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<th><strong>Title</strong></th>
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<td><strong>Author(s)</strong></td>
<td>Wei, Fengxia; Baikie, Tom; An, Tao; Schreyer, Martin; Kloc, Christian; White, Timothy John</td>
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The Five-Dimensional Incommensurate Structure of the Melilite Electrolyte \([\text{CaNd}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2\)

Fengxia Wei\(^a\), Tom Baikie\(^{a*}\), Tao An\(^a\), Martin Schreyer\(^b\), Christian Kloc\(^a\) and Tim. J. White\(^{a,c}\)

\(^a\) Division of Materials Science & Engineering, Nanyang Technological University, Singapore.
\(^b\) Institute of Chemical Engineering Sciences (ICES), Agency for Science, Technology and Research, 1 Pesek Road, Jurong Island, 627833, Singapore
\(^c\) Centre for Advanced Microscopy, Australian National University, Sullivan’s Creek Road, Canberra, ACT 0200 Australia

* Corresponding author – tbaikie@ntu.edu.sg

Abstract

Melilite-type gallium oxides are potential intermediate temperature electrolytes for solid oxide fuel cells. Single crystals of \([\text{CaNd}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2\) grown using an optical floating zone furnace have been investigated using transmission electron microscopy, powder and single crystal X-ray diffraction. The anion array topologically conforms to a \([(3.5.4.5)^2, 3.5.3.5]\) network that contains distorted pentagonal tunnels. The distortion is necessary to achieve space filling and accommodate structural misfit between the layers. Satisfactory
bond lengths and angles are obtained through two-dimensional modulation in the
tetragonal based plane, leading to five-dimensional symmetry in the superspace
group $P\bar{4}2_1m(\alpha, \alpha, 0)00s(\alpha, \alpha, 0)000$, $\alpha = 0.2319(2)$ and modulation vectors: $q_1 = \alpha (a^* + b^*)$, $q_2 = \alpha (-a^* + b^*)$. Both displacive and occupational modulations are found. Through
this mechanism, melilites are primed to accommodate mobile oxygen interstitials,
suggesting a rational approach to crystallochemical tailoring that will enhance ionic
diffusion and optimize electrolyte performance.

Introduction

Solid oxide fuel cells (SOFC) are an efficient and low polluting energy conversion
technology. A focus of current research is to reduce SOFC operating temperatures to ~
500°C through deployment of highly conductive electrolytes. Usually, oxygen transport
is mediated via anionic vacancies, typically, in yttria stabilized zirconia (YSZ) and
gadolinium doped ceria. However, in some materials oxide ions conduct via an
interstitial mechanism at ‘intermediate’ temperatures. Of particular interest are the
apatite, fergusonite and melilite families, which contain mobile superstoichiometric oxygen. Those structures often show non-rational crystallographic translations, not
accommodated within standard three dimensional crystallographic space groups, but
rather superspace groups, which describe periodicity in 4-, 5-, and 6-dimensions.
Numerous materials are now classified as higher dimensional structures including
$Na_2CO_3$, intermetallic quasicrystals and cuprate high temperature superconductors,
along with certain apatites, fergusonites, and melilites. Of the latter structure types,
the melilite family is currently the most broadly understood in terms of
incommensurability and ion conduction, but a direct causal link between crystal chemistry and electrolyte performance remains to be established.

To a first approximation, melilites adopt tetragonal $P \bar{4} 2_1 m$ symmetry, and have the general formula $[A_2][B'^4][B''_2O_7]_2$ where $A$ are large divalent or trivalent ions (e.g. Ln, Ca, Sr and Ba) and $B''_1, B''_2$ are symmetrically distinct small cations (e.g. Si and Ge). Two dimensional extended oxygen networks of the type $[(3.5.4.5)^2, 3.5.3.5]$ are created by corner-connection of $B''_1O_4$ and $B''_2O_7$ units, with these layers separated by $AO_8$ polyhedra.\textsuperscript{14} This structural framework can accommodate a large excess of oxygen, up to 0.32 per formula unit (e.g. $[Ca_{0.36}La_{1.64}]_2[Ga]_2[Ga_2O_{7.32}]_2$),\textsuperscript{15} believed responsible for the high ion conductivity. Misfit of the tetrahedral layers with the interlayer cations is accommodated by atomic displacements, leading to incommensuration, that has been extensively studied in natural and synthetic silicate-melilites,\textsuperscript{13} but not so deeply for electrolyte compositions. Seifert \textit{et al.}\textsuperscript{16} analyzed åkermanite ($[Ca]_2[Co]_2[Si_2O_7]_2$) using $^{29}$Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy and found an incommensurate to commensurate phase transition at 78°C. Synthetic $[Ca]_2[Co]_2[Si_2O_7]_2$ (Co-åkermanite) was found to be modulated using single crystal X-ray diffraction,\textsuperscript{17} and soon after, the solid solutions of $[(Sr/Na)_{2}[Co/Zn/Mg]_2[Si_2O_7]_2$ were described\textsuperscript{18-21}, with specific combinations of $A$ and/or $B''_1$ site substitutions resulting in modulation. Bindi \textit{et al.}\textsuperscript{22} reported a natural melilite $([Ca_{1.86}Sr_{0.01}Na_{0.08}K_{0.02}]_2[Mg_{0.92}Al_{0.08}]_2[Si_{1.97}Al_{0.03}O_7]_2$ was also modulated, while transmission electron microscopy (TEM) defined the incommensurate to commensurate phase transition temperatures of $[(Sr/Na)_{2}[Co/Zn/Mg/Fe/Cu]_2[(Si/Ge)_{2}O_{7}]_2$
compositions. Almost all previous work has focused on substitutions at the A (4e) and B¹ (2a) cation sites.

