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Effect of Gd substitution on structure and spectroscopic properties of $(Lu,Gd)_2O_3$:Eu ceramic scintillator

Maoqing Cao [a, b], Zewang Hu [a], Maxim Ivanov [c, d], Jiawei Dai [a], Chaoyu Li [a], Huamin Kou [a], Yun Shi [a], Haohong Chen [a], Jiayue Xu [b, **], Yubai Pan [e], Jiang Li [a, *]

[a] Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
[b] School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, China
[c] Institute of Electrophysics, Ural Branch of Russian Academy of Sciences, 106 Amundsen Street, Ekaterinburg, 620016, Russia
[d] Ural Federal University, 19 Mira Avenue, Ekaterinburg, 620002, Russia
[e] Department of Physics, Shanghai Normal University, Shanghai 200234, China

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ABSTRACT

In this paper, $(Lu_{1-x}Gd_x)_2O_3$:Eu (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) ceramics were consolidated by the solid-state reaction method combined with vacuum sintering without sintering aids. We investigated the effect of the varying contents of Gd_2O_3 on the structure and spectroscopic properties of $(Lu_{1-x}Gd_x)_2O_3$:Eu ceramics. X-ray diffraction (XRD) patterns indicate that proper amount of Gd_2O_3 can incorporate well with Lu_2O_3 and form Lu_2O_3-Gd_2O_3 solid solution. However, excessive Gd^{3+}-doping in Lu_2O_3 will lead to the cubic phase transforming into monoclinic even hexagonal phase. The Gd^{3+} substitution no more than 50% of Lu_2O_3 enhances the radioluminescence, and reduces the fluorescence lifetime. Transmittance, photoluminescence, and radiation damage of the $(Lu_{1-x}Gd_x)_2O_3$:Eu scintillation ceramics were also studied.

1. Introduction

Sesquioxides Ln_2O_3 (Ln = Y, Gd, Lu and Sc) are widely recognized as excellent hosts of laser and scintillator materials for their good physical and chemical performance such as high thermal conductivity and simple cubic structure ($Ia\bar{3}$) [1,2]. By properly doping and employing advanced processing techniques, polycrystalline transparent ceramic scintillators better than conventional single-crystal ones can be attained [3,4]. The ceramic scintillator can absorb and convert X-rays into visible photons to be applied in X-ray detection such as industrial detectors and medical diagnosis systems (computed tomography and stationary digital imaging) [5–7]. Y_2O_3 has been widely studied owing to its low cost, large band gap (5.6eV), high thermal stability, low phonon energy (380 cm^{-1}) [8,9]. Among which, Eu^{3+} doped Y_2O_3-Gd_2O_3 solid solution ceramics are developed as scintillators for X-ray computed tomography medical imaging [10]. The General Electric Company (GE) has successfully developed commercial $Y_{1.34}Gd_{0.6}O_3$:Eu ceramics to be used in medical X-ray detectors [11].

To reduce the time to expose patients to X-ray radiation and achieve high-imaging quality, scintillator should possess excellent properties such as high light yield, high absorption coefficient, short decay time and low afterglow [4]. The absorption coefficient (η_{abs}) of X-ray can be expressed as $\eta_{abs} = \rho Z_{eff}^4$ [11,12], in which ρ is theoretical density and Z_{eff} is the effective atomic number. Thus high atomic number and theoretical density are favorable. Nevertheless, high concentration of Y_2O_3 in the $Y_{1.34}Gd_{0.6}O_3$:Eu ceramics leads to the relatively low absorption efficiency due to low density ($\rho \approx 5.9$ g/cm^3) and effective atomic number. Among the rare earth sesquioxides, the density (~9.43 g/cm^3) and effective atomic number ($Z_{eff} \approx 69$) of Lu_2O_3 are much higher than Y_2O_3 ones, which endows lutetium oxide with high stopping power for ionizing radiation [13]. Thus, we can explore scintillator with better performance in the Eu doped Lu_2O_3 based compound.

The research showed that Gd^{3+} ion can readily sensitize the 4f-4f emission of Eu^{3+} and enhance the luminescence efficiency. Furthermore, the ionic radii of Gd^{3+} and Lu^{3+} ions are similar which enables them to mix quite well into solid solutions. At the same

* Corresponding author.
** Corresponding author.
E-mail addresses: xujiayue@sit.edu.cn (J. Xu), lijiang@mail.sic.ac.cn (J. Li).

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time, their large band gaps (5.4–5.5eV) can easily accommodate the rare-earth luminescent ions [14]. However, Gd_2O_3 may lead to phase transformation from cubic phase to monoclinic or hexagonal one when the temperature exceeds 1250 °C [15]. The phase transformation may influence the structure and optical properties of $(Lu,Gd)_2O_3$:Eu ceramic scintillator.

Whiffen et al. investigated structural and luminescence properties of Eu^{3+} doped $(Lu_xGd_{1-x})_2O_3$ (x = 1, 0.75, 0.5, 0.25 and 0) cubic phased nanocrystalline powders synthesized at lower temperature [16]. Seeley et al. have obtained high optical quality $Lu_{1.6}Gd_{0.3}O_3$:Eu ceramics scintillator by two-step sintering and the total integrated light yield reached 57,000 photons/MeV [17]. In our previous works, we investigated luminescent and thermoluminescent properties of Eu^{3+} doped $(Lu,Gd)_2O_3$:Eu ceramics scintillator [18]. The research revealed that radioluminescence intensity of the 4f→4f transitions of Eu3+ reaches up to 10 times of bismuth germanium oxide (BGO) single crystal reference scintillator. Rétot et al. [19] showed that the fluorescence and scintillation properties of Gd^{3+} co-doped $(Lu_{0.5}Gd_{0.5})_2O_3$:Eu is superior to Lu_2O_3:Eu transparent ceramics. However, systematic work still need to be researched to disclose the Gd substitution on structure and spectroscopic properties of $(Lu,Gd)_2O_3$:Eu ceramic scintillator.

