Preparation of luminescent and colored glasses and glass ceramics by the sol-gel method

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Germanium dioxide (GeO_2) has low phonon energy and high transparency in the infrared region compared with silicon dioxide (SiO_2), GeO_2 glasses are therefore very promising optical materials such as rare earth ions phosphors. The Mn^{2+} ion is well known to show different luminescence colors influenced by its coordination number and host materials. In the present study, to obtain new and superior optical materials, GeO_2-based glasses and glass ceramics doped with Mn^{2+} ions were prepared by a sol-gel method, and their optical properties were investigated. SiO_2 colored gels and glasses containing the organometallic compound, ferrocene, were also produced by a sol-gel method.

Strong green luminescence was observed at 535 nm under UV excitation of 254 nm from ZnO-GeO_2 glasses and glass ceramics doped with Mn^{2+} ions. Fluorescence and excitation spectra, ESR and XRD show that this green luminescence is due to the $^4T_1 \rightarrow {}^6A_1$ transition of tetrahedrally coordinated Mn^{2+} ions in Zn_2GeO_4 polycrystals. The energy transfer from excited ZnO-GeO_2 host materials to Mn^{2+} ions probably occurs. On the other hand, under UV excitation of 365 nm, Mn^{2+}-doped ZnO-GeO_2 glass ceramics showed the green luminescence, while Mn^{2+}-doped ZnO-SiO_2 glass ceramics didn't. Therefore, the former has an advantage in the low energy excitation compared with the latter.

Red luminescence was observed at about 665 nm under UV excitation of 254 nm from MgO-GeO_2 glasses and glass ceramics doped with Mn^{2+} ions. This red luminescence is found to be due to the $^4T_{1g} \rightarrow {}^6A_{1g}$ transition of octahedrally coordinated Mn^{2+} ions in $MgGeO_3$ polycrystals. This red luminescence of the glass ceramics is long in its wavelength compared with phosphors containing Eu^{3+} ions (612 nm), therefore the glass ceramics will be expected for applications in red phosphors with good color purity.

When the sol-gel reaction and the drying process of SiO_2 sols doped with ferrocene proceeded to wet gels, dried gels and glasses, the color of the samples turned from orange to blue. This color change is caused by the oxidation of ferrocene to ferrocenium ions.