Luminescence characteristics of yellow emitting Ba_3SiO_5:Eu^{2+} phosphor

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The luminescence process of Eu^{2+}-activated Ba_2SiO_4 phosphor is characterized by the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} acting as an activator center. And the studies on Eu^{2+}-activated Ba_2SiO_4 phosphors have been performed by many researchers. Barry and Blasse *et al.* [1, 2], investigated the luminescence characteristics of Eu^{2+} ion in barium and strontium orthosilicates. Poort *et al.* [3] reported different emission of Eu^{2+} ion on two sites (nine and ten coordination) of Ba_2SiO_4 with orthorhombic structure by comparing with the results of the Eu^{2+}-doped orthophosphates. However, the optical and luminescent properties of Eu^{2+}-doped Ba_3SiO_5 are not known yet.

It has been found that when Eu^{2+} is incorporated into a host, different kinds of emission centers can be formed. This occurs if there are several kinds of cations replaceable by Eu^{2+} in the host matrix or if there exists several different sites for a specific cation [4, 5]. Moreover, the absorption and emission due to the transition between $4f^7$ and $4f^65d$ states of Eu^{2+} strongly depend on the crystal field acting on Eu^{2+}. Consequently, the choice of host materials is a critical parameter for determining the optical properties of the Eu^{2+} ions. In the present work, we have synthesized the previously unknown Ba_3SiO_5:Eu^{2+} phosphors among barium silicate phosphors and investigated their luminescent properties of these using an ultraviolet (UV) source.

The Ba_3SiO_5:Eu^{2+} phosphor powders were prepared using a solid-state reaction method. The staring materials used in the preparation of Ba_3SiO_5:Eu^{2+} phosphor were pure powders of $BaCO_3$, SiO_2 (quartz), and Eu_2O_3. The stoichiometric amount of starting materials was thoroughly mixed and ground under acetone in an agate mortar. The mixed powders were then heat-treated at various temperature and time periods under a reducing atmosphere. The resulting powders were identified by X-ray diffraction (XRD) using Cu K_α radiation (Ni filter). The emission and excitation spectra of the phosphor powders were measured using a Perkin-Elmer LS-50 luminescence spectrometer with a xenon flash lamp.

The emission spectra of Ba_3SiO_5:Eu^{2+} phosphor heat-treated at different temperatures are shown in Fig. 1. As can be seen from this figure, two emission bands are observed at 504 and 566 nm. Since the two emission spectra of Ba_3SiO_5:Eu^{2+} phosphor are quite different, it can be presumed that Eu^{2+} ions occupy two sites in the Ba_3SiO_5 lattice and give rise to two emission centers. The main peak of this phosphor is transferred from a wavelength of 566 nm to a wavelength of 504 nm as heat-treated temperature increases. The Ba_3SiO_5:Eu^{2+} phosphor heat-treated at 1050 °C exhibits yellow emission maximum peaked near 566 nm. As increased heat-treated temperature, the green emission at about 504 nm prevails rather than the yellow emission band.

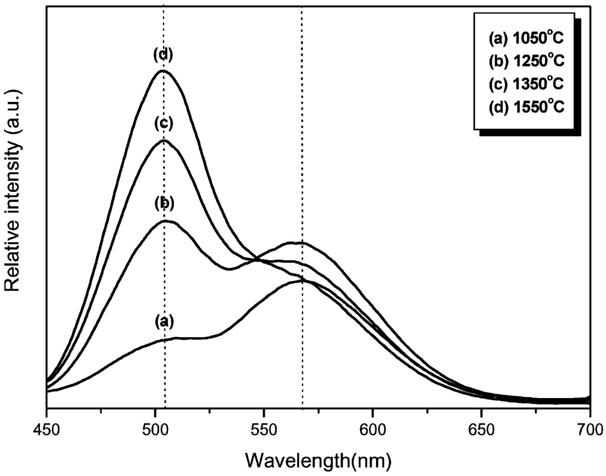

Figure 1 The emission spectra of Ba_3SiO_5:Eu^{2+} phosphor heat-treated at different temperatures.

To investigate the crystallinity of Ba_3SiO_5:Eu^{2+} phosphors heat-treated at different temperatures, XRD measurements were performed. In case of the sample heat-treated at 1050 °C, most of peaks correspond to the Ba_3SiO_5 phase that has tetragonal structure. As the heat-treated temperature is increased, the structure of the phosphor was composed of a mixture of tetragonal Ba_3SiO_5 and orthorhombic Ba_2SiO_4. Fig. 2 shows the intensity ratio of Ba_3SiO_5 phase to Ba_2SiO_4 phase as a function of the heat-treatment temperature. $I_{Ba_3SiO_5}$ is the XRD intensity of (2 0 2) plane for Ba_3SiO_5 and $I_{Ba_2SiO_4}$ is the XRD intensity of (0 3 1) plane for Ba_2SiO_4. As the heat-treatment temperature is increased from 1050 to 1550 °C, the intensity ratio of Ba_3SiO_5 phase to Ba_2SiO_4 phase decreases. This indicates that the crystalline structure of this phosphor is transformed from the tetragonal Ba_3SiO_5 phase to the orthorhombic Ba_2SiO_4 phase as the heat-treatment temperature increases. It can

