Investigation of Long Afterglow Phosphor Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ under Synchrotron Radiation

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The persistent luminescence materials are drawing more and more attentions because of a constantly growing market for their applications. As the new generation of long afterglow phosphors, lanthanide ion doped alkaline earth silicates or aluminates yield much better characteristics, such as longer duration time, brighter luminosity and improved chemical stability, than the conventional sulfide materials used earlier [1]. Although some new materials are already in commercial use, the mechanism of the persistent luminescence are still under discussion, especially the nature of the different hole traps or electron traps and their roles in the luminescence process. In this work, the luminescence from Eu²⁺ and Dy³⁺ codoped Sr₂MgSi₂O₇ was investigated under synchrotron radiation excitation as an attempt to shed some light on the luminescence mechanism of this newly developed blue-emitting long afterglow phosphor.

The powder sample, $Sr_2MgSi_2O_7$: $Eu^{2+}(0.5\%)$, $Dy^{3+}(8\%)$, was prepared by solid state reaction method in reducing atmosphere. The spectroscopic measurements were performed at the SUPERLUMI station of HASYLAB at DESY. The emission spectra are not corrected for the sensitivity of detection system.

The emission spectra shown in Figure 1 present two bands peaking at 477 and 578 nm when excited by 170 nm (curve a and b). The 477 nm broad band with FWHM of 50 nm corresponds to the transition from the lowest crystal field components of the $4f^65d^1$ excited state configuration to the $^8S_{7/2}$ ($4f^7$) ground state of Eu $^{2+}$ ions, which supposedly occupy the strontium sites in this akermanite structure host [2]. The 578 nm emission arises from intraconfigurational transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ ($4f^9$) of Dy $^{3+}$ ions. It should be noted that the transition from $^4F_{9/2}$ to the ground state $^6H_{15/2}$ of Dy $^{3+}$, located around 475 nm, overlap and are obscured by the strong Eu $^{2+}$ d-f emission, probably causing the asymmetry of 477 nm band. Under 300 nm excitation (curve c and d), the intensity of 578 nm band decreases drastically (invisible in the Figure 1, but still observable in the enlarged scale), meanwhile the 477 nm band is more symmetrical. The emission at room temperature (RT) has the same behaviour as at low temperature, except for the much lower intensity due to a strong thermal quenching effect like in singly Eu $^{2+}$ doped $Sr_2MgSi_2O_7[2]$.In the

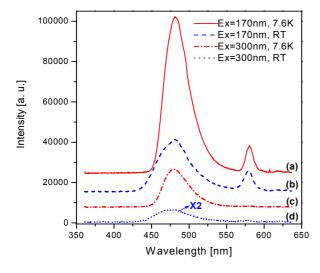


Figure 1: Emission spectra of $Sr_2MgSi_2O_7$: Eu^{2+} , Dy^{3+} under different excitation (170 and 300 nm) at 7.6 K and RT.

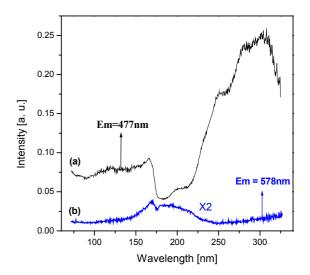


Figure 2: Excitation spectra of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ monitoring different emissions (477 and 578 nm) at 11 K.

excitation spectra monitoring 477 nm emission (Figure 2a), the dominating excitation band at wavelengths 220 nm shows a longer than complicated structure, comprising at least three subbands, which can be attributed to the transition from ⁸S_{7/2}. higher crystal components of 4f⁶5d¹ states of Eu²⁺. The excitation band below 170 nm can be assigned to the spin allowed fd transition of Dy³⁺, consistent with the results of [3]. In the excitation spectra of the 578 nm emission (Figure 2b), the long wavelength excitation bands around 300 nm are weakly pronounced, while the 170 nm band and some structures around 190 nm are dominating excitation bands. The 190 nm band is probably related to the extrinsic defects or impurities in the host. From the comparison of the two excitation curves, it can be concluded that the absorbed energy at Dy³⁺ sites can be efficiently transferred to the Eu² site, while back transfer of the energy is not significant.

The long afterglow emission spectra were also measured under 170 nm irradiation at different temperatures (see Figure 3). The long afterglow emission exists only at temperature higher than 200 K, and its intensity increases with rising temperature, at

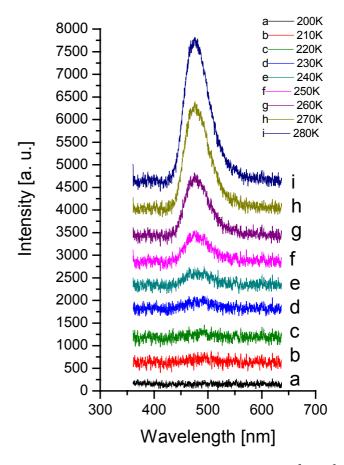


Figure 3. Long afterglow of Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ under 170 nm irradiation at different temperatures (measured after closing beam-shutter for ~30 seconds at each temperature).

least until 280 K. The long afterglow emission spectra consists of the similar band around 480 nm as that observed in emission spectra by 300 nm excitation. This indicates that the long afterglow is due to d-f transition at Eu²⁺ sites. The model supposed for the phosphorescence mechanism in SrAl₂O₄: Eu²⁺, Dy³⁺ [4] can be applied for this system. In this model, the holes trapped at Dy³⁺ sites are thermally released and can recombine with the electrons trapped at Eu²⁺ sites, resulting in the long afterglow emission. However, for the detailed information about the traps and the dynamics involved in this process, further investigations involving the thermoluminescence spectra and decay measurements of different emissions are indispensable.

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