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Acceptor Doped BiFeO$_3$ Ceramics: A New Material for Oxygen Permeation Membranes

Kyle BRINKMAN*, Takashi IIJIMA, and Hitoshi TAKAMURA[1]

Research Center for Hydrogen Industrial Use and Storage, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan
[1]Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

A new intermediate temperature mixed conducting material has been fabricated based on acceptor doping of bismuth ferrite (BiFeO$_3$). Acceptor doping at levels of 5 mol % with either Ca or Sr was found to increase the maximum operating temperature of ceramics by more than 100 °C as well as eliminate secondary phase formation often reported in the pure BiFeO$_3$ system. Mixed ionic and electronic conductivity was confirmed by measuring the oxygen permeation properties of doped ceramics which exhibited flux's on the order of 0.018 μmol/(cm^2 s) at 800 °C over the oxygen partial pressure range 0.21 atm (air) to 10^{-6} atm (He). Ceramic membranes showed an increase in oxygen flux with decreasing sample thickness indicating good surface catalysis properties of the system.   [DOI: 10.1143/JJAP.46.L93]

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Mixed electronic and ionic conducting oxide materials have important technical applications in gas sensing,[1] solid oxide fuel cells,[2] oxygen production,[3] and hydrogen generation via the partial oxidation of methane.[3] Candidate materials with mixed conductivity are currently based on both (i) single phase ABO$_3$ perovskite materials with appropriate A and B site doping to enhance oxygen vacancy concentration and electronic conductivity as well as (ii) dual phase materials composed of ceria or bismuth based ionic conductors, plus an electronic conducting component such as the noble metals Pd, Ag or electronic conductive oxides with the spinel structure.[4,5]

The current generation of single phase high oxygen flux materials are based on A'$_x$A''$_{1-x}$B'$_y$B''$_{1-y}$O$_{3-\delta}$ derivatives with various combinations of A site elements (Ba, Sr, La) and B site elements consisting of (Co, Ga, and Fe) showing intermediate temperature oxygen fluxes (above 800 °C) of between 0.1 to 1 μmol/(cm^2 s) under a oxygen partial pressure difference He to air.[6–9] In addition, high ionic conductivity materials with electrical conductivity are a necessary but not sufficient condition for high oxygen flux membranes; the surface exchange kinetics are often the rate limiting step.[5,10]

Bismuth containing compounds have been recently under investigation for high conductivity bismuth oxide electrolytes[11] and mixed composites for oxygen permeation.[5] Bismuth ferrite (BiFeO$_3$) and (Bi$_2$Fe$_4$O$_9$) have been investigated as gas sensors,[12] however there has been no reports of oxygen permeation in these material systems. Recent work on BiFeO$_3$ (subsequently referred to as BFO) perovskite materials has been focused on the materials multiferroic properties which are currently limited by high leakage currents.[13] BFO has a distorted perovskite lattice with R3c rhombohedral parameters a 3.958 Å and α 89.3[14] and is a ferroelectric and antiferromagnetic with a melting temperature of 850 °C. The high leakage currents have been described as a consequence of a multivalent Fe on the B site creating mobile oxygen vacancies. Donor doping on the B site with Nb,[15] or isovalent doping with Nd on the A site[16] has been shown to increase the ambient temperature material resistivity by reducing oxygen vacancy concentration and

subsequent internal traps which lead to bulk defect conduction under high applied fields. In contrast, acceptor doping on the A site with Sr in BFO thin films showed increased levels of DC field induced leakage.[17]

The focus of this manuscript is to describe a practical application of the high leakage current commonly observed in BFO ceramics by using them as mixed ionic and electronic conductive ceramics for the separation of oxygen from air. In this study, we turn the "disadvantages" of oxygen vacancies and low resistivity for dielectric applications into "advantages" in solid state ionic materials by producing a singly substituted perovskite with mixed conductivity. Acceptor doping was performed using Ca^{+2} (ionic radius 0.99 Å) and Sr^{+2} (ionic radius 1.12 Å) in order to facilitate A site substitution (ionic radius Bi^{+3} ionic radius 1.2 Å). In this study it is shown that acceptor doping (i) changed the crystal structure from a rhombohedral phase towards a pseudocubic phase, (ii) increased the melting point and thus maximum membrane operation temperature by over 100 °C, and (iii) resulted in flux levels of 0.018 μmol/ cm^2 at 800 °C over the oxygen partial pressure range 0.21 to 10^{-6} atm comparable with dual phase ceria[4] and bismuth[5] membranes at intermediate temperature.

