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Preparation and thermophysical properties of $(Sm_{1-x}Er_x)_2Ce_2O_7$ oxides for thermal barrier coatings

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ABSTRACT

$(Sm_{1-x}Er_x)_2Ce_2O_7$ ceramics were synthesized by sol–gel method and sintered at 1600 °C for 10 h in air. The influence of Er_2O_3-substitution on the phase structure and thermophysical properties of $Sm_2Ce_2O_7$ was investigated. The phase structures of these ceramics were identified by X-ray diffraction showing that all synthesized ceramics have fluorite-type structure. The measurements for thermophysical properties of these ceramics show that their thermal conductivities and thermal expansion coefficients remarkably decreased through Er-substitution. However, the thermal expansion coefficients were higher than that of YSZ and their thermal conductivities were much lower than that of 8YSZ. The excellent thermophysical property implies that these solid solutions are potential materials for the ceramics layer in thermal barrier coatings.

1. Introduction

To permit higher operating temperatures and hence, greater efficiency, metallic-alloy turbine blades are coated with a thin protective layer of refractory oxide. Yttria-stabilized zirconia (YSZ) in the metastable tetragonal-prime (t') phase has long been the material of choice for thermal barrier coating (TBC) applications largely due to its durability and low thermal conductivity [1]. However, at high operating temperature beyond 1200 °C, the relatively porous YSZ coatings are prone to sintering which increases thermal conductivity and makes them less effective. To further increase the operating temperature of turbine engines, new TBC ceramic materials with significantly increased phase stability, low lattice and radiation thermal conductivity, high thermal expansion coefficient and improved sintering resistance are urgently needed to provide vital thermal protection for hot-section components such as combustor liner, turbine blades, turbine vanes, etc. at gas temperature exceeding 1650 °C in harsh combustion environments [2,3].

In recent years, complex oxides with $A_2B_2O_7$ composition, where A represents trivalent rare-earth elements and B denotes tetravalent transition metal elements (Ti, Zr, Hf, Ce, Sn, etc.), exhibit a pyrochlore-type structure or a defect fluorite-type structure which is mainly governed by the radii of A- and B-site cations. They have a wide variety of attractive physical and chemical properties such as high melting point, high thermal expansion coefficient, low thermal conductivity, high thermal stability, high radiation stability and high electrical conductivity. These properties make them suitable for extensive applications such as thermal barrier coatings, solid electrolytes, nuclear waste host materials and high-temperature heating elements [4–8]. They are especially, potential thermal barrier coating materials due to their excellent thermophysical properties. Increasing the operating temperature of key metallic components in advanced turbine engines has attracted great interest worldwide [9–12].

The rare earth zirconates with general formula $Ln_2Zr_2O_7$ with pyrochlore structure or defect fluorite-type structure have been regarded as the most potential ceramic materials for thermal barrier coatings. The thermal conductivities of $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Eu, Gd, Dy, etc) ceramic materials are in the range from 1.1 to 1.2 W/m K, which are much lower than that of YSZ. Because of their promising thermophysical properties, efforts have been made to investigate the co-doped $Ln_2Zr_2O_7$ ceramics with one or more metal oxides in recent years [13–16]. However, their relative low

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thermal expansion coefficients (CETs) can result in high thermal stresses in TBC applications which are very harmful for TBC's performance.

The rare earth hafnates with $Ln_2Hf_2O_7$ type show typical pyrochlore structure [17]. However, their thermophysical properties were mainly studied by numerical simulation; further report on the thermophysical property of $Ln_2Hf_2O_7$ series was relatively less [18,19]. Thermophysical properties reported by Q. Z. Xue revealed that thermal conductivities of $Ln_2Sn_2O_7$ series were higher than that of 8YSZ and their thermal expansion coefficients were lower than that of 8YSZ [11]. These results are contrary to the requirements of thermal barrier coatings.

In recent years, rare earth cerium oxides with $Ln_2Ce_2O_7$ type (Ln = rare earth elements) have attracted considerable attention [20]. Thermophysical properties of several interesting rare-earth cerium oxides, such as $La_2Ce_2O_7$, $Nd_2Ce_2O_7$, $Gd_2Ce_2O_7$, $Sm_2Ce_2O_7$, $Er_2Ce_2O_7$ and $Yb_2Ce_2O_7$, have been reported. The thermal conductivities of unitary $Ln_2Ce_2O_7$ ceramics vary from 1.3 to 2.3 $W\,m^{-1}\,K^{-1}$ in certain temperature range, and their thermal expansion coefficients are significantly greater than 8YSZ at high temperature [21–24]. In recent studies, it has been reported that materials with low thermal conductivity and higher thermal expansion coefficient can be prepared by substitution or co-substitution with one or more rare-earth oxides (Yb_2O_3, Gd_2O_3, La_2O_3, Sm_2O_3 and Nd_2O_3) due to defect cluster formation which indicates that the thermal conductivity of $Ln_2Ce_2O_7$ ceramics may be reduced further by substitution with other elements in the cation of Ln or Ce [5,7]. Clarke and co. workers also point out that substituted cation, especially the atom with large atomic weight, at site A or B creates mass disorder on the cation sublattice which results in the lowering of thermal conductivity. Meanwhile, the thermal expansion coefficient maybe improved [25].

