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# Porous silicon nitride ceramic phosphors

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Luminescent materials have been used in a variety of display devices such as cathode ray tube, plasma display and field emission display. There also has been an application to the phosphors of light emitting diodes. Although most of the phosphors that have been used are oxides, sulfides and oxysulfides doped with rare earth or metal ions, they are not always sufficient with respect to chemical resistance and thermal resistance.

Nitride or oxynitride ceramics such as $Si_3N_4$ [1] and SiAlON [2] are well known excellent structural materials due to their high strength and high thermal and chemical resistances. Recently, $\alpha$-SiAlON ceramics has been reported as possible phosphors, [3–6] and $LaSi_3N_5$ [7] and $Ba_2Si_5N_8$ [8] phosphors have been reported as $Si_3N_4$-based luminescent ceramics. In these phosphors, rare earth ions as luminescent centers, for example, $Eu^{2+}$ and $Eu^{3+}$, are doped into interstitial sites in the host ceramics.

To our knowledge, however, there are few reports on luminescent $Si_3N_4$ ceramics because there are no sites where rare earth ions can be accommodated in the crystal structures of both $\alpha$-$Si_3N_4$ and $\beta$-$Si_3N_4$. In general, $Si_3N_4$ sintered ceramics are produced by sintering powder mixtures of $Si_3N_4$ and sintering aids such as $Y_2O_3$ and $Al_2O_3$. The resulting sintered $Si_3N_4$ ceramics are densified and have the combined microstructure of $Si_3N_4$ grains and $SiO_2$-$Al_2O_3$-$Y_2O_3$ grain boundaries. Therefore, if the grain boundary phase were luminescent, the $Si_3N_4$ sintered ceramics would be used as a phosphor.

Various yttrium silicates and yttrium silicon oxynitrides such as $Y_2SiO_7$ [9] and $Y_2Si_3N_4O_3$ [10] are well known as the host materials of phosphors. For example, Krevel *et al.* reported that a Ce-doped $Y_2Si_3N_4O_3$ showed a broadband emission with a maximum peak at about 500 nm [10].

We have developed high strength porous $Si_3N_4$ ceramics with a particular microstructure where elongated $\beta$-$Si_3N_4$ grains are connected at random in three dimensions via an Si-Er-O-N grain boundary phase. The porous $Si_3N_4$ ceramics can be fabricated by sintering powder compacts of $\alpha$-$Si_3N_4$ and $Er_2O_3$ as a sintering aid.

In this work, we focused on the porous $Si_3N_4$ ceramics including oxynitride grain boundary phases as a possible phosphor. In this paper, we report the fabrication of rare earth-doped porous $Si_3N_4$ ceramics and their luminescent properties.

Alpha-$Si_3N_4$ (99.9%, SN-E10, Ube Co. Ltd., Tokyo Japan) and various rare earth oxides ($Y_2O_3$, $Eu_2O_3$, $Tm_2O_3$, $Gd_2O_3$and $Tb_4O_7$, 99.9%, prod. by Shin-etsu Chemical Co.) were used as the starting powders. The powder mixtures of $\alpha$-$Si_3N_4$ and small amounts of $Y_2O_3$-based composite oxides as sintering aids were pressed to the dimensions of 12 mm in diameter and 5 mm thick. The total amount of the sintering aids was adjusted at 8% by weight versus $Si_3N_4$ powder. The RE (Eu, Tm, Gd or Tb) contents of $Y_2O_3$-based sintering aids were varied from 0 to 100%. The resulting powder compacts were sintered at a temperature of 1800 °C for 2 hr in a pressurized $N_2$ atmosphere of 0.3 MPa. Thus, porous $Si_3N_4$ sintered bodies having different grain boundary phases were fabricated.

Crystalline phases were identified by X-ray diffraction. The microstructure of the fracture surfaces of the sintered bodies was observed with a scanning electron microscope (SEM). Emission spectra were measured at room temperature using a fluorescent spectrophotometer (Model F-4500, Hitachi).

Fig. 1 shows typical SEM micrographs of porous $Si_3N_4$ sintered bodies fabricated with various sintering aids. All the sintering aids promoted the anisotropic grain growth of columnar grains. There was no significant difference in microstructure among their specimens, and also the specimens had high porosity of 41 to 51%.

