Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 583–588

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Thermal expansion and fracture toughness of $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=La, Sm, Dy, Er) ceramics

Lei Guo[a,b,c,*], Yu Zhang[a,b], Xiaoxiang Zhao[a,b], Caimei Wang[a,b], Fuxing Ye[a,b,c]

[a]School of Materials Science and Engineering, Tianjin University, China
[b]Tianjin Key Laboratory of Advanced Joining Technology, Tianjin University, China
[c]Key Lab of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, No. 92, Weijin Road, Tianjin 300072, China

Received 6 June 2015; received in revised form 26 August 2015; accepted 27 August 2015
Available online 5 September 2015

Abstract

$(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ and pure $RE_2Zr_2O_7$ (RE=La, Sm, Dy, Er) compounds were synthesized by a chemical-coprecipitation and calcination method, and their phase structure, thermal expansion behavior and fracture toughness were investigated. Compared with pure $RE_2Zr_2O_7$, $(La_{0.9}Sc_{0.1})_2Zr_2O_7$ and $(Sm_{0.9}Sc_{0.1})_2Zr_2O_7$ exhibited larger lattice parameters mainly due to the presence of Sc^{3+} interstitial ions, while $(Dy_{0.9}Sc_{0.1})_2Zr_2O_7$ and $(Er_{0.9}Sc_{0.1})_2Zr_2O_7$ had smaller lattice parameters, might attributable to the substitution of Sc^{3+} for RE^{3+}. With the addition of 10 mol% Sc_2O_3, the thermal expansion coefficients of $La_2Zr_2O_7$ and $Sm_2Zr_2O_7$ were obviously enhanced, while those of $Dy_2Zr_2O_7$ and $Er_2Zr_2O_7$ decreased, which was considered to have close relationship with the solid-solution mechanisms of Sc_2O_3 in $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$. 10 mol% Sc_2O_3 doping benefited the fracture toughness of $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=La, Sm, Dy, Er), which could be attributed to the increased cohesive energy due to the lattice distortion.

Keywords: Ceramics; $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$; Phase structure; Thermal expansion coefficients; Fracture toughness

1. Introduction

Rare earth zirconates ($RE_2Zr_2O_7$, RE=rare earth) have attracted much attention because of their interesting chemical and physical properties, which render them suitable for applications such as nuclear waste forms, solid electrolytes and thermal barrier coatings (TBCs) [1–3]. $RE_2Zr_2O_7$ has ordered pyrochlore structure or defect fluorite structure, which mainly depends on the radius ratio of RE^{3+} and Zr^{4+}. For $RE_2Zr_2O_7$ with pyrochlore structure, the formula can be written as $RE_2Zr_2O_6O'$, the RE^{3+} ions occupy 16d sites, the Zr^{4+} ions are incorporated at 16c sites, the O^{2-} ions occupy the 48f sites, and the O'^{2-} ions occupy 8b sites, while 8a sites are unoccupied [4,5]. For $RE_2Zr_2O_7$ with defect fluorite structure, all cations have similar kind of chemical environment, and the O^{2-} ions get only one crystallographic position; thus the formula can be written as $AO_{1.75}$ [6,7].

The applications of $RE_2Zr_2O_7$ mainly involve high-temperature processes, so the thermal expansion compatibility between these materials and the components in the device is essential for alleviating the thermal expansion mismatch stress [8,9]. The components in the device usually have large TECs, for example, the TECs of the bond coat in a TBC system of gas turbine fall in the range of $(16–18)\times10^{-6}\,K^{-1}$ [10,11]. However, $RE_2Zr_2O_7$ materials have relatively lower TECs, in the range of $(8–11)\times10^{-6}\,K^{-1}$ from 298K to 1500 K [12]. Therefore, large thermal stress would be generated in the system during thermal cycling, which could lead to the failure of the whole device. Besides the thermal expansion compatibility, high fracture toughness is also desirable for materials

*Corresponding author at: School of Materials Science and Engineering, Tianjin University, China. Tel.: +86 22 2740 6261; fax: +86 22 2740 7022.
E-mail address: glei028@tju.edu.cn (L. Guo).

http://dx.doi.org/10.1016/j.ceramint.2015.08.151
0272-8842/

used as TBCs, solid electrolytes and other applications [13,14]. However, the toughness of $RE_2Zr_2O_7$ is relatively low due to lack of energy dissipative mechanisms, which largely hinders their wide application [15,16].

In order to enlarge the TECs and improve the fracture toughness of $RE_2Zr_2O_7$, many attempts have been made. Kutty et al. have reported that the TECs of $RE_2Zr_2O_7$ pyrochlores increase with the decrease of RE^{3+} radius [12]. Ouyang et al. have found that Gd_2O_3 doping can enhance the TECs of $Sm_2Zr_2O_7$ and $Nd_2Zr_2O_7$, but the magnitude of the enhancement is limited when the doping content is low [17,18]. Qu et al. have found that substituting Sm^{3+} with smaller Mg^{2+} in $Sm_2Zr_2O_7$ leads to a significant enhancement of TECs [19]. Additionally, it has been found that doping smaller Ti^{4+} to $Gd_2Zr_2O_7$ can improve the fracture toughness [20]. In our previous study, it has been found that Sc_2O_3 doped $Nd_2Zr_2O_7$ or $Gd_2Zr_2O_7$ exhibits enhanced thermal expansion and improved fracture toughness, and the optimal Sc_2O_3 content is around 10 mol% [21,22]. The solid-solution mechanism of Sc^{3+} in $Nd_2Zr_2O_7$ and $Gd_2Zr_2O_7$ lattices was discussed in detail. Since Sc^{3+} ions have small radius, they prefer to occupy the interstitial sites of host pyrochlore, accompanied by the formation of extra oxygen ions. This would reduce the crystal energy and increase the cohesive energy, resulting in the enlarged TECs and the improved fracture toughness. However, high Sc_2O_3 doping leads to reduced TECs and has negligible effect on improving the toughness, mainly attributable to Sc^{3+} substituting for Nd^{3+} or Gd^{3+} [21,22].