Our previous study has shown that incorporation of Gd_2O_3 into $La_2Ce_2O_7$ decreases the thermal conductivity [26]. However, no data on phase structure and thermophysical properties of samarium- erbium oxides have been reported up to now. In the present study, the $(Sm_{1-x}Er_x)_2Ce_2O_7$ ceramic powders were synthesized by sol–gel method. They were then pressureless-sintered at 1600 °C in air. The structural evolution and thermophysical properties of $(Sm_{1-x}Er_x)_2Ce_2O_7$ ceramics were analysed.

2. Experiment

Samarium oxide, erbium oxide and cerium oxide powders (Rare-Chem Hi-Tech Co., Ltd., Huizhou, China, purity ≥ 99.9%) were chosen as raw materials. Rare earth oxides powders were heated at 900 °C for 2 h before further use. Ceramic powders of $(Sm_{1-x}Er_x)_2Ce_2O_7$ were synthesized by sol–gel method as introduced in reference [26]. The obtained powders were compacted into a disk form under uniaxial pressure of 50 MPa followed by cold isostatic pressing with 150 MPa. Finally, the bulks were pressureless-sintered at 1600 °C for 10 h in air.

The phase structure of each ceramic was characterized by X-ray diffraction (XRD, X'Pert PRD MPD, The Netherlands) with Cu Kα radiation at a scan rate of 4°/min. The bulk density of the samples was measured by the Archimedes method with an immersion medium of deionized water. The theoretical density of each composition was calculated using lattice parameters acquired from XRD results and the molecular weight in an elementary cell. The morphology of surface of polished and thermally etched pellet was observed using scanning electron microscopy (SEM, Model Hitachi S-4800, Japan). Qualitative X-ray element analysis of various phases was carried out using SEM equipped with energy dispersive spectroscopy (EDS).

The specific heat capacities (C_p) were determined as a function of temperature from the chemical compositions of $(Sm_{1-x}Er_x)_2Ce_2O_7$ and the heat capacity data of the constituent element (O, Er, Sm and Ce) obtained from references [27,28] in conjunction with the Neumann–Kopp rule. The linear thermal expansion coefficients of these ceramics were determined with high-temperature dilatometer (Netzsch DIL402C/7, Germany) from ambient to 1000 °C at a heating rate of 5 °C/min in an argon atmosphere. The size of samples is approximately 5 × 5 × 25 mm. Thermal diffusivity testing of these ceramics was carried out using laser flash apparatus (Netzsch LFA427, Germany) in an argon atmosphere. Cylindrical disc-shaped sample was about 12.7 mm in diameter and about 1.2 mm in thickness. Each sample was grounded so that both surfaces were coplanar. In order to avoid any transmission of the laser beam through the samples, both the front and back faces of the samples were coated with a thin layer of graphite. The thermal diffusivity measurements were made at 200 °C intervals from 200 to 1000 °C. The thermal diffusivity measurement of these samples was carried out three times at each temperature. The thermal conductivity (k) of the specimen was calculated by Eq. (1) with specific heat capacity (C_p), density (ρ) and thermal diffusivity (λ) as follows:

$$k = \lambda \times \rho \times C_P \qquad (1)$$

because the sintered specimen was not fully dense, the measured thermal conductivity was modified for the actual value k_0 using Eq. (2), where φ is the fractional porosity and the coefficient 4/3 is used to eliminate the effect of porosity on actual thermal conductivity [22].

$$\frac{k}{k_0} = 1 - \frac{4}{3}\varphi \qquad (2)$$

3. Results and discussion

3.1. XRD

Fig. 1 shows the room temperature X-ray diffraction patterns of $(Sm_{1-x}Er_x)_2Ce_2O_7$ ceramics sintered at 1873 K for 10 h in air. It can be seen that $(Sm_{1-x}Er_x)_2Ce_2O_7$ ceramics have single phase structure. All patterns are coincident with the standard spectrum of CeO_2, and no evidence of pyrochlore phase can be found. The peaks of $Sm_2Ce_2O_7$ at 2θ = 28.3, 32.79, 47.22, 55.9, 58.7 and 75.9° corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (3 3 1) reflections of fluorite structure, respectively. The absence of diffraction peaks around 36.9 and 44.5° in their XRD patterns are always considered as the characteristic of the fluorite structure

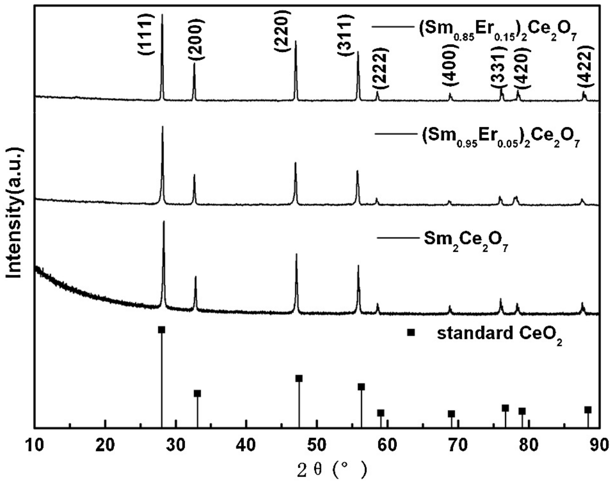

Fig. 1. XRD patters of $(Sm_{1-x}Er_x)_2Ce_2O_7$ bulk ceramics.