FLSEVIER



Contents lists available at ScienceDirect

# Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Influence of $MoO_3$ doping on structure and electrical conductivity of defect fluorite-type $Gd_2Zr_2O_7$

## Zhan-Guo Liu, Shuai Gao, Jia-Hu Ouyang\*, Xiao-Liang Xia

Institute for Advanced Ceramics, Department of Materials Science, Harbin Institute of Technology, No. 92 West Da-Zhi Street, Harbin 150001, China

#### A R T I C L E I N F O

Article history: Received 8 June 2010 Received in revised form 8 July 2010 Accepted 10 July 2010 Available online 17 July 2010

Keywords:  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$ Electrolyte Impedance spectroscopy Electrical conductivity

#### 1. Introduction

Solid oxide fuel cells (SOFCs) are generally considered as a clean, efficient and silent technology with a variety of potential applications [1]. Typically, SOFCs consist of an ionic conducting electrolyte and mixed ionic and electronic conducting electrodes (cathode and anode). The conventional electrolyte is 8 mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (YSZ), and the anode is Ni-YSZ cermets and cathode is La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> oxide, respectively [2-4]. However, unwanted chemical reactions generally take place at the cathode/electrolyte interface when SOFCs are operated at high temperatures for a long time. It will generate insulating La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and SrZrO<sub>3</sub> at the interface, which may have a detrimental effect on SOFCs performance [5,6]. In last several decades, great efforts can be found on improving the electrical conductivity of solid electrolytes [7–9]. It is well known that the electrical conductivity of solid electrolytes is affected by a lot of factors such as microstructure, ionic radius and valence of doping elements, and oxygen vacancy concentration, etc. [10-12]. There is a great deal of interest in the reducing the operating temperature of SOFCs. Complex oxides with the  $A_2B_2O_7$ -type structure, where A is a trivalent rare-earth element and B represents a tetravalent transition metal element, show an excellent electrical properties owing to high compositional diversity, structural flexibility and intrinsic concentration of oxygen vacancies [13,14]. van Dijk et al. [15,16] prepared  $Gd_xZr_{1-x}O_{2-x/2}$  (0.2 < x < 0.6) ceramics,

### ABSTRACT

In this paper, we report the preparation, structure and electrical conductivity of MoO<sub>3</sub>-doped zirconates with a nominal chemical formula of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  (x = 0, 0, 1, 0.2). X-ray diffraction measurements indicate that  $Gd_2Zr_2O_7$  exhibits a defect fluorite-type structure, and  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  (x = 0.1, 0.2) have a single phase of pyrochlore-type structure. The alternating current (AC) impedance measurements show that the electrical conductivity of  $Gd_2(Zr_{1-x}Nb_x)_2O_{7+2x}$  ceramics obeys the Arrhenius equation, and gradually increases with increasing temperature from 673 to 1173 K. The activation energy and pre-exponential factor for electrical conductivity gradually decrease with the increase of MoO<sub>3</sub> content.  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics are oxide-ion conductors in the oxygen partial pressure range of  $1.0 \times 10^{-4}$  to 1.0 atm at all test temperature levels. The electrical conductivity of defect fluorite-type  $Gd_2Zr_2O_7$  is not improved by MoO<sub>3</sub> doping.

© 2010 Elsevier B.V. All rights reserved.

and found that the stoichiometric Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> had a maximum in ionic conductivity and a minimum in activation energy at temperatures between 773 and 1023 K. Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> ceramics doped with different cations at A sites were widely investigated as potential solid electrolytes for SOFCs [17-22]. Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> doped with 5 and 10 mol% Sr showed a higher electrical conductivity than undoped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in the temperature range of 773–973 K [17]. A significant increase in electrical conductivity was found by suitable substitution of Sm or Nd at the Gd site in  $Gd_2Zr_2O_7$  ceramic [18,19]. However, the electrical conductivity of  $(Gd_{1-x}La_x)Zr_2O_7$  $(0 \le x \le 1.0)$  ceramics was almost La-content independent from 773 to 1023 K [5,6]. For  $(Gd_{1-x}Yb_x)_2Zr_2O_7$  ( $0 \le x \le 1.0$ ) ceramics, the electrical conductivity gradually decreases with the increase of Yb content at identical temperature levels [20]. Moon and Tuller [21] found that Gd<sub>2</sub>(Zr<sub>0.9</sub>Ti<sub>0.1</sub>)<sub>2</sub>O<sub>7</sub> had the highest electrical conductivity in  $Gd_2(Zr_{1-x}Ti_x)_2O_7$  ( $0 \le x \le 1.0$ ) ceramics, and the electrical conductivity was comparable to YSZ at identical temperature levels.