As recently shown, the gallate melilite [Sr₀.₄⁶La₁.₅₄]₂[Ga]₂[Ga₂O₇.₂₇]₂ possesses high oxide conductivity (0.02-0.1 S cm⁻¹) over the temperature range 600-900°C, and for the [Ca₁₋ₓLa₁₊ₓ]₂[Ga]₂[Ga₂O₇₊ₓ/₂]₂ series phase transitions from tetragonal (x ≤ 0.5) to orthorhombic (0.5 < x ≤ 0.6) to triclinic symmetry (0.6 < x ≤ 0.64) were found as lanthanum content increased. It was also observed that x > 0.5 gave lower conductivities, attributed to the reduction of symmetry, however, no information concerning the nature of the incommensurate modulation in these gallium melilites was provided. Here, we report for the first time the 5D incommensurate structure of the gallium oxide melilite [CaNd]₂[Ga]₂[Ga₂O₇]₂ using superspace formalism, and consider the implications with respect to preferential oxygen ion migration pathways, tailoring interstitial oxygen content and enhancing ion mobility.

Experimental Details

**Powder Synthesis**

Single crystals of [CaNd]₂[Ga]₂[Ga₂O₇]₂ were grown using an optical floating zone furnace. In 10 gram batches, stoichiometric mixtures of Nd₂O₃ (99.99% Alfa Aesar), CaCO₃ (99.9%, Alfa Aesar) and Ga₂O₃ (99.999%, Aldrich) were ground and homogeneously mixed in ethanol, dried in air (100°C/6 hours), then fired (800°C/10 hours) to decompose CaCO₃. The Nd₂O₃ was dehydrated and decarbonated (1000°C/6 hours) before use. The calcines were reground, pressed into pellets and sintered (1400 °C/12 hours) to yield single phase products according to powder X-ray diffraction.
(see below). For these experiments, a neodymium melilite rather than the lanthanum analogue was prepared, as the blue color of the former better absorbs infrared radiation which simplifies single crystal growth.

**Single crystal growth**

The polycrystalline materials were isostatically pressed into duplicate cylinders (5cm ×0.5cm), to serve as the feed and seed rods, and sintered (1400°C/6 hours) before mounting in the mirror furnace. Crystal growth took place in an FZ-T-4000-H-VPO-VII-PC optical floating zone furnace (Crystal Systems Corporation, Japan) containing four 1.5 kW halogen lamps, with corresponding ellipsoidal mirrors to focus the infrared irradiation to a region ~5 mm in extent, while a constant flow of dry air (2 L/min) passed through the growth chamber. With the onset of melting, tips of the feed and seed rods were brought into contact to form the floating-zone, and upon stabilization, the entire mirror stage was raised at a rate of 5 mm/h for crystal growth. The rods were counter-rotated at constant speed (27 rpm) to maintain a stable and well-mixed molten zone. Initially, polycrystalline rods were used as seeds, however, once an appreciable single crystal was obtained, it was cut and oriented with c parallel to the growth direction for subsequent experiments.

**Structural Characterization**

*Powder X-Ray Diffraction:* The top and bottom parts of the single crystal rods were cut and ground for analysis by powder X-ray diffraction (PXRD) to confirm melilite synthesis and check for secondary phases. The PXRD patterns were collected on a Bruker Advance D8 X-ray diffractometer (Cu Kα, λX = 1.54187Å) equipped with a Cu Kα X-ray tube operated at 40 kV and 40 mA. The crushed powders were mounted in a
top-loaded trough and data accumulated from 5-140° 2θ using a step size of 0.02° with a dwell time of 1s per step. Under these conditions the intensity of the strongest peak was ≈ 30000 counts (Figure 1). Rietveld refinement of the patterns was carried out with TOPAS V4.1,\textsuperscript{26} using the fundamental parameters approach\textsuperscript{27} and a full axial divergence model.\textsuperscript{28} The data were refined from the average three dimensional structure ($P \overline{4} 2_1 m$), based on the atomic positions of Skakle \textit{et al.}\textsuperscript{29}, in addition to the zero error, Chebyshev polynomial fitting of the background, and the ‘Crystallite Size’ to account for microstructure-controlled line broadening. Only isotropic atomic displacement parameters (ADPs) were refined with a common ADP taken for all O positions and Nd and Ca occupying the same crystallographic site.

![Figure 1](image)

**Figure 1.** PXRD Rietveld refinement for the [CaNd$_2$][Ga$_2$][Ga$_2$O$_7$]$_2$ subcell ($R_B = 1.6\%$).

\textit{Single Crystal X-ray Diffraction:} A single crystal fragment (0.1mm×0.08mm×0.15mm) was cleaved and mounted on a glass fiber. Data was collected on a Bruker Smart Apex II single crystal diffractometer (X-ray radiation Mo $K\alpha$, "$..."
\(\lambda=0.71073\text{ Å}\), over an angular range of \(2.07^\circ \leq \theta \leq 33.68^\circ\), with an exposure time of 200s/degree to give a total collection time of \(~50\) hours. The modulation vectors were calculated by the least-squares method from 1891 satellites, and reflections indexed with Apex II software using five integer values. The Saint module, deployed within Apex II, was used for reflection integration, performing Lorentz polarization and multi-scan absorption corrections. The data were refined using Jana 2006\(^{30}\) and no extra absorption correction was applied.

**Selected Area Electron Diffraction:** Selected area electron diffraction patterns (SAED) of single crystals were obtained from powders finely crushed under ethanol with several drops of the suspension deposited on a holy carbon mesh supported by a copper grid. A JEOL field emission TEM 2100F operated at 200 kV and fitted with a CCD camera was used to record the diffraction patterns. A Gatan double tilt holder was employed to tilt crystals to the principle crystallographic orientations and observations were made with a defocused electron beam. The satellite reflections were extremely weak and long exposure times (up to 80s) were required to record these features; only first order satellites were observed. In general, preferred cleavage favored the location of the [100] zone axis rather [001], although the latter was most informative for direct observation of modulation vectors (Figure 2). Using this procedure, long observation times were possible using a parallel, defocused beam. However, high resolution microscopy was not feasible as more converged electron probes lead to rapid amorphization.
Figure 2. [001] selected area diffraction pattern of [CaNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$, showing the $q_1$ and $q_2$ modulation.

Results

Crystal Growth: Single crystals up to 5mm in the long dimension were obtained; it was not possible to grow larger crystals due to crack propagation initiated by crystallographic stresses arising from misfit of the tetrahedral network and the interlayer cations. In this respect, it is noted that single crystals with larger interlayer species (e.g. Sr rather Ca) were easily obtained even with very a high growth speed (10mm/h); the structural details of the commensurate Sr-melilites that conform to $P\bar{4}2_1m$ will be reported elsewhere.

