Mixed Proton and Electron Conduction in Doped $BaPrO_3$ and $SrPrO_3$

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Many doped perovskite oxides including $BaCeO_3$, $BaZrO_3$, $SrCeO_3$ and $SrZrO_3$ have received recent attention as proton conductors [1]. Introduction of a trivalent dopant onto the quatravalent site results in the creation of oxygen vacancies. Upon exposure of the material to humid atmospheres OH groups are dissolved onto the formerly vacant oxygen sites and additional protons are incorporated at other oxygen ion sites. Protons, present in the form of hydroxyl ions, can easily jump from one oxygen ion to the next, giving rise to the observed high proton conductivity. To date, few mixed proton and electron conducting oxides, as would be useful in a variety of applications, have been examined. In this work we present the high temperature properties of doped $BaPrO_3$ and $SrPrO_3$, materials which have similar proton incorporation properties to other perovskites, but additionally exhibit electron transport due to the variable valence of praseodymium.

Samples of composition $BaPr_{1-x}Gd_xO_{3-\delta}$ and $SrPr_{1-x}Gd_xO_{3-\delta}$ (x = 0 to 0.4) were obtained by solid state reaction from stoichiometric mixtures of Pr_6O_{11}, Gd_2O_3 and $BaCO_3$ or $SrCO_3$. X-ray powder diffraction showed that all samples crystallized in an orthorhombic perovskite structure. In the case of the barium series, the unit cell volume first decrease then increased with Gd dopant content, exhibiting a minimum at x = 0.2. This result is interpreted in terms of the variable valence of Pr, and suggests that at low dopant concentrations a significant portion of the praseodymium ions are in the trivalent state

Dense polycrystalline pellets for electrical characterization were prepared by isostatic pressing at 0.4 GPa and subsequent sintering at 1400°C in air for $BaPr_{1-x}Gd_xO_{3-\delta}$ and in oxygen for $SrPr_{1-x}Gd_xO_{3-\delta}$. Densities ≥ 94% of theoretical were obtained. Conductivities were measured by a.c. impedance spectroscopy under both H_2O- and D_2O-saturated argon, whereas electromotive force (EMF) measurements were obtained from samples exposed to H_2O saturated on one face and H_2O saturated O_2 on the other. The conductivity of $BaPr_{1-x}Gd_xO_{3-\delta}$ (under H_2O) generally increased with Gd content, while the activation energy for transport decreased from ~ 0.3 eV for x = 0 to ~ 0.1 eV for x = 0.3, values which are substantially lower than encountered in similar perovskites such as doped $BaCeO_3$ and $SrCeO_3$ [1]. The conductivity of undoped samples was unaffected by a change in atmosphere to D_2O-saturated argon, suggesting either electronic or oxygen ion transport. In contrast, the conductivity of doped samples decreased measurably, suggesting $H^+(D^+)$ transport. The EMF results indicate an ionic transference number of 0.13 for x = 0 (undoped $BaPrO_3$) at 168 °C, of ~ 0.7 for x = 0.1 and of ~ 0.8 for x = 0.2, 0.3 at 208°C. These latter results indicate electronic transport in undoped compositions and proton transport in doped compositions, in agreement with the isotope dependence of the conductivity.

References

[1] N. Fukatsu, N. Jurita, T. Yajima, K Koide and T. Ohashi, J. Alloy Compd. 231 (1995) 706.