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**Structural Study of the Apatite $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ by Laue Neutron Diffraction and
Single Crystal Raman Spectroscopy**

Tao An,^{†a*} Alodia Orera,[‡] Tom Baikie,[§] Jason S. Herrin,[†] Ross O. Piltz,^{||}

Peter R. Slater,[¶] Tim J. White[†] and María L. Sanjuán^{‡*}

* Correspondence to: an-tao@imre.a-star.edu.sg; and sanjuan@unizar.es

[†] School of Materials Science and Engineering, Nanyang Technological University, 50
Nanyang Avenue, Singapore 639798, Singapore

[‡] ICMA, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

[§] Energy Research Institute @ NTU (ERI@N), Research Technoplaaza, Nanyang
Technological University, Nanyang Drive, 637553, Singapore

^{||} Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas
Heights, NSW 2234, Australia

[¶] School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT,
UK

^a Present address: Institute of Materials Research and Engineering (IMRE), 3 Research
Link, Singapore 117602, Singapore

Abstract

A single crystal structure determination of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ apatite, a prototype intermediate temperature electrolyte for solid oxide fuel cells grown by the floating-zone method, was completed using a combination of Laue neutron diffraction and Raman spectroscopy. While neutron diffraction was in good agreement with $P6_3/m$ symmetry, the possibility of $P6_3$ could not be convincingly excluded. This ambiguity was removed by the collection of orientation dependent Raman spectra that could only be consistent with $P6_3/m$. The composition of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ was independently verified by powder X-ray diffraction in combination with electron probe microanalysis, with the latter confirming a homogenous distribution of Sr and the absence of chemical zonation commonly observed in apatites. This comprehensive crystallochemical description of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ provides a baseline to quantify the efficacy of cation vacancies, oxygen superstoichiometry and symmetry modification for promoting oxygen ion mobility.

Keywords: apatite; solid electrolyte, neodymium silicate; single crystal; Raman spectrum; neutron diffraction

Introduction

Lanthanide silicates/germanates $[Ln_{9.33}\square_{0.66}]_{\Sigma 1}[(MO_4)_6][O_2\square_1]$ (Ln = lanthanide; M = Si, Ge; $\square$ = Ln/O vacancy)) with the apatite structure are promising intermediate temperature electrolytes for solid oxide fuel cells (IT-SOFC) and show greater oxygen mobility compared to yttria-stabilised zirconia (YSZ) from 500-700°C.^{1, 2} The structural formula of the prototypical hexagonal apatite ($P6_3/m$) can be expressed as $[A^F_4][A^T_6][(BO_4)_6]X_2$, where A are larger rare earth or alkaline earth metals, B are crystallogens or pnictogens, and X are anions. A framework constructed from A^FO_6 metaprisms corner-connected to rigid SiO_4 tetrahedra, encloses one-dimensional c -axis tunnels containing the X anions surrounded by A^T cations. The superior oxygen transport of apatites at lower temperatures arises due to the smaller activation energies for interstitial oxygen, compared to vacancy mediated transport in YSZ,^{3, 4} that arises when oxygen interstitials are concomitantly introduced with partial filling of Ln vacancies ($2\square_{Ln}^{3+} + 3\square_{O}^{2-} \rightarrow 2Ln^{3+} + 3O^{2-}$). For example, in $[La_{9.33+2/3x}][(\text{SiO}_4)_6][O_{2+3/2x}]$, $0 \leq x < 1$,⁵ the increasing La content leads to progressively more mobile oxygen,⁶ although the putative end-member $La_{10}(\text{SiO}_4)_6O_3$ ($x = 1$) may not exist. In contrast, the apatite $[La_8Sr_2][(\text{SiO}_4)_6][O_2]$ is charge balanced through $2La^{3+} \leftrightarrow 3Sr^{2+}$ exchange with the absence of superstoichiometric oxygen (26 oxygen per formula unit) and consequently shows much lower O^{2-} conductivity than La-rich compositions. To date, the influence of structural defects on oxygen transport in silicate apatites has not been examined

rigorously due to the lack of high quality single crystals. In particular, anisotropic characteristics are rarely reported, as this information is not readily extracted from polycrystalline ceramics where pores and grain boundaries attenuate ion transport.⁷

Raman spectroscopy has proven invaluable for identifying interstitial oxide ions,^{8, 9} order-disorder effects^{10, 11} and oxygen dynamics in apatites.¹² However, spectral interpretation has been controversial due to: 1) low occupancy and positional disorder of the mobile oxygen coupled to the infilling of Ln vacancies and/or inclusion of large cation dopants, 2) lower or mixed crystallographic symmetries and 3) Raman mode overlap in polycrystalline materials. Furthermore, the uniaxial optical character of hexagonal apatites will alter selection rules and introduce spectral artefacts not generally considered.

In this work, we have undertaken a joint neutron diffraction and Raman spectroscopic study of single crystal $Nd_8Sr_2Si_6O_{26}$.¹³ The rare earth chosen was neodymium, rather than the more common lanthanum, as the former better absorbs infrared wavelengths and provides a more stable melt during crystal growth.⁷ Despite their low conductivity, stoichiometric $Ln_8A_2Si_6O_{26}$ apatites are of interest as the elimination of cation vacancies, and very low interstitial oxygen content, provides a baseline chemical and crystallographic model onto which the contributions of different defect types towards oxygen mobilisation are overlaid. Single crystal Raman spectroscopy most clearly identifies mode symmetries, and reveals the angular dependence of mode intensities affected by uniaxial character. The results presented here for $Nd_8Sr_2Si_6O_{26}$ provide

reference crystallochemistry to further the investigation of non-stoichiometry apatite electrolytes.