Bi$_{1-x}$A$_x$FeO$_3$ acceptor doped ceramics were prepared with $x = 0$ and 0.05 and A = Ca and Sr. Stoichiometric amounts of Bi$_2$O$_3$, Fe$_2$O$_3$, SrO, and CaO (High Purity Chemical Co., Japan) were weighed and ball milled in ethanol for 24 h, dried and calcined at 750 °C for 5 h in air. After a second grinding and sieving step, the ceramics were mixed with a binder and uniaxially pressed into pellets of 16 mm diameter with a force of 20 kN. Sintering conditions varied with dopant and concentration, $x = 0$ samples were sintered at 780 °C for 5 h, while $x = 0.05$ Sr was sintered at 920 °C 5 h and $x = 0.05$ Ca was sintered at 900 °C for 5 h. All sintered samples had relative densities greater than 90%.

The crystal structure of the calcined powders and sintered ceramics were examined by X-ray diffraction on a Philips X-pert and the microstructure was determined by scanning electron microscopy (SEM; Hitachi) after polishing and thermal etching. After background and Kα_2 corrections, the lattice parameters of the powder spectra in the range 20 to 70° two-theta were calculated from the peak maximum using regression analysis following Cohen's method.[18]

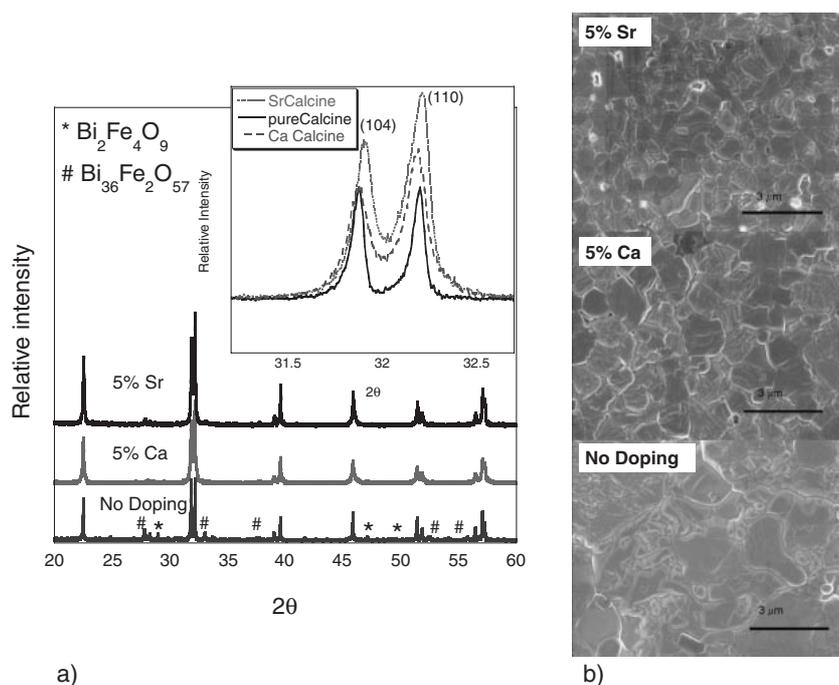*E-mail address: kyle.brinkman@aist.go.jp

Fig. 1. (a) Undoped, 5%Sr and Ca powder spectra calcined at 750 °C 5 h. Inset: Comparison of the (104) and (110) peaks for doped and undoped powder samples. (b) SEM determined microstructure of undoped (sintered 800 °C 5 h), and 5% doped Ca (900 °C 5 h) and Sr sintered ceramics (920 °C 5 h).

Oxygen flux measurements were made on polished ceramic samples of nominal thickness of 1 mm and a diameter of 13 mm. Ceramic samples were placed between two quartz tubes using a glass ring (melting point 620 °C) for gas sealing, and a metal spacer with a diameter of 5 mm to control the area of gas flux. Air at 1 atm was supplied to the feed side of the ceramic membrane while flowing He (20 sccm) was supplied to the permeate side. The gas concentration of O_2 and N_2 was measured on the membrane permeate side using a gas chromatograph (GC323; GL Sciences Co.). The leakage of oxygen was calculated by measuring the volume of N_2 gas from air on the permeate side. The oxygen permeation flux was corrected using the total measured oxygen on the permeate side minus the physical leakage of oxygen.

