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$La_{1-x}Ba_{1+x}GaO_{4-x/2}$: a novel high temperature proton conductor

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In this communication we demonstrate high temperature proton conduction in the phase $La_{1-x}Ba_{1+x}GaO_{4-x/2}$, with conductivities significantly higher than reported for other phases containing tetrahedral ions, such as doped $LaPO_4$.

Materials showing proton conduction at elevated temperatures are attracting considerable interest for possible use in technological devices such as solid oxide fuel cells (SOFCs), hydrogen separation membranes. The vast majority of the studies on high temperature (>400 °C) proton conductors has focused on materials with the perovskite (ABO_3) structure. In these materials the B cations are octahedral, and the introduction of acceptor dopants results in the incorporation of oxygen vacancies. Proton conduction then occurs due to the incorporation of water into the vacancies according to the equation

$$H_2O + V_O^{\gg} + O_O \leftrightarrow 2OH^{>}$$

More recently, high temperature proton conduction has been reported in acceptor doped $LaPO_4$.[1–3] In this system, we have tetrahedral PO_4^{3-} and the acceptor doping results in oxygen vacancies, which can then incorporate water as before. Although these systems are very interesting the conductivities are comparatively low when compared to the perovskite systems.

As part of our research in the area of SOFCs, we have been investigating ionic conduction in gallate based systems. Our research in this area has been driven by the large interest in the perovskite $LaGaO_3$ doped with Sr and Mg.[4,5] This system shows excellent ionic conductivity (in this case, oxide ion) and is attracting considerable interest as an electrolyte material for SOFCs. Investigations into the conductivity of the related K_2NiF_4 type system, $LaSrGaO_4$, have shown, however, that the conductivity is low in this case. If Sr is replaced by Ba, we have the phase $LaBaGaO_4$, the structure of which has been reported by Rueter and Müller-Buschbaum.[6] The structure itself is similar to that of β-K_2SO_4, possessing an orthorhombic cell with tetrahedral coordination for Ga (Fig. 1).

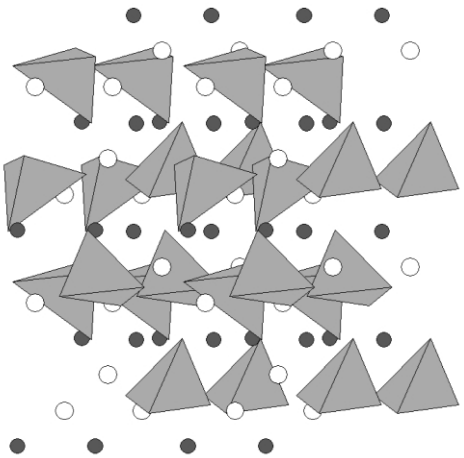

Fig. 1 The structure of $LaBaGaO_4$ (dark spheres = La, light spheres = Ba, tetrahedra = GaO_4).

The conductivity of this phase has not been previously examined, and in this communication we report that by varying the La/Ba ratio to incorporate oxygen vacancies, high conductivities are obtained. Measurements in different atmospheres indicate a significant proton conductivity in this system, with values significantly higher than reported for other phases containing tetrahedral ions, such as doped $LaPO_4$.

Samples, $La_{1-x}Ba_{1+x}GaO_{4-x/2}$, were prepared from high purity La_2O_3, $BaCO_3$ and Ga_2O_3. The powders were intimately mixed in the correct ratios and heated to 1100 °C for 12 h, reground and then reheated to 1200 °C for a further 12 h. Phase purity was examined using X-ray powder diffraction (Seifert 3003TT diffractometer). Pellets for conductivity measurements were prepared by ball milling the powder for 30 minutes, and then pressing at 6000 kg m^{-2} and heating at 1250 °C for 12 h. Both sides of the pellet were coated with Pt paste and then heated to 850 °C to ensure bonding to the pellet. Conductivity measurements were made using AC impedance spectroscopy (Hewlett Packard 4192A impedance analyser). Measurements were made in a range of atmospheres (wet atmospheres were obtained by bubbling the gas through water or D_2O).

