

## Enhanced CO<sub>2</sub> stability of oxyanion doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> systems co-doped with La, Zr

Shin, Jaegil; Slater, Peter

DOI:

[10.1016/j.jpowsour.2011.06.03](https://doi.org/10.1016/j.jpowsour.2011.06.03)

[10.1016/j.jpowsour.2011.06.003](https://doi.org/10.1016/j.jpowsour.2011.06.003)

*Citation for published version (Harvard):*

Shin, J & Slater, P 2011, 'Enhanced CO<sub>2</sub> stability of oxyanion doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> systems co-doped with La, Zr', *Journal of Power Sources*, vol. 196, no. 20, pp. 8539-8543. <https://doi.org/10.1016/j.jpowsour.2011.06.03>, <https://doi.org/10.1016/j.jpowsour.2011.06.003>

[Link to publication on Research at Birmingham portal](#)

### General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

### Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.

Enhanced CO<sub>2</sub> stability of oxyanion doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> systems co-doped with La, Zr

J.F. Shin, P.R. Slater\*

School of Chemistry, University of Birmingham, Birmingham. B15 2TT. UK

\*Correspondence to

Dr. P.R. Slater  
School of Chemistry  
University of Birmingham  
Birmingham B15 2TT  
UK

[p.r.slater@bham.ac.uk](mailto:p.r.slater@bham.ac.uk)

Tel. +44 (0)1214148906

Fax +44 (0)1214144403

## 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<sub>2</sub>. Recently we have reported enhanced oxide ion/proton conductivity in oxyanion (silicate, phosphate) doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>, and in this paper we extend this work to examine the stability at elevated temperatures towards CO<sub>2</sub>. The results show improved CO<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub> and BaCeO<sub>3</sub>, suitably doped. However, a major problem with such proton conducting perovskites is the issue of stability towards CO<sub>2</sub>. Thus, although doped BaCeO<sub>3</sub> shows excellent proton conductivity, it suffers from a distinct instability towards CO<sub>2</sub> at typical fuel cell operating temperatures (600-800 °C), leading to the formation of BaCO<sub>3</sub>. Doped BaZrO<sub>3</sub> shows much greater stability, but has been shown to suffer from poor grain boundary conductivity leading typically to significantly lower total conductivities than BaCeO<sub>3</sub> based systems. However, it should be noted that recently there have been significant improvements in the performance of BaZrO<sub>3</sub> based electrolytes through appropriate synthesis/processing to ensure the grain size is large and the samples are well sintered [5, 6].

Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>In<sub>2</sub>O<sub>5</sub> show significant proton conductivity at intermediate temperatures in a wet atmosphere. In this earlier work on Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>, 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  $\text{Ba}_2\text{In}_2\text{O}_5$  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  $\text{CO}_2$  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  $\text{CO}_2$  stability.

## 2. Experimental

High purity  $\text{BaCO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{SiO}_2$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  were used to prepare  $\text{Ba}_2\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.1}$ ,  $\text{Ba}_2\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.3}$  and La, Zr co-doped samples. In order to overcome Ba loss at elevated temperatures, a 3% excess of  $\text{BaCO}_3$  was employed. Without this small Ba excess, low levels of Ba deficient impurity phases, such as  $\text{BaIn}_2\text{O}_4$  and  $\text{Ba}_4\text{In}_6\text{O}_{13}$ , 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  $\text{Cu K}\alpha_1$  radiation).

In order to determine the CO<sub>2</sub> 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<sub>2</sub> 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<sup>-1</sup> to 1000 °C in 1:1 CO<sub>2</sub> and N<sub>2</sub> mixture to determine at what temperature CO<sub>2</sub> pick up occurred.

