Stability and oxide ion conductivity in rare-earth aluminium cuspidines

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Abstract

\(\text{RE}_4(\text{Al}_{2-x}\text{Ge}_x\text{O}_{7.5-x}2\square_{1-x}2)\text{O}_2\) (\(\text{RE} = \text{Gd}^{3+}\) and \(\text{Nd}^{3+}\)\) oxy-cuspidine series have been prepared by ceramic method (\(\text{RE} = \text{Gd}^{3+}\)\) and freeze-dried precursor method (\(\text{RE} = \text{Nd}^{3+}\)\). The compositional ranges and the high temperature stability have been determined for both series. Gadolinium aluminium cuspidines are stable at very high temperatures but the analogous neodymium compounds are only stable below 1273 K. Joint Rietveld analyses of neutron powder diffraction (NPD) and laboratory X-ray powder diffraction (LXRPD) have been carried out for \(\text{Nd}_4(\text{Al}_2\square_1\text{O}_2)\text{O}_2\) and \(\text{Nd}_4(\text{Al}_1.5\text{Ge}_0.5\text{O}_{7.25}\square_0.75)\text{O}_2\) compositions. Furthermore, Rietveld refinement of synchrotron X-ray powder diffraction (SXRPD) data were carried out for \(\text{Gd}_4(\text{Al}_{1.0}\text{Ge}_{1.0}\text{O}_{7.5}\square_0.5)\text{O}_2\) composition. The refinements have confirmed the known structural features of the cuspidine framework. These cuspidines series are oxide ion conductors with negligible electronic contribution as determined from impedance spectroscopy at variable oxygen partial pressures. The enhancement in the overall oxide conductivity along the two oxy-cuspidine series is two orders of magnitude. Typical ionic conductivity values for doped samples are around \(4 \times 10^{-5} \text{Scm}^{-1}\) at 973 K.

Keywords: SOFC; Oxide conductor; Cuspidine; Synchrotron and neutron diffraction

1. Introduction

Solid oxide fuel cells (SOFCs) are being intensively studied as a result of the increasing interest in the development of more efficient, and environmentally friendly, ways of energy transformation [1–3]. SOFCs devices allow the direct conversion of chemical to electrical energy through an electrochemical reaction. In the SOFC technology, the electrolyte is an oxygen ion conductor of yttria-stabilised zirconia, for instance \(\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}\) (YSZ). However, the elevated operation temperatures (1073–1273 K) induces restrictions in the choice of stable materials for SOFC components which enforces the use of expensive materials with relatively low lifetimes. Therefore, there is a great need to find and develop new oxide ion conductors with improved properties at lower operation temperatures.

Most important oxide ion conductors belong principally to four different structural groups, which include the fluorite-type oxide (\(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\) [4–6] and \(\delta\text{Bi}_2\text{O}_3\) [7]), doped perovskite-type oxide (for instance: \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) [8]), Aurivillius-type oxides (\(\text{BIMEVOX}, \text{Bi}_2\text{V}_{0.86}\text{Ni}_{0.14}\text{O}_{5.29}\) [9]) and \(\text{Gd}_2\text{Ti}_2\text{O}_7\) pyrochlores-derived phases [10,11]. Besides, new kinds of oxide ions conductors have been deeply studied such as oxy-apatites, for instance \(\text{La}_{0.33}\square_{0.67}(\text{SiO}_4)\text{O}_2\) [12–16] and \(\text{La}_2\text{Mo}_2\text{O}_9\) derived phases [17–21]. Nevertheless, the applicability of these materials is limited by the difficulty to obtain high density ceramics (>90%), existence of phase transition which produces a drop in conductivities values, or the low stability under reducing conditions.

As part of the attempts to discover alternative structures, a new family of oxide ion conductors derived from cuspidine structure has been recently reported [22–25]. Minerals of the cuspidine group can be described with the general formula \(\text{A}_4(\text{Si}_2\text{O}_7)\text{X}_2\), where \(\text{A}\) is a large divalent cation and \(\text{X}\) is a monovalent or divalent anion (\(\text{OH}^-, \text{F}^-\)).
O\(^{2-}\)). The archetype compound of cuspidine family is, Ca\(_4\)(Si\(_2\)O\(_7\))(OH)\(_2\) [26], which crystallises in the space group \(P2_1/c\). The cuspidine framework is built up from ribbons of edge sharing CaO\(_7\)/CaO\(_8\) polyhedra running parallel to the \(a\)-axis with tetrahedral disilicate groups, Si\(_2\)O\(_7\), interconnecting these chains through the vertexes. The structural formula of cuspidine is better described as Ca\(_4\)(Si\(_2\)O\(_7\))(OH)\(_2\) to show the empty site between disilicate group, which can be considered as an anion vacancy in the crystal structure. Several oxy-cuspidine compounds are known, such as Eu\(_4\)(Al\(_2\)O\(_7\))O\(_2\) [27], Y\(_4\)(Al\(_2\)O\(_7\))(OH)\(_2\) [28,29], Pr\(_4\)(Ga\(_2\)O\(_7\))(OH)\(_2\) [30] and La\(_4\)(Ga\(_2\)O\(_7\))(OH)\(_2\) [23]. The crystal structure of La\(_4\)(Ga\(_2\)O\(_7\))(OH)\(_2\) is shown in Fig. 1 and the positions of the oxygen vacancies have been highlighted.