Powder X-ray Diffraction: Rietveld refinement of the average structure confirmed single phase melilite, with no evidence of secondary byproducts (Figure 1). The resultant isotropic ADPs are 0.67(3)Å for Nd/Ca, 0.66(3)Å for Ga, and 3.05(18)Å for oxygen.
(Table 1), with the latter a probable indication of modulation, but as no satellite reflections were observed, detailed examination was not attempted.

**Table 1.** Atomic coordinates and isotropic ADP from PXRD for the $P\overline{4}2_1m$ average structure of $[\text{CaNd}]_2[\text{Ga}_2\text{O}_7]_2$

<table>
<thead>
<tr>
<th>atoms</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>occupancy</th>
<th>$Biso$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^1$</td>
<td>0.16081(14)</td>
<td>0.66081(14)</td>
<td>0.49232(3)</td>
<td>0.5</td>
<td>0.666(3)</td>
</tr>
<tr>
<td>Nd$^1$</td>
<td>0.16081(14)</td>
<td>0.66081(14)</td>
<td>0.49232(3)</td>
<td>0.5</td>
<td>0.666(3)</td>
</tr>
<tr>
<td>Ga$^I$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.658(3)</td>
</tr>
<tr>
<td>Ga$^II$</td>
<td>0.35730(18)</td>
<td>0.85730(18)</td>
<td>0.03628(3)</td>
<td>1</td>
<td>0.658(3)</td>
</tr>
<tr>
<td>O$^I$</td>
<td>0.5</td>
<td>0</td>
<td>0.1928(2)</td>
<td>1</td>
<td>3.05(18)</td>
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<tr>
<td>O$^II$</td>
<td>0.3555(10)</td>
<td>0.8555(10)</td>
<td>-0.3126(12)</td>
<td>1</td>
<td>3.05(18)</td>
</tr>
<tr>
<td>O$^III$</td>
<td>-0.1634(10)</td>
<td>0.09030(19)</td>
<td>0.2134(11)</td>
<td>1</td>
<td>3.05(18)</td>
</tr>
</tbody>
</table>

**Single Crystal X-ray Diffraction:** As a two-dimensionally modulated structure, all reflections for $[\text{CaNd}]_2[\text{Ga}_2\text{Ga}_2\text{O}_7]_2$, were indexed using five integers ($h\ k\ l\ m\ n$):

\[ \mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + mq_1 + nq_2, \]

where $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the reciprocal lattice vectors.

The modulation vectors $q_1 = 0.2319(2)\ (a^* + b^*),\ q_2 = 0.2319(2)\ (-a^* + b^*)$ were determined by 637 main reflections and 1891 satellites reflections. Experimental and refinement details are collected in Table 2.

**Table 2**

**Experimental details**

<table>
<thead>
<tr>
<th>Crystal data</th>
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<tr>
<td>Chemical formula</td>
<td>CaNdGa$_3$O$_7$</td>
</tr>
<tr>
<td>Chemical formula weight</td>
<td>505.47</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
</tr>
<tr>
<td>Cell Setting</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Superspace group</td>
<td>$P\overline{4}2_1m(\alpha,\alpha,0)00s(\overline{\alpha},\alpha,0)000$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>7.8868(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.2243(3)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>324.96(4)</td>
</tr>
<tr>
<td>Formula units (Z)</td>
<td>2</td>
</tr>
</tbody>
</table>
$D_x$ (Mg m$^{-3}$)  5.139  
Modulation wave vectors  
\[ q_1 = 0.2319(2) \left( a^* + b^* \right) \]
\[ q_2 = 0.2319(2) \left( -a^* + b^* \right) \]
Crystal form  Irregular  
Crystal size (mm)  0.10 $\times$ 0.08 $\times$ 0.15  
Crystal colour  Purple under sunlight  Blue under fluorescent lamp  

Data collection  
Diffractometer  Bruker Smart ApexII Four circle diffractometer  
Radiation type  Mo $K\alpha$  
Wavelength (Å)  0.71073  
Absorption correction type  Multi-scan  
Absorption coefficient $\mu$ (mm$^{-1}$)  20.777  
Range of $h$, $k$, $l$, $m$, $n$  
\[-12 \rightarrow h \rightarrow 9 \]
\[-12 \rightarrow k \rightarrow 9 \]
\[-7 \rightarrow l \rightarrow 5 \]
\[-1 \rightarrow m \rightarrow 1 \]
\[-1 \rightarrow n \rightarrow 1 \]
No. of measured reflections  17097  
No. of unique reflections  5249  
No. of observed reflections  2219  
No. of main reflections  637  
No. of satellites  
For $\pm(1, 0) \pm(0, 1)$  1531  
For $\pm(1, 1) \pm(-1, 1)$  51  
Criterion for observed reflections  $I > 3\sigma(I)$

Refinement  
Refinement on  $F$  
$R$, $wR$ (all reflections)  0.0378, 0.0519  
$R$, $wR$ (main reflections)  0.0236, 0.0316  
$R$, $wR$ (satellites) for $\pm(1, 0) \pm(0, 1)$  0.0645, 0.0721  
\[\text{For } \pm(1, 1) \pm(-1, 1)\]  0.1690, 0.1567  
$S$  2.20  
No. of parameters  322  
Weighting scheme  $w = \left[ \sigma^2(F) + (0.01F)^2 \right]^{-1}$  
(\(\Delta F/s.u.)\) max  0.0195  
$\Delta \rho_{\text{max}}$ (e Å$^{-3}$)  1.41  
$\Delta \rho_{\text{min}}$ (e Å$^{-3}$)  -1.23  
Extinction correction  B-C type I Lorentzian isotropic (Becker & Coppens, 1974)  
Extinction coefficient  4600(300)  
**Selected Area Diffraction Pattern:** The [001] pattern was composed of the main reflections and first order satellites that can be indexed by five integers, $H = ha^* + kb^* + lc^* + mq_1 + nq_2$ (Figure 2). The first order satellites form a square around the principle reflections, consistent with tetragonal symmetry. The modulation vectors $q_1^s = 0.234 (a^* + b^*)$, $q_2^s = 0.234(-a^* + b^*)$, are in good agreement to those obtained by single crystal X-ray diffraction.