Experimental methods

The $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ single crystal (Figure 1) was grown using the floating-zone technique.¹⁴ An earlier reconnaissance study found that anisotropic ionic conductivity was consistent with crystal chemical characterisation by scanning transmission electron microscopy (STEM) and a preliminary single crystal X-ray diffraction analysis.¹³ In this work, a portion of the single crystals was sectioned and pulverised for analysis by powder X-ray diffraction (PXRD) for comparison with single crystal neutron diffraction. Patterns were accumulated on a Bruker D8 Advance diffractometer using $\text{Cu } K\alpha$ X-rays generated at 40 kV and 40 mA, from $10 - 130^\circ 2\theta$ range with a step size 0.02° and dwell time 1.2s per step. The intensity of the strongest reflection was over 10,000 counts, and Rietveld refinements were carried out with *TOPAS* software.¹⁵ Quantitative wavelength dispersive X-ray spectroscopy (WDS) was performed on a mirror polished specimen using a JXA-8530F field emission source electron probe X-ray microanalyser (EPMA). A 15nm conductive carbon coating was applied to the sample prior to analysis. Point analyses were acquired using a $10 \mu\text{m}$ diameter beam with a current of 40 nA and an accelerating voltage of 15 kV. X-ray lines were monitored using the spectrometer crystals indicated: Si $K\alpha$ (TAP), Sr $L\alpha$ (PET), Nd $L\alpha$ (LIF-H), O $K\alpha$ (LDE1-H), with peak counting times of 20 seconds for O, Si, and Nd and 40 seconds for Sr. Background measurements bracketed each peak for combined counting times equalling the corresponding peak counting times,

with the exception of Si, for which a slope factor was applied to a single background measurement in order to avoid interference from Sr *L*-lines. Measured peak and background regions of all analytes were free of interferences within the sample and standard matrices. Results were quantified against well-characterised natural and synthetic external calibration standards. Reproducibility of repeat analysis of standards was within 1% of measured values using the Armstrong/Love Scott¹⁶ matrix correction algorithm and the FFAST mass absorption coefficient dataset.^{17, 18}

Single crystal neutron diffraction patterns were collected at 100K on the Koala Laue diffractometer at the Open Pool Australian Lightwater (OPAL) reactor operated by the Australian Nuclear Science and Technology Organisation (ANSTO). This Laue diffractometer uses polychromatic thermal-neutrons coupled with a large solid-angle (8 steradians) cylindrical image-plate detector. An Nd₈Sr₂Si₆O₂₆ crystal of approximate dimensions 1.5 × 1.5 × 1.5 mm was mounted on an aluminium pin with silicone grease. The diffraction patterns were indexed using LAUEGEN^{19, 20} and the reflections integrated using a 2D version of the $\sigma(I)/I$ algorithm described by Wilkinson *et al*²¹ and Prince *et al*.²² No absorption correction was necessary. The reflections were normalised to the same incident wavelength using a curve derived by comparing equivalent reflections and multiple observations via the program LAUENORM.²³ Only reflections with wavelengths between 1.0 Å and 2.9 Å were accepted for the normalisation procedure as those outside this range were too weak, or had too few equivalents to allow determination of the normalisation curve confidently. The structure was determined using Jana 2006²⁴

with the starting model derived from the single crystal X-ray diffraction.²⁵ VESTA²⁶ was used for 3D visualisation of the difference Fourier maps to identify structural disorder.

Raman measurements were recorded in backscattering geometry on selected planes of the single crystals using a DILOR XY spectrometer with excitation through an X10 microscope objective lens. Entrance and exit polarizers were used to minimise polarization losses. Initially, different excitation wavelengths allowed discrimination of Raman bands and possible Nd³⁺ emission lines with $\lambda_{\text{laser}} = 496.5$ nm found optimal in order to avoid Nd³⁺ luminescence bands overlapped with the Raman bands.

Results and discussion

Composition analysis by EPMA

Chemical compositions were determined by EPMA analyses (10 replicates) and the atomic abundances normalised to 6 silicon atoms as *B* site non-stoichiometry is unlikely (Table S1). The mean element totals are within 1% of unity, suggesting >99% accuracy. Oxygen concentration was derived from measured values of O *K* α . The reproducibility of concentration values for replicates was < 1% RSD for all elements, with the exception of Sr (1.3%), indicating the sample is homogeneous at the precision of this methodology. The resultant cation abundances are within error of the idealised formula Nd₈Sr₂Si₆O₂₆. Oxygen yields a slightly higher value of 26.37 $\pm$ 0.23 atoms that may reflect genuine excess, but caution must be exercised due to uncertainty in the thickness of the

conductive carbon coating applied to the sample surface, compared to the standards and the relatively high absorption of O $K\alpha$ by C.²⁷

Structure solution by Laue neutron diffraction

Masubuchi *et al.* reported $P6_3/m$ symmetry for $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$.²⁸ In this model, Sr solely locates at the $\text{Nd}^{\text{F}}(1)$ site, and $[\text{Sr}/\text{Nd}(1)]\text{O}_6$ metaprisms are corner-connected to the SiO_4 tetrahedra (each consists of one O(1), one O(2) and two O(3)) to form a framework structure²⁹ that surrounds the $\text{Nd}^{\text{T}}(2)$ and O(4) in the tunnel (Figure 2). However, a separate study on the La-analogue ($\text{La}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$) found $P6_3$ symmetry,³⁰ in which the $4f$ cation site splits into two $2b$ sites, and the $12i$ O(3) site splits into two $6c$ sites, O(3) and O(4), with O(5) being the tunnel O^{2-} site. Given this ambiguity, neutron diffraction data were tested against both $P6_3/m$ and $P6_3$ (Tables 1 & 2). For the higher symmetry, the determination found Sr locates solely at the $\text{Nd}^{\text{F}} 4f$ site. In lower symmetry $P6_3$ this $4f$ site splits into two $2b$ sites, but unexpectedly, the refinement converged to a favoured distribution of Sr to one $(1/3, 2/3, z)$ site, that led to a better goodness-of-fit (GOF) of 1.24, as compared to 1.48 with the $P6_3/m$ model. However, it was readily shown to be a statistical artefact as calculations performed with an equal distribution of Nd:Sr constrained across the two $2b$ sites gave an identical GOF and only slightly increased reliability values (GOF = 1.24; $R = 6.60\%$; $R_w = 3.32\%$). To investigate Sr-partitioning further, high quality powder X-ray diffraction data from pulverised $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ was undertaken to better separate Nd:Sr. Rietveld refinement of this PXRD data starting with the $P6_3$ model derived from the single crystal neutron diffraction refinements with only

