Vanadium-doped and mixed Si/Ge-based apatites : synthesis, crystal chemistry and ionic conductivity

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NANYANG
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UNIVERSITY

**VANADIUM-DOPED AND MIXED SI/GE-BASED
APATITES: SYNTHESIS, CRYSTAL CHEMISTRY
AND IONIC CONDUCTIVITY**

LI HENAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Apatite-type oxides taking the general formula $[A^I_4][A^{II}_6][(BO_4)_6][X_{2\pm y}]$, particularly those of the rare earth silicate and germanate systems, are among the more promising materials being considered as alternative solid oxide fuel cell electrolytes. Nonstoichiometric lanthanum silicate and germanate apatites display pure ionic conductivities exceeding those of yttria-stabilized zirconia at moderate temperatures (500 – 800 °C). Indeed, it is the underlying complexity and flexibility of these substances that endows them with such promise as ion conductors. Many factors influence the ionic mobility, the most important being the concentration of cation vacancies and excess anions incorporated in the structure, the valence and atomic size of the substitutional elements, crystal/grain orientations, and phase purity. In this thesis, the main focus falls on the synthesis and characterization of various apatite electrolyte materials and establishing underlying correlations between oxygen ion percolation and crystal chemistry. Apatites can be synthesized in various ways, including solid state sintering, sol-gel methods and hydrothermal reactions. The former is favored since large quantities are readily fabricated for division and multi-technique characterization, while the latter has the advantage of lower synthesis temperature. This thesis examined two synthesis methods (solid state and hydrothermal) for powdered apatites, and the growth of single-crystal apatites for investigating anisotropic ion migration. Laboratory X-ray, synchrotron, and neutron diffraction were employed to refine crystal structures by the Rietveld method. The microstructures, local structures and chemical compositions were analyzed by electron diffraction, spectroscopic and microscopic methods.

Vanadium-doped apatites of nominal composition $[La_8AE_2][Ge_{6-x}V_x]O_{26+x/2}$ ($AE = Ca, Sr, Ba; 0 \leq x \leq 1.5$) were prepared by conventional solid state sintering. Single-phase products were obtained for $x \leq 0.5$, with a combination of powder synchrotron X-ray and neutron diffraction confirming these products to be $P6_3/m$ apatites. The ionic conductivities extracted by complex impedance spectroscopy showed that small vanadium amendments enhanced oxygen mobility at

intermediate temperatures (500 – 800 °C) by more than one order of magnitude, as the incorporation of V^{5+} through displacement of Ge^{4+} is charge balanced with interstitial O^{2-} that improves ionic conduction. The most promising composition was $La_{7.88}Ca_2Ge_{5.35}V_{0.65}O_{26.15}$ that delivered $\sigma = 3.44 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 500 °C. The superstoichiometric oxygen was delocalised, without fixed X-ray or neutron scattering centres. Crystal chemistry systematics demonstrate that the Ca-apatite was superior because the relatively small framework expanded through (La/AE) O_6 metaprism twisting (ϕ) that widened the tunnel, ensuring $P6_3/m$ symmetry was adopted, which favours the passage of O^{2-} with lower activation energy.

Mixed Si/Ge-based apatites were prepared by hydrothermal synthesis under mild conditions, rather than the conventional solid-state method at high temperatures. Single-phase and highly-crystalline nanosized apatite powders were obtained with the morphology changing across the series from spheres for the Si-based end-member to hexagonal rods for the Ge-based end-member. Powder X-ray and neutron analysis found all these apatites to be hexagonal ($P6_3/m$). Quantitative X-ray microanalysis established the partial (< 15 atomic percent) substitution of La^{3+} by Na^+ (introduced from the NaOH hydrothermal reagent) showed a slight preference to enter the A^I 4f framework position over the A^{II} 6h tunnel site. Moreover, retention of hydroxide (OH^-) was confirmed by infrared spectroscopy and thermogravimetric analysis, and these apatites are best described as oxyhydroxyapatites. To prepare dense pellets for conductivity measurements, both conventional heat treatment and spark plasma sintering methods were compared, with the peculiar features of hydrothermally synthesized apatites and influence of sodium on ionic conductivity considered.

Growth of single-crystal apatites $[Nd_{9.33-x+y/3}La_x][Si_{6-y}Ga_y]O_{26}$ ($0 \leq x \leq 2$; $0 \leq y \leq 0.2$) was successful by the floating-zone method and preliminary work undertaken on these materials. It was shown that the growth direction of the single crystals without a seed was distinct, and the ionic conductivity was anisotropic and higher, than that for powdered apatites. Future investigations of the correlations between

crystal chemistry and ionic conductivity on this apatite series will be necessary to establish the optimal electrolyte composition.

Publications

T. An, T. Baikie, F. Wei, **H. Li**, F. Brink, J. Wei, S. L. Ngoh, T. J. White and C. Kloc (2011). "Single crystal growth of apatite-type Al-doped neodymium silicates by the floating zone method." *J. Cryst. Growth* 333: 70-73.

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Table of Contents

Acknowledgements.....	i
Abstract.....	iii
Publications.....	vii
Table of Contents.....	ix
List of Tables	xiii
List of Figures.....	xv
List of Abbreviations	xxi

Chapter 1	Introduction.....	1
1.1	Problem Statement	2
1.2	Objectives and Scope	4
1.3	Dissertation Overview.....	5
1.4	Findings and Outcomes.....	7
Chapter 2	Literature Review.....	9
2.1	Solid Oxide Fuel Cells	10
2.1.1	Chemistry	11
2.1.2	Construction.....	13
2.2	Oxide electrolytes: Chemistry and Structure	13
2.3	Apatite Crystallographic Family	17

2.3.1	Structure and Crystallographic Modification	17
2.3.2	Extended Apatite Family.....	20
2.4	Doping Strategies for Apatite-type Electrolytes	21
2.5	Conduction Mechanisms in Apatite	22
2.6	Conclusion: Optimization of Structure, Functionality and Performance	25
 Chapter 3 Research Methodologies		27
3.1	Precepts	28
3.2	Synthesis Methods	28
3.2.1	Solid State Reaction	29
3.2.2	Hydrothermal synthesis.....	29
3.2.3	Single Crystal Growth.....	29
3.3	Structural Characterization Methods.....	30
3.3.1	Diffraction Techniques	31
3.3.2	Rietveld Refinement	33
3.3.3	Scanning Electron Microscopy (SEM)	35
3.3.4	Transmission Electron Microscopy (TEM)	36
3.4	Physical Property Measurements	37
3.4.1	Raman and Fourier transform infrared spectroscopy	37
3.4.2	Thermogravimetric Analysis (TGA).....	37
3.4.3	Impedance spectroscopy	37
3.5	Integrated Synthesis and Characterization	39
 Chapter 4 Vanadium Doped Alkaline Earth Lanthanum Germanate Oxyapatite Electrolyte		41
4.1	Introduction	42

4.2	Experimental methods.....	42
4.2.1	Synthesis	42
4.2.2	Characterization	43
4.3	Results	49
4.3.1	Phase assemblage and lattice metric	49
4.3.2	Crystal structures.....	63
4.3.3	Microstructure and local structure	67
4.3.4	Raman and FTIR spectroscopy	72
4.3.5	Oxide ion conductivities	75
4.4	Discussion	79
4.5	Conclusion	82
Chapter 5 Mixed Si/Ge-Based Apatite-Type Phases.....		85
5.1	Introduction.....	86
5.2	Synthesis	86
5.3	Characterization	87
5.3.1	Powder Diffraction.....	87
5.3.2	Electron microscopy and spectroscopy	88
5.4	Results and Discussion.....	88
5.4.1	Synthesis and Phase Assemblage.....	88
5.4.2	Microstructure and local structure	90
5.4.3	Hydroxyl incorporation — FTIR spectroscopy and TGA	92
5.4.4	Crystal chemistry	94
5.4.5	Rietveld refinement and crystal structures	95
5.4.6	Oxide ion conductivities	102
5.5	Conclusion	106

Chapter 6	Conclusions and Future Work	107
6.1	Conclusions.....	108
6.2	Future Work	110
6.2.1	Introduction.....	110
6.2.2	Reconnaissance Single Crystal Growth	111
6.2.3	Outstanding Questions	114
	References.....	117

List of Tables

Table 2-1 Conductivity for selected electrolytes (at 800 °C unless stated).

Table 2-2 Possible Compositions of Apatite-type Electrolytes.

Table 4-1 The atomic ratios for La, AE, and O were scaled to a total Ge + V content of 6 atoms per formula unit, derived from quantitative EDS microanalyses of single-phase samples with nominal composition $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr, Ba).

Table 4-2 Refined crystal and atomic parameters from synchrotron powder X-ray diffraction of $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (x = 0, 0.25, and 0.5).

Table 4-3 Refined crystal and atomic parameters from neutron powder diffraction of $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (x = 0, 0.25, and 0.5).

Table 4-4 Isotropic and anisotropic displacement parameters refined from neutron powder diffraction for $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (x = 0, 0.25, and 0.5).

Table 4-5 Selected bond lengths and angles of $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal x = 0, 0.25, and 0.5) from synchrotron and neutron powder diffraction.

Table 4-6 Refined crystal and atomic parameters from synchrotron powder X-ray diffraction of $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal x = 0, 0.25, and 0.5).

Table 4-7 Refined crystal and atomic parameters from neutron powder diffraction of $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal x = 0, 0.25, and 0.5).

Table 4-8 Isotropic and anisotropic displacement parameters refined from neutron powder diffraction for $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal x = 0, 0.25, and 0.5).

Table 4-9 Refined crystal and atomic parameters from synchrotron powder X-ray diffraction of $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal x = 0, 0.25, and 0.5).

Table 4-10 Refined crystal and atomic parameters from neutron powder diffraction of $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal x = 0, 0.25, and 0.5).

Table 4-11 Isotropic and anisotropic displacement parameters refined from neutron powder diffraction for $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Table 4-12 Quantitative EDS microanalyses of co-existing non-apatite phases found in a preparation with nominal composition $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($x=1.5$).

Table 4-13 Conductivity data for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$; $0 \leq x \leq 0.5$) samples.

Table 4-14 The bond lengths and BVS for cations on *A* and *B* sites in $[\text{A}^{\text{I}}_4][\text{A}^{\text{II}}_6][(\text{BO}_4)_6][\text{X}_2]$ system for $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series.

Table 5-1 The atomic ratios for La, Na, and O were scaled to a total Si + Ge content of 6 atoms per formula unit, derived from quantitative EDS and EPMA for mixed $\text{Si}_{6-x}/\text{Ge}_x$ apatites.

Table 5-2 Refined cell parameter data (hexagonal cell with the space group $P6_3/m$) from laboratory X-ray and neutron powder diffraction on mixed Si/Ge-based lanthanum apatites.

Table 5-3 Atomic coordinates and equivalent isotropic ADPs for $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ from neutron powder diffraction.

Table 5-4 Anisotropic ADPs for $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ from neutron powder diffraction.

Table 5-5 Selected bond lengths and angles for $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ from neutron powder diffraction.

Table 5-6 Refined cell parameter data (hexagonal cell with the space group $P6_3/m$), atomic coordinates and equivalent isotropic ADPs of Si end-member apatite from neutron powder diffraction collected at 1100°C .

Table 5-7 Conductivity data for pellets prepared from conventional sintering and SPS (H0–6 represent samples with nominal $x = 0 - 6$, and H0a & b are SPS samples of different TD).

Table 6-1 A comparison of the two solid solution series studied in this research.

List of Figures

Figure 2-1 Concept diagram of SOFC based on oxygen-ion conductors [Reproduced from Stambouli and Traversa⁷⁶].

Figure 2-2 Ionic conductivity of (a) fluorite, (b) perovskite, and (c) apatite at various temperatures. The conductivities at intermediate temperatures (~500 °C) are marked by blue circles [Adapted from Kharton *et al.*⁸⁷].

Figure 2-3 Phase diagram of $\text{Nd}_2\text{O}_3 - \text{SiO}_2$ [Taken from Higuchi *et al.*¹⁰⁴].

Figure 2-4 Polyhedral representation of $[\text{A}^{\text{I}}_4][\text{A}^{\text{II}}_6][(\text{BO}_4)_6]\text{X}_2$ apatite emphasizing the $\text{A}^{\text{I}}\text{O}_6$ metaprisms (stripped) and BO_4 tetrahedra (green). (a) The [001] projection that shows the topological relationship between the polyhedra and A^{II} and X tunnel ions. (b) Clinographic projection of a single one-dimensional channel [Adapted from Srinivasan *et al.*¹⁰⁵].

Figure 2-5 An apatite taxonomy with the frameworks divided into three genera: neutral apatites containing only (BO_4) tetrahedra; reduced apatites made up of (BO_3) units; and oxidized apatites with (BO_5) polyhedra. Hybrid apatites with $\text{BO}_3/\text{BO}_4/\text{BO}_5$ provide a means for crystallochemically tailoring functionality [Taken from Pramana *et al.*¹⁰⁸].

Figure 2-6 The interstitial oxygen site at the periphery of the channels and surrounding lattice relaxation [Reproduced from Kendrick *et al.*¹¹⁰].

Figure 2-7 Interstitial oxide-ion migration pathway in $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ from atomistic simulation studies; (a) view down the c axis; (b) view perpendicular to the c axis [Reproduced from Kendrick *et al.*¹¹⁰].

Figure 2-8 Proposed conduction pathway between adjacent oxide-ion channels obtained from computer simulation results of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The incorporation of a periphery interstitial oxide-ion (yellow) (a) forces a silicate oxygen (orange) in between the two SiO_4 units forming an Si_2O_9 unit (b), the top silicate unit rotates to form an Si_2O_9 unit with a neighboring silicate unit (c), and an oxygen on the top silicate unit (green) is released as an interstitial in a different channel (d) [Reproduced from Kendrick *et al.*¹¹⁰].

Figure 3-1 Nyquist plot and the simple equivalent circuit.

Figure 4-1 Schematic diagram of refinement methods for La/AE and Ge/V occupancies in $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr, Ba; nominal $x = 0, 0.25, 0.5$).

Figure 4-2 Rietveld plots of the (a) synchrotron and (b) neutron powder diffraction data of nominal $\text{La}_8\text{Sr}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$ collected at room temperature. The observed intensity is shown by dots, with the solid line representing the calculated intensity. Differences between observed and calculated intensities are plotted beneath. Vertical markers indicate the Bragg reflections of CaF_2 standard (top) and apatite (bottom).

Figure 4-3 PXRD patterns and enlarged segments for (a) & (b) $[\text{La}_8\text{Ca}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$, (c) & (d) $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ and (e) & (f) $[\text{La}_8\text{Ba}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series with nominal $x=0, 0.25, 0.5, 0.75, 1, 1.25$, and 1.5 synthesised with two calcination cycles at 1300 and 1350 °C for 16 hours separately. Under these preparative conditions the solid-solution limit is $x = 0.5$. In (b), (d) & (f) peaks from secondary phases are labelled with * for $x > 0.5$.

Figure 4-4 Refined lattice parameters from synchrotron powder X-ray diffraction data for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr, Ba) (a) a , (b) c , (c) c/a , (d) unit cell volume. The x -values are those derived from Rietveld analysis.

Figure 4-5 Refined lattice parameters from synchrotron powder X-ray diffraction data for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr and Ba). The x -values are those derived from Rietveld analysis.

Figure 4-6 Twist angle (a) Polyhedral representation of the refined $\text{La}_{7.99}\text{Sr}_2\text{Ge}_{5.58}\text{V}_{0.42}\text{O}_{26.20}$ structure with metaprism twisting (ϕ) labelled, face-sharing $\text{A}^{\text{I}}\text{O}_6$ metaprisms (yellow) are corner connected to BO_4 tetrahedra (orange) forming the framework, which surrounds the tunnel A^{II} atoms (blue), (b) Plot of twist angles with respect to x , (c) Plot of $\text{A}^{\text{I}}/\text{A}^{\text{II}}$ atomic size ratio with respect to x , (d) Plot of oxygen nonstoichiometry with respect to ϕ , (e) Plot of ionic conductivity with respect to ϕ , (f) Plot of activation energy with respect to ϕ for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr, Ba).

Figure 4-7 BSE micrographs for $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series with nominal (a) $x = 0.25$ and (b) $x = 1.5$, respectively. By contrast, the dark background reflects resin and the relatively bright regions represent the embedded powder samples.

Figure 4-8 Low angle backscattered electron micrographs (5.0kV) for $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series with (a) AE = Ca, $x = 0$; (b) AE = Sr, $x = 0$; (c) AE = Ba, $x = 0$; (d) AE = Ca, $x = 0.5$; (e) AE = Sr, $x = 0.5$; (f) AE = Ba, $x = 0.5$.

Figure 4-9 Low angle backscattered electron image for $\text{La}_{7.67}\text{Ba}_2\text{Ge}_{5.29}\text{V}_{0.71}\text{O}_{25.86}$ (nominal composition: $\text{La}_8\text{Ba}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$) pellet of unpolished surface.

Figure 4-10 XRD profile for the sintered pellet surface with nominal composition $[\text{La}_8\text{Ba}_2][\text{Ge}_{5.5}\text{V}_{0.5}]\text{O}_{26.25}$. Peaks of abnormally strong intensities (comparing with a randomly oriented diffraction pattern) are indexed, which are resulted from preferred orientations and poor statistics of the bulk surface.

Figure 4-11 EBSD analyses on polished pellet of nominal $\text{La}_8\text{Ba}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$. The all-Euler map (with grain boundaries shown by black lines) is shown on the left and crystal orientations for six elongated grains (marked on the map by numbers) are presented on the right; the growth directions of these crystals are all along *c*-axis.

Figure 4-12 TEM images (low-magnification and high-resolution) and diffraction patterns for nominal (a) & (b): $[\text{La}_8\text{Sr}_2][\text{Ge}_6]\text{O}_{26}$, (c) & (d): $[\text{La}_8\text{Sr}_2][\text{Ge}_{5.5}\text{V}_{0.5}]\text{O}_{26.25}$.

Figure 4-13 Raman spectra of normalised intensities for (a) $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (b) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (c) $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ series with nominal $x = 0, 0.25$, and 0.5 , measured at room temperature.

Figure 4-14 Raman spectrum for the initial reactant V_2O_5 powder measured at room temperature. Peaks located at $283, 405$ and 480 cm^{-1} are assigned to the bending vibrations of $\text{V}=\text{O}$, $\text{V}=\text{O}$, $\text{V}_2\text{-O}$ (doubly coordinated oxygen) bonds; peaks located at $530, 699$ and 990 cm^{-1} are assigned to the stretching modes of $\text{V}_3\text{-O}$ (triply coordinated oxygen), $\text{V}_2\text{-O}$, and $\text{V}=\text{O}$ bonds.

Figure 4-15 FTIR spectra for (a) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ with $x=0, 0.25$, and 0.5 , (b) $\text{La}_8\text{AE}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$ with $\text{AE} = \text{Ca}, \text{Sr}$, and Ba .

Figure 4-16 The impedance plots for (a) $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (b) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (c) $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ series with nominal $x = 0, 0.25$, and 0.5 at $500\text{ }^\circ\text{C}$.

Figure 4-17 Variation of conductivities with temperatures for (a) $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (b) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (c) $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ series with nominal $x = 0, 0.25$, and 0.5 .

Figure 5-1 XRD data for Ge end-member apatite prepared with prolonged reaction time of 60 days, peaks from the secondary phase $\text{La}(\text{OH})_3$ are labeled with *.

Figure 5-2 Low angle backscattered electron micrographs (5.0 kV) for (A) Si end-member, (B) intermediate composition of nominal equivalent Si/Ge, and (C) Ge end-member apatites synthesized at 240 °C for 16 hours.

Figure 5-3 Low angle backscattered electron micrographs (5.0 kV) for Ge end-member apatites with synthesis condition of (A) 220 °C, 3 hours; (B) 220 °C, 6 days; (C) 220 °C, 60 days; (D) 200 °C, 1 day; (E) 220 °C, 1 day; (F) 240 °C, 1 day.

Figure 5-4 TEM images (low-magnification and high-resolution) and diffraction patterns for (A) & (B) Si end-member, (C) & (D) intermediate composition of nominal equivalent Si/Ge, (E) & (F) Ge end-member apatites.

Figure 5-5 FTIR spectra for mixed $\text{Si}_{6-x}/\text{Ge}_x$ -based lanthanum apatites with wavenumber ranges from (A) 400–1800 cm^{-1} and (B) 2000–4000 cm^{-1} . The intensities were normalized to refined Si or Ge content with (a) Si_6 , (b) $\text{Si}_{5.82}$, (c) $\text{Si}_{5.44}$, (d) $\text{Si}_{4.70}$, (e) $\text{Ge}_{3.13}$, (f) $\text{Ge}_{4.49}$, (g) $\text{Ge}_{5.24}$.

Figure 5-6 TGA plots for (A) Si end-member, (B) intermediate composition of nominal equivalent Si/Ge, and (C) Ge end-member apatites synthesized at 240 °C for 16 hours.

Figure 5-7 Rietveld plots of the (a) laboratory X-ray and (b) neutron powder diffraction data of mixed $\text{Si}_{6-x}/\text{Ge}_x$ -based apatite of nominal $x = 3$ collected at room temperature. The observed intensity is shown by dots, with the solid line representing the calculated intensity. Differences between observed and calculated intensities are plotted beneath.

Figure 5-8 Refined lattice parameters and the linear fits from powder X-ray (square) and neutron (triangle) diffraction data for the analogue of mixed $\text{Si}_{6-x}/\text{Ge}_x$ -based lanthanum apatites with refined x from 0 – 6.

Figure 5-9 2-D and 3-D Fourier mapping for the Si end-member apatite with (A) and (B) $2a$ oxygen position, (C) and (D) $4e$ oxygen and hydrogen positions.

Figure 5-10 *In situ* high temperature neutron diffraction data for Si end-member apatite collected between room temperature (25 °C) and 1100 °C.

Figure 5-11 Variation of conductivities with temperature for pellets of mixed $\text{Si}_{6-x}/\text{Ge}_x$ -based lanthanum apatites (H0–6 represent samples with nominal $x = 0 - 6$, and H0b is the SPS sample of lower TD) prepared from (A) conventional sintering and (B) SPS.

Figure 5-12 Backscattered electron micrographs (5.0 kV) for pellets of Ge end-member apatite prepared from (A) conventional sintering and (B) SPS.

Figure 5-13 Impedance spectra for Ge end-member apatite in dry ● and wet ○ N₂ at 450°C showing a small reduction in resistance in wet N₂.

Figure 6-1 Optical floating zone furnace (a) Photograph of the mirror furnace (Model: FZ-T-4000-H-VPO-VII-PC), (b) Schematic diagram of the image furnace with double ellipsoidal mirrors [(b) adapted from Higuchi *et al.*¹⁰⁴].

Figure 6-2 Processes of single crystal growth by the floating-zone method.

Figure 6-3 Photographs of the as grown crystal rods of (a) Nd_{8.33}LaSi₆O₂₆, (b) Nd_{9.37}Si_{5.9}Ga_{0.1}O₂₆ with embedded pictures of partial crystal taken under luminescent lamp.

List of Abbreviations

AC	Alternating Current
ADP	Atomic Displacement Parameters
AE	Alkaline Earth
ANSTO	Australian Nuclear Science and Technology Organization
APFU	Atoms Per Formula Unit
A.U.	Arbitrary Units
BEI	Backscattered Electron Images
BSE	Backscattered Electron
BVS	Bond Valence Sum
CBED	Convergent Beam Electron Diffraction
CHP	Combined Heat and Power
CN	Coordination Number
C _s	Spherical Aberration
DI	De-Ionized
E _a	Activation Energy
EBSD	Electron Backscatter Diffraction
EDS/EDX	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
EPMA	Electron Probe Microanalysis
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
LSGM	Lanthanum Strontium Gallate Magnesite
MAS	Magic-Angle Spinning
NMR	Nuclear Magnetic Resonance
OPAL	Open Pool Australian Lightwater
PXRD	Powder X-ray Diffraction
QPA	Quantitative Phase Analysis
R _{wp}	Weighted R-Bragg

SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
SOFC	Solid Oxide Fuel Cell
SPS	Spark Plasma Sintering
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
WDS	Wavelength Dispersive Spectrometers
WT. %	Weight Percent
XRD	X-ray Diffraction
YSZ	Yttria Stabilized Zirconia
Z	Atomic Number

Chapter 1

Introduction

Rare-earth silicates and germanates adopting the apatite-type structure have attracted widespread interest as electrolytes for solid oxide fuel cells. To provide an essential underpinning for the delivery of fuel cell longevity and reliability, it is important to understand the role of crystallochemical modifications, develop a comprehensive description of conduction pathways, and detect the correlation between crystallographic structure and ion mobility.

1.1 Problem Statement

In common with other electrochemical devices, the solid oxide fuel cell (SOFC) is composed of an anode, electrolyte and a cathode. As a key component in the cell, an electrolyte with high oxygen transport and limited electronic conduction is required, that must remain stable as an ionic conductor in both oxidizing and reducing environments for optimal performance.¹⁻² Many oxide ion conducting materials are under consideration, and one of the most widely used electrolytes is yttria-stabilized zirconia (YSZ), which exhibits high ionic conductivity at temperatures beyond 800 °C.³⁻⁵ Such high temperatures required to achieve acceptable ion fluxes can lead to many technological problems such as materials aging, mechanical instability, undesirable chemical reactions between cell components, and shortened lifetime. To reduce the operating temperature of SOFCs, oxide ion electrolytes with high conductivity at low temperatures are favored.

