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Luminescent Eu^{3+}-doped transparent alumina ceramics with high hardness

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ABSTRACT

The Eu^{3+}-doped transparent aluminas were prepared by wet shaping technique followed by pressureless sintering and hot isostatic pressing. The effect of dopant amount on microstructure, real in-line transmission (RIT), photoluminescence (PL) properties, hardness and fracture behaviour was studied. The RIT decreased with increasing amount of the dopant. The PL emission spectra of Al_2O_3:Eu^{3+} ceramics exhibited predominant red light emission with the highest intensity (under 394 nm excitation) for material containing 0.125 at.% of Eu^{3+} and colour coordinates (0.645, 0.355) comparable with commercial red phosphors. The doping resulted in hardness increase from 26.1 GPa for undoped alumina to 27.6 GPa for Eu-doped sample. The study of fracture surfaces showed predominantly intergranular crack propagation micro-mechanism.

1. Introduction

Corundum (α-Al_2O_3) can be under certain conditions an optical material of great technological importance due to its high optical transparency in a wide spectral range from ultraviolet to near-infrared combined with excellent thermal stability, chemical inertness and good mechanical properties [1]. Contrary to its single crystal form (sapphire), submicron polycrystalline alumina ceramics exhibit even better mechanical properties which in combination with reasonable price could eventually lead to replacement of single crystals in optical applications.

It is well known that addition of rare-earth elements (RE) ions into various host materials results in an improvement of their structural, electronic and optical properties, expanding the areas of their use to various applications, including laser materials, optical amplifiers, phosphors, photocatalysts etc. [2–4]. Among the trivalent RE ions that exhibit characteristic f-f intraconfigurational narrow emission lines, the Eu^{3+} ion is a potential candidate for creation of luminescent materials due to its exceptional properties [5]. As trivalent cation, Eu^{3+} ion exhibits strong red monochromatic emission colour. For divalent Eu^{2+}, matrix tunable emission is ranging from blue to green spectral region. Thus, the Eu^{3+} ion has been frequently used as efficient luminescence probe due to its electronic/spectral properties [6]: (*i*) the excited $^5D_0$ state is well separated (~12,000 cm^{-1}) from $^7F_{0\text{-}6}$ states; (*ii*) $^5D_0$ and $^7F_0$ states are non-degenerate, so that $^5D_0 \rightarrow {}^7F_0$ transition exhibits a single peak when Eu^{3+} occupies only one site of symmetry type C_s, C_n, C_{nv} (proving the existence of more than one site of symmetry); (*iii*) long decay time (in millisecond range) from excited $^5D_0$ state; (*iv*) exceptionally large Stokesí shift and (*v*) the intensity of $^5D_0 \rightarrow {}^7F_1$ transition (magnetic dipole in origin) is formally insensitive to the crystal field environment and consequently can be used as a reference transition. Moreover, the ligand-to-metal charge transfer (LMCT) of Eu^{3+} corresponds to the reduction $4f^6 \rightarrow 4f^7L^{-1}$ and the Eu^{3+} tends to reduce in order to obtain the stable half-filled shell configuration [6,7].

The Eu^{3+}-doped alumina was already prepared and characterized in the form of powders [8–10], microspheres [11] or in our previous work in the form of translucent ceramics [12]. Translucent Eu^{2+}-doped alumina (0.1 at.% Eu) was prepared and characterized by Yang et al. [13], who combined gel-casting and vacuum sintering and obtained the ceramics with in-line transmittance of 22% at 800 nm and typical blue light emission. In addition to our previously published results [12] this is to our best knowledge the

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only work dealing with europium doped transparent/translucent alumina. The lack of published data is primarily caused by the fact that the preparation of transparent luminescent ceramics is a major difficulty due to the significant decrease of optical transparency at higher dopant levels required for obtaining PL properties [14].

Unlike extensive studies of electronic, structural and optical properties of doped polycrystalline aluminas, investigation of their mechanical and/or fractographic properties is often neglected, and is largely limited to commonly used metallic dopants, such as magnesium [15,16] or zirconium [16]. With exception of lanthanum-doped alumina, no reports on mechanical properties of RE-doped aluminas are available [17].

The main goal of this study was to enhance optical transparency of Eu^{3+}-doped alumina ceramics. Our previous work [18] reporting successful preparation of Er^{3+}-doped transparent alumina showed the highest PL intensity and transparency at the optimal dopant concentration of 0.1 at.%. Based on these results, the amount of Eu^{3+} dopant in the range of 0.05–0.15 at.% was introduced into alumina using the optimised processing developed and described in our previous works [12,18]. The second aim was to characterize the light emission, mechanical and fractographic properties of Eu^{3+}-doped aluminas and to discuss them in terms of dopant concentration and microstructure and to compare them with the data available in literature.

