Control of valence states of europium in sodium-aluminosilicate glasses

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Glasses doped with well-controlled Eu^{3+} and Eu^{2+} ions have attracted considerable interest due to the possibility of tuning the wavelength range of the emitted light from violet to red by using their $^5D_0 \rightarrow ^7F_j$ and 5d–4f electron transitions. However, in silicate glasses, the Eu atoms are stably doped in the trivalent state, with no indication of divalent Eu. Special techniques, melting and/or secondary heating in a reducing atmosphere, are needed to reduce Eu^{3+}. If the valence state of Eu ions could be easily controlled in silicate glasses, numerous opportunities for glass applications would open up.

Now, we successfully found out the sodium-aluminosilicate glasses, in which the oxidation states of Eu ions are easily controlled by heating in ambient or reducing atmosphere. In the Na_2O–Al_2O_3–SiO_2 system (see figure), the Eu atoms primarily exist in the trivalent state in all glasses melted in air. On the other hand, large differences were observed in the glasses heated under H_2, that is, the Eu^{3+} ions doped in the glasses with Al/Na > 1 (region colored with blue) were only reduced to Eu^{2+}, whereas the Eu^{3+} ions were stable not to be reduced in the glasses with Al/Na < 1(region colored with yellow). The spectra shown in figure are fluorescence of Eu^{2+} and Eu^{3+}, respectively. Important finding was that the coexistence of Al^{3+} ions is essential for reducing Eu^{3+} ions. In particular, in the glass compositions with Al/Na > 1.0, the Eu^{3+} ions are coordinated by the oxygens bound with AlO_4 and SiO_4 units, and are reduced to the Eu^{2+} by heating in H_2 gas. The local structure of Eu^{3+} ions was investigated using the extended X-ray absorption fine-structure (EXAFS) spectroscopy, magic-angle spinning solid state nuclear magnetic resonance (MAS-NMR) spectroscopy, and infrared spectroscopic experiments, and the results were discussed in the context of the reaction of Eu^{3+} ions with H_2 gas. The present results provide useful guideline for controlling the valence state of RE ions in host materials; then numerous opportunities for glass applications can be opened up.

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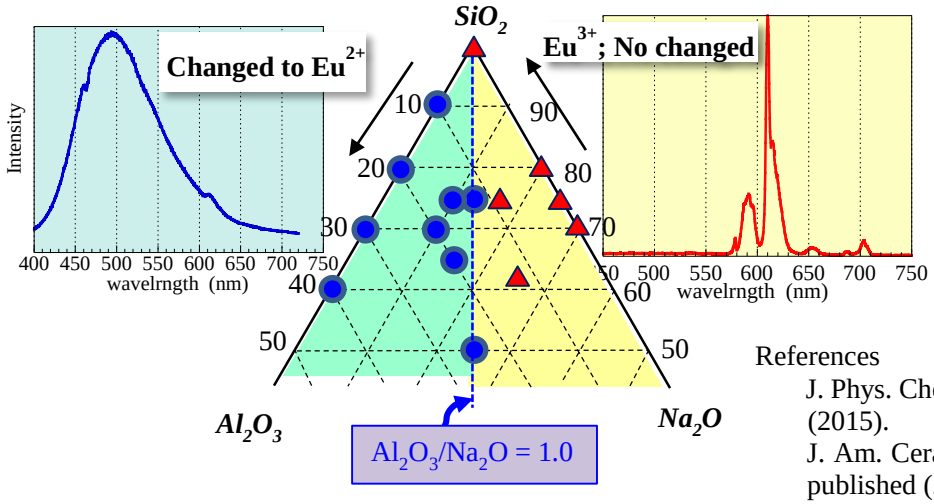

References

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