The possibilities of cation substitution in the tetrahedral site for the cuspidine structure have been already studied for \(RE\(_4\)(Ga\(_2\)O\(_7\))(OH)\(_2\)\) (\(RE = La\(^{3+}\), Nd\(^{3+}\), Gd\(^{3+}\)) [22–25]. These studies showed that partial aliovalent substitution of Ga\(^{3+}\) by Ge\(^{4+}\) or Ti\(^{4+}\) is accompanied by introduction of extra oxygen to charge compensation with the result of an enhancement of the oxide conductivity. In the obtained series, for instance La\(_4\)(Ga\(_2\)-x,Ti\(_x\)O\(_7\))(OH)\(_2\) [22,25], the isolated pyrogroups transforms to infinite chains of trigonal bipyramids with some interruptions due to the oxygen vacancies. Full infinite chains of TiO\(_5\) units are present in the end-member compound, La\(_4\)(Ti\(_2\)O\(_8\))O\(_2\). In addition, the complete electrochemical characterisation under different atmospheres revealed a significant proton contribution to the overall conductivity for Ti-doped cuspidines [25]. Finally, it must be underlined that for Ga-cuspidines, the Ge\(^{4+}\) doping leads to higher conductivity values than Ti\(^{4+}\) substitution.

Here we report the synthesis and characterisation of new oxygen ion conductors based on aluminium cuspidines, \(RE\(_4\)(Al\(_2\)-x,Ge\(_x\)O\(_7\))(OH)\(_2\)\) (\(RE = Gd\(^{3+}\), Nd\(^{3+}\))). Freeze-dried precursor method was used to prepare Nd-containing series, which cannot be obtained by standard ceramic route. Some members of the series have been investigated by neutron and synchrotron powder diffraction to describe the crystal structures, including the oxygen sublattice. The electrochemical characterisation has allowed establishing the main oxide conductivity features.

2. Experimental section

2.1. Synthesis

Two cuspidine series have been prepared: \(RE\(_4\)(Al\(_2\)-x,Ge\(_x\)O\(_7\))(OH)\(_2\)\) (\(RE = Gd\(^{3+}\), x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6; \(RE = Nd\(^{3+}\), x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0). Gd-containing cuspidines were synthesised by conventional ceramic method using high purity oxides as starting materials: Gd\(_2\)O\(_3\) (Alfa, 99.999%), GeO\(_2\) (Aldrich, 99.998%) and \(\gamma\)-Al\(_2\)O\(_3\) (Alfa, 99.997%). Gadolinium oxide was precalcined at 1273 K for 2 h in order to achieve decarbonation. The reagents, in stoichiometric amounts, were mixed in an agate mortar for 10 min and heated at 1373 K for 12 h. After cooling, the samples were milled for 3 h in a Fritsch ball mill (model Pulverisette 7, 45 cm\(^3\) agate vessel containing seven agate balls with a diameter of 15 mm) at 100 rpm with reverse rotation every 20 min. The resulting powders were pelletised at 100 MPa and heated at 1673 K for 48 h in ZGS–Pt–10%Rh crucibles. Gd\(_4\)(Al\(_2\)O\(_7\))(OH)\(_2\) needed an extra thermal treatment at 1873 K for 5 h. Pellets weight losses due to germanium volatilisation were found negligible at these temperatures and heating times. The cuspidine structure cannot be obtained by ceramic method for Nd\(^{3+}\), a larger lanthanide ion (see Results section). Hence a second synthesis method based in freeze-dried precursor was used [19,21].

Nd\(_4\)(Al\(_2\)-x,Ge\(_x\)O\(_7\))(OH)\(_2\) series was prepared by a freeze-dried precursor method from a stoichiometric cation solution with ethylenediamine-tetraacetic acid (EDTA) as complex agent. Neodymium oxide was dissolved in the minimum volume of nitric acid (1:1) and the pH was slowly raised up to 4 by adding ammonia. An EDTA solution 0.55 M was added under continuous stirring in a molar ratio metal/EDTA = 1/1.1 maintaining the pH between 4 and 6 with ammonia. The amorphous GeO\(_2\) is readily soluble in water, and so, stoichiometric quantities of this compound were dissolved in the minimum volume of water, giving a solution with a final pH of \(\approx 5\). Then, EDTA and ammonia were added to obtain a final pH value close to 5. It is important to avoid a drastic decrease of pH values below 2 to avoid EDTA precipitation. An aqueous solution of aluminium nitrate Al(NO\(_3\))\(_3\)·9H\(_2\)O was also prepared and the overall water content of this reagent was previously determined by thermogravimetric analysis. This solution had an initial pH \(\approx 2\), which was slowly raised to 4 by addition of ammonia. The complexation step of Al\(^{3+}\) ions with EDTA was done carefully maintaining the pH between 4 and 6 with ammonia under continuous stirring to avoid the precipitation of the metal hydroxide or EDTA at high or low pH values, respectively. The stoichiometric

