Synthesis and characterization of oxyanion (phosphate, sulfate) doped Ba$_2$Sc$_{2-y}$Ga$_y$O$_5$

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Abstract

In this paper we examine the effect of partial substitution of Ga for Sc in the oxyanion (phosphate, sulfate) containing perovskites, $\text{Ba}_2\text{Sc}_{2-x}\text{P}_x\text{O}_{5+x}$ and $\text{Ba}_2\text{Sc}_{2-x}\text{S}_x\text{O}_{5+3x/2}$ with the samples analysed through a combination of X-ray diffraction, TGA, Raman spectroscopy and conductivity measurements. The results demonstrate that in both cases, Ga can be incorporated in place of Sc up to 40%. In order to accommodate the increasing Ga content, a reduction in the oxyanion content is required. Thus for the highest Ga content sample achieved, only 10% oxyanion incorporation was achieved giving endmember compositions of $\text{Ba}_2\text{ScGa}_{0.8}\text{P}_{0.2}\text{O}_{5.2}$ and $\text{Ba}_2\text{ScGa}_{0.8}\text{S}_{0.2}\text{O}_{5.3}$ for phosphate and sulfate doping respectively. While the Ga doping was shown to significantly improve the stability of the systems towards CO$_2$ containing atmospheres, conductivity measurements showed a reduction in the conductivity with increasing Ga content.

Keywords: Perovskite, proton conductor, phosphate, scandate, gallate, sulfate
**Introduction**

Perovskite-related materials have attracted significant interest in the fuel cell area for use either as electrolytes or electrode materials. In terms of the electrolyte, both systems displaying high oxide ion conductivity and high proton conductivity have been investigated [1,2,3]. An integral aspect to the optimization of the properties of these electrolyte material is an appropriate doping strategy to introduce oxide ion defects, with the most common being vacancy defects. Such oxide ion vacancy defects either allow the conduction of oxide ions, or the incorporation of water to introduce protons, and hence allow proton conduction [1,2,3]. The traditional approach to introduce oxide ion vacancies is to dope with aliovalent cations of similar size, e.g. Ba(Ce/Zr)O$_3$ doped with Y on the Ce/Zr site [4,5,6]. Such doped Ba(Ce/Zr)O$_3$ have attracted considerable interest as high temperature proton conductors in wet atmospheres, due to water incorporation into the oxide ion vacancies according to equation 1.

$$\text{V}_o^{\cdot\cdot} + \text{O}_o + \text{H}_2\text{O} \leftrightarrow 2 \text{OH}_o^\cdot$$ (eqtn 1)

While doped BaCeO$_3$, in particular, shows very high proton conductivity, a major problem with this and many other proton conducting perovskites is the instability towards CO$_2$ at typical fuel cell operating temperatures (600-800 °C), leading to the formation of BaCO$_3$ [7]. Improvements in the stability can be achieved by changing from BaCeO$_3$ to BaZrO$_3$, although there have been problems with this latter material in terms of poor grain boundary conductivity [8, 9]. Some advances have been made through appropriate
synthesis/processing (use of sintering aids) to ensure the grain size is large and the samples are well sintered or by moving to mixed Zr/Ce systems [10,11].

Another system that has attracted considerable interest is Ba$_2$In$_2$O$_5$ [12-15], which adopts the brownmillerite structure. In this system, there is a large number of vacant oxide ion sites (1/6 of the available sites are vacant), but these vacancies are ordered leading to alternating layers of octahedral and tetrahedral In, and hence the oxide ion conductivity is low. In this system doping with similar size aliovalent cations with higher charge (e.g. Zr$^{4+}$, Ti$^{4+}$ for In$^{3+}$) has been exploited to introduce disorder on the oxygen sublattice and hence increase the oxide ion conductivity. Recently we have demonstrated an alternative doping strategy for this system, involving the use of oxyanion ($\text{MO}_4^{n-}$; M= Si, P, S), to synthesise new proton conducting perovskites. In this doping strategy, the P, S, Si of the oxyanion group resides on the perovskite B cation site, with the oxide ions of this group filling 4 or the available 6 oxide ion positions around this site. This doping strategy has been shown to enhance the oxide ion conductivity through the introduction of disorder on the oxygen sublattice, with proton conduction observed in wet atmospheres due to water incorporation in the remaining vacant sites surrounding In. In addition to the beneficial effect on the conductivity this strategy has also been shown to enhance the stability towards CO$_2$ [16,17,18], which is attributed to the introduction of these acidic dopants reducing the basicity of the system [19]. Following our initial work on Ba$_2$In$_2$O$_5$, which demonstrated that silicate, phosphate and sulfate could be successfully doped into this system, leading to samples with high proton conductivity and enhanced CO$_2$ stability [16-19], we have shown that this strategy could be extended to Ba$_2$Sc$_2$O$_5$, with phosphate doping leading once more to samples with high conductivity and improved CO$_2$ stability.
However, an issue with these particular systems is their general high cost, due to the presence of Sc, In. In this paper we examine the effect of Ga doping into these phosphate doped barium scandate systems, with a view to reducing the Sc content, and analyzing the effect on the conductivity and CO$_2$ stability. We also demonstrate that comparable sulfate doped systems can be prepared, and compare the results to the phosphate doped systems.

