Mechanical properties of Ba$_{1-x}$K$_x$Ce$_{0.6}$Zr$_{0.2}$Y$_{0.2}$O$_{3-δ}$ oxides by nanoindentation

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Abstract

The microstructural and nanomechanical characteristics Ba$_{1-x}$K$_x$Ce$_{0.6}$Zr$_{0.2}$Y$_{0.2}$O$_{3-δ}$ (K-doped BCZY, 0.0 ≤ x ≤ 0.15) oxides affected by the various K doping concentrations are investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and nanoindentation techniques in this study. All BKCZY samples are produced by a combination of the citrate-ethylenediaminetetraacetic acid (EDTA) complexing sol-gel process and the composition-exchange method, formed by uniaxial pressure and sintered at 1600 °C for 4 h. XRD results indicated that the BKCZY samples are predominantly the perovskite-type cubic structure. The hardness and Young’s modulus of BKCZY samples are measured by a Berkovich nanoindenter operated with the continuous contact stiffness measurements (CSM) mode. The results indicated that the hardness and Young’s modulus of BKCZY sample decreased with increasing the K doping concentrations.

Keywords: Ba$_{1-x}$K$_x$Ce$_{0.6}$Zr$_{0.2}$Y$_{0.2}$O$_{3-δ}$ electrolytes; XRD; SEM; Nanoindentation; Hardness

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1. Introduction

Solid oxide fuel cells (SOFCs) are one of the alternative techniques for the production of clean energy, promising high efficiencies and low environment impact [1-2]. Generally, SOFCs are composed of oxygen-ion-conducting electrolytes (O\textsuperscript{2−}-SOFCs) and operated at 800-1000°C to high conversion efficiency and power density [3]. However, such a high operation temperature introduces many practical problems, such as high costs, materials degradations, thermal expansion mismatch, reactions between the components, and slow start-up and shut-off [4], etc. Therefore, there is increasing interest in developing SOFCs based on proton-conducting electrolytes (H\textsuperscript{+}-SOFCs) operating at the intermediate temperatures (400-800°C) that facilitates the selection of sealing and interconnection materials, control of the interactions between the electrode/electrolyte, and thereby prolongs the operational lifetime of devices [5-6]. Moreover, H\textsuperscript{+}-SOFCs have higher theoretical electromotive force and electrical efficiency than O\textsuperscript{2−}-SOFCs [7].

The key issue in the development of H\textsuperscript{+}-SOFC is the use of a highly proton-conductive electrolyte with sufficient thermal stability at intermediate temperatures in various environments.

The perovskite-type oxides including BaCe\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{3}, BaZrO\textsubscript{3}, SrCe\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{3}, and SrZrO\textsubscript{3} have been reported to exhibit predominant proton conduction at elevated temperature in hydrogen containing or humidified atmosphere [8]. Among these proton-conductive electrolytes, BaCeO\textsubscript{3}-based oxides are generally believed to have the highest conductivity [9]. However, their chemical instability has been confirmed under CO\textsubscript{2}, H\textsubscript{2}O, or H\textsubscript{2}S containing atmospheres at high temperature [10-11]. Unfavorable reactions with carbon species and H\textsubscript{2}S could lead to the decomposition of BaCeO\textsubscript{3}-based electrolyte and performance degradation of H\textsuperscript{+}-SOFCs. Many efforts have been devoted to partially substitute Ce with Zr in the hope to improve the chemical stability [12-13]. In addition, to enhance the protonic conduction in BaCe\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{3}, doping with lower-valence cations is also essential. A trivalent dopant such as Y\textsuperscript{3+} can lead to the creation of oxygen vacancies, thus resulting in enhanced protonic conduction. Many studies have reported the promising performance of proton-conducting BaCe\textsubscript{1-x}Zr\textsubscript{x}Y\textsubscript{y}O\textsubscript{3-d} since it maintains the good chemical stability of BaZrO\textsubscript{3} but with improved electrical conductivity compared to BaCe\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{3} [14-15].