instrumental parameters and Nd/Sr cation occupancies released showed no preference for the Nd and Sr over the two alternative $2b$ sites. Thus, there was no case to support Nd/Sr ordering over the framework $Ln^F O_6$ metaprisms (see Figure S1 for the PXRD refinement profile and the distribution of the Nd/Sr over the $2b$ sites). Also, no supercell reflections were observed in either the neutron or X-ray diffraction studies to indicate such ordering of the Nd/Sr cations, which was justified by a parallel TEM study (to be published elsewhere).¹³ Therefore, the correct symmetry could not be discerned between $P6_3/m$ and $P6_3$ solely by X-ray or neutron diffraction, and Raman spectroscopy was thus performed, as described in the subsequent section. Table 3 contains the anisotropic atomic displacement parameters, while Tables S2 and S3 show selected bond lengths, angles, and bond valence sums from the neutron refinements in each space group.

EPMA measures the local compositions to a depth of $\sim 1 \mu m$ and was in agreement with neutron diffraction that inspects the entire volume of the crystal shard and yielded the refined composition $Nd_{8.0(2)}Sr_{2.0(2)}Si_6O_{26}$ ($P6_3/m$). This agrees well with the idealised value and provides further confirmation of the chemical homogeneity at the millimetre scale. Nonetheless, difference Fourier maps reveal weak intensity centres, possibly arising from low occupancy oxygen interstitial sites. The atomic positions and interatomic distances to respective nearest atomic neighbours for these Fourier peaks are listed in Table 4. In addition, from the Fourier intensity and neutron scattering lengths (Table S4), the oxygen concentration at each interstitial site can be calculated. Some of these potential oxygen interstitial sites are close to the SiO_4 tetrahedra, and likely to promote localised structural distortion as the SiO_4 units (being essentially rigid bodies)

tilt away from their ideal locations. Such tilting is characteristic of apatites, as has recently been described for mimetite ($\text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$),³¹ where AsO_4 tetrahedra rotate to accommodate the stereochemically active $6s^2$ lone pair electrons of the Pb^{2+} , leading to a monoclinic supercell ($a_{\text{mon}} = b_{\text{mon}} = 2a_{\text{hex}}$; $c_{\text{mon}} = c_{\text{hex}}$). In the present context, it is possible that the Pb^{2+} lone pair electrons in $\text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$ occupy similar positions to the interstitial oxygens of electrolyte material, as stereochemically active lone pairs are of a similar volume to an O^{2-} ion.^{32, 33} However, for $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ the low abundance of oxygen interstitials does not drive the formation of a supercell, nor can they be detected as neutron scattering centres in the single crystal.

Raman Spectral Characteristics of $P6_3/m$ and $P6_3$ Symmetry

For $P6_3/m$ $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ there are 33 Raman active modes ($12 A_g + 8 E_{1g} + 13 E_{2g}$) where 15 belong to SiO_4 internal modes, 4 to SiO_4 librations and 14 to Nd, SiO_4 and O(4) translations (Table 5). Internal modes for an isolated and regular tetrahedron are: ν_1 (symmetric stretching), ν_2 (symmetric bending), ν_3 (asymmetric stretching) and ν_4 (asymmetric bending), and in silicate apatites typically appear at: $\nu_1 \sim 850 \text{ cm}^{-1}$; $\nu_3 \sim 930 \text{ cm}^{-1}$; $\nu_2 \sim 400 \text{ cm}^{-1}$; $\nu_4 \sim 530 \text{ cm}^{-1}$.^{8-10, 12, 34} Insertion of the tetrahedron into a crystal lattice splits the number of modes by lowering symmetry and through correlated vibrations between different tetrahedra. These effects lead to the appearance of multiple bands in the region of ν_1 , ν_2 , ν_3 and ν_4 (Table 6).

Should the symmetry be lowered to $P6_3$, the number of Raman active modes increases to 63 (Table 7), which decomposes as $21 A + 21 E_1 + 21 E_2$. For completeness, the decomposition of the 27 internal modes expected in this space group is given in Table 6. Removing inversion symmetry activates in Raman spectra polar modes that manifest with different frequencies according to their longitudinal or transverse character. Because A and E_1 modes are polar, the observed frequencies should multiply to 105 ($21A_{TO}$, $21A_{LO}$, $21E_{1,TO}$, $21E_{1,LO}$, $21E_2$, where “LO” and “TO” denote longitudinal and transverse optical modes respectively).

