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OPTICAL PROPERTIES OF Eu^{3+} AND Cr^{3+} DOPED LaCaZrSiBORATE

A. BROWN*, A. BRUCE*, J.A. CAPOBIANCO, D. KRASHKEVICH** and D.J. SIMKIN*

Concordia University, Department of Chemistry, H3G 1M8 Montreal, (Quebec), Canada

*McGill University, Department of Chemistry, H3A 2K6 Montreal, (Quebec), Canada

**Schott Glass Technologies, Inc., Duryea, PA 18642, U.S.A.

Various compositions within the LaCaZrSiBorate system may be used to prepare glasses and glass-ceramics (referred to as LaKN14) of excellent optical quality. Since these materials readily accept most rare earth and transition metal ions in solid solution, they are of considerable interest as potential laser materials. Before this potential can be exploited, the optical properties must be fully characterized. Of particular interest in this regard is the detailed behavior of the luminescence, and the nature of the sites occupied by the activator ions. Previous experience with glass-ceramics (1) has shown that fluorescence line narrowing (FLN) of the $^5\text{D}_0 \rightarrow ^7\text{F}_0, 1, 2$ emission of Eu^{3+} can be used to probe the Eu^{3+} environment, and in particular, to study the distribution of Eu^{3+} ions between two phases - crystalline and glass. We report here our first results of these measurements. Other workers (2, 3, 4) have been actively studying Cr^{3+} emission from glasses and glass-ceramics because of potential usefulness of the broad $^4\text{T}_2 \rightarrow ^4\text{A}_2$ emission for tunable laser applications. We also include here results on the emission studies we have begun on $\text{Cr}^{3+}\text{LaKN14}$.

The materials studied were prepared by Schott Glass Technologies Incorporated, Duryea, Pennsylvania. The samples studied contained either Eu^{3+} (2 % w/w) or Cr^{3+} (2500 ppm and 500 ppm); heat treated specimens had been heated at 914 °C for one hour. Emission spectra of the Eu^{3+} samples were recorded at 8 °K, 77 °K, and room temperature, both under excitation into the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ (462 nm - 466 nm) using Coumarin 460, and under resonance excitation of $^7\text{F}_0 \rightarrow ^5\text{D}_0$ (572 nm - 581 nm) with Rhodamine 6G. Time resolved emission spectra, and decay time measurements of the Cr^{3+} doped samples were also recorded at 8 °K, 77 °K, and at room temperature, using Coumarin 460 (470 nm) excitation. Resonant excitation studies into $^4\text{A}_2 \rightarrow ^2\text{E}$, using Nile blue (640 nm - 710 nm) were performed at 77 °K.

The Eu^{3+} , $^7\text{F}_0 \rightarrow ^5\text{D}_0$ could be located from the emission spectra excited in the range 462 nm - 466 nm, with Coumarin 460 at 77 °K. The corresponding spectra obtained are shown in FIGURE 1. The salient feature of these spectra is that two different sites are occupied by Eu^{3+} , having $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission maxima at 575.5 nm and at 579.1 nm. FIGURE 2 shows the 8 °K emission spectra of the LaCaZrSiBorate glass, excited at various wavelengths within the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission band. The most important features are: (1) the sharpness of the lines and the excitation dependent shift of the lowest component of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission, and (2) the full Stark splitting of the $^7\text{F}_1$ (three components) and $^7\text{F}_2$ (five components) manifolds, indicating a site symmetry of C_{2v} or lower. The variation of the Stark components peak positions with excitation wavelength confirms that there are two sites, one being excited from 572 nm to 578 nm, and the other from 578 nm to 580 nm.

Although the true site symmetry of Eu^{3+} is probably C_1 in the glass, the crystal field calculations are based on the assumption of C_{2v} point group symmetry. This is the highest noncentrosymmetric symmetry for which the full Stark splitting of the J manifolds occurs, and the lowest which permits this distinction of most of the components. Using the equations for C_{2v} symmetry of Lempicki et al. (5), a set of crystal field parameters, $B_{\lambda\mu}$, giving the best fit to all eight components, are derived for each spectrum.

