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Preparation and Characterization of Aluminum-doped $SiO_2:Sm^{3+}$ Phosphor

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Samarium ions in Al-doped $SiO_2:Sm^{3+}$ phosphor were revealed to be atomically dispersed in small Al_2O_3 crystallites by forming Sm-O-Al bonding, which contributes to improvements in the fluorescent intensity of $SiO_2:Sm^{3+}$ phosphor.

One of the important applications of quartz glasses is a laser medium, where[1)] rare metal ions are highly dispersed. A glass containing Nd^{3+} ions is utilized as a typical glass laser and its preparation techniques and characterization have been extensively studied.[2)] It has been known that fluorescent intensity from Nd^{3+} ions is significantly improved by an addition of a small amount of Al^{3+} ions into $SiO_2:Nd^{3+}$ phosphor,[3)] and this has been attributed to the formation of almost atomically dispersed Nd^{3+} ions. However, few studies on the fluorescent properties of glasses dispersing other rare metal ions and on the effects of dopants have been reported.[4)]

In this work, the fluorescence of Sm^{3+} ions in $SiO_2:Sm^{3+}$ phosphors with various Al^{3+} concentrations and the local structures around Sm^{3+} ions were studied by EXAFS (extended x-ray absorption fine structure) and TEM (transmission electron microscope)to understand the role of Al^{3+} dopant for fluorescent property.

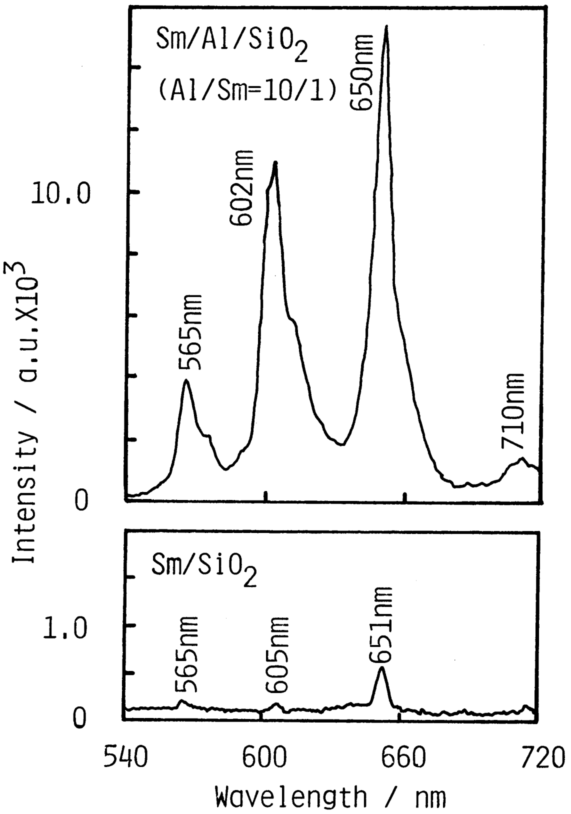

Fig. 1. Emission spectra of Sm/SiO_2 and $Sm/Al/SiO_2$ (Excitation 403 nm).

An Al-doped $SiO_2:Sm^{3+}$ phosphor was prepared by hydrolysis of ethyl silicate mixed with Sm (III) and Al (III) nitrates dissolved in an enough amount of ethylene glycol (EG) or ethanol at 75 °C. A gel formed was dried at 110 °C, followed by calcination at 500 °C for 2 h. The fine and white powder thus prepared was fired at 950 °C for 4 h prior to the measurements of fluorescent intensity using Spex Fluorolog by 403 nm excitation. In the case of $SiO_2:Sm^{3+}$ phosphor, hydrolysis of ethyl silicate mixed with Sm(III) nitrate dissolved in EG or ethanol was performed and a gel obtained was dried and calcined under the same conditions as employed for the preparation of Al-doped phosphor. The molar ratios of Sm/SiO_2 and Al/Sm in the phosphors were varied.

