

Investigation on Valence State Change of Persistent Phosphors

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1 Introduction

Persistent phosphors, a kind of specific luminescent materials that can exhibit “self-sustained” persistent luminescence (PersL) in the dark for minutes, hours or even days after ceasing external excitation, have achieved a big commercial success for civil applications, such as emergency signage, safety indication, luminous paints, watch dials, *etc.* It features energy storage capabilities, for which not all the energy absorbed upon external excitation is immediately emitted as light. A fraction of absorbed energy is used to transfer a charge carrier from the luminescent center to a so-called trap center, generating a metastable state. The trapping-detrapping process of charge carriers is regarded as the key mechanism dominating the performance (luminescent duration & intensity) of persistent phosphors, in which the valence state of activators and/or trap centers may change before/after light excitation [1].

2 Experiment

$Y_3Ga_5O_{12}$ (YGG):Cr-Eu0.05 and YGG:Cr-Eu0.5 transparent ceramics are prepared by solid-state reaction and vacuum sintering method. The doping concentration of Cr^{3+} is kept constant to be 0.5 mol% in two samples, and the doping concentration of Eu^{3+} is varied from 0.05 mol% to 0.5 mol%. The chemicals of Y_2O_3 , Ga_2O_3 , Eu_2O_3 and Cr_2O_3 with purity of >4N were used as raw materials. The starting powder was mixed by ball-milling method with anhydrous alcohol for several hours. The mixture powder was dried at 80°C for 36 h and compacted to form a ceramic green body, then pre-heated at 800°C for 20 h in air to remove the organic substances, and finally sintered at 1600-1650°C for 10-20 h in vacuum atmosphere. The as-sintered samples were double-mirror polished using a copper plate and diamond slurry. The X-ray absorption spectroscopy (XAS) was performed at the beamline BL9A of Photon Factory (KEK, Japan). The photon flux density of X-ray at 7 keV is 4×10^{12} photons/sec/mm². The Cr K and Eu L_{III} X-ray absorption near edge structure (XANES) were recorded for all the samples in fluorescence mode before/after 6 W UV (254 nm) illumination from mercury lamp. The ceramic sample rotation is controlled by piezo rotation stage (PDR1/M, Thorlabs)

3 Results and Discussion

PL and PersL images of two YGG:Cr-Eu ceramic samples are demonstrated in Fig. 1(a) under/after ceasing 254 nm UV illumination for 5 min. It gives typical orange emission under UV light from Eu^{3+} : ${}^5D_0 \rightarrow {}^7F_1$. The intense bands observed are due to ${}^5D_0 \rightarrow {}^7F_4$ at 708 nm and

${}^5D_0 \rightarrow {}^7F_1$ (magnetic dipole, MD) transition at 590 nm. The integrated intensity ratio of ${}^5D_0 \rightarrow {}^7F_2$ electric dipole (ED) to ${}^5D_0 \rightarrow {}^7F_1$ transitions here is very small compared with other Eu^{3+} doped red phosphors, such as Y_2O_3 . However, after stopping the UV excitation, both of two samples show deep-red PersL from Cr^{3+} : ${}^4T_2/{}^2E \rightarrow {}^4A_2$, which gives the evidence that Eu^{3+} acts as the electron trapping center while Cr^{3+} acts as the emission center for PersL.

Further investigation on the expected valence state change after the UV charging is shown in Fig. (b)/(c) in which the most famous green persistent phosphor, $SrAl_2O_4:Eu^{2+}-Dy^{3+}$ is also measured as a reference. With the help of rotation stage, we tried to avoid fast saturation behavior from synchrotron beam charging by rotating the sample during XANES measurements. The results suggest that the decrease of Eu^{2+} and increase amount of Eu^{3+} are observed in $SrAl_2O_4$, in which Eu^{2+} acts as the emission center. However, Eu^{3+} signal keeps almost constant in YGG, which indicates that metastable state of $(Eu^{3+}+e^-)^*$ may be reasonable for PersL as trapping center instead of direct formation of Eu^{2+} . Other XANES studies on Yb^{3+} in YAGG:Ce-Yb persistent phosphor and Ni^{2+} in $LaAlO_3$ NIR phosphor can be referred to Ref. (2) and (3), respectively using the same beam-station in PF

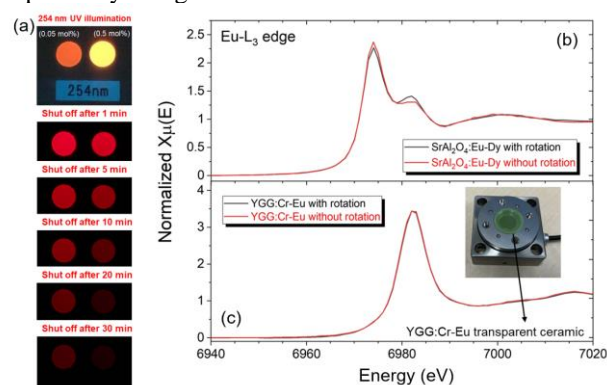


Fig. 1 (a) Images of the YGG:Cr-Eu0.05 and YGG:Cr-Eu0.5 ceramic samples under and after mercury lamp (254 nm, 6 W output) illumination for 5 min; XANES of (b) $SrAl_2O_4:Eu-Dy$ and (c) YGG:Cr-Eu monitoring $Eu^{2+/3+}$ energy using rotation stage

References

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