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Determination of electronic and ionic conductivity in mixed ionic conductors: HiTEC and in-situ impedance spectroscopy analysis of isovalent and aliovalent doped $BaTiO_3$

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ABSTRACT

The ionic and electronic conductivities of nonstoichiometric $BaTiO_3$ (undoped, Ca-doped, and Zr-doped $BaTiO_{3-\delta}$) ceramics were investigated through high temperature equilibrium conductivity (HiTEC) and in-situ impedance measurements at various equilibrium conditions with different oxygen partial pressures over a temperature range of 950–1050 °C. Contribution of mobile oxygen vacancies on the electrical conductivity has been determined by HiTEC measurement as a function of oxygen partial pressure; the electrical conductivity with mobile oxygen vacancies shows a broad transition from p-type to n-type, and thereby there is an increase of the minimum conductivity at the n–p transition point. Through combining in-situ impedance spectroscopy measurements with the HiTEC measurements, it was confirmed clearly that the mobile oxygen vacancy contributes to the total conductivity, and the oxides become mixed conductors around the n–p transition regime (minimum electronic conductivity regime). It was found that Warburg impedance can be observed at the condition of $t_{ion}/t_{electronic} \gtrsim 0.05$ in the temperature range of 950–1050 °C and pO_2 range of $0.95–10^{-16}$ atm. The ionic conductivity varied with the concentration of extrinsic oxygen vacancies and dopants, and the activation energy for mobility of oxygen vacancy in Ca-doped $BaTiO_{3-\delta}$ was found to be 1.04 ± 0.05 eV using the two techniques in a very good agreement.

1. Introduction

Many of the important functional oxides have mixed electronic and ionic conduction. In a given oxide, the relative contribution on conduction depends on the processing, chemical doping, and impurity types and their respective concentrations, which can all modify the defect chemistry, and the electroneutrality conditions can change, altering the ionic and electronic compensation. These important effects are known, but typically not considered, as there is a lack of techniques to easily assess these physical changes. The objective of this paper is to demonstrate the power of a combination of in-situ impedance spectroscopy and high temperature equilibrium conductivity (HiTEC) to determine the mixed conduction characteristics using a model system of a Ca-doped $BaTiO_3$. Earlier, Jamnik and Maier [1] and Boukamp et al. [2] investigated intensively the electrochemical impedance treatment for mixed conductors taking into account the parameters impacting on the Warburg diffusion.

Building from that important work, we successfully used with the high temperature impedance spectroscopy to determine mixed electronic and ionic conduction in electroceramic systems, such as $Pb(Zr,Ti)O_3$, and were able to quantify the ambipolar diffusion in PZT controlling the superoxidation reaction [3,4]. This change in defect compensation from ionic compensation of $[V''_{Pb}] \approx [V^{\bullet\bullet}_{O}]$ caused from high temperature process, involving the volatility of PbO, followed by the oxidation of the oxygen vacancies on cooling re-oxidizes through to obtain electronic compensation, $2[V''_{Pb}] \approx p$ [5,6]. In addition, we have also considered other important cases, such as the oxidation of Mn^{2+} doping in the linear dielectrics $Ca(Hf,Ti)O_3$ [7], Mg-doped $BaTiO_3$ [8], and the oxidation of $BaTiO_3$ multilayer capacitors after low oxygen partial pressure sintering [9].

The Ca-doped $BaTiO_3$ is an interesting case, as Ca^{2+} is a dopant that can occupy either the octahedral B-site as an acceptor or as an isovalent substitution on the twelve-fold coordinated A-site. This interesting phenomenon of site occupancy of Ca in $BaTiO_3$ has been previously investigated by a number of authors, including Smyth et al. [10–12], Tiwari et al. [13], and Lee and Randall [14]. It has been known that extrinsic oxygen vacancy by acceptor dopants can contribute to the total conductivity in the HiTEC around n–p transition region in the $BaTiO_3$-based materials, which are mostly electronic conductors. However, there has been no direct evidence for the ionic conduction by using an in-situ measurement for mixed ionic conductors in this family of materials.