In $RE_2Zr_2O_7$ series, apart from $Nd_2Zr_2O_7$ and $Gd_2Zr_2O_7$, other compounds have also been explored for high-temperature applications [19,23,24]. Also, the main obstacle hindering their wide application is the low TEC and the poor fracture toughness. Inspired by our previous work, Sc_2O_3 may be still an excellent dopant for all the $RE_2Zr_2O_7$ series, which could enhance their TECs and toughness. In the present study, 10 mol% Sc_2O_3 was doped in $RE_2Zr_2O_7$ (RE=La, Sm, Dy, Er) in order to enlarge the TECs and improve the toughness. $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=La, Sm, Dy, Er) ceramics were produced by a chemical co-precipitation and calcination method, and their phase structure, thermal expansion behavior and facture toughness were investigated. The effects of Sc_2O_3 doping on the TECs and toughness were discussed based on the solid-solution mechanisms of Sc_2O_3 in $RE_2Zr_2O_7$. Additionally, $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=Nd, Gd) and $RE_2Zr_2O_7$ (RE=La, Nd, Sm, Gd, Dy, Er) ceramics were also produced, and the data was collected for comparison.

2. Experimental procedure

$RE_2Zr_2O_7$ and $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=La, Nd, Sm, Gd, Dy, Er) powders were synthesized by the chemical co-precipitation and calcination method. La_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Sc_2O_3 (purity 99.99%) and $ZrOCl_2 \cdot 8H_2O$ (purity 99.95%) were used as raw materials. RE_2O_3 powders were weighted and dissolved in nitric acid, $ZrOCl_2 \cdot 8H_2O$ was dissolved in distilled water, and then the solutions were mixed in appropriate proportion and stirred for 30 min. The mixed solutions were slowly added to excess ammonia water (pH > 12) with mechanical and ultrasonic agitating to obtain gel-like precipitates, followed by filtering and washing with distilled water several times until pH 7 was reached. The washed precipitates were dried at 120 °C for 20 h and then calcined at 800 °C for 5 h for crystallization. The acquired powders were cold pressed at ~250 MPa and then sintered at 1650 °C for 10 h in air to obtain bulk materials for TEC and mechanical properties measurements.

Phase structure of the sintered bulks was identified by X-ray diffraction (XRD, Bruker D8 Advanced, CuKα radiation). The TECs of the bulks were determined using a high-temperature dilatometer (Netzsch DIL 402E, Germany). Values were continuously recorded from room temperature to 1500 °C at a scanning rate of 5 °C/min during heating as well as during cooling, and they were corrected using the standard sapphire sample. To avoid systematic errors, the specimens were fabricated to the same dimensions of 4 mm × 4 mm × 25 mm.

Mechanical properties of the ceramics were measured by the indentation method. Although this method for determining mechanical properties of a material is uncertain, it can be used for the qualitative comparison of the samples produced by similar procedure [25]. Therefore, the indentation method was used in this study to reveal the variation trend of the mechanical properties. Vickers hardness (HV) of the polished specimens was measured at the load of 200 g using a microhardness tester (HV-1000A, China). At least 10 valid indentations were made for each sample. The indentation and crack patterns were used to calculate the fracture toughness (K_{IC}) using the following equation [26].

$$K_{IC} = 0.16 H_v a^2 c^{-3/2} \quad (1)$$

Where a is the half length of the indent diagonal, c is the half-crack length measured from the middle of the indent to the tip of the crack.

3. Results and discussion

Fig. 1a shows the XRD patterns of $RE_2Zr_2O_7$ and $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=La, Sm, Dy, Er) ceramics; the data of $RE_2Zr_2O_7$ and $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=Nd, Gd) ceramics is from Refs. [21,22] for comparison. Be similar to $Nd_2Zr_2O_7$ and $Gd_2Zr_2O_7$, $RE_2Zr_2O_7$ (RE=La, Sm) ceramics exhibit pyrochlore phase, which is distinguished from fluorite phase by the presence of superlattice peaks at $2\theta \approx 28°$ (311), 37° (331), 45° (511) [25,27]. These superlattice peaks can also be detected in $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$ (RE=La, Sm) ceramics, indicating the presence of pyrochlore phase. It can be seen that Sc_2O_3 doping in $RE_2Zr_2O_7$ (RE=La, Nd, Sm, Gd) results in the XRD peaks of pyrochlore phase shifting toward lower angles, suggesting that the unit cell of $RE_2Zr_2O_7$ pyrochlore expands after Sc_2O_3 doping. A second phase (fluorite phase) can be found in $(La_{0.9}Sc_{0.1})_2Zr_2O_7$, mainly attributable to the large size mismatch between La^{3+} and Sc^{3+}. This indicates that the solubility of Sc_2O_3 in $La_2Zr_2O_7$ is less than 10 mol%. In the XRD patterns of $RE_2Zr_2O_7$ and $(RE_{0.9}Sc_{0.1})_2Zr_2O_7$