2. Experimental procedure

Commercial high purity Al_2O_3 powder (99.99%, TM-DAR, Taimei Chemicals Co., Japan) with the primary particle size of 150 nm was used as a base material. The Eu^{3+}-doped alumina samples were prepared according to optimised procedure as described in [12,18] using Eu_2O_3 powder (purity 99.99%, particle size 30–50 nm, GNM – Getnanomaterials, USA). The final concentration of optically active dopant (Eu^{3+}) was in range to 0–0.15 at.% with respect to Al_2O_3.

Pressure-less sintering of green bodies was carried out to achieve 95.0–97.3% of theoretical density, i.e. only closed porosity was present. Two-stage pre-sintering regime (TSP) was used [12].

The sintered samples were hot isostatically pressed (HIP, ABRA Shirp, Switzerland) at 1280 °C/3 h in argon atmosphere and pressure of 200 MPa. The reference undoped alumina was HIPed at 1250 °C/3 h.

The density of sintered samples was determined according to the Archimedes' principle by double weighing in deionised water. The theoretical density was calculated from the theoretical densities of Al_2O_3 and Eu_2O_3 by the rule of mixtures.

Scanning electron microscopy (Lyra 3, Tescan, Czech Republic) was used to examine the microstructures of sintered bodies. The mean grain size (MGS) was determined by the linear intercept method using a correction factor of 1.56 [19]. 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 determined using a non-polarized He–Ne laser (λ = 632.8 nm). RIT values were measured in at least five different positions for each sample and were related to constant thickness of 0.8 mm.

The excitation and emission fluorescence spectra were recorded using Fluorolog FL3-21 spectrometer (Horiba, USA) equipped with PMT (R928) detector. The Xe-lamp (450 W) was used as an excitation source. To eliminate the second-order diffraction of the radiation source, a cut-off filter was used in the measurements. The luminescence spectra of studied samples presented herein were recorded at room temperature in front face mode and corrected for spectrometer response and lamp (except of excitation spectra).

One kilogram load indentations (20 measurements for each sample) were made on polished cross sections using an instrumented hardness tester (Z2.5/ZHU0.2, Zwick/Roel, Germany). The fracture toughness was calculated from Young's modulus E [MPa], hardness H [MPa], the indentation load P [N] and crack length c [m] as follows [20]:

$$K_{Ic} = \alpha \sqrt{\frac{E}{H}} \frac{P}{c^{\frac{3}{2}}}. \quad (1)$$

The calibration factor α [–] has a value of 0.018. The Vickers imprint diagonals and crack lengths were measured by confocal laser microscope (LS3100, Olympus, Japan). Elastic modulus was estimated for each individual hardness measurement from the slope of the unloading curve using the method described by Oliver and Pharr [21].

Table 1
Pre-sintering regimes for individual samples and achieved relative densities.

Eu^{3+} concentration (at.%)	TSP – regime[a]	Relative density (%)
0	1380 °C → 1230 °C/10 h	95.0
0.05	1440 °C → 1280 °C/10 h	96.7
0.075	1440 °C → 1280 °C/10 h	97.1
0.1	1440 °C → 1280 °C/10 h	97.0
0.125	1440 °C → 1280 °C/10 h	96.1
0.15	1470 °C → 1280 °C/10 h	97.3

[a] TSP – without dwell time in first step.

Table 2
Mean grain size and real in-line transmittance of rare earth doped alumina after HIP.

Eu^{3+} concentration (at.%)	Mean grain size (nm)	Standard deviation (nm)	RIT (%)
0	500	80	60.3
0.05	390	50	57.3
0.075	400	50	56.5
0.1	350	40	56.5
0.125	360	40	56.4
0.15	340	40	45.1

3. Results and discussion

3.1. Microstructure and real in-line transmission

Pre-sintering was carried out in order to prepare materials with only closed porosity, i.e. suitable for HIP. Higher content of Eu^{3+} suppressed densification, so the temperatures needed for pre-sintering of doped samples were slightly higher than that for pure alumina (Table 1). The same applies for the temperature of HIP (1280 °C for doped samples, 1250 °C for pure alumina).

All samples were HIPed to full density; any possible minimal differences in relative density could not be distinguished with the use of applied measuring method. The values of mean grain size of HIPed samples are summarized in Table 2. The microstructure of pure alumina was slightly coarser than in doped samples, which confirmed, similarly to another additives segregating preferably at grain boundaries – e.g. Mg, Zr, Y, Er [12,22], the grain growth inhibiting effect of Eu doping. However, in terms of their influence on measured properties (RIT, photoluminescence, mechanical properties), all microstructures could be considered as similar.

Optical transparency of doped alumina decreased with increasing dopant content (Table 2). Up to 0.125 at.% of Eu^{3+}, the decrease was negligible and the RIT remained relatively high. However, the addition of 0.15 at.% of the dopant resulted in significant drop of transparency. This effect was attributed to the excess of the dopant segregated at grain boundaries and subsequent formation of second phase inclusions [23]. Taking into account the RIT values, 0.125 at.% of Eu^{3+} could be considered as the maximum content of dopant which still allows relatively high level of transparency in studied

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