Rare-earth silicates⁶⁻¹⁵ and germanates¹⁶⁻²⁵ adopting the apatite-type structure have attracted widespread interest as electrolytes for SOFCs. Besides those actual and potential applications as catalyst,²⁶⁻²⁷ non-toxic dyes,²⁸ and hosts for radioactive wastes,²⁹ apatite-type materials are also promising ionic conductors with good performance at moderate temperatures (500 – 800 °C).³⁰⁻⁴³ Apatite electrolytes are conventionally synthesized by solid-state reaction through high-temperature sintering (> 1000 °C), but an alternate route is by sol-gel processing⁴⁴⁻⁴⁷ where lower temperature (> 800 °C) calcination is possible. The synthesis of Ge-containing apatites is somewhat problematic, as compared to silicates, due to Ge volatilization leading to mixed phase products.^{16, 19, 48} Mild hydrothermal synthesis⁴⁹⁻⁵⁰ could avoid prolonged sintering at high temperatures, but to date, there have been no systematic studies to establish the optimal hydrothermal conditions for silicate apatite preparation, and analogous germanates have never been produced in this way. For all these preparative routes, obtaining single-phase, polycrystalline apatite (> 99%) is challenging, especially for complex chemistries.

Furthermore, deviations from the ideal composition could occur, since the apatite structure possesses zeolitic character with large one-dimensional tunnels responding flexibly to chemical substitutions.⁵¹ For example, oxy-, hydroxyl-, and carbonated-apatite can crystallize from notionally the same starting materials through variation in redox conditions, humidity and temperature.⁵² As a consequence, controlling the final composition is difficult and tailoring synthesis parameters is required.

The general formula for electrolyte oxyapatite of hexagonal structure $P6_3/m$ is $[A^I_4][A^{II}_6][(BO_4)_6]O_2$, where A are rare-earths or alkaline-earths and B is Si or Ge. Apatites contain several cation acceptor sites leading to a wide range of substitutional possibilities⁵³⁻⁶⁷ with ion mobility modified by varying cation type and proportions. Extensive studies of the factors influencing electrolyte performance have appeared, which show that A^I cation-deficient or oxygen excess systems deliver higher conductivity than stoichiometric compositions,^{7, 68-71} and that larger A^{II}/A^I species promote oxygen migration through lower activation energy.⁵¹ Consequently, the larger lanthanum (La^{3+}) apatite analogues usually show superior electrolyte performance, compared to smaller rare earth (Yb^{3+}) compounds.^{6, 43, 72-73}

Developing a comprehensive description of oxygen migration through the electrolyte will provide an essential underpinning for the delivery of fuel cell longevity and reliability. To date however, the details of conduction pathways remain the subject of debate and the correlation between crystallographic structure and ion mobility is unclear. Moreover, most of the studies were on powdered apatites, and consequently, micrographic defects such as porosity, grain boundaries, and grain textures unavoidably degrade conductive performance and bring additional difficulties for identifying ion migration pathways within the crystal structure.

1.2 Objectives and Scope

The objectives of this research were to:

- (i) *tailor synthesis parameters* to obtain single-phase apatites with high crystallinity;
- (ii) *establish correlations* between apatite crystallochemistry and ionic conductivity; and
- (iii) *design and optimize the performance* of lanthanum germanate and lanthanum silicate based apatites.

The scope of this PhD comprises:

- (I) Fabrication of apatites through a variety of routes including:
 - (I-i) Solid state sintering: High temperature ($> 1000\text{ }^{\circ}\text{C}$) fabrication with repeated grinding and heating minimizes impurities. This method has the advantages of high yield and high crystallinity, and complex chemistries can be easily handled.
 - (I-ii) Sol-gel synthesis: Alkoxides are often used as a chemical precursor to yield pure and finely divided polycrystalline powders *via* lower temperature reactions ($> 800\text{ }^{\circ}\text{C}$). However, residual amorphous phases may degrade overall product crystallinity. This method was tried in the initial reconnaissance but not selected for syntheses, due to the doping difficulties and poor product crystallinity.
 - (I-iii) Hydrothermal reactions: The starting materials must be soluble in aqueous alkaline or acidic media, and nano-crystalline powders can be synthesized in autoclaves at low temperatures $\leq 240\text{ }^{\circ}\text{C}$. This method has a low yield and only a small amount of apatite powder can be synthesized in each batch.
- (II) Comprehensive characterization by:
 - (II-i) Powder diffraction: Laboratory X-ray, fixed wavelength synchrotron and neutron diffraction were employed to conduct quantitative phase analysis and obtain crystallochemical information (unit cell

parameters, symmetry, occupancy, anisotropic thermal parameters, and distortion of polyhedra).

(II-ii) Electron microscopy: Scanning electron microscopy was applied for the visualization of particle morphology, grain size, macroscopic defects and phase segregation. Energy dispersive X-ray can be used to validate the material chemistry, and with care, deliver quantitative analyses. The collection of nano-scale information is best accomplished by transmission electron microscopy. Selected area electron diffraction, due to the high coherence of the electron beam and small probe volume, can be used to verify the space group of the synthesized materials and observe superlattice formation. High resolution electron microscopy can identify atomic segregation, examine defect abundance, and confirm crystal structures.

(II-iii) Spectroscopic methods: Raman and Fourier-transformed infrared spectroscopy were conducted to probe the coordination and bonding. Thermogravimetric analysis was necessary to monitor loss of water (proton content) and volatiles.

(III) Conductivity measurements were gathered by impedance spectroscopy that measures oxygen ion mobility.

1.3 Dissertation Overview

Germanates and silicates of the apatite family display high ionic conductivity at a relatively modest 500 °C. Silicates are more stable than germanates, as the latter are volatile upon prolonged sintering at high temperatures. However, germanate apatites are predisposed to contain interstitial sites compared to silicates, and the volatilization can be avoided by control of sintering conditions. Lanthanide group elements are commonly present in silicate and germanate apatites and enhance chemical and structural stability. Among the lanthanide group, lanthanum apatites show superior conductivity and were chosen for this study. To fulfill the objectives

of this research, two chemical analogues of powdered apatites were designed and fabricated with different routes, then analysed using the same characterization regime. The first analogues were vanadium-doped alkaline earth lanthanum germanate oxyapatites that included three sub-series containing calcium, strontium, and barium. The second group comprised mixed Si/Ge-based lanthanide apatites.

This thesis starts with an introduction (Chapter 1) followed by a literature review (Chapter 2). Research methodologies are described in Chapter 3, and in the next two chapters, comprehensive descriptions of the work on vanadium-doped apatites (Chapter 4), and mixed Si/Ge-based lanthanide apatites (Chapter 5) are provided where the experimental methods, results and discussion are presented separately. Last Chapter 6 collects the outcomes of the entire project with a proposal for future work given.

Chapter 1 provides a short review of the apatite structure and the rationale for pursuing this study. It also presents the research justification and experimental design strategies with objectives and scope established.

Chapter 2 reviews the basis of solid oxide fuel cell design, compares and contrasts the properties of conventional electrolyte materials. Details of the apatite structure are given, with emphasis on crystallochemical flexibility and oxide ion conduction mechanisms.

Chapter 3 explores the range of techniques employed for synthesis and crystallographic structure characterization. Their deployment for phase and composition confirmation, and investigation of microscopic morphologies and defects are described, including their limitations and complementarities.

Chapter 4 targeted vanadium substituted germanate oxyapatites with fully occupied cation sites $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}; 0 \leq x \leq 1.5$) to assess the impact of a high-valency ion (V^{5+}) on functionality, search for interstitial oxygen,

and identify those factors which enhance electrolyte conductivity. As better conductivity can be achieved by the introduction of excess charge carriers, pentavalent element doping was attempted here in order to inject superstoichiometric oxygen. Conventional solid state reactions were chosen for syntheses of this series due to the complex chemistries involved. A significant enhancement in conductivity was observed even with low-level vanadium doping, and the best performance was for the calcium doped series. This result confirmed the general principles for crystallochemical tailoring on performance enhancement.

Chapter 5 focuses on mixed Si/Ge-based lanthanide apatites of composition $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$, from hydrothermal synthesis. Conventional heat treatment was coupled with spark plasma sintering to fabricate dense products where oxygen mobility is maximized. In addition, the role of sodium, introduced from the reaction fluid, was quantified as $\text{La}_{8.50}\text{Na}_{1.29}\text{Si}_{6-x}\text{Ge}_x\text{O}_{24}(\text{OH})_{2.79-2y}\text{O}_y\Box_{y-0.79}$ and the impact on micro-structure and conductivity was evaluated.

Chapter 6 summarizes the outcomes of this research and provides guidance for designing future apatite electrolyte materials. A description on how the chemical and crystallographic changes correlate to the conductive property is presented. Suggestions are made on how to exploit these new concepts through addressing correlations of crystal chemistry, ion migration mechanisms and device fabrication. Following the discussion of future research directions, preliminary work on the growth and study of single-crystal apatites is given, although complete investigation would require a follow-up project that is beyond the scope of this thesis.

1.4 Findings and Outcomes

The achievements of this research and several novel findings and outcomes include:

- (i) *tailored solid state synthesis procedures* that yield vanadium doped germanate apatites of high purity and little germanium loss;
- (ii) *a well-developed hydrothermal approach* to obtain the germanate varieties;
- (iii) *the systematical examination of the hydrothermal conditions* for single-phase nano-crystalline silicate-germanate apatites;
- (iv) *confirmation that all the apatites adopt the $P6_3/m$ hexagonal crystallographic structure* and validated compositions of these synthesized apatites;
- (v) *demonstrated anisotropic growth of crystallites* from loose powder and grains in sintered pellets;
- (vi) *fabrication of dense pellets to maximize oxygen mobility* through conventional heat treatment coupled with spark plasma sintering;
- (vii) *achieving enhanced conductivity* even with low-level vanadium-doping;
- (viii) *formulated the chemical impact on conductive property* when sodium and hydroxyl incorporation occur; and
- (ix) *proved the general principles for crystallochemical tailoring* on performance enhancement.

Chapter 2

Literature Review

Rapidly increasing energy prices and climate change are dominant global issues where technological solutions are urgently needed. Although worldwide energy demand is continuously increasing, non-renewable energy resources, principally oil, coal and natural gas, are predicted to shortly reach peak production. For many countries, poor energy supply security coupled with high energy costs threatens their economic wellbeing and national integrity. In his testimony to the U.S. Senate, Prof. Richard E. Smalley (Nobel laureate in Chemistry) rated the challenge of delivering sustainable energy production and its distribution as the largest issue for humanity in the coming 50 years. It is now axiomatic that sources of abundant, renewable and cost-effective energy will be crucial for the continuance of modern civilization, an equitable sharing of wealth, and expansion of civil society.

2.1 Solid Oxide Fuel Cells

While there will be many components of renewable energy systems, fuel cells have emerged as one of the most effective solutions to the energy crisis, due to their high fuel-to-electricity conversion efficiency.^{3, 74-75} A fuel cell is an electrochemical conversion device that directly transforms the chemical energy held in a fuel into electricity through reaction with oxygen or other oxidizing agent; since combustion is avoided such devices offer superior efficiency and are environmentally benign.⁷⁶ Large fuel cell installations can be deployed for commercial electricity generation and automotive applications, and can be scaled-down for consumer electronics. As distinct from electrochemical batteries or supercapacitors, fuel cells will not discharge or need re-energizing, and will operate as long as fuel and oxidant are supplied. The working principle of the fuel cell was established by Christian Friedrich Schönbein in 1838 and the first operating fuel cell was developed in 1839 by Welsh scientist and barrister Sir William Robert Grove.⁷⁷ This prototype was called a “gas voltaic battery”, where two platinum strips were brought in contact with a common mineral-acid electrolyte, and when the upper half of one Pt strip was exposed to hydrogen gas and the other half exposed to oxygen, the flow of electricity was measured.

Nowadays, the power supplied by fuel cells varies hugely from portable power sources that produce a few watts of electricity, right up to megawatts of electricity generated by fuel cell power plants. Fuel cells come in many varieties, utilizing different fuels and electrolytes, and can operate from room temperature up to 1000 °C (polymer based 23–120 °C, solid oxide based 800–1000 °C).^{75, 78} However, the device structure is always similar with three major parts: the anode and the cathode, where the redox reactions take place, and the electrolyte which provides a conducting channel for the ions. These segments are connected such that fuel (commonly H₂ or CH₄) is consumed at the anode to generate water or carbon dioxide as exhaust, while an electric current flows to the cathode to power electric motors.

2.1.1 Chemistry

Fuel cells are generally classified according to the chemical composition of the electrolyte materials used for ionic conduction. Common types of fuel cells include polymer electrolyte membrane (PEM) fuel cells,⁷⁹ direct methanol fuel cells,⁸⁰ solid oxide fuel cells,⁸¹ alkaline fuel cells,⁸² molten carbonate fuel cells⁸³ and phosphoric acid fuel cells.⁸⁴ Each type requires particular materials and fuels and is suitable for different applications. For example, in PEM fuel cells, a proton conductive membrane is used as the electrolyte separating the anode from the cathode. These devices are attractive for smaller scale applications due to their high power density and relatively low operating temperature (<90 °C). However, besides the low proton flow, a major challenge for PEM fuel cells can be their poor durability due to degradation of both the catalyst and the polymer membrane.⁷⁹

Compared to PEM fuel cells, a SOFC uses a refractory oxide or ceramic as the electrolyte.⁸⁵⁻⁸⁶ The key difference from other technologies is that these materials allow the cells to operate at temperatures as high as 1000 °C. Consequently, the high quality exhaust gas is ideal for integrating heat and power applications in combined-cycle electric power plants. In this manner, the SOFC can deliver many advantages including high efficiency, long-term stability, fuel flexibility, low emissions and relatively low cost. The direct fuel-to-electricity efficiencies of SOFC can reach 70%, and if the calorific value of the hot exhaust is captured and exploited, the total inherent generation efficiency can be 90%.⁷⁶ On the other hand, since SOFCs operate at temperatures from 500 °C to 1000 °C, the start-up time to working temperature is long, and the mechanical integrity and chemical compatibility of the cell may be compromised with extended use.

The typical structure and chemistry of a SOFC is shown in Figure 2-1. The anode and cathode electrodes form a sandwich structure separated by a solid state electrolyte.

Figure 2-1 Concept diagram of SOFC based on oxygen-ion conductors [Reproduced from Stambouli and Traversa⁷⁶].

For a SOFC using H_2 gas as the fuel, oxygen ions formed from air in the cathode migrate through the electrolyte to the fuel gas passing over the anode, and oxidize the fuel. Electrons generated at the anode move to the external circuit and generate electricity. Therefore, the electrochemical reactions in SOFCs can be described using the equations:

Typical electrode metals are Ni, Co, Ru and Pt used in the reducing environment at the anode, while on the cathode side, the doped LaMnO_3 perovskite and $(\text{La,Sr})\text{CoO}_3$ cobaltite are commonly employed.¹ The electrolyte is usually a high melting point oxide, especially zirconia doped with yttria that is favourable for the transport of oxygen ions. In the cubic fluorite-phase YSZ, the conduction is improved by increasing the concentration of oxygen vacancies.

It is fundamentally important to control the mobility of ionic and electronic charge carriers in the electrolyte, since good ionic conduction in solid electrolyte reduces impedance and electronic isolation prevents leakage currents.

2.1.2 Construction

The SOFC can be designed in various geometrical configurations, such as rolled tubes (tubular) or flat plates, and the fabrication process is compatible with the techniques developed for the electronics industry, such as bulk ceramic processing methods, including tape casting and screen-printing, while spray pyrolysis and magnetron sputtering techniques can be used to deposit porous electrodes.^{1, 86} Among the different fabrication methods, tape casting is particularly versatile due to its low cost, scalability and applicability to many SOFC components such as porous anode materials, dense electrolyte and interconnect materials. Tape casting significantly reduces the cost and fabrication time since fuel cells can be fabricated simultaneously and virtually continuously. Screen-printing is the second most common ceramic processing method for SOFCs, especially for the production of uniform cathode layers on top of electrolyte-supported cells. As thickness is readily controlled, it is also a promising way to apply thin layers of dense electrolyte on anode-supported SOFCs. Electrophoretic deposition is also cost effective as it requires a simple apparatus and short deposition time, and it is easy to scale-up with little restriction on the shape of deposition substrates. Moreover, it is binder free and suitable for laminates deposition. The ability of forming thin and dense deposits makes electrophoretic deposition a unique technique for SOFCs.

2.2 Oxide electrolytes: Chemistry and Structure

The nature of the electrolyte fundamentally controls the performance of the fuel cell via its contribution to the ohmic internal resistance, with the essential material requirement being high ionic conductivity (typically $>1 \times 10^{-3} \text{ Scm}^{-1}$ at $\sim 600^\circ\text{C}$), low electronic conduction, good thermal shock resistance, promising chemical stability, and compatibility with the electrodes.¹⁻² Mobility is associated with various defects, among which anion vacancies are the most common charge carriers in oxide-ion conductors. Oxide-ion conductors (mainly ceramics) that contain highly mobile O^{2-} are already deployed in SOFCs. There are a large

variety of electrolyte materials available and four well studied examples are illustrative:

- (i) The oxygen ion conductivity of fluorite-structured binary oxide systems^{5, 87-91} is one of the most widely studied topics in high-temperature electrochemistry. YSZ is the benchmark for reduced-temperature SOFC, and it is the most widely used zirconia-based solid electrolyte for practical applications due to the low dopant cost. The conduction is improved by increasing the concentration of oxygen vacancies ($2\text{Zr}^{4+} + \text{O}^{2-} \rightarrow 2\text{Y}^{3+} + \square_{\text{O}^{2-}}$) ($\sigma = 0.04 \text{ Scm}^{-1}$ at 800 °C) and the optimum concentration of yttria was found to be ~ 8–11 mol%, as complex defects of low mobility form with further doping.⁸⁸ Several interconnect issues arise since the solid electrolyte is in contact with the anode and cathode. For example, the YSZ electrolyte could react with the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) cathode leading the formation of interconnect products such as $\text{La}_2\text{Zr}_2\text{O}_7$,⁹² SrZrO_3 ,⁹³ or a combination of phases with lower ionic conductivities that detract from performance.
- (ii) The perovskite-type phases derived from lanthanum gallate, LaGaO_3 , possess a higher ionic conductivity than stabilized zirconia at reduced temperatures (~500–800 °C).⁹⁴⁻⁹⁶ Higher oxygen vacancy concentration can be achieved by substituting La and Ga with alkaline earth elements and divalent metals respectively. Consequently, the series of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM) with incorporation of Sr and Mg showed improved oxide ion conduction ($\sigma_{\text{max}} = 0.15 \text{ Scm}^{-1}$ at 800 °C)⁹⁶ at $x = 0.10\text{--}0.20$ and $y = 0.15\text{--}0.20$. Surprisingly, the introduction of a small amount of transition metal dopants such as cobalt and iron can further increase the ionic conductivity, yet the electronic conductivity increases simultaneously leading to an overall degradation of fuel cell performance.^{94, 96} The disadvantages of LaGaO_3 -based electrolytes include the high cost of gallium, possible reduction and volatilization of gallium oxide, significant reactivity with certain electrodes, and formation of secondary phases in the course of processing.

(iii) The Aurivillius phase⁹⁷ of $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ consists of alternating $\text{Bi}_2\text{O}_2^{2+}$ and perovskite-like $\text{VO}_{3.5}^{2-}$ layers, with oxygen vacancies in the perovskite layers providing ion migration. The crystal structure can be stabilized by partial substitution of vanadium with transition metal cations such as Co, Cu or Ni, and these solid solutions exhibit higher ionic conductivity than that of YSZ and LSGM.⁹⁸⁻⁹⁹ However, similar to the Bi_2O_3 -based oxides, the phase stability of doped γ -bismuth vanadate remains an issue, and further complexity arises from the high chemical reactivity and low mechanical strength. Thus, it is difficult to utilize these phases practically.⁸⁷

(iv) Rare earth apatite materials have recently attracted considerable interest with relatively high oxide ion conductivity reported for silicate and germanate systems. In doping studies, it was shown that to achieve high conductivities in apatites, non-stoichiometry in the form of either cation vacancies, or excess oxygen, is required.^{6, 70} As shown in Figure 2-2, Ge/Si-based apatite materials and their doped variants exhibit conductivities comparable to, or better than, the conventional fluorite-type and perovskite-type ceramics at moderate temperatures.⁸⁷ Table 2-1 compares the four groups of electrolyte conductivities and the apatite family shows good overall performance at intermediate temperatures with relatively high conductivity and promising phase stability.

Figure 2-2 Ionic conductivity of (a) fluorite, (b) perovskite, and (c) apatite at various temperatures. The conductivities at intermediate temperatures ($\sim 500^\circ\text{C}$) are marked by blue circles [Adapted from Kharton *et al.*⁸⁷].

Table 2-1 Conductivity for selected electrolytes (at 800 °C unless stated).

Electrolytes	Conductivity (Scm^{-1})
<i>Fluorite(zirconia) derivatives</i>	
8 mol% (Y ₂ O ₃)-YSZ ⁸⁸	4.3×10^{-2}
10 mol% (Y ₂ O ₃)-YSZ ⁸⁹	2.0×10^{-2}
10 mol% (CaO)-CaSZ ⁸⁹	9.3×10^{-4}
9 mol% (In ₂ O ₃)-InSZ ⁹¹	9.3×10^{-3}
<i>Perovskite derivatives</i>	
La _{0.9} Sr _{0.1} Ga _{0.8} Mg _{0.2} O _{3-δ} ⁹⁴	1.0×10^{-1}
La _{0.8} Sr _{0.2} Ga _{0.8} Mg _{0.15} Co _{0.05} O _{3-δ} ¹⁰⁰	1.6×10^{-1}
La _{0.9} Sr _{0.1} (Ga _{0.8} Mg _{0.2}) _{0.95} Co _{0.05} O _{3-δ} ¹⁰¹	9.3×10^{-2}
La _{0.9} Sr _{0.1} In _{0.9} Mg _{0.1} O _{3-δ} ¹⁰²	2.0×10^{-3}
<i>Aurivillius phases</i>	
Bi ₂ Sr ₂ Ta ₂ GaO _{11.5} ⁹⁹	9.3×10^{-3}
Bi ₂ Sr ₂ Nb ₂ GaO _{11.5} ⁹⁹	2.0×10^{-2}
Bi ₂ Sr ₂ Nb ₂ AlO _{11.5} ⁹⁹	1.2×10^{-2}
Bi ₂ V _{0.9} Cu _{0.1} O _{5.35} ⁹⁹	5×10^{-2} (500 °C)
Bi ₂ V _{0.9} Co _{0.1} O _{5.35} ⁹⁹	7×10^{-2} (500 °C)
Bi ₂ V _{0.93} Ni _{0.07} O _{5.395} ⁹⁹	1×10^{-1} (500 °C)
<i>Apatite phases</i>	
La _{9.33} (SiO ₄) ₆ O ₂ ¹⁰³	2.0×10^{-3}
La _{9.33} (GeO ₄) ₆ O ₂ ¹⁰³	1.0×10^{-2}
La _{9.5} (GeO ₄) _{5.5} (AlO ₄) _{0.5} O ₂ ⁵³	1.6×10^{-1}
La ₁₀ Si ₆ O ₂₇ ⁷	4.3×10^{-3} (500 °C)
La ₉ BaSi ₆ O _{26.5} ⁶³	6.6×10^{-3} (500 °C)
La ₁₀ Si ₅ GaO _{26.5} ⁶³	2.4×10^{-3} (500 °C)

2.3 Apatite Crystallographic Family

Apatite usually appears as the most common phosphate mineral of composition $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ that refers to hydroxylapatite, fluorapatite and chlorapatite, and a more complete crystallochemical expression in $P6_3/m$ symmetry would be $[\text{Ca}_4][\text{Ca}_6][(\text{PO}_4)_6][\text{OH}, \text{F}, \text{Cl}]_2$ by the unit cell content. Another group of apatite-type minerals are the silicate analogues, while no germanate natural apatites are presently known. Synthetic oxyapatites can be obtained with a high-temperature treatment $> 900^\circ\text{C}$, and the phosphate and silicate hydroxylapatite will dehydrate to form oxyapatite when heated. The phase diagram of Nd_2O_3 – SiO_2 surrounding the apatite $\text{Nd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ composition is shown in Figure 2-3,¹⁰⁴ and it is notable that Nd_2SiO_5 and $\text{Nd}_2\text{Si}_2\text{O}_7$ can co-crystallize for certain temperatures and compositions.

Figure 2-3 Phase diagram of Nd_2O_3 – SiO_2 [Taken from Higuchi *et al.*¹⁰⁴].

2.3.1 Structure and Crystallographic Modification

Apatites are ideally represented as $[\text{A}^{\text{I}}_4][\text{A}^{\text{II}}_6][(\text{BO}_4)_6][\text{X}_2]$ compounds of hexagonal structure with space group $P6_3/m$ (176) (Figure 2-4), where an $\text{A}^{\text{I}}_4(\text{BO}_4)_6$ framework surrounds the $\text{A}^{\text{II}}_6\text{O}_2$ tunnel contents occupying the one-dimensional channels along the c -axis.¹⁰⁵ Crystallographically larger A cations occupy the two

A sites: the 6+3-coordinated A^I position ($4f$, $(1/3, 2/3, z)$ according to Wyckoff notation) in the framework and the 7-coordinated A^{II} site ($6h$ ($x, y, 1/4$)) located near the tunnel periphery, whereas the smaller B cations occupy the $6h$ ($x, y, 1/4$) site that is usually 4-coordinated. It is instructive to describe the framework as a motif of $A^I O_6$ metaprisms that are corner-connected to BO_4 tetrahedra. The bore of this conduit is controlled by (001) twisting of the triangular faces of the metaprisms through an angle φ so that the framework can expand or contract to accommodate the tunnel components. Both the framework and tunnel show varying degrees of nonstoichiometry, and cation vacancies appear to be concentrated on the framework A^I position. The B -site is apparently fully occupied, but the coordination to oxygen is variable with magic-angle spinning (MAS) nuclear magnetic resonance (NMR) and neutron diffraction revealing BO_5 and BO_6 polyhedra in addition to the BO_4 tetrahedra.

Figure 2-4 Polyhedral representation of $[A_4^I][A_6^{II}][(BO_4)_6]X_2$ apatite emphasizing the $A^I O_6$ metaprisms (stripped) and BO_4 tetrahedra (green). (a) The [001] projection that shows the topological relationship between the polyhedra and A^{II} and X tunnel ions. (b) Clinographic projection of a single one-dimensional channel [Adapted from Srinivasan *et al.*¹⁰⁵].