**Experimental**

High purity BaCO$_3$, Sc$_2$O$_3$, Ga$_2$O$_3$, NH$_4$H$_2$PO$_4$, and (NH$_4$)$_2$SO$_4$ were used to prepare Ba$_2$Sc$_{2-x-y}$Ga$_y$P$_x$O$_{5+x}$ and Ba$_2$Sc$_{2-x-y}$Ga$_y$S$_x$O$_{5+3x/2}$ samples. A small (3%) excess of BaCO$_3$ was employed, in order to overcome Ba loss at elevated temperatures, and eliminate Ba deficient impurity phases, such as Ba$_3$Sc$_4$O$_9$, as has been seen in other studies synthesising similar Ba containing phases [17,18]. The powders were intimately ground and heated initially to 1000°C for 12 hours. They were then ball-milled (350 rpm for 1 hour, Fritsch Pulverisette 7 Planetary Mill) and reheated to 1100°C for 12 hours. The resulting powders were then ball-milled (350 rpm for 1 hour, Fritsch Pulverisette 7 Planetary Mill) a second time and pressed as pellets (1.3 cm diameter) and sintered at 1400°C for 12 hours. The pellets were covered in sample powder and the crucible was covered with a lid to limit the amount of Ba loss during the sintering process. Powder X-ray diffraction (Bruker D8 diffractometer with Cu Ka$_1$ radiation) was used to demonstrate phase purity as well as for preliminary structure determination. For the latter, the GSAS suite of programs was used [21].
The CO₂ stability of samples was determined using thermogravimetric analysis (Netzsch STA 449 F1 Jupiter Thermal Analyser). Samples were heated at 10 °C min⁻¹ to 1000 °C in 1:1 CO₂ and N₂ mixture to determine at what temperature CO₂ pick up occurred. Raman spectroscopy measurements were made in order to provide further evidence for the successful incorporation of phosphate, or sulfate. These measurements utilised a Renishaw inVia Raman microscope with excitation using a Cobolt Samba CW 532 nm DPSS Laser.

The water contents of hydrated samples were determined from thermogravimetric analysis (Netzsch STA 449 F1 Jupiter Thermal Analyser). Samples were heated at 10°C min⁻¹ to 1000°C in N₂, and the water content was determined from the observed mass loss.

For the conductivity measurements, the sintered pellets were coated with Pt paste, and then heated to 800°C for 1 hour to ensure bonding to the pellet. Conductivities were then measured by AC impedance measurements (Hewlett Packard 4182A impedance analyser) in the range from 0.1 to 10³ kHz. Measurements were made in dry N₂ and wet N₂ (in which the gas was bubbled at room temperature through water) to identify any protonic contribution to the conductivity. Measurements were also made in dry O₂ to determine if there was a p-type electronic contribution to the conductivity. The impedance spectra typically showed a single broad semicircle, corresponding to overlapping of bulk and grain boundary components (see figure S2 in the supplementary material). The total resistance was determined by the low frequency intercept of this semicircle.

