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Photoluminescence Inhomogeneity of LGSO : Ce Scintillator Crystal

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Spatial distribution of photoluminescence (PL) parameters in $Lu_2SiO_5 : Ce$ (LSO : Ce) and $Lu_{2x}Gd_{2-2x}SiO_5 : Ce$ (LGSO : Ce) are investigated using confocal microscopy. The PL spectra of both crystals are dominated by a single band peaked at ~ 510 nm. A low intensity sub-band peaked at 600 nm is observed in LGSO:Ce. Spatial inhomogeneities down to submicron size are observed in spectral center of mass mapping images of LGSO : Ce while the spatial distributions of spectrally-integrated PL intensity and PL peak position showed no large variations. The inhomogeneities in LGSO : Ce are caused by the spectral variation of the long-wavelength sub-band and are attributed to Ce^{3+} located in CeO_6 polyhedra. The results are explained by Lu / Gd ratio fluctuations in mixed LGSO : Ce crystals.

Keywords: Confocal microscopy, Luminescence, LGSO, Scintillator.

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1. INTRODUCTION

High luminous efficiency is one of the most important properties of in scintillator materials. The improvement of scintillation yield can be achieved by isovalent cation or anion substitution. In general, the mixed crystals obtained this way exhibit higher light yield and energy resolution compared to those of their constituents. The origin of the yield enhancement is still under discussion, however, it is usually explained by the carrier trapping phenomena. For example, it is assumed that gallium doping in Al-Ga substituted garnet leads to the elimination of shallow electron traps promoting electron capture by Ce^{3+} [1]. Simultaneously, as the bandgap decreases with increasing gallium content, the quantity of generated electron-hole pairs per absorbed quantum is increased, thus improving the light yield.

Lu / Gd cation substitutions are formed in $Lu_{2x}Gd_{2-2x}SiO_5 : Ce$ (LGSO : Ce) crystals by mixing $Gd_2SiO_5 : Ce$ (GSO : Ce) and $Lu_2SiO_5 : Ce$ (LSO : Ce). The mixed crystal contains structural inhomegeneities which affect carrier dynamics. The highest inhomogeneity is believed to be at 1 : 1 ratio of the constituents. Previously, an enhanced inhomogeneity in local distribution of constituents was evidenced for metal alloys, where formation of atomic domains of hundreds of nanometers in size were observed [2, 3].

The optimal crystal content is essential for efficient scintillation yield. It was shown that the scintillation yield in LGSO : Ce at certain Lu / Gd ratio value can be up to 130 % and 300 % of that in LSO : Ce and GSO : Ce, respectively [4]. The increase of the light yield can be explained by the formation of Lu- and Gd-rich regions in LGSO : Ce crystal. This variation of the crystal content induces the bandgap fluctuations which are pronounced at the domain boundaries. The fluctuations limit the diffusion of excited carriers promoting their capture at Ce^{3+} and subsequent radiative transitions at the ion.

The compositional inhomogeneity is found to be favorable for carrier multiplication efficiency in LGSO : Ce, [4] Ce-doped $Lu_{1-x}Y_xAlO_3 : Ce$ [5] and Y_2SiO_5 crystals [6]. However, all the results rely on the indirect evidences. In this work compositional inhomogeneity of LGSO : Ce is directly reveled in nanometer domain using confocal microscopy.

2. EXPERIMENTAL

LGSO and LSO crystals doped with Ce were grown by the Czochralski method at $Ar + O_2$ atmosphere in iridium crucibles. Lu_2O_3, Gd_2O_3, CeO_2, and SiO_2 oxides with 99.99 % purity were used as the starting materials. The growth conditions were kept the same for both crystals. For our study, the samples with the dimensions of $10 \times 10 \times 2$ mm were cut from the central parts of the crystals and polished.

The cerium weight fractions in the crystals were determined using atomic emission spectroscopy based on the complete evaporation of the material in an arc discharge and recording the emission by using spectrograph DFS-1. The spectra were measured in the range from 250 to 350 nm. Cerium content was determined to be 0.2 at. % in LSO : Ce and 0.32 at. % in LGSO : Ce.

The X-ray luminescence spectra were measured using spectrometer KSVU-23. X-ray emitter with Cu anode ($U = 40$ kV, $I_a = 25$ mA) was used for excitation.