During aliovalent substitution, smaller trivalent ions will partition to the A^I site while larger ions will show a disposition for the A^{II} site. The volume of the framework $A^I O_6$ metaprism is less than the channel $A^{II} O_7$ capped prisms, as for example, $La^I O_6$ and $La^{II} O_7$ in $La_{10}(GeO_4)_5(GeO_5)O_2$. Therefore, a smaller rare

earth (e.g. Sm^{3+}) will preferentially displace La^{3+} in the framework as $[\text{La}_{4-x}\text{Sm}_x][\text{La}^{\text{II}}_6][(\text{BO}_4)_5(\text{BO}_5)][\text{O}_2]$. This reduces the framework dimensions, and so, the metaprism twist angle becomes smaller, in turn promoting hexagonal symmetry which enhances ionic conductivity. During altrivalent substitutions, monovalent and divalent A ions will preferentially partition to the framework A^{I} site, while trivalent and tetravalent ions will be concentrated in the tunnel A^{II} site irrespective of size. Because higher valence ions will always attempt to distribute charge widely through maximizing co-ordination number, such ions will invariably occupy the tunnel positions before filling the framework. For example in $[(\text{La}_2\text{Sr}_2)][\text{La}_6][(\text{GeO}_4)_6][\text{O}_2]$ larger Sr^{2+} (ionic radius = 1.18 Å) partitions to the small framework metaprism, while the smaller (ionic radius = 1.03 Å), but more highly charged La^{3+} enters the tunnel. Vacancies are confined to the A^{I} site (cation vacancies) and the X position (anion vacancies), while the A^{II} and B sites are fully occupied. Much attention has been paid to the occurrence of cation vacancies in apatite, and in electrolytes, high ionic conductivity occurs in $[\text{La}_{0.833}^{\text{I}}]_4[\text{La}^{\text{II}}]_6(\text{SiO}_4)_6\text{O}_2$. In fact, an analogous compound $\text{Nb}_2(\text{PO}_4)_2 \equiv \text{Nb}_6(\text{PO}_4)_6$ can be described as an apatite framework in which 50% of the A^{I} sites are vacant, suggesting that such absences are energetically favored.

The $A^{\text{I}}\text{O}_6$ metaprism twist angle ϕ is a key apatite variable such that the tunnel volume can be fine-tuned to accommodate different contents,⁵¹ either in terms of ionic size or occupancy. Larger rotations constrict the tunnel when either the size or abundance of the A^{II} and X atoms decreases and vice versa. To discuss in another way, by adjusting the oxygen positions and abundance when X = oxygen, larger twist angles can be indicative of the introduction of extra-stoichiometric oxygen in the framework, whereas smaller twist angles might suggest incorporation of interstitial tunnel oxygen. The experimentally derived ϕ can be correlated with unit cell parameters as well as possible structural symmetry changes. Apatites metrically distort from hexagonal at larger metaprism twist angles ($> 24\text{-}25^\circ$) in order to maintain acceptable bond valence sum limits,¹⁰⁶⁻¹⁰⁷ and this reduces the symmetry from $P6_3/m$ to monoclinic $P2_1/m$ or triclinic $P-1$ with a diminution of oxygen mobility as the transport pathways become more tortuous.¹⁰⁵

2.3.2 Extended Apatite Family

The compositions of most apatite chemical end-members can be generalized as $A_{10}(BO_4)_6X_2$ as detailed in section 2.3.1. However, this genus is not the only representative of the apatite family as the framework is exceedingly adaptive. White *et al.* classified apatites in a taxonomy containing three genera: $A_{10}(BO_3)_6X_2$, $A_{10}(BO_4)_6X_2$, $A_{10}(BO_5)_6X_2$ (Figure 2-5),¹⁰⁸ where A and B are larger and smaller cations and X are anions.

The different genera are crystallographically distinguished by the different polyhedron (BO_3 , BO_4 or BO_5) contained in the framework, and chemically they are differentiated through the varying oxidation state of the cations required for charge balance. All three apatite genera are hettotypes derived from $P6_3/mcm$ Mn_5Si_3 alloy type.¹⁰⁹ With the descent of anion-stuffed derivatives from this common structural type, it is possible to predicate feasible stoichiometries of apatites and chemically tailor their functionality. Moreover, there is in principle no impediment to the creation of apatite hybrids that contain mixtures of BO_3 , BO_4 , and BO_5 framework elements, as only the oxygen sub-structure is modified without disturbing the cation array.

Of these genera, only the $A_{10}(BO_4)_6X_2$ apatites, and their non-stoichiometric derivatives, have been examined as electrolytes. However, $A_{10}(BO_3/BO_4/BO_5)_6X_2$ hybrids may exhibit superior low temperature ion conduction, mediated by super-stoichiometric oxygen or metal vacancies in the framework.

Figure 2-5 An apatite taxonomy with the frameworks divided into three genera: neutral apatites containing only (BO_4) tetrahedra; reduced apatites made up of (BO_3) units; and oxidized apatites with (BO_5) polyhedra. Hybrid apatites with $BO_3/BO_4/BO_5$ provide a means for crystallochemically tailoring functionality [Taken from Pramana *et al.*¹⁰⁸].

2.4 Doping Strategies for Apatite-type Electrolytes

Stoichiometric apatite-type oxide-ion conductors, crystallochemically described as $A^I_4A^{II}_6(BO_4)_6O_2$, do not show superior ion-conducting performance as there are no interstitial and vacancy defects that could facilitate ion migrations. Various doping strategies can be applied in order to synthesize non-stoichiometric apatites with interstitials or vacancies. Moreover, it is essential that the tunnel anion is O^{2-} , rather than OH^- or a vacancy, for significant ion mobility.

A summary of the possible compositions of apatite-type electrolytes ($X = O$) is provided in Table 2-2. While some of the apatite genera (e.g. $[La]_{10}[(SiO_4)_4(AlO_4)_2]O_2$) have been studied previously, it will be prudent to re-

examine these materials specifically to search for high concentrations of ‘interstitial’ oxygen.

Table 2-2 Possible Compositions of Apatite-type Electrolytes.

FRAMEWORK TAXONOMY	COMPOSITION		
	A-CATIONS	B-CATIONS	TYPICAL FORMULA
GENERA			
$A_{10}(BO_3)_6O_2$	Pb^{2+}, Bi^{3+}	As^{3+}, Sb^{5+}	$[Pb_8Bi_2][(AsO_3)_6]O_2$
$A_{10}(BO_4)_6O_2$	La^{3+}, Na^+, Sr^{2+}	$Al^{3+}, Fe^{3+}, Si^{4+}$	$[La]_{10}[(SiO_4)_4(AlO_4)_2]O_2$
$A_{10}(BO_5)_6O_2$	$La^{3+}, Ba^{2+}, Sr^{2+}$	Re^{7+}, Mn^{7+}	$[La_2Ba_8][(ReO_5)_6]O_2$
HYBRIDS			
$A_{10}(BO_3/BO_4)_6O_2$	La^{3+}, Ca^{2+}	Si^{4+}, C^{4+}	$[La_6Ca_4][[(CO_3)(SiO_4)_5]O_2$
$A_{10}(BO_4/BO_5)_6O_2$	$La^{3+}, Ca^{2+}, Ba^{2+}$	$Ge^{4+}, Re^{7+}, Mn^{7+}$	$[La_9Ba_1][[(GeO_4)_4(ReO_5)(GeO_5)]O_2$
$A_{10}(BO_3/BO_5)_6O_2$	La^{3+}, Ba^{2+}	B^{3+}, Re^{7+}, Mn^{7+}	$[La_2Ba_8][(ReO_5)_5(BO_3)]O_2$

2.5 Conduction Mechanisms in Apatite

In the development of new oxygen ion conductors, rare earth apatite materials have attracted considerable interest for their higher ionic conductivities at moderate temperatures as compared with conventional electrolytes. Apatite-type oxides taking the general formula $A_{10-\delta}(BO_4)_6X_{2\pm y}$, can accommodate a number of stoichiometries including anion/cation-deficient and anion-excess compositions. Reports have shown that the cation-deficient and anion-excess materials exhibit much higher conductivity than fully stoichiometric compositions, with the best performance found for the oxygen-excess lanthanum based silicates and germanates.³⁴

Tolchard *et al.* (2003)⁶⁸ carried out a series of calculations, atomistic modeling and NMR studies on two types of apatites: $La_8Sr_2Si_6O_{26}$ and $La_{9.33}Si_6O_{26}$, in order to investigate the oxide ion transport mechanism. Based on the fact that ionic

conduction is aided by intrinsic atomic defects, calculation of formation energies for various types of defects on different atomic sites were performed, including isolated point defects (vacancies and interstitials), Frenkel and Schottky-type disorder. It was found that the most favorable oxygen vacancy site is the channel center position, whereas the preferred oxygen interstitial site, rather than being located within the channel as initially thought, is accommodated at the channel periphery close to the framework wall (Figure 2-6).¹¹⁰ This oxide interstitial position is stabilized by the displacement of the nearby silicate tetrahedron towards the La channels, accounting for the high thermal displacement parameters observed for the silicate oxygen atoms.

Figure 2-6 The interstitial oxygen site at the periphery of the channels and surrounding lattice relaxation [Reproduced from Kendrick *et al.*¹¹⁰].

Atomistic simulations examined possible conduction models including both vacancy and interstitial migration. The results suggested that conduction for the fully stoichiometric apatite ($\text{La}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$) was via a vacancy mechanism, in which the migration route was predicted to be a linear path with saddle-points mid-way between the channel centre positions. Since poor ionic conductivity and high activation energy were observed for this type of conduction, it will not be discussed further in detail. On the other hand, a cation-deficient ($\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) or oxygen-excess apatite yielded high conductivity with an interstitial conduction mechanism.⁶⁸ Interstitial oxygen migration proceeds via a non-linear (sinusoidal-like) pathway along the c-axis channel, as shown in Figure 2-7.¹¹⁰ The saddle-point is away from the channel centre, and at the location where the interstitial

anion needs to pass by a channel oxygen atom, the pathway site lies close to the channel periphery position. Furthermore, this route involves migration across the face of a tetrahedral unit coupled with local relaxation (displacements away from the channel) around it.

Figure 2-7 Interstitial oxide-ion migration pathway in $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ from atomistic simulation studies; (a) view down the c axis; (b) view perpendicular to the c axis [Reproduced from Kendrick *et al.*¹¹⁰].

Previous studies have shown that the conductivity is anisotropic and parallel to the channel direction. In single crystal studies, it was found that besides intra-tunnel conduction, there is also significant conduction perpendicular to the channels.^{17, 21, 111} As shown in Figure 2-8, transfer of interstitial O^{2-} between channels is facilitated by the rotation of two isolated SiO_4 tetrahedra in the framework to form a Si_2O_9 unit.

For the oxygen excess series $\text{La}_{9.33+x}(\text{Si/Ge})_6\text{O}_{26+3x/2}$ with ample interstitial oxide-ions, higher conductivity is realized by interstitial aided ion migration.^{110, 112-113} It has been found that germanate apatites are predisposed to contain interstitial sites compared to silicates,^{21, 71, 110} and thus, can accommodate higher oxygen excess compositions. For the hyperstoichiometric germanate $\text{La}_{10}(\text{GeO}_4)_6\text{O}_3$, the framework interstitial oxygen provide a reservoir of ions that can migrate into the conducting channels, via a mechanism of inter-tunnel oxygen diffusion that transiently converts GeO_4 tetrahedra to GeO_5 distorted trigonal bipyramids.^{21, 111}

Figure 2-8 Proposed conduction pathway between adjacent oxide-ion channels obtained from computer simulation results of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The incorporation of a periphery interstitial oxide-ion (yellow) (a) forces a silicate oxygen (orange) in between the two SiO_4 units forming an Si_2O_9 unit (b), the top silicate unit rotates to form an Si_2O_9 unit with a neighboring silicate unit (c), and an oxygen on the top silicate unit (green) is released as an interstitial in a different channel (d) [Reproduced from Kendrick *et al.*¹¹⁰].

2.6 Conclusion: Optimization of Structure, Functionality and Performance

Rare-earth silicates and germanates adopting the apatite-type structure have attracted widespread interest as electrolytes for SOFCs, as they are superior ionic conductors compared to YSZ at moderate temperatures ($< 800\text{ }^\circ\text{C}$). The general formula for electrolyte oxyapatite is $[\text{A}^{\text{I}}_4][\text{A}^{\text{II}}_6][(\text{BO}_4)_6]\text{O}_2$, where A are rare-earths or alkaline-earths and B is Si or Ge. High degrees of structural and compositional flexibility allow the possibility of designing new hybrid apatite electrolytes. A wide range of chemical substitutions and non-stoichiometry (cation vacancies and/or oxygen excess) can be adjusted to modify ion migration and electrical properties.

This thesis is concerned with tuning oxygen mobility by controlling the metaprisism twist angle and introducing altrivalent cation substitutions that favor oxygen interstitial and metal vacancy formation. The crystallochemical manipulations employed in these studies to enhance electrolyte performance include:

- (i) adjusting the size of the apatite framework, relative to the tunnel, to give acute metaprism twist angles that open intra-tunnel conduction pathways;
- (ii) exploiting counter-ion substitutions, to accommodate extrastochiometric oxygen in the framework reservoir, that in turn, reduces activation energy and introduces more mobile oxygen; and
- (iii) stabilizing *A* cation vacancies in tandem with increasing the concentration of framework oxygen to maximize inter-tunnel conduction.

These three mechanisms will operate co-operatively. By recognizing these fundamental concepts, strategies for creating structures that deliver optimal performance can be devised.

Chapter 3

Research Methodologies

This investigation of new apatite electrolyte materials follows a standard procedure of synthesis, characterization and property measurement. Distinct preparative routes were adopted to synthesize different apatite analogues. Various characterization techniques were deployed for crystallochemical investigations. The functionality was explored by ionic conductivity measurements.

3.1 Precepts

This investigation of new apatite electrolyte materials follows a standard procedure of synthesis, characterization and property measurement. Distinct preparative routes were adopted to synthesize different analogues of apatite materials in the form of powders or large single crystals. Several structure characterization techniques involving laboratory and synchrotron X-ray and neutron diffraction were deployed and the data analysed by Rietveld methods. In addition, electron microscopy and spectroscopic techniques were selectively applied as complementary probes to obtain a thorough understanding of the structure and chemistry of each solid solution series. Finally, to explore functionality, the ionic conductivity of the electrolytes was measured over a range of temperatures. This Chapter provides a general description of the methods and techniques employed in this research, with specific operational aspects and parameters used for particular chemical analogues provided in the following chapters.

3.2 Synthesis Methods

Conventionally, apatite electrolyte materials are synthesized in powder form through solid state sintering, where the starting reactants are mixed and calcined at a high temperature ($>1000\text{ }^{\circ}\text{C}$). This route is appropriate, as in general, volatilization of the components is insignificant, but usually, repeated grinding and firing cycles are required to ensure good yields. Alternatively, sol gel and hydrothermal methods are feasible and yield nano-crystalline powders *via* low temperature reactions, where the precursor materials are salts soluble in aqueous alkaline or acidic media. Compared to traditional solid state chemistry, soft chemistry techniques possess the merits of reduced synthesis temperature, shortened reaction time, and/or improved phase purity, yet the finely divided and small crystallite size of the apatite products may cause detailed crystallographic

analyses to be challenging. The majority of published studies are based on powdered apatites, but the value of large apatite crystals is considerable, as those allow more precise and detailed crystallochemical information to be extracted and anisotropic features and physical properties to be examined. In this thesis, solid state and hydrothermal methods were employed for powdered apatite syntheses, and the growth of large centimeter-sized crystals having critical compositions was achieved using the floating zone method.

3.2.1 Solid State Reaction

The starting materials for solid state synthesis were oxides and carbonates that were dehydrated by pre-heating. The powdered reactants were mixed in stoichiometric quantities, ground together homogeneously, and then fired at high temperatures (≥ 1200 °C). Repeated grinding and compaction was needed to obtain homogeneous products and remove persistent intermediate phases to yield phase pure products. For single crystal growth, solid state synthesis was performed initially to obtain compact rods of polycrystalline apatites that were used as feed for floating zone growth.

3.2.2 Hydrothermal synthesis

The starting reactants were separately dissolved in de-ionized (DI) water to form clear stock solutions that were then mixed together with stirring to form a homogeneous gel. An alkali solution (sodium hydroxide) was required to dissolve oxides that were sparingly soluble in water and maintain a strong basic pH environment. The mixture was sealed in a Teflon-lined stainless steel autoclave before heat treatment in an oven (180 – 240 °C / 3 h – 60 days). The product was finally centrifuged, washed with DI water and dried.

3.2.3 Single Crystal Growth

Single crystals of electrolyte apatites were obtained by a floating-zone mirror furnace. In these experiments, the growth process begins by preparing

polycrystalline feed rods through cold isostatic pressing of powdered apatite followed by sintering at high temperature (~ 1650 °C/20 h). One rod is mounted on the top rotator and another rod (sometimes called the seed rod) of the same composition (either polycrystalline or single crystal) is mounted below. At the start of growth process, a set of four halogen lamps have their radiation focused to melt the tip of the feed rod, before bringing it into contact with the lower rod and slowly solidifying. The mirror stage continues moving upwards slowly (~ 1 – 20 mm/h), and at the same time, the two rods are rotated in opposite directions during the growth process. As the mirror stage shifts upwards, so does the molten zone, and during this slow solidification process, the grains become progressively larger until a large single crystal eventually forms.

3.3 Structural Characterization Methods

The crystal structure of a material fundamentally determines its properties, and determining atomic arrangements is a basic requirement for designing functional materials. A comprehensive characterization methodology of SOFC apatite electrolytes should include: (a) quantitative phase analysis to confirm there is only apatite, as secondary phases may detract from performance; (b) quantitative elemental analysis to verify the concentration of dopants and vacancies in a formula unit; (c) recognition of topological distortions and appearance of polymorphs as a function of composition or temperature; (d) location of interstitial oxygen and metal vacancies that control the mechanism of ion conduction; and (e) the correlation of crystal chemical properties with ion flux and activation energy for migration. In order to extract this information, a suite of tools are required including diffraction, electron microscopy and spectroscopic methods. These techniques can probe the electrolyte structurally and chemically from atomic to micron scales, and taken in combination, a more complete description of the apatite electrolyte can be obtained more effectively.

3.3.1 Diffraction Techniques

3.3.1.1 Laboratory Powder X-ray Diffraction (PXRD)

Laboratory PXRD patterns were collected on a Bruker D8 Advance diffractometer fitted with a LynxEye silicon strip detector and a Cu X-ray tube operated at 40 kV and 40 mA. The samples were mounted in a top-loaded holder and data accumulated from CuK_α radiation ($\lambda_{\text{av}} = 1.54056 \text{ \AA}$) using a Bragg-Brentano ($\theta - 2\theta$) geometry. A step-scan was adopted over a 2θ range $10 - 130^\circ$ at intervals of 0.02° with a counting time of 1s per step. As a readily available and simple technique, PXRD was the primary characterization tool and is suitable for phase analysis and extraction of crystallographic information. However, a limitation of X-ray diffraction arises from the difficulty in acquiring low atomic number (Z) information, especially when both heavy and light elements are present because the weak interaction with light atoms (oxygen in the present context) would be masked by strong X-ray scattering from the heavy atoms. In addition, the angular dependence of X-ray scattering results in limited intensity at high diffraction angles, yet this region contains information for determining anisotropic atomic displacements (ADP) and crystal site occupancy factors. Overall, PXRD delivers accurate unit cell parameters for apatite materials, but the geometry of oxygen sublattice, which controls ionic conductivity, cannot be extracted with high reliability.

3.3.1.2 Single Crystal X-ray Diffraction

Because single crystal X-ray diffraction avoids the convolution of Bragg reflections it is more information rich compared to powder diffraction. Single-crystal fragments ($0.1 \text{ mm} \times 0.08 \text{ mm} \times 0.15 \text{ mm}$) were cleaved from the as-grown and annealed crystal rods. The crystals were mounted on a glass fiber and data collected using a Bruker Smart Apex II three-circle diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda_{\text{av}} = 0.71073 \text{ \AA}$) over the angular range $5 - 65^\circ$ 2θ , with an exposure time of 60 s/deg to give a total collection time of $\sim 15 \text{ h}$. SmartApex II software was used for reflection integration, Lorentz polarisation and multi-scan absorption corrections.

3.3.1.3 Powder Neutron Diffraction

Neutron diffraction is used in conjunction with electron and X-ray diffraction to provide a more complete description of the crystallographic structure. While X-rays interact with the electron density surrounding the atoms, neutrons scatter from the nuclei with the strength of the interaction being isotope dependent. For apatite electrolytes, neutron methods are highly reliable as the neutron scattering length of oxygen is large and the location of oxygen atoms and the distortion of polyhedra can be detected with greater confidence. Neutron powder diffraction data were gathered using the Echidna (high resolution powder diffractometer) beamline at Australian Nuclear Science and Technology Organization (ANSTO), Sydney, Australia, drawing neutrons from the Open Pool Australian Lightwater (OPAL) reactor. A Ge (335) monochromator with 140° take-off angle yielded a neutron wavelength of $1.622 \text{ \AA}$. Samples were contained in vanadium cans (10 mm in diameter) and detected at ambient temperature over the range of $4 - 164^\circ 2\theta$ with a step size of 0.05° for 3 h. By introducing an internal standard (CaF_2) spiked to 20 weight percent (wt.%), the amorphous content of the sample can be estimated.

3.3.1.4 Single Crystal Neutron Diffraction

Neutron diffraction is the application of elastic neutron scattering for the determination of the atomic structure. A major difference from X-rays is that the scattering is mostly due to the nuclei of the atoms. Therefore, it gives information about the nuclei position rather than the shape of electron density. White neutron radiation (wavelength peaked as $1.3 \text{ \AA}$) on the Laue diffractometer KOALA at ANSTO was applied for the diffraction experiments for apatite crystals ($> 0.1 \text{ mm}^3$). Liquid helium cooling of the sample allowed data collection down to 4 K. In the Laue method, the crystal is exposed to a very broad spectrum of wavelengths, and a large area imaging plate is used to record the arrangement of diffraction spots. Approximately one day is required for the measurement of a single sample at a specific temperature.

3.3.1.5 Synchrotron Powder X-ray Diffraction

For conventional laboratory-based X-ray source and neutron powder diffraction, intrinsic limitations such as broad peaks, overlapping reflections and low reflection intensity can degrade the accuracy of extracted lattice parameters, and determination of site occupancy factors for elements that have relatively similar X-ray scattering factors or neutron scattering lengths is troublesome. These limitations can be partially overcome by using the high intensity radiation and monochromatic illumination produced by a synchrotron. High resolution synchrotron powder X-ray diffraction patterns were collected at room temperature using the Powder Diffraction Beamline at the Australian Synchrotron Light Source fitted with a Si (111) double crystal monochromator. A wavelength of 0.61885 Å (20.0349 keV) was selected to avoid absorption edges and secondary fluorescence, and probe a large volume of reciprocal space. The apatites were mixed with 20 wt.% CaF₂ as an internal calibrant of peak position and intensity ($a = 5.47093$ Å, space group $Fm\bar{3}m$), and loaded into 0.3 mm diameter low X-ray absorption soda lime glass capillaries that were rotated during the experiment. Patterns were accumulated at a 0.00375° step size over the angular range 5-66.6° 2θ .

3.3.2 Rietveld Refinement

Rietveld refinement¹¹⁴⁻¹¹⁵ is a whole pattern algorithm that calculates the entire powder pattern using a variety of refinable parameters. The position and intensities of the peaks from the calculated diffraction profile are fitted to the experimental data set. The calculated intensity $y_i(calc)$ at any arbitrarily chosen point, i , in the pattern is

$$y_i(calc) = s \cdot \sum_K |F_K(calc)|^2 L_K \phi(2\theta_i - 2\theta_K) P_K A + B_i(obs) \quad (3-1)$$

which includes the contributions from all Bragg reflections K , with the scale factor s , the square absolute value of the structure factor for the K th Bragg reflection $|F_K(calc)|^2$, the Lorentz polarization and multiplicity factors represented by L_K , the

absorption correction A , the preferred orientation function P_K , the reflection profile function ϕ and the background contribution $B_i(obs)$ at i th step. The calculated intensity for a mixture of phases would be the summation of the reflections from every phase present in addition to the background intensity. The weighted sum of the squared differences between the observed and calculated powder pattern is

$$\sum_i w_i (y_i(obs) - y_i(calc))^2; w_i = \frac{1}{\sigma^2(y_i(obs))} \quad (3-2)$$

where $\sigma(y_i(obs))$ is the standard deviation in $y_i(obs)$.

With a reliable starting model, this method minimizes the differences between the calculated and experimental data through variation of instrumental and crystallographic parameters to arrive at a structure refinement. Besides, constraints and restraints can be applied to these parameters that may converge to unreliable values at false minima in the least square refinement. Many different statistical agreement factors or criteria-of-fit are used to assess the Rietveld refinement quality such as:

$$R_p = \frac{\sum_i |y_i(obs) - y_i(calc)|}{\sum_i y_i(obs)} \quad (3-3)$$

$$R_{wp} = \sqrt{\frac{\sum_i w_i (y_i(obs) - y_i(calc))^2}{\sum_i w_i y_i(obs)^2}} \quad (3-4)$$

$$R_{exp} = \sqrt{\frac{\sum M - P}{\sum_i w_i y_i(obs)^2}} \quad (3-5)$$

$$GOF = \chi^2 = \frac{R_{wp}}{R_{exp}} \quad (3-6)$$

$$R_B = \frac{\sum_k |I_k(obs) - I_k(calc)|}{\sum_k I_k(obs)} \quad (3-7)$$

where M is the number of data points, P is the number of parameters, $I_k(obs)$ and $I_k(calc)$ are the observed and calculated intensities of the k^{th} reflection.¹¹⁴⁻¹¹⁵ Moreover, certain of the parameters (p) should be refined simultaneously as they are strongly correlated and can converge to non-physical values (e.g., zero shift correction and specimen displace correct). Here, the Rietveld methodology as

implemented in the programs TOPAS¹¹⁶⁻¹¹⁷ and JANA¹¹⁸ were employed for evaluating powder X-ray and neutron diffraction patterns.

