

## OXYGEN ION CONDUCTION IN PURE AND YTTRIA-DOPED BARIUM CERATE

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### Summary

Electrical conductivity of pure and  $Y_2O_3$ -doped  $BaCeO_3$  has been measured as a function of oxygen partial pressure (down to  $10^{-14}$  atm) in the temperature range 600 - 1000 °C. In the high partial pressure region the specimens behave as mixed conductors with significant electron-hole conduction. However, below about  $10^{-6}$  atm they become predominantly ionic conductors. The observed conductivity variation has been explained on the basis of annihilation of existing oxygen vacancies with excess oxygen. The ionic transference number has been determined as a function of oxygen partial pressure.

### 1. Introduction

Oxygen ion conductors have received considerable attention due to their use as electrolytes in oxygen sensors, oxygen pumps, fuel cells, etc. To improve the performance of these devices, it is necessary to seek new and better electrolytes. The electrolytes most widely studied for this purpose are those with the fluorite structure. They include calcia and yttria-doped  $ZrO_2$  [1, 2],  $HfO_2$  [3],  $ThO_2$  [4 - 7] and  $CeO_2$  [8, 9]. In recent years mixed oxides having the perovskite structure ( $A^{2+}B^{4+}O_3$ ) have also been reported to exhibit significant oxygen ion conduction [10 - 12].

Usually ionic conduction is not favoured in these oxides because of their close-packed structure. The oxygen ion conduction in perovskites, however, can be strongly enhanced by partially substituting cations of lower valency for the A or B cation so as to introduce oxygen vacancies in the structure [13, 14]. Therefore, a distinct possibility of their application as oxide electrolytes exists. The conductivities of some of the oxygen deficient perovskites such as  $CaTi_{0.7}Al_{0.3}O_{2.85}$ ,  $CaTi_{0.95}Mg_{0.05}O_{2.95}$  are comparable with those of stabilized zirconia [15].

The compounds  $BaZr_{0.9}Bi_{0.1}O_{2.95}$ ,  $BaCe_{0.9}Bi_{0.1}O_{2.95}$  and  $BaTh_{0.95}La_{0.05}O_{2.975}$  have also been reported to show high ionic conductivity [16]. Stephenson and Flanagan [17] have reported evidence of oxygen ion conduc-

tion from e.m.f. measurements in  $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$  (PZT). The electrical conductivity of  $\text{SrCeO}_3$  is also reported to be due to the mobility of oxygen ions [18]. A preliminary investigation by Longo *et al* [18] indicated the possibility of oxygen ion conduction in pure  $\text{BaCeO}_3$ . The dependence of the electrical conductivity of  $\text{Y}_2\text{O}_3$ -doped  $\text{BaCeO}_3$  on dopant concentration has been reported by Virkar *et al* [19]. In this paper, we report a more detailed investigation into the ionic conductivity of pure and yttria-doped  $\text{BaCeO}_3$ .

## 2. Experimental

The samples studied, *i.e.*, pure and  $\text{Y}_2\text{O}_3$ -doped  $\text{BaCeO}_3$  with dopant concentrations of 1, 2 and 10 mole % (expressed as mole percent. of  $\text{CeO}_2$ ), were prepared by a solid state sintering process using 'AnalaR' grade  $\text{BaCO}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CeO}_2$ . Details are given elsewhere [19]. The formation of the compound and the solid solubility were confirmed by X-ray diffraction measurements ( $\text{Cu K}\alpha$  radiation).