For the conductivity measurements a Norecs Probostat<sup>TM</sup> 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<sup>3</sup> kHz, with an applied voltage of 100 mV. Since Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> displays a small p-type contribution to the conductivity in oxidising conditions, measurements were made in dry N<sub>2</sub> to eliminate this contribution. In addition, measurements were made in wet N<sub>2</sub> (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<sup>-1</sup>) 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  $\text{Ba}_2\text{In}_2\text{O}_5$  to cubic for  $\text{Ba}_2\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.1}$ , and  $\text{Ba}_2\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.3}$  [21-23]. The stability of these systems towards  $\text{CO}_2$  was examined by heating in  $\text{CO}_2$  at different temperatures between 600 and 800 °C, and through TGA studies in a 1:1  $\text{N}_2:\text{CO}_2$  atmosphere between 10 and 1000 °C. The results showed that on heating to 600 °C,  $\text{BaCO}_3$  impurities were visible for all samples (figure 2). However, compared to undoped  $\text{Ba}_2\text{In}_2\text{O}_5$ , the Si, P doped samples showed significantly lower sensitivity towards  $\text{CO}_2$ , with much smaller  $\text{BaCO}_3$  impurities observed at this temperature. The results were also compared to Y doped  $\text{BaCeO}_3$  which is known to be very sensitive towards  $\text{CO}_2$ . As for undoped  $\text{Ba}_2\text{In}_2\text{O}_5$ , this phase showed the presence of large  $\text{BaCO}_3$  impurities when heated in  $\text{CO}_2$  at 600 °C. The TGA results provided further indication of the relative stabilities of the samples towards  $\text{CO}_2$  (figure 3). For undoped  $\text{Ba}_2\text{In}_2\text{O}_5$  a clear increase in mass, consistent with  $\text{CO}_2$  pick up and formation of  $\text{BaCO}_3$ , was observed at 600 °C. Similarly, for  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  a significant increase in mass was observed above 500 °C. In contrast, for phosphate and silicate doped  $\text{Ba}_2\text{In}_2\text{O}_5$ , 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  $\text{Ba}_2\text{In}_2\text{O}_5$  towards  $\text{CO}_2$  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  $\text{CO}_2$  stability and conductivity. Single phase

$\text{Ba}_{2-x}\text{La}_x\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.3+x/2}$ ,  $\text{Ba}_{2-x}\text{La}_x\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.1+x/2}$  ( $0 \leq x \leq 0.4$ ) and  $\text{Ba}_2\text{In}_{1.7-x}\text{Zr}_x\text{P}_{0.3}\text{O}_{5.3+x/2}$ ,  $\text{Ba}_2\text{In}_{1.8-x}\text{Zr}_x\text{Si}_{0.2}\text{O}_{5.1+x/2}$  ( $0 \leq x \leq 0.4$ ) were prepared, and the  $\text{CO}_2$  stability and conductivities were examined. The preliminary studies showed that as the La, Zr content increased, so the stability towards  $\text{CO}_2$  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  $\text{CO}_2$  stability but detrimental in terms of the conductivity. In terms of a balance between high conductivity and  $\text{CO}_2$  stability, the compositions  $\text{Ba}_{1.7}\text{La}_{0.3}\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.45}$ ,  $\text{Ba}_2\text{In}_{1.5}\text{Zr}_{0.2}\text{P}_{0.3}\text{O}_{5.4}$ ,  $\text{Ba}_{1.6}\text{La}_{0.4}\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.3}$ ,  $\text{Ba}_2\text{In}_{1.6}\text{Zr}_{0.2}\text{Si}_{0.2}\text{O}_{5.2}$  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  $\text{Ba}_2\text{In}_2\text{O}_5$  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  $\text{Zr}^{4+}$ ,  $\text{La}^{3+}$  compared to  $\text{In}^{3+}$ ,  $\text{Ba}^{2+}$  respectively, with the larger difference between the sizes of  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  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  $\text{Ba}_2\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.3}$  and  $\text{Ba}_2\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.1}$  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  $\approx 650$  °C in wet atmospheres due to proton conductivity. For  $\text{Ba}_2\text{In}_{1.6}\text{Zr}_{0.2}\text{Si}_{0.2}\text{O}_{5.2}$  a conductivity of  $2.7 \times 10^{-3} \text{ Scm}^{-1}$  at 500 °C was observed in wet  $\text{N}_2$ , which represents a promising value for technological applications.



Measurements of the CO<sub>2</sub> stability of these four co-doped samples showed no evidence by X-ray diffraction for any BaCO<sub>3</sub> formation on heating in CO<sub>2</sub> at 600 °C, where small BaCO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> was visible, highlighting the excellent CO<sub>2</sub> stability of these latter phases (figure 6). The TGA studies in a 1:1 CO<sub>2</sub>:N<sub>2</sub> 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<sub>2</sub> stability for these co-doped systems, especially for the La/Si and Zr/Si co-doped samples.