3.3.2.1 TOPAS

The starting refinement model of germanate and silicate apatite used the atomic positions of $P6_3/m$ $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$.²⁰ The fundamental parameters or pseudo-Voigt peak-shape profile as implemented in TOPAS and corresponding X-ray form factor or neutron scattering lengths were used. The instrumental parameters are fixed during the crystallographic refinement. For each data set, a four-coefficient Chebychev polynomial and $1/x$ profile background, zero error, scale factors, lattice dimensions and crystal size were refined sequentially, followed by site occupancies, atom positions and isotropic/anisotropic ADPs for all atoms.

3.3.2.2 JANA

The basic principle for JANA data extraction is similar to TOPAS with a “profile fit” performed before structural refinement. An additional feature for JANA refinement is the generation of Fourier maps: JANA used to create 2D sections of Fourier difference maps to identify structural disorder, and VESTA¹¹⁹ allowed visualisation of the difference Fourier maps in three dimensions. For instance, a site is “split” when positive electron density is concentrated about a high symmetry lattice position in the difference Fourier map. In these cases, the structure may be better described by lower symmetry or as a superstructure. Negative electron density, on the other hand, indicates anomalously high scattering, and therefore, site chemistry adjusted with lower atomic number species or reduced occupancy.

3.3.3 Scanning Electron Microscopy (SEM)

Secondary electron images (SEI) and backscattered electron images (BEI) were collected using two types of scanning electron microscopes: a JEOL JSM 6400 and a JEOL JSM 7600F. Energy dispersive X-ray spectroscopy (EDX/EDS) point analysis and mapping were used to correlate microstructure and chemistry. The

quantitative analyses were carried out at 15kV and 1nA using a JEOL JSM 6400 SEM optimized for quantitative chemical analysis and equipped with an Oxford Instruments light element energy dispersive spectrometer and Link ISIS SEMquant software. Suplementarily, electron probe microanalysis (EPMA) was performed for selected samples on a JEOL JXA-8530F equipped with five wavelength dispersive spectrometers (WDS), and a Zeiss UltraPlus Field Emission Scanning Electron Microscope (FESEM) equipped with an HKL electron backscatter diffraction (EBSD) system was used to examine the crystal texture. To examine crystal/grain morphology, the powdered samples were platinum sputter coated before fixing with double sided carbon tape to an aluminum or brass sample holder. For quantitative analysis and observations of phase contrast from compositionally distinct regions, the samples were embedded in thermal epoxy resin disks (diameter 25 mm and thickness 5 mm), mirror-polished ($< 1\ \mu\text{m}$ finish) and carbon coated for quantitative analyses.

3.3.4 Transmission Electron Microscopy (TEM)

High-resolution (HR) images and selected area electron diffraction (SAED) patterns were collected using a JEOL JEM-2010 and 2100F TEM operating at 200keV. High resolution TEM (HRTEM) was employed to study atomic scale structural disorder of thin ($< 10\ \text{nm}$) crystals and is extremely beneficial for examining nano-sized particles or crystallographic domains. Electron diffraction can establish the space group of materials, or at least exclude non-conforming symmetries. Compared to X-ray and neutron diffraction that examine the average structure, the high coherence of the electron beam and small probe diameter make it able to detect superlattice formation. In the present work, the apatites were finely ground under ethanol, then ultrasonically dispersed for ~10 mins. Several drops of the suspension were deposited on a holey carbon film supported by a copper grid that was dried before introduction to the microscope.

3.4 Physical Property Measurements

3.4.1 Raman and Fourier transform infrared spectroscopy

The Raman spectra were collected in a WITec CRM200 confocal Raman microscopy system (laser wavelength 488 nm and spot size $\sim 0.5\ \mu\text{m}$), with the Si band at $520\ \text{cm}^{-1}$ used for wavenumber calibration. Fourier transform infrared (FTIR) spectroscopy measures the molecular absorption and transmission characteristics of a material when exposed to infrared radiation. In this manner, resonant frequencies associated with rotation or vibration are easily detected. In this study, distinguishing oxyapatite from hydroxyapatite is essential for confirmation of the mobile carrier type, especially for hydrothermally synthesized apatites. FTIR spectra were gathered at room temperature from 400 and $4000\ \text{cm}^{-1}$ using a Perkin Elmer (Spectrum 2000) spectrophotometer with a spectral resolution of $4\ \text{cm}^{-1}$. Translucent pellets were prepared by mixing and pelletising apatite powder with oven-dried ($120\ ^\circ\text{C}$) potassium bromide (KBr).

3.4.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was conducted using a Mettler Toledo TGA/SDTA851 to monitor loss of water (proton content) and volatiles. Powders (60 mg) were placed in an alumina crucible and heated under flowing air at a heating rate of $10\ ^\circ\text{C}/\text{min}$ from room temperature to $1000\ ^\circ\text{C}$.

3.4.3 Impedance spectroscopy

Impedance is a measure of the ability of a circuit to resist the flow of electrical current. In electrochemical devices (cells), the measurement of ionic conductivity is based on studies made on the measurement of cell alternating current (AC) impedance over a range of temperatures and frequencies. The complex impedance Z , which is the sum of resistance and reactance, can be written as

$$Z = Z' + iZ'' \quad (3-8)$$

where Z' is the real part and Z'' the imaginary part of Z . The function is plotted in the complex plane that is known as Nyquist diagrams (Figure 3-1 a), where low frequency data are on the right side of the plot and higher frequencies are on the left. The simple equivalent circuit is a parallel connection of resistor and capacitor as shown in Figure 3-1 b. Different contributors (i.e. bulk, grain boundary and electrode) to the total conductivity can be distinguished however in the case when impedance is measured from pressed polycrystalline pellets, resolution and quantification of bulk and grain boundary conductivity may be difficult.

Figure 3-1 Nyquist plot and the simple equivalent circuit.

Conventionally sintered pellets that are not fully dense will lead to a deterioration of ionic conductivity. Spark plasma sintering can be used to produce pellets of near theoretical density, yet the smaller grain size produces more severe grain boundary effects. Additionally in apatites where the structure is inherently anisotropic, maximum conductivity is assumed to take place along the c -axis. Single crystal measurements are thus essential to eliminate the effects of grain boundary resistance and access the anisotropic conductivities, but this can only be validated with large crystals. In general, the activation energy for the powder bulk response will be similar to a single crystal only for isotropic conductors.

In this study, conventional compact pellets of polycrystalline samples (10 mm diameter) were prepared as follows: the apatite powders were mixed with binder (isopropyl alcohol with 3% polyvinyl butyral), pelletised (300 bar) uniaxially, and sintered at 1500 °C for six hours. Both sides of the pellets were coated with Au paste and then heated to 750 °C to ensure bonding to the pellet. For comparison, spark plasma sintering (SPS),¹²⁰⁻¹²² a hot-pressing technique with a high heating

rate, was applied to fabricate dense ($> 95\%$ theoretical density (TD)) polycrystalline pellets using a Dr Sinter SPS-825 (SPS Syntex Inc., Japan) apparatus. Apatite powders were loaded in a $\varnothing$ 20 mm graphite die set and uniaxially pressed at a constant pressure of 50 MPa during the entire process. The temperature was first ramped to 600 °C at a rate of 150 °C/min, and then to 850 °C at a rate of 100 °C/min. After this rapid heating, the temperature was slowly raised to 950 °C in 3 min, with increment of 50 °C, 30 °C and 20 °C in each respective minute. The sample was pressed for 5 min at this temperature for the sintering to complete, after which both pressure and heating power were released for the samples to cool naturally. Finally, the materials were burnt in air at 850 °C for 2 h to remove residual carbon. The ionic conductivity was evaluated by AC impedance spectroscopy (Hewlett Packard 4182A impedance analyzer), with measurements taken in air at an applied voltage 0.1 V over a frequency range of 100 Hz – 10 MHz from 300 to 800 °C. For single crystals, discs were cut from the as-grown crystal rods with approximate dimensions $5 \times 5 \times 3$ mm. Opposing faces of the discs were coated with gold paste and then heated at 700 °C for 1 h to ensure bonding. Conductivity measurements were made in air from 370 °C to 860 °C using AC impedance spectroscopy (frequency range 10 Hz to 13 MHz, applied voltage of 0.1 V).

3.5 Integrated Synthesis and Characterization

A primary objective of this study was to establish unequivocal relationships between structure and functionality. In this work, polycrystalline apatites were usually prepared by solid-state sintering or hydrothermally, and single crystal apatites were obtained by floating zone growth. The synthesis parameters for various chemical analogues will be examined systematically in the following Chapters. Various diffraction techniques including X-ray, synchrotron and neutron were applied for the materials characterization, while Raman, FTIR and TGA spectroscopy, and HRTEM provide more direct information of the local atomic arrangement and coordination. Care was taken to ensure that the data interpretation

was consistent with X-ray and neutron diffraction that average rather large volumes.

Impedance testing of oxide ion conductivity was introduced to establish clear linkages between materials processing, crystal chemistry and functionality. However, as measurements from single crystals showed, additional effects result in polycrystalline ceramics due to the presence of secondary phases, grain boundaries, pores, and chemical heterogeneity. Therefore, it is challenging to reduce this complexity and deconvolute the combined influences to relate ion mobility solely to the crystal structure. Nonetheless, this research has used multiple experimental methods to obtain a self-consistent description of the electrolytes studied. In this way, examination of the apatite electrolytes over a range of scales (nm to cm) suggest the extracted properties can be considered reliable, and used to guide to electrolyte design and synthesis.

Chapter 4

Vanadium Doped Alkaline Earth Lanthanum Germanate Oxyapatite Electrolyte*

The crystal chemistry and oxygen conductivity of vanadium-doped apatites of nominal composition $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$; $0 \leq x \leq 1.5$) were studied to establish their potential as intermediate temperature SOFC electrolytes. Single-phase products obtained for $x \leq 0.5$ were found, using a combination of powder synchrotron X-ray and neutron diffraction, to be $P6_3/m$ apatites. The ionic conductivities extracted by complex impedance spectroscopy showed that small vanadium amendments enhanced oxygen mobility at intermediate temperatures (500 – 700 °C) by more than one order of magnitude. Crystal chemistry systematics demonstrate that the Ca-apatite was superior because the relatively small framework expanded through $(\text{La}/\text{AE})\text{O}_6$ metaprism twisting that widened the tunnel, ensuring $P6_3/m$ symmetry was adopted, which favours the passage of O^{2-} with lower activation energy.

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4.1 Introduction

As introduced in the Chapter 2 Literature Review, high oxide ion mobility at intermediate temperatures (500 – 700 °C) has been observed in non-stoichiometric $[A^I_4][A^{II}_6][(BO_4)_6]O_2$ apatite-type rare earth silicates by Nakayama *et al.*,⁶⁻⁸ triggering ongoing investigation of the synthesis, structure, and conductivity of these materials. Contrary to the traditional fluorite-type or perovskite-type oxides, where oxide ions are transported via a vacancy mechanism achieved through specific cation doping,⁸⁷ migration in apatite-type silicates/germanates, prototypically $La_{9.33}(Si/Ge)_6O_{26}$, is often mediated by the creation of oxygen interstitials.^{9, 68-69, 123-124} Apatites contain several cation acceptor sites leading to a wide range of substitutional possibilities³⁴ with ion mobility modified by varying cation type and proportions. Extensive studies of the factors influencing electrolyte performance have appeared, which show that cation-deficient or oxygen excess systems deliver higher conductivity than stoichiometric compositions. Specifically, penta-valent element doping can be used to inject superstoichiometric oxygen as attempted in vanadium doped silicate apatites.^{63, 125-126} Here, we targeted vanadium-substituted germanate oxyapatites with fully occupied cation sites $[La_8AE_2][Ge_{6-x}V_x]O_{26+x/2}$ ($AE = Ca, Sr, Ba; 0 \leq x \leq 1.5$) to assess the impact of a high-valency ion (V^{5+}) on functionality, search for interstitial oxygen, and identify those factors which enhance electrolyte conductivity.

4.2 Experimental methods

4.2.1 Synthesis

Powdered apatites of nominal composition $[La_8AE_2][Ge_{6-x}V_x]O_{26+x/2}$ ($AE = Ca, Sr, Ba; 0 \leq x \leq 1.5$) were prepared by solid-state synthesis using stoichiometric quantities of oxides and carbonates: La_2O_3 (Aldrich, 99.9%), GeO_2 (Alfa, 99.999%), $SrCO_3$ (BDH, 98.5%), $BaCO_3$ (Fluka, 98.5%), $CaCO_3$ (Kanto, 99.5%),

and V_2O_5 (Fluka, 98%). Lanthanum oxide was pre-calcined at 1000 °C for 4 h to ensure dehydration and decarbonation, while germanium oxide and the carbonates were treated at 600 °C and 500 °C, respectively. The oxide and carbonate reactants were manually ground for 20 minutes with an agate mortar and pestle, and calcined in air for two cycles (1300 °C/16 h followed by 1350 °C/16 h) with intermediate regrinding. The overall ideal reaction is

4.2.2 Characterization

4.2.2.1 Powder diffraction

For the electrolyte compositions considered here, it was essential to combine X-ray and neutron diffraction to arrive at complete crystallographic descriptions. Specifically, X-ray methods are unable to differentiate La from Ba, and the form factors for V and Ge are similar. On the other hand, neutrons are essential to derive oxygen positions, but lack the sensitivity to distinguish Sr from La, and V cannot be detected directly.

Laboratory powder X-ray, high resolution synchrotron powder X-ray (Australian Synchrotron Light Source), and neutron (Echidna beamline, ANSTO) powder diffraction patterns were acquired at room temperature from $[La_8(Ca/Sr/Ba)_2][Ge_{6-x}V_x]O_{26+x/2}$ ($0 \leq x \leq 1.5$), and the detailed equipment setup and parameters used was described in Chapter 3.

4.2.2.2 Rietveld refinement procedures and strategies

For both synchrotron and neutron powder X-ray diffraction data, Rietveld analysis of $[La_8AE_2][Ge_{6-x}V_x]O_{26+x/2}$ was conducted using *TOPAS 4*¹¹⁷ base on the general procedure given in Chapter 3. A pseudo-Voigt peak shape function modelled the Bragg reflections using $La_{9.33}Ge_6O_{26}$ ($P6_3/m$) as the starting structure.²⁰ A four-

coefficient Chebychev polynomial and $1/x$ profile background, a zero error, scale factors, and lattice dimensions were refined sequentially. [La/AE] and [Ge/V] occupancies were refined, followed by atom positions and isotropic ADPs in groups as follows: framework A^I cations; tunnel A^{II} cations; Ge; and all oxygen (framework, tunnel, interstitial). Anisotropic atomic displacement factors were refined for oxygen only using the neutron diffraction patterns.

Initially, full site occupancies were assumed for all atomic sites, but this approach always resulted in an overall alkaline earth dopant AE (Ca, Sr, or Ba) stoichiometry larger than expected (i.e. > 2 atoms per formula unit (apfu)). As earlier studies suggested the involvement of A^I $4f$ vacancies,³⁶ the refinement strategy was modified to allow for framework substoichiometry and ensure the large cation content ($A^I + A^{II}$) agreed with the nominal synthetic composition. The La/AE occupancies on the A^{II} $6h$ site were fixed at 6 apfu as there are no reports of vacancies at this position, and the number of AE atoms on the A^I site calculated ($= 2 - \text{alkaline earth on the } A^{II} \text{ site}$) and fixed. Finally, the La occupancy on the A^I site was released without any constraint. In this manner, the sum of $A^I + A^{II}$ cations are always equal or less than 10 apfu within error, and the number of vacancies can be determined ($= 10 - \text{total cations on the } A \text{ sites}$).

As noted, the relative occupancies La/Sr derived from neutron data are unreliable because of the similar bound coherent scattering lengths (La : Sr = 8.24 fm : 7.02 fm).¹²⁷ Similarly, La/Ba occupancies from synchrotron refinement are imprecise because of the close atomic numbers (La : Ba = 57 : 56). The X-ray scattering power on the B site is only slightly changed by minor (0.5 apfu) vanadium replacement of germanium. On the other hand, for neutron diffraction, the Ge/V scattering lengths are quite different (8.185 fm : -0.3824 fm),¹²⁷ although the determination is indirect, since the coherent neutron scattering length of vanadium is extremely low and the V occupancy is inferred from the reduction in scattering at the Ge/V sites.

To exploit these diffraction characteristics, a refinement strategy that combined the merits of both techniques was devised (Figure 4-1). (i) For the Ca series, the synchrotron refinements took the Ge/V ratio derived from neutron diffraction. (ii) For the Sr series, Ge/V occupancies were taken from the neutron data and fixed, while the La/Sr occupancies were refined from the synchrotron pattern. This process of establishing Ge/V and La/Sr ratios from neutron and synchrotron refinements was cycled until stable occupancies were reached. (iii) For the Ba series, both La/Ba and Ge/V occupancies in synchrotron refinements were fixed at values derived from neutron diffraction.

Figure 4-1 Schematic diagram of refinement methods for La/AE and Ge/V occupancies in $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr, Ba; nominal x = 0, 0.25, 0.5).

While in principle a joint refinement of synchrotron X-ray and neutron data should be feasible, attempts to conduct the refinements in this fashion were unsuccessful. The poor convergence is attributed to the vastly different intensity of the two patterns (Figure 4-2) with the X-ray counts dominating the minimization, leading to non-physical crystallographic parameters.

Figure 4-2 Rietveld plots of the (a) synchrotron and (b) neutron powder diffraction data of nominal $\text{La}_8\text{Sr}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$ collected at room temperature. The observed intensity is shown by dots, with the solid line representing the calculated intensity. Differences between observed and calculated intensities are plotted beneath. Vertical markers indicate the Bragg reflections of CaF_2 standard (top) and apatite (bottom).

4.2.2.3 Electron microscopy and spectroscopy

To investigate the microstructure, JEOL JSM 6400 and JEOL JSM 7600F were used for SEI and BEI collection. As a supplementary investigation on the material chemistry, quantitative analyses were carried out (JEOL JSM 6400) for the whole analogue with calibration reference standards of pure V and the end member $\text{La}_8\text{Sr}_2\text{Ge}_6\text{O}_{26}$. Crystal texture of the sintered pellet with selected composition $\text{La}_8\text{Ba}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$ was examined by an HKL EBSD system equipped on a Zeiss UltraPlus field emission scanning electron microscope. For transmission electron microscopy, HR images and SAED patterns were collected using a JEOL JEM-2010 TEM at 200keV.

The infrared and Raman spectroscopy was conducted at room temperature as introduced in Chapter 3. FTIR is complementary to Raman spectroscopy for qualitative confirmation of vanadium incorporation, but assignment of specific Ge-O and V-O absorption bands was not possible due to the extensive convolutions from 580 – 1000 cm^{-1} .

Conventional compact pellets (1.0 cm diameter) for conductivity measurements were prepared to study the ionic conductivity by AC impedance spectroscopy (Hewlett Packard 4182A impedance analyser). The measurements were taken in air at an applied voltage 0.1 V over a frequency range of 100 Hz – 10 MHz from 300 to 800 °C.

4.3 Results

4.3.1 Phase assemblage and lattice metric

Laboratory powder X-ray diffraction patterns confirmed the synthesis of single phase, crystalline products for the Ca, Sr, and Ba substituted $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series with nominal compositions $0 \leq x \leq 0.5$ (Figure 4-3). Beyond $x = 0.5$, secondary phases appeared, that could not be identified against known compounds and became more abundant as vanadium content increased. Consequently, the balance of these studies focussed on $x \leq 0.5$ preparations.

Although germanium volatilisation has been reported when firing at $1500\text{ }^\circ\text{C}^{128}$ or at $1300\text{ }^\circ\text{C}^{129}$ for long periods (120 h), losses here were not significant under the relatively mild and short firing time used. Moreover, energy dispersive X-ray microanalysis (Table 4-1) and diffraction did not detect secondary phases or departures from expected compositions. Further, the introduction of vanadium oxide reduces the apatite crystallization temperature, thereby suppressing evaporative loss of germanium.

Table 4-1 The atomic ratios for La, AE, and O were scaled to a total Ge + V content of 6 atoms per formula unit, derived from quantitative EDS microanalyses of single-phase samples with nominal composition $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (AE = Ca, Sr, Ba).

<i>Nominal x</i>	<i>La</i>		<i>AE</i>		<i>Ge</i>		<i>V</i>		<i>O</i>	
	<i>avg no.</i>	<i>std dev</i>	<i>avg no.</i>	<i>std dev</i>	<i>avg no.</i>	<i>std dev</i>	<i>avg no.</i>	<i>std dev</i>	<i>avg no.</i>	<i>std dev</i>
<i>AE = Ca</i>										
<i>x=0.00</i>	7.81	0.12	1.93	0.03	6.00	0.00	0	0	25.64	0.20
<i>x=0.25</i>	7.81	0.07	1.96	0.03	5.73	0.03	0.27	0.03	25.81	0.11
<i>x=0.50</i>	7.82	0.08	1.98	0.03	5.58	0.03	0.42	0.03	25.93	0.13
<i>AE = Sr</i>										
<i>x=0.00</i>	7.95	0.10	2.00	0.02	6.00	0.00	0	0	25.92	0.16
<i>x=0.25</i>	7.89	0.14	1.95	0.12	5.72	0.05	0.28	0.05	25.92	0.17
<i>x=0.50</i>	7.88	0.08	2.02	0.05	5.57	0.05	0.43	0.05	26.06	0.13
<i>AE = Ba</i>										
<i>x=0.00</i>	7.93	0.08	1.97	0.03	6.00	0.00	0	0	25.87	0.15
<i>x=0.25</i>	7.92	0.13	1.93	0.06	5.75	0.03	0.25	0.03	25.93	0.26
<i>x=0.50</i>	7.99	0.11	1.79	0.06	5.62	0.03	0.38	0.03	25.97	0.14

Figure 4-3 PXRD patterns and enlarged segments for (a) & (b) $[\text{La}_8\text{Ca}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$, (c) & (d) $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ and (e) & (f) $[\text{La}_8\text{Ba}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series with nominal $x=0, 0.25, 0.5, 0.75, 1, 1.25$, and 1.5 synthesised with two calcination cycles at 1300 and 1350 °C for 16 hours separately. Under these preparative conditions the solid-solution limit is $x = 0.5$. In (b), (d) & (f) peaks from secondary phases are labelled with $*$ for $x > 0.5$.

Rietveld quantitative phase analysis (QPA) of both synchrotron and neutron powder diffraction data (Tables 4-2 to 4-11) confirmed apatite and the calcium fluoride internal standard, however, the apparent fluoride content derived from X-ray patterns exceeds the weighted 20 wt.%. This can be attributed to a co-existing non-diffracting component, but represents a substantial overestimate due to the influence of X-ray microabsorption,¹³⁰ especially for vanadium-rich materials where crystal sizes are larger (see Section 4.3.3). In contrast, neutron QPA is reliable and shows that within error, fully crystalline products were achieved, with only the possibility of minor glassy phases at grain boundaries.

Table 4-2 Refined crystal and atomic parameters from synchrotron powder X-ray diffraction of $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.93}\text{Sr}_2\text{Ge}_6\text{O}_{25.90}$	$\text{La}_{7.93}\text{Sr}_2\text{Ge}_{5.84}\text{V}_{0.16}\text{O}_{25.98}$	$\text{La}_{7.99}\text{Sr}_2\text{Ge}_{5.58}\text{V}_{0.42}\text{O}_{26.20}$
R_{exp} (%)	2.29	2.30	2.39
R_{wp} (%)	4.48	4.88	7.71
R_{p} (%)	3.29	3.57	5.32
R_{b} (%)	1.48	1.56	2.10
<i>GOF</i>	1.95	2.12	3.23
Amorphous phase wt.% ^a	7.3(5)	13.6(5)	15.6(7)
Apatite wt.% ^a	92.70(10)	86.38(12)	84.44(17)
a (Å)	9.920979(14)	9.920248(14)	9.92016(2)
c (Å)	7.329844(14)	7.331756(14)	7.33324(2)
V (Å ³)	624.791(2)	624.861(2)	624.977(3)
c/a	0.7388	0.7391	0.7392
twist angle φ (°)	24.2 ₆	23.8 ₄	24.4 ₄
La/Sr(1), 4f, (1/3 2/3 z)			
z	0.00039(13)	0.00039(14)	-0.0001(2)
B (Å ²)	0.329(10)	0.483(12)	0.48(2)
Occ La/Sr(1)	0.561(4)/ 0.422(7)	0.534(5)/ 0.449(8)	0.511(8)/ 0.486(13)
La/Sr(2), 6h, (x y 1/4)			
x	0.23036(4)	0.23002(5)	0.22942(8)
y	-0.01099(6)	-0.01127(6)	-0.01159(10)
B (Å ²)	0.106(7)	0.183(7)	0.223(12)
Occ La/Sr(2)	0.948(5)/ 0.052(5)	0.966(5)/ 0.034(5)	0.991(9)/ 0.009(9)
Ge/V, 6h, (x y 1/4)			
x	0.39966(7)	0.39950(8)	0.39904(12)
y	0.37198(7)	0.37213(8)	0.37206(13)
B (Å ²)	0.097(13)	0.158(15)	0.03(3)
Occ Ge/V ^b	1.00/0.00	0.9741/0.0259	0.9308/0.0692
O(1), 6h, (x y 1/4)			
x	0.3116(5)	0.3125(5)	0.3114(8)
y	0.4859(5)	0.4848(5)	0.4839(8)
B (Å ²)	0.55(8)	0.55(9)	0.50(15)
O(2), 6h, (x y 1/4)			
x	0.6011(5)	0.6017(5)	0.6003(8)
y	0.4759(5)	0.4757(5)	0.4756(8)
B (Å ²)	0.42(8)	0.67(9)	0.19(13)
O(3), 12i, (x y z)			
x	0.3396(3)	0.3397(4)	0.3395(6)
y	0.2486(3)	0.2481(4)	0.2491(6)
z	0.0630(4)	0.0639(4)	0.0642(7)
B (Å ²)	1.03(7)	1.31(8)	1.60(13)
O(4), 2a, (0 0 1/4)			
B (Å ²)	1.30(13)	1.37(15)	2.0(3)

^a Spiked with 20 wt.% CaF_2 standard.^b The occupancies for Ge and V were fixed to values derived from neutron diffraction.