![Fig. 1. Ball and stick crystal structure of La\(_4\)(Ga\(_2\)O\(_7\))(OH)\(_2\). The positions of the oxygen vacancies (\(\square\)), are highlighted.](image-url)
cation solutions prepared separately were mixed under constant stirring and slow heated in a hot plate to reduce the solution volume. The volume and cation concentration of the resulting solutions were \( \approx 200 \text{mL} \) and 0.15 M of Nd\(^{3+}\). Droplets of these solutions were subsequently flash frozen over liquid nitrogen and freeze-dried in a Heto Lyolab freeze-dryer for 2 days. The dried precursor powders were calcined at 573 K for 30 min, which produces the release of a large volume of gases and a voluminous blackish powder. The resulting solids were ground in an agate mortar and heated up to the decomposition temperature (873 K for 6 h) estimated by a TGA/DTA instrument (Pyris Diamond TG/DTA, model Perkin-Elmer).

The Gd-cuspidine series prepared by the ceramic method and Nd-cuspidine prepared by freeze-dried precursor method are hereafter labelled as GdGe\(_x\) and NdGe\(_x\), respectively.

### 2.2. Powder diffraction

All samples were characterised by laboratory X-ray powder diffraction (LXRPD) at room temperature (RT). The powder patterns were collected for NdGe\(_x\) series on a Siemens D5000 automated diffractometer, using graphite-monochromated CuK\(_{α1,2}\) radiation. The compounds were load in flat aluminium holders and scanned between 10° and 100° (2\(θ\)) in 0.03° steps, counting 16 s per step. High-resolution LXRPD patterns were collected for GdGe\(_x\) series in a Philips X'Pert Pro automated diffractometer, equipped with a Ge(111) primary monochromator and a X'celerator detector. The patterns were collected from 15° to 100° (2\(θ\) range) in 0.02° steps. In order to determine the thermal expansion coefficients of NdGe\(_{0.2}\) and NdGe\(_{0.6}\), LXRPD patterns were collected on heating each 100 K in an Anton-Paar TTK 450 camera under air conditions in the temperature range from 373 to 1073 K.

Neutron powder diffraction (NPD) patterns were collected for NdGe\(_{0.0}\) and NdGe\(_{0.5}\) at RT on HRPT diffractometer (SINQ neutron source at Paul Scherrer Institut, Villigen, Switzerland) with the samples loaded in vanadium cans. The wavelength \( \sim 1.886 \text{Å} \), was selected by the vertically focusing Ge (511) monochromator. The overall measuring time was \( \sim 6\text{h} \) per pattern to have good statistics over the 20 angular range of 5°–165° [21–0.95 Å] with 0.05° step size. Synchrotron X-ray powder diffraction (SXRPD) pattern for GdGe\(_{1.0}\) was collected on ID31 diffractometer [European Synchrotron Radiation Facility (ESRF), Grenoble, France]. The sample was loaded in a borosilicate glass capillary (\( φ = 1 \text{mm} \)) and rotated during data collection. A short penetrating wavelength, \( λ = 0.40084(5) \text{Å} \) (30.9 keV), was selected with a double-crystal Si (111) monochromator and calibrated with Si standard sample from NIST (\( α = 5.43094 \text{Å} \)). The overall measuring time was \( \sim 1\text{h} \) to have very good statistics over the angular range 2–30° (in 2\(θ\)) [11.5–0.77 Å]. The data from the multi-analyser Si (111) stage coupled with the nine

scintillation detectors were normalised and summed up to 0.003° step size with local software to produce the final raw data.

Full structural characterisation was carried out for NdGe\(_{0.0}\) and NdGe\(_{0.5}\) by a joint Rietveld analysis of LXRPD and NPD data at RT. The structure of GdGe\(_{1.0}\) has been determined from high-resolution SXRPD data because Gd has very high neutron absorption. All Rietveld [31] analyses were done using the GSAS suite of programs [32].

### 2.3. Microstructural characterisation

The morphology and microstructural studies of powders and sintered pellets were carried out using a JEOL SM 840 scanning electron microscope. The pellet surfaces were polished with diamond paste (12, 9, 6, 3 and 1 \(µ\)m) and thermally etched at 50 K below the sintering temperature for 15 min. Finally, the samples were metallised by gold sputtering for better image definition.