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3. RESULTS AND DISCUSSION

Typical X-ray excited luminescence spectra of LSO : Ce and LGSO : Ce are shown in the inset in Fig. 1. Single band peaked at ~ 400 nm dominates in LSO : Ce spectra, while two sub-bands peaked at ~ 420 nm and ~ 510 nm are observed in LGSO : Ce spectra. The sub-bands are attributed to $5d$-$4f$ transitions of Ce^{3+} at Ce1 (CeO_7) and Ce2 (CeO_6) polyhedra. In LSO : Ce, Ce^{3+} ionsare predominantly situated at Ce1 sites [7, 8], thus only one band is observed. The addition of gadolinium leads to relaxation of the crystal lattice, and the fraction of cerium at sites Ce2 increases. This redistribution can be evaluated from the relative intensity of the Ce1 and Ce2 bands in the luminescence spectrum (see Fig. 1). Therefore, relative Lu / Gd content in mixed crystal can be evaluated using luminescence spectra.
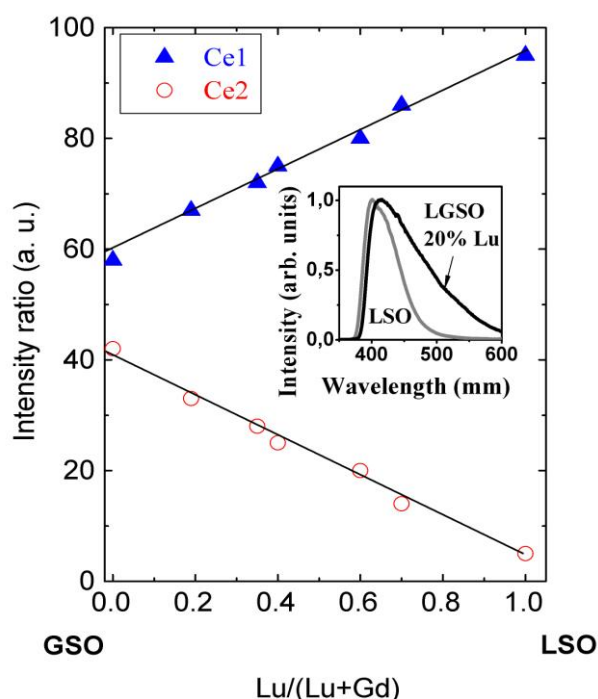
Fig. 1 – Intensity ratio of Ce1 (CeO_7) and Ce2 (CeO_6) luminescence bands as a function of LGSO : Ce composition. The inset shows X-ray excited luminescence of LSO : Ce and LGSO : Ce

Confocal microscopy was used to study the spatial distribution of PL parameters (spectrally-integrated PL intensity, full width at half maximum (FWHM), and PL spectral center-of-mass). Due to the rough polishing the crystal surface was covered by deep scratches which strongly disturbed PL measurements. However, the exclusive feature of confocal microscopy to eliminate out-of-focus light allowed us to separate distorted surface spectra and measure PL deeper inside the crystal. The obtained spatial distributions of all the PL parameters were nearly homogeneous. Spatial variations were observed only in the center-of-mass mapping images (see Fig. 2). In LSO : Ce (Fig. 2, left), a gradual shift of PL band to longer wavelength can be explained the increasing reabsorption deep inside the crystal. Meanwhile, in LGSO:Ce (Fig. 2, right), we observed spatial inhomogeneities of the order of 1-3 µm in diameter (marked by squares) scattered in the crystal volume.
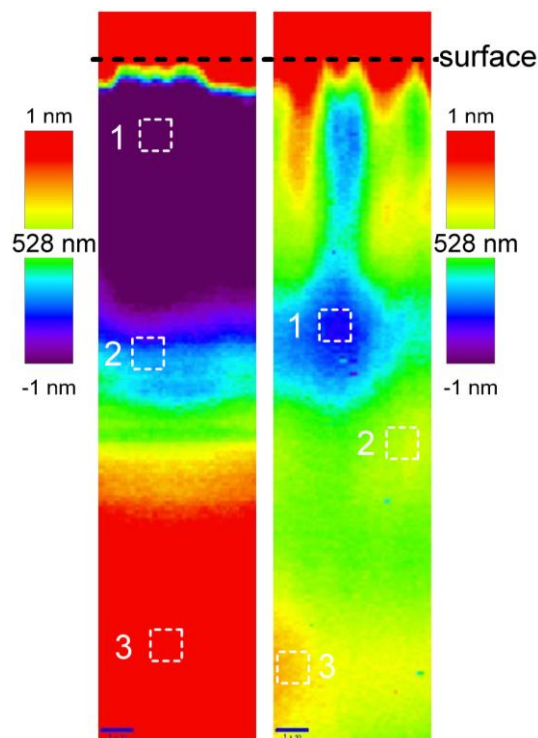