The ratios B_{44}/B_{40} are plotted against $-B_{22}/B_{20}$ in FIGURE 3 for the glass. Brecher and Riseberg's (6) ratios, calculated from the geometric model, ranging from pure eightfold coordination to pure ninefold coordination, are also included. The LaCaZrSiBorate glass values follow the theoretical ones quite well, indicating the presence of sites covering the full range of 8 to 9 coordination.

The room temperature absorption spectrum of Cr^{3+} activated sample revealed two broad bands corresponding to ${}^4A_2 \rightarrow {}^4T_2$ ($16,234 \text{ cm}^{-1}$) and ${}^4A_2 \rightarrow {}^4T_1$ ($23,041 \text{ cm}^{-1}$). The position of the 4T_2 leads to a value $D_4 = 1623 \text{ cm}^{-1}$. This, combined with the position of the 4T_1 gives $B = 692 \text{ cm}^{-1}$. The emission maximum for the low field sites gives the position of the 2E level ($14,409 \text{ cm}^{-1}$), which allows the determination of C for these values of D_4 and B . The value of C was found to be 2726 cm^{-1} or $C/B = 3.94$. Decay measurements showed that both emission bands decayed nonexponentially with a range of decay times of 0.5 ms to 1.5 ms for 2E and 25 s to 85 s for 4T_2 . The resonance FLN emission from the 2E at 70 °K showed sidebands at about 75 cm^{-1} from the resonance.

REFERENCES

1. J.A. Capobianco, T.F. Belliveau, G. Lord, and D.J. Simkin, *Phys. Rev.*, **B34**, 4204 (1986).
2. L.J. Andrews, A. Lempicki, and B.C. McCollum, *J. Chem. Phys.*, **74**, 5526 (1981).
3. F. Durville, B. Champagnon, E. Duval, and G. Boulon, *J. Phys. Chem. Solids*, **46**, 701 (1985).
4. A. Kisilev, R. Reisfeld, A. Buch, and M. Ish-Shalom, *Chem. Phys. Letters*, **129**, 450 (1986).
5. A. Lempicki, H. Samelson, and C. Brecher, *J. Mol. Spectrosc.*, **27**, 375 (1968).
6. C. Brecher and L.A. Riseberg, *Phys. Rev.*, **B13**, 81 (1976).

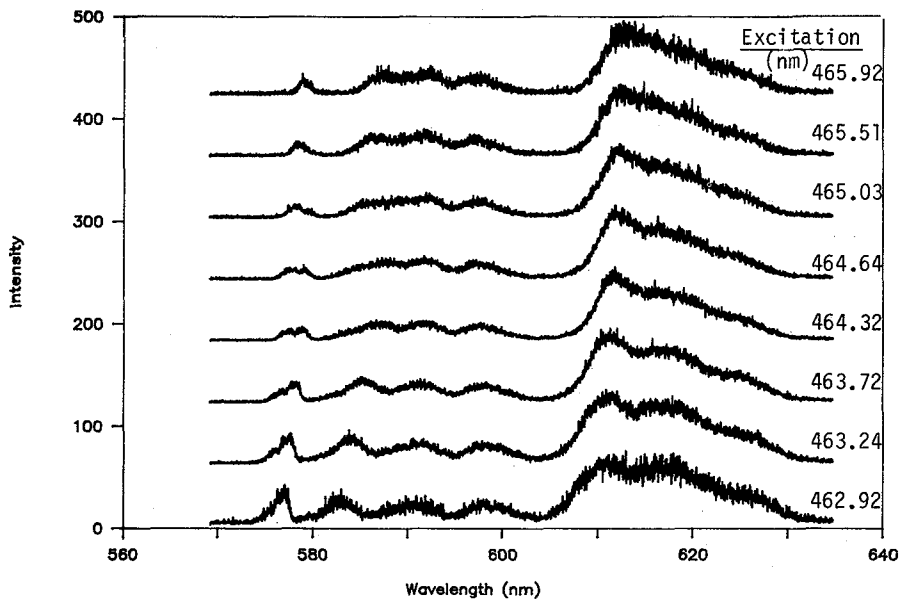


FIGURE 1. Emission Spectra of Eu^{3+} in LaCaZrSiBorate at 77 °K Using Different Excitation Wavelengths.