Results and discussion
**Phosphate doping: \( \text{Ba}_2\text{Sc}_{2-x-y}\text{Ga}_y\text{P}_x\text{O}_{5+x} \)**

In our previous studies on phosphate doped \( \text{Ba}_2\text{Sc}_2\text{O}_5 \), we showed that for high temperature synthesis without phosphate doping, no perovskite phase (but rather \( \text{Ba}_3\text{Sc}_4\text{O}_9 \)) was observed [20]. On incorporation of phosphate, the presence of perovskite peaks was observed, with single phase samples observed for \( \text{Ba}_2\text{Sc}_{2-x}\text{P}_x\text{O}_5 \) with \( x=0.4, 0.5 \). Since the \( x=0.4 \) phase showed the highest conductivity, Ga doping was targeted at this system. These Ga doping studies showed that while Ga could be incorporated into the perovskite phase, there was a need to lower the phosphate content as the Ga level increased, as otherwise the formation of phosphate rich impurities, e.g. \( \text{Ba}_5(\text{PO}_4)_3(\text{OH}) \), were observed. However, too low a phosphate content also led to impurities, in this case \( \text{Ba}_3\text{Sc}_4\text{O}_9 \). The lower phosphate content required on gallium doping is most likely due to the gallium as well as the phosphorus preferring tetrahedral coordination, although further work is required to confirm this. The successfully prepared \( \text{Ba}_2\text{Sc}_{2-x-y}\text{Ga}_y\text{P}_x\text{O}_{5+x} \) samples are listed in table 1 with X-ray powder diffraction data for selected samples shown in figure 1. The cell parameters for these systems are also given in table 1, and these data show a general decrease in lattice parameter on increased substitution of \( \text{Sc}^{3+} \) with \( \text{Ga}^{3+} \) consistent with the smaller ionic radius of \( \text{Ga}^{3+} \) compared with \( \text{Sc}^{3+} \). From preliminary structure refinements using the X-ray diffraction data, the phosphate composition was found to be within 2\% of the nominal compositions for all the phases, in agreement with its successful incorporation. Further structural characterisation using neutron diffraction data is required to get more detailed information regarding the oxygen sites.
Raman data were collected for all the phosphate doped $\text{Ba}_2\text{Sc}_{2-y}\text{Ga}_y\text{O}_5$ and showed the presence of bands due to phosphate at $\sim 940 \text{ cm}^{-1}$ consistent with its incorporation (figure 2). Since, theoretically there should be no Raman active bands if the sample is purely cubic, apart from weak second order effects, the appearance of these bands suggests that there are significant local distortions from cubic symmetry. Such a situation was previously demonstrated for oxyanion doped $\text{Ba}_2\text{In}_2\text{O}_5$ from total scattering studies [22], which showed that while the average structure was cubic, the local structure was orthorhombic.

The conductivities of selected phosphate doped phases were then analysed. Initially measurements were performed in $\text{N}_2$ to eliminate any p-type contribution to the conductivity as is seen in the related phosphate doped $\text{Ba}_2\text{Sc}_2\text{O}_5$ [20]. The data showed high conductivities, with a further enhancement in wet $\text{N}_2$, consistent with a protonic contribution (table 2, figure 3). A comparison of the conductivities for $\text{Ba}_2\text{Sc}_{2-x-y}\text{Ga}_y\text{P}_x\text{O}_{5+x}$ showed a decrease for the higher phosphate content, which can be attributed to the filling of the oxide ion vacancies. The data also showed that increasing the gallium content lowered the conductivity, which may indicate some trapping of the oxide ion vacancy/proton defects on $\text{Ga}^{3+}$ incorporation, consistent with the earlier suggestion that $\text{Ga}$ is incorporated in tetrahedral coordination. Nevertheless, the conductivity of $1.2 \times 10^{-3} \text{ Scm}^{-1}$ at $500^\circ \text{C}$ in wet $\text{N}_2$ for $\text{Ba}_2\text{Sc}_{1.5}\text{Ga}_{0.1}\text{P}_{0.4}\text{O}_{5.4}$ is comparable with other proton conducting perovskites [1,3]. Similarly the activation energies for all samples were in the range 0.33-0.41 eV, which are comparable with values observed for other perovskite proton conductors, such as $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$ (0.44 eV) [23].
Subsequent measurements in dry O\textsubscript{2} confirmed the presence of a p-type contribution at elevated temperatures (above \(\approx 400^\circ\text{C}\)) leading to an increase in conductivity (figure 4).