In Fig. 1 is depicted a significant enhancement in the emission intensity of the Al-doped phosphor, comparing with the phosphor without dopant. Molar ratio of Sm/SiO_2 was $5x10^{-3}$ in both the phosphors here and that of Al/Sm in the Al-doped one was 10. By monitoring the emission intensity at maximum, that is 650 nm, the most effective Sm/SiO_2 ratio was studied using Al-doped phosphors with a constant Al/Sm ratio of 10. As can be seen in Fig. 2, maximum intensity was observed for the phosphors with Sm/SiO_2 ratio of about $7x10^{-3}$. Then, an optimum Sm/Al ratio for the fluorescent intensity at 650 nm was found to be about 10 (see Fig. 3), where Sm/SiO_2 molar ratio was kept to be $7x10^{-3}$. Thus, an extreme improvement in the fluorescent intensity of Al-doped $SiO_2:Sm^{3+}$ phosphor is achieved when the phosphor is prepared so that the Sm/SiO_2 and Al/Sm molar ratios are about $7x10^{-3}$ and 10, respectively. A TEM photograph of the Al-doped phosphor, observed at an accelerating voltage of 200 kV, is given in Fig. 4. The Sm/SiO_2 and Al/Sm ratios were $7x10^{-3}$ and 15, respectively. It is

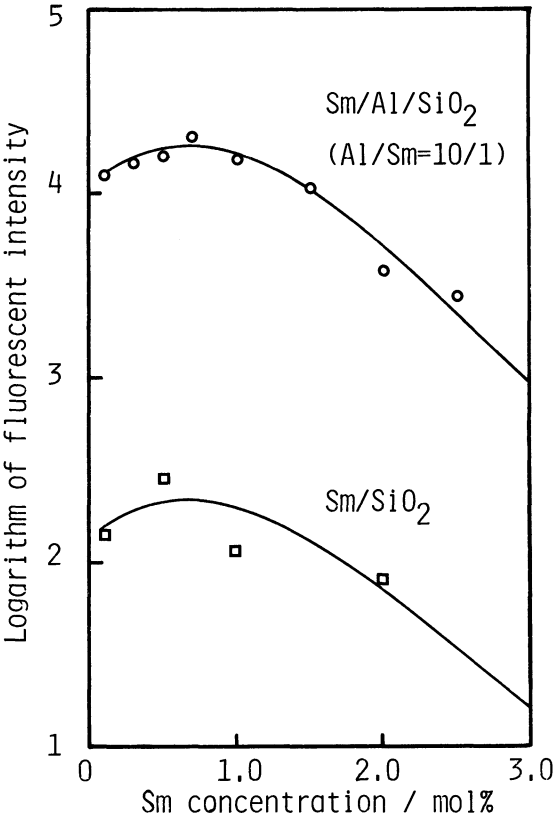

Fig. 2. Relationship between Sm concentration and fluorescent intensity (650 nm).

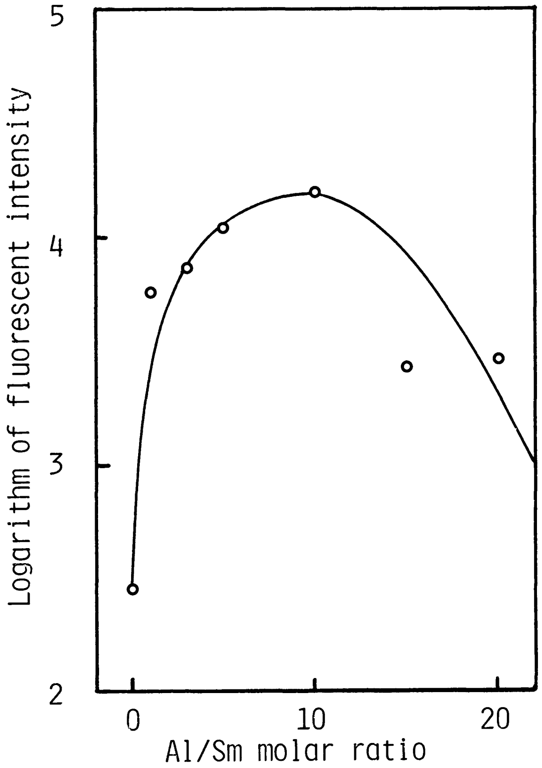

Fig. 3. Relationship between Al/Sm and fluorescent intensity (650 nm).

