Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 3823–3826

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Determination of the maximum Ca content in $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ by XRD intensity ratio

Zetian Tao*, Guihua Hou, Ning Xu

Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, China

Received 23 July 2013; received in revised form 23 July 2013; accepted 9 August 2013
Available online 16 August 2013

Abstract

Complex oxides $La_{2-x}Ca_xZr_2O_{7\pm\delta}$($x$=0.06–0.10) were prepared by a modified Pechini method and a novel strategy based on the X-ray diffraction intensity ratio was developed to determine the maximum Ca content in $La_{2-x}Ca_xZr_2O_{7\pm\delta}$. Computer simulation predicted that the intensity ratio of (662) and (331) reflections for $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ increased with the increasing Ca content x. XRD analysis showed that with increasing x until 0.08, the ratio increased as predicted, then leveled off with further increase of x. An abrupt change in electrical conductivity was also observed at x of 0.08. It was concluded that the maximum Ca content lay in 0.08 for $La_{2-x}Ca_xZr_2O_{7\pm\delta}$.

Keywords: C. Ionic conductivity; Ceramics; Inorganic compounds; Sol–gel chemistry; X-ray diffraction

1. Introduction

Ceramic proton conductors receive much attention from the solid oxide fuel cells (SOFCs) community because the proton-conducting SOFCs would permit lowering the working temperature to the range of 500–700 °C [1–4]. In addition, no fuel gas circulation is necessary for proton-conducting SOFCs compared to the conventional SOFCs with YSZ electrolyte as water is produced at the cathode side. Among these ceramic proton conductors, much attention has been paid to ABO_3-type perovskites, particularly to the rare earth doped $BaCeO_3$ materials that exhibit the highest protonic conductivities. One of the major challenges for this type of proton conductors is a proper compromise between conductivity and chemical stability. For example, doped $BaCeO_3$ has sufficiently high ionic conductivity, but the chemical stability in an atmosphere containing CO_2 and H_2O is inadequate for fuel-cell applications [5,6]. The doped pyrochlore $La_2Zr_2O_7$ which shows desirable proton conductivity and high chemical stability is an interesting electrolyte material candidate for proton-conducting SOFCs [7–10].

The lanthanum zirconate ($La_2Zr_2O_7$) is cubic (space group Fd-3m) with eight A2B2O6O′ molecules (88 atoms) per unit cell. There are four crystallographically nonequivalent kinds of atoms: the cations A and B and the oxygen ions O and O″. Expressed in Wyckoff notation they occupy crystallographic positions 16d, 16c, 48f and 8b, respectively [11,12]. The pure material $La_2Zr_2O_7$ cannot accommodate any appreciable amounts of protons and does not show proton conduction [13]. Thus, lower valence ions such as Ca^{2+} is introduced to the La sites by forming the oxygen vacancies, which can be replaced by protonic defects under humid atmosphere [14,15].

The maximum Ca-doping content in $La_2Zr_2O_7$ has been studied for getting the largest proton conductivity, but the results are conflicting. Omata et al. report a value of 0.05 for $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ beyond which a second phase $CaZrO_3$ appears [9–16]. A higher value of 0.08 is also reported [8]. The discrepancy in the reported literature may arise partly from the different sample preparation routes used, and/or the different characterization methods adopted. One method to determine the maximum Ca-doping content is to investigate the impurity phase of $CaZrO_3$ with the XRD diffraction. But a higher value than the real one is gained because of the detection limit of the instrument. In this paper, we use a simple and available method to determine the maximum Ca-doping content, in which the intensity ratio of XRD reflections (662) and

*Corresponding author. Tel.: +86 515 88298923; fax: +86 515 88298927.
E-mail address: newton@mail.ustc.edu.cn (Z. Tao).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.08.046

(331) for $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ is examined as a function of the Ca-doping content. We also measure the conductivity to validate the results got from the method refers above.