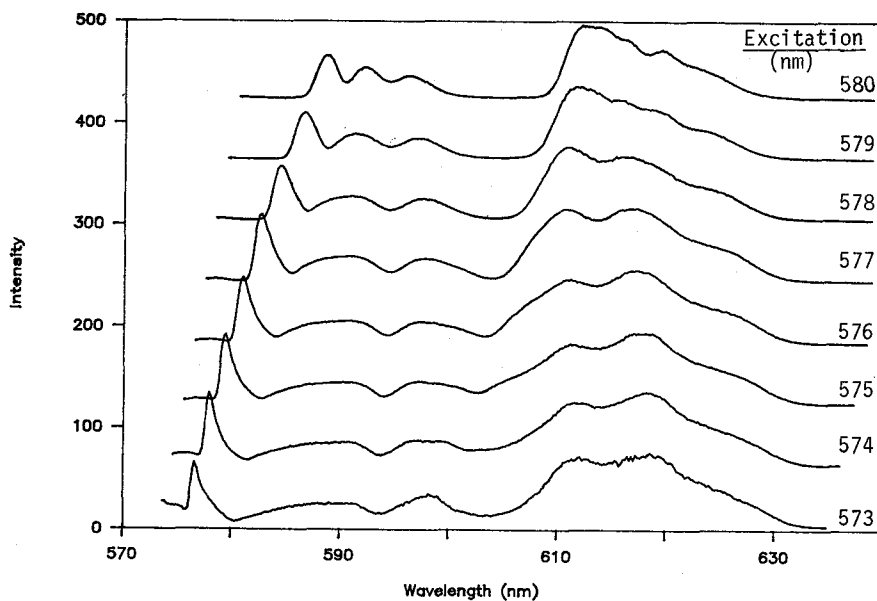


FIGURE 2. Emission Spectra of Eu^{3+} in LaCaZrSiBorate at 8 °K Using Different Excitation Wavelengths.

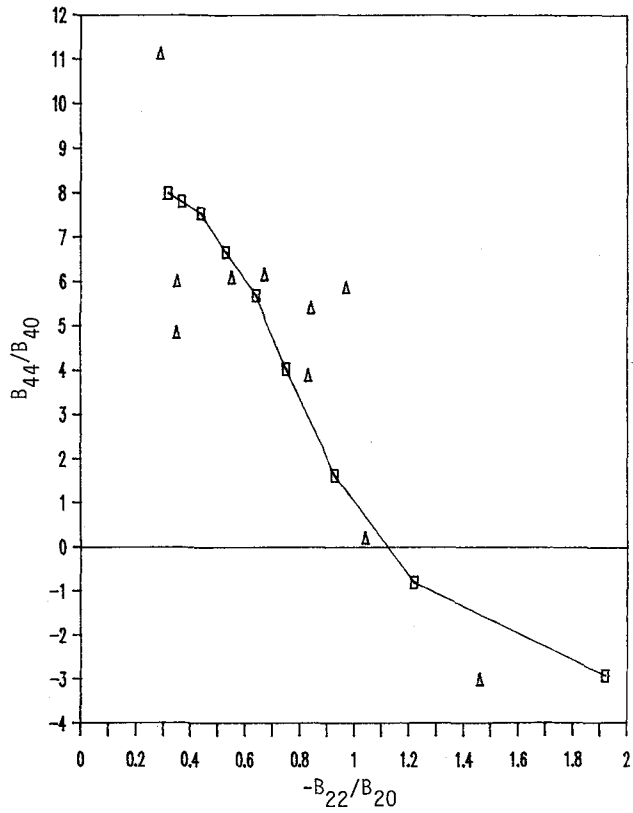


FIGURE 3. Behavior of the major crystal-field ratios B_{22}/B_{20} and B_{44}/B_{40} , which contain purely geometric information about the coordination. The line and \square symbols represent values calculated from the geometric model (Breckner and Riseberg, Reference 6). The Δ symbol indicates experimental values for LaCaZrSiBorate glass.