For the electrical measurements, platinum paste (Engelhard No 6082) electrodes were applied on the flat surfaces of the specimens. Platinum foils attached to lead wires were pressed against the specimen surfaces by a spring loading arrangement. Alternating current (1 kHz) electrical conductivity measurements were carried out with an LCR bridge. The temperature of the specimen was controlled within  $\pm 1^\circ\text{C}$  and the desired oxygen partial pressure around the sample was generated using an electrochemical oxygen pump, fabricated in this laboratory using a stabilised zirconia tube. The construction is similar to that described by Agarwal *et al* [20]. The oxygen partial pressure of the flowing gas was varied by manual control of the current through the electrochemical oxygen cell. The gas, with controlled oxygen partial pressure, was transferred to the specimen holder through a copper tube. The exact oxygen partial pressure of the gas around the specimen holder was determined using a stabilised zirconia oxygen sensor, sited close to the specimen. During measurement, sufficient time was allowed to establish equilibrium.

## 3. Results and discussion

The effect of the oxygen partial pressure ( $P_{\text{O}_2}$ ) on the conductivity ( $\sigma$ ) of these specimens, measured at fixed temperatures of 600, 700 and 800  $^\circ\text{C}$ , is shown in Fig 1. It will be seen that, in each case, the conductivity drops initially with decreasing  $P_{\text{O}_2}$ . At still lower  $P_{\text{O}_2}$ , however, it becomes independent of partial pressure and continues so to be down to a value of  $10^{-14}$  atm. As expected, the conductivity at each  $P_{\text{O}_2}$  increases with temperature and  $\text{Y}_2\text{O}_3$  content [19]. In the high  $P_{\text{O}_2}$  region the slope of the curve varies slightly (between 1/7 and 1/9) with temperature as well as with  $\text{Y}_2\text{O}_3$  addition [4]. The slope tends to increase with temperature but to decrease with

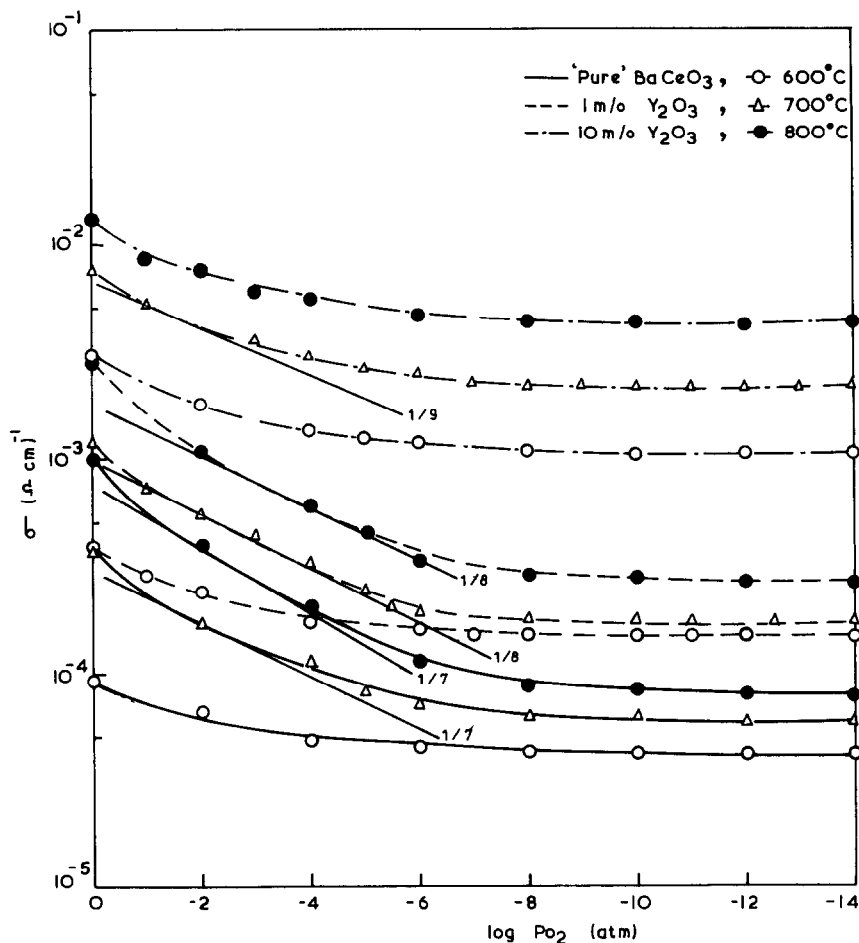


Fig 1 Electrical conductivity as a function of  $\log P_{O_2}$  at 600, 700 and 800 °C for 'pure' and  $Y_2O_3$ -doped  $BaCeO_3$