In order to determine the level of water incorporation in these samples, they were heated under wet N\textsubscript{2} to 800\(^\circ\text{C}\), before slow cooling (0.4 °C min\(^{-1}\)) to room temperature. The water contents were then determined by TGA measurements, and the results are shown in table 3, indicating low water contents of \(\approx 0.1\) moles per formula unit. The data show that it is not possible to completely fill all the oxide ion sites in these phosphate doped systems. This inability to completely fill all the available oxygen vacancy sites with water can be explained partially by the requirement for vacancies around the phosphate to maintain the tetrahedral coordination of this oxyanion [18,20]. However, for the high Ga content samples with low phosphate contents, the water content remains low, which further supports the assumption of a preference for tetrahedral coordination for the Ga, which hence limits water incorporation. Additional measurements, heating at low temperatures, 200-300\(^\circ\text{C}\), in wet N\textsubscript{2} for 1 week, did not lead to any increase in these water contents, suggesting that the low water content is related to the materials themselves, rather than being a kinetic limitation of the experiment.

One concern regarding proton conducting perovskites for fuel cell applications is their stability towards CO\textsubscript{2} containing atmospheres. Thus, for example, while doped BaCeO\textsubscript{3} shows excellent proton conductivity, it suffers from a distinct instability towards CO\textsubscript{2} at typical fuel cell operating temperatures (500–700\(^\circ\text{C}\)), leading to the formation of BaCO\textsubscript{3} [7]. Therefore the stability of the Ba\(_2\)Sc\(_{2-x-y}\)Ga\(_y\)P\(_x\)O\(_{5+x}\) samples were examined and compared with BaCe\(_{0.9}\)Y\(_{0.1}\)O\(_{2.95}\). For phosphate doped Ba\(_2\)Sc\(_{2-x}\)Ga\(_x\)O\(_5\), TGA studies showed improved stability relative to BaCe\(_{0.9}\)Y\(_{0.1}\)O\(_{2.95}\). BaCe\(_{0.9}\)Y\(_{0.1}\)O\(_{2.95}\) showed a clear
mass increase above 500°C consistent with CO₂ pick up whereas phosphate doped Ba₂Sc₂₋ₓGaₓO₅ showed a mass increase at temperatures greater than 750°C, table 4, and the compositions with a gallium content greater than 0.5 showed no mass increase up to 1000°C. The data showed that on increased gallium content the temperature for the mass increase increased, while in the samples examined the relative phosphate content did not appear to significantly affect the temperature of the CO₂ pick up. Thus, while Ga doping is detrimental towards the conductivity, it does lead to a significant improvement in the CO₂ stability. In addition, although the conductivity is lowered on Ga doping, they remain higher than other recently reported CO₂- stable proton conducting electrolytes, such as doped LaPO₄ [24].

**Sulfate doping: Ba₂Sc₂₋ₓ₋ₚGaₓSₓO₅₊₃ₓ/2**

Following the successful synthesis of phosphate doped Ba₂Sc₂₋ₓGaₓO₅, attempts were made to prepare sulfate doped samples. Initially, we examined the possibility of stabilising the perovskite structure on sulfate doping into Ba₂Sc₂O₅ without Ga co-doping. As shown in our previous study on phosphate doped Ba₂Sc₂O₅, there was no sign of any perovskite phase without sulfate doping, with Ba₃Sc₄O₉ formed instead. The introduction of sulfate showed that single phase perovskite samples could be obtained for 20% sulfate doping, i.e. Ba₂Sc₁.₆S₀.₄O₅.₆ (figure 5). The possibility to partially replace Sc by Ga was then examined, with the results showing that, as for the phosphate doped samples, while Ga could be incorporated into the perovskite phase, there was a need to lower the sulfate content as the Ga level was increased.

The successfully prepared Ba₂Sc₂₋ₓ₋ₚGaₓSₓO₅₊₃ₓ/2 samples are listed in table 5 with X-ray powder diffraction data for selected samples shown in figure 6. The cell parameters for
these systems are also given in table 5, and these data show a general decrease in lattice parameter on increased substitution of Sc$^{3+}$ with Ga$^{3+}$ consistent with the smaller ionic radius of Ga$^{3+}$ compared with Sc$^{3+}$. Raman data confirmed the incorporation of sulfate groups into the structure, as indicated by the presence of a peak at around 990 cm$^{-1}$ (figure 7).