The Raman tensors, R_{is} , for $6/m$ symmetry (as in $P6_3/m$) are:

$$A_g = \begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}$$

$$E_{1g} = \begin{pmatrix} & c & \\ c & d & \\ & d & \end{pmatrix}, \begin{pmatrix} & -d & \\ -d & c & \\ & c & \end{pmatrix}$$

$$E_{2g} = \begin{pmatrix} e & f & \\ f & -e & \\ & & \end{pmatrix}, \begin{pmatrix} f & -e & \\ -e & -f & \\ & & \end{pmatrix}$$

Raman tensors for the 6 factor group (as in $P6_3$ space group) are the same as for $6/m$ except for the parity labelling and polarity of the A and E_1 modes. The expressions “parallel” and “crossed” will be used for configurations with $\mathbf{e}_i // \mathbf{e}_s$ and $\mathbf{e}_i \perp \mathbf{e}_s$, respectively,

where $\mathbf{e}_i$ and $\mathbf{e}_s$ stand for the polarization directions of incident and scattered electric fields respectively.

Mode identification is straightforward if measurements are performed along crystal directions in which only one type of symmetry is active. In addition, the discussion about optical anisotropy is easier if measurements are performed with the z axis either perpendicular to the surface or contained in it. Thus, most of the results presented in this work were recorded within a plane that contains the z axis so that both the incident and scattered beams are perpendicular to the optical axis (see scheme in Figure 4). We denote as u the direction perpendicular to the c axis in such a plane. This u - z plane provides the crystal directions required for mode identification in the centrosymmetric $P6_3/m$ space group: zz and uz spectra give A_g and E_{1g} modes, respectively, whereas the uu spectrum presents a superposition of A_g and E_{2g} symmetries, which allows identification of the E_{2g} modes.

The situation is more complicated for the non-centrosymmetric space group $P6_3$. As mentioned previously, A and E_1 modes are now polar and will manifest with different frequencies depending on their longitudinal or transverse character, which in turn depends on the relative orientation of mode propagation ($\mathbf{q}$) and polarization ($\mathbf{p}$). According to the tables, the polarity of A modes is along z and that of E_1 modes is along $\{x, y\}$ directions. Then, in a backscattering configuration onto the u - z plane, with $\mathbf{q} \perp z$, A_{TO} , E_{1LO} and E_{1TO} are the excited components. In contrast, if spectra are collected from the (001) plane ($\mathbf{q} \parallel z$) only the LO component of the A modes would be observed (E_1

modes are not active in this plane). In an arbitrary case, with z neither parallel nor perpendicular to the direction of incidence, we should expect the simultaneous presence of the LO and TO components of all polar modes will be present. In summary, if the lattice is polar, A and E_1 modes should appear either split or with a different frequency when comparing spectra measured in different planes. The polarity does not affect the behaviour of the non-polar E_2 modes.

Raman spectral Analysis

Figure 5 shows zz , uz and uu spectra of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ single crystals recorded at room temperature within the u - z plane. By comparison to other Si apatites,¹² the bands arising from internal vibrations of SiO_4 tetrahedra are readily identified: ν_1 and ν_3 stretching modes around 860 and 920 cm^{-1} and bending modes ν_2 and ν_4 at about 400 and 530 cm^{-1} , respectively. These values are slightly higher than those of $\text{La}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$, due to the smaller lattice parameters of the Nd compound.⁹ Translation external modes are expected below 600 cm^{-1} . Vibration of the tunnel oxygen O(4), in particular, is expected at relatively high frequencies of the order of 400-500 cm^{-1} ,⁸ thus possibly overlapping with the bending internal modes. As regards to the libration of SiO_4 tetrahedra, they are expected also at low or moderate frequencies ($< 300 \text{ cm}^{-1}$).

The readily identifiable bands are 12 A_g , 8 E_{1g} and 11 E_{2g} modes, in close expectation for $P6_3/m$ symmetry (12 A_g + 8 E_{1g} + 13 E_{2g}). To have a full picture of Raman activity and accurate frequencies, spectra were decomposed as a sum of pseudo-Voigt band profiles

using LabSpec software with position, width, integrated area and Gaussian/Lorentzian mixing fitted. This procedure accentuates weak and broad bands that might arise from lower symmetry, oxygen disorder coupled to Sr incorporation, or second order effects (Table 8). Even including the secondary features, the number of observed bands is significantly less than expected for $P6_3$. Moreover, as LO/TO splitting was not detected for any mode there is no evidence for long-range symmetry reduction. For example, the uu spectra measured in different crystallographic planes appear similar (Figure 5) and the A modes, in particular, present the same frequencies as in the zz spectrum without splitting.

Spectral decomposition also found the A_g part of the ν_1 band consists of two components (see inset in Figure 5), the one at lower frequency (850 cm^{-1}) having about one tenth of the intensity of the main feature at 859 cm^{-1} . The splitting of the ν_1 band is quite unexpected in $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ but has been detected in other apatites, where it has been attributed to perturbation of SiO_4 tetrahedra by either nearby cation vacancies or interstitial oxide ions.^{10, 34} As previous Raman studies¹⁰ were performed on polycrystalline samples, the superposition of the E_{2g} and A_g components of the ν_1 band may mask the A_g splitting shown in this work. In $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$, without cation vacancies and negligible interstitial oxygen concentration,³⁵ this splitting may indicate perturbation of the SiO_4 tetrahedron caused by disorder on the Nd sublattice induced through the incorporation of strontium.

Raman Spectra Angular Dependence

Away from the principal crystal orientations, the selection rules appear to fail in the case of the A_g modes, something that can be explained by the optically anisotropic character of the $Nd_8Sr_2Si_6O_{26}$ apatite. Raman spectra of $Nd_8Sr_2Si_6O_{26}$ were measured in backscattering configuration within the u - z plane as a function of the angle (α) formed by the electric field and the u axis in “parallel” and “crossed” configurations (Figures 6 and 7 respectively). In the absence of uniaxial effects, Raman intensities are proportional to the usual expression –

$$I \propto |\sum e_i R_{is} e_s|^2$$

where R_{is} and e_i , e_s were defined above. Making use of the appropriate Raman tensors for A_g mode symmetry it can be shown the angular dependences of the mode intensities in the u - z plane with u along an unknown direction ($\cos\beta$, $\sin\beta$, 0) are expressed as -

$$A_g (//) = (a \cos^2\alpha + b \sin^2\alpha)^2 \quad (1)$$

$$A_g (\perp) = (a - b)^2 \sin^2\alpha \cos^2\alpha \quad (2)$$

It is noted that the β dependence disappears in the final expressions.