Several synthesis techniques have been utilized to prepare BaCe\textsubscript{1-x}Zr\textsubscript{x}Y\textsubscript{y}O\textsubscript{3-d} powders, including solid-state reaction [16], combustion [17] and sol-gel [18] methods. The sol-gel process has gained considerable attention because it can produce powders with great compositional uniformity, low residual carbon level, and nano-scale particle size [19-20], which is important to make dense products at lower sintering temperatures. In addition, the nano-crystalline conductors have been reported to have the higher conductivity compared to micro-scale oxides prepared using other processes due to favorable ionic mobility along the grain boundaries [21]. On the other hand, the protonic conductivity of perovskites is found to be strongly affected by the basicity of the constituent oxides due to its dominant influence on water uptake capacity [8]. Therefore, introducing highly basic alkaline cations into perovskite oxides should further improve the protonic conductivity. A significantly higher conductivity has been shown in K-doped BaZrO\textsubscript{3} than that in undoped BaZrO\textsubscript{3} [22]. In addition, Xu et al. [23] demonstrated that the water uptake of Y-doped BaZrO\textsubscript{3} synthesized by solid state reaction was increased with 5% K doped at the A-site of perovskites. However, both works found that introducing K into perovskites may lead to poor sinterability, high porosity and second phase formation, possibly due to the limit of K doping at A-site and high volatility of K-doped oxide at high process temperatures. Herein, in this work, we synthesize the proton-conducting Ba\textsubscript{1-x}K\textsubscript{x}Ce\textsubscript{0.6}Zr\textsubscript{0.2}Y\textsubscript{0.2}O\textsubscript{3-d} (BKCZY\textsubscript{y}, x = 0 ~ 0.15 at%) ceramics oxides by a combination of the citrate-ethylenediaminetetraacetic acid (EDTA) complexing sol-gel process and the composition-exchange method.

On the other hand, a successful fabrication of an SOFC demands a highly conductive and mechanical stable electrolyte, which is the key part of an SOFC assembly. In ceramic materials, crack behaviors are often initiated because of the microstructural defects introduced during manufacturing and/or the operation processes. The elements should be handled without breaking during manufacture and stack assembly and, also survive during the thermal cycling under operation. Thus, it is necessary that they withstand the mechanical stresses generated during processing and service. Many works have been focused on the electrical properties of SOFCs electrolytes [24-26]; however, their mechanical properties are almost ignored. Mechanical properties of electrolytes are also important when considering the necessarily long term service of SOFCs, which is susceptible to thermal stress and mechanical stress during the cell operation. Because of this, various non-conventional techniques have been developed for measuring the mechanical properties of solid materials, among high-resolution, nanoindentation has been successfully in the examination of electrolytes ceramics [27-29]. In this work, the microstructural and
nanomechanical characteristics of BKCZY oxides with various K doping levels have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nanoindentation techniques.

2. Experimental details

The citrate-EDTA complexing sol-gel process was used for preparing Ba_{1-x}K_xCe_{0.2}Zr_{0.2}Y_{0.2}O_{3-δ} (BKCZY, 0.0 ≤ x ≤ 0.15) oxides. The raw materials were commercial KNO_3 (99.9%), Ba(NO_3)\_2 (99.3%), ZrO(NO_3)\_2·2H_2O (99.0%), Ce(NO_3)\_3·6H_2O (99.5%), and Y(NO_3)\_3·6H_2O (99.9%). Citric acid was used as a chelating agent to the precursor solution, and EDTA acid as a solvent. The molar ratio of citric and EDTA acid to the total metal cations content was set at 2:2:3. The pH value of the solution was adjusted to be ~ 6 using NH_4OH. The mixed solutions were heated to 100 °C under stirring until obtaining viscous gels. By further heated at 250 °C to evaporate residual water and organics, these gels were converted into yellow powders. The synthesized powders were then calcined at 1000 °C for 12 h with a heating rate of 5 °C /min. To obtain dense samples, the calcined powders were uniaxially pressed into cylindrical pellets (1 cm in diameter and 1 mm in thickness) at 250 MPa for 20 s and then sintered in an air atmosphere. Sintering was performed at 1600 °C for 4 h. The phase identification of the sintered ceramics was performed with a powder diffractometer (Bruker D8A) with Ni-filtered Cu Kα radiation and the diffraction angle from 2θ° to 80° with a step of 0.01°. Microstructural analysis of samples is performed by using scanning electron microscopy (SEM, Hitachi S-4700).

The nanoindentation measurements were performed on a Nanoindenter MTS NanoXP® system (MTS Cooperation, Nano Instruments Innovation Center, TN, USA) with a pyramid-shaped Berkovich-type diamond indenter tip. The mechanical properties (the hardness and Young’s modulus) of BKCZY oxides were measured by nanoindentation with a continuous stiffness measurements (CSM) technique [30]. In this technique, a small sinusoidal load with known frequency and amplitude was superimposed onto the quasi-static load. It results in a modulation of the indenter displacement that is phase shifted in response to the excitation force. The stiffness, S, of the material, and the damping, wC, along indentation loading can be respectively calculated using Eq.(1) and Eq.(2) expressed below.