The conductivities of selected sulfate doped phases were then analysed, and the results were similar to those for the phosphate doped samples, with high conductivities observed, with a further enhancement in wet N$_2$, consistent with a protonic contribution (table 6, figure 8), along with comparable activation energies to the phosphate doped samples (0.34-0.41 eV). There was a similar decrease in conductivity on increasing Ga content, while the CO$_2$ stability was enhanced (table 8).

The level of water incorporation in these samples (table 7) was also similar to the results as for the phosphate doped systems, with water contents of 0.05-0.08 moles per formula unit, indicating incomplete filling of all the available oxygen vacancy sites with water.

**Conclusions**

The results demonstrate that it is possible to stabilize the cubic perovskite phase on phosphate or sulfate doping into Ba$_2$Sc$_2$O$_5$. Furthermore, Ga can be partially substituted into these phases leading to significant improvements in the CO$_2$ stability. This improved CO$_2$ stability is, however, at the detriment to the conductivity, and therefore highlights the issues with developing proton conducting electrolyte materials with both high conductivity and high CO$_2$ stability; demonstrating that strategies to improve the latter lower the former. Nevertheless, high conductivities, and good CO$_2$ stabilities are
observed for samples with low (e.g. 5%) Ga contents, leading to promising potential for fuel cell electrolyte applications. The results further highlight the potential of oxyanion doping in perovskites with a view to forming new phases with high conductivities.

Acknowledgements

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References


19. J. F. Shin, P. R. Slater; *J. Power Sources*, 2011, **196**, 8539.


Table 1 Cell parameter data for Ba$_2$Sc$_{2-x-y}$Ga$_y$P$_x$O$_{5+x}$

<table>
<thead>
<tr>
<th>Sample (nominal composition)</th>
<th>Unit cell parameters (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>2$Sc$</em>{1.6}$P$<em>{0.4}$O$</em>{5.4}$</td>
<td>4.150(1)</td>
<td>71.49(3)</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.5}$Ga$<em>{0.1}$P$</em>{0.4}$O$_{5.4}$</td>
<td>4.1426(7)</td>
<td>71.097(4)</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.4}$Ga$<em>{0.2}$P$</em>{0.4}$O$_{5.4}$</td>
<td>4.1374(6)</td>
<td>70.827(3)</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.3}$Ga$<em>{0.4}$P$</em>{0.3}$O$_{5.3}$</td>
<td>4.1343(6)</td>
<td>70.670(3)</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.3}$Ga$<em>{0.5}$P$</em>{0.2}$O$_{5.2}$</td>
<td>4.1401(7)</td>
<td>70.964(4)</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.2}$Ga$<em>{0.6}$P$</em>{0.2}$O$_{5.2}$</td>
<td>4.1352(9)</td>
<td>70.714(5)</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.1}$Ga$<em>{0.7}$P$</em>{0.2}$O$_{5.2}$</td>
<td>4.1320(8)</td>
<td>70.549(4)</td>
</tr>
<tr>
<td>Ba$<em>2$ScGa$</em>{0.8}$P$<em>{0.2}$O$</em>{5.2}$</td>
<td>4.1233(1)</td>
<td>70.108(5)</td>
</tr>
</tbody>
</table>
Table 2. Conductivity data for Ba$_{2}$Sc$_{2-x-y}$Ga$_{y}$P$_{x}$O$_{5+x}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>(nominal composition)</th>
<th>Conductivity (S cm$^{-1}$)</th>
<th>500 °C</th>
<th>800 °C</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>Dry N$_2$</td>
<td>Wet N$_2$</td>
<td>Dry N$_2$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.6}$P$<em>{0.4}$O$</em>{5.4}$</td>
<td></td>
<td>2.9 x 10$^{-3}$</td>
<td>5.9 x 10$^{-3}$</td>
<td>7.9 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.5}$Ga$<em>{0.1}$P$</em>{0.4}$O$_{5.4}$</td>
<td></td>
<td>1.1 x 10$^{-3}$</td>
<td>1.2 x 10$^{-3}$</td>
<td>3.4 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.4}$Ga$<em>{0.2}$P$</em>{0.4}$O$_{5.4}$</td>
<td></td>
<td>6.1 x 10$^{-4}$</td>
<td>7.8 x 10$^{-4}$</td>
<td>2.3 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.3}$Ga$<em>{0.4}$P$</em>{0.3}$O$_{5.3}$</td>
<td></td>
<td>3.5 x 10$^{-4}$</td>
<td>6.4 x 10$^{-4}$</td>
<td>2.9 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.3}$Ga$<em>{0.5}$P$</em>{0.2}$O$_{5.2}$</td>
<td></td>
<td>8.3 x 10$^{-4}$</td>
<td>1.2 x 10$^{-5}$</td>
<td>3.5 x 10$^{-5}$</td>
</tr>
<tr>
<td>Ba$<em>2$ScGa$</em>{0.8}$P$<em>{0.2}$O$</em>{5.2}$</td>
<td></td>
<td>8.2 x 10$^{-6}$</td>
<td>4.3 x 10$^{-5}$</td>
<td>5.9 x 10$^{-5}$</td>
</tr>
</tbody>
</table>
Table 3 Water content for $\text{Ba}_2\text{Sc}_{2-x-y}\text{Ga}_y\text{P}_x\text{O}_{5+x}$