**Superspace Group Description:** The five-dimensional incommensurate structure can be visualized as a 3-dimensional physical object combined with 2 higher dimensions. The corresponding superspace group contains the symmetry of the basic structure, plus the symmetry elements in the higher dimension, and for melilite, the superspace group symbol $P_{4_1}^{32}_{m}$ (notation according to Janner et al.) was adopted; a comprehensive explanation of this terminology is given by Bindi et al. The upper terms refer to the basic structure, with the lower part representing the respective higher dimensional symmetry operations. For example, the $4_{4}^{4}$ superscript directly above the 4 subscript means there is 4-fold inversion in physical space and 4-fold rotation in the higher dimension; 2$_{1}$ over $m$ indicates a mirror plane in addition to the screw axis in the 3D space; while the last pair shows a glide related to the mirror symmetry $m$.

Stokes et al. have recently derived all the (3+2) superspace groups, and suggested an extended formalization. Accordingly, [CaNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$ adopts the melilite basic metric $a = 7.8868(4)$, $c = 5.2243(3)$Å with two incommensurate modulation vectors: $q_1^s = 0.2319(2)(a^*+b^*)$, $q_2^s = 0.2319(2)(-a^*+b^*)$, resulting in a superspace group $P_{4}^{2}m(\alpha,\alpha,0)00s(\bar{\alpha},\alpha,0)000$, where $\alpha = 0.2319(2)$ is the magnitude of
modulation vectors, and $s = 1/2$ indicates an intrinsic translation, which corresponds to the glide plane in the notation of Janner.\textsuperscript{32}

**Refinement of Single Crystal XRD Data:** The average structure in physical space was refined using the 637 main reflections with $I > 3\sigma(I)$, and quickly converged to $R_{all}^{obs} = 0.0297$, with the composition $[\text{Ca}_{1.023(3)}\text{Na}_{0.977(3)}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2$, that is close to the notional $[\text{CaNd}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2$. Table 3 lists the refined atomic coordinates and anisotropic displacement parameters for the average structure. To refine the 5D structure, modulation of both atomic position and displacement parameters were applied using the satellite reflections (1, 0), (0, 1), (1, 1), and (-1, 1). The number of observed (1,1) and (1,-1) satellites was found to be very low due to the fact that $\alpha \sim 1/4$, and the 2\textsuperscript{nd} order satellites ($h, k, l, 1, 1$), ($h+1, k, l, -1, 1$), ($h, k, l, 1, -1$) ($h, k+1, l, -1, -1$) cannot be separated, leading to a relatively high $R_{2nd}^{obs}$ factor (~0.17) for 2\textsuperscript{nd} order satellites. Overlap correction was applied during the refinement by treating pairs of combined satellites as fully overlapped reflections. Separate refinements of 1\textsuperscript{st} and 2\textsuperscript{nd} order satellites were performed, and inclusion of the small number of observed 2\textsuperscript{nd} order satellites, together with 1\textsuperscript{st} order satellites lowered $R_{obs}$ factors, especially $R_{1st}^{obs}$ by about 12% (0.072 to 0.064). Nd/Ca also exhibit occupational modulations, leading to a significant $R_{all}^{obs}$ reduction (0.049 to 0.036).

**Table 3.** Atomic coordinates and anisotropic displacement parameters for average structure

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occu</th>
<th>Uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd\textsuperscript{1}</td>
<td>4e .m</td>
<td>0.15917(5)</td>
<td>0.65917(5)</td>
<td>0.49516(10)</td>
<td>0.489(4)</td>
</tr>
<tr>
<td>Ca\textsuperscript{1}</td>
<td>4e .m</td>
<td>0.15917(5)</td>
<td>0.65917(5)</td>
<td>0.49516(10)</td>
<td>0.511(4)</td>
</tr>
</tbody>
</table>
Discussion

Average structure

In the average structure, the GaO$_4$ tetrahedra form pentagonal rings that stack along [001] to create channels. The Nd/Ca cations align as chains inside these channels and are positioned between the layers (Figure 3). The average structure features a strong anisotropy of the Nd/Ca and O displacement ellipsoids; O$^2$ has the longest ellipsoidal axis directed along [110]. Ga$^{II}$-O$^2$-Ga$^{II}$ is linear but the O$^2$ has a large atomic displacement parameter perpendicular to the Ga$^{II}$-O$^2$ vector; this suggests bending of the Ga$^{II}$-O$^2$-Ga$^{II}$ bond and the real Ga$^{II}$-O$^2$ distance is longer. This observation is consistent with twisting of the Ga$^{II}_2$O$_7$ tetrahedral dimers around [001], accommodated by a slight rotation of the Ga$^{IV}$O$_4$ tetrahedra, probably also along [001]. O$^3$ elongates towards the A site atoms, due to the size misfit of the interstices and the Nd/Ca ionic size.
Figure 3. The average structure of \([\text{Ca}_2\text{Nd}_2][\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2\), obtained through single crystal X-ray diffraction. (a) projected along \(\langle 001 \rangle\), and (b) \(\langle 010 \rangle\). Atoms are represented by 50% probability displacement ellipsoids.