2. Experimental

$La_{2-x}Ca_xZr_2O_{7\pm\delta}$ (x=0, 0.06, 0.07, 0.08, 0.09, 0.10) powders were synthesized by Pechini method. Appropriate amounts of $CaCO_3$ and La_2O_3 that had been calcined at 1000 °C were dissolved in nitric acid and mixed with Zr $(NO_3)_4$ solution, then citric acid was added, which was used as complexation agent. Molar ratio of citric acid/metal was set at 1.5. The solution was heated under stirring to evaporate water until it changed into viscous gel and finally ignited to flame, resulting in the white ash. The ash was calcined at 1000 °C for 3 h to form fine $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ powders. The as-prepared powders were isostatiacally pressed into wafers (Φ15) under 300 MPa pressure, sintered in air at 1550 °C for 10 h, and then cooled.

The phase of the obtained powders and the intensity ratio of reflections (662) and (331) were measured with X-ray diffractometer (XRD) using CuKα radiation in the Bragg–Branteno geometry. The powders used for analysis were sieved with 250 mesh. The theoretic intensity ratio was conducted by using a computer simulation. The intensity ratio was calculated using program POWDERCELL [17]. Calculation was also performed to examine the effect of oxygen nonstoichiometry on the intensity ratio. Parameters used for simulation were given as follows: Bragg–Branteno geometry, radiation CuKa1; space group Fd-3m, $a=b=c=10.7997$ Å; lanthanum ion site in 16d, site occupation factor (SOF)=1.000−0.950; calcium ion in 16d, SOF=0.000−0.050; zirconium ion in 16c, SOF=1.000−0.972; oxide ion site two positions, one is 48f, the other one 8b.

The electrical conductivity of a whole series of samples $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ with x ranging from 0.06 to 0.10 was measured at elevated temperatures in humidified hydrogen (~ 3% H_2O) with an electrochemical station CHI604C (0.1 Hz to 100 KHz) using AC impedance spectroscopy.

3. Results and discussion

As shown in Fig. 1, all the samples of $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ (x=0, 0.06, 0.07, 0.08, 0.09, 0.10) exhibits pyrochlore phase structure without impurity phase such as CaZrO3, implying that the maximum Ca-doping content may be greater than 0.10. However, the second phase $CaZrO_3$ might have appeared at x less than 0.10 and could not be found while its quantity is below the detection limit of the XRD method. Thus, the precise value of the maximum Ca-doping content needs be determined by other methods.

Fig. 2 shows the calculated intensity ratio of reflections (662) and (331) for $La_{2-x}Ca_xZr_2O_7$. It can be seen clearly that the intensity ratio increases with increasing Ca-doping value x. With the increase of x from 0 to 0.10, the intensity ratio increases by 15% from 8.14 to 9.37. The lanthanum zirconate normally exhibits oxygen nonstoichiometry as represented by formula $La_2Zr_2O_{7\pm\delta}$. The effect of oxygen nonstoichiometry

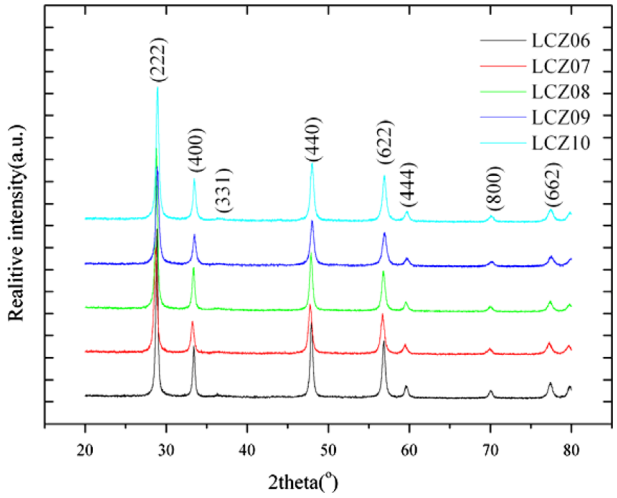

Fig. 1. X-ray diffraction patterns of the samples of $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ (x=0, 0.06, 0.07, 0.08, 0.09, 0.10).