Figure 8 shows the angular dependence of the intensity of the A_g component of the SiO_4 breathing mode at 859 cm^{-1} and of the A_g modes at 530 and 925 cm^{-1} . When the experimental points (circles) are superimposed on the intensity evolution (dashed line) given by equations (1) and (2) that simplify to $I = a^2$ and $I = b^2$ for $\alpha = 0$ and 90° , the

correspondence is unsatisfactory. The discrepancy is attributed to the depolarization of light induced by the optical anisotropy of the material. In an optically uniaxial system the incident light decomposes into two waves: the ordinary wave, propagating with refraction index n_0 (ordinary index), and the extraordinary wave, propagating with refraction index n_{eff} that depends on the angle (θ) formed by the direction of propagation of light and the optical axis in the form:

$$\frac{1}{n_{eff}^2} = \frac{\cos^2 \theta}{n_0^2} + \frac{\sin^2 \theta}{n_e^2}$$

n_e being the extraordinary refraction index. The difference between n_0 and n_e produces a dephasing between the ordinary and extraordinary waves that result in a depolarisation of light as it travels through the medium. For $\theta = 90^\circ$, as in our measurements in the u - z plane, $n_{eff} = n_e$ and the uniaxial effects are maximised.

These effects are consistent with the formalism of Alonso-Gutiérrez *et al.*³⁶ that decomposes the electric field at each step of the Raman process as the sum of an ordinary and an extraordinary component and introducing a dephasing factor $\exp(i\delta)$ on one of the components, such that:

$$\delta = -\frac{2\pi}{\lambda}(n_{eff} - n_0)d, \quad (3)$$

where λ is the laser wavelength and d the path run by the light either at the entrance or at the exit of the point where the Raman events take place. According to equation (3) δ is different for each plane (θ) but is the same for all modes and is independent of the measurement angle within the plane, α .

It can be shown that the angular dependences for A_g mode intensities when measuring onto a u - z plane are expressed as:

$$A_g (//) = (a \cos^2 \alpha \cos 2\delta + b \sin^2 \alpha)^2 + a^2 \cos^4 \alpha \sin^2 2\delta \quad (4)$$

$$A_g (\perp) = (a^2 + b^2 - 2ab \cos 2\delta) \sin^2 \alpha \cos^2 \alpha \quad (5)$$

These relationships successfully fit the experimental intensities for parallel and crossed configurations within the u - z plane (Figure 8). All three sets of data were fitted with $\delta = 50 \pm 1^\circ$.

As suggested by Alonso-Gutiérrez *et al.*,³⁶ a qualitative estimate of the absolute value of the birefringence ($\Delta = n_e - n_o$) can be obtained from the value of δ and equation (3) provided that the optical path is known. Taking for instance $d = 10$ microns it is found that $|\Delta| = 0.00643$, which is close to the values reported for the apatite phosphate mineral $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.³⁷

Conclusions

Neutron diffraction of a large untwinned $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ crystal was indistinguishably modelled in $P6_3/m$ and $P6_3$ models with a slightly improved GOF associated with the latter. In both cases, the refined average compositions conform to the nominal chemistry, verified by EPMA study that found a homogeneous distribution of strontium. The ambiguous structure determination was resolved through Raman spectroscopy that found modes consistent with the higher symmetry ($P6_3/m$). Moreover, angular dependent single crystal Raman spectroscopy detected the optical uniaxial character of hexagonal $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$. The Raman results suggest that any deviation from $P6_3/m$ is so small that it has little effect in the Raman activity. Overall, the results are consistent with a centrosymmetric space group $P6_3/m$ as the number of modes is far fewer than expected for $P6_3$ and no LO/TO split frequencies were observed. Splitting of the A_g component of the SiO_4 internal mode can be attributed to Sr doping, although a low concentration of Frenkel interstitial oxide ions may also perturb the SiO_4 tetrahedra. Optical uniaxial effects are proposed to explain the apparent non-fulfillment of selection rules if spectra are recorded out of the main crystal directions. If there is such a symmetry lowering, as analogous to $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$,³⁰ it gives only broad bands with weak activity.

Associated Content

One figure showing PXRD refinement profile; four tables listing EPMA data, selected bond lengths and angles for $P6_3/m$ and $P6_3$, and selected neutron scattering lengths; two Crystallographic Information Files (CIF) for single crystal neutron diffraction data in $P6_3/m$ and $P6_3$ symmetry. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

Author Information

Corresponding Authors

* Email: an-tao@imre.a-star.edu.sg.

* Email: sanjuan@unizar.es.

Notes

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Figures and Tables

Table 1. Specimen dimensions of the $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ crystal, parameters of neutron diffraction and lattice parameters.