addition of  $Y_2O_3$ . It is difficult to identify the exact knee of the curves; however, for all the specimens it lies in the  $P_{O_2}$  range of  $10^{-5}$  -  $10^{-7}$  atm.

These results indicate that both pure and  $Y_2O_3$ -doped  $BaCeO_3$  specimens are not fully ionic conductors throughout the  $P_{O_2}$  range of measurement. Above about  $10^{-6}$  atm the material behaves as a mixed conductor with significant electron-hole conductivity, while below this pressure it behaves as a predominantly ionic conductor indicated by the  $P_{O_2}$ -independent conductivity. This is very similar to that observed in  $ThO_2$ -base electrolytes [4].

Partial hole conduction in the high partial pressure range may be explained on the basis of two probable defect reactions. One of these alter-

natives is that the oxygen from the gas phase is introduced in the lattice as doubly charged interstitials. Accordingly, the defect reaction and the corresponding neutrality condition are written as (using conventional notations)



$$2[O_i''] = [h] \quad (2)$$

These lead to a 1/6 dependence of  $\log \sigma$  on  $\log P_{O_2}$  [21]

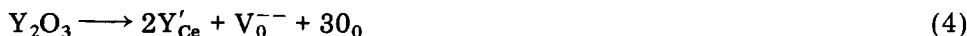
The other possible defect reaction is that the existing oxygen vacancies are annihilated by the excess oxygen according to the defect reaction



which leads to a 1/4 dependence of  $\log \sigma$  on  $\log P_{O_2}$  [21]. The theoretical slopes of either 1/6 or 1/4 may, however, be observed only when the material is prepared in the extremely pure state and the measurements are carried out in the high  $P_{O_2}$  range sufficiently far from the knee region. It is unrealistic to assume that even 'pure' material does not contain traces of aliovalent impurities. The lower slopes observed are due to the fact that the  $P_{O_2}$  range of measurement is close to the knee region and there is appreciable ionic transport along with hole conduction [4].

It may be mentioned that reaction (3) is more likely to take place in these materials than reaction (1) since the creation of oxygen interstitials is quite difficult in the closely packed perovskite lattice.

When  $BaCeO_3$  is doped with  $Y_2O_3$  it is expected that  $Y^{3+}$  ions go preferably to the  $Ce^{4+}$  sites, creating negatively charged defects such as  $Y'_{Ce}$ . It may be assumed that the charge compensation takes place by the formation of doubly charged oxygen vacancies. Therefore the defect reaction is written as



leading to the formation of a high concentration of oxygen vacancies, responsible for enhanced ionic conduction. In the high  $P_{O_2}$  region, on the other hand, reaction (3) is still valid and contributes to the partial pressure dependence of the conductivity. The increased ionic contribution is, however, responsible for the observed lower slope for the higher dopant concentration (Fig. 1).

From the experimental results, the variation of hole conductivity ( $\sigma_h$ ) with  $P_{O_2}$  may be obtained by subtracting the  $P_{O_2}$  independent ionic conductivity from the measured total conductivity in the mixed conduction region, assuming that the magnitude of ionic conductivity remains constant, even in this range. Such plots of the difference between total and ionic conductivities ( $\sigma_T - \sigma_i$ ) against  $\log P_{O_2}$  for different specimens are shown in Fig. 2. It may be noted that the slopes of these plots compare quite well with the predicted value of 1/4 (eqn (3)), particularly for the 'pure' sample