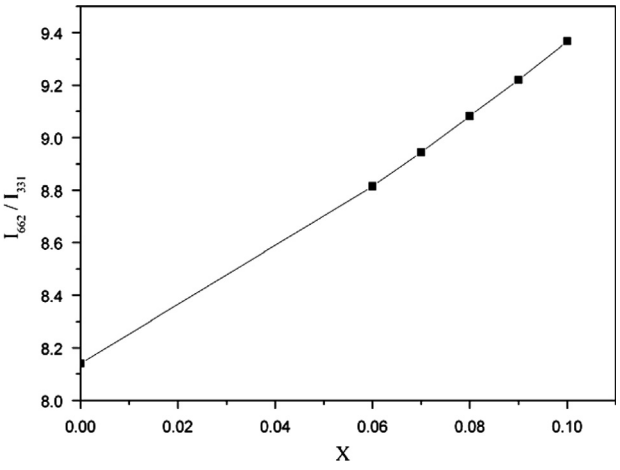

Fig. 2. Calculated intensity ration of the (662) and (331) reflections as a function of Ca-doping content x in $La_{2-x}Ca_xZr_2O_7$.

on the intensity ratio is also accessed by computer simulation, and the results are presented in Fig. 3. Since the pyrochlore-structured oxide cannot contain excessive oxygen at interstitial positions, the incorporation of excessive oxygen leads to the creation of cation vacancies at both La and Zr sites. Thus, oxygen-excessive $La_2Zr_2O_{7+\delta}$ is more appropriately represented by the formula $La_{2-y}Zr_{2-y}O_7$ with $y=2\delta/(7+\delta)$, and simulation was done with this defect chemistry model. From Fig. 3, it can be seen that the intensity ratio decreases with the increase of oxygen excess δ and increases with the increase of oxygen deficiency δ. Compared with the result of $La_{2-x}Ca_xZr_2O_7$, the effect is much smaller. At oxygen excess δ=0.20, the intensity ratio is decreased by ~1%. At deficiency δ of 0.20, the intensity ratio is increased by 9%.

The real intensity ratio, measured from the XRD, is shown in Fig. 4. We can investigate from the figure and know that the intensity ratio increases with increasing x until x=0.08; the intensity ratio increases by 24% from 8.14 at x=0.00 to 10.09 at x=0.08. Compared with the computer simulation, we can know that the increase of the intensity can be attributed to

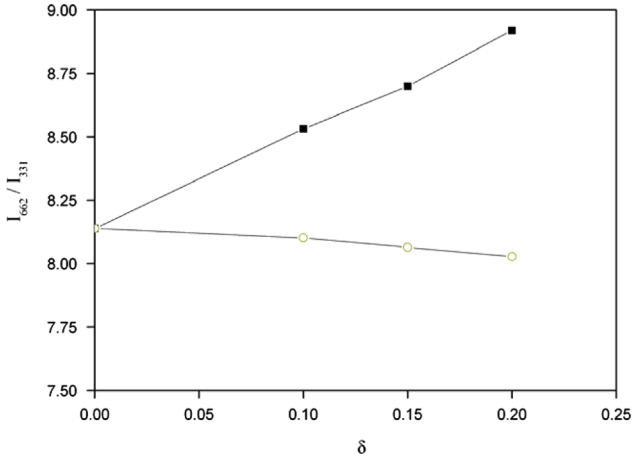

Fig. 3. Calculated intensity ration of the (662) and (331) reflections as a function of oxygen nonstoichiometry in $La_2Zr_2O_{7\pm\delta}$. (■) oxygen deficient. (○) oxygen excess.