Crystal size	1.5×1.5×1.5mm	1.5×1.5×1.5mm
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3/m$ (No.176)	$P6_3$ (No.173)
Temperature	100K	100K
Unit cell dimensions		
a (Å)	9.5812(3)	9.5812(3)
c (Å)	7.0655(5)	7.0655(5)
V (Å ³)	561.71(5)	561.71(5)
Density (g cm ⁻³)	5.6515	5.6702
μ (cm ⁻¹)	0.029	0.029
Wavelength (Å)	0.71069	0.71069
Collection limits (θ ,°)	3.79 – 41.31	3.79 – 41.31
Data measured	2006	2006
Unique reflections	1016	1924
Reflections with $I \geq 3\sigma(I)$	774	1412
R	0.0567	0.0658
R_w	0.0344	0.0331
GOF	1.48	1.24
D residual (fm·Å ⁻³)		
+	0.90	0.69
-	0.95	0.79

Table 2. Refined atomic positions, site occupancy and isotropic atomic displacement parameters (ADPs) from Laue neutron diffraction of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ at 100K. The Sr was found to solely locate at the $4f$ site in the $P6_3/m$ model, and the $(1/3, 2/3, z)$ $2b$ site in the $P6_3$ model.

Site	Wyckoff	x	y	z	Occupancy	U_{Iso}
$P6_3/m$						
Nd(1)	$4f$	$1/3$	$2/3$	-0.00015(9)	0.49(5)	0.0074(2)
Sr	$4f$	$1/3$	$2/3$	-0.00015(9)	0.51(5)	0.0074(2)
Nd(2)	$6h$	0.01063(5)	0.24229(5)	$1/4$	1	0.0060(2)
Si	$6h$	0.3983(1)	0.3699(1)	$1/4$	1	0.0065(3)
O(1)	$6h$	0.31607(9)	0.48180(9)	$1/4$	1	0.0127(2)
O(2)	$6h$	0.59438(8)	0.47298(8)	$1/4$	1	0.0117(2)
O(3)	$6h$	0.34076(7)	0.25096(6)	0.06767(8)	1	0.0140(2)
O(4)	$2a$	0	0	$1/4$	1	0.0144(3)
$P6_3$						
Nd(1)	$2b$	$1/3$	$2/3$	-0.0027(3)	0.04(7)	0.0063(5)
Sr	$2b$	$1/3$	$2/3$	-0.0027(3)	0.96(7)	0.0063(5)
Nd(2)	$2b$	$2/3$	$1/3$	-0.0024(3)	1	0.0087(5)
Nd(3)	$6c$	0.01067(4)	0.24234(4)	0.2490(3)	1	0.0061(1)
Si	$6c$	0.39836(8)	0.36986(9)	0.2457(5)	1	0.0065(2)
O(1)	$6c$	0.31609(7)	0.48174(7)	0.2486(4)	1	0.0128(2)
O(2)	$6c$	0.59433(6)	0.47299(7)	0.2485(5)	1	0.0118(2)
O(3)	$6c$	0.3423(2)	0.2514(2)	0.0660(3)	1	0.0131(6)
O(4)	$6c$	-0.3390(3)	-0.2506(2)	-0.0692(3)	1	0.0155(7)
O(5)	$2a$	0	0	0.2538(8)	1	0.0140(3)

Table 3. Refined anisotropic ADPs from Laue neutron diffraction of Nd₈Sr₂Si₆O₂₆ at 100K.

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
<i>P6₃/m</i>						
Nd(1)/Sr	0.0091(2)	0.0091(2)	0.0040(3)	0.0046(1)	0	0
Nd(2)	0.0063(2)	0.0064 (2)	0.0051(2)	0.0029(2)	0	0
Si	0.0072(3)	0.0064(3)	0.0063(4)	0.0036(3)	0	0
O(1)	0.0166(3)	0.0127(3)	0.0134(3)	0.0109(2)	0	0
O(2)	0.0082(3)	0.0096(3)	0.0152(4)	0.0028(2)	0	0
O(3)	0.0231(3)	0.0115(2)	0.0084(3)	0.0094(2)	-0.0061(2)	-0.0028 (2)
O(4)	0.0103(3)	0.0103(3)	0.0227(8)	0.0051(2)	0	0
<i>P6₃</i>						
Nd(1)/Sr	0.0084(6)	0.0084(6)	0.002(1)	0.0042(3)	0	0
Nd(2)	0.0101(5)	0.0101(5)	0.006(1)	0.0051(3)	0	0
Nd(3)	0.0064(1)	0.0066(2)	0.0050(2)	0.0030(1)	-0.0009(5)	-0.0007(5)
Si	0.0072(3)	0.0065(2)	0.0061(3)	0.0037(2)	-0.0023(9)	-0.0004(9)
O(1)	0.0168(3)	0.0129(2)	0.0135(3)	0.0110(2)	0.0049(9)	0.0012(9)
O(2)	0.0082(2)	0.0097(2)	0.0153(3)	0.0028(2)	0.0002(10)	0.0020(9)
O(3)	0.0225(8)	0.0125(7)	0.010(1)	0.0131(7)	-0.0097(6)	-0.0083(5)
O(4)	0.0242(9)	0.0110(7)	0.007(1)	0.0055(7)	-0.0027(6)	0.0028(5)
O(5)	0.0104(3)	0.0104(3)	0.0213(8)	0.0052(1)	0	0

Table 4. Oxygen interstitial positions, their respective peak concentrations and nearest neighbours at 100K, arranged from highest to lowest concentration.

	x	y	z	Conc. ($\text{\AA}^{-3}$)	Nearest to	x	y	z	Distance ($\text{\AA}$)
O _{Int} 1	0.7375	0.2011	$\frac{1}{4}$	0.041	Si	0.6302	0.0285	$\frac{1}{4}$	1.45
O _{Int} 2	0.3684	0.1010	$\frac{1}{4}$	0.040	Nd(2)	0.2317	-0.0106	$\frac{1}{4}$	1.21
O _{Int} 3	0.1533	0.4994	0.1574	0.040	O(1)	0.3161	0.4818	$\frac{1}{4}$	1.78

Table 5. Raman activity in $P6_3/m$.

