Enhanced CO$_2$ stability of oxyanion doped Ba$_2$In$_2$O$_5$ systems co-doped with La, Zr

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Abstract
In the Solid Oxide Fuel Cell (SOFC) field, proton conducting perovskite electrolytes offer many potential benefits. However, an issue with these electrolytes is their stability at elevated temperatures in the presence of CO$_2$. Recently we have reported enhanced oxide ion/proton conductivity in oxyanion (silicate, phosphate) doped Ba$_2$In$_2$O$_5$, and in this paper we extend this work to examine the stability at elevated temperatures towards CO$_2$. The results show improved CO$_2$ stability compared to the undoped system, and moreover this can be further improved by co-doping on either the Ba site with La, or the In site with Zr. While this co-doping strategy does reduce the conductivity slightly, the greatly improved CO$_2$ stability would suggest there is technological potential for these co-doped samples.

Keywords: Perovskite, Proton Conductivity, Solid Oxide Fuel Cell, Electrolyte, Silicon
1. Introduction

Materials displaying high proton conductivity have attracted considerable attention due to potential applications in solid oxide fuel cells, hydrogen sensors and separation membranes [1-4]. The systems showing the highest proton conductivity are the Ba containing perovskites, BaZrO$_3$ and BaCeO$_3$, suitably doped. However, a major problem with such proton conducting perovskites is the issue of stability towards CO$_2$. Thus, although doped BaCeO$_3$ shows excellent proton conductivity, it suffers from a distinct instability towards CO$_2$ at typical fuel cell operating temperatures (600-800 °C), leading to the formation of BaCO$_3$. Doped BaZrO$_3$ shows much greater stability, but has been shown to suffer from poor grain boundary conductivity leading typically to significantly lower total conductivities than BaCeO$_3$ based systems. However, it should be noted that recently there have been significant improvements in the performance of BaZrO$_3$ based electrolytes through appropriate synthesis/processing to ensure the grain size is large and the samples are well sintered [5, 6].

Ba$_2$In$_2$O$_5$ has also attracted substantial interest in terms of both oxide ion conductivity and proton conductivity [7-20]. While the conductivity of the undoped material is comparatively low at intermediate temperatures, due to ordering of the oxide ion vacancies, oxide ion disorder can be introduced through doping on the In and/or Ba site, leading to a substantial enhancement in the oxide ion conductivity. In addition, both doped and undoped Ba$_2$In$_2$O$_5$ show significant proton conductivity at intermediate temperatures in a wet atmosphere. In this earlier work on Ba$_2$In$_2$O$_5$, the dopants chosen were cations with similar size e.g. La for Ba, Zr for In. Recently we have been
investigating an alternative doping strategy involving the incorporation of oxyanions. This work showed that enhanced oxide ion conductivities could be achieved by doping Ba$_2$In$_2$O$_5$ with oxyanions (phosphate, sulphate, silicate) [21-23], along with significant proton conductivities in wet atmospheres below $\approx 650$ °C. In this paper, we extend this work to investigate the CO$_2$ stability of these doped samples. We also investigate the effect of co-doping on the Ba or In site with La and Zr respectively, with regards to the conductivity and the CO$_2$ stability.