Fig. 2 shows the X-ray diffraction diagrams of Y/Eu co-doped specimens. It is found that the specimen sintered with 100% $Y_2O_3$ consists of $\beta$-$Si_3N_4$ and $Y_2Si_3N_4O_3$, where $Y^{3+}$ ions are present as the secondary phase. There is no significant change of the X-ray diffraction diagrams when $E_2O_3$ is added to the sintering aid. Also in the specimen with 100% $Eu_2O_3$, almost all the peaks appear at the same positions as those of the specimen with 100% $Y_2O_3$. The secondary phase in the specimen with 100% $Eu_2O_3$ is possibly $Eu_2Si_3N_4O_3$ although we cannot identify their peaks due to no data of the compound in the up-to-date powder diffraction data files (ICDD 2000). Several unidentified peaks were also seen in the diagrams, and their relative intensity was almost equivalent in the specimens with 20% $Eu_2O_3$ and 100% $Eu_2O_3$ (for example, the relative peak intensity $I/I_0$ values of peaks at 35° ($2\theta$) were the same). These unidentified phases are possibly trace amounts of europium silicates such as $Eu_2SiO_4$ and $Eu_3Si_2O_7$. However, they could not be determined in the present work.

Fig. 3 shows the emission spectra of the Y/Eu co-doped specimens. The specimens have broadband emissions with maximum peaks at a constant $\lambda$ value of 451 nm, independent of Eu concentration, and the

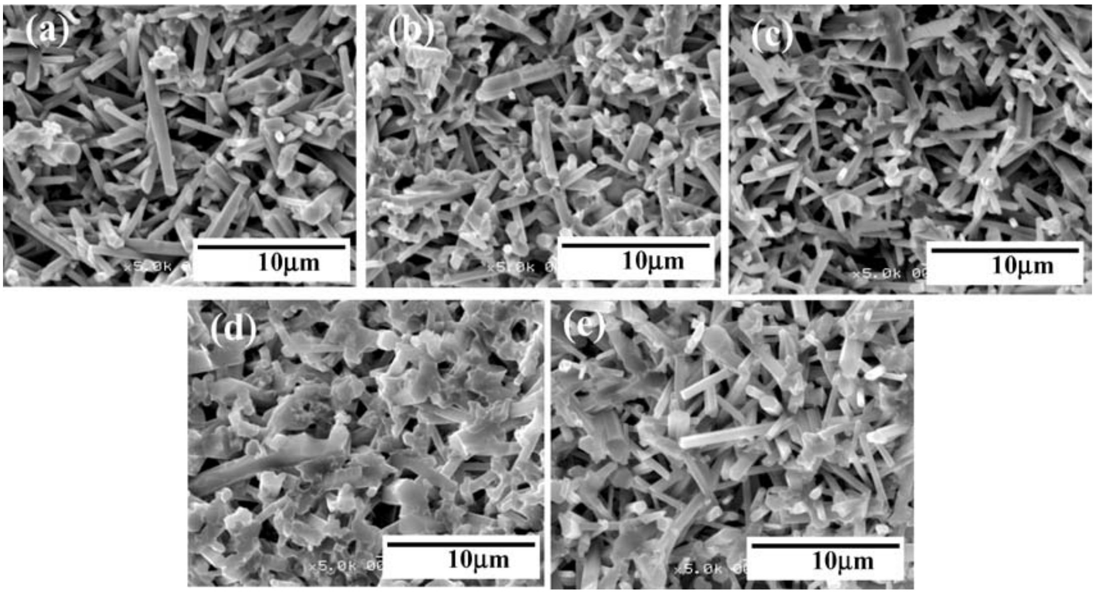

*Figure 1* Typical SEM micrographs of porous $Si_3N_4$ ceramics sintered with: (a) $Y_2O_3$, (b) $Eu_2O_3$, (c) $Tm_2O_3$, (d) $Gd_2O_3$ and (e) $Tb_4O_7$ as sintering aids.

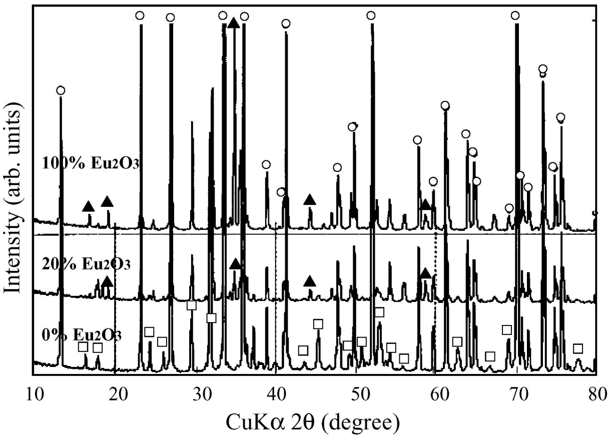

*Figure 2* X-ray diffraction diagrams Y/Eu co-doped porous $Si_3N_4$ ceramics with various Eu/(Eu + Y) values: ○: $\beta$-$Si_3N_4$, □: $Y_2Si_3N_4O_3$, and ▲: unidentified.

