

Proton Transport in Perovskites Containing Variable Valence Elements

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Many doped perovskite oxides including BaCeO₃, BaZrO₃, SrCeO₃ and SrZrO₃ have received recent attention as proton conductors [1]. Introduction of a trivalent dopant onto the quadravalent 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 BaPrO₃, a compound which has similar proton incorporation properties to other perovskites, but also exhibits electron transport due to the variable valence of praseodymium. In addition, substitution of a portion of the Pr by Zr leads to increased chemical stability.

Samples of composition BaPr_{1-y}M_yO_{3-δ} and BaPr_{0.8-y}Zr_{0.2}M_yO_{3-δ} (M = Y, Gd, Nd and x = 0 to 0.4) were obtained by solid state reaction from stoichiometric mixtures of BaCO₃, Pr₆O₁₁, ZrO₂ and M₂O₃. X-ray powder diffraction showed that all samples crystallized in an orthorhombic perovskite structure. Dense polycrystalline pellets for electrical characterization were prepared by isostatic pressing at 0.4 GPa and subsequent sintering at 1400°C in air. Densities ≥ 94% of theoretical were obtained. Conductivities were measured by a.c. impedance spectroscopy under both H₂O- and D₂O-saturated gases, for a range of oxygen partial pressures. Water content in saturated samples was measured by both thermo-gravimetric (TGA) methods and prompt-gamma activation analysis (PGAA) using neutron guide NG-7 at the NIST Center for Neutron Research. Electromotive force (EMF) measurements were obtained from samples exposed to gases in several different configurations:

1. H₂ / H₂O | sample | O₂ / H₂O
2. H₂ / H₂O(I) | sample | H₂ / H₂O(II)
3. O₂ / H₂O(I) | sample | O₂ / H₂O(II)

The conductivity of BaPr_{1-y}M_yO_{3-δ} first increased then decreased with dopant content, peaking at ~ 10⁻² S/cm (200°C) at x = 0.2, whereas the activation energy for transport reached a minimum of ~ 0.1 eV at x = 0.15. Zirconium substitution did not significantly impact conductivity, but did dramatically increase chemical stability. For example, Zr-substituted samples gained, on average ~ 2 wt% when exposed to flowing CO₂ at elevated temperatures, whereas BaPrO₃ typically gained ~ 11 wt%. In addition, the X-ray diffraction patterns of Zr-containing samples were unchanged after exposure to H₂O-saturated atmospheres, in contrast to compositions not containing Zr, which showed measurable changes. The magnitudes of the conductivities in BaPrO₃-based materials are much greater than those encountered in those based on BaCeO₃ or SrCeO₃ [1] and suggest

electronic transport. The EMF results, however, were generally consistent with a high ionic transport number. Chemical analysis by PGAA showed the proton content to be comparable to the doping level, demonstrating that protons were incorporated, despite the variable valence of Pr.

References

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