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Luminescent rare-earth-doped transparent alumina ceramics

K. Bodišová[a,*], R. Klement[b], D. Galusek[b], V. Pouchlý[c], D. Drdlík[c], K. Maca[c]

[a] Faculty of Food and Chemical Technology, STU Bratislava, Slovakia
[b] Joint Glass Centre of the IIC SAS, TnU AD, and FChFT STU, Trenčín, Slovakia
[c] CEITEC—Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic

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ABSTRACT

Present study aims at development and characterization of transparent polycrystalline alumina ceramics doped with optically active additives exhibiting light induced emission properties. Tested materials were prepared using wet shaping technique (slip casting) followed by pressure-less sintering and hot isostatic pressing (HIP). Three different rare-earth dopants (Nd, Eu, Er-0.2 at.% with respect to Al_2O_3) were introduced into alumina in order to obtain induced light emission properties. The samples were pre-sintered using two different regimes: single step – SSP and two-step pre-sintering – TSP. Final microstructure of HIP-ed samples pre-sintered by TSS was similar to that of the SSP pre-sintered samples; any differences in the average grain size were within the range of standard deviation of the measurement. The real in-line transmittance (RIT) ranged between 8 and 34%, depending on the type of dopant and the pre-sintering regime. The highest RIT values were obtained for Er-doped alumina, the lowest for Nd-doped alumina. The RIT was correlated with the size of the alumina matrix grains and decreased with increasing average grain size of the material. Despite the similarity of microstructure and density, significantly higher RIT was determined in the samples pre-sintered with the use of the two stage regime, irrespective of the dopants used. The photoluminescence spectra of rare-earth-doped samples both in visible and NIR spectral region showed typical absorption/emission/excitation bands due to the presence of optically active Nd^{3+}, Eu^{3+} or Er^{3+} ions in the host matrix.

1. Introduction

Transparent polycrystalline alumina ceramics have been studied for decades as cheaper alternative to sapphire single crystals, for optical applications [1]. The economic and ecological benefits of such replacement are undisputed: moreover, the applications could be extended due to better mechanical properties and possibility of production of large size and complex shaped parts.

The properties (optical, mechanical, etc.) of ceramics as the polycrystalline materials, contrary to single crystals, are generally closely linked to their microstructure. Especially the optical transparency is strongly influenced by presence of pores, second phase inclusions and in the case of alumina as a birefringent material also by grain size. Therefore, the effort is focused at the preparation of dense, fine grained ceramics without second phase inclusions, which limits the choice of starting materials to high purity powders and imposes strict requirements on the proper selection and conduction of shaping and sintering methods.

Doping represents another option how to influence the final microstructure of dense alumina. Our recent work demonstrates the influence of various dopants on microstructure refinement of polycrystalline alumina in the final stage of sintering [2]. Other authors report an increase of the in-line transmittance through addition of dopants such as Zr, Y and La, mostly as a result of decreasing the average grain size of transparent alumina [3,4].

Besides the microstructure refinement, the doping with certain elements could lead to obtaining of new interesting functional properties and therefore extend the application potential of transparent alumina (dosimeters, phosphors for high-brightness LED or laser host materials). However, adding the required amount of dopant (higher than 0.1 at.% for photoluminescent materials) inevitably leads to the formation of inclusions deteriorating the transparency, making the preparation of transparent alumina with luminescence properties a challenging topic.

To the best of our knowledge, there are only few works dealing with transparent or translucent alumina doped with optically (photoluminescence) active rare earth (RE) and transition metal (TM) ions. Cr-doped transparent alumina exhibiting thermoluminescence (TL) and optically stimulated luminescence was designed as a potential TL dosimetry material [5]. Doping of alumina with

* Corresponding author.
E-mail address: katarina.bodisova@stuba.sk (K. Bodišová).

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Ti and Mg was proposed for the same purpose [6]. However, the mean grain size of prepared material is well within the micrometer size range as the result of pressure-less sintering at relatively high temperature, with adverse impact on transparency.

Penilla et al. [7]. prepared Tb^{3+} doped transparent alumina with fine-grained microstructure with 75% of total transmission at a wavelength of 800 nm and with characteristic Tb^{3+} emission by spark plasma sintering. To the best of the author's knowledge, this was the first instance when a birefringent (non-cubic) polycrystalline oxide bulk ceramic possessed both high transparency and induced light emission properties. They also suggested that only high heating and cooling rates accessible by SPS technique and operating out of thermodynamic conditions can result in achieving high concentration of dopant while maintaining the transparency.

This study is aimed at finding an alternative way for producing transparent alumina exhibiting photoluminescent properties, utilizing colloidal processing for green body preparation, followed by pre-sintering and subsequent hot isostatic pressing. Transparent alumina ceramics doped with RE elements (Nd, Eu, Er) were prepared in this way and characterized in terms of their microstructure, real in-line transmittance and photoluminescence properties.

2. Experimental

High purity 99.99% commercial alumina powder Taimicron TM-DAR, Taimei Chemicals Co., Ltd., Tokyo, Japan, with the primary particle size of 150 nm and specific surface area of 13.7 $m^2\,g^{-1}$ was used as a starting material (the values were determined by the producer from SEM micrographs and by BET analysis, respectively).

