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Fabrication and characterization of Eu^{3+}-doped Lu_2O_3 scintillation ceramics

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ABSTRACT

Density, morphology, optical transmittance and luminescence of undoped and europium-doped Lu_2O_3 ceramics have been studied. It has been revealed that europium ions in concentration of 5 at.% act as a solid-state sintering aids in Lu_2O_3 ceramics promoting its densification. Lu_2O_3:Eu^{3+} optical ceramics with relative density of 98 ± 2%, with an average grain size of 50 μm and in-line transmittance of 41% in the visible wavelength range has been produced by vacuum sintering at T = 1850 °C. The scintillation characteristics of Lu_2O_3:Eu^{3+} ceramics under excitation with α-particles (^{238}Pu source, E = 5.46 MeV) have been determined for the first time (S = 500 ± 50 photons/MeV, R = 26.5%).

1. Introduction

Development of new functional materials based on optical ceramics is an urgent task of the modern materials sciences. Optical ceramics are promising materials for utilization as phosphors [1], solid state lasers host materials [2–4], transparent armor [5], lamp envelopes [6], scintillation detectors [7–10] and they possess several advantages over traditional materials – glasses and single crystals. These advantages include improved processability, lower cost of fabrication, wider range of compositions [11], etc. Despite partial segregation of activators at the grain boundaries [12] advanced scintillation ceramics have higher light output in comparison with crystals of the same composition due to better structural and compositional uniformity and consequently better optical perfection [13].

Europium-doped lutetium oxide is a material of significant interest for application in digital radiography as a scintillator screen due to its high density (ρ = 9.44 g/sm^3) and high X-ray to visible light conversion efficiency. Lu_2O_3:Eu^{3+} has high effective atomic number (Z_{eff} = 63) and high value of attenuation cross-section of X-ray radiation. Linear luminescence with a maximum at ~611 nm is perfectly matched with the spectral sensitivity range of modern Si-photodiodes and charge-coupled devices [14,15]. Taking into account the unique physico-chemical properties as well as functional and exploitation characteristics of lutetia ceramics they can compete with traditional scintillation materials on the basis of single crystals and ceramics in the near future [7,16]. Despite several publications on growth of Lu_2O_3 (see, for example [17] and references cited therein), there is no commercial technology on single crystals fabrication due to extremely high melting point of the compound (~2450 °C). Thus production of optical ceramics is considered as the sole alternative to produce bulky Lu_2O_3.

Optical transparency and outstanding scintillation performance of ceramic comparable with the single crystals can only be achieved by precise control of its phase and chemical composition, crystalline structure and density during all the processing steps, including synthesis of low agglomerated nanopowders with controllable morphology and development of advanced sintering conditions. Traditionally, to fabricate pore-free ceramic with a near theoretical density (>99.999%) high pressure consolidation methods of nanopowders are used (hot pressing, hot isostatic pressing, spark plasma sintering) which provide excellent driving force for densification [2,14,18–20]. However, sintering under pressure can lead to contamination of ceramics by graphite tooling or even to deviation from the stoichiometry due to reducing conditions of sintering. For this reason pressure-less sintering method such as vacuum sintering are considered as alternative ones for production of transparent ceramics with high optical quality. The relatively low driving potential for densification of these methods may be substantially increased by using of sintering additives accelerating mass transport kinetics [21]. However, utilization of sintering additives could lead to formation of scattering centers (glassy, secondary phases) or charge carriers traps which may alert optical and scintillation performance of ceramics [22,23]. According to [24] europium ions having tendency to change their valence state not only provide functional response of Y_2O_3 ceramics but also act as effective sintering aids. Incorporation of Eu^{2+} ions into cationic sublattice of yttrium oxide increases effective diffusion constants that results in improved densification of europium-doped ceramics

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[24]. Taking into account that lutetium and yttrium oxides are the structural analogues, one can expect that europium ions will also lead to enhanced densification of Lu_2O_3 ceramics. The aim of this work was to sinter Lu_2O_3:Eu^{3+} ceramics using europium ions as the sintering aids and to determine its functional characteristics.

2. Experimental

2.1. Production of Lu_2O_3:Eu^{3+} ceramics

Undoped and Eu^{3+}-doped Lu_2O_3 nanocrystalline powders were obtained by normal-strike co-precipitation technique from water solution. Lutetium and europium chlorides were used as the starting materials and NH_4HCO_3 was used as a precipitant. After precipitation the formed precipitate was collected, filtered, washed several times with water and absolute ethanol and dried in air at T = 25 °C. Then the powders were grinded and calcined in a muffle furnace in the 700–1200 °C temperature range for 2 h. To produce optical ceramics Lu_2O_3 and Lu_2O_3:Eu^{3+} (5 at.%) nanopowders were at first formed into disks by uniaxial pressing method to achieve relative densities of 45–50% from the theoretical one. Then Lu_2O_3, Lu_2O_3:Eu^{3+} (5 at.%) compacts were sintered at T = 1800–1850 °C in high vacuum furnace with graphite or tungsten heaters and annealed in air at T = 1350 °C for 15 h. Finally, the resultant ceramics were polished on the both sides to a thickness of 1 mm.

2.2. Characterization of ceramics

Density of the sintered bodies was estimated by standard Archimedes method. Phase identification was performed via X-ray diffraction (XRD) method on SIEMENS D-500 X-ray difractometer (Cu Kα radiation, graphite monochromator). The ceramics microstructure and grain size were studied by scanning electron microscopy (SEM) on JEOL JSM-6390LV microscope. Optical investigations of ceramics were conducted using 1 mm thick pellets polished on both surfaces. In-line transmittance in the 190–1100 nm wavelength range was determined by Perkin–Elmer "LAMBDA-35" spectrophotometer. Luminescence was studied on an automated SDL-2 setup (LOMO) under excitation with REIS-I X-ray tube (Cu anticathode, U = 30 kV) at room temperature.