Table 4-3 Refined crystal and atomic parameters from neutron powder diffraction of $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.93}\text{Sr}_2\text{Ge}_6\text{O}_{25.90}$	$\text{La}_{7.93}\text{Sr}_2\text{Ge}_{5.84}\text{V}_{0.16}\text{O}_{25.98}$	$\text{La}_{7.99}\text{Sr}_2\text{Ge}_{5.58}\text{V}_{0.42}\text{O}_{26.20}$
R_{exp} (%)	3.06	3.04	3.06
R_{wp} (%)	4.36	4.22	4.40
R_{p} (%)	3.48	3.38	3.52
R_{b} (%)	1.73	1.65	1.65
GOF	1.42	1.39	1.44
Amorphous phase wt.% ^a	2.9(9)	2.1(10)	1.5(10)
Apatite wt.% ^a	97.1(2)	97.9(2)	98.5 (2)
a (Å)	9.91022(13)	9.90847(18)	9.90941(13)
c (Å)	7.32094(14)	7.32192(16)	7.32414(15)
V (Å ³)	622.68(2)	622.54(3)	622.85(2)
c/a	0.7387	0.7390	0.7391
twist angle φ (°)	23.5 ₈	23.9 ₉	24.2 ₄
La/Sr(1), $4f$, ($1/3$ $2/3$ z)			
z	0.4980(5)	0.4984(5)	0.4977(5)
Occ La/Sr(1) ^b	0.5611/0.4217	0.5337/0.4490	0.5112/0.4860
La/Sr(2), $6h$, (x y $1/4$)			
x	0.2309(2)	0.2311(2)	0.2304(2)
y	-0.0094(3)	-0.0095(3)	-0.0096(3)
Occ La/Sr(2) ^b	0.9478/0.0522	0.9660/0.0340	0.9906/0.0094
Ge/V, $6h$, (x y $1/4$)			
x	0.4003(3)	0.3999(3)	0.3993(3)
y	0.3724(2)	0.3723(2)	0.3723(2)
Occ Ge/V	1.00/0.00	0.974(7)/0.026(7)	0.931(7)/ 0.069(7)
O(1), $6h$, (x y $1/4$)			
x	0.3118(4)	0.3103(4)	0.3098(4)
y	0.4861(4)	0.4848(4)	0.4846(4)
O(2), $6h$, (x y $1/4$)			
x	0.6038(3)	0.6037(3)	0.6035(3)
y	0.4765(4)	0.4767(3)	0.4761(4)
O(3), $12i$, (x y z)			
x	0.3396(3)	0.3390(3)	0.3393(3)
y	0.2471(3)	0.2465(3)	0.2469(3)
z	0.0628(3)	0.0636(3)	0.0640(3)
O(4), $2a$, (0 0 $1/4$)			

^a Spiked with 20 wt.% CaF_2 standard.

^b The occupancies for La and Sr were fixed to values derived from synchrotron diffraction.

Table 4-4 Isotropic and anisotropic displacement parameters refined from neutron powder diffraction for $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.93}\text{Sr}_2\text{Ge}_6\text{O}_{25.90}$	$\text{La}_{7.93}\text{Sr}_2\text{Ge}_{5.84}\text{V}_{0.16}\text{O}_{25.98}$	$\text{La}_{7.99}\text{Sr}_2\text{Ge}_{5.58}\text{V}_{0.42}\text{O}_{26.20}$
La/Sr(1), 4f, (1/3 2/3 z)			
B ($\text{\AA}^2$)	0.46(4)	0.46(4)	0.46(4)
La/Sr(2), 6h, (x y 1/4)			
B ($\text{\AA}^2$)	0.32(3)	0.27(3)	0.31(3)
Ge/V, 6h, (x y 1/4)			
B ($\text{\AA}^2$)	0.51(4)	0.55(5)	0.49(5)
O(1), 6h, (x y 1/4)			
U_{11}	0.0196(17)	0.0180(16)	0.0161(17)
U_{22}	0.0084(16)	0.0125(17)	0.0102(18)
U_{33}	0.0086(15)	0.0071(15)	0.0064(16)
U_{12}	0.0112(15)	0.0134(15)	0.0117(15)
$U_{13} = U_{23} = 0$			
O(2), 6h, (x y 1/4)			
U_{11}	0.0068(15)	0.0037(14)	0.0044(15)
U_{22}	0.0094(15)	0.0069(14)	0.0047(15)
U_{33}	0.0098(16)	0.0134(16)	0.0129(17)
U_{12}	0.0013(13)	-0.0008(12)	-0.0015(13)
$U_{13} = U_{23} = 0$			
O(3), 12i, (x y z)			
U_{11}	0.0318(18)	0.0371(18)	0.0392(19)
U_{22}	0.0158(13)	0.0138(12)	0.0110(12)
U_{33}	0.0101(10)	0.0090(10)	0.0107(10)
U_{12}	0.0126(11)	0.0152(11)	0.0160(11)
U_{13}	-0.0112(10)	-0.0097(10)	-0.0104(11)
U_{23}	-0.0037(9)	-0.0030(9)	-0.0019(9)
O(4), 2a, (0 0 1/4)			
U_{11}	0.0191(17)	0.0145(16)	0.0139(17)
U_{22}	0.0191(17)	0.0145(16)	0.0139(17)
U_{33}	0.024(3)	0.021(3)	0.022(3)
U_{12}	0.0095 (9)	0.0073(8)	0.0069(9)
$U_{13} = U_{23} = 0$			

Table 4-5 Selected bond lengths and angles of $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5) from synchrotron and neutron powder diffraction.

Nominal x	0	0.25	0.5
Refined from Synchrotron X-ray Diffraction Data			
Bond Length (Å)			
La/Sr(1)-O(1) $\times 3$	2.495 (3)	2.505 (4)	2.510(6)
La/Sr(1)-O(2) $\times 3$	2.591(4)	2.587(4)	2.591(7)
La/Sr(1)-O(3) $\times 3$	2.953(3)	2.953(4)	2.956(6)
Average	2.680	2.682	2.686
La/Sr(2)-O(1)	2.747(3)	2.747(4)	2.736(6)
La/Sr(2)-O(2)	2.526(4)	2.531(4)	2.537(7)
La/Sr(2)-O(3) $\times 2$	2.464(3)	2.471(3)	2.472(6)
La/Sr(2)-O(3) $\times 2$	2.626(3)	2.620(3)	2.629(6)
La/Sr(2)-O(4)	2.3418(5)	2.3397(6)	2.3354(9)
Average	2.542	2.543	2.544
Ge/V-O(1)	1.740(6)	1.720(6)	1.718(10)
Ge/V-O(2)	1.731(4)	1.737(4)	1.729(7)
Ge/V-O(3) $\times 2$	1.733(3)	1.731(3)	1.724(5)
Average	1.734	1.730	1.724
Bond Angle (°)			
O(1)-Ge-O(3)	110.61(15)	110.90(16)	110.6(3)
O(1)-Ge-O(2)	114.7(2)	115.0(2)	115.0(4)
O(3)-Ge-O(3)	104.6(2)	104.0(2)	104.4(4)
O(3)-Ge-O(2)	107.90(14)	107.72(16)	107.8(3)
Refined from Neutron Powder Diffraction Data			
Bond Length (Å)			
La/Sr(1)-O(1) $\times 3$	2.482(4)	2.489(4)	2.486(4)
La/Sr(1)-O(2) $\times 3$	2.586(4)	2.587(4)	2.587(4)
La/Sr(1)-O(3) $\times 3$	2.948(3)	2.952(3)	2.952(3)
Average	2.672	2.676	2.675
La/Sr(2)-O(1)	2.760(4)	2.744(4)	2.741(4)
La/Sr(2)-O(2)	2.513(4)	2.509(3)	2.521(4)
La/Sr(2)-O(3) $\times 2$	2.466(2)	2.469(2)	2.474 (3)
La/Sr(2)-O(3) $\times 2$	2.600(3)	2.594(3)	2.596(3)
La/Sr(2)-O(4)	2.336(3)	2.338(3)	2.332(3)
Average	2.534	2.531	2.533
Ge/V-O(1)	1.741(5)	1.738(5)	1.736(6)
Ge/V-O(2)	1.746(4)	1.749(4)	1.752(4)
Ge/V-O(3) $\times 2$	1.742(2)	1.740(2)	1.737(3)
Average	1.743	1.742	1.741
Bond Angle (°)			
O(1)-Ge-O(3)	110.80(16)	110.72(16)	110.92(17)
O(1)-Ge-O(2)	115.10(18)	115.43(18)	115.69(19)
O(3)-Ge-O(3)	103.77(18)	103.31(17)	103.37(19)
O(3)-Ge-O(2)	107.85(16)	107.95(16)	107.58(18)

Table 4-6 Refined crystal and atomic parameters from synchrotron powder X-ray diffraction of $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{8.05}\text{Ca}_{1.95}\text{Ge}_6\text{O}_{26.03}$	$\text{La}_{7.98}\text{Ca}_2\text{Ge}_{5.62}\text{V}_{0.38}\text{O}_{26.16}$	$\text{La}_{7.89}\text{Ca}_2\text{Ge}_{5.35}\text{V}_{0.65}\text{O}_{26.16}$
R_{exp} (%)	6.88	6.76	6.93
R_{wp} (%)	7.21	7.61	8.08
R_p (%)	5.39	5.67	6.07
R_b (%)	1.83	1.81	1.96
GOF	1.05	1.13	1.17
Amorphous phase wt.% ^a	6.1(8)	7.1(7)	9.7(8)
Apatite wt.% ^a	93.87(16)	92.93(15)	90.31(17)
a (Å)	9.88216(3)	9.88067(2)	9.88194(3)
c (Å)	7.23238(3)	7.23349(2)	7.23396(3)
V (Å ³)	611.668(4)	611.578(4)	611.774(4)
c/a	0.7319	0.7321	0.7320
twist angle φ (°)	22.3 ₈	22.5 ₄	22.6 ₉
La/Ca(1), 4f, (1/3 2/3 z)			
z	-0.0012(3)	-0.0015(2)	-0.0011(3)
B (Å ²)	0.41(2)	0.43(2)	0.58(3)
Occ La/Ca(1)	0.525(3)/0.475(3)	0.509(2)/0.485(6)	0.512(2)/0.460(6)
La/Ca(2), 6h, (x y 1/4)			
x	0.22997(7)	0.22950(7)	0.22943(8)
y	-0.01218(9)	-0.01221(9)	-0.01235(10)
B (Å ²)	0.266(12)	0.287(10)	0.373(13)
Occ La/Ca(2)	0.992(4)/0.008(4)	0.990(4)/0.010(4)	0.973(4)/0.027(4)
Ge/V, 6h, (x y 1/4)			
x	0.40299(12)	0.40298(11)	0.40309(13)
y	0.37511(12)	0.37514(12)	0.37497(14)
B (Å ²)	0.14(2)	0.11(2)	0.21(3)
Occ Ge/V ^b	1.00/0.00	0.937/0.063	0.891/0.109
O(1), 6h, (x y 1/4)			
x	0.3184(7)	0.3192(7)	0.3196(8)
y	0.4907(7)	0.4919(6)	0.4933(7)
B (Å ²)	0.22(13)	0.26(12)	0.48(15)
O(2), 6h, (x y 1/4)			
x	0.6019(8)	0.6004(7)	0.5996(9)
y	0.4738(8)	0.4733(7)	0.4724(9)
B (Å ²)	0.82(14)	0.98(13)	1.33(16)
O(3), 12i, (x y z)			
x	0.3385(6)	0.3385(5)	0.3383(6)
y	0.2512(6)	0.2512(6)	0.2515(6)
z	0.0668(7)	0.0667(6)	0.0670(7)
B (Å ²)	2.03(13)	1.92(12)	2.16(14)
O(4), 2a, (0 0 1/4)			
B (Å ²)	2.1(3)	1.9(2)	2.8(3)

^a Spiked with 20 wt.% CaF_2 standard.

^b The occupancies for Ge and V were fixed to values derived from neutron diffraction.

Table 4-7 Refined crystal and atomic parameters from neutron powder diffraction of $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.8}\text{Ca}_2\text{Ge}_6\text{O}_{25.7}$	$\text{La}_{7.82}\text{Ca}_2\text{Ge}_{5.62}\text{V}_{0.38}\text{O}_{25.92}$	$\text{La}_{7.88}\text{Ca}_2\text{Ge}_{5.35}\text{V}_{0.65}\text{O}_{26.15}$
R_{exp} (%)	2.97	2.99	3.72
R_{wp} (%)	4.54	4.45	5.27
R_{p} (%)	3.59	3.55	4.19
R_{b} (%)	1.77	1.59	1.83
GOF	1.53	1.49	1.42
Amorphous phase wt.% ^a	5.0(11)	-2.2(12)	3.4(14)
Apatite wt.% ^a	95.0(2)	102.2(2)	96.6(3)
a (Å)	9.87089(15)	9.86956(14)	9.87087(16)
c (Å)	7.22428(17)	7.22553(16)	7.22604(19)
V (Å ³)	609.59(2)	609.53 (2)	609.74(3)
c/a	0.7319	0.7321	0.7321
twist angle ϕ (°)	22.0 ₇	21.7 ₉	21.0 ₁
La/Ca(1), $4f$, $(1/3\ 2/3\ z)$			
z	0.4994(6)	0.4981(5)	0.4998(7)
Occ La/Ca(1)	0.57(2)/0.38(3)	0.56(2)/0.40(3)	0.56(2)/0.41(4)
La/Ca(2), $6h$, $(x\ y\ 1/4)$			
x	0.2311(3)	0.2311(2)	0.2310(3)
y	-0.0115(3)	-0.0108(3)	-0.0108(4)
Occ La/Ca(2)	0.92(2)/0.08(2)	0.93(2)/0.07(2)	0.94(2)/0.06(2)
Ge/V, $6h$, $(x\ y\ 1/4)$			
x	0.4021(3)	0.4030(3)	0.4021(4)
y	0.3735(3)	0.3741(3)	0.3741(3)
Occ Ge/V	1.00/0.00	0.937(7)/0.063(7)	0.891(8)/0.109(8)
O(1), $6h$, $(x\ y\ 1/4)$			
x	0.3158(4)	0.3169(4)	0.3165(5)
y	0.4905(4)	0.4909(4)	0.4909(5)
O(2), $6h$, $(x\ y\ 1/4)$			
x	0.6064(4)	0.6062(4)	0.6061(5)
y	0.4751(4)	0.4749(4)	0.4743(5)
O(3), $12i$, $(x\ y\ z)$			
x	0.3408(5)	0.3412(5)	0.3416(5)
y	0.2506(4)	0.2508(4)	0.2514(4)
z	0.0626(3)	0.0628(3)	0.0637(4)
O(4), $2a$, $(0\ 0\ 1/4)$			

^a Spiked with 20 wt.% CaF_2 standard.

Table 4-8 Isotropic and anisotropic displacement parameters refined from neutron powder diffraction for $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.8}\text{Ca}_2\text{Ge}_6\text{O}_{25.7}$	$\text{La}_{7.82}\text{Ca}_2\text{Ge}_{5.62}\text{V}_{0.38}\text{O}_{25.92}$	$\text{La}_{7.88}\text{Ca}_2\text{Ge}_{5.35}\text{V}_{0.65}\text{O}_{26.15}$
La/Ca(1), $4f$, $(1/3 \ 2/3 \ z)$			
$B \ (\text{\AA}^2)$	0.80(7)	1.12(7)	1.25(8)
La/Ca(2), $6h$, $(x \ y \ 1/4)$			
$B \ (\text{\AA}^2)$	0.50(4)	0.60(4)	0.76(5)
Ge/V, $6h$, $(x \ y \ 1/4)$			
$B \ (\text{\AA}^2)$	0.63(4)	0.57(5)	0.56(7)
O(1), $6h$, $(x \ y \ 1/4)$			
U_{11}	0.037(2)	0.037(2)	0.040(3)
U_{22}	0.0167(19)	0.0224(19)	0.024(2)
U_{33}	0.0024(16)	0.0081(16)	0.0056(19)
U_{12}	0.0251(19)	0.0268(18)	0.029(2)
$U_{13} = U_{23} = 0$			
O(2), $6h$, $(x \ y \ 1/4)$			
U_{11}	0.0090(16)	0.0069(15)	0.0106(19)
U_{22}	0.0081(16)	0.0060(15)	0.0093(19)
U_{33}	0.044(2)	0.046(2)	0.051(3)
U_{12}	0.0049(14)	0.0019(13)	0.0064(16)
$U_{13} = U_{23} = 0$			
O(3), $12i$, $(x \ y \ z)$			
U_{11}	0.103(3)	0.100(3)	0.107(4)
U_{22}	0.0205(16)	0.0251(16)	0.0230(19)
U_{33}	0.0176(14)	0.0177(13)	0.0174(15)
U_{12}	0.0414(19)	0.0409(18)	0.040(2)
U_{13}	-0.0297(15)	-0.0309(14)	-0.0288(17)
U_{23}	-0.0089(12)	-0.0096(12)	-0.0046(14)
O(4), $2a$, $(0 \ 0 \ 1/4)$			
U_{11}	0.012(2)	0.0072(19)	0.008(2)
U_{22}	0.012(2)	0.0072(19)	0.008(2)
U_{33}	0.067(6)	0.079(6)	0.101(8)
U_{12}	0.0062(11)	0.0036(9)	0.0038(12)
$U_{13} = U_{23} = 0$			

Table 4-9 Refined crystal and atomic parameters from synchrotron powder X-ray diffraction of $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.88}\text{Ba}_2\text{Ge}_6\text{O}_{25.82}$	$\text{La}_{7.88}\text{Ba}_2\text{Ge}_{5.66}\text{V}_{0.34}\text{O}_{25.99}$	$\text{La}_{7.67}\text{Ba}_2\text{Ge}_{5.29}\text{V}_{0.71}\text{O}_{25.86}$
R_{exp} (%)	2.26	2.30	6.63
R_{wp} (%)	5.78	7.33	9.20
R_{p} (%)	4.18	5.52	5.89
R_{b} (%)	1.95	2.10	1.96
GOF	2.56	3.18	1.39
Amorphous phase wt.% ^a	5.9(5)	9.5(6)	7.3(7)
Apatite wt.% ^a	94.11(10)	90.50(12)	92.70(14)
a (Å)	9.990695(17)	9.987150(17)	9.98963(3)
c (Å)	7.419536(15)	7.421694(16)	7.42060(2)
V (Å ³)	641.355(3)	641.087(3)	641.311(4)
c/a	0.7426	0.7431	0.7428
twist angle ϕ (°)	24.7 ₈	25.0 ₅	23.9 ₂
La/Ba(1), $4f$, $(1/3\ 2/3\ z)$			
z	-0.00012(12)	-0.00030(15)	-0.0000(2)
B (Å ²)	0.293(8)	0.436(10)	0.392(14)
Occ La/Ba(1) ^b	0.601/0.369	0.582/0.390	0.609/0.307
La/Ba(2), $6h$, $(x\ y\ 1/4)$			
x	0.23006(5)	0.22956(6)	0.22954(9)
y	-0.01064(7)	-0.01063(9)	-0.01085(12)
B (Å ²)	0.285(7)	0.354(8)	0.602(12)
Occ La/Ba(2) ^b	0.912/0.088	0.926/0.0737	0.872/0.128
Ge/V, $6h$, $(x\ y\ 1/4)$			
x	0.39766(8)	0.39710(10)	0.39738(14)
y	0.37046(8)	0.37041(10)	0.37051(14)
B (Å ²)	0.325(14)	0.293(17)	0.40(2)
Occ Ge/V ^c	1.00/0.00	0.944/0.056	0.882/0.118
O(1), $6h$, $(x\ y\ 1/4)$			
x	0.3114(6)	0.3106(7)	0.3127(10)
y	0.4840(6)	0.4835(7)	0.4821(10)
B (Å ²)	1.27(11)	1.47(15)	2.2(2)
O(2), $6h$, $(x\ y\ 1/4)$			
x	0.5985(6)	0.5978(7)	0.6001(10)
y	0.4760(6)	0.4771(7)	0.4767(10)
B (Å ²)	1.22(11)	1.31(14)	2.2(2)
O(3), $12i$, $(x\ y\ z)$			
x	0.3400(4)	0.3393(6)	0.3379(7)
y	0.2502(4)	0.2500(5)	0.2515(7)
z	0.0645(5)	0.0668(6)	0.0650(8)
B (Å ²)	1.29(8)	1.52(10)	2.03(15)
O(4), $2a$, $(0\ 0\ 1/4)$			
B (Å ²)	2.25(18)	2.0(2)	2.6(3)

^a Spiked with 20 wt.% CaF_2 standard.^b The occupancies for La and Ba were fixed to values derived from neutron diffraction.^c The occupancies for Ge and V were fixed to values derived from neutron diffraction.

Table 4-10 Refined crystal and atomic parameters from neutron powder diffraction of $\text{La}_8\text{Ba}_2\text{Ge}_6$ - $x\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.88}\text{Ba}_2\text{Ge}_6\text{O}_{25.82}$	$\text{La}_{7.88}\text{Ba}_2\text{Ge}_{5.66}\text{V}_{0.34}\text{O}_{25.99}$	$\text{La}_{7.67}\text{Ba}_2\text{Ge}_{5.29}\text{V}_{0.71}\text{O}_{25.86}$
R_{exp} (%)	3.06	3.06	2.98
R_{wp} (%)	4.52	4.43	4.52
R_{p} (%)	3.60	3.54	3.61
R_{b} (%)	2.02	1.90	1.83
GOF	1.48	1.44	1.52
Amorphous phase wt.% ^a	4.1(9)	-1.2(10)	2.0(10)
Apatite wt.% ^a	95.93(18)	101.2(2)	98.0(2)
a (Å)	9.97963(16)	9.97623(15)	9.97861(17)
c (Å)	7.41046(17)	7.41273(16)	7.41128(18)
V (Å ³)	639.15(3)	638.91(2)	639.09(3)
c/a	0.7426	0.7430	0.7427
twist angle ϕ (°)	24.7 ₄	25.7 ₆	25.4 ₈
La/Ba(1), $4f$, ($1/3$ $2/3$ z)			
z	0.5014(5)	0.5005(5)	0.5007(6)
Occ La/Ba(1)	0.601(19)/0.37(3)	0.582(19)/0.39(3)	0.61(2)/0.31(3)
La/Ba(2), $6h$, (x y $1/4$)			
x	0.2313(3)	0.2302(3)	0.2308(3)
y	-0.0086(3)	-0.0096(3)	-0.0087(4)
Occ La/Ba(2)	0.912(19)/0.088(19)	0.926(19)/0.074(19)	0.87(2)/0.13(2)
Ge/V, $6h$, (x y $1/4$)			
x	0.3978(3)	0.3968(3)	0.3973(3)
y	0.3704(2)	0.3703(2)	0.3706(3)
Occ Ge/V	1.00/0.00	0.944(7)/0.056(7)	0.882(7)/0.118(7)
O(1), $6h$, (x y $1/4$)			
x	0.3094(5)	0.3076(5)	0.3075(5)
y	0.4842(5)	0.4833(5)	0.4829(5)
O(2), $6h$, (x y $1/4$)			
x	0.6005(4)	0.5983(4)	0.5998(5)
y	0.4787(5)	0.4781(5)	0.4777(5)
O(3), $12i$, (x y z)			
x	0.3390(4)	0.3386(4)	0.3386(4)
y	0.2466(3)	0.2463(3)	0.2466(4)
z	0.0641(3)	0.0649(3)	0.0655(3)
O(4), $2a$, (0 0 $1/4$)			

^a Spiked with 20 wt.% CaF_2 standard.

Table 4-11 Isotropic and anisotropic displacement parameters refined from neutron powder diffraction for $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5).

Nominal x	0	0.25	0.5
Refined Composition	$\text{La}_{7.88}\text{Ba}_2\text{Ge}_6\text{O}_{25.82}$	$\text{La}_{7.88}\text{Ba}_2\text{Ge}_{5.66}\text{V}_{0.34}\text{O}_{25.99}$	$\text{La}_{7.67}\text{Ba}_2\text{Ge}_{5.29}\text{V}_{0.71}\text{O}_{25.86}$
La/Ba(1), $4f$, $(1/3\ 2/3\ z)$			
$B\ (\text{\AA}^2)$	0.55(6)	0.59(5)	0.62(6)
La/Ba(2), $6h$, $(x\ y\ 1/4)$			
$B\ (\text{\AA}^2)$	0.77(4)	0.78(4)	0.82(4)
Ge/V, $6h$, $(x\ y\ 1/4)$			
$B\ (\text{\AA}^2)$	0.63(5)	0.50(5)	0.49(6)
O(1), $6h$, $(x\ y\ 1/4)$			
U_{11}	0.040(3)	0.040(3)	0.044(3)
U_{22}	0.022(3)	0.019(2)	0.020(3)
U_{33}	0.025(2)	0.026(2)	0.029(3)
U_{12}	0.026(2)	0.025(2)	0.025(2)
$U_{13} = U_{23} = 0$			
O(2), $6h$, $(x\ y\ 1/4)$			
U_{11}	0.0158(19)	0.0171(18)	0.022(2)
U_{22}	0.0141(18)	0.0153(19)	0.016(2)
U_{33}	0.035(2)	0.032(2)	0.039(3)
U_{12}	-0.0009(16)	0.0013(16)	-0.0001(18)
$U_{13} = U_{23} = 0$			
O(3), $12i$, $(x\ y\ z)$			
U_{11}	0.050(2)	0.052(2)	0.058(3)
U_{22}	0.0243(14)	0.0213(14)	0.0265(16)
U_{33}	0.0143(13)	0.0168(13)	0.0171(14)
U_{12}	0.0231(15)	0.0227(15)	0.0253(17)
U_{13}	-0.0188(14)	-0.0170(14)	-0.0194(15)
U_{23}	-0.0088(11)	-0.0067(10)	-0.0072(12)
O(4), $2a$, $(0\ 0\ 1/4)$			
U_{11}	0.019(2)	0.019(2)	0.021(3)
U_{22}	0.019(2)	0.019(2)	0.021(3)
U_{33}	0.077(6)	0.073(6)	0.099(8)
U_{12}	0.0094(11)	0.0093(11)	0.0107(13)
$U_{13} = U_{23} = 0$			

The refined unit cell constants (a , c , and c/a) from synchrotron powder X-ray diffraction of $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$, and 0.5) (Figure 4-4) found Ba apatites have the largest lattice metric compared to the intermediate Sr analogues and the smallest Ca series, as expected due to the ascending ionic radii of the framework cations: Ca^{2+} (CN 8, 1.12 Å) < Sr^{2+} (CN 8, 1.26 Å) < Ba^{2+} (CN 8, 1.42 Å).¹³¹ Within the same alkali-earth series, the lattice parameters are without obvious trend with increasing x , because Ge^{4+} and V^{5+} are of similar size (Ge^{4+} (CN 4) = 0.39 Å; V^{5+} (CN 4) = 0.36 Å).¹³¹ However, in plots with expanded scales (Figure 4-5), a and c are seen to react oppositely, but slightly, with increasing V^{5+} content. In general, a contracts while c expands, such that the unit cell volume is essentially constant.

