14. The Slow Temporal Relaxation of Meta-Phosphate Glass containing Europium as revealed by Inhomogeneous Linewidth Change in Fluorescence Spectra due to 5D_0 - 7F_0 Transition of Eu^{3+} Ions

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(Communicated by Masao KOTANI, M. J. A., Feb. 12, 1985)

Recently there has been much interest in the origin of the optical homogeneous and inhomogeneous linewidths of rare-earth ions in amorphous materials and glasses.¹⁾⁻¹⁰⁾ We tried to find phenomena that would indicate that the inhomogeneous linewidths are temporally dependent. In this communication we wish to show that the inhomogeneous linewidth of 5D_0 - 7F_0 fluorescence line of Eu^{3+} in meta-phosphate glass is a function of time at room temperature.

Measurements of inhomogeneous linewidth were carried out for five samples. Sample compositions were 100 mol% $\text{Ca}(\text{PO}_3)_2$ with 50, 60, 65, 70 and 82 mol% Eu^{3+} . A high pressure mercury lamp (USHIO 500W) was used as the source of excitation. Fluorescence spectra were dispersed with a 50 cm grating monochromator (1200 lines/mm). Details of glass preparation and experimental apparatus are given in ref. 11). An energy level diagram and a spectrum profile of the Eu^{3+} ion (5D_0 - 7F_0) are shown in Fig. 1.

Fig. 1. Spectral shape of the inhomogeneously broadened transition of 5D_0 - 7F_0 emission spectrum of Eu^{3+} ion (70 mol%) in $\text{Ca}(\text{PO}_3)_2$ glass at room temperature.

The temporal shift of the full width at half-maximum (FWHM) of the inhomogeneously broadened 5D_0 - 7F_0 transition spectra of Eu^{3+} ion in glass are shown in Figs. 2, 3 and 4 plotted against time. The gradual change of FWHM exists in the range from 0.40 Å to 1.85 Å for 50, 60, 65, 70 and 82 mol% Eu^{3+} ions, respectively.

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Fig. 2. Time dependence of the half width of ⁵D₀-⁷F₀ emission spectra of Ca(PO₃)₂:Eu³⁺ (70 mol%) at room temperature under the excitation of UV light from a high pressure mercury lamp. The abscissa means the time which has elapsed after the glass sample was taken out of the furnace and cooled to room temperature. A temporal shift of spectral width is observed about 1.85 Å at the time between 2 and 800 h after glass was formed.

Fig. 3. Time dependence of the half width of ⁵D₀-⁷F₀ emission spectra of Ca(PO₃)₂:Eu³⁺_X (X=50, 60 and 65 mol%) at room temperature. Temporal shifts of spectral width are observed and show the gradual increase of the spectral width with time.

Fig. 4. Time dependence of the half width of $^5D_0-^7F_0$ emission spectra of $\text{Ca}(\text{PO}_3)_2:\text{Eu}^{3+}$ (82 mol%) at room temperature. Spectral width of about 3.5 Å is very narrow compared with the other concentrations (about 20–21 Å). This high concentration doped Eu^{3+} glass would be in the crystalline state.

In conclusion, judging from the relationship between linewidth increase and time, our results suggest that there exists a variation of the crystal field acting on the Eu^{3+} ions after the glass was formed. We believe that the relaxation, which is a result of the renormalization of the strain in the glass, may be largely responsible for the behavior of these temporal variations in the spectral width.

Finally, an observation of the temporal variation (or shift) of the emission spectra of rare earth ions in glass would give a useful information on the structural changes of glasses and amorphous materials.

The authors would like to thank Mr. Cartis Cairns for comments.

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