

Electrical properties of Tb-doped barium cerate

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Received 13 October 2012; received in revised form 27 December 2012; accepted 22 January 2013

Available online 6 February 2013

Abstract

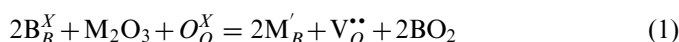
The electrical conductivity of $\text{Ba}_{0.8}\text{Ce}_{1-x}\text{Tb}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.15$) has been studied in air and moist reducing atmosphere (5% H_2 in Ar) in the temperature range between 550 and 900 °C. The powders of such materials are prepared by the combustion synthesis technique. The microstructure of the sintered specimens correlates well with its electrical properties. Electrical conduction mechanism of sintered specimens in various atmospheres is explained with respect to defect sites formed within the material. The generation of hydroxyl vacancy, proton and hole in moist reducing atmosphere increases the protonic conductivity significantly compared to hole/oxide ion conductivity in air atmosphere. Grain and grain boundary conductivity have been determined from the impedance measurements. The complex mechanism of electrical conduction of the sintered materials does not follow the linear behaviour in the Arrhenius plot. Maximum electrical conductivity obtained under moist reducing atmosphere is 0.049 S cm^{-1} for $\text{Ba}_{0.8}\text{Ce}_{0.85}\text{Tb}_{0.15}\text{O}_{3-\delta}$ at 900 °C.

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Keywords: B. X-ray methods; B. Defects; C. Electrical Properties; C. Impedance; Microstructure

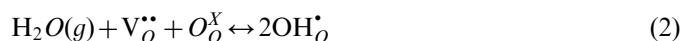
1. Introduction

The rare earth doped barium cerate perovskite materials are being investigated over the decades for variety of applications such as gas separation membrane, gas sensor, electrolyte for solid oxide fuel cell, catalyst and in nuclear power plant [1–11]. These oxides have both the oxide ion conductivity as well as proton conductivity depending upon the operating temperature, surrounding gas atmosphere etc. The oxide ion vacancies through which the oxide ion migrates are being created by substitution of higher valance cations in B^{4+} site with lower valance cations (M^{3+}) in ABO_3 perovskite structure Eq. (1). On the other hand, the conversion of oxide ion conductivity to protonic conductivity is primarily due to the hydration of oxide ion vacancies Eq. (2) [5,7,12]. These vacancies are only able to migrate inside the materials whereas the dopants remain fixed in the B site of the ABO_3 perovskite structure.



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However, the factors responsible for electrical conduction in these materials are the surrounding gas atmosphere, operating temperature, concentration of defect sites as well as charged species in the lattice structure, thickness of the material, materials synthesis procedure and the electric potential applied across the material [1,8,13–15]. Therefore, the conduction mechanism for this type of oxide is very complex. Understanding of the mechanism of electrical conduction in different atmospheres and operating temperatures is very much essential to enhance the performance of the material. However, a concrete study on the conduction mechanism particularly for this Tb-doped perovskite material has not been done extensively. In this investigation an attempt has been made to explore the conduction mechanism of Tb-doped barium cerate [$\text{Ba}_{0.8}\text{Ce}_{1-x}\text{Tb}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.15$)] in air and moist reducing atmosphere.

2. Experimental

Tb-doped barium cerate powder of compositions $\text{Ba}_{0.8}\text{Ce}_{1-x}\text{Tb}_x\text{O}_{3-\delta}$ ($x = 0.3, 0.5$ and 0.7) are prepared by the combustion synthesis technique using $\text{Ba}(\text{NO}_3)_2$ [99+%, ACROS Organics], $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [99.5%, ACROS

Organics], $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [99.9%, Sigma Aldrich] and $\text{CH}_2\text{NH}_2\text{COOH}$ [99+%, ACROS Organics] as primary constituents. The nitrates of Ba, Ce and Tb are used as oxidants and glycine is used as fuel in this synthesis. Table 1 shows the four different compositions along with their respective identification codes which are used in this study. Barium deficient pure barium cerate is not stable at higher temperature but with addition of dopants the stability increases for such barium deficient compositions. In this study, the barium deficient composition is chosen because of its better chemical stability than stoichiometric or barium excess compositions [16,17]. All the combustion experiments have been performed in fuel rich condition (nitrate: fuel=0.17). The thermal decomposition of gel precursor has been analyzed by DTA/TGA in air atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ using Simultaneous Thermal Analyzer (STA 409C, Netzsch, Germany). The as-synthesized powder is calcined at $1100^\circ\text{C}/6\text{ h}$ in air to form the phase-pure perovskite structure which is then confirmed by X-ray diffraction (XRD) analysis using X'Pert Pro software (PANalytical, Philips, Holland). The calcined powder is then planetary milled at a speed of 250 rpm for 6 h in isopropyl alcohol followed by air drying and pressing the powder uniaxially in the form of pellets (dia: 10 mm and thickness: 1–2 mm) under an applied pressure of 250 MPa followed by sintering at $1550^\circ\text{C}/6\text{ h}$ in air. The densities of the sintered specimens are measured by Archimedes principle using xylene as the immersion liquid. The compositional homogeneity across the sample equilibrated under air as well as moist reducing atmosphere at 900°C is also confirmed by the SEM EDX (Leo S430i). The fractured surface morphology of the sintered samples has been observed by FESEM (Model no. SUPRA 35VP). The electrical conductivity is measured by complex plane AC impedance spectroscopy using a Frequency Response Analyser (ModuLab, Solartron, UK) in the frequency range of $10\ \mu\text{Hz}$ to 1 MHz. A symmetric cell configuration of Pt-barium cerate-Pt has been used for all the measurements. For this purpose, the electrodes are prepared by screen printing of pure platinum paste on the both sides of the sintered specimens followed by curing at $1000^\circ\text{C}/2\text{ h}$ in air. The electrical conductivity is measured in the temperature range between 550 and 900°C in air as well as in moist reducing atmosphere ($5\% \text{H}_2$ in Ar). The moist reducing atmosphere is created by passing the mixture gas ($5\% \text{H}_2 + 95\% \text{Ar}$) continuously through the water bubbler kept at room temperature during the electrical measurement. To obtain the environmental equilibrium the sintered pellet is