### 2.4. Sintering conditions and conductivity measurements

Fine powders of GdGe\(_x\) and NdGe\(_x\) compositions were obtained by grinding the initial powdered samples in a vibratory ball mill (Retsch, 2 zirconia balls with a diameter of 12.25 mm and a vessel volume of 8 \(cm^3\)) at 15 Hz for 20 min. The resulting average particle sizes were small [\(d_{50} \sim 1.5–3 \text{µm}\)]. The particle/agglomerate size distribution was measured on a Coulter LS130 laser diffraction analyser. Electrical characterisation was carried out on cylindrical pellets (\( 6 \text{mm} \) of diameter and \( 1 \text{mm} \) of thickness) obtained by pressing \( \sim 0.08 \text{g} \) of the fine powder samples at 175 MPa for 1 min. The pellets were sintered at 1773 and 1273 K for 6 h for GdGe\(_x\), and NdGe\(_x\), series, respectively. Electrodes were made by coating opposite pellet faces with METALOR® 6082 platinum paste and gradually heating to 1223 K at a rate of 5 K\( min^{-1}\) for 15 min in air to decompose the paste and to ensure a good conductivity and adherence. Successive treatments were made to achieve an electrical resistance lower than 1 \(Ω\) on both pellet faces.

Impedance spectroscopy data in static air were collected for GdGe\(_x\) series using a Hewlett-Packard 4284A impedance analyser over the frequency range 20 Hz–1 MHz. Similar data were recorded for NdGe\(_x\) series using a Solartron 1260 FRA instrument over the frequency range from 0.1 Hz to 1 MHz. The applied voltage was 200 mV in the temperature range of 1223–673 K and 250 mV between 623 and 573 K. Electrical measurements were acquired on cooling every 50 K (accuracy of ±1K) at 5 K\( min^{-1}\) and a delay time of 20 min at each selected temperature to ensure thermal stabilisation.

High-temperature conductivity measurements as a function of oxygen partial pressure [\(p(O_2)\)] ranges from air to \(10^{-20} \text{atm}\) were performed in a closed tube furnace cell for GdGe\(_{1.0}\) and NdGe\(_{0.5}\) compositions. The \(p(O_2)\) values
were monitored by using a YSZ oxygen sensor, placed next to the pellet inside the cell. The conductivity values were continually recorded as a function of \( p(O_2) \). The process consists of flushing the system with a dry 5% \( \text{H}_2 - \text{N}_2 \) gas mixture for 12 h at 1173 K to reach a minimum in oxygen activity inside the furnace. After that, the oxygen partial pressure was slowly raised back to atmospheric pressure by free diffusion, because the system is not airtight. The isothermal measurement took over 72 h to complete.

3. Results and discussion

3.1. Single phase existence ranges

Gd\(_{4}(\text{Al}_{2-x}\text{Ge}_{x}\text{O}_{7+\frac{1}{2}x})\) series from Rietveld refinements at room temperature\(^a\)

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>( \beta/\alpha ) (deg)</th>
<th>( V/Z ) (Å(^3))</th>
<th>( R_{wp} ) (%)</th>
<th>( R_{f} ) (%)</th>
<th>GdAlO(_3) (%)</th>
<th>GdGeO(_3) (%)</th>
<th>( \sigma_T ) (S cm(^{-1}))</th>
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<td>109.465(9)</td>
<td>213.85(2)</td>
<td>2.12</td>
<td>3.81</td>
<td>0.5(1)</td>
<td>2.75</td>
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<td>2.19</td>
<td>3.42</td>
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<td>2.19</td>
<td>3.42</td>
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<td>3.81</td>
<td>0.5(1)</td>
<td>2.75</td>
<td>10.0×10(^{-6})</td>
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The overall isothermal conductivities (at 973 K) are also given.

\(^{a}\)The unit cell edges relationship for the two reported settings is given for the sake of comparison of the evolution along the series: \( a(P2_1/n11) = b(P12_1/c) \) and \( b(P2_1/n11) = c(P12_1/c) \).

\(^{b}\)SXRPD data refinement.

\(^{c}\)Space group \( P12_1/c \).

\(^{d}\)Space group \( P2_1/n11 \).

\(^{e}\)This sample contained 1.3(2) wt% of GdGeO\(_3\).
obtained from freeze-dried, must be heated quickly at 573 K for 30 min to avoid rehydration and to start the auto-ignited process. Finally, the samples were calcined at 873 K for 6 h to obtain a light violet amorphous precursor, as revealed by the LXRPD pattern (Fig. 2b for NdGe0.0), free of carbonaceous residues because there were no appreciable mass losses above 873 K by TG. In order to follow the crystallisation process, the samples were heated for 6 h at different temperatures between 873 and 1273 K (see Figs. 2b–d). Fig. 2d shows that crystalline cuspidine-type structure is obtained at 1273 K.

In Figs. 3a and b are shown the scanning electron microscopy (SEM) images for NdGe0.0 sample heated at 973 and 1273 K, respectively. NdGe0.0 heated at 973 K (amorphous by LXRPD, Fig. 2c) is formed by layers of 15–20 μm of length. This compound is polycrystalline after calcined at 1273 K (Fig. 2d) and the microstructure is formed by agglomerates of small particles in the submicrometric range (Fig. 3b) with a specific surface area of ~8 m² g⁻¹ calculated from nitrogen adsorption, using the BET method.