Modulated Structure
An approximant \(4a \times 4a \times 1c\) cell illustrates the modulation (Figure 4). Deformation of the pentagonal rings is clear and gives rise to a change of coordination around the \(A\) cations. Six-, seven- and eight-coordinate \(A\) cations exist in different parts of the structure, assuming \(A–O\) distances \(> 2.9\AA\) are disregarded. The \(A–O\) bonds, especially the longest ones, are strongly influenced by the displacive modulation, whereby lengthening and shortening are imposed in different regions of the crystal, leading to a change in the \(A\) site coordination (Figure 5). For example, the largest modulations are observed at the longest bonds \(A–O^3-v,vii\), with a deviation of bond lengths up to \(1.18(2)\AA\), while the second longest bonds \(A–O3-iv,viii\) have differences below \(0.52(2)\AA\). Smaller influences are exerted on the shorter \(A–O^1-i\) bond; the regular \(Nd/Ca–O^1-i\) bond is \(2.383(2)\ \AA^{35}\), while the stretched average distances are \(2.45(8)\AA\), varying from \(2.37(8)\AA\) to \(2.53(8)\AA\) in the modulated structure. Variations of bond distances caused by modulation can be observed as a function of \(t\) and \(u\), the additional two-dimensional space coordinates. For instance, in Figure 5, at some regions, the \(A–O^3\) bonds show the greatest variance in excess of \(2.9\AA\), while the strong short bonds \(A–O^2\), and \(A–O^1\) are more constant (Table 4). The \(A–O\) bond distributions at \(t=0, u=0\) show that there are 35.9\% eight-, 29.6\% seven-, and 34.5\% six-coordinate \(A–O\) polyhedra. Occupational modulation is also found for the \(A\) site \(Nd/Ca\) atoms; at \(u = 0\), the occupancy of \(Nd\) varies from \(0.518(12)\) to \(0.580(12)\), while \(Ca\) ranges from \(0.420(13)\) to \(0.472(13)\) as a function of \(t\) (Figure 7). Nd-rich and Ca-rich areas can be found at different regions of \(t\) and \(u\). Areas of strongest polyhedral distortion correspond to a Ca-rich area, where almost all the six-coordinated polyhedra emerge (Figure 4).
Figure 4. The approximate modulated structure of $4a \times 4a \times 1c$ cell, projected along the $c$ axis. Nd/Ca-O bonds $< 2.9 \, \text{Å}$ are represented by sticks. 6-coordinate Nd/Ca pentagons are highlighted in aqua, 7-coordinate pentagons are orange, and 8-coordinated are yellow. The Ga$^I$O$_4$ and Ga$^{II}$O$_4$ tetrahedra are shown as grey.

Because the interlayer $A$ cations are too small, compared with the space between the layers, the tetrahedral sheets must distort. The strongest distortion occurs for the Ga$^I$O$_4^3$ tetrahedra (Figure 8), which is compromised by bending of the Ga$^{II}_2$O$_7$ tetrahedral dimers (Figure 9) to stabilize the structure. Positional disorder is introduced into the structure because of this distortion, and consequently, modulation develops. Smaller $A$ cations give
rise to larger distortions, and therefore the structure is more likely to be incommensurate.

For a regular Ga$^I$O$_3$ tetrahedron in the average structure, the Ga-O bond is 1.8242(4) Å; however, the modulation distributes the Ga$^I$O$_3$ bond lengths from 1.68(6) Å to 1.98(6) Å (Table 4). The O$^3$-Ga$^I$-O$^3$ bond angle variations are shown in Figure 10, with the largest deviation from around 21.50(11)° from the regular tetrahedral angle of 109.49°. In the Ga$^{II}$O$_4$ tetrahedron, the largest distortion occurs for the O$^3$-iv-Ga$^{II}$-O$^3$-viii angle as well as the Ga$^{II}$-O$^3$ bonds, with variation of ±17.25(4)° from the average structure (99.246°) and bond length variation of 0.36(12) Å can be found throughout the structure (Figure 11).

**Table 4.** Modulated structure: Interatomic distances (Å) and tetrahedral angles (°)

<table>
<thead>
<tr>
<th></th>
<th>average</th>
<th>minimum</th>
<th>maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A-O polyhedra</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>O$^3$-i</td>
<td>2.45(7)</td>
<td>2.37(8)</td>
<td>2.53(8)</td>
</tr>
<tr>
<td>O$^3$-ii</td>
<td>2.58(8)</td>
<td>2.38(8)</td>
<td>2.82(8)</td>
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<tr>
<td>O$^3$-iv</td>
<td>2.57(8)</td>
<td>2.38(8)</td>
<td>2.83(8)</td>
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<tr>
<td>O$^2$-i</td>
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<td>2.28(5)</td>
<td>2.56(5)</td>
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<tr>
<td>O$^3$-iv</td>
<td>2.48(6)</td>
<td>2.24(6)</td>
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<tr>
<td>O$^3$-v</td>
<td>2.90(6)</td>
<td>2.42(6)</td>
<td>3.64(6)</td>
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<td>O$^3$-vii</td>
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<td>3.65(6)</td>
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<tr>
<td>O$^3$-viii</td>
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<td>2.76(6)</td>
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<tr>
<td><strong>Ga$^{IV}$O$_4$ tetrahedra</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ga$^I$O$^3$</td>
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<td>1.68(6)</td>
<td>1.98(6)</td>
</tr>
<tr>
<td>O$^3$-i-Ga$^I$-O$^3$-ii</td>
<td>110(3)°</td>
<td>90 (2)°</td>
<td>131(3)°</td>
</tr>
<tr>
<td>O$^3$-i-Ga$^I$-O$^3$-iv</td>
<td>107(3)°</td>
<td>102(3)°</td>
<td>113(3)°</td>
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<tr>
<td>O$^3$-i-Ga$^I$-O$^3$-v</td>
<td>110(3)°</td>
<td>90(2)°</td>
<td>131(3)°</td>
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<tr>
<td>O$^5$-ii-Ga$^I$-O$^4$-iv</td>
<td>110(3)°</td>
<td>90(2)°</td>
<td>131(3)°</td>
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<tr>
<td>O$^3$-ii-Ga$^I$-O$^3$-v</td>
<td>107(3)°</td>
<td>102(3)°</td>
<td>113(3)°</td>
</tr>
<tr>
<td>O$^3$-iv-Ga$^I$-O$^3$-v</td>
<td>110(3)°</td>
<td>90(2)°</td>
<td>131(3)°</td>
</tr>
<tr>
<td><strong>Ga$^{IV}$O$_4$ tetrahedra</strong></td>
<td></td>
<td></td>
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<tr>
<td>Ga$^{III}$O$^1$</td>
<td>1.79(8)</td>
<td>1.72(9)</td>
<td>1.87(9)</td>
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<td>Ga$^{III}$O$^3$</td>
<td>1.84(6)</td>
<td>1.69(6)</td>
<td>2.05(6)</td>
</tr>
</tbody>
</table>
Symmetry codes: (i) $x, y, z$; (ii) $y, -x, 1-z$; (iii) $x, y, -1+z$; (iv) $-x, -y, -1+z$; (v) $-y, x, 1-z$; (vi) $x, y, 1+z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (viii) $\frac{1}{2}-y, \frac{1}{2}-x, z$; $x, y, z$ are the average atomic coordinates in space group $P\bar{4}2_1m$.