obvious that the doped Al ions coagulated to form, probably, small alumina crystallites sized 200-500 Å during the firing at 950 °C, because no such crystallites are observed in the undoped phosphors.

Since a key to understand the role of Al dopant lies in the difference of local structures around Sm^{3+} ions between Al-doped phosphors and phosphors without dopant, EXAFS[5)] was applied to both the phosphors with Sm/SiO_2 and Al/Sm molar ratios of $7x10^{-3}$ and 10, respectively.

Figure 5 shows Fourier transforms of Sm L_{III} EXAFS spectra of $SiO_2:Sm^{3+}$ and the Al-doped one. Fourier transforms of EXAFS spectra of pure Sm_2O_3 and $SmAlO_3$ powders are also given, for comparison.

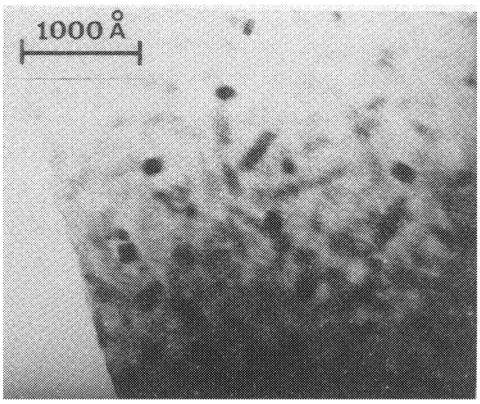

Fig. 4. TEM photograph of $Sm/Al/SiO_2$ (Al/Sm = 15/1).