To the best of our knowledge, there is no report on structure and electrical conductivity of MoO<sub>3</sub>-doped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in the open literatures. It is interesting to study the influence of the substitution of hexavalent Mo at the Zr site on the structure and electrical conductivity of Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> ceramic. In this work, the preparation, structure and electrical conductivity of Gd<sub>2</sub>(Zr<sub>1-x</sub>Mo<sub>x</sub>)<sub>2</sub>O<sub>7+2x</sub> (x=0, 0.1, 0.2) ceramics were investigated in detail.

#### 2. Experimental

Zirconate ceramics with a nominal chemical formula of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  (x=0, 0.1, 0.2) were prepared by a conventional solid-state reaction method in

<sup>\*</sup> Corresponding author. Tel.: +86 451 86414291; fax: +86 451 86414291. *E-mail address:* ouyangjh@hit.edu.cn (J.-H. Ouyang).

<sup>0925-8388/\$ -</sup> see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2010.07.101



**Fig. 1.** XRD patterns of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics sintered at 1973 K for 10 h in air: (a) in  $2\theta$  range of  $10-70^{\circ}$ ; (b) (3 1 1)<sub>F</sub>/(6 2 2)<sub>Py</sub> peak in  $2\theta$  range of 56.5–59.5°.

air using stoichiometric amounts of Gd<sub>2</sub>O<sub>3</sub> (Grirem Advanced Materials Co. Ltd., China; purity  $\geq$  99.99%), ZrO<sub>2</sub> (Dongguan SG Ceramics Technology Co. Ltd., China; purity  $\geq$  99.98) and MoO<sub>3</sub> (Shanghai Colloid Chemical Plant, China; purity  $\geq$  99.5%). The powders were mechanically mixed for 24 h at rotating speed of 300 rpm using zirconia ball and absolute ethyl alcohol as milling media. The mixed powders were dried and then pressed into pellets using a uniaxial stress. Subsequently, the pellets were further compacted by an isostatic pressure of 280 MPa for 5 min. The pressed pellets were measured by the Archimedes principle with an immersion medium of deionized water. The phase structure of sintered samples was characterized by an X-ray diffractometer (Rigaku D/Max 2200VPC, Japan) with Cu K $\alpha$  radiation at a scan rate of 4°/min. A step scan procedure (0.02°/2 $\theta$  step, time per step 3 s) on the diffraction peaks of (3 1 1)<sub>F</sub>/(62 2)<sub>Py</sub> was recorded to determine the evolution of X-ray spectrum.

The impedance measurements were performed on sintered pellets (~1 mm in thickness, ~8 mm in diameter) in air using platinum electrodes. Platinum paste was applied on both sides of the sintered pellets, and cured at 1223 K for 2 h in air to remove the organic binders. The alternating current (AC) impedance spectra were obtained using an impedance/gain-phase analyzer (Solartron<sup>TM</sup> SI 1260, UK). Impedance measurements were conducted on heating from 673 to 1173 K in a frequency range from 2 MHz to 200 Hz with an increment interval of 50 K. The impedance spectra were also measured in an oxygen partial pressure  $p(O_2)$  range of 1.0 × 10<sup>-4</sup> to 1.0 atm. Software equivalent circuit Zview 3.1c was used to analyze the AC impedance data.

#### 3. Results and discussion

Fig. 1 shows the XRD patterns of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics sintered at 1973 K for 10 h in air. From Fig. 1(a),  $Gd_2Zr_2O_7$  ceramic

Relative densities of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics sintered at 1973 K for 10 h in air.