2. Experimental

High purity BaCO$_3$, La$_2$O$_3$, In$_2$O$_3$, ZrO$_2$, and SiO$_2$, NH$_4$H$_2$PO$_4$ were used to prepare Ba$_2$In$_{1.8}$Si$_{0.2}$O$_{5.1}$, Ba$_2$In$_{1.7}$P$_{0.3}$O$_{5.3}$ and La, Zr co-doped samples. In order to overcome Ba loss at elevated temperatures, a 3% excess of BaCO$_3$ was employed. Without this small Ba excess, low levels of Ba deficient impurity phases, such as BaIn$_2$O$_4$ and Ba$_4$In$_8$O$_{13}$, were observed after sintering, as has been seen in other studies synthesising similar Ba containing phases [24,25]. The powders were intimately ground and heated initially to 1000 °C for 12h, before dry-milling (350 rpm for 1 hour, Fritsch Pulverisette 7 Planetary Ball Mill) and reheating to 1000 °C for a further 50h. The resulting powders were then pressed as pellets (1.3 cm diameter) and sintered at 1400 °C for 10h. In order to limit the amount of Ba loss during the sintering process, the pellets were covered in sample powder and the crucible was covered with a lid. Phase purity was determined using X-ray powder diffraction (Bruker D8 diffractometer with Cu K$\alpha$_1 radiation).
In order to determine the CO$_2$ stability of samples, two sets of experiments were performed. In the first set of experiments, samples were heated at temperatures between 600 and 800 °C for 12 hours in a tube furnace under flowing CO$_2$ gas, and the samples were analysed for partial decomposition by X-ray diffraction. In the second experiment samples were analysed using thermogravimetric analysis (Netzsch STA 449 F1 Jupiter Thermal Analyser). Samples were heated at 10 °C min$^{-1}$ to 1000 °C in 1:1 CO$_2$ and N$_2$ mixture to determine at what temperature CO$_2$ pick up occurred.

For the conductivity measurements a Norecs Probstat$^{\text{TM}}$ measurement cell was employed [26, 27]. The sintered pellets (>85% theoretical density) 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 10$^3$ kHz, with an applied voltage of 100 mV. Since Ba$_2$In$_2$O$_5$ displays a small p-type contribution to the conductivity in oxidising conditions, measurements were made in dry N$_2$ to eliminate this contribution. In addition, measurements were made in wet N$_2$ (in which the gas was bubbled at room temperature through water) to identify any protonic contribution to the conductivity. The impedance data for the P, Si singly doped and La/P, La/Si co-doped samples showed a single broad semicircle in both dry and wet atmospheres (figure 1). The capacitance of the semicircle ($\approx$10$^{-12}$ Fcm$^{-1}$) was typical of a bulk response, suggesting that the resistance of the grain boundary was small compared to that of the bulk. For the Zr/Si and Zr/P co-doped samples, a single semicircle was observed above 400 °C, while below this temperature a small grain boundary component was also observed. The conductivities reported represent total conductivities.
3. Results and discussion

As shown in our previous work, X-ray powder diffraction analysis indicated that on Si, P doping there is a change in symmetry from orthorhombic for Ba$_2$In$_2$O$_5$ to cubic for Ba$_{2}$In$_{1.8}$Si$_{0.2}$O$_{5.1}$, and Ba$_2$In$_{1.7}$P$_{0.3}$O$_{5.3}$ [21-23]. The stability of these systems towards CO$_2$ was examined by heating in CO$_2$ at different temperatures between 600 and 800 °C, and through TGA studies in a 1:1 N$_2$:CO$_2$ atmosphere between 10 and 1000 °C. The results showed that on heating to 600°C, BaCO$_3$ impurities were visible for all samples (figure 2). However, compared to undoped Ba$_2$In$_2$O$_5$, the Si, P doped samples showed significantly lower sensitivity towards CO$_2$, with much smaller BaCO$_3$ impurities observed at this temperature. The results were also compared to Y doped BaCeO$_3$ which is known to be very sensitive towards CO$_2$. As for undoped Ba$_2$In$_2$O$_5$, this phase showed the presence of large BaCO$_3$ impurities when heated in CO$_2$ at 600 °C. The TGA results provided further indication of the relative stabilities of the samples towards CO$_2$ (figure 3). For undoped Ba$_2$In$_2$O$_5$ a clear increase in mass, consistent with CO$_2$ pick up and formation of BaCO$_3$, was observed at 600 °C. Similarly, for BaCe$_{0.9}$Y$_{0.1}$O$_{2.95}$ a significant increase in mass was observed above 500 °C. In contrast, for phosphate and silicate doped Ba$_2$In$_2$O$_5$, the TGA traces were much flatter, with a large mass increase only observed when the temperature was raised further to above 800 °C.