The La/Ba ratio was varied to investigate the possibility of introducing oxygen excess and oxygen vacancies. Attempts to increase the La content above 1 and so introduce oxygen excess, *i.e.* $La_{1+x}Ba_{1-x}GaO_{4+x/2}$, were unsuccessful, with impurities being observed even for small values of x. In contrast, lowering the La content to give oxygen vacancies was found to be successful, with X-ray diffraction indicating that it was possible to prepare single phases samples of $La_{1-x}Ba_{1+x}GaO_{4-x/2}$ for $0 \leq x \leq 0.2$. For samples with $x > 0.2$ small impurities were observed. For the pure samples ($0 \leq x \leq 0.2$), the cell parameters showed an increase with increasing Ba content (x = 0, a = 10.016(5), b = 7.267(4), c = 5.911(4) Å; x = 0.2, a = 10.086(5), b = 7.349(4), c = 5.944(4) Å), which is consistent with the larger size of Ba^{2+} compared to La^{3+}, and supports the successful preparation of these phases.

Initially conductivity measurements were performed in air. These preliminary results showed that the conductivity of the undoped phase $LaBaGaO_4$ was comparatively low, while the doped phases, $x > 0$, showed significantly higher conductivities (Fig. 2), again consistent with the successful incorporation of extra Ba to give oxygen vacancies.

Measurements were then performed in a range of atmospheres, dry and wet N_2, wet H_2/Ar (5%/95%), dry and wet O_2. The data for $LaBaGaO_4$ is shown in Fig. 3.

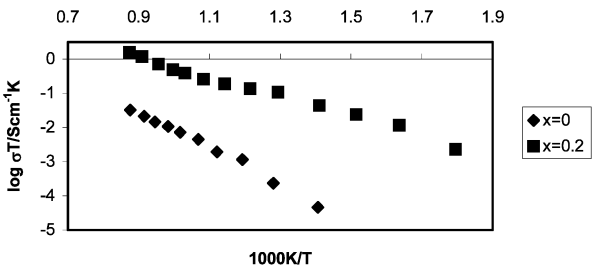

Fig. 2 Conductivity data for $La_{1-x}Ba_{1+x}GaO_{4-x/2}$ in air.

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A small reduction in the conductivity is observed in changing from dry O_2 to dry N_2, which suggests the presence of electronic (p-type) conduction. In wet N_2 and H_2/Ar, there is an increase in conductivity compared to the dry N_2 data, suggesting some proton conduction. Overall, however, the conductivities are rather low, which is consistent with the fact that this phase is nominally fully stoichiometric.

For the samples with $x > 0$, the conductivity showed a significant increase. The data for different atmospheres for the sample, $La_{0.8}Ba_{1.2}GaO_{3.9}$ are shown in Figs. 4 and 5.

The data clearly shows a significant increase in the conductivities in wet atmospheres especially at temperatures below 650 °C. Although the differences are most clearly seen at these lower temperatures, the conductivities in wet atmospheres are always higher than for dry atmospheres over the range of temperatures studied (200–800 °C).

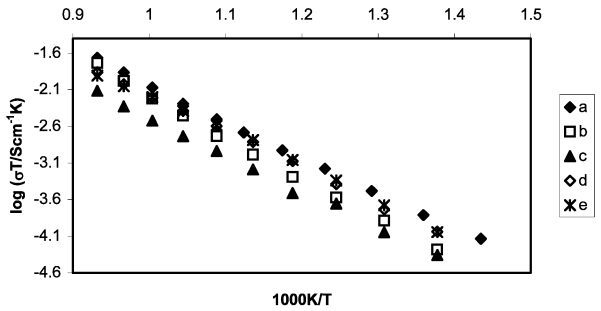

Fig. 3 Conductivity data for $LaBaGaO_4$ in (a) O_2/H_2O, (b) dry O_2 (c) dry N_2, (d) N_2/H_2O, (e) H_2/Ar (5%/95%)/H_2O.

