O U R N A L O F

Ceramic Processing Research

Luminescent properties of Eu-activated Mg-Y-Si-O-N glass and crystalline phosphors

Sosuke Sato^a, Shinnosuke Kamei^a, Kazuyoshi Uematsu^a, Tadashi Ishigaki^b, Kenji Toda^{a,b}, Mineo Sato^{b,c}, Hideki Sasaoka^d, Masahiro Ooka^d and Kazuhito Nishimura^d

^aDepartment of Chemistry and Chemical Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata, 950-2181, Japan

^bCenter for Transdisciplinary Research, Niigata University, 8050 Ikarashi 2-nocho, Niigata, 950-2181, Japan

^cGraduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Niigata, 950-2181, Japan

^dKochi FEL, 3-1 Shinonome-cho, Kochi, 780-0805, Japan

Eu-activated Mg-Y-Si-O-N glass and MgYSi₂O₅N phosphors were prepared by a conventional solid-state reaction method. The samples were sintered at 1573-1673 K for 2 h in NH₃ atmosphere. MgYSi₂O₅N phosphors show red emission at 611 nm. On the other hand, emissions of Mg-Y-Si-O-N glass phosphors were shifted from blue (at about 450 nm) to yellow (at about 550 nm) with increasing concentration of Eu ions. The different luminescent characteristics between MgYSi₂O₅N and Mg-Y-Si-O-N glass are ascribed to different valence of doped Eu ions respectively.

Introduction

In recent years, oxynitride glass such as Y-Si-Al-O-N [1], Ca-Si-Al-O-N [2] and Mg-Si-O-N [3] have received attention as luminescent materials because of their good thermalstability, mechanical characteristic and chemical properties. The glass phosphors have investigated to apply for white light-emitting diodes (LEDs) and often shown interesting luminescent properties. For example, Euactivated Y-Si-Al-O-N glass having the emission wavelength shifts from below 500 nm to 640 nm with controlling Eu concentration is reported by Graaf et al. [4].

The Mg-Y-Si-O-N glass is known as a precursor of the MgYSi₂O₅N [5, 6] and well investigated about the glass properties [7-9]. However, the Mg-Y-Si-O-N glass has not been reported as an oxinitride glass phosphor. Therefore, we focus on the Mg-Y-Si-O-N glass which is colorless and transparence. The Mg-Y-Si-O-N glass is often produced by melting of crystalline MgYSi₂O₅N whose crystal structure is analogous to diopside (CaMgSi₂O₆). The Eu-activated diopside is well known as a phosphor for plasma display panels (PDPs) [10]. The luminescent property of $Mn^{2+}-Ce^{3+}$ co-doped MgYSi₂O₅N phosphor has already investigated by W. Xie et al [11], however Eu-activated MgYSi₂O₅N has not been investigated. In this study, we synthesized Eudoped Mg-Y-Si-O-N glass and MgYSi₂O₅N ceramic phosphor to compare luminescence property of crystals with that of the glasses.

Experimental

Mg-(Y, Eu)-Si-O-N glass and Mg(Y_{1-x}Eu_x)Si₂O₅N phosphors were prepared by a conventional solid-state reaction method. The starting materials, MgO (Kanto Chemical Co., Inc. 99.99%), Y₂O₃ (Sin-Etsu Chemical Co., Ltd. 99.99%), Si₃N₄ (Ube Ind., Ltd. 99.5%), SiO₂ (Wako Pure Chemical Ind., Ltd. 99.9%) and Eu₂O₃ (Sin-Etsu Chemical Co., Ltd. 99.99%), were mixed in homogeneous stoichiometry using an agate mortar. After mixing, the sample was placed in an alumina boat inside a tubular furnace and sintered at 1573 K - 1673 K under NH₃ atmosphere. The sample was held at this temperature for 2 h and then cooled to room temperature. In the glass synthesis, starting materials compositions of Mg-(Y, Eu)-Si-O-N glass are the same of crystalline MgYSi₂O₅N compositions.

The crystal structures of the samples were identified by powder X-ray diffraction analysis (MAC Science; MX Labo) with Cu Ká radiation (40 kV, 25 mA) at room temperature. Photoluminescence (PL) and PL excitation spectra for these compositions were measured with a spectrofluorometer (JASCO FP-6500) at room temperature.

Results and Discussion

Figure 1 shows XRD patterns of crystalline MgYSi₂O₅N prepared at 1573 K. All samples conformed to the diffraction patterns of MgYSi₂O₅N phase. Although the Eu 7 mol% sample was also matched the diffraction patterns of MgYSi₂O₅N, it seems that the crystallinity has become lower than the other samples because the Eu 7 mol% sample was caused partially melting. The Eu 10 mol% sample completely melted at 1573 K due

^{*}Corresponding author:

Tel:+81-25-262-6771

Fax:

E-mail: ktoda@eng.niigata-u.ac.jp



Fig. 1. XRD patterns of the samples fired at 1573 K.