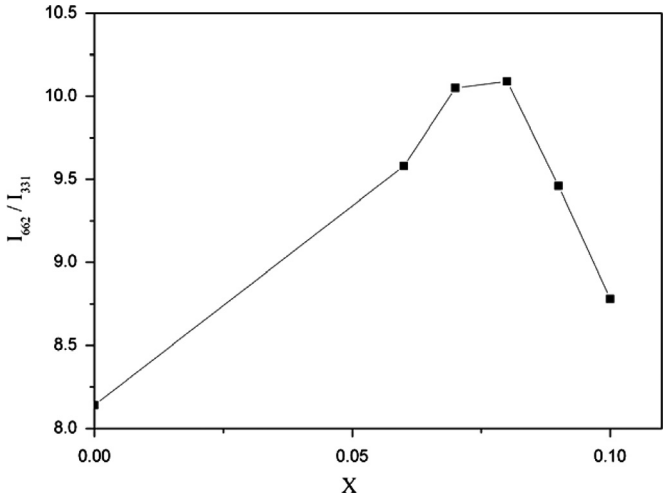

Fig. 4. Measured intensity ratio I_{662}/I_{331} as a function of Ca-doping value x in $La_{2-x}Ca_xZr_2O_{7\pm\delta}$.

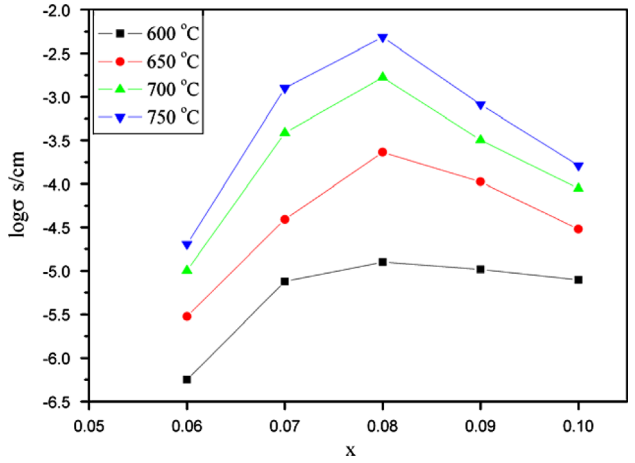

Fig. 5. Measured electrical conductivity σ at various temperatures as a function of Ca-doping content x in $La_{2-x}Ca_xZr_2O_{7\pm\delta}$.

Ca-doping at the La site and the oxygen deficiency. At x larger than 0.08, the intensity ratio becomes smaller which reveals that the maximum Ca-doping content is about 0.08. Beyond the value 0.08, the impurity phase $CaZrO_3$ may form and decrease the intensity ratio, consequently.

The electrical conductivities of the dense wafers are measured at elevated temperatures of 600 °C–750 °C in humidified hydrogen (~3% H_2O) and the results are shown in Fig. 5. It can be seen that the electrical conductivity increases with the increased temperatures and an obviously change happens at $x=0.08$. The largest electrical conductivity at $x=0.08$ indicates the maximum Ca-doping content is 0.08 beyond which an impurity phase forms and leads to the decrease of the electrical conductivity. This result well accord with the conclusion made from the intensity ratio.

4. Conclusions

In the present study, a simple and available method based on the XRD intensity ratio was employed to determine the Ca-doping content in pyrochlore-structured $La_{2-x}Ca_xZr_2O_{7\pm\delta}$. Computer simulation showed that the intensity ratio I_{662}/I_{331} for $La_{2-x}Ca_xZr_2O_{7\pm\delta}$ increased significantly with increasing Ca-doping content x at the La site and oxygen deficient δ. XRD analysis showed that the intensity ratio increased with x until $x=0.08$, beyond which it leveled off. The measurement of electrical conductivity revealed that the largest conductivity was got at $x=0.08$. Both the XRD intensity ratio analysis and the electrical measurement confirmed that the maximum Ca-doping content at La site was 0.08. The XRD intensity ratio method combined with the measurement of electrical conductivity offers us a useful way to determine the element doping or deficiency content and this interesting method may be applied in other materials.