These initial results therefore indicated that the stability of Ba$_2$In$_2$O$_5$ towards CO$_2$ was improved by silicate or phosphate doping, although the samples still showed some instability at higher temperatures. Therefore, the effect of co-doping with La, Zr was examined to determine the effect on both the CO$_2$ stability and conductivity. Single phase
Ba_{2-x}La_xIn_{1.7}P_{0.3}O_{5.3+x/2}, Ba_{2-x}La_xIn_{1.8}Si_{0.2}O_{5.1+x/2} (0 ≤ x ≤ 0.4) and Ba_{2-x}Zr_xP_{0.3}O_{5.3+x/2}, Ba_{2-x}Zr_xSi_{0.2}O_{5.1+x/2} (0 ≤ x ≤ 0.4) were prepared, and the CO$_2$ stability and conductivities were examined. The preliminary studies showed that as the La, Zr content increased, so the stability towards CO$_2$ appeared to increase, although this was at the expense of a general reduction in the conductivity. Thus, La, Zr co-doping appears beneficial in terms of the CO$_2$ stability but detrimental in terms of the conductivity. In terms of a balance between high conductivity and CO$_2$ stability, the compositions Ba$_1.7$La$_{0.3}$In$_{1.7}$P$_{0.3}$O$_{5.45}$, Ba$_2$In$_{1.5}$Zr$_{0.2}$P$_{0.3}$O$_{5.4}$, Ba$_{1.6}$La$_{0.4}$In$_{1.8}$Si$_{0.2}$O$_{5.3}$, Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$ were identified as the most promising, and so these compositions were analysed in more detail. XRD patterns for these samples are shown in figure 4, with their cell parameters and those for undoped Ba$_2$In$_2$O$_5$ and singly Si/P doped samples given in table 1. These data show a decrease in cell volume on Zr, La incorporation consistent with the smaller size of Zr$^{4+}$, La$^{3+}$ compared to In$^{3+}$, Ba$^{2+}$ respectively, with the larger difference between the sizes of La$^{3+}$ and Ba$^{2+}$ leading to a greater decrease in cell volume for La doping.

The conductivities of these co-doped samples are shown in figure 5, and a comparison with those of singly doped Ba$_2$In$_{1.7}$P$_{0.3}$O$_{5.3}$ and Ba$_2$In$_{1.8}$Si$_{0.2}$O$_{5.1}$ shown in table 2. As can be seen from these data, the Si doped samples show the highest conductivities, and Zr co-doping appears to show a lower decrease than for La co-doping. This may reflect the larger cell size for the former Zr doped samples. Overall the conductivities show high values, with a significant enhancement below ≈650 °C in wet atmospheres due to proton conductivity. For Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$ a conductivity of 2.7 x 10$^{-3}$ Scm$^{-1}$ at 500 °C was observed in wet N$_2$, which represents a promising value for technological applications.
Measurements of the CO\textsubscript{2} stability of these four co-doped samples showed no evidence by X-ray diffraction for any BaCO\textsubscript{3} formation on heating in CO\textsubscript{2} at 600 °C, where small BaCO\textsubscript{3} impurities were seen for the singly doped samples. Further studies were performed at higher temperatures up to 800 °C. These studies showed the presence of small BaCO\textsubscript{3} impurities for the Zr/P and La/P co-doped systems at 800 °C, while for the Si/Zr and La/Si co-doped materials, no BaCO\textsubscript{3} was visible, highlighting the excellent CO\textsubscript{2} stability of these latter phases (figure 6). The TGA studies in a 1:1 CO\textsubscript{2}:N\textsubscript{2} atmosphere also showed no significant mass change for the Zr/Si and La/Si co-doped systems, although expanding the scale of the data showed that there was a small mass increase for the Zr/P and La/P co-doped systems above 600 °C (figure 7). Overall the results therefore showed improved CO\textsubscript{2} stability for these co-doped systems, especially for the La/Si and Zr/Si co-doped samples.