Here, we build upon our and other earlier works to demonstrate high temperature impedance spectroscopy in conjunction with HiTEC measurement to provide quantification of ionic conductivity. The

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concentration of oxygen vacancies is particularly important in electroceramic, piezoelectric, and dielectric materials that involve operation under continuous electrical bias and require long time operation for commercial products. The electromigration of oxygen vacancies frequently determine the limiting lifetimes and require better understanding of the details of this mechanism [15–22].

2. Experimental

The nonstoichiometric compositions, undoped $BaTiO_3$ ($BaTi_{0.998}O_{2.996}$) and Ca-doped $BaTiO_3$, were synthesized by using a modified citrate process (see the details in related papers) [23,24]. Here the nonstoichiometries were determined from earlier work with XRF analysis [14,25]. The raw materials were Ti-isopropoxide ethanol solution, $BaCO_3$, $CaCO_3$, and citric acid monohydrate all with over 99.99% purity and obtained from Alfa Aesar. The Zr-doped $BaTiO_3$ powder was synthesized by using conventional sol–gel process with high purity barium acetate, titanium isopropoxide, and zirconium propoxide. The calcined powders were pressed by cold isostatic pressing in 30,000 psi and then sintered for 30 h in air at 1350 °C for undoped and Ca-doped $BaTiO_3$ and 1600 °C for Zr-doped $BaTiO_3$. The relative density of the sintered samples was over 94%, and the XRD analyses revealed all single phase with tetragonal perovskite structure at room temperature (not shown here).

The high temperature electrical conductivity measurements were conducted using a conventional 4-probe method in a tube furnace with gasses controlling the atmosphere, schematically represented in Fig. 1. Four Pt electrodes were pasted, as shown in Fig. 1 (right upper corner), and then cured at 1200 °C in air. The Pt wires were wound on the Pt paste. The oxygen partial pressures (pO_2) were controlled with O_2/Ar, CO/CO_2, and H_2/Ar gas mixtures and monitored by YSZ oxygen sensor positioned immediately below the samples. The resistance was obtained from a voltage drop between the inner electrodes with applying constant current through outer electrodes, and the conductivity was evaluated with the sample dimension, ~1.74 × ~3.18 × ~3.5 mm^3, between the inner electrodes (see Fig. 1). To obtain near equilibrium conductivity at each condition, the samples were held from 24 h to several days after changing temperature and pO_2.

In-situ impedance measurements were performed using the two inner electrodes after approaching the equilibrium conditions using a Solartron SI1287 electrochemical interface and 1255B frequency response analyzer under a V_{rms} of 50 mV or 100 mV ac signal over the temperature range of 950 °C to 1050 °C and frequency range from 1 MHz to 0.1 Hz. The impedance spectroscopy data was analyzed with Z-view (Scribner Associates, Southern Pines, NC, USA) in the form of Nyquist and Bode plots.

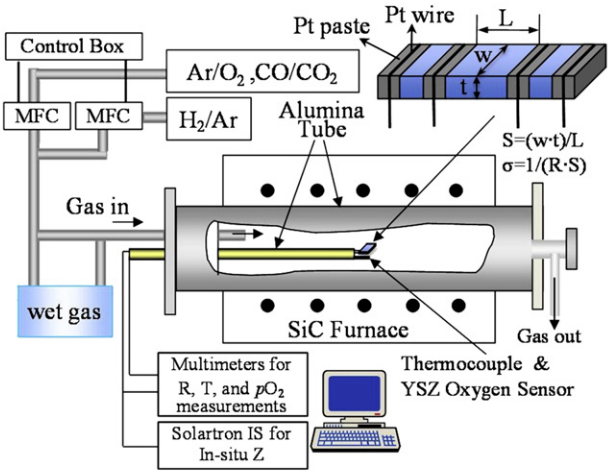

Fig. 1. A schematic diagram for high temperature equilibrium conductivity (HiTEC) and in-situ impedance measurements.