<table>
<thead>
<tr>
<th>Sample (nominal composition)</th>
<th>Moles of water per formula unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.6}\text{P}<em>{0.4}\text{O}</em>{5.4}$</td>
<td>0.12(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.5}\text{Ga}<em>{0.1}\text{P}</em>{0.4}\text{O}_{5.4}$</td>
<td>0.11(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.4}\text{Ga}<em>{0.2}\text{P}</em>{0.4}\text{O}_{5.4}$</td>
<td>0.10(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.3}\text{Ga}<em>{0.4}\text{P}</em>{0.3}\text{O}_{5.3}$</td>
<td>0.11(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.3}\text{Ga}<em>{0.5}\text{P}</em>{0.2}\text{O}_{5.2}$</td>
<td>0.11(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.2}\text{Ga}<em>{0.6}\text{P}</em>{0.2}\text{O}_{5.2}$</td>
<td>0.12(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.1}\text{Ga}<em>{0.7}\text{P}</em>{0.2}\text{O}_{5.2}$</td>
<td>0.14(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{ScGa}</em>{0.8}\text{P}<em>{0.2}\text{O}</em>{5.2}$</td>
<td>0.11(1)</td>
</tr>
</tbody>
</table>
Table 4 Temperature for uptake of CO₂ for Ba₂Sc₂₋ₓGaₓPₓO₅₊ₓ from TGA studies up to 1000°C

<table>
<thead>
<tr>
<th>Sample (nominal composition)</th>
<th>Temperature of mass gain (°C)</th>
</tr>
</thead>
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<tr>
<td>Ba₂Sc₁.₆P₀.₄O₅.₄</td>
<td>750</td>
</tr>
<tr>
<td>Ba₂Sc₁.₅Ga₀.₁P₀.₄O₅.₄</td>
<td>750</td>
</tr>
<tr>
<td>Ba₂Sc₁.₄Ga₀.₂P₀.₄O₅.₄</td>
<td>800</td>
</tr>
<tr>
<td>Ba₂Sc₁.₃Ga₀.₄P₀.₃O₅.₃</td>
<td>825</td>
</tr>
<tr>
<td>Ba₂Sc₁.₃Ga₀.₅P₀.₂O₅.₂</td>
<td>850</td>
</tr>
<tr>
<td>Ba₂Sc₁.₂Ga₀.₆P₀.₂O₅.₂</td>
<td>no mass gain</td>
</tr>
<tr>
<td>Ba₂Sc₁.₁Ga₀.₇P₀.₂O₅.₂</td>
<td>no mass gain</td>
</tr>
<tr>
<td>Ba₂ScGa₀.₈P₀.₂O₅.₂</td>
<td>no mass gain</td>
</tr>
<tr>
<td>BaCe₀.₉Y₀.₁O₂.₉₅</td>
<td>500</td>
</tr>
<tr>
<td>Sample (nominal composition)</td>
<td>Unit cell parameters (Å)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>(\text{Ba}<em>2\text{Sc}</em>{1.6}\text{S}<em>{0.4}\text{O}</em>{5.6})</td>
<td>4.1674(2)</td>
</tr>
<tr>
<td>(\text{Ba}<em>2\text{Sc}</em>{1.4}\text{Ga}<em>{0.3}\text{S}</em>{0.3}\text{O}_{5.45})</td>
<td>4.16770(9)</td>
</tr>
<tr>
<td>(\text{Ba}<em>2\text{Sc}</em>{1.3}\text{Ga}<em>{0.4}\text{S}</em>{0.3}\text{O}_{5.45})</td>
<td>4.1656(1)</td>
</tr>
<tr>
<td>(\text{Ba}<em>2\text{Sc}</em>{1.2}\text{Ga}<em>{0.6}\text{S}</em>{0.2}\text{O}_{5.3})</td>
<td>4.14827(8)</td>
</tr>
<tr>
<td>(\text{Ba}<em>2\text{Sc}</em>{1.1}\text{Ga}<em>{0.7}\text{S}</em>{0.2}\text{O}_{5.3})</td>
<td>4.14056(7)</td>
</tr>
<tr>
<td>(\text{Ba}<em>2\text{ScGa}</em>{0.8}\text{S}<em>{0.2}\text{O}</em>{5.3})</td>
<td>4.1386(1)</td>
</tr>
</tbody>
</table>
Table 6 Conductivity data for Ba$_2$Sc$_{2-x-y}$Ga$_y$S$_x$O$_{5+3/2x}$