**Figure 5.** The eight-, seven-, and sixfold coordination of the A site cations. Bonds longer than 2.9 Å are represented by dashed lines. The atomic coordinates were at $t=0$, $u=0$; $t=0.5$, $u=0.5$; $t=0.6$, $u=0$; respectively. For the symmetry codes refer to Table 4.
**Figure 6.** Variation of A-O bond distances as a function of $t$, at $u=0$ and $u=0.610$. At some regions, A-O$^3$ bonds exceed 2.9 Å. Symmetry codes are in Table 4.

**Figure 7.** Occupancy variation for the A site atoms Nd and Ca at different $u$ as a function of $t$.

**Figure 8.** (a) Distorted and (b) undistorted Ga$^1$O$^3_4$ tetrahedra, viewed along c axis, (a) is extracted from the approximant $4a \times 4a \times 1c$ cell of the modulated structure. Symmetry codes are shown in Table 4.
Figure 9. The bent $\text{Ga}^{\text{II}}\text{O}_7$ tetrahedral dimmers, dashed lines show the ideal position, viewed along $c$ axis. Symmetry codes are listed in Table 4.

![Diagram](image)

Figure 10. Bond angle variations for $\text{Ga}^{\text{I}}\text{O}_3$ tetrahedra at a function of $t$, (a) at $u=0$, (b) $u=0.5$. Symmetry codes are in Table 4.
Figure 11. Bond angle (a), (b) and bond length (c), (d) variations for Ga\textsuperscript{III}O\textsubscript{4} tetrahedron as a function of $t$, at (a) (c) $u=0$, (b) (d) $u =0.50$. The symmetry codes are the same as in Table 4.

**Bond valence summations**

The bond valence sums (BVS) for all the cations were calculated in order to evaluate the validity of the structure (Table 5.) The BVS of Nd/Ca were obtained by summing the partial bond valence of Nd and Ca through the occupancy ratios along $t$ and $u$, using the
parameters of Altermatt & Brown\textsuperscript{36} (Figure 12). Similar to the reported incommensurate structure \([\text{Ca}_2\text{Co}_2\text{Si}_2\text{O}_7]_2\),\textsuperscript{21} the values for Nd/Ca are remarkably lower than the formal charges, consistent with the interstices being too large for the A site cations. High BVS regions correspond to the areas with Nd occupancy dominant, probably because of the larger affinity of Nd\textsuperscript{3+} ions to oxygen. The BVS values for Ga\textsuperscript{I} and Ga\textsuperscript{II} show large variations, but their mean values are within a tolerable range. In fact, aside from the remarkable variation, the mean values of BVS for all cations in the modulated structure are closer to the formal values than those calculated for the average structure (Table 5).

Table 5. Bond Valence Sums

<table>
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<th>Average structure</th>
<th>Modulated structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean value</td>
</tr>
<tr>
<td>Nd/Ca</td>
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<td>2.02(10)</td>
<td>2.09(12)</td>
</tr>
<tr>
<td>Ga\textsuperscript{I}</td>
<td>3</td>
<td>3.14(2)</td>
<td>3.09(3)</td>
</tr>
<tr>
<td>Ga\textsuperscript{II}</td>
<td>3</td>
<td>3.21(2)</td>
<td>3.15(11)</td>
</tr>
</tbody>
</table>
Figure 12. Bond valence sum (BVS) variations for A site atoms as a function of $t$ and $u$. BVS was calculated according to the ratio of Nd/Ca at different $t$ and $u$.

**Modulation vectors**

While the number of fully determined modulated melilitie structures remains quite small, sufficient data is now available to search for crystallochemical correlations. The value of $\alpha$ for $q_1$ and $q_2$ can be related to chemical composition, particularly the A/B ionic radius ratio (Figure 13). Cation substitutions at the different sites are found to have distinct effects on the modulation vector. For example, substitutions of larger ions at the B site leads to an increase in $\alpha$, while similar substitutions at the A site generally induce the opposite effect, e.g. in $[\text{Ca}_2]_2[\text{Fe}_x\text{Mg}_{1-x}]_2[\text{Si}_2\text{O}_7]_2^{37}$ increasing the Fe content.
(r(Fe^{2+}) > r(Mg^{2+})) causes \( \alpha \) to increase, while \( \alpha \) decreases when Sr content increases in 

\([\text{Ca}_{1-x}\text{Sr}_x]_2[\text{Mg}]_2[\text{Si}_2\text{O}_7]_2^{38} \) and 

\([\text{Ca}_{1-x}\text{Sr}_x]_2[\text{Co}]_2[\text{Si}_2\text{O}_7]_2^{21} \) \( (r(\text{Sr}^{2+}) > r(\text{Ca}^{2+})) \). Both situations accommodate increasing \( \alpha \) when the \( A/B \) ratio decreases, which results in less structural distortion. However, some melilite compositional joins do not always obey the same trend, indicating that along with the \( A/B \) size ratio, different charge combinations for species occupying the same crystallographic site are also important. For example, it is seen that \( \alpha \) increases along with \( A/B \) ratio when 4\% of Ca is replaced by Sr in 

\([\text{Ca}_2]_2[\text{Mg}]_2[\text{Si}_2\text{O}_7]_2^{20} \) and this may reflect ordering of the \( A \) cations. Similarly, for 

\([\text{CaNd}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2 \) and 

\([\text{CaLa}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2 \) enhanced ordering expected for the latter because the larger cation size difference, will give a larger \( \alpha \). In another example, the tetrahedral size deviation of \( \text{ZnO}_4 \) and \( \text{GeO}_4 \) is probably responsible for the abrupt \( \alpha \) discontinuity of 

\([\text{Ca}]_2[\text{Zn}]_2[\text{Ge}_2\text{O}_7]_2 \). In this review of melilite modulation, the only case that cannot be explained by these systematics is for 