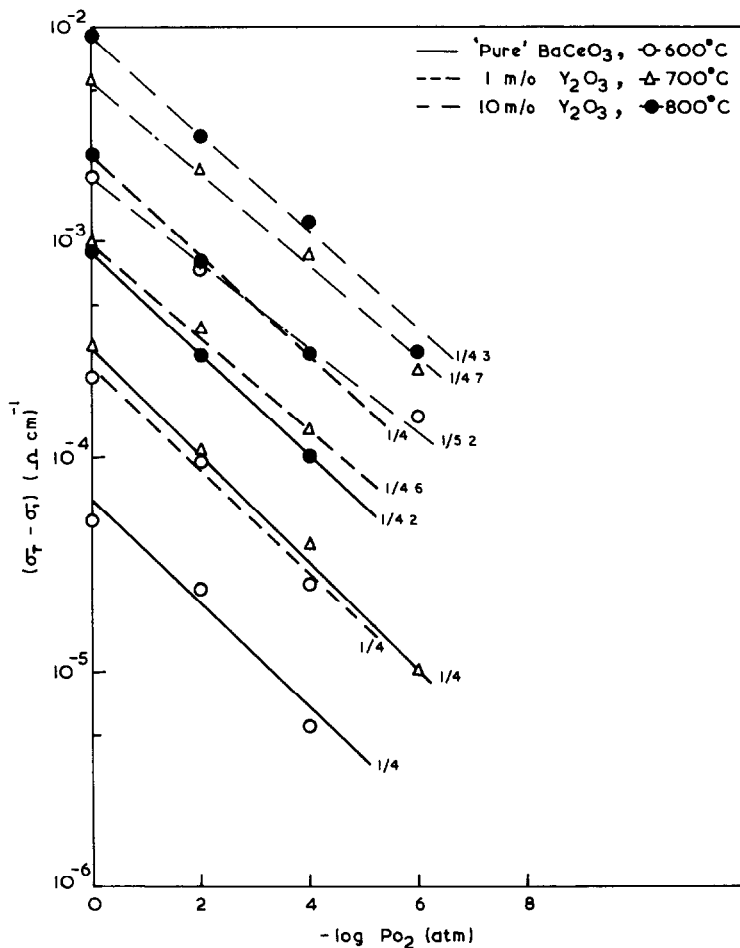


Fig 2 Plot of  $(\sigma_T - \sigma_{ion})$  vs  $\log P_{O_2}$  for 'pure' and doped  $\text{BaCeO}_3$  at different temperatures

and that with lower dopant concentration. A small deviation in the slope for the highly doped specimen is due to the larger contribution of the ionic conduction [4].

It is observed that both pure and doped specimens of  $\text{BaCeO}_3$  become predominantly ionic conductors only at lower partial pressures. The values of ionic conductivity in the lower  $P_{O_2}$  range are lower compared with those measured in air (i.e., in high  $P_{O_2}$ ).

The variation of ionic conductivity with temperature and  $\text{Y}_2\text{O}_3$  content is shown in Fig. 3. As in the case of air, the conductivity increases with temperature; however, with a lower activation energy, except for the 10 mole %

