Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Characterization of $Ln_4Al_2O_9$ (Ln = Y, Sm, Eu, Gd, Tb) rare-earth aluminates as novel high-temperature barrier materials

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ARTICLE INFO

Keywords:
Thermal barrier coatings
Cuspidine-type rare-earth aluminates
X-ray powder diffraction
Thermal diffusivity
Thermal expansion coefficient

ABSTRACT

A family of cuspidine-type rare-earth (RE) aluminates with the general formula $Ln_4Al_2O_9$ (Ln = Y, Sm, Eu, Gd, Tb) was prepared for potential use as thermal-barrier coating (TBC) materials with appropriate properties. Various trivalent lanthanides were applied to tailor the properties of the oxides for use as ceramic top coat (TC) materials intended for high-temperature applications. Following various heat treatments, the X-ray diffraction (XRD) results obtained demonstrated that $Eu_4Al_2O_9$ (EuAM) possessed the greatest structural stability of all the samples at 1200 and 1300 °C. Moreover, $Y_4Al_2O_9$ (YAM) had a long lifetime at 1000 °C, and was stable at 1100 °C. At 1200 °C, $Sm_4Al_2O_9$ (SmAM) and $Gd_4Al_2O_9$ (GdAM) were more stable than $Tb_4Al_2O_9$ (TbAM). However, at 300–1000 °C, the TbAM exhibited the highest thermal expansion coefficient (TEC) of all the samples. At 600 °C, the thermal diffusivity values of the five compositions were favourable, and were lower than that of yttria-stabilised zirconia (YSZ) oxides.

1. Introduction

The use of thermal barriers is vital when the operating temperature of a device is increased to increase its efficiency [1]. Conventional thermal barrier coating (TBC) systems consist of three layers, which are coated onto the alloy substrate: (i) a metallic bond coat (BC), (ii) an intermediate thermally grown oxide (TGO), and (iii) a ceramic top coat (TC). All these layers have different physical, mechanical, and thermal properties, which are strongly affected by the processing conditions [2]. The TC is the outer layer, which first has contact with the hot working gases; it is expected to thermally isolate the other TBC layers. These ceramic barriers should offer: (i) a high melting temperature, (ii) low thermal conductivity, (iii) a thermal expansion coefficient (TEC) similar to that of the underlying alloy substrate, (iv) strain tolerance, (v) morphological and structural stability at high temperatures, (vi) oxidation and corrosion resistance, and be (vii) inexpensive [3,4]. To date, the most commonly used TBC materials are 6–8% (in wt%) yttria-stabilized zirconia oxides (YSZ: Y_2O_3-ZrO_2). They possess sufficient porosity and microstructural defects, reducing their thermal conductivity and rendering them compliant in accommodating thermal strain. However, YSZ coatings undergo enhanced sintering and phase transformation at high temperatures (> 1200 °C). The decomposition of tetragonal zirconia with the formation of a monoclinic or cubic phase is usually accompanied by volume changes and extensive cracking. Hence, it is important to identify TBCs that possess all the desirable attributes of 6–8YSZ, which could be used to address the aforementioned critical issues [5–13].

Rare earth (RE) zirconate pyrochlores have received intense interest because of their low thermal conductivity and high phase stability. However, the interaction that occurs between pyrochlores and TGO may impair the durability of the system. Moreover, in a previous study on the thermochemical compatibility of $GdO_{1.5}$-ZrO_2 compositions with TGOs (Al_2O_3), a $GdAlO_3$ interphase was formed [3]. This gives a useful compositional guideline with regard to the design of TBC materials. Therefore, the use of materials based on zirconia (ZrO_2) and stabilized with rare and/or alkaline earth oxides (Pr_2O_3, Nd_2O_3, Sm_2O_3, CeO_2, CaO, MgO, etc.) as thermal barriers would be interesting. In addition, the co-doping of YSZ with trivalent RE is considered an effective method for the development of alternative ceramic materials with high phase stability and low thermal conductivity. This will be extended to non-metal dopants; recent preliminary works have shown that these fluorite-type systems are able to accommodate low levels of phosphate (up to 5 mol%) [14]. As part of the attempt to discover alternative structures, a new family of materials, derived from a cuspidine structure, with high thermal stability, has been recently reported [15,16]. Minerals of the cuspidine-oxide group can be described as having the