LXRPD data for NdGeₓ series indicated that the main crystalline phase for the seven members (x = 0–1.0) has cuspidine-type structure. A minor crystalline secondary phase, NdAlO₃ (PDF 76-1336), was detected in some samples (see Table 2). The analysis of the LXRPD data by the Rietveld method showed that NdGe0.8 contained 1.9(1) and 1.3(1) wt% of Nd₂O₃ (PDF 74-2139) and NdAlO₃, respectively. NdGe₁.₀ sample contained 1.1(1), 11.8(3), and 1.2(1) wt% of Nd₂O₃ (PDF 74-2139) and NdAlO₃, respectively. NdGe₁.5 sample contained 1.1(1), 11.8(3), and 1.2(1) wt% of Nd₂O₃ (PDF 74-2139) and NdAlO₃, respectively. NdGe₂.₀ sample contained 1.1(1), 11.8(3), and 1.2(1) wt% of Nd₂O₃ (PDF 74-2139) and NdAlO₃, respectively.

The overall isothermal conductivities (at 973 K) are also given.

The unit cell values for GdGeₓ and NdGeₓ series, determined from the Rietveld refinements of LXRPD data, are given in Tables 1 and 2, respectively. The unit cell parameters are larger for NdGe₁.₀ than for GdGe₁.₀, as expected based on the variation of the ionic radii of the rare-earth cations [33]. For the two series, the overall trend is a volume increasing with germanium content (Tables 1 and 2) due to the oxygen loading. However, the variation is anisotropic due to the structural features of the cuspidine-framework. Tables 1 and 2 show that a and c parameters (in the P2₁/c setting) smoothly increase, and b parameter decreases, with x. This anisotropic variation is likely due to the interplay of three factors. Firstly, the introduction of extra oxygen in an empty position, to balance the charges, should expand the structure, but there is also an associate tilting of the tetrahedral groups [23] that decreases the b parameter. Secondly, the oxygens are distributed over two available sites [23,25], which may lead to slightly different unit cell parameters. Thirdly, the sizes of Al³⁺ and Ge⁴⁺ are very similar but not identical. Finally, it must be underlined that the smooth variation of the unit cell parameters up to x = 1.2 for GdGeₓ (Table 1) and x = 0.8 for NdGeₓ (Table 2) confirms the formation of the solid solutions in the reported compositional ranges.

### Table 2

Unit cell parameters and R-factors for Nd₄(Al₂₋ₓGeₓ)O₁₂₋ₓ (x = 0.0, 0.2, 0.4, 0.5, 0.6 and 0.8) series from Rietveld refinements at room temperature in c.g. P12₁/c.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>V/Z (Å³)</th>
<th>R_p(%)</th>
<th>R_w(%)</th>
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<td>109.7203(1)</td>
<td>224.38(2)</td>
<td>6.05/—</td>
<td>1.31/—</td>
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<td>224.66(1)</td>
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<td>Nd₄(Al₁.₂Ge₀.₈O₁₂)O₁₂</td>
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<td>10.8147(4)</td>
<td>11.4118(5)</td>
<td>109.9315(1)</td>
<td>224.98(2)</td>
<td>6.24/—</td>
<td>2.65/—</td>
<td>1.4(1)</td>
<td>36.5 × 10⁻⁶</td>
</tr>
<tr>
<td>Nd₄(Al₁.₀Ge₁.₀O₁₂)O₁₂</td>
<td>7.7629(3)</td>
<td>10.8122(5)</td>
<td>11.4155(7)</td>
<td>109.8147(1)</td>
<td>225.35(2)</td>
<td>8.71/—</td>
<td>2.10/—</td>
<td>1.3(1)</td>
<td>44.3 × 10⁻⁶</td>
</tr>
</tbody>
</table>

The overall isothermal conductivities (at 973 K) are also given.

*All atoms are located at the general position: 4e, Wyckoff notation.

*Joint LXRPD and NPD data refinement at RT.

*LXRPD data refinement.

3.2. Chemical and thermal stability

The stability of the GdGeₓ and NdGeₓ cuspidine series has been studied under different temperatures, atmospheres and time. Fig. 4 show the LXRPD patterns of NdGe₀.₀ and NdGe₀.₅ compositions under different conditions as representative members of the series: (1) pellets for all compositions were heated at 1273 K for 24 h to investigate the thermal stability at that temperature. The samples are stable at 1273 K since they do not undergo degradation, excepting NdGe₀.₀, which develops small amounts of Nd₂O₃ and NdAlO₃ (see Fig. 4a-left). (2) In
aluminium cuspidines present higher stability with smaller rare-earth cations like Gd$^{3+}$.