Aqueous suspensions with the solid content of 45 vol.% of Al_2O_3 were stabilized electrosterically with the use of a commercial dispersant Darvan CN. De-ionized water with electric conductivity $25 \pm 5 \times 10^{-4}$ S m^{-1} at room temperature was used as a dispersion medium. The suspensions were doped by RE elements (0.2 at.% of Nd, Eu or Er with respect to Al_2O_3). In order to ensure homogeneous distribution of dopants rare earth elements were added in the form of nanoparticles $XAlO_3$ (X = Nd, Eu or Er), which were prepared by mixing appropriate amounts of $Al(NO_3)_3{\cdot}9H_2O$ (p.a., Centralchem, Slovakia) dissolved in deionized water with RE nitrate prepared by dissolution of X_2O_3 powders (Treibacher Industrie AG, Austria) in 65% HNO_3. Citric acid dissolved in deionized water and ethylene glycol was added to the mixture of the nitrates and heated in oil bath for 2 h at 85–90 °C. The solvent was evaporated under continuous stirring. The product was dried, and calcined at 800 °C for 1 h to remove organic residua. The powder was then milled in planetary mill in order to reduce the number of aggregates. Residual aggregates were removed from diluted water suspensions by centrifugation at 800 rpm for 2 min. Only unsedimented particles were dried and used for doping.

The suspensions with added rare earth aluminates were homogenized on rollers for 24 h. 40 g of alumina milling balls with diameter 4 mm were added to 10 ml of the suspension. After homogenization the suspensions were poured into PVC dishes (S = 12.6 cm^2) and allowed to dry at ambient conditions for three days. Green bodies were then dried at 80 °C for 5 h.

The pressureless sintering experiments were carried out in an electrical furnace (Classic, Czech Republic) with $MoSi_2$ heating elements in the air. The samples were sintered up to closed porosity corresponding to 95–96% of the theoretical density. The samples were pre-sintered using two different regimes: single step pre-sintering (SSP) and two-step pre-sintering (TSP). SSP was performed by heating the samples at the rate of 20 °C min^{-1} up to the maximal temperature from the interval between 1390 and 1550 °C without isothermal dwell, with subsequent cooling at the same rate. When the two-step pre-sintering (TSP) was applied, the specimens were first heated to a temperature T1 without isothermal dwell (whereby achieving the relative theoretical density of 88–90%), and subsequently cooled down to a temperature T2 (which ranged between 1150 and 1350 °C) at the rate of 20 °C min^{-1}. The isothermal dwell at the temperature T2 was 10 h. The samples sintered to closed porosity were hot isostatically pressed (HIP ABRA Shirp, Switzerland) with maximal operating temperature 1500 °C and the pressure of 200 MPa in argon. Molybdenum heating and shielding enables sintering without carbon contamination, which is usual in furnaces with graphite heating elements.

The density of sintered specimens was determined according to the Archimedes' principle using the value of 3.997 g cm^{-3} as the theoretical density for all samples (the value was calculated from the theoretical density of Al_2O_3 and the respective rare earth oxide by the rule ox mictures).

The microstructures were examined by scanning electron microscopy on polished and thermally etched cross sections (JEOL 7600F, Jeol Ltd., Japan and Lyra 3, Tescan, Czech Republic). The mean grain size was determined using the linear intercept method using a correction factor of 1.56. Minimum of 200 grains were measured in order to obtain statistically robust set of data.

The real in-line transmission (RIT) of polished samples was measured with a non-polarized He–Ne laser (λ = 632.8 nm). The distance from the sample to the detector was 860 mm, with an opening angle of 0.5°. The real in-line transmission was measured on two to four samples in at least five different positions on each sample and was recalculated to constant thickness of 0.8 mm.

The excitation and emission fluorescence spectra of studied samples were measured using Fluorolog FL3-21 spectrometer (Horiba, Ltd., Japan) with Xe-lamp (450 W) as an excitation source. The luminescence spectra of studied samples were recorded at room temperature.

3. Results

3.1. Pre-sintering: the effect of additives on densification

The amount of dopant added to achieve relevant photoluminescent properties should be in the order of tenths of a percent, which obviously strongly influences the densification behaviour of alumina. Due to their similar chemical nature and ionic diameter, all dopants have almost the same retarding effect on densification (Fig. 1). For comparison, the densification data of alumina doped with Zr in significantly lower amount (250 ppm) are also present. The retarding effect on densification seems to slightly increase with

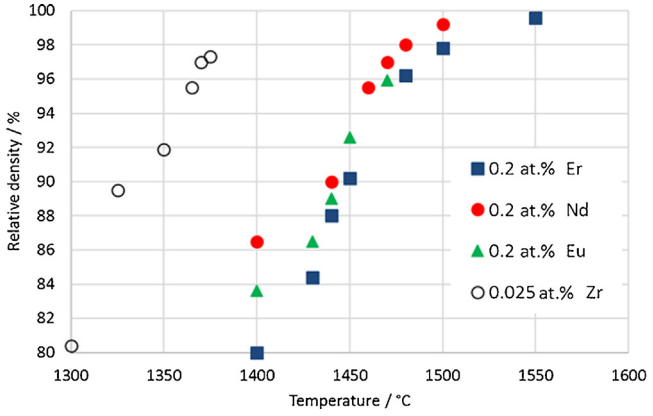

Fig. 1. Dependence of relative density on the sintering temperature (pressureless sintering).