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https://doi.org/10.1016/j.ceramint.2018.01.225
Received 21 December 2017; Received in revised form 19 January 2018; Accepted 26 January 2018

Please cite this article as: Moran-Ruiz, A., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.01.225

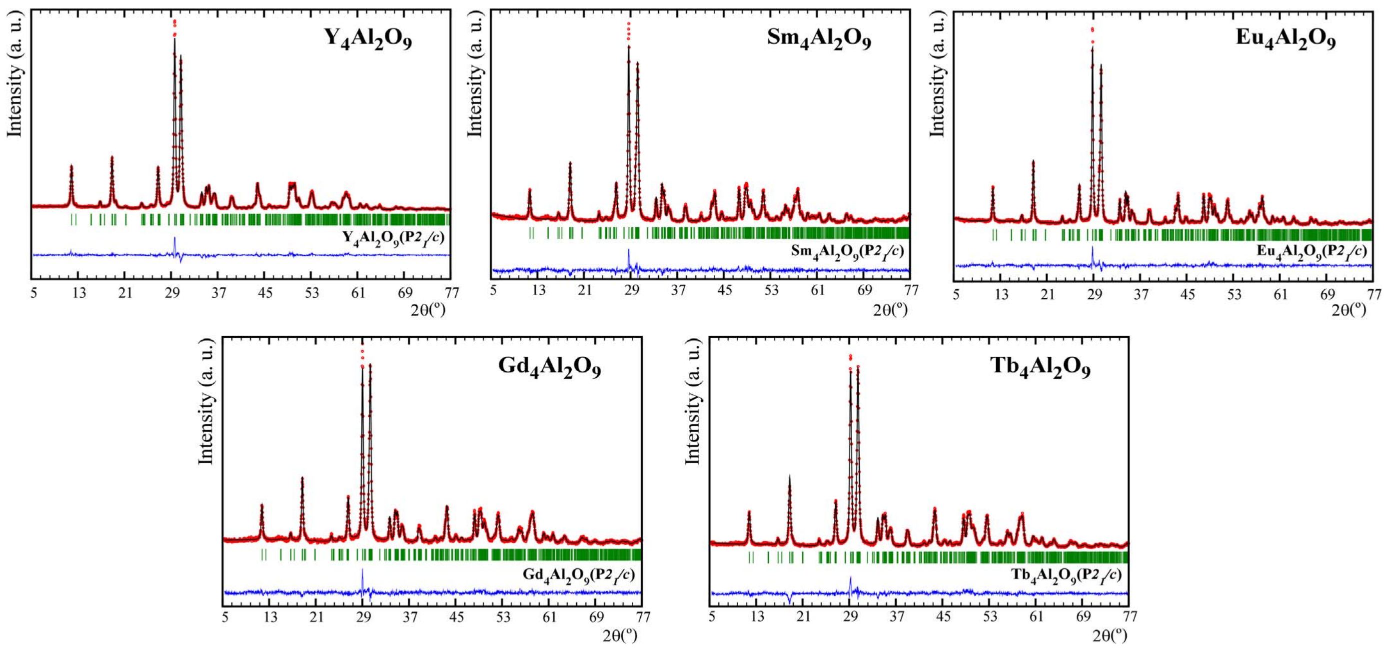

Fig. 1. Rietveld X-ray diffraction pattern refinement results obtained for the prepared $Y_4Al_2O_9$, $Sm_4Al_2O_9$, $Eu_4Al_2O_9$, $Gd_4Al_2O_9$, and $Tb_4Al_2O_9$ oxides. The circles denote the experimental results, and the upper solid line represents the calculated profile. The theoretical peak positions (vertical lines) and difference lines are shown in the bottom of each pattern.

general formula $Ln_4Al_2O_9$, where Ln is a trivalent lanthanide. The archetype compound of the cuspidine family is $Y_4Al_2O_9$ (YAM), which crystallises in the space group $P2_1/c$. According to previous studies, YAM shows a reversible thermal phase transformation, from a low-temperature monoclinic phase to a high-temperature monoclinic phase, at 1377 °C [17]. Here, we report the synthesis and characterization of new oxides based on cuspidine-type RE aluminates, $Ln_4Al_2O_9$ (Ln = Y, Sm, Eu, Gd, Tb). The combustion method was used to prepare analogues of YAM to study their microstructure, structural stability, thermal diffusivity, and thermal expansion behaviour.