\([\text{Ca}_2]_2[\text{Mg}]_2[\text{Si}_2\text{O}_7]_2-[\text{Ca}_2]_2[\text{Co}]_2[\text{Si}_2\text{O}_7]_2 \), where the \( \text{Co}^{2+} \) (0.56Å) ionic radius is slightly smaller than \( \text{Mg}^{2+} \) (0.57Å), but \( \alpha \) is significantly larger. Possibly, crystal field effects for \( \text{Co}^{2+} \) account for this apparent anomaly. Moreover, at room temperature 

\([\text{Ca}_2]_2[\text{Mg}]_2[\text{Si}_2\text{O}_7]_2 \) is close to its incommensurate-commensurate phase transition temperature (~80°C), and the abrupt decrease in \( \alpha \) may precede the onset of this transformation.\(^{39}\) It is notable that for the related 

\([\text{A}_2]_2[\text{B}]_2[\text{M}_2\text{O}_8]_2 \) fresnoite materials similar trends have not yet established. It is suggested this may be due to the prevalence of nanoscale intergrowths of commensurate and incommensurate domains which mask simple correlations between \( \alpha \) and compositions.\(^{40}\)
Figure 13. Relationship of $\alpha$ with cation ratio $A/B$: (a) for end member compositions, (b) for cation substitutions at A or B sites. Ionic radii of B site cations are calculated according to their respective ratio. The $\alpha$ for $[\text{Ca}_2]_2[\text{Fe}_x\text{Mg}_{0.1-x}]_2[\text{Si}_2\text{O}_7]_2$ is re-calculated from the Seifert et al.;\textsuperscript{37} $[\text{Ca}_2]_2[\text{Co}_{0.9}\text{Zn}_{0.1}]_2[\text{Si}_2\text{O}_7]_2$ from Jia. et al.;\textsuperscript{38} $[\text{Ca}_{2-x}\text{Sr}_x]_2[\text{Co}]_2[\text{Si}_2\text{O}_7]_2$ from Bagautdinov et al.;\textsuperscript{21} $[\text{Ca}_{2-x}\text{Sr}_x]_2[\text{Mg}]_2[\text{Si}_2\text{O}_7]_2$ from Jiang et al.;\textsuperscript{20} $[\text{CaLa}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2$ and $[\text{Ca}_2]_2[\text{Ga}]_2[\text{GaGeO}_7]_2$ are obtained from SAED (see Figure 14).
The existence of eight-, seven- and six-coordinated A site polyhedra is a distinct feature of the [CaNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$ incommensurate structure. Strong distortions of the Ga-O tetrahedra are induced by the variation of interatomic distances. As the incommensurate modulation is due to the misfit between the tetrahedral layers and the size of interlayer cations, smaller A-site cations with respect to the B-tetrahedra, give rise to greater structural misfit resulting in incommensurate structures and the internal strain that makes the growth of appreciable single crystals more difficult. Therefore, modulation is predicted when Nd/Ca is substituted with smaller lanthanides such as Sm and Gd, or if a larger metalloid enters the B-site (e.g. Mg).

**Figure 14.** SAED for [CaLa]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$ and [Ca$_2$]$_2$[Ga]$_2$[GaGeO$_7$]$_2$, showing that the modulation vectors of $\sim$0.24 and $\sim$0.26 respectively.
Figure 15. Distorted trigonal bi-pyramidal Ga\textsuperscript{II}O\textsubscript{5}, O4 represents the interstitial oxygen, viewed along c direction. This graph was adopted from Kuang et al.\textsuperscript{5}

Preferred diffusion pathways

The preferred crystallochemical formula is [Ca\textsubscript{1-x}Nd\textsubscript{x+3}]\textsubscript{2}[Ga]\textsubscript{2}[Ga\textsubscript{2}O\textsubscript{7+3x/2}]\textsubscript{2} as this provides insight into the location of interstitial oxygen. A greater concentration of Nd than Ca (i.e. Nd/Ca\textgreater{}1) leads to the introduction of mobile oxygen interstitials that fill the pentagonal rings of the tetrahedral layer. The Ga\textsuperscript{I}O\textsubscript{4} tetrahedron is connected via all four oxygen ions to tetrahedral dimers, while the Ga\textsuperscript{II}O\textsubscript{4} tetrahedron contains the non-bridging oxygen O\textsubscript{1} that provides the flexibility to accommodate interstitials through the repositioning of the O\textsubscript{1} to enter the coordination environment of the Ga\textsuperscript{II} resulting in a distorted trigonal bi-pyramidal Ga\textsuperscript{II}O\textsubscript{5} polyhedron (Figure 15).\textsuperscript{5} Stabilization of interstitial oxygen requires dynamical deformation of the framework that is an important feature of the modulated structure. Large cations at the A site can readily accommodate the change of coordination number, and the corner-connected gallium oxide tetrahedral network can stabilize the interstitial oxygen by binding them into the polyhedral network. The preferred interstitial migration path along O\textsubscript{2} and O\textsubscript{3} is shown as oxygen ellipsoid
elongation and excess electron density (Figure 16). Members of the flexible layered-structure melilite family can readily accommodate mobile interstitial oxygen.

**Figure 16.** Interstitial oxygen preferred migration path along O$^2$ and O$^3$, with no excess electron density indicating migration involving O$^1$. Fourier peaks are included in the form of oxygen in this representation and are shown in red. The structural representation was derived from a single crystal X-ray diffraction refinement of [Ca$_{0.5}$Nd$_{1.5}$]$_2$[Ga$_2$Ga$_3$O$_{7.25}$]$_2$. 
Figure 17. Projected topologies of the [(3.5.4.5)$^2$, 3.5.3.5] tetrahedron-pentagon oxygen nets of melilite. The ideal net is from O’Keeffe and Hyde,\textsuperscript{14} [SrNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$ is a commensurate derivative and [CaNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$ is modulated. Obvious pentagon distortion can be observed in both non-modulated and modulated nets. 6-, 7- and 8-coordinated polyhedra are filled by aqua, orange and yellow colors, respectively.