3. Results and discussion

3.1. High temperature equilibrium conductivity (HiTEC) ($\sigma(pO_2, T)$)

Basically, in oxide materials the ionic conduction is dominated by the concentration and mobility of oxygen vacancies. The oxygen vacancies can be generated by three major routes, such as reduction reaction, acceptor dopants, and partial Schottky defect reactions, the energetics of which have been quantified earlier [26,27]. All these reactions affect the electrical conductivity, changing carrier type and concentration, varying the electroneutrality conditions with different charge compensation mechanisms. The defect reactions are given by using the Kröger–Vink notation [28]:

Reduction reaction:

$$O_O^X \leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g) \tag{1}$$

$$\sigma_e \approx e\mu_e n \approx e\mu_e (2K_{Re})^{1/3} pO_2^{-1/6}. \tag{2}$$

Acceptor solubility reaction:

$$BaO + AO \rightarrow Ba_{Ba}^X + 2O_O^X + A_{Ti}'' + V_O^{\bullet\bullet} \tag{3}$$

$$\sigma_e \approx e\mu_e n \approx e\mu_e C_1 K_{Re}^{1/2} K_{acceptor}^{-1/4} pO_2^{-1/4} \approx e\mu_e C_1 \left(\frac{K_{Re}}{[A_{Ti}'']}\right)^{1/2} pO_2^{-1/4} \tag{4}$$

at high pO_2 region the *p*-type conductivity is given by

$$\sigma_h \approx e\mu_h p \approx e\mu_h \frac{K_i}{C_1}\left(\frac{[A_{Ti}'']}{K_{Re}}\right)^{1/2} pO_2^{+1/4} \tag{5}$$

and

$$\sigma_h \approx e\mu_h C_1 \left(K_{Ox}[A_{Ti}'']\right)^{1/2} pO_2^{+1/4}. \tag{6}$$

Partial Schottky reaction (x = 1 and y = 0 for Ba-rich; x = 0 and y = 1 for Ti-rich):

$$Ba_xTi_yO_{x+2y} \rightarrow xBa_{Ba}^X + yTi_{Ti}^X + (x+2y)O_O^X + yV_{Ba}'' + xV_{Ti}'''' + (2x+y)V_O^{\bullet\bullet} \tag{7}$$

$$\sigma_e \approx e\mu_e n \approx e\mu_e C_2 K_{Re}^{1/2} K_{PS}^{-1/(6x+4y)} pO_2^{-1/4} \approx e\mu_e C_2 \left(\frac{K_{Re}}{[V_{Ba}'']^y (2[V_{Ti}''''])^x}\right)^{1/2} pO_2^{-1/4} \tag{8}$$

at high pO_2 region the *p*-type conductivity is given by

$$\sigma_h \approx e\mu_h \frac{K_i}{C_2}\left(\frac{[V_{Ba}'']^y (2[V_{Ti}''''])^x}{K_{Re}}\right)^{1/2} pO_2^{+1/4} \tag{9}$$

and

$$\sigma_h \approx e\mu_h C_2 \left(K_{Ox}[V_{Ba}'']^y (2[V_{Ti}''''])^x\right)^{1/2} pO_2^{+1/4} \tag{10}$$

where: K_{Re}, K_{Ox}, $K_{acceptor}$, and K_{PS} are the equilibrium constants for the reduction, oxidation, acceptor substitution, and partial Schottky reactions, respectively. [N] represents the concentration of N defect species. C_1 is a constant, including activities of BaO and AO, and C_2 for activities of BaO or TiO_2. The earlier work by Tsur and Randall [29] demonstrates that a universal analytical model can approximate to the limiting Brouwer cases. However, in this paper the Brouwer approximation (e.g., $n \approx 2[V_O^{\bullet\bullet}]$), which is more standard, is employed to extract ionic and electronic