### 3.3. Crystal structures

A joint refinement of NPD and LXRPD data for Nd$_4$(Al$_{2-x}$O$_x$)O$_2$ and Nd$_4$(Al$_{1.5}$Ge$_{0.5}$O$_{7.25}$)O$_2$ were carried out at RT in $P$2$_1$/c space group as previously described for La$_4$(Ga$_2$-x,Ge$_x$O$_{7.5}$)O$_2$ [23] and La$_4$(Ga$_2$-x,Ti$_x$O$_{7.5}$)O$_2$ [25] cuspidine series. The neutron wavelength was refined in the simultaneous analysis of Nd$_4$(Al$_2$O$_2$)O$_2$ and it converged to 1.88551(6) Å. This value was used in all subsequent Rietveld analyses. The occupation factors of O(5) and O(10), which join the trigonal bypiramid chains [23,25], were freely refined given 0.52(4) and 0.81(4), respectively. The occupation factors of the two Al/Ge sites were also refined but constrained to full occupancy of each site. The refined structural stoichiometry for NdGe$_{0.5}$ was Nd$_4$(Al$_{1.45(8)}$Ge$_{0.55(8)}$O$_{7.33(8)}$)O$_2$ which is in good agreement with the nominal stoichiometry, Nd$_4$(Al$_{1.5}$Ge$_{0.5}$O$_{7.25}$)O$_2$.

The temperature factors of O(5) and O(10) were constrained to be the same to avoid correlations in the refinements. The final fits were very good for both compositions and the refined atomic parameters are given in Table 3. Bond distances and selected bond angles are given in the supplementary material in Tables S1 and S2. The Rietveld fits of the neutron and X-ray data for NdGe$_{0.5}$ sample are shown in Fig. 5.

The insertion of oxygen into the vacant position, O(10), and the partial emptying of O(5) in the NdGe$_x$ series equalise the two different distances initially present in the dialuminate groups and between them, respectively. So, the isolated tetrahedral dialuminate present in Nd$_4$(Al$_2$O$_2$)O$_2$ are converted to infinite bipyramid chains with some interruptions due to partial occupancy of both oxygens in Nd$_4$(Al$_{1.5}$Ge$_{0.5}$O$_{7.25}$)O$_2$ (see Fig. 6). The observed trend in the Al–O bond distances is fully consistent with the previous findings for the Ga–O distances, also obtained by NPD, in related doped cuspidines [23,25].

The crystal structure of Gd$_4$(Al$_{1.0}$Ge$_{1.0}$O$_{7.5}$)O$_2$ at RT has been described from SXRPD data using the structure of La$_4$(Ga$_{1.0}$Ti$_{1.0}$O$_{7.5}$)O$_2$ as starting model in the non-standard monoclinic space group $P$2$_1$/n1. NPD data were not acquired due to the high absorption of the Gadolinium cations. The absence of neutron data does not allow to describe the structure in $P$2$_1$/c space group and hence, an approximate (simplified) structure is described in $P$2$_1$/n1 with half-unit cell. The occupation factors of Al(1) and Ge(1) were fixed to their nominal values and they were refined later. The occupation factor of O(3) was fixed to its nominal value and it was not refined. The temperature factors of O(1), O(2), O(4) and O(5) were constrained to be the same to avoid correlations in the refinements. The synchrotron pattern showed anisotropic broadening with asymmetric tails for some reflections, which is likely linked
to the morphology of the crystallites plus some lack of oxygen ordering in the crystals, which has recently been pointed out [24]. The final refined atomic parameters are given in Table 3 and bond distances and selected bond angles are given in the supplementary material in Tables S1 and S2. The Rietveld plot of the synchrotron X-ray data is displayed in Fig. 7.

The volume thermal expansion coefficient for NdGe0.2 and NdGe0.6 samples, derived from high-resolution LXRPD data taken each 100 K, was $\alpha_v = 16.0(4) \times 10^{-6}$

Table 3

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$ (Å²)</th>
</tr>
</thead>
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<tr>
<td>RE(1)</td>
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<td>0.2501(9)</td>
<td>0.009(1)</td>
</tr>
<tr>
<td>RE(2)</td>
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<td>0.7455(9)</td>
<td>0.014(1)</td>
</tr>
<tr>
<td>RE(3)</td>
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<td>-</td>
<td>-</td>
<td>0.525(4)</td>
</tr>
<tr>
<td>RE(4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0989(2)</td>
</tr>
<tr>
<td>M(1)</td>
<td>0.1793(3)</td>
<td>0.3774(3)</td>
<td>0.2894(9)</td>
<td>0.011(1)</td>
</tr>
<tr>
<td>M(2)</td>
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<td>0.1856(9)</td>
<td>0.1171(8)</td>
<td>0.006(3)</td>
</tr>
<tr>
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<td>0.1064(9)</td>
<td>0.7133(9)</td>
<td>0.004(2)</td>
</tr>
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<td>O(2)</td>
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<td>0.8305(9)</td>
<td>0.004(2)</td>
</tr>
<tr>
<td>O(3)</td>
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<td>0.3851(9)</td>
<td>0.6707(9)</td>
<td>0.006(5)</td>
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<tr>
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<td>0.2723(9)</td>
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<td>0.2805(9)</td>
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<td>O(5)</td>
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<td>0.004(2)</td>
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<td>-</td>
<td>-</td>
<td>0.4362(9)</td>
</tr>
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<td>O(7)</td>
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<td>-</td>
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<td>0.2297(9)</td>
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<tr>
<td>O(8)</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>O(10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5638(9)</td>
</tr>
</tbody>
</table>