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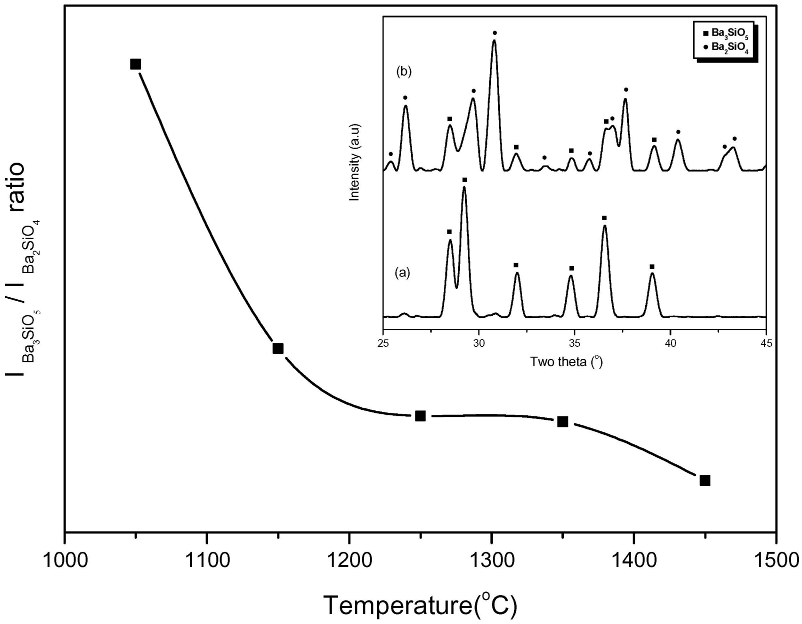

Figure 2 The intensity ratio of Ba_3SiO_5 phase to Ba_2SiO_4 phase in terms of various heat-treatment temperatures. ($I_{Ba_3SiO_5}$ is the XRD intensity of (2 0 2) plane for Ba_3SiO_5, $I_{Ba_2SiO_4}$ is the XRD intensity of (0 3 1) plane for Ba_2SiO_4.) The inset shows the XRD patterns of Ba_3SiO_5:Eu^{2+} phosphor heat-treated at (a) 1050 °C and (b) 1550 °C.

be confirmed from the XRD patterns of the samples heat-treated at 1050 and 1550 °C as shown in the inset of Fig. 2.

Because the Eu^{2+}-doped compounds strongly depend on the neighboring Eu^{2+} ions, it can be presumed that Eu^{2+}-doped barium silicate phosphors have a different emission band which changes with the crystalline environment. Tetragonal Ba_3SiO_5 has the same structure as Cs_3CoCl_5 in which there are two barium sites that appear in equal numbers in the lattice. Consequently, Ba_3SiO_5:Eu^{2+} phosphor has two emission bands which occur at the wavelength of 504 and 566 nm as shown in Fig. 1. The excitation spectra of Ba_3SiO_5 phosphor with 0.1 mol Eu^{2+} are investigated as shown in Fig. 3. The excitation spectra were obtained by monitoring two emission bands of 504 and 566 nm, respectively. The excitation spectra of Ba_3SiO_5:Eu^{2+} correspond to the $4f^7 \rightarrow 4f^6 5d$ transition of Eu^{2+} and depend on the emission wavelength. The excitation spectrum for 504 nm emission center has one excitation band at 350 nm, whereas the excitation spectrum for 566 nm emission center has two excitation bands at 335 and 398 nm.

The effect of Eu^{2+} concentration on the emission of Ba_3SiO_5:Eu^{2+} phosphors was also investigated. In general, the Ba_2SiO_4:Eu^{2+} phosphor having the orthorhombic structure showed a typical concentration quenching and shift to longer wavelength as the concentration of Eu^{2+} increases due to some changes of the crystal field around Eu^{2+}. However, the Ba_3SiO_5:Eu^{2+} phosphor showed some different luminescence features. The emission spectra of Ba_3SiO_5:Eu^{2+} phosphors prepared at various concentrations of Eu^{2+} are shown in Fig. 4. In the emission spectrum of

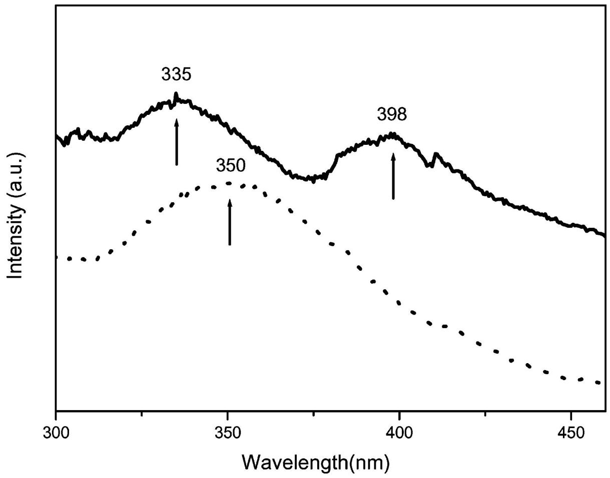

Figure 3 The excitation spectrum of Ba_3SiO_5:Eu^{2+} (0.1 mol) phosphor heat-treated at 1050 °C (solid line: excitation spectrum by monitoring at 566 nm emission center, dotted line: excitation spectrum by monitoring at 504 nm emission center).

