XANES studies of Eu in Mn^{2+} and Eu^{3+} co-doped ZnO-GeO_2 long-lasting afterglow phosphors and of Mn in alkali borate glasses

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1. Introduction

We have reported optical properties of Mn-doped glasses and glass ceramics prepared by sol-gel method. Samples consisting of ZnO and GeO_2 as host matrices and Mn as a luminescence center, ZnO-GeO_2:Mn^{2+}, showed strong green luminescence under UV irradiation due to the transition of Mn^{2+} ions. Furthermore, Mn^{2+} and Eu^{3+} ions co-doped ZnO-GeO_2 (ZnO-GeO_2:Mn^{2+},Eu^{3+}) glasses and glass ceramics showed afterglow luminescence lasting for 180 min after stopping UV irradiation. For considering the mechanism of this afterglow luminescence, it is important to clarify the valence of Eu ions in the samples. Therefore, we carried out Eu L-edge XANES spectral measurements for revealing the Eu valence in ZnO-GeO_2:Mn^{2+},Eu^{3+}.

Mn^{2+} shows green luminescence in ZnO-GeO_2 systems as described above, and red luminescence in MgO-GeO_2 systems. Moreover, Mn^{4+} is also known as a red luminescence center. Red luminescence from Mn^{4+} appeared at longer wavelength than that of Mn^{2+}, it is thus considered that red luminants having good color purity can be obtained with Mn^{4+}. To investigate the relation between luminescence properties and the valence of Mn, we prepared Mn-doped alkali borate glasses by melting method, and measured Mn K-edge XANES spectra.

2. Experimental

Mn^{2+} and Eu^{3+} ions co-doped ZnO-GeO_2 (ZnO-GeO_2:Mn^{2+},Eu^{3+}) glasses and glass ceramics were prepared by sol-gel method. The samples were ground into powders and heat

treated under reduce atmosphere (Ar : H_2 = 95 : 5), and then characterized by Eu L-edge XANES measurements (BL-3, SR center, Ritsumeikan University).

Mn-doped alkali borate glasses (K_2O-B_2O_3, Li_2O-B_2O_3) were prepared by melting method, using Li_2MnO_3 as an Mn source. Mn K-edge XANES measurements were also carried out at BL-3.

3. Results

Fig. 1 shows Eu L-edge XANES spectra of ZnO-GeO_2:Mn^{2+},Eu^{3+} samples. Commercial luminants of LP-RE1 and LP-B4 (Kasei Optonics, LTD. (at present: Phosphor Department, Mitsubishi Chemical)) were measured as reference samples for Eu^{3+} and Eu^{2+}, respectively. Spectrum A is for the mixture of LP-RE1 and LP-B4. Peaks due to Eu^{2+} at 6972 and 6996 eV, and those due to Eu^{3+} at 6979 and 7016 eV were found. It was cleared that almost all of the Eu ions existed as Eu^{3+} in the samples B ~ G, irrelevant to Mn concentrations.

Fig. 2 shows Mn K-edge XANES spectra of Mn-doped alkali borate glasses. $MnCO_3$ and Li_2MnO_3 were measured as references of Mn^{2+} and Mn^{4+}, respectively. The spectra showed the following tendency: increasing the amounts of Li_2MnO_3 and alkali metal oxides (K_2O or Li_2O) in the samples, it was likely that the Mn^{4+} peak intensity increased (③→⑦). Luminescence peaks due to Mn^{n+} except for Mn^{2+} at around 580 ~ 600 nm were obtained from these samples under UV irradiation (not shown), it is therefore concluded that the possibility of the Mn^{4+} existence is high in the sample.

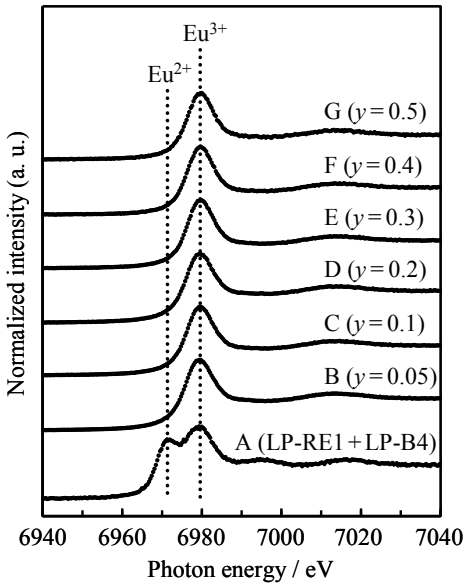

Fig. 1. Eu L-edge XANES spectra of yMnO-1.5Eu_2O_3-25ZnO-75GeO_2 samples heat treated at 900 ºC in a mixed gas of 95 % Ar and 5 % H_2.

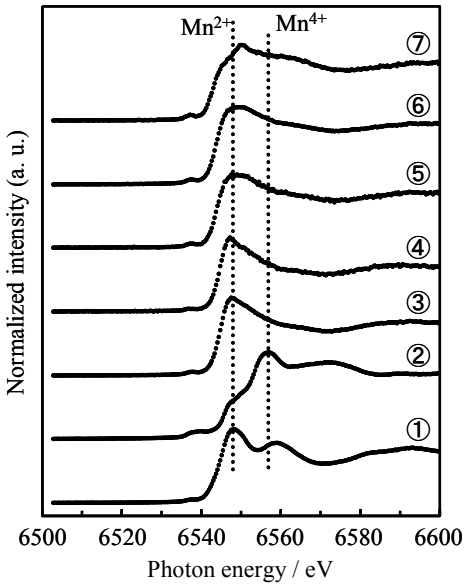

Fig. 2. Mn K-edge XANES spectra of Li_2MnO_3-doped alkali borate glasses: ① $MnCO_3$, ② Li_2MnO_3, ③ 1Li_2MnO_3-100B_2O_3, ④ 0.1Li_2MnO_3-10Li_2O-90B_2O_3, ⑤ 0.1Li_2MnO_3-30Li_2O-70B_2O_3, ⑥ 1Li_2MnO_3-30Li_2O-70B_2O_3, ⑦1Li_2MnO_3-30K_2O-70B_2O_3.