Figure 1(a) compares the powder spectra for undoped, Ca and Sr doped samples calcined at 750 °C for 5 h. It is seen that acceptor doping facilitates the formation of a pure perovskite phase resulting in an elimination of the secondary phases commonly observed in pure BFO.[15] Doped and undoped powder spectra were indexed to a rhombohedral phase and the inset in Fig. 1(a) shows the detail of the (104) vs (110) diffraction peaks indicating a structural change with dopant additions.

The results of lattice parameter regression analysis of the powder spectra is presented in Table I comparing the rhombohedral lattice parameter *a* and the rhombohedral angle α of undoped, Ca and Sr doped samples synthesized in this work with literature values. It is seen that doping with 5% Sr increases the lattice parameter *a*, and the rhombohedral angle α towards 90° (a pseudocubic phase); even though the ionic radius of the Sr^{+2} dopant ion is smaller than the Bi^{+3} ion by 7%. Simple electronegativity arguments as well as recent theoretical studies suggest this may be due to the greater ionicity in the Sr–O bond as compared to the covalent Bi–O bond.[19] A recent study in Sr doped BFO thin films found that Sr was indeed substituted at the "A" site

Table I. X-ray determined rhomobohedral lattice parameters for undoped, 5% Ca and 5% Sr doped $BiFeO_3$ calcined powders as compared with literature values.[14]

Sample	Lattice parameter *a* (Å)	α (deg)
$BiFeO_3$[14]	3.958	89.300
$BiFeO_3$ (This work)	3.997(6)	89.420(2)
5%Ca	3.990(5)	89.448(2)
5%Sr	4.000(0)	89.442(4)

in the perovskite structure, and the Sr–O ionic bond was a likely source of the discrepancy between the estimated and experimentally observed raman shift.[17]

Addition of acceptor dopants Ca and Sr at levels of 5% was also found to increase the sintering temperature (melting point) of ceramics over 100 °C. Undoped ceramics were sintered at 780 °C, while Sr and Ca dopes samples were sintered in excess of 900 °C reaching densities greater than 90%. Figure 1(b) shows the SEM determined microstructure of undoped and doped ceramics showing an decrease in grain size with doping; although all a samples showed grain size in the 1–3 µm range. Secondary phase formation was also seen to remain in the undoped samples even after sintering.