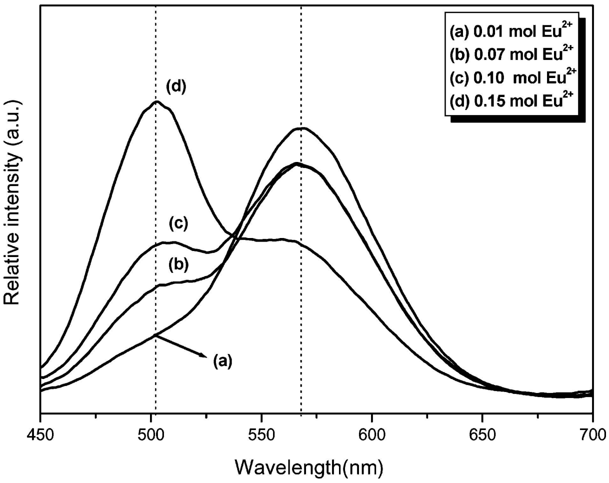

Figure 4 The emission spectra of Ba_3SiO_5:Eu^{2+} phosphor with various amounts of Eu^{2+} concentration.

Ba_3SiO_5:Eu^{2+} the phosphor having a 0.01 mol Eu^{2+} concentration showed one broad emission band at 568 nm. As the concentration of Eu^{2+} increases, however, the emission band of Ba_3SiO_5:Eu^{2+} phosphor is split into two emission bands with a main peak at 504 nm and a less intense band at 568 nm. At higher concentration of Eu^{2+} (0.15 mol), the intensity of 568 nm emission band is drastically reduced and Ba_3SiO_5:Eu^{2+} phosphor has maximum intensity at 504 nm. This may be attributed to energy transfer between two Eu^{2+} sites [4, 6]. As the Eu^{2+} concentration increases, the distance between Eu^{2+} ions becomes less, and the probability of energy transfer among Eu^{2+} ions increases [7]. In other words, the probability of Eu^{2+} ions at higher levels of 5d, which make an energy transfer to the lowed 5d levels of Eu^{2+} ions, increases with an increase of Eu^{2+} concentration. Blasse *et al.* [6], explained the energy transfer from the Eu_1-site to Eu_2-site in strontium silicate phosphate with apatite structure through energy overlap of the emission band and excitation band of the Eu_1-site and the Eu_2-site. It makes it possible to explain the energy transfer from Eu_1-site and Eu_2-site in present case. However, further investigation seems necessary to prove the energy transfer between Eu^{2+} ions in Ba_3SiO_5 phosphor.

In summary, the Ba_3SiO_5:Eu^{2+} phosphor has been synthesized and the luminescence properties have been investigated. The emission spectrum and the crystalline structure of Ba_3SiO_5:Eu^{2+} phosphor strongly depends on the heat-treatment temperature. The crystalline structure of Ba_3SiO_5:Eu^{2+} is transformed from tetragonal-type Ba_3SiO_5 to orthorhombic-type Ba_2SiO_4, as heat-treatment temperature increases. According to the transformed structure, the Eu^{2+}-doped barium silicate phosphors display different emission bands because the Eu^{2+}-doped compounds are strongly affected by the surrounding Eu^{2+} ions. The energy transfer from the Eu_1-site to the Eu_2-site is confirmed through the emission band of Ba_3SiO_5 as the Eu^{2+} concentration increases.

References

1. T. L. BARRY, *J. Electrochem. Soc.* **115** (1968) 1181.
2. G. BLASSE, W. L. WANMAKER, J. W. TER VRUGT and A. BRIL, *Philips Res. Repts.* **23** (1968) 189.
3. S. H. M. POORT, W. JANSSEN and G. BLASSE, *J. Alloys Comp.* **260** (1997) 93.
4. M. LESKELÄ, T. KOSKENTALO and G. BLASSE, *J. Solid State Chem.* **59** (1985) 272.
5. G. BLASSE, *J. Sold State Chem.* **62** (1986) 207.
6. G. BLASSE and A. BRIL, *Phys. Lett.* A **28** (1969) 572.
7. J. QIU, K. MIURA, N. SUGIMOTO and K. HIRAO, *J. Non-Cryst. Solids* **266** (1997) 213.

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