The origin of the enhancement in CO<sub>2</sub> stability can be attributed to two factors, as illustrated by work by Yi *et al.* on the stability of Ba(Fe,Co, Nb)O<sub>3-x</sub> perovskite cathode materials [28]. In this work the authors showed that improved stability of the perovskite towards CO<sub>2</sub> 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  $\text{Ba}_2\text{In}_2\text{O}_5$  leads to an improvement in the stability towards  $\text{CO}_2$ . Furthermore, co-doping with La or Zr leads to even greater stability, with the composition  $\text{Ba}_2\text{In}_{1.6}\text{Zr}_{0.2}\text{Si}_{0.2}\text{O}_{5.2}$  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**

1. T. Norby, Y. Larring, *Current Opinion in Solid State and Materials Science* 2 (1997) 593.

2. K.D. Kreuer, *Annu. Rev. Mater. Res.*, 33 (2003) 333.
3. L. Malavasi, C.A.J. Fisher, M.S. Islam, *J. Mater. Chem.* 39 (2010) 4370.
4. A. Orera, P.R. Slater, *Chem. Mater.* 22 (2010) 675.
5. P. Babilo, S.M. Haile, *J. Am. Ceram. Soc.* 88 (2005) 2362.
6. S.W. Tao, J.T.S. Irvine, *J. Solid State Chem.* 180 (2007) 3493.
7. J.B. Goodenough, J.E. Ruizdiaz, Y.S. Zhen, *Solid State Ionics* 44 (1990) 21.
8. S.A. Speakman, J.W. Richardson, B.J. Mitchell, S.T. Misture, *Solid State Ionics* 149 (2002) 247.
9. T. Schober, *Solid State Ionics* 109 (1998) 1.
10. V. Jayaraman, A. Magrez, M. Caldes, O. Joubert, M. Ganne, Y. Piffard, L. Brohan, *Solid State Ionics* 170 (2004) 17.
11. A. Rolle, R.N. Vannier, N.V. Giridharan, F. Abraham, *Solid State Ionics* 176 (2005) 2095.
12. T. Schrober, J. Friedrich, *Solid State Ionics* 113 (1998) 369.
13. G.B. Zhang, D.M. Smith, *Solid State Ionics* 82 (1995) 153.
14. E. Quarez, S. Noirault, M.T. Caldes, O. Joubert, *J. Power Sources* 195 (2010) 1136.
15. M. Karlsson, A. Matic, C.S. Knee, I. Ahmed, S.G. Eriksson, L. Borjesson, *Chem. Mater.* 20 (2008) 3480.
16. F. Giannici, A. Longo, A. Balerna, K.D. Kreuer, A. Martorana, *Chem. Mater.* 19 (2010) 5714.
17. S. Noirault, S. Celerier, O. Joubert, M.T. Caldes, Y. Piffard, *Solid State Ionics* 178 (2007) 1353.

18. I. Ahmed, S.G. Eriksson, E. Ahlberg, C.S. Knee, P. Berastegui, L.G. Johansson, H. Rundlof, M. Karlsson, A. Matic, L. Borjesson, D. Engberg, *Solid State Ionics* 177 (2006) 1395.
19. K. Kakinuma, A. Tomita, H. Yamamura, T. Atake, *J. Mater. Sci.* 41 (2006) 6435.
20. C.A.J. Fisher, M.S. Islam, *Solid State Ionics* 118 (1999) 355.
21. J.F. Shin, L. Hussey, A. Orera, P.R. Slater, *Chem. Commun.* 46 (2010) 4613.
22. J.F. Shin, A. Orera, D.C. Apperley, P.R. Slater, *J. Mater. Chem.* 21 (2011) 874.
23. J.F. Shin, D.C. Apperley, P.R. Slater, *Chem. Mater.* 22 (2010) 5945.
24. T. Omata, T. Fuke, S. Otsuka-Yao-Matsuo, *Solid State Ionics* 177 (2006) 2447.
25. A.M. Abakumov, M.D. Rossell, O.Y. Gutnikova, O.A. Drozhzhin, L.S. Leonova, Y.A. Dobrovolsky, S.Y. Istomin, G. Van Tendeloo, E.V. Antipov, *Chem. Mater.* 20 (2008) 4457
26. [www.norecs.com](http://www.norecs.com)
27. R. Haugrud, Y. Larring, T. Norby; *Solid State Ionics* 176 (2005) 2957.
28. J.X. Yi, M. Schroeder, T. Weirich, J. Maier, *Chem. Mater.* 22 (2010) 6246.