$^a$ All atoms are located at the general position 4c, Wyckoff notation.
$^b$ All atoms are located at the general position 4e, Wyckoff notation.
$^c$ SXRPD data refinement.
$^d$ Joint LXRPD and NPD refinement.
$^e$ $M = Al/Ge$ with occupation factors: Al(1) = 0.46 (1), Ge(1) = 0.54 for GdGe1.0 and Al(1) = 0.63(4), Ge(1) = 0.37, Al(2) = 0.82(4), Ge(2) = 0.18 for NdGe0.5.
$^f$ Nominal occupation factors for O(3) is 0.75 for GdGe1.0.
$^g$ Occupation factors for O(5) and O(10) are 0.52(4) and 0.81(4), respectively, for NdGe0.5.
and 20.2(7) x 10^{-6} K^{-1}, respectively [\chi_v is defined as m/n for the \( V(T) = n + mT(K) \) linear fitting]. Under the isotropic thermal expansion approximation, the linear expansion coefficient, \( \beta_{\text{calc}} \), can be derived as \( \beta_{\text{calc}} = \chi_v/3 \) being 5.3(1) x 10^{-6} and 6.7(2) x 10^{-6} K^{-1} for NdGe_{0.2} and NdGe_{0.6}, respectively.

3.4. Sintering conditions and impedance study

The sintering conditions for the pellets of GdGe_x series at 1773 K led to dense specimens with compactions ranging between 96% and 99% of the theoretical value (taking into account the pellets mass, volume and the crystallographic density). Fig. 8a shows a SEM micrograph for GdGe_{1.0} sintered pellet, showing the microstructure with average grain size ranging between 1 and 2 \mu m and low porosity. However, it can be observed that some grains are not well interconnected. No indications of liquid phase formation or phase segregations at the grain boundary were found in any studied samples. Additionally, no contamination due to the ball-milling process was detected in the sintered pellets. On the other hand, the limited thermal stability range for NdGe_x series resulted in porous samples. The pellets density values are \sim 65\%, at the highest possible sintering temperature 1273 K, which are low for an accurate measurements of ionic conductivities. Successive grinds were carried out in a vibratory ball mill for 20 min at 15 Hz to improve the compactions at 1273 K without success. Fig. 8b shows a SEM micrograph for NdGe_{0.5} sintered pellet, where large pores are observed. The porosity makes difficult to estimate the corresponding
grain sizes, although the material has good connectivity between the microparticles.

Representative impedance data for one composition of each series, GdGe\textsubscript{1.0} and NdGe\textsubscript{0.5}, at 773 K are shown as impedance complex plane plots in Fig. 9; similar plots were obtained for all compositions. For GdGe\textsubscript{1.0}, an almost non-deformed semicircle is observed with an associated capacitance at the maximum of 9.3 pF cm\textsuperscript{-1}. For NdGe\textsubscript{0.5}, a set of overlapped semicircles can be observed. This set of semicircles indicates that at least two different contributions due to grain interior (bulk) and internal interfaces (grain boundary and porosity) are present. Lower frequency processes are observed at high temperature in the form of a well-developed spike, with an associated capacitance of 0.031 mF cm\textsuperscript{-1} at 20 Hz and 1173 K for GdGe\textsubscript{1.0} (not shown). From these data, it may be concluded that the samples show principally ionic conductivity as previously reported for related cuspidine materials [22–25].

To investigate the electrical microstructure of the pellets is useful to analyse the spectroscopic plots (−Z′′/M′ vs. log f) for the same impedance data since it allows determining whether the overall pellet resistances represent the bulk resistance of the grains or were influenced by grain boundary effects. Spectroscopic plots for GdGe\textsubscript{1.0} (Fig. 10a) have the maxima of both curves quite close (less than one order of magnitude in frequency) which indicates that the impedance peak is associated with the same RC element responsible of the modulus peak, however the associated capacitances (8.4 pF cm\textsuperscript{-1} for M′ and 9.3 pF cm\textsuperscript{-1} for Z′) are somewhat larger than those expected for a homogeneous bulk value (∼2 pF cm\textsuperscript{-1} is expected assuming a typical high-frequency permittivity ε′ of 10–20). Furthermore, the M′ peak shows a shoulder at high frequencies that corresponds to a more conductive element. This relaxation is not well defined at low temperatures because the data dispersion likely due to the high electrical resistance of the material. To further examine this point, we have plotted the real part of the complex capacitance as a function of frequency (not shown). At low frequencies, the blocking electrode effect can be observed and, at higher frequencies, the curves show a clear relaxation from ∼9 pF toward lower values in the pF range as frequency increases. The relaxation at ∼9 pF is attributed to a very thick grain boundary or constriction resistance at the region of grain–grain contacts that may be observed in the SEM micrograph (Fig. 8a). This component dominates the Z′ spectrum and represents the main part of the total resistance of the samples.

