Blue Light Excitable Red-Emitting Oxide Phosphor

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The orthophosphates with the general formula $ABPO_4$ (A: monovalent cations and B: divalent cations) have been widely investigated as host material for phosphors because of excellent thermal stability and the tetrahedral rigid three-dimensional matrix of the phosphates is thought to be ideal for charge stabilization.[1-3] Therefore, the Eu^{2+}-doped orthophosphate phosphors can shows good luminescence efficiency as phosphor for use in white LEDs. However, the luminescence properties of the orthophosphates phosphors with the $ABPO_4$ (A: monovalent cations and B: small divalent cations such as Be, Mg, and Zn) formula were rarely reported.[4] In particular, there is no report on the research of olivine-type $NaMgPO_4:Eu^{2+}$ for potential application as a phosphor, although photoluminescence of glaserite-type $NaMgPO_4:Eu^{2+}$ has been reported,[5,6] which shows blue emission under excitation at 336 nm.

In this letter, novel red-emitting olivine-type $NaMgPO_4:Eu^{2+}$ phosphor was synthesized by melt synthesis technique using arc-imaging furnace for first time, and their crystal structure and photoluminescence properties were characterized.

To investigate the crystal structure, the Rietveld refinement analysis is carried out on the sample prepared in this study. As a result, the obtained XRD pattern of $NaMgPO_4:Eu^{2+}$ phosphor is well indexed to the single phase of orthorhombic olivine-type $LiMgPO_4$ structure (JCPDS #20-1138). This indicates that the $NaMgPO_4:Eu^{2+}$ phosphor has an orthorhombic olivine-type structure with a space group of *Pnma*. Na^+ ion has an ionic radius of 0.102 nm for 6 coordination, while Mg^{2+} has an ionic radius of 0.072 nm for 6 coordination.[7] Therefore, in the case of present phosphors, the doping Eu^{2+} ions preferably occupy the Na^+ site in the host lattice, because the ionic radius of Eu^{2+} (0.117 nm for 6 coordination)[7] is similar to that of Na^+ (0.102 nm) which is much larger than that of the Mg^{2+} ion (0.072 nm).

Figure 1 presents the photoluminescence excitation and emission spectra of a $NaMgPO_4:2.5mol\%Eu^{2+}$ phosphor. The excitation spectrum is consisted of broad band covering the region from the UV to visible light part, which indicates that the phosphor is very suitable for a color converter using any excitation wavelength as the primary light source. The first small broad band located under about 270 nm is caused by the electronic transition between the valence and the conduction band of the $NaMgPO_4$ host material, and another strong broad band from 270 to 580 nm are attributed to the $4f^7$-$4f^65d^1$ transition of Eu^{2+}. The emission spectrum exhibit a red emission band centering at 628 nm, which correspond to the allowed transition from $4f^65d^1$ to $4f^7$ of Eu^{2+}, and no red line emissions from Eu^{3+} are observed even in a phosphorescence mode. By the optimization of the Eu^{2+} concentration, the maximum emission intensity was obtained for $NaMgPO_4:2.5mol\%Eu^{2+}$.

In the white LEDs application, the temperature dependence of phosphor is important because it has great influence on the light output and color-rendering index. Figure 2 shows temperature dependence of the emission intensity of the $NaMgPO_4:2.5mol\%Eu^{2+}$ phosphors normalized with respect to the value at 25 °C. It can be seen that the $NaMgPO_4:Eu^{2+}$ phosphor has an excellent thermal stability on the temperature quenching effect. With an increase in the temperature up to 150 °C, the emission intensity of the $NaMgPO_4:Eu^{2+}$ phosphor decreases to 82 % of the initial value at 25 °C. These results indicate that the $NaMgPO_4:Eu^{2+}$ phosphors are expected to find application as red-emitting phosphor for use in white LEDs.

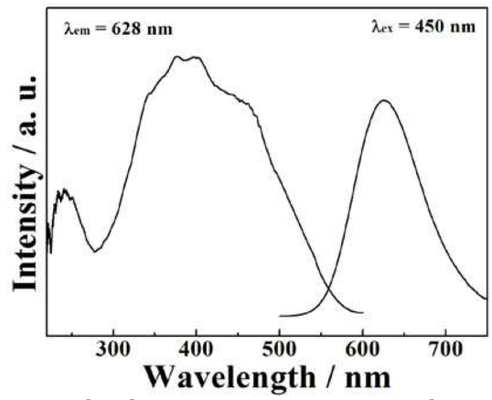

Fig. 1. Photoluminescence excitation and emission spectra of $NaMgPO_4:2.5mol\%Eu^{2+}$.

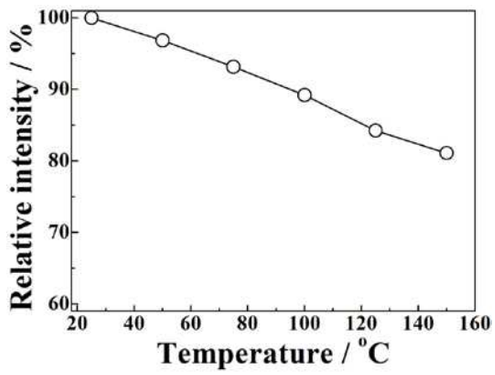

Fig. 2. The temperature dependece of the emission intensity of the $NaMgPO_4:2.5mol\%Eu^{2+}$.

This work was supported by a project from NEDO, New Energy and Industrial Technology Development Organization (Rare Metal Substitute Materials Development Project Development of Technology for Reducing Tb and Eu Usage in Phosphors for Fluorescent Lamp by High-speed Material Synthesis and Evaluation).

References

1. Z.C. Wu et al., *Mater. Chem. Phys.*, **103**, 415 (2007).
2. Y.-S. Tang et al., *Appl. Phys. Lett.*, **90**, 151108 (2007).
3. C.C. Lin et al., *J. Lumin.*, **129**, 1682 (2009)
4. S. Zhang et al., *Opt. Mater.*, **32**, 1545 (2010).
5. W. Tang et al., *Luminescence*, **25**, 364 (2010).
6. W. Tang et al., *Appl. Phys. A*, **103**, 263 (2011).
7. R.D. Shannon, *Acta Crystallogr., Sect.* A, **32**, 751 (1976).