Atom	Site	Raman activity in $P6_3/m$
Nd1	$4f$	$A_g + E_{1g} + E_{2g}$
Nd2	$6h$	$2 A_g + E_{1g} + 2 E_{2g}$
Si	$6h$	$2 A_g + E_{1g} + 2 E_{2g}$
O1	$6h$	$2 A_g + E_{1g} + 2 E_{2g}$
O2	$6h$	$2 A_g + E_{1g} + 2 E_{2g}$
O3	$12i$	$3 A_g + 3 E_{1g} + 3 E_{2g}$
O4	$2a$	E_{2g}
Total = 12 A_g + 8 E_{1g} + 13 E_{2g} (33 modes)		

Table 6. Internal modes of SiO_4 tetrahedra in $P6_3/m$ and $P6_3$ space group.

Tetrahedra	Raman activity in $P6_3/m$	# of modes	Raman activity in $P6_3$	# of modes
ν_2 (E)	$A_g + E_{1g} + E_{2g}$	3	$2A + 2E_1 + 2E_2$	6
ν_4 (T ₂)	$2A_g + E_{1g} + 2E_{2g}$	5	$3A + 3E_1 + 3E_2$	9
ν_1 (A ₁)	$A_g + E_{2g}$	2	$A + E_1 + E_2$	3
ν_3 (T ₂)	$2A_g + E_{1g} + 2E_{2g}$	5	$3A + 3E_1 + 3E_2$	9
Total	$6A_g + 3E_{1g} + 6E_{2g}$	15	$9A + 9E_1 + 9E_2$	27

Table 7. Raman activity in $P6_3$.

Atom	Site	Raman activity in $P6_3$
Nd1	$2b$	$A + E_1 + E_2$
Nd2	$2b$	$A + E_1 + E_2$
Nd3	$6c$	$3A + 3E_1 + 3E_2$
Si	$6c$	$3A + 3E_1 + 3E_2$
O1	$6c$	$3A+3E_1+3E_2$
O2	$6c$	$3A+3E_1+3E_2$
O3	$6c$	$3A+3E_1+3E_2$
O4	$6c$	$3A+3E_1+3E_2$
O5	$2a$	$A + E_1 + E_2$
Total = 21 A + 21 E₁ + 21 E₂ (63 modes)		

Table 8. Experimental frequencies and assignment within in $P6_3/m$ space group. Numbers in italics indicate weak and broad bands evidenced only through the fitting procedure.

A _g modes (cm ⁻¹)	E _{1g} modes (cm ⁻¹)	E _{2g} modes (cm ⁻¹) (from <i>uu</i> spectrum)	Assignment
111.8	97.1	104.3	Nd and SiO ₄ translations and SiO ₄ librations
127.8	132		
	164.1	160	
189.2	196.7	189.6	
227.8	224.3	222	
		236.3	
250	243.7		
264.4	259.8	261.3	
292.9	293.5	290.6 <i>leak</i>	
386.1	384.8		v ₂ + O(4)
405	395.5	403.2	
	427 <i>leak</i>	424.7	
		431.6	
		517.7	v ₄ + O(4)
529.6	523.8	572.9 <i>vw</i>	
850.2+858.7	858.7 <i>leak</i>	850 +858.6	v ₁
895.8	876.3	888	v ₃
923.7	924 <i>leak</i>	919.8	
954.1	947.7	943.5

Figure 1. $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ single crystal grown via floating-zone method.

Figure 2. The apatite structure of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ with $P6_3/m$ symmetry. The Nd(1) and Sr dopant atoms occupy the framework sites (4f) and their occupancy is represented by the filled area of the sphere. Each Nd(1)/Sr forms a metaprism with three O(1) atoms (6h) and three O(2) atoms (6h). A framework structure is formed when these metaprisms are corner-connected to SiO_4 tetrahedra (with centered Si (6h) bonded to one O(1) (6h), one O(2) (6h) and two O(3) atoms (12i)). This framework surrounds the Nd(2) atoms (6h), which in turn enclose the O(4) atoms (2a) located along the c axis tunnel.

Figure 3. Locations of oxygen interstitials in $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ ($P6_3/m$) at 100K. No interstitials were found to be in the [001] tunnel.

Figure 4. Schematic diagram showing the single crystal surface and the main directions used in this study. k_i and k_s stand for the directions of incident and scattered light; q is the direction of phonon propagation. u is perpendicular to the z axis; both are contained within the horizontal plane.

Figure 5. Raman spectra of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ recorded in (a) zz , (b) uz and (c) uu configurations within the u - z plane, and (d) uu spectrum measured onto a plane nearly perpendicular to the z axis. The inset shows the decomposition of the zz spectrum in the region of the ν_1 breathing mode as a sum of pseudo-Voigt profiles. The points are the experimental data and the lines are the result of the fitting.

Figure 6. Raman spectra of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ measured in backscattering geometry onto a u - z plane of the single crystal, u being an unknown direction within the hexagonal (001) plane, as a function of the angle formed by the incident electric field and the u axis. Spectra were recorded in parallel configuration (the electric field of the scattered light is parallel to that of the incident light). From top to bottom $\alpha = 0^\circ, 35^\circ, 70^\circ, 90^\circ$.

Figure 7. Raman spectra of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ recorded in crossed configuration (the electric field of the scattered light is perpendicular to that of the incident light). From top to bottom $\alpha = 0^\circ, 35^\circ, 70^\circ, 90^\circ$.

Figure 8. Plots of intensity versus angle dependence for three selected A_{1g} modes. Circles are experimental data for integrated intensities either in parallel or in crossed configurations (filled and open symbols, respectively). Solid lines are the best fits using equations (4) and (5). Dotted lines in (a) represent the angular evolution obtained through equations (1) and (2) without uniaxial effects.