Fig. 2 – Spatial distribution of PL band center-of-mass position in LSO : Ce (left) and LGSO : Ce (right). The length of blue scale bar is 1 µm

Different locations of the samples were selected in Fig. 2 (marked by dashed squares) to collect PL spectra (Fig. 3(a) and (b)). To better reveal differences, spectra were subtracted after their normalization to the peak value (Fig. 3(c) and (d)). The PL spectra of LSO : Ce sample shifts to long-wavelength with increasing distance from the surface, as it is expected due to reabsorbtion (note the sharp shift in subtracted spectra in Fig.3 (c)).

Meanwhile, a band peaked at ~ 600 nm is observed in the subtracted spectra of LGSO : Ce, though it is absent in LSO : Ce sample (Fig. 3(d)). The spectral position of this band matches well with that observed in X-ray excited luminescence of LGSO : Ce (see the inset of Fig. 1) and it can be attributed to the increase in relative intensity of Ce2 luminescence centers. The plausible cause of the observed variation is small irregularities in Gd concentration across the LGSO : Ce sample. The increase of Gd increases the contribution of Ce2 band in the luminescence spectrum, as it shown in Fig. 1. Using the data presented in Fig. 3, we deduce that the highest local Gd concentration is in the areas like that marked as 2, while the lowest contentration is in areas like 1. To the best of our knowledge, this is the first direct experimental evidence showing submicrometer-scale fluctuations of Gd concentration in mixed crystals.

4. CONCLUSIONS

Spatial distributions of PL parameters in LSO : Ce and LGSO : Ce crystals were measured using confocal microscopy. Spatial inhomogeneities of spectral center of mass observed in LGSO : Ce sample are attributed to
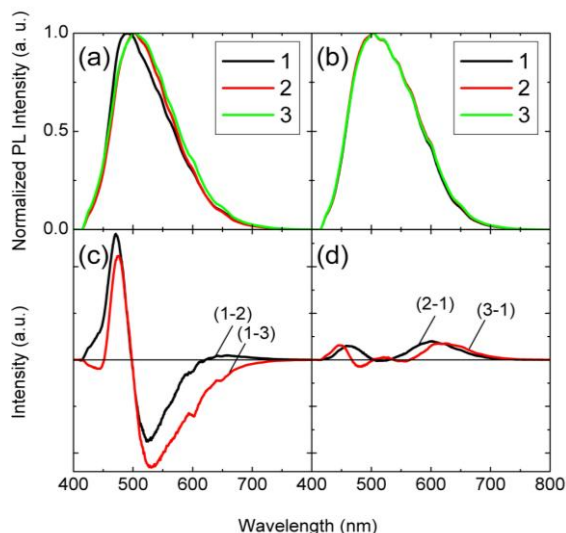
Fig. 3 – Normalized PL spectra from different areas (marked in Fig. 2) of LSO : Ce and LGSO : Ce, (a) and (b), respectively. Subtracted spectra of LSO : Ce and LGSO : Ce are shown in (c) and (d), respectively.

$5d$-$4f$ transitions of Ce^{3+} at Ce2 (CeO_6) polyhedra which, in turn, are influenced by Lu / Gd ratio in the crystal. The spatial inhomogeneity of the spectral component peaked at ~ 600 nm in LGSO : Ce reflect fluctuations in Lu / Gd ratio across the crystal. Such submicron-scale fluctuations in crystal composition might influence the process of carrier migration to luminescence centers and should be taken into account in designing and fabrication of scintillators based on mixed crystals.

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