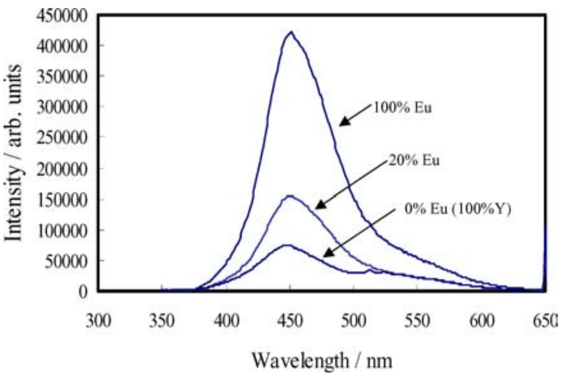

*Figure 3* Emission spectra of the Y/Eu co-doped porous $Si_3N_4$ ceramics.

luminescence intensity increases with increasing Eu content.

$Y_2Si_3N_4O_3$ oxynitride should show no emission because $Y^{3+}$ ion does not have any 4f and 5d electrons. Nevertheless, the specimen sintered with 100% $Y_2O_3$ also shows blue emission even though its intensity is weak. At the current stage, a possible cause for this emission is explained by impurities in the starting powder, especially the other rare earth ions in $Y_2O_3$.

No remarkably sharp line emission peaks of $Eu^{3+}$ are observed in the spectra, indicating the reduction of $Eu^{3+}$ to $Eu^{2+}$ because of sintering atmosphere of $N_2$. The energy level scheme of $Eu^{2+}$ has been known for long [11]. In the emission spectra, either sharp 4f-4f transitions or very broad band emission due to 5d-4f transitions are observed depending on the fact that how large the ligandfield splitting of 5d-levels is [12].

We discussed whether the luminescence of the unidentified phases formed with $Y_2Si_3N_4O_3$ was attributed to the overall luminescence of specimens or not. However, we consider that the broadband emissions are assigned to the $5d^14f^6$-$4f^7$ transitions in $Y_2Si_3N_4O_3$: Eu phosphors because the peak intensity of the unidentified phases does not vary with increasing Eu content (see Fig. 2b and c).

Fig. 4 shows an emission spectrum of a Tb-doped specimen sintered with 100% $Tb_3O_4$. Special sharp line emissions characteristic of $Tb^{3+}$ are observed at λ values of 489, 545, 585 and 623 nm. According to the energy levels of the 4f-4f transitions [13], these

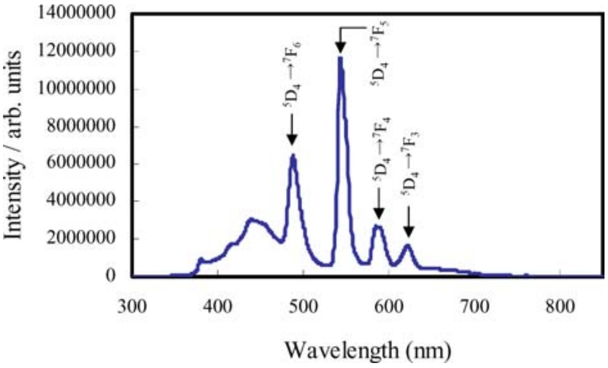

*Figure 4* Emission spectrum of a Tb-doped porous $Si_3N_4$ ceramic sintered with 100% $Tb_3O_4$.

emissions can be assigned to the following 4f-4f transitions: $^5D_4 \rightarrow {}^7F_6$ (~490 nm), $^5D_4 \rightarrow {}^7F_5$ (~545 nm), $^5D_4 \rightarrow {}^7F_4$ (~590 nm) and $^5D_4 \rightarrow {}^7F_3$ (~620 nm). The reason for broadband emission around 450 nm is probably the same as those in the specimen sintered with 100% $Y_2O_3$.

The luminescence characterization of specimens sintered with $Gd_2O_3$and $Tm_2O_3$ is under consideration.

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