<table>
<thead>
<tr>
<th>Sample (nominal composition)</th>
<th>Conductivity (S cm$^{-1}$)</th>
<th>500 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry N$_2$</td>
<td>Wet N$_2$</td>
<td>Dry N$_2$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.6}$S$<em>{0.4}$O$</em>{5.6}$</td>
<td>8.9 x 10$^{-4}$</td>
<td>8.9 x 10$^{-4}$</td>
<td>3.5 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.4}$Ga$<em>{0.3}$S$</em>{0.3}$O$_{5.45}$</td>
<td>3.8 x 10$^{-4}$</td>
<td>8.7 x 10$^{-4}$</td>
<td>1.6 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.3}$Ga$<em>{0.4}$S$</em>{0.3}$O$_{5.45}$</td>
<td>2.2 x 10$^{-4}$</td>
<td>5.2 x 10$^{-4}$</td>
<td>1.0 x 10$^{-3}$</td>
</tr>
<tr>
<td>Ba$<em>2$Sc$</em>{1.2}$Ga$<em>{0.6}$S$</em>{0.2}$O$_{5.3}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>6.0 x 10$^{-4}$</td>
<td>4.4 x 10$^{-4}$</td>
</tr>
<tr>
<td>Ba$<em>2$ScGa$</em>{0.8}$S$<em>{0.2}$O$</em>{5.3}$</td>
<td>4.6 x 10$^{-5}$</td>
<td>2.0 x 10$^{-4}$</td>
<td>1.9 x 10$^{-4}$</td>
</tr>
</tbody>
</table>
Table 7 Water contents for $\text{Ba}_2\text{Sc}_{2-x-y}\text{Ga}_y\text{S}_x\text{O}_{5+3/2x}$

<table>
<thead>
<tr>
<th>Sample (nominal composition)</th>
<th>Moles of water per formula unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.4}\text{Ga}<em>{0.3}\text{S}</em>{0.3}\text{O}_{5.45}$</td>
<td>0.07(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.3}\text{Ga}<em>{0.4}\text{S}</em>{0.3}\text{O}_{5.45}$</td>
<td>0.08(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.2}\text{Ga}<em>{0.6}\text{S}</em>{0.2}\text{O}_{5.3}$</td>
<td>0.08(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{Sc}</em>{1.1}\text{Ga}<em>{0.7}\text{S}</em>{0.2}\text{O}_{5.3}$</td>
<td>0.08(1)</td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{ScGa}</em>{0.8}\text{S}<em>{0.2}\text{O}</em>{5.3}$</td>
<td>0.06(1)</td>
</tr>
</tbody>
</table>
Table 8 Temperature for uptake of CO\(_2\) for Ba\(_2\)Sc\(_{2-x-y}\)Ga\(_x\)S\(_x\)O\(_{5+3/2x}\) from TGA studies up to 1000\(^\circ\)C