Spectroscopic plots for NdGe\textsubscript{0.5} show a large separation between the two maxima of almost two orders of magnitude in frequency (Fig. 10b). The associated capacitance to the M′ maximum (2.5 pF cm\textsuperscript{-1}) is bulk characteristic, meanwhile the associated capacitance of the Z′ maximum (7.2 pF cm\textsuperscript{-1}) can be ascribed to a grain boundary contribution. The Z′ peak is not symmetric and an overlapped shoulder is observed at high frequencies close to the maximum of the M′ peak. It must be noted that the grains in NdGe\textsubscript{0.5} are well interconnected, as
The variation of total conductivity with Ge-content (at 973 K) under static air for GdGe<sub>x</sub> and NdGe<sub>x</sub> series, are given in the insets of Fig. 11. These values increase with Ge content, likely reaching a maximum for the highest Germanium-loaded materials, GdGe<sub>1.2</sub> and NdGeO<sub>0.8</sub> compositions. The conductivity values for GdGe<sub>x</sub> and NdGe<sub>x</sub> series at 973 K are given in Tables 1 and 2, respectively. These conductivity values are slightly lower than those previously reported for the Nd<sub>d</sub>(Ga<sub>2-x</sub>Ge<sub>x</sub>O<sub>7+y/2</sub>□<sub>1-y/2</sub>)O<sub>2</sub> series [24] at the same temperature: 3.7 × 10<sup>-5</sup> S cm<sup>-1</sup> for Nd<sub>d</sub>(Ga<sub>1.6</sub>GeO<sub>0.4</sub>O<sub>7.2</sub>□<sub>0.8</sub>)O<sub>2</sub>. However, the values are not directly comparable because the high porosity of the NdGe<sub>x</sub> samples. Furthermore, cuspidine materials with a large cation, i.e. Ga<sup>3+</sup>, at the tetrahedral site seems to display higher conductivity values compared to those derived from smaller cations like Al<sup>3+</sup>. The lower volume cell for Nd<sub>d</sub>(Al<sub>3</sub>O<sub>7</sub>□)O<sub>2</sub> (223.96 Å<sup>3</sup>) compared to Nd<sub>d</sub>(Ga<sub>2</sub>O<sub>7</sub>□)O<sub>2</sub> (231.5 Å<sup>3</sup>) probably reduce the free space for oxygen diffusion and consequently the conductivity decreases.

The ionic conductivity is independent of the oxygen partial pressure, <i>p(O<sub>2</sub>)</i>, for a pure ionic conductor. However, the conductivity increases for a mixed ionic–electronic conductor as <i>p(O<sub>2</sub>)</i> increases or decreases, depending on the predominant electronic contribution (p- and n-type, respectively). The conductivity data for GdGe<sub>1.0</sub> at 1173 K as a function of <i>p(O<sub>2</sub>)</i> are shown in the inset of Fig. 9. As it can be observed, the conductivity is almost independent of oxygen partial pressure, which suggests pure oxide-ion conduction with negligible electronic contribution within the studied oxygen partial pressure range. In addition, the conductivity of NdGeO<sub>0.5</sub>, which is stable under a constant flow of 5% H<sub>2</sub>–Ar at 1073 K, was also studied as function of <i>p(O<sub>2</sub>)</i>, and it also remains constant.

**4. Conclusions**

Two cuspidine series, <i>RE</i><sub>d</sub>(Al<sub>2-x</sub>Ga<sub>x</sub>O<sub>7+y/2</sub>□<sub>1-y/2</sub>)O<sub>2</sub> (<i>RE</i> = Gd<sup>3+</sup> and Nd<sup>3+</sup>), have been prepared as solid solutions up to <i>x</i> = 1.2 for Gd<sup>3+</sup> and 0.8 for Nd<sup>3+</sup>. The Gd-containing series could be prepared by ceramic method at high temperature, 1673 K, but the Nd-containing phases are not stable at high temperatures and cannot been prepared by standard solid-state reaction route. The Nd series was prepared at much lower temperatures, 1273 K, from freeze-dried precursor method. Neutron and synchrotron powder diffraction data have confirmed the known structural features of the cuspidine framework. The enhancement in the overall oxide conductivity along the two oxy-cuspidine series is two orders of magnitude with negligible electronic contribution. However, the reported oxide conductivity values are somewhat smaller than those previously reported for similar doped oxy-cuspidine-containing Ga<sup>3+</sup> cations.

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Fig. 11. Arrhenius plots of log σ<sub>T</sub> for (a) Gd<sub>d</sub>(Al<sub>2-x</sub>Ga<sub>x</sub>O<sub>7+y/2</sub>□<sub>1-y/2</sub>)O<sub>2</sub> (0.0 ≤ <i>x</i> ≤ 1.2) series and (b) Nd<sub>d</sub>(Al<sub>2-x</sub>Ga<sub>x</sub>O<sub>7+y/2</sub>□<sub>1-y/2</sub>)O<sub>2</sub> (0.0 ≤ <i>x</i> ≤ 0.8) series. The insets show the variation of the overall conductivity as function of Ge content at 973 K, the dashed line is a guide to the eyes.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.07.009.

References