Figure 4-4 Refined lattice parameters from synchrotron powder X-ray diffraction data for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca, Sr, Ba}$) (a) a , (b) c , (c) c/a , (d) unit cell volume. The x -values are those derived from Rietveld analysis.

Figure 4-5 Refined lattice parameters from synchrotron powder X-ray diffraction data for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}$ and Ba). The x-values are those derived from Rietveld analysis.

4.3.2 Crystal structures

Rietveld crystal structure refinement of $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ (nominal $x = 0, 0.25$ and 0.5) in hexagonal $P6_3/m$ for synchrotron and neutron data yielded good agreement between calculated and observed patterns (Tables 4-2 to 4-11, Figure 4-2). In every case, the X-ray diffraction analysis found that most, if not all, the alkaline earth (Ca/Sr/Ba) resides on the $4f$ framework sites in agreement with previous work.^{56, 68, 70} The type of nonstoichiometry was distinct however: the Sr series was negligibly substoichiometric on the A^I ($4f$) site (less than 2% vacant), while for the Ca and Ba analogues, A^I was 3%–8% under-occupied, leading in some cases to oxygen-deficient (< 26 oxygen apfu) compositions with partial occupancy of the tunnel $2a$ anion position; this is especially evident for Ba of

nominal $x = 0.5$. Mechanisms for the incorporation of vanadium, cation vacancies, and oxygen interstitials can be collated as:

A general scheme that includes (4-2) and (4-3) can be written as:

A further mechanism, believed to be less significant, may be:

Although the incorporation of vanadium ions into apatite should introduce excess oxygen via mechanism (4-2), the lack of direct diffraction evidence for an interstitial oxygen site in the hexagonal channel or elsewhere, suggests charge balance arises primarily by the creation of La^{3+} vacancies (mechanism (4-3)), or more likely, the extra oxygen is delocalised and does not contribute to Bragg diffraction of neutrons as suggested by Beaudet-Savignat *et al.*⁵⁶ It is noted that the oxide ions in the channel have large [001] anisotropic displacements for all compositions, as would be expected if static disorder (mechanism (4-2)) is operative. In practice, the combined mechanism (4-4) will be active, though the x and y proportions will be specific for the stoichiometry and firing temperature. The refined vanadium content x for Sr series are smaller than those for Ca and Ba analogues, because the A^I site vacancies for the latter series exceed those for the Sr series, as follows (nominal $x = 0.5$, ratios were derived from Rietveld refined neutron diffraction patterns):

Mismatch between the flexible framework and tunnel ions distorts the structure through $A^I\text{O}_6$ metaprism twisting (counter-rotation of the opposing triangular faces of the metaprism through a [001] projected angle), with the twist angles (ϕ) calculated from neutron diffraction refinements providing superior reliability of oxygen positions (Figure 4-6 a). As anticipated, the twist angles follow the trend

Ba > Sr > Ca (Figure 4-6 b) because the alkaline-earths primarily occupy the framework and control the tunnel diameter. Consequently, when Ba is accommodated in the $A^I\text{O}_6$ metaprism, this polyhedron must have a large ϕ ($\sim 25^\circ$) to constrict the framework around the relatively small tunnel contents ($\text{La}^{II}_6\text{O}_2$). At the other extreme, Ca insertion reduces framework polyhedra volumes, and so ϕ ($\sim 21.5^\circ$) must become more acute to open the channel sufficiently to satisfy bonding to its contents. Being of intermediate size, Sr analogues show $\phi \sim 24^\circ$.

The trends for any given alkaline earth series as a function of V^{5+} content (x) are subtle, as V^{5+} and Ge^{4+} are of similar size, and because the relative importance of substitution mechanisms (4-2) and (4-3) will vary. As V^{5+} is slightly smaller than Ge^{4+} , increasing x reduces framework size and ϕ is more acute. The trends for all three series result from the combined effects of varying A^I/A^{II} size ratios, A^I site vacancy concentrations, and the extent of vanadium substitution (Figure 4-6 c).

Figure 4-6 Twist angle (a) Polyhedral representation of the refined $\text{La}_{7.99}\text{Sr}_2\text{Ge}_{5.58}\text{V}_{0.42}\text{O}_{26.20}$ structure with metaprism twisting (ϕ) labelled, face-sharing $A^I\text{O}_6$ metaprisms (yellow) are corner connected to BO_4 tetrahedra (orange) forming the framework, which surrounds the tunnel A^{II} atoms (blue), (b) Plot of twist angles with respect to x, (c) Plot of A^I/A^{II} atomic size ratio with respect to x, (d) Plot of oxygen nonstoichiometry with respect to ϕ , (e) Plot of ionic conductivity with respect to ϕ , (f) Plot of activation energy with respect to ϕ for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$).

4.3.3 Microstructure and local structure

The backscattered electron (BSE) micrographs for the $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series show homogeneous contrast for single-phase apatites ($x \leq 0.5$), but for $x > 0.5$ several distinct regions arise from the secondary phases (as also observed by XRD) (Figure 4-7). For the Sr series, the chemical compositions for $x \leq 0.5$ were probed by EDS with variance established by averaging (over 15 analyses) (Table 4-1). There is an apparent deviation from the nominal compositions, which correlates well with the refined compositions from Rietveld analysis. The La content is lower than expected, which is attributed to vacancies on the A^{I} cation sites. The Ge/V ratios are close to nominal, however, the low concentration of vanadium leads to a relatively large standard deviation. For samples with $x > 0.5$, the proportion of secondary phases is significant and three compounds, in addition to apatite, were detected in the $x = 1.5$ material (Table 4-12) containing an excess of La and/or V. The identity of these phases remains to be determined.

Figure 4-7 BSE micrographs for $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ series with nominal (a) $x = 0.25$ and (b) $x = 1.5$, respectively. By contrast, the dark background reflects resin and the relatively bright regions represent the embedded powder samples.

Table 4-12 Quantitative EDS microanalyses of co-existing non-apatite phases found in a preparation with nominal composition $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($x=1.5$).

	wt. %		
	Phase 1	Phase 2	Phase 3
La₂O₃	79.87	66.95	62.39
SrO	1.04	3.81	7.26
GeO₂	5.63	13.06	17.62
V₂O₅	12.86	16.48	9.73
Total	99.40	100.30	97.00

BSE images of the sintered pellets show equiaxed grains (Figure 4-8 a , b and d) for Ca- and Sr- substituted apatites with grain sizes ranging from 6 - 10 μm , while the Ba- substituted crystals are elongated along [001] (Figure 4-8 c) to 10 - >100 μm , which is similar to the morphology of Sr-substituted lanthanum silicate apatite.³³ Existence of intergranular material was observed (Figure 4-9), which may be glassy, as suggested earlier by neutron QPA. The obvious, complex features at some interfaces are of similar contrast and composition with the apatite phase. On the other hand, the clean grain boundaries sometimes contain narrow darker contrast and are possibly germanium/vanadium rich glasses. The crystal masses are without texture, and XRD of pellet surfaces confirmed only a minor degree of (100), (011) and (210) preferred orientations (Figure 4-10). Apatite crystals become increasingly *c*-axis acicular with the introduction of larger alkaline earth ions ($\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$), because incipient melting progressively contributes to fluxing; BaO has the lowest melting point followed by SrO and CaO, and grain growth would be more rapid at near-melting eutectic temperatures.¹³² Moreover, the addition of vanadium accentuates anisotropic growth (Figure 4-8 e and f), as V_2O_5 melts at 690 °C which is the lowest among all oxides used here. It is well

known that the liquid phase formed by V_2O_5 addition drastically alters the microstructure and increases the density of sintered ceramics,¹³³⁻¹³⁴ as observed here. EBSD of nominal $[La_8Ba_2][Ge_{5.5}V_{0.5}]O_{26.25}$ confirmed preferential *c*-axis growth (Figure 4-11) with six selected grains of different orientations.

Figure 4-8 Low angle backscattered electron micrographs (5.0kV) for $[La_8AE_2][Ge_{6-x}V_x]O_{26+x/2}$ series with (a) $AE = Ca$, $x = 0$; (b) $AE = Sr$, $x = 0$; (c) $AE = Ba$, $x = 0$; (d) $AE = Ca$, $x = 0.5$; (e) $AE = Sr$, $x = 0.5$; (f) $AE = Ba$, $x = 0.5$.

Figure 4-9 Low angle backscattered electron image for $La_{7.67}Ba_2Ge_{5.29}V_{0.71}O_{25.86}$ (nominal composition: $La_8Ba_2Ge_{5.5}V_{0.5}O_{26.25}$) pellet of unpolished surface.

Figure 4-10 XRD profile for the sintered pellet surface with nominal composition $[\text{La}_8\text{Ba}_2][\text{Ge}_{5.5}\text{V}_{0.5}]\text{O}_{26.25}$. Peaks of abnormally strong intensities (comparing with a randomly oriented diffraction pattern) are indexed, which are resulted from preferred orientations and poor statistics of the bulk surface.

Figure 4-11 EBSD analyses on polished pellet of nominal $\text{La}_8\text{Ba}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$. The all-Euler map (with grain boundaries shown by black lines) is shown on the left and crystal orientations for six elongated grains (marked on the map by numbers) are presented on the right; the growth directions of these crystals are all along *c*-axis.

TEM imaging and diffraction of $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ with $x = 0$ (Figure 4-12 a, b) and $x = 0.5$ (Figure 4-12 c, d) was consistent with $P6_3/m$ symmetry when viewed along $\langle 101 \rangle$ and $\langle 211 \rangle$ orientations. HRTEM contrast was not uniform, especially for vanadium-rich compositions, and rapid damage under the highly energetic electron probe may arise from vanadium volatilisation.¹³⁵

Figure 4-12 TEM images (low-magnification and high-resolution) and diffraction patterns for nominal (a) & (b): $[\text{La}_8\text{Sr}_2][\text{Ge}_6]\text{O}_{26}$, (c) & (d): $[\text{La}_8\text{Sr}_2][\text{Ge}_{5.5}\text{V}_{0.5}]\text{O}_{26.25}$.

4.3.4 Raman and FTIR spectroscopy

Figure 4-13 shows the Raman spectra for $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ ($x = 0, 0.25$ and 0.5). Following Orera *et al.*¹³⁶⁻¹³⁷ the strong band at $\sim 340\text{ cm}^{-1}$ was assigned to the ν_2 symmetric bending mode of the GeO_4 tetrahedra, and those at lower energies ($< 300\text{ cm}^{-1}$) are mainly due to the translational and librational external modes of the GeO_4 group. The bands from 400 to 500 cm^{-1} arise from the ν_4 bending modes of the GeO_4 tetrahedra, and those observed from 700 to 800 cm^{-1} correspond to the symmetric ν_1 and asymmetric ν_3 stretching modes. A shoulder at around $800\text{-}850\text{ cm}^{-1}$ is due to the vanadium in apatite and not unreacted V_2O_5 (Figure 4-14).¹³⁸⁻¹³⁹ Additional features observed in the Raman spectra are substantial band broadening and shifting towards lower energies with vanadium doping, possibly indicating greater strain, as $x = 0.5$ is approaching the vanadium solid-solution limit.

Figure 4-13 Raman spectra of normalised intensities for (a) $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (b) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (c) $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ series with nominal $x = 0, 0.25$, and 0.5 , measured at room temperature.

Figure 4-14 Raman spectrum for the initial reactant V_2O_5 powder measured at room temperature. Peaks located at 283, 405 and 480 cm^{-1} are assigned to the bending vibrations of $\text{V}=\text{O}$, $\text{V}=\text{O}$, $\text{V}_2\text{-O}$ (doubly coordinated oxygen) bonds; peaks located at 530, 699 and 990 cm^{-1} are assigned to the stretching modes of $\text{V}_3\text{-O}$ (triply coordinated oxygen), $\text{V}_2\text{-O}$, and $\text{V}=\text{O}$ bonds.

The FTIR transmission spectra for $[\text{La}_8\text{Sr}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ ($x = 0, 0.25$ and 0.5) and $[\text{La}_8\text{AE}_2][\text{Ge}_{5.5}\text{V}_{0.5}]\text{O}_{26.25}$ show a broad peak ($550\text{--}950\text{ cm}^{-1}$) assigned to O-Ge-O stretching and deformation modes (Figure 4-15).¹²⁸ For the vanadium-doped apatites, there is an additional shoulder at $\sim 850\text{ cm}^{-1}$ assigned to a VO_4 band¹⁴⁰ whose intensity increases with x , which is consistent with the Raman observations. In comparing different A-cation substitutions, the GeO_4 band shifts to lower frequencies as larger alkali ions are incorporated. The decrease of the Ge-O vibration frequency is associated with a decrease in bond strength, accompanied by bond lengthening in the GeO_4 tetrahedra for Ca, Sr and Ba substituted apatites from $1.731\text{ \AA}$ to $1.741\text{ \AA}$ to $1.746\text{ \AA}$, respectively, as determined by neutron diffraction.¹⁴¹

Figure 4-15 FTIR spectra for (a) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ with $x=0, 0.25$, and 0.5 , (b) $\text{La}_8\text{AE}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$ with $\text{AE} = \text{Ca}, \text{Sr}, \text{and Ba}$.

4.3.5 Oxide ion conductivities

The impedance data were variable, with some compositions showing a single semicircle, with a capacitance typical of a bulk response, indicating very little grain boundary contribution, while in other samples there was evidence for a second grain boundary semicircle (Figure 4-16). The conductivity data (bulk conductivities) are displayed in Figure 4-17. As expected, the fully stoichiometric apatite ($\text{La}_8\text{AE}_2\text{Ge}_6\text{O}_{26}$) showed the lowest conductivity (e.g. $\text{AE} = \text{Sr}$, $\sigma = 3.53 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$) at intermediate temperature (500°C). However, as the oxygen content rises with the addition of vanadium (nominal $x = 0.25$), the conductivity increased

by more than one order of magnitude ($AE = \text{Sr}$, $\sigma = 6.49 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$), but less obviously with further doping to $x = 0.5$ ($AE = \text{Sr}$, $\sigma = 9.39 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$). The conductivities are comparable to those reported for equivalent apatite germanates with similar nominal oxygen excess but without doping on the Ge site (i.e. $\text{La}_{8.5}\text{Ba}_{1.5}\text{Ge}_6\text{O}_{26.25}$, $\sigma \approx 8 \times 10^{-5} \text{ S cm}^{-1}$ at 500°C ,⁵⁹ compared to $6.68 \times 10^{-5} \text{ S cm}^{-1}$ for $AE = \text{Ba}$, $x = 0.5$), suggesting that the key influence on the conductivity is the introduction of excess oxygen rather than the specific dopant site. Comparing the three series, the calcium apatites proved superior with a high ionic conductivity of $3.44 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ ($x = 0.5$) at 500°C and a relatively low activation energy (E_a) of 0.95 eV (Table 4-13).

Figure 4-16 The impedance plots for (a) $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (b) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (c) $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ series with nominal $x = 0, 0.25$, and 0.5 at 500°C .

Figure 4-17 Variation of conductivities with temperatures for (a) $\text{La}_8\text{Ca}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (b) $\text{La}_8\text{Sr}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$, (c) $\text{La}_8\text{Ba}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ series with nominal $x = 0, 0.25$, and 0.5 .

Table 4-13 Conductivity data for $\text{La}_8\text{AE}_2\text{Ge}_{6-x}\text{V}_x\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca, Sr, Ba}$; $0 \leq x \leq 0.5$) samples.

Apatite (nominal composition)	Density of pellet (% theoretical)	σ ($\text{S}\cdot\text{cm}^{-1}$) at 500 °C	E_a (eV)
$\text{La}_8\text{Ca}_2\text{Ge}_6\text{O}_{26}$	84	1.84×10^{-5}	0.75
$\text{La}_8\text{Ca}_2\text{Ge}_{5.75}\text{V}_{0.25}\text{O}_{26.125}$	86	1.97×10^{-4}	0.93
$\text{La}_8\text{Ca}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$	93	3.44×10^{-4}	0.95
$\text{La}_8\text{Sr}_2\text{Ge}_6\text{O}_{26}$	81	3.53×10^{-6}	0.91
$\text{La}_8\text{Sr}_2\text{Ge}_{5.75}\text{V}_{0.25}\text{O}_{26.125}$	97	6.49×10^{-5}	1.06
$\text{La}_8\text{Sr}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$	97	9.39×10^{-5}	1.08
$\text{La}_8\text{Ba}_2\text{Ge}_6\text{O}_{26}$	92	4.16×10^{-6}	1.10
$\text{La}_8\text{Ba}_2\text{Ge}_{5.75}\text{V}_{0.25}\text{O}_{26.125}$	94	4.45×10^{-5}	1.08
$\text{La}_8\text{Ba}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$	97	6.68×10^{-5}	1.08

4.4 Discussion

Bond valence summing (BVS) for each cation in the Sr substituted $[\text{A}^{\text{I}}_4][\text{A}^{\text{II}}_6][(\text{BO}_4)_6][\text{O}_2]$ system¹⁴²⁻¹⁴³ (Table 4-14) was used to validate metal distribution over the polyhedra, with large deviations from formal valence indicative of unsuitable sites. Moreover, BVS can probe the relative occupancy numbers of disordered sites and detect lattice strain. As expected, the calculated BVS show La^{3+} and V^{5+} to be underbonded and those for Sr^{2+} and Ge^{4+} overbonded, but the average BVS for A^{I} and B sites close to ideal with 2.45/2.51 and 4.13/4.07 ($\text{AE} = \text{Sr}$, $x = 0.5$; bond lengths refined from neutron diffraction).

Table 4-14 The bond lengths and BVS for cations on *A* and *B* sites in $[A^I_4][A^{II}_6][(BO_4)_6][X_2]$ system for $[La_8Sr_2][Ge_{6-x}V_x]O_{26+x/2}$ series.

Polyhedron	Metaprism (CN=9)				Tetrahedra (CN=4)			
	A^I-O_{avg} (Å)	BVS for La	BVS for Sr	BVS for A^{I*} / Valence of A^{I*}	$B-O_{avg}$ (Å)	BVS for Ge	BVS for V	BVS for B^* / Valence of B^*
Synchrotron refined compositions								
$La_{7.93}Sr_2Ge_6O_{25.90}$	2.680	2.58	2.23	2.39 / 2.53	1.734	4.15	-	4.15 / 4.00
$La_{7.93}Sr_2Ge_{5.84}V_{0.16}O_{25.98}$	2.682	2.56	2.21	2.36 / 2.50	1.730	4.20	4.88	4.22 / 4.03
$La_{7.99}Sr_2Ge_{5.58}V_{0.42}O_{26.20}$	2.686	2.53	2.19	2.36 / 2.51	1.724	4.27	4.96	4.32 / 4.07
Neutron refined compositions								
$La_{7.93}Sr_2Ge_6O_{25.90}$	2.672	2.65	2.29	2.45 / 2.53	1.743	4.06	-	4.06 / 4.00
$La_{7.93}Sr_2Ge_{5.84}V_{0.16}O_{25.98}$	2.676	2.62	2.26	2.41 / 2.50	1.742	4.07	4.72	4.09 / 4.03
$La_{7.99}Sr_2Ge_{5.58}V_{0.42}O_{26.20}$	2.675	2.63	2.27	2.45 / 2.51	1.741	4.08	4.74	4.13 / 4.07

* BVS for A^I and *B* sites are calculated from BVS of each element, and the valences for both sites are calculated from ideal valence of each element:

$$BVS \text{ for } A^I = BVS_{La} \times A^I \text{ Occupancy}_{La} + BVS_{Sr} \times A^I \text{ Occupancy}_{Sr}$$

$$BVS \text{ for } B = BVS_{Ge} \times B \text{ Occupancy}_{Ge} + BVS_V \times B \text{ Occupancy}_V$$

$$\text{Valence for } A^I = 3 \times A^I \text{ Occupancy}_{La} + 2 \times A^I \text{ Occupancy}_{Sr}$$

$$\text{Valence for } B = 4 \times B \text{ Occupancy}_{Ge} + 5 \times B \text{ Occupancy}_V$$

The metaprism twist angles (ϕ) for the Ca and Sr series are well below an upper limit $\sim 25^\circ$, beyond which hexagonal symmetry cannot sustain acceptable bond valence sum limits without rotation of the tetrahedra.¹⁰⁶⁻¹⁰⁷ Typically, at larger metaprism twist angles, apatites metrically distort from hexagonal $P6_3/m$ symmetry to monoclinic $P2_1/m$ or triclinic $P\bar{1}$ with a diminution of oxygen mobility. Since ϕ for the Ba-series is near the phase transition, this offers a partial explanation for the low conductivity.

The introduction of vanadium generally increases the total oxygen content (mechanism (4-2) dominant), although some oxygen-deficient apatites appear due to the creation of La^{3+} cation vacancies (mechanism (4-3) dominant). Superstoichiometric oxygen facilitates an interstitial conducting mechanism,^{7, 33, 68, 144} and cation vacancies located at $4f$ sites could cause $2a$ O^{2-} ion displacement and

creation of “interstitial-like” positions, which provide favourable diffusion paths across and through the tunnels.^{110-111, 145} The variable vacancy concentration makes the evaluation of conductivities with increasing x more complex, although the evolution of conductivity correlates with the relative proportions of oxygen interstitials and cation vacancies. Specifically, oxygen nonstoichiometry, conductivity, and activity energy can be rationalised when plotted against metaprism twist angle (Figure 4-6 d, e & f). In general, the Ca series displays opposite trends compared to the Ba and Sr series because $\text{Ca}^{2+} < \text{La}^{3+}$ while Sr^{2+} , $\text{Ba}^{2+} > \text{La}^{3+}$ with respect to ionic size. Most obviously, ionic conductivity correlates well with the oxygen nonstoichiometry, with σ generally increasing with greater oxygen stoichiometry. Comparing the three analogues, the conductivity decreased in the order $\text{Ca} > \text{Sr} > \text{Ba}$ following the observations of Pramana *et al.*¹⁴⁶ for the alkaline earth lanthanum germanate oxyapatite; this behaviour is contrary to the silicate apatites where Ba-doped apatites were superior.⁵⁶ The lowest activation energies arise when the large tunnel is greatly expanded (ϕ small) that facilitates oxygen migration with the trend across the three analogues following the order $\text{Ca} < \text{Sr} < \text{Ba}$. Besides intrinsic factors, several extrinsic properties influence conductivity, especially porosity, grain size and crystal habit. For example, grain morphology is compositionally dependent: the calcium-doped series have isotropic grains, while the strontium and barium series are acicular crystals with the largest $c : a$ aspect ratios observed for the latter. Moreover, vanadium not only causes crystal chemical changes, but also promotes phase and microstructural changes. For example, amorphous material is less abundant in vanadium doped products indicative of better crystallisation, although the crystals were more anisotropic. As conductivity along c axis is much larger than that along a axis,⁸ textural modification of the compact pellets would influence bulk conductivities. Although there was no evidence of severe textural phenomena in the pellets as observed in EBSD map, clusters of crystals showing preferred orientation could exist in local areas.

4.5 Conclusion

Three series of vanadium doped electrolyte apatites with nominal composition $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}; 0 \leq x \leq 1.5$) were synthesised and characterised by laboratory X-ray, synchrotron and neutron diffraction followed by Rietveld refinement. The chemical compositions, microstructures, and local structures were analysed by SEM and TEM. Single-phase apatites were obtained for nominal $x \leq 0.5$ and structural investigations were invariably consistent with $P6_3/m$ symmetry. All the three series show an order of magnitude enhancement in conductivity, even with low-level vanadium doping; the best performance was for the calcium doped series. The conductivities and activation energy are controlled by dopant size, melting temperature, crystallinity, and the microstructure of the sintered pellets. Compositions with $\text{AE} = \text{Sr}, x > 0$ and $\text{AE} = \text{Ba}, x \geq 0$ show particularly strong anisotropic grain growth, and therefore their conductive properties are likely to be texturally limited. Overall, the vanadium-doped apatites show potential as electrolytes for intermediate temperature SOFCs, with $\sigma = 3.44 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 500 °C and a relatively low activation energy (0.95 eV) achieved.

For these apatite electrolytes, crystallochemical tailoring to enhance performance confirmed four general principles:

- a. *Smaller $\text{A}^{\text{I}}\text{O}_6$ metaprism twist angles open the channel to promote conductivity.* Consequently, the Ca series shows the greatest oxygen mobility, as the smaller average ionic size of the framework cations reduces twisting and enlarges the tunnel diameter. In addition, ϕ is well below 25°, beyond which, lower symmetries are favoured that create more intricate ion migration paths and reduce conductivity. In general, smaller A^{I} cations will enhance oxygen mobility (the conductivity $\text{Ca} > \text{Sr} > \text{Ba}$).
- b. *Excess oxygen allows interstitial mobility, leading to higher conductivity.* The introduction of V^{5+} in Ge^{4+} is offset by the incorporation of superstoichiometric oxygen that leads to greater σ at intermediate temperatures. Therefore, to

increase oxygen interstitial concentration higher valent B cations should be used.