$$ S = \left[ \frac{1}{P_{\text{max}} \cos \Phi - (K_s - mw^2)} \right]^{-\frac{1}{2}} $$  \hspace{1cm} (1)

$$ wC = \frac{P_{\text{max}}}{h(w)} \sin \Phi $$  \hspace{1cm} (2)

where \( P_{\text{max}} \) and \( h(w) \) are denoted as the driving force and the displacement response of the indenter, respectively; \( \Phi \) is the phase angle between \( P_{\text{max}} \) and \( h(w) \); \( m \) is the mass of the indenter column; \( K_s \) is spring constant at the vertical direction; \( K_f \) is frame stiffness; \( m, K_s, K_f \) are all constant values for specified indentation system; \( w \) is angular speed which equals to \( 2\pi f \); \( f \) is the driven frequency of the \( ac \) signal of 45 Hz for this work, which is used to avoid the sensitivity to thermal drift. The loading resolution of the system was 50 nN. The hardness and elastic modulus are, then, calculated by putting the obtained stiffness data into Eq. (3) and Eq. (4) shown below, respectively.

$$ H = \frac{P_{\text{max}}}{A_c} $$  \hspace{1cm} (3)

$$ E = \frac{1}{1-\nu^2} \frac{1}{2} \frac{1}{A_c} S $$  \hspace{1cm} (4)

Here, \( \nu \) is the Possion’s ratio of the material and is set to be 0.25 for the current analysis, and \( A_c \) is contact area when the material in contact with indenter being loaded at \( P_{\text{max}} \). In this way, the hardness and modulus as a function of the penetration depth can be determined for a single loading/unloading cycle [31].

The area function, which is used to calculate contact area, \( A_c \), from contact depth, \( h_c \), was carefully calibrated by using fused silica as the standard sample prior to the nanoindentation experiments. The nanoindentation tests were carried out in the following sequence: first of all, the Berkovich indenter was brought into contact with the surface at a constant strain rate of 0.05 s\(^{-1}\) until ~500 nm of penetration was achieved. The load was then held at the maximum
value for 10 s in order to determine the creep behavior. The Berkovich indenter was then withdrawn from the surface at the same rate until 10 % of the maximum load was reached. This constant strain rate was chosen such that the strain-hardening effect can be avoided during the measurements. At least 20 indents were performed on each BKCZY sample in order to achieve the statistical significance. The nanoindentations were sufficiently spaced to prevent each test from mutual interactions. All experimental results for each sample are an average of values of at least 20 indents.

3. Results and discussion

In Fig. 1, BKCZY (K = 0 and 0.15 at%) oxides are predominantly the perovskite-type cubic structure, showing five major diffraction signals, namely those from the (110), (200), (211), (220), and (310) planes (JCPDS card no. 89-2485). In addition, three very weak peaks associated with the cubic (Zr,Ce,Y)O$_2$-like structure indicated by “▲” are displayed. These peaks most possibly correspond to a CeO$_2$-like phase since their XRD peaks close to main peaks of CeO$_2$ [32]. It has been reported that an addition of K atoms into perovskite-type materials can stabilize the perovskite structure in terms of increased tolerance factor and enhanced electronegativity difference [33-34]. Therefore, we speculate that with an increase in the K doping, the perovskite structure of BKCZY oxides can be more stabilized in sintering and in the meanwhile, the formation of CeO$_2$-like second phase is more suppressed. Under the circumstances, Ce$^{4+}$ cations (0.87 Å) tend to remain at the B-site of perovskite and their larger ionic radius than Zr$^{4+}$ (0.72 Å) results in an increase in lattice parameter [32]. This inference is also consistent with the inset of XRD results, in which the CeO$_2$-like peak appears to diminish with increasing the K doping. It implies that the formation of CeO$_2$-like phase in sintered oxides can be further suppressed through the composition-exchange process for the calcined powders.

The surface morphologies of BKCZY oxides with various K doping level are shown in Fig. 2. All BKCZY oxides are well densified and very few pores are observed on the surface. The pores can be ascribed to the oxide volume shrinkage, which results from the release of structural water and residual organics, and volatilization of K-doped oxide at high sintering temperature [22]. In addition, the average grain size was increased from 1.5 to 3.2 μm as the K doping concentration was increased from 0 at% to 0.15 at%, respectively.