<table>
<thead>
<tr>
<th>Sample (nominal composition)</th>
<th>Temperature of mass gain (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(<em>2)Sc(</em>{1.4})Ga(<em>{0.3})S(</em>{0.3})O(_{5.45})</td>
<td>800</td>
</tr>
<tr>
<td>Ba(<em>2)Sc(</em>{1.3})Ga(<em>{0.4})S(</em>{0.3})O(_{5.45})</td>
<td>850</td>
</tr>
<tr>
<td>Ba(<em>2)Sc(</em>{1.2})Ga(<em>{0.6})S(</em>{0.2})O(_{5.3})</td>
<td>950</td>
</tr>
<tr>
<td>Ba(<em>2)Sc(</em>{1.1})Ga(<em>{0.7})S(</em>{0.2})O(_{5.3})</td>
<td>950</td>
</tr>
<tr>
<td>Ba(<em>2)ScGa(</em>{0.8})S(<em>{0.2})O(</em>{5.3})</td>
<td>no mass gain</td>
</tr>
<tr>
<td>BaCe(<em>{0.9})Y(</em>{0.1})O(_{2.95})</td>
<td>500</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 XRD patterns for Ba$_2$Sc$_{1.5}$Ga$_{0.1}$P$_{0.4}$O$_{5.4}$, Ba$_2$Sc$_{1.3}$Ga$_{0.4}$P$_{0.3}$O$_{5.3}$ and Ba$_2$ScGa$_{0.8}$P$_{0.2}$O$_{5.2}$.

Fig. 2 Raman spectra of Ba$_2$Sc$_{1.5}$Ga$_{0.1}$P$_{0.4}$O$_{5.4}$ and Ba$_2$Sc$_{1.1}$Ga$_{0.7}$P$_{0.2}$O$_{5.2}$ with peak showing the presence of phosphate indicated.

Fig. 3 Conductivity data between 350°C and 800°C for Ba$_2$Sc$_{1.5}$Ga$_{0.1}$P$_{0.4}$O$_{5.4}$ (circle) and Ba$_2$ScGa$_{0.8}$P$_{0.2}$O$_{5.2}$ (square) in dry (empty) and wet (filled) N$_2$.

Fig. 4 Conductivity data between 350°C and 800°C for Ba$_2$ScGa$_{0.8}$P$_{0.2}$O$_{5.2}$ in dry N$_2$ (filled square) and dry O$_2$ (empty square).

Fig. 5 XRD pattern for Ba$_2$Sc$_{1.6}$S$_{0.4}$O$_{5.6}$ and undoped Ba$_2$Sc$_2$O$_5$, the latter leading to the formation of Ba$_3$Sc$_4$O$_9$ rather than a perovskite phase.

Fig. 6 XRD patterns for Ba$_2$Sc$_{1.4}$Ga$_{0.3}$S$_{0.3}$O$_{5.45}$, Ba$_2$Sc$_{1.3}$Ga$_{0.4}$S$_{0.3}$O$_{5.45}$, Ba$_2$Sc$_{1.2}$Ga$_{0.6}$S$_{0.2}$O$_{5.3}$, Ba$_2$Sc$_{1.1}$Ga$_{0.7}$S$_{0.2}$O$_{5.3}$ and Ba$_2$ScGa$_{0.8}$S$_{0.2}$O$_{5.3}$.

Fig. 7 Raman spectra of Ba$_2$Sc$_{1.3}$Ga$_{0.4}$S$_{0.3}$O$_{5.45}$ and Ba$_2$Sc$_{1.1}$Ga$_{0.7}$S$_{0.2}$O$_{5.3}$ with peak showing the presence of sulfate indicated.

Fig. 8 Conductivity data between 350°C and 800°C for Ba$_2$Sc$_{1.4}$Ga$_{0.3}$S$_{0.3}$O$_{5.45}$ (circle), and Ba$_2$ScGa$_{0.8}$S$_{0.2}$O$_{5.3}$ (square) in dry (empty) and wet (filled) N$_2$.

Fig. 9 Conductivity data between 500°C and 800°C for Ba$_2$Sc$_{1.3}$Ga$_{0.4}$S$_{0.3}$O$_{5.45}$ in dry N$_2$ (filled circle) and dry O$_2$ (empty circle).
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5

Intensity (A.U.)

"Ba$_3$Sc$_2$O$_5$"

Ba$_2$Sc$_{1.6}$S$_{0.4}$O$_{5.6}$

2$\theta$ (°)
Fig. 7
Fig. 8
Fig. 9