- c. *Activation energy is lower in expanded tunnels*, where the barriers to ion migration are more easily overcome. Therefore, compositional series with smaller ϕ and enlarged tunnel are generally preferred. Smaller A^I cations open the channel which structurally and thermodynamically favors tunnel migration.
- d. *Superstoichiometric oxygen may be ordered or disordered*. In $\text{La}_{10}(\text{GeO}_4)_5(\text{GeO}_5)\text{O}_2$ perfect correlation of superstoichiometric oxygen was observed.²¹ However, in the materials studied here there is no direct evidence for interstitial sites, but the cation contents derived from structure refinement require O^{2-} for charge balance. The localization of interstitial oxygen can be controlled by thermal treatment. Long term annealing will favor ordering, but this will not be practical for producing electrolytes due to time and energy costs.

Chapter 5

Mixed Si/Ge-Based Apatite-Type Phases^{*}

In this study, mixed Si/Ge-based apatites were prepared by hydrothermal synthesis under mild conditions, rather than the conventional solid-state method at high temperatures. Single-phase and highly-crystalline nanosized apatite powders were obtained with the morphology changing across the series from spheres for the Si-based end-member to hexagonal rods for the Ge-based end-member. Powder X-ray and neutron analysis found all these apatites to be hexagonal ($P6_3/m$). Quantitative X-ray microanalysis established the partial (< 15 atomic percent) substitution of La^{3+} by Na^+ (introduced from the NaOH hydrothermal reagent) that showed a slight preference to enter the $A^{\text{I}} 4f$ framework position over the $A^{\text{II}} 6h$ tunnel site. Moreover, retention of hydroxide (OH^-) was confirmed by infrared spectroscopy and thermogravimetric analysis, and these apatites are best described as oxyhydroxyapatites. To prepare dense pellets for conductivity measurements, both conventional heat treatment and spark plasma sintering methods were compared, with the peculiar features of hydrothermally synthesized apatites and influence of sodium on ionic conductivity considered.

^{*} Li, H. *et al.* Hydrothermal synthesis, structure investigation, and oxide ion conductivity of mixed Si/Ge-based apatite-type phases. *Inorg. Chem.*, accepted 2014, doi: 10.1021/ic402370e.

5.1 Introduction

Apatite electrolytes are mostly obtained at high temperatures ($> 800\text{ }^{\circ}\text{C}$) through calcination of homogeneous precursor powders prepared by grinding oxides or sol-gel methods.^{7, 45} The synthesis of Ge-containing apatites is somewhat problematic, as compared to silicates, due to Ge volatilization leading to mixed phase products.^{103, 147-148} Recently, a mild hydrothermal synthesis of silicate oxyhydroxyapatites was found to deliver a pure and highly crystalline product at low temperature ($230\text{ }^{\circ}\text{C}$).⁴⁹⁻⁵⁰ To date however, there is a lack of systematic studies to establish the optimal hydrothermal conditions for silicate apatite preparation, and analogous germanates have not been produced in this way. Here, we targeted mixed Si/Ge-based lanthanide apatites of composition $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$, for hydrothermal synthesis, with subsequent studies of crystal chemistry, defect concentration and powder morphology used to explore the relationship between structure and ionic conductivity. It was found that germanate apatites are superior electrolyte materials, but for hydrothermally prepared materials care is needed to control sodium contamination, which lowers the total oxide ion content, and hence also the conductivity.

5.2 Synthesis

Apatites of nominal composition $\text{La}_{9.33}\square_{0.67}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$ ($\square$ represents the A^{I} vacancy, $0 \leq x \leq 6$) were hydrothermally synthesized from gels with the chemical composition (molar ratio) of $2.5\text{-}4.1\text{La}_2\text{O}_3:5.3\text{SiO}_2+\text{GeO}_2:19.3\text{Na}_2\text{O}:1722\text{H}_2\text{O}$. The amount of lanthanum was adjusted empirically to obtain single-phase apatites. In a typical synthesis with $\text{Si/Ge}=1$, 2.13 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Strem, 99.9%) was dissolved in 13 ml of DI water (Solution I). Subsequently, 0.16 g of silicic acid (Merck, 99%) and 0.28 g of GeO_2 (Alfa, 99.999%) were dissolved in the base solution containing 1.54 g of NaOH (Schedelco, 99.9%) in 18 ml of DI water (Solution II). These stock solutions were combined by introducing Solution I to

Solution II dropwise, with stirring continued for two hours at ~70 °C to ensure a homogeneous gel was formed. This mixture was sealed in a 45 ml Teflon-lined stainless steel autoclave and reconnaissance crystallization performed at 180 – 240 °C from 3 h to 60 days. Based on yield and crystallinity, a static condition of 240 °C / 16 hours was selected for bulk synthesis of powders used for X-ray and neutron powder diffraction and ionic conductivity tests. After cooling to room temperature the product was centrifuged, washed with DI water and dried at 60 °C overnight. The overall ideal reaction can be expressed as:

The situation is not as straightforward as Equation (5-1) suggests, since apatites contain several cation acceptor sites leading to a wide range of substitutional possibilities²⁴, and as considered shortly, monovalent Na⁺ ions can potentially displace La³⁺. Both H⁺ and OH⁻ ions could also be incorporated.

5.3 Characterization

5.3.1 Powder Diffraction

While XRD delivers accurate lattice parameters, the technique is insensitive to oxygen in the lanthanum-rich matrix, and to arrive at more complete crystallographic descriptions, neutron experiments are essentially needed. Laboratory powder X-ray and neutron (Echidna beamline, ANSTO) powder diffraction patterns were acquired at room temperature and the detailed equipment setup and parameters used were described in Chapter 3. In order to gain additional information on the effect of water incorporation and possible loss at elevated temperature, the silicate and germanate end-members were subjected to *in situ* high temperature neutron diffraction studies from 25 to 1100 °C.

5.3.2 Electron microscopy and spectroscopy

Quantitative analyses were carried out using a JEOL JSM 6400 for the whole analogues and both JEOL JSM 6400 and JEOL JSM 7600F were used for SEI and BEI collection. To confirm the bulk composition, EPMA was performed for three selected samples on a JEOL JXA-8530F equipped with five WDS. The accelerating voltage and current used were 10 kV and 40 nA, respectively. Standards employed were monazite (La) and albite (Na, Si and Al) minerals obtained from Astimex, while synthetic GeO₂ (Ge) was from Alfa Aesar. The peak counting time for La, Na, Si, Al and Ge was 30, 60, 30, 60 and 30s, respectively and the background counting time was half of the characteristic peak. HR images and SAED patterns were collected using a JEOL JEM-2010 operated at 200 keV. The infrared spectroscopy was conducted at room temperature as introduced in Chapter 3.

Both conventional and spark plasma sintering methods were applied to produce compact pellets of powders for conductivity measurements. The ionic conductivity was evaluated by AC impedance spectroscopy (Hewlett Packard 4192A impedance analyzer), with measurements taken in air, with an applied voltage of 0.1 V over a frequency range of 100 Hz – 10 MHz from 300 to 800 °C. The impedance spectra showed a single broad semicircle consistent with a combination of bulk and grain boundary components, and so it was not possible to accurately extract individual bulk resistivities. Consequently the data reported represent total conductivities.

5.4 Results and Discussion

5.4.1 Synthesis and Phase Assemblage

Laboratory powder X-ray diffraction patterns confirmed the synthesis of a single phase apatite for the Ge end-member when the reaction was conducted above 200

°C; for synthesis at 240 °C the single-phase product formed within 3 hours. The Si end-member was obtained similarly. Based on a fixed ratio of Si/Ge sources and base concentration, the introduced La content was always < 85% of the stoichiometric quantity, as preliminary experiments found stoichiometric combinations produce significant amounts of secondary phases (mainly the unreacted $\text{La}(\text{OH})_3$), and although longer synthesis times reduced these, they were not eliminated completely even after 60 days reaction (Figure 5-1).

Figure 5-1 XRD data for Ge end-member apatite prepared with prolonged reaction time of 60 days, peaks from the secondary phase $\text{La}(\text{OH})_3$ are labeled with *.

Because SiO_2 and GeO_2 dissolve in hot (~ 80 °C), concentrated NaOH while $\text{La}(\text{OH})_3$ precipitates, extra-stoichiometric Si and Ge oxides are required to promote the fast crystallization of apatite. After many trials, it was concluded that with the La source fixed at 60% of the stoichiometric value, the optimized condition of 240 °C and 16 hours produced well crystallized single-phase apatite across the whole mixed Si/Ge series. These parameters are more robust than reported previously⁴⁹⁻⁵⁰ (230 °C / 6 days), and there remains a degree of flexibility to choose various combinations of temperature, time, stoichiometry and reagent-to-water ratio to manipulate crystal size and morphology.

5.4.2 Microstructure and local structure

Backscattered electron images of the apatite powders found the Si end-member composed of spherical nanoparticles (30 – 100 nm), but as the Ge content increased, the average particle size increases (~40 to 200 nm), and the spherical crystals elongate, until for the germanate end-member, the crystals become hexagonal rods (100 – 600 nm) (Figure 5-2).

Figure 5-2 Low angle backscattered electron micrographs (5.0 kV) for (A) Si end-member, (B) intermediate composition of nominal equivalent Si/Ge, and (C) Ge end-member apatites synthesized at 240 °C for 16 hours.

The microstructures for apatites synthesized under different conditions are collated in Figure 5-3, and while growth is slow, the rod length increases by an order of magnitude (from 100 nm to several microns) after 60 days. Single-phase germanate apatite forms at 220 °C and 240 °C, but at < 200 °C, the large hexagonal apatite rods co-exist with acicular $\text{La}(\text{OH})_3$.

Figure 5-3 Low angle backscattered electron micrographs (5.0 kV) for Ge end-member apatites with synthesis condition of (A) 220 °C, 3 hours; (B) 220 °C, 6 days; (C) 220 °C, 60 days; (D) 200 °C, 1 day; (E) 220 °C, 1 day; (F) 240 °C, 1 day.

To confirm the particles are well crystallized, SAED and phase contrast imaging was carried out for the two end-members and one intermediate composition ($x = 3$) (Figure 5-4). The microstructures shown in the low-magnification images are consistent with the BEI images. HRTEM contrast was not uniform as rapid damage under the highly energetic electron probe may arise from volatilization of hydrogen-bearing species.

Figure 5-4 TEM images (low-magnification and high-resolution) and diffraction patterns for (A) & (B) Si end-member, (C) & (D) intermediate composition of nominal equivalent Si/Ge, (E) & (F) Ge end-member apatites.

5.4.3 Hydroxyl incorporation — FTIR spectroscopy and TGA

The FTIR transmission spectra across the Si/Ge series (Figure 5-5) contains a broad band from 2600 to 3700 cm^{-1} arising from hydroxyl groups and water, but distinct from calcium phosphate hydroxyapatite, the O-H bond stretching mode does not appear as a narrow peak¹⁴⁹ at $\sim 3570 \text{ cm}^{-1}$ and the OH librational mode ($\sim 630 \text{ cm}^{-1}$) was not detected. These differences are suggestive of a low OH^- ion content that

are consistent with the previous research⁴⁹⁻⁵⁰ indicating the coexistence of OH^- and O^{2-} ions and the formation of oxy-hydroxyapatites. The bands at 962 and 910 cm^{-1} belong to asymmetric stretching modes of the SiO_4 group, while those at 542 and 490 cm^{-1} result from asymmetric bending modes of the SiO_4 group and La-O vibration modes.¹⁵⁰⁻¹⁵¹ Analogously, the bands at 786, 764, 451, 416 cm^{-1} are assigned to the stretching and bending modes of the GeO_4 group but moved to shorter wavenumbers compared to SiO_4 .¹⁶ Further evidence of the presence of hydrous species was obtained by TGA (Figure 5-6) with significant weight losses (~2%) observed; the initial ~1.3% weight loss up to 300 °C should be due to evaporation of absorbed and crystalline H_2O , and the subsequent minor loss till 1200 °C could be caused by removal of OH groups, accompanied by conversion to oxyapatite.

Figure 5-5 FTIR spectra for mixed $\text{Si}_{6-x}/\text{Ge}_x$ -based lanthanum apatites with wavenumber ranges from (A) 400–1800 cm^{-1} and (B) 2000–4000 cm^{-1} . The intensities were normalized to refined Si or Ge content with (a) Si_6 , (b) $\text{Si}_{5.82}$, (c) $\text{Si}_{5.44}$, (d) $\text{Si}_{4.70}$, (e) $\text{Ge}_{3.13}$, (f) $\text{Ge}_{4.49}$, (g) $\text{Ge}_{5.24}$.

Figure 5-6 TGA plots for (A) Si end-member, (B) intermediate composition of nominal equivalent Si/Ge, and (C) Ge end-member apatites synthesized at 240 °C for 16 hours.

5.4.4 Crystal chemistry

Quantitative microanalyses (Table 5-1) were performed by SEM-EDS and EPMA; aside from establishing the La/Ge/Si content, these analyses were used to investigate the incorporation of sodium. There is an apparent deviation from the nominal compositions, which correlates well with the refined compositions from Rietveld analysis. The La content is lower than expected, which is attributed to the incorporation of Na, and through the whole series, the Si/Ge ratio is larger than nominal values. As both silicon and germanium were always in excess with respect to the lanthanum source and the dissolution kinetics of SiO_2 ¹⁵² and GeO_2 ¹⁵³ are distinct, some departure from nominal product compositions is expected. As the Ge content increases, the Si/Ge ratio approaches its putative value. It is noted that minor Si (< 0.2 wt.%) was detected in the germanate end-member, and is probably introduced by corrosion of glass containers used for the strong alkaline solution.

Table 5-1 The atomic ratios for La, Na, and O were scaled to a total Si + Ge content of 6 atoms per formula unit, derived from quantitative EDS and EPMA for mixed $\text{Si}_{6-x}\text{Ge}_x$ apatites.

Nominal x	La		Na		Si		Ge		O	Departure from Nominal x (%)
	avg no.	std dev	avg no.	std dev	avg no.	std dev	avg no.	std dev	avg no.	
x=0	8.14	0.30	1.30	0.06	6.00	0.00	0.00	0.00	24.86	0.0
<i>*x=0</i>	<i>8.47</i>	<i>0.11</i>	<i>1.24</i>	<i>0.02</i>	<i>6.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>25.33</i>	<i>0.0</i>
x=1	8.53	0.39	1.28	0.06	5.76	0.02	0.24	0.02	25.44	76.0
x=2	8.63	0.41	1.17	0.08	5.21	0.03	0.79	0.03	25.53	60.5
x=3	8.62	0.36	1.14	0.05	4.10	0.04	1.90	0.04	25.50	36.7
<i>*x=3</i>	<i>8.17</i>	<i>0.09</i>	<i>1.22</i>	<i>0.02</i>	<i>4.31</i>	<i>0.06</i>	<i>1.69</i>	<i>0.06</i>	<i>24.87</i>	<i>43.7</i>
x=4	8.50	0.39	1.11	0.08	2.76	0.07	3.24	0.07	25.31	19.0
x=5	8.17	0.27	1.05	0.07	1.41	0.03	4.59	0.03	24.78	8.2
x=6	8.28	0.47	1.04	0.04	0.10	0.02	5.90	0.02	24.94	1.7
<i>*x=6</i>	<i>8.31</i>	<i>0.02</i>	<i>1.42</i>	<i>0.00</i>	<i>0.06</i>	<i>0.01</i>	<i>5.94</i>	<i>0.01</i>	<i>25.18</i>	<i>1.0</i>

* EPMA

Because of the close characteristic X-ray line energies for Na ($K\alpha_{1,2}$ 1.041 keV), La ($M\alpha_1$ 0.833 keV) and Ge ($L\alpha_{1,2}$ 1.188 keV),¹⁵⁴ the Na contents detected by EDS are potentially inaccurate. However, these characteristic X-rays are readily

separated by wavelength dispersive X-ray analysis (Na = 1.192 nm; La = 1.490 nm; Ge = 1.045 nm), and for confirmation, EPMA on three selected samples (two end-members and one mixed Si/Ge of nominal $x = 3$) were performed and the analyses found in reasonable agreement with EDS (Table 5-1).

Several charge balance mechanisms can be formulated to accommodate sodium. As the ionic radii of La^{3+} (CN 6, 1.03Å) and Na^+ (CN 6, 1.02Å) are similar,¹³¹ monovalent Na^+ ions may substitute for trivalent La^{3+} by creating oxygen vacancies (Equation (5-2)), or occupy La^{3+} cation vacancies together with the incorporation of oxygen interstitials (Equation (5-3)).

A general scheme that includes (5-2) and (5-3) can be written as:

Driven by the charge balancing and characteristics of the synthesis method, it is possible that hydrogen is involved in the form of hydroxide and the valance imbalance caused by sodium substitutions could be solved by replacing oxygen with hydroxide ions (Equation (5-5)).

5.4.5 Rietveld refinement and crystal structures

The powder X-ray data were refined with TOPAS¹¹⁶ and the starting composition of $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ in space group $P6_3/m$ (No. 176). A fundamental parameter peak function was adopted and the background (four-coefficient Chebychev polynomial and 1/x profile), zero error, scale factors, and lattice dimensions were refined sequentially followed by [La/Na] and [Si/Ge] fractional occupancies, atom positions and isotropic ADPs. The refinement of neutron diffraction data was conducted with JANA2006¹¹⁸ using the same starting model, but the profile fitting was performed with a pseudo-Voigt peak shape function and a five-coefficient

Chebyshev polynomial background, while simultaneously refining the lattice and zero shift parameters. Finally, the occupancies, atom fractional coordinates and anisotropic ADPs were released simultaneously to complete the crystal structure modeling.

All the profiles were satisfactorily modeled in $P6_3/m$ with low R_{wp} values ($< 6\%$) for both X-ray and neutron data (Figure 5-7). The refined lattice parameters ($a = b$, c) and unit cell volumes dilate linearly with increasing Ge content (x) as Ge^{4+} (CN 4, $0.39\text{\AA}$) has a larger ionic radius than Si^{4+} (CN 4, $0.26\text{\AA}$)¹³¹ (Table 5-2, Figure 5-8).

Figure 5-7 Rietveld plots of the (a) laboratory X-ray and (b) neutron powder diffraction data of mixed $\text{Si}_{6-x}\text{Ge}_x$ -based apatite of nominal $x = 3$ collected at room temperature. The observed intensity is shown by dots, with the solid line representing the calculated intensity. Differences between observed and calculated intensities are plotted beneath.

Table 5-2 Refined cell parameter data (hexagonal cell with the space group $P6_3/m$) from laboratory X-ray and neutron powder diffraction on mixed Si/Ge-based lanthanum apatites.

X-ray diffraction Refined composition	Unit cell parameters (Å)		Volume(Å ³)	R (%)				GOF
	$a = b$	c	V	R_p	R_{wp}	R_{exp}	R_b	
La _{8.59} Na _{1.13} Si ₆ O _{25.45}	9.72743(10)	7.17977(10)	588.351(14)	3.59	4.57	3.41	1.51	1.34
La _{8.77} Na _{1.03} Si _{5.80} Ge _{0.20} O _{25.67}	9.73420(9)	7.18823(9)	589.865(13)	3.40	4.32	3.31	1.45	1.30
La _{8.97} Na _{0.91} Si _{5.21} Ge _{0.79} O _{25.91}	9.74885(9)	7.19304(9)	592.038(13)	3.42	4.36	3.29	1.36	1.32
La _{8.74} Na _{1.02} Si _{4.42} Ge _{1.58} O _{25.62}	9.78960(15)	7.20219(13)	597.76(2)	4.12	5.39	3.28	1.62	1.64
La _{8.70} Na _{0.98} Si _{3.22} Ge _{2.78} O _{25.54}	9.84343(16)	7.21513(14)	605.43(2)	4.44	5.83	3.26	1.65	1.79
La _{8.64} Na _{1.07} Si _{1.93} Ge _{4.07} O _{25.50}	9.89589(10)	7.22902(9)	613.083(15)	3.92	5.06	3.23	1.56	1.57
La _{8.92} Na _{0.92} Si _{0.72} Ge _{5.28} O _{25.84}	9.93039(6)	7.23768(7)	618.106(10)	3.39	4.40	3.31	1.41	1.33
Neutron diffraction Refined composition	Unit cell parameters (Å)		Volume(Å ³)	R (%)				GOF
	$a = b$	c	V	R_p	R_{wp}	$R(obs)$	$R(all)$	
La _{8.42} Na _{1.42} Si ₆ O _{25.88} H _{0.63}	9.7272(3)	7.1816(3)	588.48(3)	2.83	3.54	4.14	4.14	1.69
La _{8.40} Na _{1.54} Si _{5.82} Ge _{0.18} O _{26.12} H _{0.98}	9.7332(3)	7.1863(3)	589.59(3)	3.15	3.93	4.19	4.19	1.91
La _{8.59} Na _{1.23} Si _{5.44} Ge _{0.56} O _{25.71} H _{0.63}	9.7503(2)	7.1955(2)	592.42(3)	3.09	3.85	4.38	4.39	1.86
La _{8.40} Na _{1.31} Si _{4.70} Ge _{1.30} O _{25.58} H _{0.44}	9.7912(3)	7.2058(2)	598.26(3)	2.79	3.51	3.90	3.90	1.68
La _{8.58} Na _{1.17} Si _{2.87} Ge _{3.13} O _{25.62} H _{0.43}	9.8442(4)	7.2185(2)	605.82(4)	3.13	3.97	4.74	4.74	1.82
La _{8.46} Na _{1.17} Si _{1.51} Ge _{4.49} O _{26.02} H _{0.96}	9.8973(3)	7.2309(2)	613.42(3)	3.16	3.93	3.97	3.97	1.72
La _{8.63} Na _{1.19} Si _{0.76} Ge _{5.24} O _{25.88} H _{1.06}	9.9451(2)	7.2431(2)	620.40(3)	3.61	4.48	4.26	4.26	1.96

Figure 5-8 Refined lattice parameters and the linear fits from powder X-ray (square) and neutron (triangle) diffraction data for the analogue of mixed Si_{6-x}/Ge_x-based lanthanum apatites with refined x from 0 – 6.

As the Na⁺ ions could reside on both $6h$ and $4f$ sites, the occupancies of La³⁺ and Na⁺ were allowed to vary, with the constraint of full occupation applied to the $6h$ [La/Na], but not to the $4f$ [La/Na] site, as vacancies usually appear at the latter position. To maintain neutrality, the substitution of monovalent Na⁺ cations on trivalent La³⁺ sites may be balanced by the creation of anionic vacancies. As the FTIR data indicated the existence of –OH groups, the incorporation of OH[–] ions at

the expense of O^{2-} ions should also be taken into account. The overall effect makes the expression of the chemical compositions in hydrothermal products rather more complex, as compared to solid-state synthesized apatites, and these phases are best described as oxy-hydroxyapatites, however, the details cannot be established by X-ray diffraction. More directly, the $6h$ [Si/Ge] sites can be regarded as fully tenanted and the average scattering power of the tetrahedrally coordinated cation is readily determined.

As neutron diffraction is better able to detect light elements (O and H), this technique was ultimately used for the final structural analysis. To model the tunnel oxygen, the $2a$ site was initially selected, but Fourier mapping showed a pair of symmetrical excess scattering centers along z (Figure 5-9 (A) & (B)), that could be accounted for using a $4e$ position with a refined occupancy of $\leq 50\%$. For all other oxygen positions full occupancies were appropriate. The remaining negative peaks around the tunnel center (0 0 0) in the Fourier map could be accounted for by placing H^+ ions at these positions (Figure 5-9 (C) & (D)). This finding is consistent with crystal chemistry and the demand for charge balance.

Figure 5-9 2-D and 3-D Fourier mapping for the Si end-member apatite with (A) and (B) $2a$ oxygen position, (C) and (D) $4e$ oxygen and hydrogen positions.

The refined occupancies yielded 2 – 9% vacancies on A^I (4f) site. Moreover, the partitioning of Na^+ across A^I (4f) and A^{II} (6h) sites was almost equal, with a slight preference for the A^I framework site (Table 5-3). The chemical compositions derived from Rietveld analysis were generally consistent with EDS/EPMA chemical analyses. However, the complexity of La/Na/□ and O/OH/□ distributions and occupations mean the chemistries established by Rietveld refinement do not exactly charge balance. Taking the nominal $x = 3$ as an example, the refined composition is $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ (overall charge = -0.21) while charge balanced expression would be $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{24}(\text{OH})_{2.51-2y}\text{O}_y\text{□}_{y-0.51}$. The whole analogue can be represented as $\text{La}_{8.50}\text{Na}_{1.29}\text{Si}_{6-x}\text{Ge}_x\text{O}_{24}(\text{OH})_{2.79-2y}\text{O}_y\text{□}_{y-0.79}$ by taking the average La and Na content of the 7 samples.

Table 5-3 Atomic coordinates and equivalent isotropic ADPs for $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ from neutron powder diffraction.

Atom	Wyck	x	y	z	S.O.F.	$U_{\text{iso}} (\text{\AA}^2)$
La/Na(2)	6h	0.2372(4)	-0.0092(4)	1/4	0.899(12)/0.101(12)	0.0216(13)
La/Na(1)	4f	1/3	2/3	0.4993(6)	0.753(10)/0.175(13)	0.0154(11)
Si/Ge	6h	0.4033(5)	0.3729(5)	1/4	0.783(14)/0.217(14)	0.0146(19)
O(1)	6h	0.3210(5)	0.4859(5)	1/4	1	0.034(3)
O(2)	6h	0.5982(5)	0.4713(5)	1/4	1	0.032(2)
O(3)	12i	0.3475(4)	0.2566(4)	0.0694(4)	1	0.0441(19)
O(4)	4e	0	0	0.1873(13)	0.396(10)	0.023(4)
H	4e	0	0	0.03155(6)	0.109(10)	0.02(fixed)

Space group = $P6_3/m$ (no. 176), $a = 9.7912(3)$, $c = 7.2058(2)$ Å. Cell volume = $598.26(3)$ Å³. $R_{\text{wp}} = 3.28\%$.