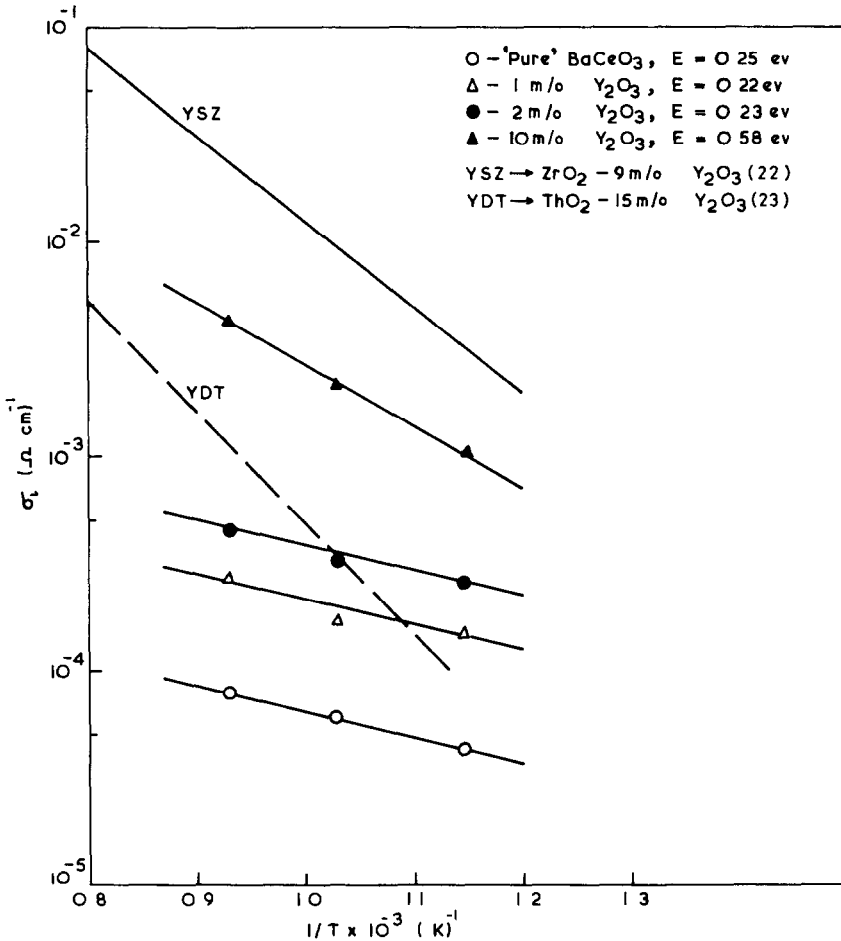


Fig. 3 Ionic conductivity vs  $1/T$  for 'pure' and  $Y_2O_3$ -doped  $BaCeO_3$  (1, 2 and 10 mole %)

$Y_2O_3$  specimen for which the value is slightly higher than that observed in air [19]. The ionic conduction activation energy,  $\epsilon e$ , measured in the low  $P_{O_2}$  region, is lower in the case of 1 and 2 mole %  $Y_2O_3$ -doped  $BaCeO_3$  than in those obtained for conductivity measured in air,  $\epsilon e$ , in the high  $P_{O_2}$  region [19]. This might be due to the predominant ionic conduction at low  $P_{O_2}$  in doped  $BaCeO_3$ . However, the activation energy (0.57 eV) of highly doped  $BaCeO_3$  is high as compared with that calculated for lower dopant concentration ( $\approx 0.22$  eV) which might be the result of ordering of the oxygen vacancies. Ordering occurs readily at higher dopant concentration.

For comparison, the ionic conductivities of two commercial solid electrolytes, yttria stabilized zirconia (YSZ) [22] and yttria doped thoria