In this work, $(Lu_{1-x}Gd_x)_2O_3$:Eu (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) ceramics were successfully fabricated using the solid-state reaction method, and the effects of Gd^{3+} doping on the structure, luminescence, and optical performances of the materials were studied.

2. Experimental procedures

Six composition samples of $(Lu_{1-x}Gd_x)_2O_3$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) doped with Eu^{3+} ions (6 at.%) were synthesized. High-purity powders of Lu_2O_3 (Rare-Chem. Hi.-Tech. Co., Ltd., 99.99%, Guangzhou, China), Eu_2O_3 (Alfa Aesar Co., Inc., 99.99%, Tianjin, China), and Gd_2O_3 (Alfa Aesar Co., Inc., 99.999%, Tianjin, China) were used as raw materials. The powders were mixed in ethanol and ball-milled with high-purity corundum balls for 12 h, then the as-milled slurry was dried at 70 °C for 4 h to remove the ethanol. The dried powers were sieved through 200-mesh screen and calcined at 600 °C for 4 h to remove the organic components. Green pellets were uniaxially pressed at 40 MPa and then cold isostatically pressed at 250 MPa. The pellets were sintered at 1700–1850 °C for 30 h in a tungsten mesh-heated vacuum furnace under vacuum (10^{-3} Pa) during holding. After sintering, the as-sintered bodies were annealed at 1450 °C for 10 h in air to remove the oxygen vacancies. The ceramics were mirror-polished on both surfaces to 1.5 mm for the following characterization.

The specific surface areas of the powders were determined using a gas sorption analyzer (Model Micromeritics ASAP 2010, Norcross, USA) based on the Brunauer-Emmett-Teller (BET) method. XRD measurements were performed on a Japan D/max2200 PC instrument. For the analysis the ceramic samples were grinded into powder. The 2θ ranged from 10° to 80° with 0.02° step and data analysis was performed on a Huber Imaging Plate Guinier Camera G670 (Cu $K_{\alpha 1}$ radiation, λ = 1.54056 Å, 40 kV/30 mA, Ge monochromator). Micrographs of the raw materials and ball-milled powers were observed with a field emission scanning electron microscopy (FESEM, SU8220, Hitachi, Japan).

Transmission spectra were measured using the Cary-5000 Scan UV–vis–NIR spectrophotometer. The photoluminescence and fluorescence lifetime were analyzed by an FSL 920 Spectrometer using xenon lamp (450 W) as a light source at room temperature. And the X-ray excited luminescence spectra was performed with homemade system of test equipment. The X-ray tube was set at 70 kV, 1.5 mA. The radioluminescence curves were recorded by Ocean Optics QE65000 spectrometer. The setup allowed to record full spectra in the range of 200–900 nm, simultaneously. In the test of radiation damage of the ceramics, the samples were exposed to X-ray for 5 min before the radiation induced optical absorption measurement. In the measurements including transmittances, the photoluminescence and X-ray excited luminescence spectra, the spectral resolutions are 1 nm.

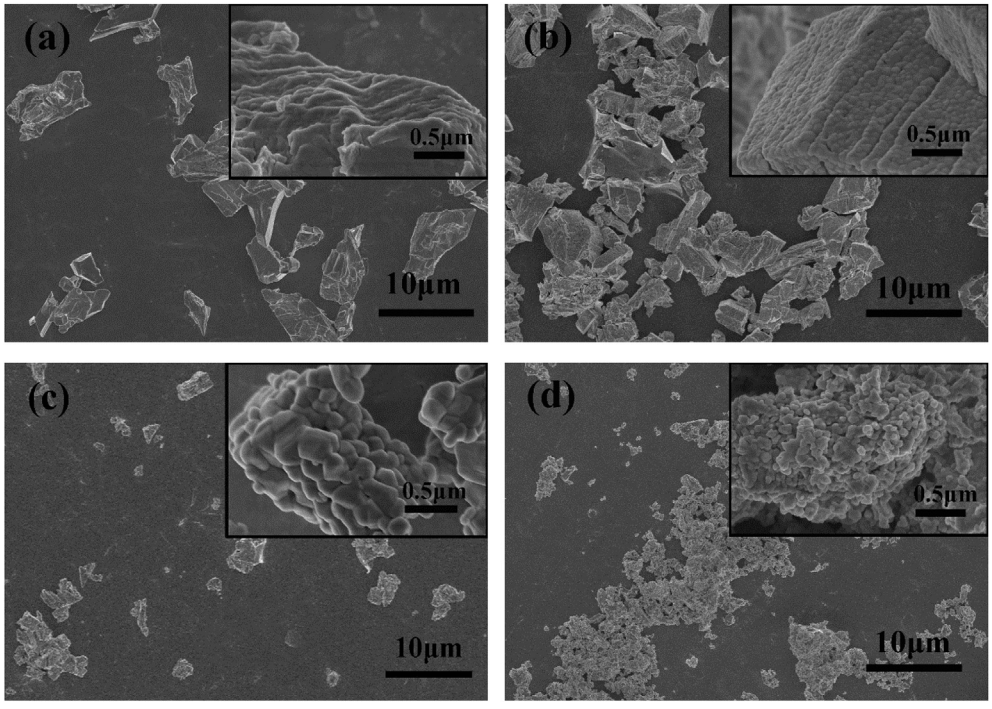

Fig. 1. SEM micrographs of the raw powders (a) Lu_2O_3, (b) Gd_2O_3, (c) Eu_2O_3, (d) the powder mixture after ball-milling.