Conclusion

Melilites contain a 2D tetrahedral network with pentagons that are distorted even in the non-modulated structures (e.g. [SrNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$), but most evidently in the incommensurate form of [CaNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$ (Figure 17). This long range distortion enables the flexible deformation which is prerequisite for high interstitial oxygen mobility. Network systematics may be a powerful tool to predict modulation, and also identify compounds as potential low temperature ion conductors. Similar structures containing triangle-quadrangle-pentagon nets include (1) the [(3.5.4.5)$^2$, 3.5.3.5] net as found for Ca$_5$Al$_6$O$_{18}$\textsuperscript{41} and fresnoite-types (such as Ba$_2$TiSi$_2$O$_8$,\textsuperscript{42} K$_2$MoAs$_2$O$_9$\textsuperscript{43} and K$_2$V$_3$O$_8$\textsuperscript{44}) that contain pentagons formed from alternate connections of tetrahedral dimers with pyramids TiO$_5$ (or Mo/VO$_5$), (2) the [5.4$^3$, 5.4.3.4, 5.4$^3$,(5.4.3.4)$^2$] net as in
K₃W₅O₁₅,14 where 5 corner-connected tetrahedra form pentagon-triangles, with other tetrahedra edge-shared to form the extended network, (3) the [(5³.3)², 5³, 5³.3, 5³] net for hexagonal structures such as K₃V₅O₁₄45 and CaTa₄O₁₁,46 (4) the [(3.4.5.4)², (3.5.4.5)²] net such as Ba₃Si₄Ta₆O₂₆ and Ba₃Si₄Ta₆O₂₃,47 where all tetrahedra are corner-connected, (5) the [3.5.3.5, (3.4.5³)²] net, e.g. Ta₂O₅,48 and (6) the [3.5.3.5, (3.4.5²)²] net, as in UVO₅49 (see Table 6). The connected pentagons are likely to provide favorable diffusion pathways for oxygen (Figure 18).14 Other tetrahedral network candidates include one dimensional net such as Na₂SiO₅50 and La₂TiO₅51, two dimensional nets including LaSrGaO₅,52 Ba₂CuSi₂O₇,53 Na₂Si₂O₅,54 BaSi₂O₅55 and nordite LaSrNa₃ZnSi₆O₁₇,56 and three dimensional nets as found in langasite La₃Ga₅SiO₁₄57 where a 2-dimensional tetrahedral net is connected through octahedra.

Table 6. Planar pentagonal nets with the highest proportion of pentagons may be especially suitable for ion conduction.

<table>
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<tr>
<th>Net14</th>
<th>Vertices</th>
<th>% pentagon/quadrangle/triangle</th>
<th>Examples</th>
</tr>
</thead>
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<td>[(3.5.4.5)², 3.5.3.5]</td>
<td>40/20/40</td>
<td>melilite, fresnoite, Ca₅Al₆O₁₈41</td>
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<tr>
<td>21</td>
<td>[5.4³, 5.4.3.4, 5.4³, (5.4.3.4)²]</td>
<td>20/60/20</td>
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<td>[(5³.3)², 5³.5³.3, 5³]</td>
<td>66.7/0/33.3</td>
<td>K₃V₅O₁₄42, CaTa₄O₁₁46</td>
</tr>
<tr>
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<td>[(3.4.5.4)², (3.5.4.5)²]</td>
<td>33.3/33.3/33.3</td>
<td>Ba₃Si₄Ta₆O₂₆ and Ba₃Si₄Ta₆O₂₃47</td>
</tr>
<tr>
<td>24</td>
<td>[3.5.3.5, (3.4.5²)²]</td>
<td>50/25/25</td>
<td>Ta₂O₅48</td>
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<tr>
<td>25</td>
<td>[3.4.5.4, (3.4.5²)²]</td>
<td>33.3/33.3/33.3</td>
<td>UVO₅49</td>
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</table>
Figure 18. Ideal triangle-quadrangle-pentagon nets with lines showing likely preferred ion diffusion paths.

In the present case, non-bridging oxygen $O^1$ in the Ga$^{II}\text{O}_4$ serves as a key for the interstitial stabilization and mobility in melilite, and in general modulated structures with terminal oxygen and a distorted network are potential candidates for high oxide mobility. Many well-known oxide ion conductors such as fresnoite$^{58}$ and fergusonite (e.g.CeNbO$_{4+x}$)$^{12}$ are all layered structures. Ba$_{18}$Al$_{12}$O$_{36}$$^{41}$ also has tetrahedra containing terminal oxygen. One other possible electrolyte is the bismuth calcium aluminate $\text{Bi}_2\text{Ca}_6\text{Al}_{12}\text{O}_{27}$$^{59}$ where corner-connected AlO$_4$ tetrahedra form corrugated six- and three-membered rings, edge-sharing with CaO$_8$ polyhedra aligned along $c$ that create three-dimensional nets, with Bi located in large hexagonal tunnels parallel to $c$ to form
Bi$_2$O$_3$ pairs. Another target ceramic may be Na$_2$Si$_3$O$_7$ that is a (3+1) dimensional incommensurate structure with distorted silicate tetrahedral layers connected by Na. Certain brownmillerites (e.g. Ca$_2$Fe$_2$O$_5$) are also incommensurate structures with distorted tetrahedral chains that are ready to accommodate interstitials. Moreover, further reduction of brownmillerites can form infinite-layer oxides (Sr/CaFeO$_2$) with square-planar oxygen coordination that have very high oxygen mobility. Material families sharing these key crystal chemical features with melilite are potential fast oxide ion conductors.

Supporting information available: The CIF for average and modulated structure [CaNd]$_2$[Ga]$_2$[Ga$_2$O$_7$]$_2$. This material is available free of charge via the Internet at http://pubs.asc.org.

Author Information

Corresponding Author

*Division of Materials Science & Engineering, Nanyang Technological University, Singapore. Email: tbaikie@ntu.edu.sg

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Reference


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The Five-Dimensional Incommensurate Structure of the Melilite Electrolyte $[\text{CaNd}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_7]_2$

Fengxia Wei$^a$, Tom Baikie$^a$, Tao An$^a$, Martin Schreyer$^b$, Christian Kloc$^a$ and Tim. J. White$^{a,c}$