Supplementary Information

Figure S1. Rietveld refinement profile of the PXRD data of $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ crystal using the derived $P6_3$ model with good reliability values ($\text{GOF} = 1.47$, $R_{\text{exp}} = 3.69\%$, $R_{\text{wp}} = 5.43\%$, $R_p = 4.25\%$, $R_B = 4.215\%$). This result show no preferential distribution of Nd and Sr over the two $2b$ sites ($\text{Nd}:\text{Sr} = 0.52(41) : 0.48(41)$ at one $2b$ site and $0.50(40) : 0.50(40)$ at the other $2b$ site).

Table S1. Concentrations expressed as mass percentages and atomic abundances normalized to 6 Si atoms for 10 repeat analyses by EPMA. The average (Avg) composition was found to be $\text{Nd}_{8.00}\text{Sr}_{2.02}\text{Si}_6\text{O}_{26.37}$ with low standard deviation (SD) and relative standard deviation (RSD).

	Weight percent (%)					Atomic abundance normalised to 6 Si			
	Si (K α)	Sr (L α)	Nd (L α)	O(K α)	Total	Si (K α)	Sr (L α)	Nd (L α)	O(K α)
736G	8.74	9.07	59.50	21.71	99.01	6	2.00	7.96	26.17
737G	8.76	9.27	59.81	21.90	99.74	6	2.04	7.98	26.32
738G	8.75	9.29	59.60	21.71	99.36	6	2.04	7.96	26.13
739G	8.71	9.09	59.26	21.90	98.96	6	2.01	7.95	26.47
740G	8.70	9.23	59.56	21.75	99.23	6	2.04	8.00	26.35
741G	8.70	8.96	59.68	21.68	99.02	6	1.98	8.02	26.26
742G	8.66	9.12	59.19	21.76	98.73	6	2.03	7.99	26.47
743G	8.62	8.94	59.57	21.61	98.74	6	2.00	8.08	26.42
744G	8.51	9.05	59.57	21.76	98.90	6	2.05	8.18	26.93
745G	8.77	9.11	59.24	21.80	98.92	6	2.00	7.89	26.19
Avg	8.69	9.11	59.50	21.76	99.06	6	2.02	8.00	26.37
SD	0.08	0.12	0.20	0.09	0.31	-	0.02	0.08	0.23
RSD	0.91%	1.32%	0.34%	0.41%	0.31%	-	1.18%	1.00%	0.87%

Table S2. Selected bond lengths and angles for $P6_3/m$.

Bond (Å)	
Nd(1)/Sr-O(1)	2.4486(8)
Nd(1)/Sr-O(2)	2.5125(8)
Nd(1)/Sr-O(3)	2.8525(7)
Nd(2)-O(1)	2.6673(7)
Nd(2)-O(2)	2.455(1)
Nd(2)-O(3)	2.4057(6); 2.5327(6)
Nd(2)-O(4)	2.2722(6)
Si-O(1)	1.617(2)
Si-O(2)	1.628(1)
Si-O(3)	1.6227(7)
Bond valence sum	
Nd1	2.665(2)
Sr	2.672(2)
Nd2	2.851(2)
Si	4.015(6)
O1	2.061(4)
O2	2.078(3)
O3	1.924(2)
O4	1.972(2)
Angle (°)	
O(1)-Si-O(3)	111.00(5)
O(1)-Si-O(2)	113.23(6)
O(3)-Si-O(3)	105.11(5)
O(3)-Si-O(2)	108.06(5)
φ	24.4 ₅

Table S3. Selected bond lengths and angles for $P6_3$.

Bond (Å)	
Nd(1)/Sr-O(1)	2.455(3)
Nd(1)/Sr-O(2)	2.508(3)
Nd(1)/Sr-O(4)	2.866(2)
Nd(2)-O(1)	2.443(3)
Nd(2)-O(2)	2.518(3)
Nd(2)-O(3)	2.840(2)
Nd(3)-O(1)	2.6668(6)
Nd(3)-O(2)	2.455(1)
Nd(3)-O(3)	2.537(2); 2.406(3)
Nd(3)-O(4)	2.404(3); 2.529(2)
Nd(3)-O(5)	2.2728(5)
Si-O(1)	1.617(1)
Si-O(2)	1.6269(9)
Si-O(3)	1.607(4)
Si-O(4)	1.640(4)
Bond valence sum	
Nd1	2.558(7)
Sr	2.649(7)
Nd2	2.597(7)
Nd3	2.761(6)
Si	4.02(2)
O1	2.040(5)
O2	2.056(4)
O3	1.94(1)
O4	1.85(1)
O5	1.906(2)
Angle (°)	
O(1)-Si-O(3)	112.15(9)
O(1)-Si-O(4)	109.73(9)
O(1)-Si-O(2)	113.22(6)
O(3)-Si-O(4)	105.1(2)
O(3)-Si-O(2)	108.39(9)
O(2)-Si-O(4)	107.8(1)
φ	24.4 ₅

Table S4. Neutron scattering length of respective atoms.³⁸

Atom	Coherent scattering length (fm)
-------------	--

Nd1	7.69
Sr	7.02
Si	4.1491
O	5.803

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Table of Contents synopsis

Full Raman study and neutron diffraction on high quality $\text{Nd}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$ single crystals have been performed for structural solution, demonstrating the application of Raman spectroscopy in the confirmation of symmetry between $P6_3$ and $P6_3/m$, which are too similar to be discerned with diffraction methods alone. The obtained Raman spectra from this stoichiometric composition could thus serve as baseline information for further study of non-stoichiometry apatite compounds.