The atomic displacement parameters (Table 5-4) of the channel oxygens (4e) showed significant anisotropy with high U_{33} displacements suggestive of diffusion along the channel, or the presence of OH groups displaced off the ideal site to allow for efficient hydrogen bonding to neighbouring oxide ions.¹⁵⁵ Large oxygen ADPs are indicative of average scattering of the Si/GeO₄ tetrahedra, as a result of stoichiometric mixing of Si and Ge, together with cooperative relaxation of the BO₄ units that facilitates oxygen ion migration. In addition, the small positive scattering

centers inside the tunnels located by Fourier mapping supports the presence of a low concentration of interstitial sites at the channel periphery. This is consistent with previous studies of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ that linked these interstitial sites to silicate sublattice distortions. As expected, the smaller Si has a significantly lower BVS compared to Ge, while the La^{I} atom in the metaprism is underbonded and Na is slightly overbonded. The average BVS for A^{I} and B sites are close to ideal with 2.35/2.43 and 4.24/4 for the composition of $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ (Table 5-5).

Table 5-4 Anisotropic ADPs for $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ from neutron powder diffraction.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23} ($\text{\AA}^2$)
La/Na(2)	0.0268(16)	0.0267(17)	0.0118(12)	0.0138(13)	0	0
La/Na(1)	0.0150(13)	0.0150(13)	0.0163(19)	0.0075(7)	0	0
Si/Ge	0.024(2)	0.010(2)	0.012(2)	0.0090(19)	0	0
O(1)	0.062(3)	0.046(3)	0.019(3)	0.046(3)	0	0
O(2)	0.036(3)	0.027(2)	0.030(3)	0.015(2)	0	0
O(3)	0.085(3)	0.040(2)	0.0207(13)	0.041(2)	-0.0230(13)	-0.0001(12)
O(4)	0.011(3)	0.011(3)	0.046(8)	0.0054(17)	0	0

Table 5-5 Selected bond lengths and angles for $\text{La}_{8.40}\text{Na}_{1.31}\text{Si}_{4.70}\text{Ge}_{1.30}\text{O}_{25.58}\text{H}_{0.44}$ from neutron powder diffraction.

Bond	Bond Length ($\text{\AA}$)	Bond	Bond Angle ($^\circ$)
La/Na(2)-O(1)	2.7684(2)	O(1)-Si/Ge-O(2)	114.470(3)
La/Na(2)-O(2)	2.4735(2)	O(1)-Si/Ge-O(3)	111.0706(16)
La/Na(2)-O(3) $\times$ 2	2.47519(13)	O(2)-Si/Ge-O(3)	107.0245(16)
La/Na(2)-O(3) $\times$ 2	2.61183(17)	O(3)-Si/Ge-O(3)	105.693(3)
La/Na(2)-O(4)	2.41098(14)		
La/Na(1)-O(1) $\times$ 3	2.48200(13)	BVS for La1	2.87
La/Na(1)-O(2) $\times$ 3	2.53867(14)	BVS for Na1	1.06
La/Na(1)-O(3) $\times$ 3	2.8700(3)	BVS for $A^{\text{I}*}$ / Valence of $A^{\text{I}*}$	2.35 / 2.43
Si/Ge-O(1)	1.66261(5)	BVS for Si	3.95
Si/Ge-O(2)	1.65287(14)	BVS for Ge	5.28
Si/Ge-O(3) $\times$ 2	1.63272(8)	BVS for B^* / Valence of B^*	4.24 / 4

* BVS for A^I and B sites are calculated from BVS of each element, and the valences for both sites are calculated from ideal valence of each element:

$$\text{BVS for } A^I = \text{BVS}_{\text{La}} \times A^I \text{ Occupancy}_{\text{La}} + \text{BVS}_{\text{Na}} \times A^I \text{ Occupancy}_{\text{Na}}$$

$$\text{BVS for } B = \text{BVS}_{\text{Si}} \times B \text{ Occupancy}_{\text{Si}} + \text{BVS}_{\text{Ge}} \times B \text{ Occupancy}_{\text{Ge}}$$

$$\text{Valence for } A^I = 3 \times A^I \text{ Occupancy}_{\text{La}} + 1 \times A^I \text{ Occupancy}_{\text{Na}}$$

$$\text{Valence for } B = 4 \times B \text{ Occupancy}_{\text{Si}} + 4 \times B \text{ Occupancy}_{\text{Ge}}$$

The *in-situ* high temperature neutron diffraction studies proved the loss of hydroxyl species at elevated temperatures because the profile background, with a significant incoherent scattering component from ^1H , decreases through the whole process (Figure 5-10). The major loss was found within 300 °C, which is consistent with the result from TGA. The refined neutron diffraction data collected at 1100 °C showed obvious proton loss and oxygen enrichment (Table 5-6), and more free charge carriers could thus be obtained by the oxidization of the apatites.

Figure 5-10 *In situ* high temperature neutron diffraction data for Si end-member apatite collected between room temperature (25 °C) and 1100 °C.

Table 5-6 Refined cell parameter data (hexagonal cell with the space group $P6_3/m$), atomic coordinates and equivalent isotropic ADPs of Si end-member apatite from neutron powder diffraction collected at 1100 °C.

Unit cell parameters (Å)			Volume (Å ³)		R (%)			GOF
$a = b$	c		V		R_p	R_{wp}	$R(obs)$	$R(all)$
9.7978(4)	7.2452(4)		602.33(5)		3.86	4.91	4.95	4.97
								2.45
atom	Wyck	x	y	z	S.O.F.		U_{iso} (Å ²)	
La/Na(2)	6h	0.2308(5)	-0.0174(5)	1/4	0.911(14)/0.089(14)		0.0304(17)	
La/Na(1)	4f	1/3	2/3	0.4983(8)	0.688(11)/0.164(14)		0.0291(18)	
Si/Ge	6h	0.3987(9)	0.3734(12)	1/4	1/0		0.056(5)	
O(1)	6h	0.3268(6)	0.4894(7)	1/4	1		0.046(3)	
O(2)	6h	0.5958(6)	0.4727(7)	1/4	1		0.058(3)	
O(3)	12i	0.3404(5)	0.2564(5)	0.0690(5)	1		0.061(2)	
O(4)	4e	0	0	0.225(5)	0.552(9)		0.118(7)	

5.4.6 Oxide ion conductivities

Pellets prepared by conventional sintering showed poorer conductivity (Table 5-7), in line with prior studies of apatite systems, where the comparatively low temperature (particularly for the Si rich samples) and the short heat treatment (6 h) to limit Ge loss, was insufficient for full densification. The recorded conductivities are comparatively low for apatite silicate/germanate electrolytes. Starting from the silicate end-member, the conductivity does not change appreciably with Ge doping until $x = 3$, with an obvious increase for $x \geq 4$ that continues to the Ge end-member (Figure 5-11 (A)). This observation can be partly attributed to trends in pellet density, as the silicate rich electrolytes have lower density (< 85% TD) while the germanate rich electrolytes show significantly improved density (up to 97% TD). A major factor, however, affecting the conductivities is likely to be the incorporation of Na, which has the effect of reducing the cation vacancy and oxide ion interstitial contents, both likely to reduce conductivities.

Table 5-7 Conductivity data for pellets prepared from conventional sintering and SPS (H0–6 represent samples with nominal $x = 0 - 6$, and H0a & b are SPS samples of different TD).

Samples prepared by conventional sintering	Density of pellet (% theoretical)	σ (S·cm ⁻¹) at 500 °C	E_a (eV)
H0	68	2.17×10^{-7}	1.07
H1	72	2.27×10^{-7}	1.08
H2	85	1.74×10^{-7}	1.12
H3	79	1.38×10^{-7}	1.13
H4	89	3.41×10^{-7}	1.12
H5	97	1.60×10^{-6}	1.06
H6	95	8.88×10^{-6}	1.01
Samples prepared by SPS	Density of pellet (% theoretical)	σ (S·cm ⁻¹) at 500 °C	E_a (eV)
H0a	96	3.66×10^{-5}	0.87
H0b	83	1.30×10^{-7}	1.15
H1	98	1.49×10^{-5}	0.89
H2	100	1.05×10^{-5}	0.88
H3	100	3.93×10^{-6}	1.00
H4	99	1.31×10^{-6}	1.13
H5	100	8.71×10^{-7}	1.12
H6	100	7.43×10^{-7}	1.11

Figure 5-11 Variation of conductivities with temperature for pellets of mixed $\text{Si}_{6-x}/\text{Ge}_x$ -based lanthanum apatites (H0–6 represent samples with nominal $x = 0 - 6$, and H0b is the SPS sample of lower TD) prepared from (A) conventional sintering and (B) SPS.

Slater *et al.* reported that conductivity increases with Ge content only for a single-phase hexagonal apatite, and the optimum Si/Ge ratio for high conductivity was found to be 2/4 in solid-state synthesized $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$ system.¹⁰³ In our case, Na substitution for La may play a positive role in maintaining the hexagonal structure and suppressing Ge loss, so the highest conductivity was observed for the Ge-based end-member. However, overall the conductivities are lower than observed from these prior studies, which can be related to the presence of Na reducing both cation vacancy and interstitial content. The activation energy initially increases with Ge doping and reaches the maximum at Si : Ge = 1 : 1, then drops back with further Ge doping, but the absolute change is not large. As germanate apatites usually have higher activation energies than silicates, the trend observed here for Si rich samples is accounted for by the low pellet density.

For comparison, pellets of near TD were fabricated using the SPS method. These materials showed significantly improved conductivity for Si-rich apatites, while the conductivity was similar or slightly lower than that of the conventionally sintered pellets for Ge-rich apatites, as the density discrepancies were not large (Figure 5-11 (B)). In terms of the latter, the nanoscaled grain size (Figure 5-12) of SPS pellets may prove negative towards the total conductivity as grain boundary contributions will be more important. The biggest change in conductivity was for the Si end-member (2.17×10^{-7} to $3.66 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 500 °C) matching a higher pellet density (68% to 96% TD) for conventionally sintered and SPS samples. To confirm the negative effect of porosity, a less dense pellet of Si end-member apatite (83%) was made by the SPS method and the conductivity dropped by two orders of magnitude (Table 5-7, Figure 5-11). For dense pellets composed of micron sized crystals, the bulk conductivity will be intrinsic to the material and independent of microstructure (e.g. grain size). This may not be true for nanostructured materials and grain size will be influential. Therefore, the SPS pellets showed lower conductivity than conventionally sintered samples of similar compaction. Additionally, the conductivity decreases with Ge content, which is the opposite of conventionally sintered pellets. The corresponding activation energies for Si rich samples are relatively low (~0.88 eV) while that for Ge rich samples are much

higher (~ 1.12 eV). As there is no significant difference in pellet density and grain size across the chemical series, and very minor Ge loss is expected as SPS does not require long sintering time, the observed conductivity changes through the series are intrinsic and controlled by both the cation vacancies and oxygen defects, with some attenuation of performance arising from the incorporation of Na^+ and possible retention of H^+ .

Figure 5-12 Backscattered electron micrographs (5.0 kV) for pellets of Ge end-member apatite prepared from (A) conventional sintering and (B) SPS.

Since the structural studies had indicated the presence of protons in the sample, some measurements were performed in different atmospheres, in particular comparing results in dry and wet N_2 . The results indicated a small improvement in the conductivity in wet N_2 , which for vacancy conductor systems (e.g. perovskite) can be attributed to a protonic contribution to the conductivity (Figure 5-13). However, as described previously,¹⁵⁶ the oxide ion conduction in these apatite systems is mediated by oxide ion interstitials, and the presence of water can lead to incorporation of both protons and oxide ion interstitials, and so the enhancement in this case could be due to either of these effects.

Figure 5-13 Impedance spectra for Ge end-member apatite in dry ● and wet ○ N_2 at $450^\circ C$ showing a small reduction in resistance in wet N_2 .

5.5 Conclusion

Single-phase and highly crystalline Si/Ge lanthanide oxy-hydroxyapatite powders were obtained by hydrothermal synthesis. The morphology across the series changes from nanosized spheres for Si-based end-member to hexagonal rods for Ge-based end-member. EDS and EPMA found limited contamination by sodium, while FTIR spectroscopy and TGA proved the hydroxyl incorporation as processing artifacts. The Rietveld refinement was consistent with $P6_3/m$ structure and these electrolytes can be represented as $La_{8.50}Na_{1.29}Si_{6-x}Ge_xO_{24}(OH)_{2.79-2y}O_y \square_{y-0.79}$. Overall the conductivities were lower than conventionally synthesized systems, which can be related to the presence of Na lowering the cation vacancy and oxide ion interstitial content.

Chapter 6

Conclusions and Future Work

In this thesis, two homologous chemical series of germanate and silicate apatites were investigated as novel electrolytes for SOFCs. The completed work has led to a deeper understanding of the structure-to-conductivity relationship, and the impact of crystallochemical modification on oxygen migration. A plan for future work was designed that will exploit large single-crystal apatites of various compositions, and to this end, reconnaissance studies have demonstrated the successful growth of lanthanum and gallium-doped neodymium silicate apatite.

6.1 Conclusions

Solid oxide fuel cells, as environmentally-friendly electrochemical devices, will be one of the key technologies replacing non-renewable fossil fuels through direct conversion of chemical energy into electricity. Because the electrolyte is a core component, that determines the ion transport mechanism, the efficiency of ionic mobility and the operational temperature,² a substantial body of research has been directed towards the development of new electrolyte materials, amongst which apatite-type ceramics stand out as promising intermediate-temperature solid oxide ion conductors.

In this thesis, two homologous chemical series of germanate and silicate apatites were investigated as novel electrolytes for SOFCs. The vanadium doped electrolyte apatites with nominal composition $[\text{La}_8\text{AE}_2][\text{Ge}_{6-x}\text{V}_x]\text{O}_{26+x/2}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}; 0 \leq x \leq 1.5$) were synthesized and characterized by laboratory X-ray, synchrotron and neutron diffraction followed by Rietveld refinement. The chemical compositions, microstructures, and local structures were analyzed by SEM and TEM. Single-phase apatites were obtained for nominal $x \leq 0.5$ and structural investigations were invariably consistent with $P6_3/m$ symmetry. All the three alkaline earth series show an order of magnitude enhancement in conductivity, even with low-level vanadium doping; the best performance was for the calcium doped series. Compositions with $\text{AE} = \text{Sr}, x > 0$ and $\text{AE} = \text{Ba}, x \geq 0$ show particularly strong anisotropic grain growth, and therefore their conductive properties are likely to be texturally limited. Overall, the vanadium-doped apatites show potential as electrolytes for intermediate temperature SOFCs, with $\sigma = 3.44 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 500 °C and a relatively low activation energy (0.95 eV) achieved. The conductivities and activation energy are controlled by many factors such as dopant size, melting temperature, crystallinity, and the microstructure of the sintered pellet. Several general principles for crystallochemical tailoring to enhance performance were confirmed here: (i) smaller $A^{\text{I}}\text{O}_6$ metaprism twist angles

open the channel to promote conductivity; (ii) excess oxygen facilitates interstitial mobility leading to higher conductivity; (iii) activation energy is lower in expanded tunnels; and (iv) superstoichiometric oxygen may be ordered or disordered, with the latter favoring ion conduction.

For the mixed Si/Ge lanthanide oxy-hydroxyapatite analogues, single-phase and highly crystalline powders were obtained by hydrothermal synthesis. The morphology across the series changes from nanosized spheres for the Si-based end-member to hexagonal rods for the Ge-based end-member. EDS and EPMA found limited contamination by sodium, while FTIR spectroscopy and TGA proved that hydroxyl was incorporated as a processing artifact. The Rietveld refinement was consistent with $P6_3/m$ and these electrolytes can be compositionally represented as $\text{La}_{8.50}\text{Na}_{1.29}\text{Si}_{6-x}\text{Ge}_x\text{O}_{24}(\text{OH})_{2.79-2y}\text{O}_y\Box_{y-0.79}$. Overall, the conductivities were lower than conventionally synthesized systems, due to the presence of Na lowering the cation vacancy concentration and oxide ion interstitial content, both of which detract from O^{2-} transport.

The completed work for these two apatite electrolyte series has led to a deeper understanding of the structure-to-conductivity relationship, and the impact of crystallochemical modification on oxygen migration. By testing different preparative methods and doping strategies, optimized synthesis conditions and chemical compositions were established (Table 6-1). The detailed characterization was accomplished with several diffraction techniques accompanied by electron microscopy and spectroscopy, that in combination, produce a most complete analysis of crystal structure and bonding chemistry that permits discussion of how intrinsic material properties correlate with conductivity. Supplementary investigations, such as particle size and shape, grain orientation and morphology, and sintered pellet porosity, further support the assessment of ionic conductivities. Overall, these prudent investigations and detailed outcomes contribute to the current research and innovation of electrolyte materials, and serve to guide the future development of solid oxide fuel cell technologies.

Table 6-1 A comparison of the two solid solution series studied in this research.

		Vanadium Doped Apatites	Mixed Si/Ge-Based Apatites
Optimized Synthesis Condition	Method	solid-state reaction	hydrothermal synthesis
	Temperature	1300 °C, 1350 °C	240 °C
	Time	16 hours	16 hours
	No. of Cycles	2	1
Product Feature	Particle Size	~6 μm	~100 nm
	Particle Shape	rounded and equant	spherical and hexagonal cylindrical
Optimized Composition	Nominal	$\text{La}_8\text{Ca}_2\text{Ge}_{5.5}\text{V}_{0.5}\text{O}_{26.25}$	$\text{La}_{9.33}\text{Si}_6\text{O}_{26}$
	Refined	$\text{La}_{7.88}\text{Ca}_2\text{Ge}_{5.35}\text{V}_{0.65}\text{O}_{26.15}$	$\text{La}_{8.42}\text{Na}_{1.42}\text{Si}_6\text{O}_{25.88}\text{H}_{0.63}$
Best Conductivity Achieved at 500 °C		$3.44 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$	$3.66 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$

6.2 Future Work

6.2.1 Introduction

The majority of structural studies of apatite electrolyte materials have relied on powder X-ray and neutron diffraction, and the ionic conductivity measurements are taken from sintered polycrystalline pellets. However, powder methods have led to many conflicting reports regarding the positions of the interstitial ions and predictions of conduction pathways.⁶⁸ Furthermore, open porosity, grain boundaries and grain textures are all unavoidable factors that could reduce ultimate conductivity and complicate the interpretation of ion mobility data. Consequently, single crystals are indispensable for identifying structural rearrangements, and observing intrinsic bulk properties such as anisotropy of electrical conductivity. However, large apatite crystals are rare because they are technically challenging to produce and costly to grow. In a unique study, single crystal $\text{Nd}_{9.33}\text{Si}_6\text{O}_{26}$ was grown and characterized by Higuchi *et al.*¹⁰⁴ It was found that the conductivities parallel to the *c*-axis of the single crystal was about 100–200 times higher than the conductivity of the $\text{Nd}_{10}\text{Si}_6\text{O}_{27}$ polycrystalline ceramic.^{42, 70, 157} In order to improve the ionic conductivity and gain a clearer insight into the crystal structure and conducting pathways, study of the single-crystal apatite should be undertaken.

On the basis of the work completed here for powdered apatite electrolyte materials, the main thrusts for the balance of this research will be to grow large single-crystal apatites with various dopings, in order to establish baseline structural data

(especially interstitial oxygen positions) and study the extent of anisotropic conductivity (parallel and perpendicular to the channels). This approach allows precise structural characterization and more complete interpretation of ionic conductivity, and should remove the current ambiguities that presently surround the correlation of functionality and structure in ion conducting apatites. To this end, and beyond the scope of this thesis, a reconnaissance experiment on single crystal synthesis has been undertaken.

6.2.2 Reconnaissance Single Crystal Growth

The growth of single crystal apatites was carried out using an FZ-T-4000-H-VPO-VII-PC optical floating zone furnace (Crystal Systems Corporation, Japan). The furnace chamber is equipped with four 1.5 kW halogen lamps and corresponding ellipsoidal mirrors that focus the infrared irradiation to a small region (Figure 6-1 a). Compact feed rods of polycrystalline apatite were first prepared by isostatic pressing powdered apatite and solid state sintering at high temperature ($\sim 1650^\circ\text{C}$ / 20 h). One rod was mounted on the top rotator as shown (Figure 6-1 b) and another rod of the same composition (either polycrystalline or single crystal) was mounted below.

Figure 6-1 Optical floating zone furnace (a) Photograph of the mirror furnace (Model: FZ-T-4000-H-VPO-VII-PC), (b) Schematic diagram of the image furnace with double ellipsoidal mirrors [(b) adapted from Higuchi *et al.*¹⁰⁴].

A constant flow of air (2 L/min) was passed through the chamber during growth. As the feed and seed rod tips start to melt, they are brought into contact to form the floating-zone; after the molten zone stabilises, the entire mirror stage translates upwards (5 mm/h) during crystal growth. The rods are counter-rotated at constant speed (40 rpm) to maintain a stable and well mixed molten zone. As the mirror stage shifts upwards, so does the molten zone, and during this slow solidification process, the grains became progressively larger until a large single crystal eventually formed (Figure 6-2).

Figure 6-2 Processes of single crystal growth by the floating-zone method.

In these initial investigations, growth of single crystal lanthanum germanate and lanthanum silicate apatites (nominal composition: $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ / $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) were first attempted, but proved unsuccessful. The as-grown crystal rods were polycrystalline and fractured into small pieces. Furthermore, severe volatilization of germanium was observed in the germanate crystal and the monoclinic ($P2_1/c$) La_2GeO_5 was finally obtained instead of apatite. Based on this experience, compositions close to the successful example ($\text{Nd}_{9.33}\text{Si}_6\text{O}_{26}$) were chosen as a start of single crystal exploration. With La doping on Nd site and Ga doping on Si site, a series of compositions $[\text{Nd}_{9.33-x+y/3}\text{La}_x][\text{Si}_{6-y}\text{Ga}_y]\text{O}_{26}$ ($0 \leq x \leq 2$; $0 \leq y \leq 0.2$) were selected for single crystal growth by the floating-zone method. Long rods of transparent purple crystal (Figure 6-3) were prepared for the whole series in an air

atmosphere and at a growth speed of 10 mm/h. This successful crystal growth proved the feasibility of preparing single crystals over a range of compositions.

Figure 6-3 Photographs of the as grown crystal rods of (a) $\text{Nd}_{8.33}\text{LaSi}_6\text{O}_{26}$, (b) $\text{Nd}_{9.37}\text{Si}_{5.9}\text{Ga}_{0.1}\text{O}_{26}$ with embedded pictures of partial crystal taken under luminescent lamp.

The crystals were primarily characterized by single crystal X-ray diffraction and transmission electron microscopy using a Bruker AXS SMART APEXII single crystal diffractometer ($\text{CuK}_{\alpha 1}$ radiation 1.5406 Å) and a JEOL JEM 2100F respectively. Single crystal $P6_3/m$ apatites were confirmed for this compositional series, and preliminary high-resolution images suggest the hexagonal structure in perfectly ordered at the unit cell scale. As a part of ongoing work, a Laue white beam neutron experiment at ANSTO plays a complementary role to the X-ray diffraction for integrated structure refinement. To locate low occupancy oxygen interstitial sites in heavy cation matrices, neutron diffraction is essential. In addition, the presence of interstitial oxygen in combination with H_2O and OH moieties cannot be investigated by X-rays but can be solved by neutron methods, together with spectroscopy. The homogeneity of crystals can be confirmed using analytical scanning electron microscopy combined with EBSD of polished crystal facets. Further confirmation of composition can be obtained from electron probe microanalysis and electron-dispersive X-ray spectroscopy. The self-consistent interpretations of data from all these techniques yield a most complete structural description of electrolyte apatites that may be correlated with ion transport mechanisms.

6.2.3 Outstanding Questions

The research on apatite electrolyte materials is not yet closed as there remain ambiguous data interpretations and unexplored linkages of structure with performance. Some important outstanding questions include:

- a. *Unexplored doping strategies.* Because the interstitial oxygen that promotes higher conductivity is located in the framework, the synthesis of BO_4/BO_5 hybrids is an obvious means to enhance conductivity. For example, the introduction of high valence B -cations such as Re^{7+} and W^{6+} should promote interstitial oxygen incorporation and ultimately enhance SOFC performance.
- b. *Developing single crystal growth techniques.* Using the infrared mirror image furnace, it is more difficult to grow large colorless crystals (e.g. $La_{9.33}Si_6O_{26}$) as compared to strongly colored crystals (e.g. purple $Nd_{9.33}Si_6O_{26}$), as dark materials better absorb heat; this is why the $La_{9.33}Si_6O_{26}$ crystal broke into small pieces, while the $Nd_{9.33}Si_6O_{26}$ crystal could be grown as a perfect rod. To overcome this difficulty, the growth technique will be further improved by adjusting the rotation speed, supplied heat (percentage of full power), and growth speed. Another way to enhance growth would be doping light-colored apatites for better heat absorption. Due to the volatilization of germanium, it is very challenging to grow the single-crystal $La_{9.33}Ge_6O_{26}$ apatite, however doped varieties (e.g. transition metals on the Ge sites) may prove less difficult. Such compositional modifications could be attempted based on the reconnaissance experiments.
- c. *Determining ion conduction pathways.* A dynamic TEM study that exploits the high spatial and temporal resolution possible in spherical aberration (C_s) corrected instruments could be used to directly observe the tetrahedral / square pyramidal distortion that allows O^{2-} to migrate at high operating temperature. Convergent beam electron diffraction and high resolution TEM, including energy filtered imaging, may be crucial to specify crystallographic diffusion mechanisms with respect to atomic scale order-disorder phenomena and

incommensurate-commensurate modulation of apatites, together with the support of spectroscopy and computer modeling.

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