2. Experimental

$Ln_4Al_2O_9$ (Ln = Y, Sm, Eu, Gd, Tb) samples were prepared via the glycine nitrate combustion (GNC) route, under identical synthetic conditions, to study the influence of various trivalent lanthanides with regard to their use as thermal barriers for high-temperature applications. The synthesis of the samples was performed using $Y(NO_3)_3{\cdot}6H_2O$ (99.8%), $Gd(NO_3)_3{\cdot}6H_2O$ (99.9%), $Eu(NO_3)_3{\cdot}5H_2O$ (99.9%), $Sm(NO_3)_3{\cdot}6H_2O$ (99.9%), $Tb(NO_3)_3{\cdot}5H_2O$ (99.9%), and $Al(NO_3)_3{\cdot}9H_2O$ (98%) as metal precursors, and glycine (> 99%) as a combustion fuel; these materials were all purchased from Aldrich. The glycine was added to obtain a fuel/oxidizer molar ratio of 1. The details of the synthesis are reported elsewhere. The resultant powders were calcined in air at 900 °C for 8 h to obtain pure samples.

All the metal contents were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES), which was performed using a Horiba Yobin Yvon Activa spectrophotometer. For this purpose, samples were dissolved using a mixture of HNO_3 and HCl, over a period of 24 h, to obtain a clear and measurable solution.

The structural analysis of the synthesized materials, and the characterization of the crystalline phases of all the samples that were heated at 1000, 1100, 1200, and 1300 °C, with isothermal hold periods of 10 h, were performed using laboratory X-ray diffraction (XRD). Data were collected at 25 °C using a Philips X´Pert-Pro diffractometer with Cu Kα radiation (λ = 1.5418 Å), over the 2θ range of 5–80°; a step size of 0.026° was used, with a dwell time of 10 s per step. A power generator was used at 40 kV and 40 mA. Full-profile Rietveld refinements were performed using the FullProf program to determine the structural parameters of the identified phases and the weight percentage of each phase within the samples. For all the samples of $Ln_4Al_2O_9$, the space group used for the refinement was $P2_1/c$ (14). In-situ high-temperature XRD analysis was performed using heating–cooling cycles at 1000 °C. In addition, powder X-ray thermo-diffraction (TDX) analysis of the obtained powders was performed. These analyses were conducted using a Bruker D8 Advance Theta-Theta diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a HTK2000 chamber with a Pt sample holder. The power generator was set to 30 kV and 20 mA. For the TDX analysis, patterns were recorded from room temperature to 1300 °C at intervals of 20 °C; the samples were scanned over the 2θ range of 20–80°, with a step size of 0.03° and a dwell time of 2 s per step.

The morphologies of the samples were determined using a scanning electron microscope (SEM, JEOL JSM-7000F). Secondary electron images were captured at 20 kV and $1.1{\cdot}10^{-11}$ A.

The $Ln_4Al_2O_9$ pellets were sintered at 1000 °C for 10 h to produce corresponding bulk samples. A laser-flash apparatus (the Netzsch LFA 457 microflash) was used to measure the thermal diffusivity, from room temperature to 600 °C, via Parker´s method; the sample size was approximately φ 12.7 × 2.5 mm. The TEC values of the bulk samples were measured using a Unitherm Model 1161 dilatometer, over the temperature range of 30–1000 °C; the dimensions of each thermal expansion specimen were approximately 1 × 3 × 7 mm.

3. Results and discussion

3.1. Phase characterization

The room-temperature XRD patterns of all the synthesized $Ln_4Al_2O_9$ oxides are shown in Fig. 1. The patterns reveal that all the samples consist of a single phase without impurities. The Rietveld fits regarding the powder XRD data were performed using the monoclinic ($P2_1/c$) space group; the same structure is observed for the mineral cuspidine. The cell volumes of these compounds (Table 1), at room temperature, increased slightly with the ionic radii of the trivalent RE elements: $Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Y^{3+}$ [18].

The results of the chemical analyses, presented in Table 1, show that there is good agreement between the analysed chemical compositions of the prepared powders and the nominal compositions.