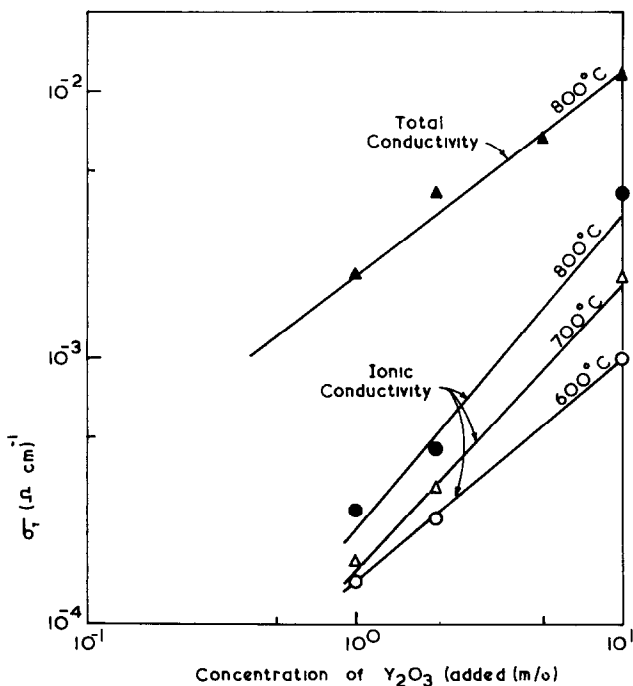


Fig 4 Conductivity as a function of  $Y_2O_3$  content at fixed temperatures

(YDT) [23] are also plotted in the Figure. It may be noted that even though the pure and low- $Y_2O_3$ -containing specimens have lower conductivities, the value for the 10 mole %  $Y_2O_3$  specimen compares quite well with those of YDT and YSZ. Due to its lower activation energy the conductivity even becomes higher than that of YSZ below about 500 °C.

It follows from reaction (4) that the ionic conductivity is proportional to the  $Y_2O_3$  content, so there should be a linear dependence between  $\log \sigma_i$  (ionic) and the logarithm of concentration. This is observed in Fig 4, in which both the ionic and the total conductivity are plotted against concentration for a fixed temperature. It is evident that the ionic conductivity is 1/4 to 1/5 of the total conductivity. Beyond 10 mole % however, the conductivity becomes almost independent of concentration, probably due to the clustering of defects.

From the data in Fig. 3 a rough estimate of the ionic transport number is made by using the relation  $t_i = \sigma_i / \sigma_T$  at different oxygen partial pressures. The values are plotted in Fig. 5. It is observed that the transference number, as expected, increases with increasing dopant concentration and becomes unity below the oxygen partial pressure of about  $10^{-8}$  atm.

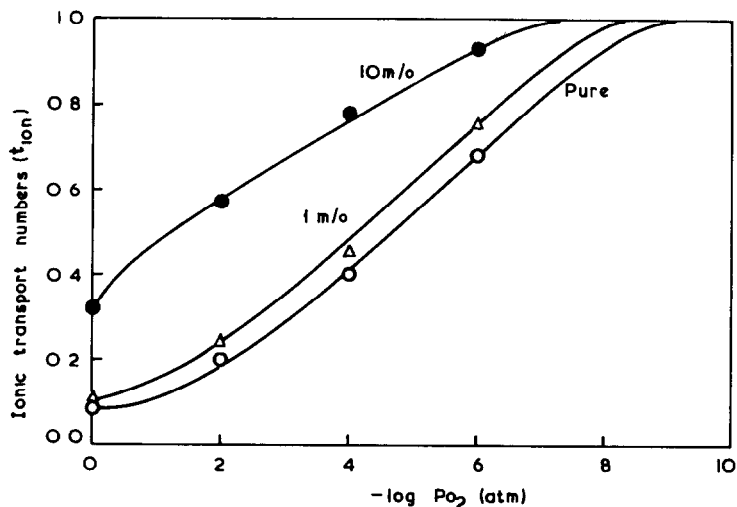


Fig 5 Ionic transference numbers for  $Y_2O_3$ - $BaCeO_3$  solid solution as a function of partial pressure of oxygen at 800 °C

#### 4. Conclusions

$BaCeO_3$ , which has a perovskite structure, shows significant oxygen ion conduction below an oxygen partial pressure of around  $10^{-6}$  atm. In the high partial pressure range it behaves as a mixed conductor with appreciable electron-hole conduction. On the addition of  $Y_2O_3$ ,  $Ce^{4+}$  ions are substituted by  $Y^{3+}$  ions with a significant increase in the vacancy concentration and a consequent increase in electrical conductivity and ionic transport number. From the point of view of electrical conductivity,  $Y_2O_3$ -doped  $BaCeO_3$  may act as a good substitute for  $Y_2O_3$ -doped  $ThO_2$  as an oxide solid electrolyte.

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