## Figure Captions

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

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

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

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

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

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

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

Fig. 7 TG profiles ( $10\text{ °C min}^{-1}$  to 1000 °C in 1:1  $\text{CO}_2$  and  $\text{N}_2$  mixture) for (a)  $\text{Ba}_{1.7}\text{La}_{0.3}\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.45}$ , (b)  $\text{Ba}_2\text{In}_{1.5}\text{Zr}_{0.2}\text{P}_{0.3}\text{O}_{5.4}$ , (c)  $\text{Ba}_2\text{In}_{1.6}\text{Zr}_{0.2}\text{Si}_{0.2}\text{O}_{5.2}$  (d)

$\text{Ba}_{1.6}\text{La}_{0.4}\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.3}$  and (e)  $\text{Ba}_2\text{In}_2\text{O}_5$ .(inset: expanded scale for (a)-(d))

Table 1a Cell parameter data for P doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> (data for the undoped and singly doped samples from ref [22])

Sample (nominal composition)	Unit cell parameters (Å)			Unit cell volume (Å <sup>3</sup> )
	a	b	c	
Ba <sub>2</sub> In <sub>2</sub> O <sub>5</sub>	6.089(2)	16.736(8)	5.963(2)	607.6(2)
Ba <sub>2</sub> In <sub>1.7</sub> P <sub>0.3</sub> O <sub>5.3</sub>	4.208(1)	-	-	74.5(1)
Ba <sub>1.7</sub> La <sub>0.3</sub> In <sub>1.7</sub> P <sub>0.3</sub> O <sub>5.45</sub>	4.183(1)	-	-	73.2(1)
Ba <sub>2</sub> In <sub>1.5</sub> Zr <sub>0.2</sub> P <sub>0.3</sub> O <sub>5.4</sub>	4.199(1)	-	-	74.0(1)

Table 1b Cell parameter data for Si doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> (data for the undoped and singly doped samples from ref [23])

Sample (nominal composition)	Unit cell parameters (Å)			Unit cell volume (Å <sup>3</sup> )
	a	b	c	
Ba <sub>2</sub> In <sub>2</sub> O <sub>5</sub>	6.089(2)	16.736(8)	5.963(2)	607.6(2)
Ba <sub>2</sub> In <sub>1.8</sub> Si <sub>0.2</sub> O <sub>5.1</sub>	4.209(1)			74.6(1)
Ba <sub>1.6</sub> La <sub>0.4</sub> In <sub>1.8</sub> Si <sub>0.2</sub> O <sub>5.3</sub>	4.167(1)			72.4(1)
Ba <sub>2</sub> In <sub>1.6</sub> Zr <sub>0.2</sub> Si <sub>0.2</sub> O <sub>5.2</sub>	4.200(1)			74.1(1)

Table 2a. Conductivity data for P doped series (conductivity enhancement in wet atmospheres was only observed below  $\approx 650$  °C)

Sample (nominal composition)	Conductivity ( $S\text{ cm}^{-1}$ )		
	500 °C		800 °C
	Wet	Dry	
$\text{Ba}_2\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.3}$	$1.9 \times 10^{-3}$	$5.0 \times 10^{-4}$	$1.2 \times 10^{-2}$
$\text{Ba}_{1.7}\text{La}_{0.3}\text{In}_{1.7}\text{P}_{0.3}\text{O}_{5.45}$	$4.4 \times 10^{-4}$	$1.8 \times 10^{-4}$	$6.0 \times 10^{-3}$
$\text{Ba}_2\text{In}_{1.5}\text{Zr}_{0.2}\text{P}_{0.3}\text{O}_{5.4}$	$9.7 \times 10^{-4}$	$4.0 \times 10^{-4}$	$5.3 \times 10^{-3}$

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

Sample (nominal composition)	Conductivity ( $S\text{ cm}^{-1}$ )		
	500 °C		800 °C
	Wet	Dry	
$\text{Ba}_2\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.1}$	$4.5 \times 10^{-3}$	$1.7 \times 10^{-3}$	$4.3 \times 10^{-2}$
$\text{Ba}_{1.6}\text{La}_{0.4}\text{In}_{1.8}\text{Si}_{0.2}\text{O}_{5.3}$	$7.7 \times 10^{-4}$	$5.3 \times 10^{-4}$	$1.8 \times 10^{-2}$
$\text{Ba}_2\text{In}_{1.6}\text{Zr}_{0.2}\text{Si}_{0.2}\text{O}_{5.2}$	$2.7 \times 10^{-3}$	$9.9 \times 10^{-4}$	$2.3 \times 10^{-2}$