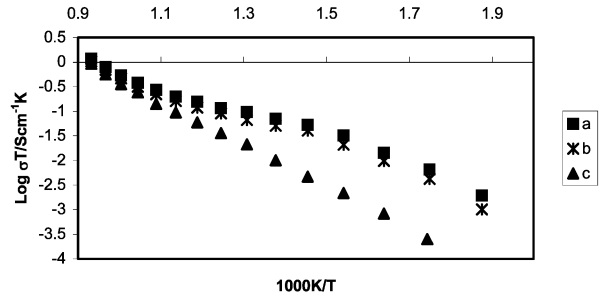

Fig. 4 Conductivity data for $La_{0.8}Ba_{1.2}GaO_{3.9}$ in (a) O_2/H_2O, (b) O_2/D_2O, (c) dry O_2.

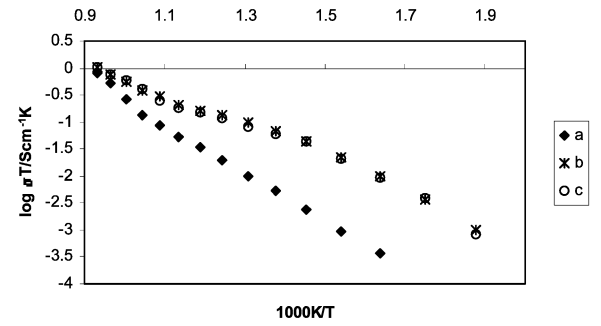

Fig. 5 Conductivity data for $La_{0.8}Ba_{1.2}GaO_{3.9}$ in (a) dry N_2 (b) N_2/H_2O (c) H_2/Ar (5%/95%)/H_2O.

As for the sample $LaBaGaO_4$, the conductivity in dry N_2 is slightly lower than that in dry O_2, which is consistent with some electronic (p-type conduction). In wet atmospheres, as the proton conduction becomes dominant, the conductivities in O_2 and N_2 become comparable.

In order to provide further evidence to support the presence of proton conduction, measurements were performed for $La_{0.8}Ba_{1.2}GaO_{3.9}$ in O_2/D_2O. The results show a clear isotope effect (Fig. 4), with an increase in resistance compared to the data for O_2/H_2O. At temperatures < 600 °C, the resistance in O_2/D_2O is approximately 1.4 times that in O_2/H_2O, in agreement with that expected. At higher temperatures the value is lower (*e.g.* 1.1 times at 800 °C), suggesting additional contributions (electronic, oxide ion) to the conductivity.

The results clearly demonstrate that the system $La_{0.8}Ba_{1.2}GaO_{3.9}$ shows significant proton conduction. This system contains tetrahedral Ga, unlike the widely studied perovskite systems, where we have an octahedral ion. Compared with the other high temperature proton conductors containing tetrahedral ions, *e.g.* Sr doped $LaPO_4$, the conductivities are significantly higher. Further work is required to investigate these systems further, including determination of the proton transport number, and further doping studies (*e.g.* varying the rare earth cation) to optimize the conductivity. The nature of the oxygen vacancy defects in these systems also needs investigating. In Sr doped $LaPO_4$ it has been reported that in dry atmospheres, rather than PO_3^- units, the vacancies are present in $P_2O_7^{4-}$ units, which then convert to HPO_4^{2-} in wet atmospheres.[3] Whether similar $Ga_2O_7^{8-}$ units are present in these systems needs further study.

We have also performed preliminary studies of the related systems, $La_{1-x}(Ba/Sr)_{2+x}GaO_{5-x/2}$, also containing tetrahedral Ga. Although the results also suggest proton conduction in these phases, these particular systems appear to be unstable to decomposition in contrast to the $La_{1-x}Ba_{1+x}GaO_{4-x/2}$ samples.

In summary, we have observed high proton conductivity in the novel system $La_{1-x}Ba_{1+x}GaO_{4-x/2}$ containing tetrahedral Ga. This work, along with recent interest in other systems containing tetrahedral ions, *e.g.* apatite oxide ion conductors, olivine-type phases as cathodes for Li batteries, suggest that structures containing tetrahedral ions may be a rich vein of research for the future.

Notes and references

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