Acknowledgments

This work is supported by Research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201318) and Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (No. 13KJB430023);

References

[1] C. Zuo, S. Zha, M. Liu, M. Hatano, M. Uchiyama, $Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\delta}$ as an electrolyte for low-temperature solid-oxide fuel cells, Advanced Materials 18 (2006) 3318–3320.

[2] K.D Kreuer, Proton-conducting oxides, Annual Review of Materials Research 33 (2003) 333–359.

[3] H. Iwahara, H. Uchida, K. Morimoto, High-temperature solid electrolyte fuel-cells using perovskite-type oxide based on $BaCeO_3$, Journal of the Electrochemical Society 137 (1990) 462–465.

[4] Y. Du, A.S. Nowick, Galvanic cell measurements on a fast proton conducting complex perovskite electrolyte, Solid State Ionics 91 (1996) 85–91.

[5] N. Bonanos, K.S. Knight, B. Ellis, Perovskite solid electrolytes: structure, transport properties and fuel cell applications, Solid State Ionics 79 (1995) 161.

[6] S. Gopalan, A.V. Virkar, Thermodynamic stabilities of $SrCeO_3$ and $BaCeO_3$ using a molten salt method and galvanic cells technical papers, Journal of The Electrochemical Society 140 (1993) 1060.

[7] J.A. Labrincha, J.R. Frade, F.M.B. Marques, Protonic conduction in $La_2Zr_2O_7$-based pyrochlore materials, Solid State Ionics 99 (1997) 33.

[8] T. Omata, K. Okuda, S. Tsugimoto, S. Otsuka-Yao-Matsuo, Water and hydrogen evolution properties and protonic conducting behaviors of Ca^{2+}-doped $La_2Zr_2O_7$ with a pyrochlore structure, Solid State Ionics 104 (1997) 249.

[9] T. Omata, S. Otsuka-Yao-Matsuo, Electrical properties of proton-conducting Ca^{2+}-doped $La_2Zr_2O_7$ with a pyrochlore-type structure, Journal of the Electrochemical Society 148 (2001) E252.

[10] T. Omata, S. Otsuka-Yao-Matsuo, Infrared absorption spectra of high temperature proton conducting Ca^{2+}-doped $La_2Zr_2O_7$, Journal of the Electrochemical Society 148 (2001) E475.

[11] M.A. Subramanian, G. Aravamudan, G.V.S. Rao, Oxide pyrochlores—a review, Progress in Solid State Chemistry 15 (1983) 55.

[12] W.R. Panero, L. Stixrude, R.C. Ewing, First-principles calculation of defect-formation energies in the $Y_2(Ti,Sn,Zr)_2O_7$ pyrochlore, Physical Review B B70 (2004) 054110.

[13] Mårten E. Björketun, Christopher S. Knee, B.Joakim Nyman, Göran Wahnström, Protonic defects in pure and doped $La_2Zr_2O_7$ pyrochlore oxide, Solid State Ionics 178 (2008) 1642–1647.

[14] Ji-De Wang, Ya-Hong Xie, Zheng-Fang Zhang, Rui-Quan Liu, Zhi-Jie Li, Protonic conduction in Ca^{2+}-doped $La_2M_2O_7$ (M=Ce, Zr) with its application to ammonia synthesis electrochemically, Materials Research Bulletin 40 (2005) 1294–1302.

[15] T Omata, K Ikeda, R. Tokashiki, S. Otsuka-Yao-Matsuo, Proton solubility for $La_2Zr_2O_7$ with a pyrochlore structure doped with a series of alkaline-earth ions, Solid State Ionics 167 (2004) 389–397.

[16] A. Rabenau, Perowskite and Fluoritphasen in den Systemen ZrO_2-$LaO_{1.5}MgO$ and $ZrO_2LaO_{1.5}CaO$, Zeitschrift für Anorganische und Allgemeine Chemie 288 (1956) 221.

[17] G. Nolze, W. Kraus, PowderCell 2.0 for windows, Powder Diffraction 13 (1998) 256–259.