Fig 1

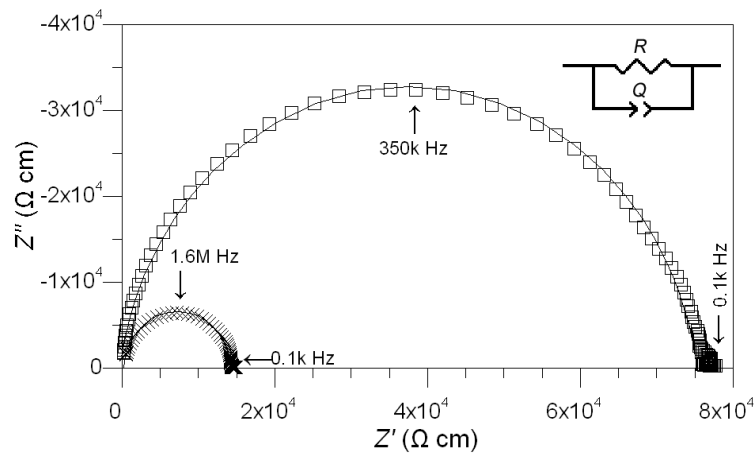


Fig 2

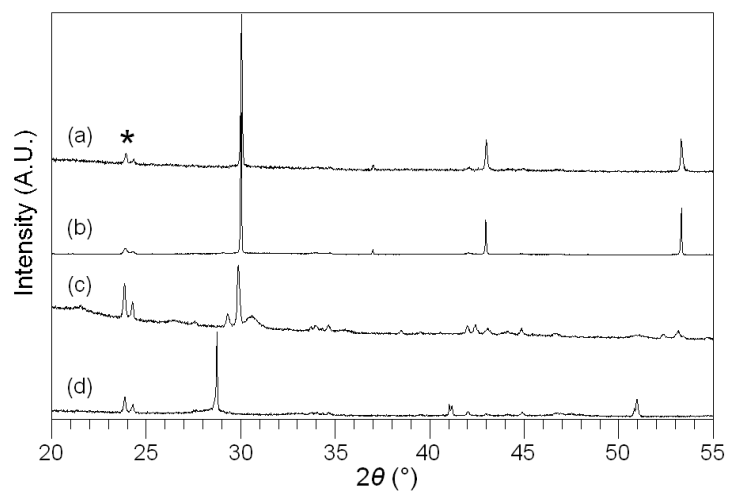


Fig. 3

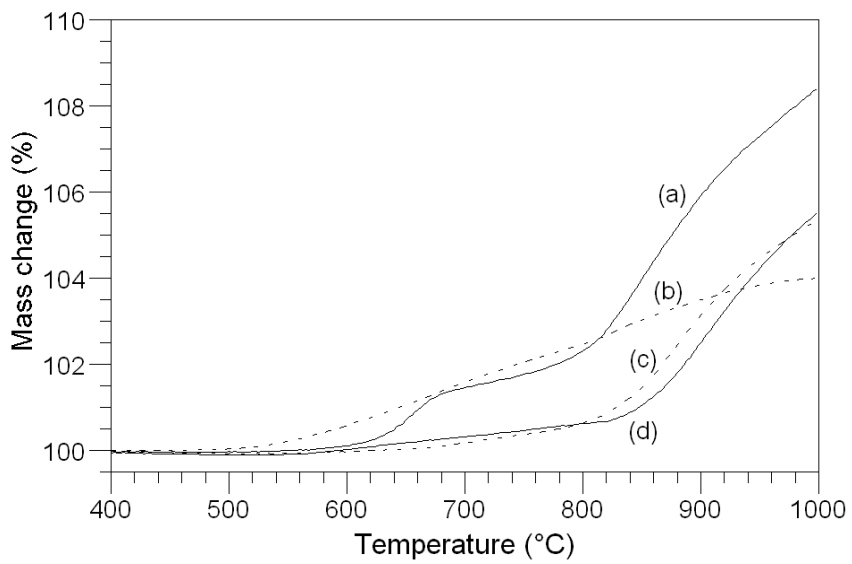


Fig 4

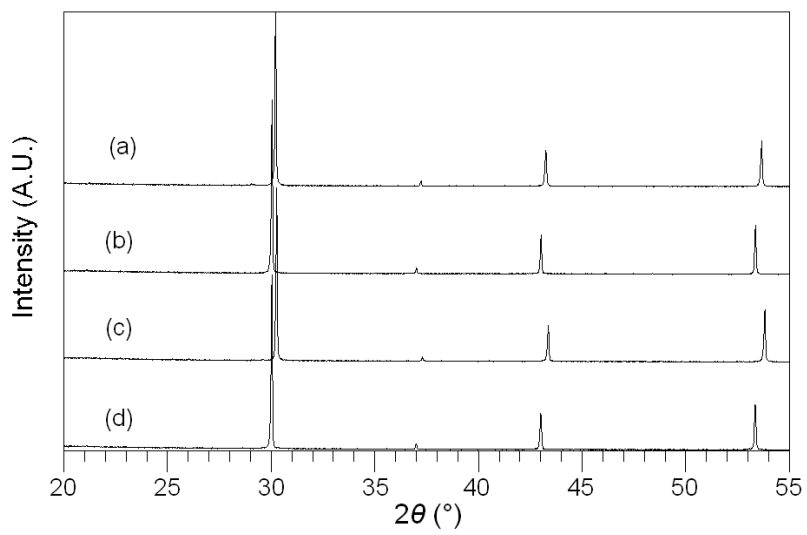