Fig. 2. PL spectra of the samples fired at 1573 K.

to melting point depression of MgYSi₂O₅N by increasing Eu concentration. When the firing temperature was at 1673 K, all samples melted and formed glass. The body color of the glass samples were colorless at low Eu concentration (1 - 5 mol%) and yellow at high Eu concentration (7 - 10 mol%).

Crystalline sample emissions were different from that of glass samples. The PL spectra of the samples fired at 1573 K are shown in Figure 2. The Eu 1 and 3 mol% samples showed the broad absorption from 200 to 400 nm and the red emission at 611 nm due to the ${}^{5}D_{J}$ \rightarrow ⁷F_{J'} transition of Eu³⁺. However, the samples higher Eu 5 mol% (glass phosphor) showed the broad emission due to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu²⁺. The emission of glass samples is explained as resulting from the sites occupied by Eu ions are different from crystalline MgYSi₂O₅N. In the glass sample, the valence of Eu ions is divalent although the sample composition was the same of crystalline MgYSi₂O₅N. The Eu ions occupied in the Y sites in the MgYSi₂O₅N, however, in Mg-Y-Si-O-N glass the Eu ions widely exist in the sample without the regular sites. Therefore, the Eu ions in the glass samples are reduced from Eu³⁺ to Eu²⁺ by the NH₃ atmosphere because the Eu ions are substituted in irregular sites in the Mg-Y-Si-O-N glass structure.

Figure 3 shows the emission spectra of glass phosphors obtained by varying Eu concentration. The



Fig. 3. PL spectra of the Mg-Y-Si-O-N glass samples.



Fig. 4. PL excitation spectra of the Mg-Y-Si-O-N glass samples.

spectra shifted to longer wavelengths (about 450 to 550 nm) with increasing Eu concentration from 1 to 7 mol%. The Eu 7 mol% sample showed the longest emission wavelength at the top of the peaks. These wavelength shifts are also shown in other oxynitride glass phosphors such as Eu-doped Y-Al-Si-O-N glass [4]. The emission shifts of Eu-doped Y-Al-Si-O-N glass to longer wavelengths with increasing Eu-contents. The emission spectra in the Mg-Y-Si-O-N glass are considered the same phenomenon with Eu-doped Y-Al-Si-O-N glasses. The wide emission spectra shifted with changing Eu²⁺ concentration in Mg-Y-Si-O-N glasses can be explained by energy transfer, where a Eu^{2+} site is excited and subsequently donates its energy to a neighboring Eu²⁺ site just like Eu-doped Y-Al-Si-O-N glass. The energy transfer can only occur if the excited state of the receiving Eu²⁺ ion is located at lower energies than that of the donating ion. This is the case in glasses where a distribution of Eu²⁺ sites is present rather than one well-defined site. The probability of energy transfer between two ions increases as the distance between the donor and the acceptor ion decreases, which is in accordance with the observed dependence of the emission energy on the Eu²⁺ concentration [4]. In the Eu concentrations at 10 mol%, the emissions shifted to shorter wavelengths compared with Eu 7 mol%. The emission of the Eu 10 mol% sample did not shift so much. The reasons of these

shorter wavelength shifts are under consideration.

The excitation spectra of Mg-Y-Si-O-N glass samples shifted to longer wavelength with increasing Eu concentrations (figure 4). As well as the emission spectra of the glass samples, the spectra indicated the longest wavelength shift when the Eu concentrations were at 7 mol%. However, no wavelength shifts were shown between the Eu 7 mol% and the Eu 10 mol%, which is different from the result comparing the emissions of the Eu 7 mol% and the Eu 10 mol% samples.

These non-linear changes of the excitation and emission spectra were interest luminescent property. A possible cause of the non-linear changes is considered the change of Eu^{2+} sites by another glass phase being present in the Eu 10 mol% sample.

Conclusions

Eu-activated MgYSi₂O₅N and Mg-Y-Si-O-N glass phosphors were synthesized by a solid-state reaction. MgYSi₂O₅N phosphors showed the red emission due to the Eu³⁺ ions. However, Mg-Y-Si-O-N glass phosphors indicate blue to yellow emission due to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu²⁺ by controlling Eu concentrations. These different emissions between MgYSi₂O₅N and Mg-Y-Si-O-N phosphors are due to the Eu ions in the different sites. The wide wavelength shifts of Mg-Y-Si-O-N glass phosphors are considered due to the energy transfer between the doped Eu ions.

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