The origin of the enhancement in CO\textsubscript{2} stability can be attributed to two factors, as illustrated by work by Yi \textit{et al.} on the stability of Ba(Fe,Co, Nb)O\textsubscript{3-x} perovskite cathode materials [28]. In this work the authors showed that improved stability of the perovskite towards CO\textsubscript{2} could be attributed to reduced oxide ion vacancy levels and increased acidity of the perovskite. In the present study, the incorporation of phosphate, silicate, zirconium and lanthanum will increase the oxygen content, and hence reduce the number of oxide ion vacancies. This reduction in oxide ion vacancies may be partly responsible, however, for the observed reduction in conductivity on co-doping with Si/P and La/Zr. All the dopants are also likely to increase the acidity of the system, although it might be expected from this that the phosphate doped system would be more stable due to both the
higher acidity and higher oxygen content. In contrast, the Si doped systems proved the most stable, and the origin of this improved stability requires further investigation.

4. Conclusions

The results show that phosphate or silicate doping into Ba$_2$In$_2$O$_5$ leads to an improvement in the stability towards CO$_2$. Furthermore, co-doping with La or Zr leads to even greater stability, with the composition Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$ showing particularly promise, due to the high conductivity and high stability.

Acknowledgements

We would like to express thanks to the University of Birmingham for funding (EPS international studentship for JFS).

The Bruker D8 diffractometer, and Netzsch thermal analyser used in this research were obtained through the Science City Advanced Materials project: Creating and Characterising Next generation Advanced Materials project, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

The funding agencies had no involvement in the collection, analysis and interpretation of data; in the writing of the report; and in the decision to submit the paper for publication.

References


26. www.norecs.com


Figure Captions

Fig. 1 Fitted impedance data for Ba$_{1.6}$La$_{0.4}$In$_{1.8}$Si$_{0.2}$O$_{5.3}$ at 310 °C: dry N$_2$ (square) and wet N$_2$ (cross).

Fig. 2 XRD patterns for (a) Ba$_2$In$_{1.8}$Si$_{0.2}$O$_{5.1}$, (b) Ba$_2$In$_{1.7}$P$_{0.3}$O$_{5.3}$, (c) Ba$_2$In$_2$O$_5$ and (d) Ba$_2$Ce$_{0.9}$Y$_{0.1}$O$_{2.95}$ after heating in CO$_2$ at 600 °C for 12h (main BaCO$_3$ impurity peaks marked *).

Fig. 3 TG profiles (10 °C min$^{-1}$ to 1000 °C in 1:1 CO$_2$ and N$_2$ mixture) for (a) Ba$_2$In$_2$O$_5$, (b) Ba$_2$Ce$_{0.9}$Y$_{0.1}$O$_{2.95}$, (c) Ba$_2$In$_{1.7}$P$_{0.3}$O$_{5.3}$ and (d) Ba$_2$In$_{1.8}$Si$_{0.2}$O$_{5.1}$.

Fig. 4 XRD patterns of (a) Ba$_{1.7}$La$_{0.3}$In$_{1.7}$P$_{0.3}$O$_{5.45}$, (b) Ba$_2$In$_{1.5}$Zr$_{0.2}$P$_{0.3}$O$_{5.4}$, (c) Ba$_{1.6}$La$_{0.4}$In$_{1.8}$Si$_{0.2}$O$_{5.3}$ and (d) Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$ showing single phase cubic perovskite systems.

Fig. 5(a) Conductivity data for Ba$_{1.7}$La$_{0.3}$In$_{1.7}$P$_{0.3}$O$_{5.45}$ in dry N$_2$ (filled square) and wet N$_2$ (open square) and for Ba$_2$In$_{1.5}$Zr$_{0.2}$P$_{0.3}$O$_{5.4}$ in dry N$_2$ (filled circle) and wet N$_2$ (open circle).

Fig. 5(b) Conductivity data for Ba$_{1.6}$La$_{0.4}$In$_{1.8}$Si$_{0.2}$O$_{5.3}$ in dry N$_2$ (filled square) and wet N$_2$ (open square) and for Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$ in dry N$_2$ (filled circle) and wet N$_2$ (open circle).