Scintillation characteristics of Lu_2O_3:Eu^{3+} (5 at.%) ceramics were determined under alpha-particles excitation (^{238}Pu source, E_α = 5.46 MeV) with spectrometric tract, including charge sensitive preamplifier, linear spectrometric amplifier (Ioffe Physical Technical Institute, RAS, Russia) and AMA-03-F multichannel pulse amplitude analyzer. The FEU-183 photomultiplier tube (PMT) (NRI "Electron", Russia) was used as a photodetector. The shaping time was 20 μs. The light output (S) of ceramics was determined as maximum position of pulse height spectra under α-particles excitation. The absolute light output of Lu_2O_3:Eu^{3+} (5 at.%) ceramics was evaluated by comparison of light outputs of ceramics and $Bi_4Ge_3O_{12}$ (BGO) single crystal of the same dimensions taking into account differences in quantum efficiency of radioluminescence spectra of Lu_2O_3:Eu^{3+} and BGO. Amplitude resolution R was determined as a ratio of the half-width maximum of pulse height spectra to its position.

3. Results and discussion

3.1. Influence of europium ions on density and morphology of Lu_2O_3 ceramics

Sinterability of nanopowders is mainly determined by their morphological features as well as by phase, chemical and granulometric composition. Commercial nanopowders usually do not satisfy all the requirements for the initial charge for optical ceramics even consolidated by hot isostatic pressing [2]. For this reason we have developed original laboratory methodic to produce Lu_2O_3 nanopowders including synthesis of the mixture of amorphous and crystalline precursor with approximate composition of $Lu(OH)_x(CO_3)_y \cdot nH_2O$ by chemical co-precipitation followed by calcination in the oxygen atmosphere. Absence of succession between crystalline structure of precursor and lutetium oxide formed allows one to synthesize Lu_2O_3:Eu^{3+} powders containing low-agglomerated equiaxed particles with uniform particle size of about 25–40 nm each of them is a single crystal.

To determine influence of europium ions on Lu_2O_3 sinterability the nominally pure and europium-doped nanopowders were synthesized. The europium concentration was selected to be 5 at.% that is close to the optimum concentration of luminescent impurity [14]. This concentration coincides well with optimal concentration of europium ions as the sintering aid in isostructural Y_2O_3:Eu^{3+} ceramics [24]. The obtained powders were compacted in equal conditions and vacuum sintered at T = 1800–1850 °C for 15 h. Finally, the synthesized pellets were polished and annealed in air. At least three samples of each composition were used for the comparison purposes. Fig. 1 shows photographs of Lu_2O_3, Lu_2O_3:Eu^{3+} ceramics after vacuum sintering. Undoped Lu_2O_3 ceramics were black and opaque (Fig. 1a), while europium-doped Lu_2O_3 ceramics were translucent and the text can be easily read through the sample (Fig. 1b). The black color of ceramics may be caused by formation of oxygen-deficient lutetium oxide. The same color was observed in RE_2O_3 (RE = Y, Lu) single crystals and ceramics obtained in reducing conditions [17,25]. Since the presence of dopant strongly affects the optical transmittance of Lu_2O_3 ceramics (Fig. 1) europium ions could be considered as effective solid state sintering aid.

Vacuum sintering of Lu_2O_3 and Lu_2O_3:Eu^{3+} ceramics at T = 1850 °C leads to formation of close porosity ($\rho \geqslant 95\%$). The relative density of activated ceramics was always higher compared to undoped one (98 ± 2% and 95 ± 2%, correspondingly). This fact confirms enhanced densification of europium-doped Lu_2O_3 samples. The translucency of Lu_2O_3:Eu^{3+} ceramic suggests that its density exceeds 99.5% [18] which still lies within the limit of 98 ± 2% determined by Archimedes method. Fig. 2 presents typical microstructure of pure and europium-doped Lu_2O_3 ceramics sintered at 1850 °C. The average grain sizes of ceramics greatly depend on the chemical composition and amounts to 17 and 51 μm for Lu_2O_3 and Lu_2O_3:Eu^{3+}, correspondingly. During sintering of lutetium ceramics at T = 1850 °C removal of residual porosity is accompanied by intensive grain growth starting in Lu_2O_3 above 1650 °C [18]. The grain growth enhancement is more pronounced in activated ceramics. Increase of density and average grain size of yttria ceramics doped with divalent cations was recently observed in [26,24]. Similar effect in Lu_2O_3:Eu^{3+} ceramics doped by trivalent europium ions suggests the change of the valence state of activator ions during vacuum sintering.

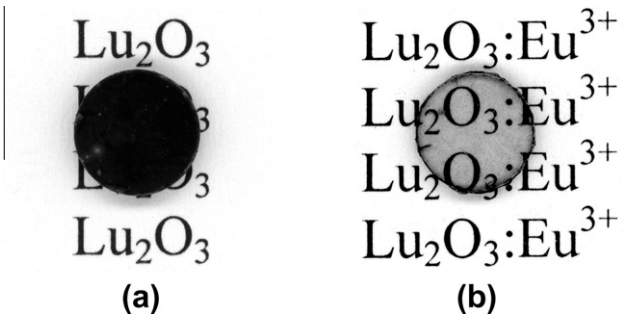

Fig. 1. Lu_2O_3 (a) and Lu_2O_3:Eu^{3+} 5 at.% (b) ceramics vacuum sintered at 1850 °C for 15 h and annealed in air at 1350 °C for 15 h.