The typical load-displacement curves for the BKCZY (K=0 at% and 15 at%) oxides are displayed in Fig. 3(a). The load-displacement responses obtained by nanoindentation contain information about the elastic and plastic deformation of the indented materials. Therefore, it is often regarded as a “fingerprint” of materials properties under identification. Mechanical properties, such as the hardness and Young’s modulus, can be readily extracted from the load-displacement curves like those displayed in Fig. 3(a). The hardness and Young’s modulus for the BKCZY (K=0 at% and 15 at%) oxides as a function of penetration depth obtained by using the analyses described above are illustrated in Fig. 3(b) and Fig. 3(c), respectively. As shown in Fig. 3(b), all of the hardness-displacement plots can be divided into two stages, namely, initial increase to a maximum value and subsequent decrease to a constant value. The increase in hardness at small penetration depth is usually attributed to the transition between purely elastic to elastic/plastic contact and at this stage the hardness is not accurately measured by the mean contact pressure. Only under the condition of a fully developed plastic zone does the mean contact pressure represent the hardness. When there is no plastic zone, or only partially formed plastic zone, the mean contact pressure is less than the nominal hardness [31]. After the first stage, the hardness decreases and reaches a constant value. The constant characteristic of hardness is consistent with that of a single material; therefore, the hardness values at this stage could be regarded as intrinsic properties of ceramics materials. As can be observed in Figs. 2(a)-2(d) and Fig. 3(b), the average grain size increases with the increasing K doping concentration, the effect of K doping concentration on the hardness of BKCZY oxides thus can be generally explained by the well-known Hall-Petch relationship \( H = H_0 + k d^{-1/2} \), where \( H_0 \) is a constant and \( d \) is the diameter of grain). Our experimental results are in consistent with the previous study [27].

Figures should be placed at the top or bottom of a page wherever possible, as close as possible to the first reference to them in the paper.

In addition, Fig. 3(c) displays a plot of Young’s modulus of BKCZY (K=0 at% and 15 at%) oxides determined using the method of Oliver and Pharr [31]. The tendency of variation is similar to the hardness results illustrated in Fig. 3(b). It is apparent that the Young’s modulus demonstrates a tendency of decrease with K doping concentration.
The previous studies [35-36] have shown that the lattice spacing of doped CeO$_2$ materials increase when increasing the doped concentration or the sintering temperature. Consequently, the enlarged lattice spacing, which usually leads to an enlarged atomic distance then affects the modulus negatively, could be the reason for the observed decreased elastic modulus, as shown in Fig. 3(c). The values of hardness and Young’s modulus obtained from the abovementioned CSM measurements for all BKCZY oxides under study are summarized in Table 1.

4. Conclusions

In summary, nanoindentation has established on the nanoscale mechanical properties of BKCZY oxides. Nanoindentation results indicated that, depending on the grain size which is intimately related to the K doping concentration, the BKCZY oxides have hardness ranging from 5.2±0.1 to 9.3±0.2 GPa and Young’s modulus ranging from 138.5±3.6 to 179.2±2.3 GPa with the higher values being corresponding to lower K doping concentration.

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Figures and Tables

Table 1. Hardness, Young’s modulus, fracture toughness and fracture energy of BKCZY oxides.

| BKCZY | H (GPa) | E (GPa) | $K_I$ (MPa·m$^{1/2}$) | $G_f$ (J/m$^2$) |
|-------|---------|---------|----------------------|-----------------|
| K@ 0 at% | 9.3±0.2 | 179.2±2.3 | 0.43±0.13 | 0.96±0.08 |
| K@ 5 at% | 7.8±0.3 | 165±13.2 | 0.32±0.11 | 0.58±0.07 |
| K@10 at% | 6.5±0.2 | 152.3±4.8 | 0.25±0.12 | 0.35±0.09 |
| K@15 at% | 5.2±0.1 | 138.5±3.6 | 0.19±0.11 | 0.24±0.08 |

Fig. 1. XRD patterns of BKCZY (K = 0 at% and 15 at%) oxides and the inset shows the enlarged XRD spectra around 30°.
Fig. 2. SEM micrographs of BKCZY oxides doped with the various K doping concentrations: (a) 0 at%; (b) 5 at%; (c) 10 at% and (d) 15 at%.

Fig. 3. Nanoindentation measurement results: (a) the load-displacement curves for BKCZY (K = 0 at% and 15 at%) oxides; (b) hardness-displacement and (c) Young’s modulus-displacement curves for BKCZY (K=0 at% and 15 at%) oxides.

Fig. 4. SEM micrograph of the fracture surface of BKCZY (K = 15 at%) and, the inset shows the corresponding load-displacement curve with a pop-in event under an nanoindentation load of 200 mN.

References

[1] N.Q. Minh, T. Takahashi, Science and Technology of Ceramic Fuel Cells, Elsevier, Amsterdam, 1995.
[2] S.M. Haile, Fuel cell materials and components, Acta Mater. 51 (2003) 5981-6000.
[3] G. Hoogers, Full cell technology handbook, Boca Raton, FL: CRC Press, 2003.
[4] I.M. Hung, H.W. Peng, S.L. Zheng, C.P. Lin, J.S. Wu, Phase stability and conductivity of Ba_{1−x}Sr_{x}Ce_{1−y}Y_{y}O_{3−δ} solid oxide fuel cell electrolyte, J. Power Sources 193 (2009) 155-159.
[5] Z.P. Shao, S.M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, Nature 431 (2004) 170-173.