The oxygen flux characteristics for acceptor doped bismuth ferrite ceramics are presented in Fig. 2(a) for 5% Sr doped and Fig. 2(b) for 5% Ca doped ceramic membranes with thickness greater than 1 mm. No leaks of nitrogen could be measured in during the experiments indicating that the physical oxygen leakage was less than 0.2 nmol/(cm^2 s). In a purely oxygen ionic conductor such as ceria or zirconia, the absence of an additional electronic conductive phase, or an externally supplied voltage results in zero net oxygen flux. In the acceptor doped BFO ceramics prepared in this study, mixed ionic and electrical conductivity is evident from the high levels of oxygen flux; 0.018 µmol/(cm^2 s) at 800 °C for a 1.24-mm-thick membrane with Sr doping.
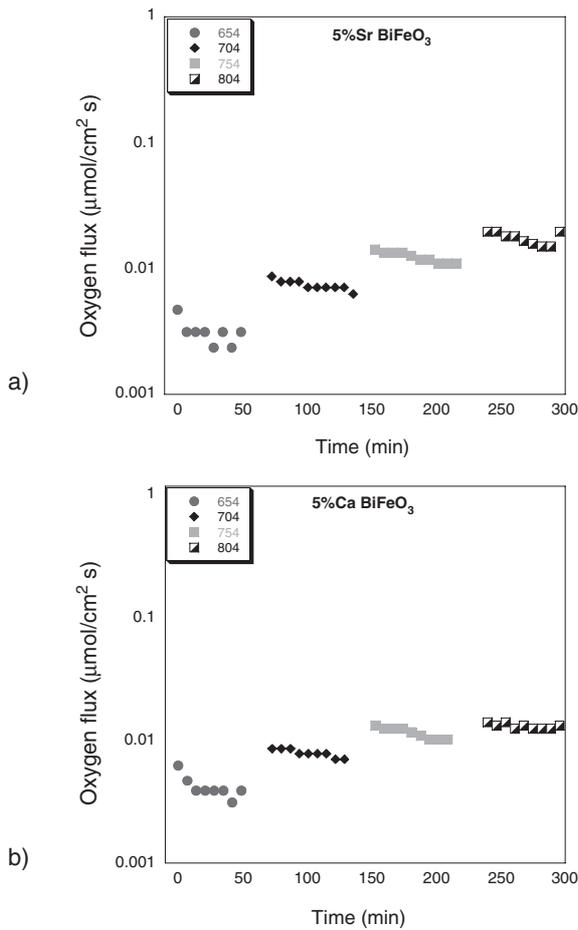
Fig. 2. Oxygen flux [$\mu mol/(cm^2\,s)$] at temperatures from 650 to 800 °C as a function of time (minutes) for (a) 1.24-mm-thick 5% Sr doped ceramics and (b) 1.16-mm-thick 5% Ca doped ceramics.
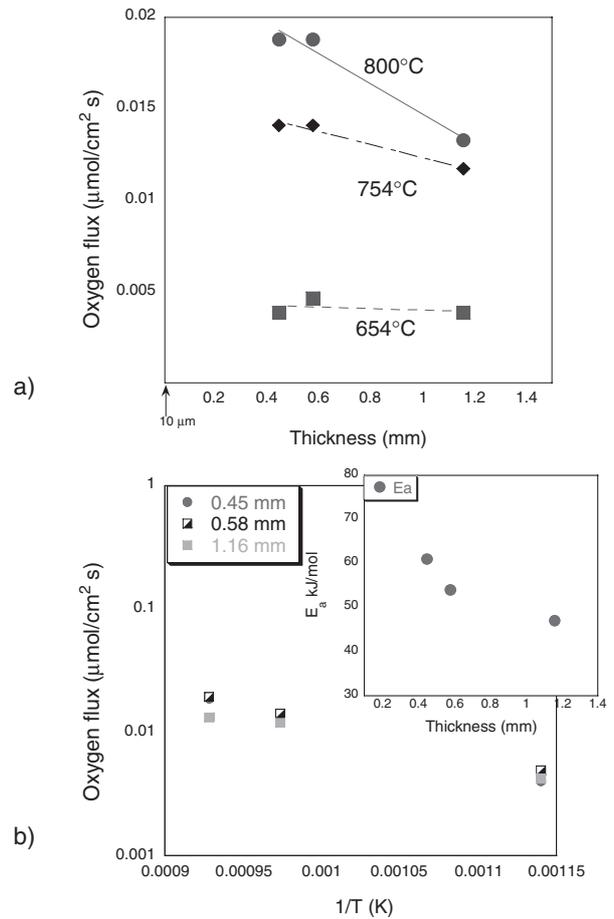

Fig. 3. (a) Oxygen flux at various temperatures as a function of ceramic membrane thickness from 1.16 to 0.45 mm of 5% Ca doped ceramics (b) activation energy (kJ/mol) for oxygen flux permeation as a function of membrane thickness.

An increase in oxygen flux with decreasing membrane thickness as seen in Fig. 3(a) indicates good surface catalysis properties of this material system. Figure 3(b) shows the increase in the activation energy of oxygen flux from 47 to 61 kJ/mol with decreasing membrane thickness from 1.16 to 0.45 mm. This behavior suggests that thin film membranes of this material may also have enhanced oxygen flux. Further opportunities for enhanced flux may result from higher levels of acceptor doping which should both enhance oxygen vacancy concentration and may further increase the melting point of the material enabling higher temperature operation.

There are however, a number of un-resolved issues with this material system. The most critical for applications involving partial oxidation is the phase stability, mechanical stability, and the materials ability to retain electronic conductivity under the extreme oxygen partial pressure gradients. In addition, doping concentration levels should be examined in combination with structural and spectroscopic techniques to confirm site substitution in ceramic materials. Measurement of total conductivity in a range of oxygen partial pressure environments and temperatures are currently underway in order to gain insight into the electronic and ionic conduction mechanisms.

A new mixed conducting perovskite material was synthesized based on acceptor doping of BFO ceramics with Sr and Ca ions in concentrations of 5 mol %. Doping was found to inhibit secondary phase formation, increase the rhombohedral angle α towards 90° approaching a pseudo-cubic phase, while increasing the materials melting point over 100 °C. Mixed ionic and electronic conductivity was confirmed by oxygen permeation measurement leading to oxygen flux of 0.018 $\mu mol/(cm^2\,s)$ at 800 °C in Sr doped samples over the oxygen partial pressure range 0.21 atm (Air) to 10^{-6} atm (He).

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