Fig 5(a)

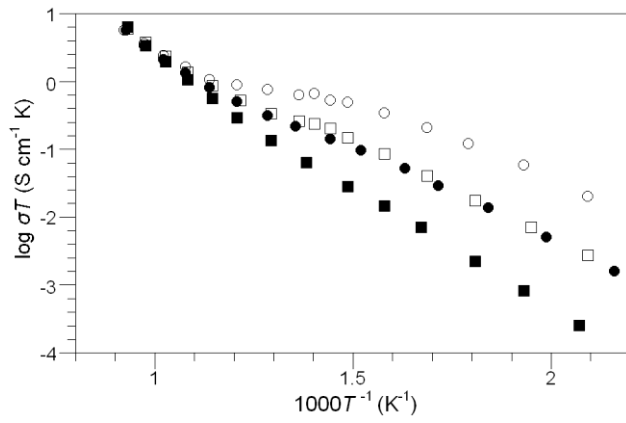


Fig 5 (b)

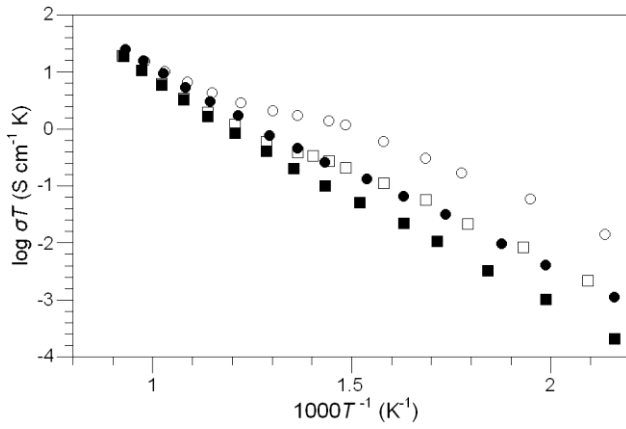


Fig 6

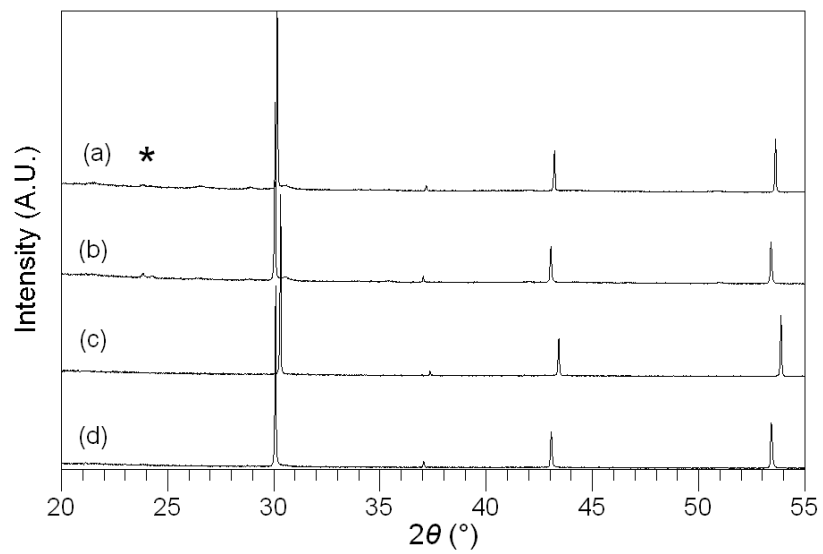


Fig 7