Ceramic materials	Relative density (%)
$\begin{array}{l} Gd_2Zr_2O_7\\ Gd_2(Zr_{0.9}Mo_{0.1})_2O_{7.2}\\ Gd_2(Zr_{0.8}Mo_{0.2})_2O_{7.4} \end{array}$	97.3 96.5 96.0

exhibits a defect fluorite-type structure, and  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$ (*x*=0.1, 0.2) ceramics have a pyrochlore-type structure, which is characterized by the presence of typical superstructure diffraction peaks at the  $2\theta$  values of about  $14^{\circ}$  (111),  $28^{\circ}$  (311),  $37^{\circ}$ (331),  $45^{\circ}$  (511) and  $51^{\circ}$  (531) using Cu K $\alpha$  radiation [22–24]. No other phases are identified from Fig. 1(a). The XRD patterns of (311)<sub>F</sub>/(622)<sub>Py</sub> peak for  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics are shown in Fig. 1(b), which indicates that these peaks gradually shift to the high angle region with the increase of MoO<sub>3</sub> content. The MoO<sub>3</sub>-doped  $Gd_2Zr_2O_7$  can be simply expressed using the defect equilibrium reaction as:

$$MoO_3 \stackrel{Gd_2Zr_2O_7}{\longrightarrow} Mo_{7r}^{\bullet\bullet} + O_i'' + 2O_0$$
(1)

where  $Mo_{Zr}^{\bullet,o}$ ,  $O_i''$  and  $2O_o$  represent a hexavalent Mo cation at a tetravalent Zr cation site, an oxygen anion at the interstitial site and two oxygen anions on regular oxygen anion sites in the crystal structure, respectively.

In the  $A_2B_2O_7$  system, the phase structure is mainly governed by the ionic radius ratio of  $r(A^{3+})/r(B^{4+})$ . The stability of pyrochlore-type structure in zirconates is limited to the range of  $1.46 \le r(A^{3+})/r(B^{4+}) \le 1.78$  at an atmospheric pressure [14]. The ionic radius of Gd<sup>3+</sup> is 0.1053 nm in eightfold coordination, and the ionic radius of Zr<sup>4+</sup> and Mo<sup>6+</sup> is 0.072 and 0.059 nm in the sixfold coordination, respectively [25]. The value of  $r(A^{3+})/r(B^{4+})$  is equal to 1.46 for Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, and Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> shows a defect fluorite-type structure owing to high sintering temperature of 1973 K used in this work, which is higher than the phase transition temperature (1803 K) of  $Gd_2Zr_2O_7$  [26]. For  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  (x=0.1, 0.2) ceramics in this work, the values of  $r(A^{3+})/r(B^{4+})$  are clearly larger than 1.46 since the ionic radius of  $Mo^{6+}$  is smaller than that of  $Zr^{4+}$ , and therefore  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  (x = 0.1, 0.2) ceramics exhibit a pyrochlore-type structure. Table 1 presents the relative densities of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics sintered at 1973 K for 10 h in air. It shows that  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics have a high relative density of 96.0-97.3%.

Fig. 2 shows typical impedance plots of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$ ceramics at 723 K in air. The contributions due to grain and grainboundary effects are obviously observed at high and low-frequency regions. In the ideal case, the frequency response of electrical conductivity of polycrystalline electrolytes can be modeled by a resistor-capacitor (RC) pair in parallel. However, in the present case, in place of capacitor a constant phase element (CPE) is required to model the experimental data [27], as shown in Fig. 2, respectively. From fitted results, for  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  (x=0, 0.1, 0.2) ceramics, the capacitance for the high-frequency semicircles at 723 K in air is determined to be  $2.08 \times 10^{-10}$  F cm<sup>-1</sup>,  $2.85 \times 10^{-10} \,\text{F}\,\text{cm}^{-1}$  and  $3.17 \times 10^{-10} \,\text{F}\,\text{cm}^{-1}$ , respectively, while the low-frequency semicircles show capacitance at 723 K in air is  $5.04 \times 10^{-7} \,\mathrm{F \, cm^{-1}}$ ,  $1.02 \times 10^{-7} \,\mathrm{F \, cm^{-1}}$ , and  $6.91 \times 10^{-8} \,\mathrm{F \, cm^{-1}}$ , respectively. These values are typical for the grain and grainboundary contributions in solid electrolyte materials. The electrical resistance value of each composition of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$ ceramics, R, is determined from the intercept of the corresponding low-frequency semicircle on the Z' axe [27]. The electrical conductivities of  $Gd_2(Zr_{1-x}Mo_x)_2O_{7+2x}$  ceramics are calculated from the values of resistance at corresponding temperatures and the geometrical dimensions of the measured samples.

Download English Version:

https://daneshyari.com/en/article/1617922

Download Persian Version:

https://daneshyari.com/article/1617922

Daneshyari.com