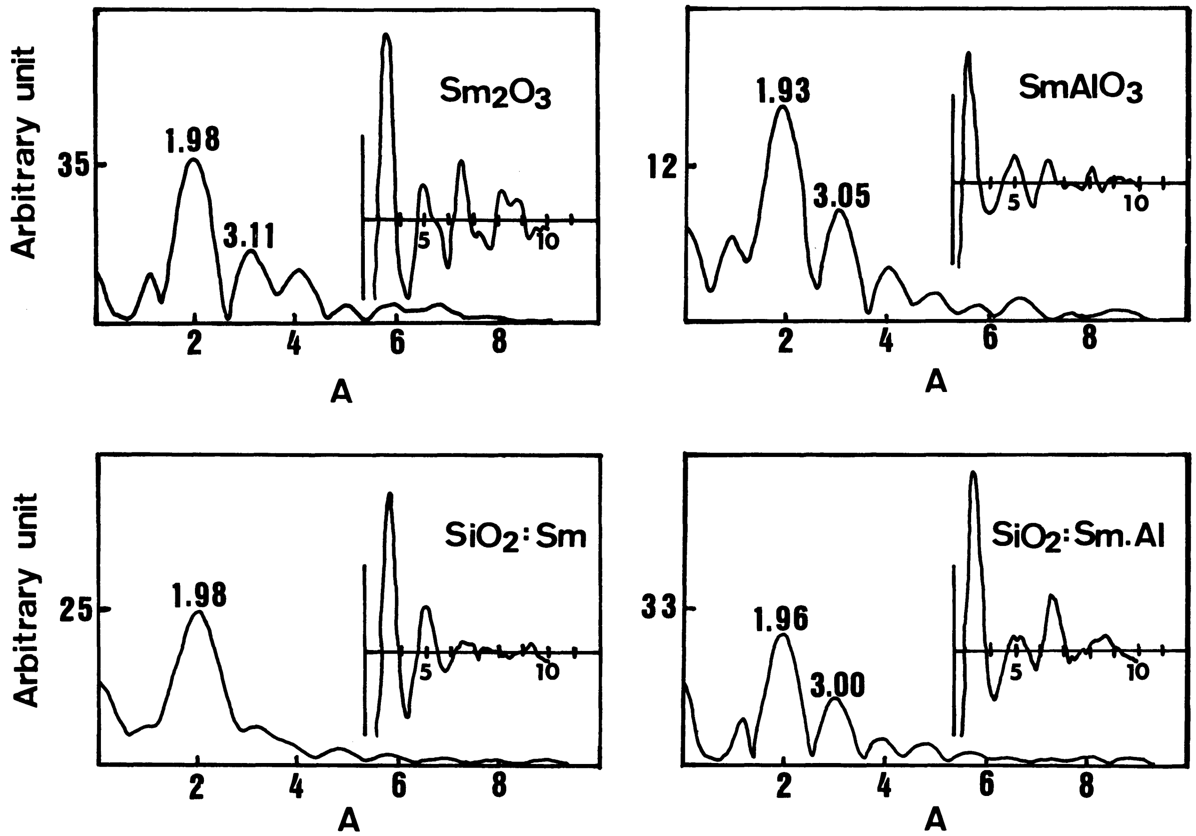

Fig. 5. Oscillations and Fourier transforms of EXAFS spectra.

Each spectrum has a peak at about 1.95 Å (phase shift uncorrected), evidently corresponding to nearest neighbor oxygen atoms to Sm. In $SiO_2:Sm^{3+}$ phosphor, EXAFS oscillation is monotonous and consequently, this is the only peak, suggesting no formation of Sm_2O_3 crystallites. It is, however, still difficult to conclude the atomical dispersion of Sm^{3+} ions in $SiO_2:Sm^{3+}$ phosphors, since amorphous Sm_2O_3 particles, if present, must exhibit the only one peak due to Sm-O bonding. On the other hand, EXAFS oscillation of the Al-doped phosphor is more complicated and the associated Fourier transform has several peaks. Repeated measurements indicated that the peaks at 1.96 and 3.00 Å (phase shift uncorrected) are reproducible, thus clearly showing the difference in local structures around Sm^{3+} ions in the Al-doped and undoped phosphors.

The second peak in Sm_2O_3 corresponds to Sm atoms at 3.58 Å, and the one in $SmAlO_3$ corresponds to Al atoms at 3.24 Å and Sm atoms at 3.76 Å, calculated from their crystallographic structures. At this moment, it is not possible to identify unambiguously the nature of the second peak of the Al-doped phosphor. It is, however, certain to conclude that Sm-Sm interaction is not a major component of this second peak, because the peak position is different from the second peak of Sm_2O_3 by as much as 0.1 Å. It is most plausible to assign this peak to Al atoms in Sm-(O)-Al bonding, suggesting the atomic dispersion of Sm^{3+} ions in the Al-doped $SiO_2:Sm^{3+}$ phosphors.

Considering all the evidences from XRD, TEM and EXAFS, the following pictures are proposed about the local structures of Sm atoms in Al-doped and undoped SiO_2: Sm^{3+} phosphors. Samarium atoms in the Al-doped phosphors are atomically dispersed by forming Sm-O-Al bonding with Al atoms in small Al_2O_3 crystallites sized several hundred A, while in the undoped phosphors it is not certain whether the Sm^{3+} ions are atomically dispersed in SiO_2 matrix or coagulate to form amorphous Sm_2O_3 particles. The preparation techniques employed here have been developed in the field of catalyst preparation such as Ni/SiO_2,[6)] where the atomic dispersion of Ni^{2+} ions in a gel formed by hydrolysis and the formation of tiny clusters of NiO by firing at 500 °C have been evidenced by EXAFS.[7)] On the analogy of these results the presence of amorphous Sm_2O_3 particles in the fired $SiO_2:Sm^{3+}$ phosphor is preferred to the atomic dispersion.

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