Fig. 6 XRD patterns for (a) Ba$_{1.7}$La$_{0.3}$In$_{1.7}$P$_{0.3}$O$_{5.45}$, (b) Ba$_2$In$_{1.5}$Zr$_{0.2}$P$_{0.3}$O$_{5.4}$, (c) Ba$_{1.6}$La$_{0.4}$In$_{1.8}$Si$_{0.2}$O$_{5.3}$ and (d) Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$ after heating in CO$_2$ at 800 °C for 12h (main BaCO$_3$ impurity peaks marked *).

Fig. 7 TG profiles (10 °C min$^{-1}$ to 1000 °C in 1:1 CO$_2$ and N$_2$ mixture) for (a) Ba$_{1.7}$La$_{0.3}$In$_{1.7}$P$_{0.3}$O$_{5.45}$, (b) Ba$_2$In$_{1.5}$Zr$_{0.2}$P$_{0.3}$O$_{5.4}$, (c) Ba$_2$In$_{1.6}$Zr$_{0.2}$Si$_{0.2}$O$_{5.2}$
Ba$_{1.6}$La$_{0.4}$In$_{1.8}$Si$_{0.2}$O$_{5.3}$ and (e) Ba$_2$In$_2$O$_5$.(inset: expanded scale for (a)-(d))
Table 1a Cell parameter data for P doped Ba$_2$In$_2$O$_5$ (data for the undoped and singly doped samples from ref [22])

<table>
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<tr>
<th>Sample (nominal composition)</th>
<th>Unit cell parameters (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
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<tr>
<td></td>
<td>a</td>
<td>b</td>
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<tr>
<td>Ba$_2$In$_2$O$_5$</td>
<td>6.089(2)</td>
<td>16.736(8)</td>
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<tr>
<td>Ba$<em>2$In$</em>{1.7}$P$_{0.3}$O$_5.3$</td>
<td>4.208(1)</td>
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<td>Ba$<em>2$In$</em>{1.5}$Zr$<em>{0.2}$P$</em>{0.3}$O$_5.4$</td>
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Table 1b Cell parameter data for Si doped Ba$_2$In$_2$O$_5$ (data for the undoped and singly doped samples from ref [23])

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<td>4.200(1)</td>
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Table 2a. Conductivity data for P doped series (conductivity enhancement in wet atmospheres was only observed below \( \approx 650 \, ^\circ C \))

<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>
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<td>Wet</td>
<td>Dry</td>
<td></td>
</tr>
<tr>
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<td>( 1.9 \times 10^{-3} )</td>
<td>( 5.0 \times 10^{-4} )</td>
<td>( 1.2 \times 10^{2} )</td>
</tr>
<tr>
<td>( \text{Ba}<em>{1.7}\text{La}</em>{0.3}\text{In}<em>{1.7}\text{P}</em>{0.3}\text{O}_{5.45} )</td>
<td>( 4.4 \times 10^{-4} )</td>
<td>( 1.8 \times 10^{-4} )</td>
<td>( 6.0 \times 10^{3} )</td>
</tr>
<tr>
<td>( \text{Ba}<em>2\text{In}</em>{1.5}\text{Zr}<em>{0.2}\text{P}</em>{0.3}\text{O}_{5.4} )</td>
<td>( 9.7 \times 10^{-4} )</td>
<td>( 4.0 \times 10^{-4} )</td>
<td>( 5.3 \times 10^{3} )</td>
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</table>

Table 2b. Conductivity data for Si doped series (conductivity enhancement in wet atmospheres was only observed below \( \approx 650 \, ^\circ C \))

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<th>Sample (nominal composition)</th>
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<th>800 °C</th>
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<td>Dry</td>
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<td>( 7.7 \times 10^{-4} )</td>
<td>( 5.3 \times 10^{-4} )</td>
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<td>( 9.9 \times 10^{-4} )</td>
<td>( 2.3 \times 10^{2} )</td>
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</tbody>
</table>
Fig. 3
Fig 4

![Graph showing intensity vs. 2θ for different samples labeled (a), (b), (c), and (d).]
Fig 5(a)

Fig 5 (b)
Fig 6