kept for half an hour at each temperature before measurement in air as well as in moist reducing atmosphere.

3. Results & discussion

The thermal analysis of the precursor gels of all four compositions shows that major weight loss is observed between 200 and 425°C (Fig. 1). This broad temperature range indicates that the thermal decomposition in the precursor gel is gradual rather than instantaneous. During the combustion of the gel precursor, adsorbed and structural water is lost at the beginning up to around 200°C . The weight loss in between 200 and 350°C is due to the thermal decomposition of glycine complex and formation of respective oxide constituents. The formation of solid solution between the oxide constituents followed by phase evaluation corresponds to the weight loss in the temperature range $350\text{--}425^\circ\text{C}$ [18]. However, a minor amount of weight loss is still observed in all the compositions at around 900°C which could be due to the formation of oxygen ion vacancy in the lattice structure [19]. It is reported that such oxygen ion vacancies are formed in undoped as well as doped barium cerate compositions which can be expressed by the Eqs. (3) and (4) [20,21]. The percentage of weight loss is found to be maximum in BC (94.03%) compared to doped compositions in the order of 84.12%, 84.71% and 83.27% for BCT1, BCT2 and BCT3 respectively (Table 1). It may be due to the presence of maximum percentage of structural water as well as glycine in the precursor gel of pristine composition (BC). By substitution of Ce with Tb, the structural water is reduced in the overall composition in the order of $\text{BCT1} > \text{BCT2} > \text{BCT3}$ because terbium nitrate contains five molecules of water compared to cerium nitrate which is hexahydrate. Therefore, the process of substitution of Ce by Tb actually reduces one molecule of water in overall composition. As the nitrate to glycine ratio is constant (0.17) for all the four compositions thus the amount of glycine is more in BC compared to doped compositions (BCT1, BCT2 and BCT3). It is also observed that there is no significant weight loss after 1100°C which is

Table 1
Sample identification codes of various Tb-doped $\text{Ba}_{0.8}\text{CeO}_{3-\delta}$ compositions.

Tb doping (mol%)	Composition	Sample identification code
0	$\text{Ba}_{0.8}\text{CeO}_{3-\delta}$	BC
5	$\text{Ba}_{0.8}\text{Ce}_{0.95}\text{Tb}_{0.05}\text{O}_{3-\delta'}$	BCT1
10	$\text{Ba}_{0.8}\text{Ce}_{0.90}\text{Tb}_{0.10}\text{O}_{3-\delta''}$	BCT2
15	$\text{Ba}_{0.8}\text{Ce}_{0.85}\text{Tb}_{0.15}\text{O}_{3-\delta'''}$	BCT3

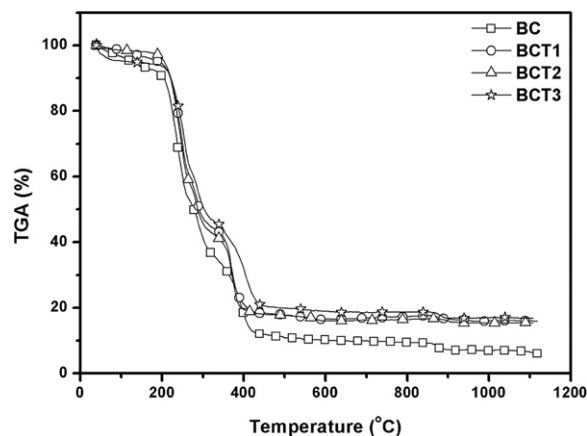


Fig. 1. TGA of $\text{Ba}_{0.8}\text{CeO}_{3-\delta}$ and Tb-doped $\text{Ba}_{0.8}\text{CeO}_{3-\delta}$.

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