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LASER SPECTROSCOPY AND FLUORESCENCE LINE NARROWING OF Cr³⁺ IN LaCaZrSiB₂ O₃ GLASS AND GLASS-CERAMIC

A. BRUCE*, J.A. CAPOBIANCO, G. CORMIER*, D. KRASHKEVICH** and D.J. SIMKIN*

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

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

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

Glasses and glass-ceramics of excellent optical quality can be prepared from melts of various compositions within the LaCaZrSiB₂O₃ system, referred to as LaKN14 glasses. Since these materials can readily serve as hosts to transition metal or rare earth ions, they are of considerable interest for their potential use as laser materials. One of the most interesting of these is Cr³⁺ activated LaKN14 glass and glass-ceramic. However, to assess their actual potential for laser application a thorough understanding of the optical spectroscopic properties is essential. For this purpose, we have undertaken a study of the absorption, excitation, and emission spectra, as well as the measurements of the decay kinetics of the Cr³⁺ luminescence, and the time evolution of the emission. We also report here some preliminary results of resonance fluorescence line narrowing (FLN) measurements, which allow us to determine the splittings of the excited ²E within the inhomogeneously broadened envelope of the emission band.

The materials studied were prepared by Schott Glass Technologies Incorporated, Duryea, Pennsylvania. They were activated with Cr³⁺ at two different concentrations: 500 ppm and 2500 ppm; the heat treated specimens were heated at 914 °C for one hour. Time resolved emission spectra and decay times were recorded at 8 °K, 77 °K, and room temperature using Coumarin 460 (470 nm) excitation from an excimer (Lumonics, XeCl) laser pumped dye laser. The fluorescence was passed through a Spex 3/4 m monochromator (1200 g/m grating), and detected with an R928 Hamamatsu multialkali photomultiplier (spectral response to about 930 nm). The signal was fed into an EGG PAR Boxcar averager with digital processing unit. To perform the resonance fluorescence measurements, a chopper was fitted to the monochromator slits. A timing pulse was picked off the chopper wheel, sent to a digital delay circuit, the output of which was used to trigger the laser. In this way, the laser could be fired during the time when the slits were blocked by the chopper, which would open to allow the resonance fluorescence signal to enter the monochromator only after the selected delay. In practice, 500 μs to 1.5 ms generally proved to be sufficient to completely eliminate scattered laser light but still permit detection of the Cr³⁺ fluorescence. The boxcar was triggered by a photodiode (from the laser pulse), and the initial delay of the gate was set to sample the signal only after the chopper blade had exposed the slits.

The room temperature absorption spectrum 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 $D_q = 1623 \text{ cm}^{-1}$. This combined with the position of 4T_1 give $B = 692 \text{ cm}^{-1}$. 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_q and B . The value of C was found to be 2726 cm^{-1} , or $C/B = 3.94$. These values are entirely consistent with those reported by Andrews et al. (1) for LiAlB_2O_3 glass ($D_q = 1642 \text{ cm}^{-1}$, $B = 732 \text{ cm}^{-1}$, and $C/B = 4.29$).

The time resolved emission spectra are shown in FIGURE 1. After an initial delay of $500 \mu\text{s}$, the 4T_2 emission is essentially gone, revealing only the emission from the high field sites (2E). Decay time measurements revealed that both emission bands decayed non-exponentially with a range of decay times of 0.5 ms to 1.5 ms for 2E and $25 \mu\text{s}$ to $85 \mu\text{s}$ for 4T_2 . The inhomogeneously broadened 2E emission had a width of about 514 cm^{-1} at $8 \text{ }^\circ\text{K}$, which results from the wide range of crystal field sites characteristic of borate glasses (1), as compared with silicate and phosphate glasses. The emission spectra and decay times were also measured for the heat treated samples. Although the emission intensity for a given Cr^{3+} concentration and temperature was noticeably greater from the heat treated samples, no other differences were observed. We were unable to detect the extent of crystallization with conventional X-ray techniques, which might indicate extremely small crystallite sizes. Further work on more extensively devitrified samples is planned.

FIGURE 2 shows the resonance FLN emission from the 2E at $70 \text{ }^\circ\text{K}$. The exciting laser was tuned through the inhomogeneously broadened band, thus selectively exciting the various Cr^{3+} sites. The side-bands, which are observed at about 75 cm^{-1} from the resonance, give the 2E splitting as described by other workers (2, 3). The wide range of high field sites is manifested in the relatively broad side bands, as compared with those found in silicates (2, 3).

It is also noteworthy that the 2E splitting observed in LaKN14 glass (75 cm^{-1}) is larger than that reported in ED2 glass (55 cm^{-1}) (2) and in magnesium aluminum silicate glass-ceramic (3) (70 cm^{-1}).

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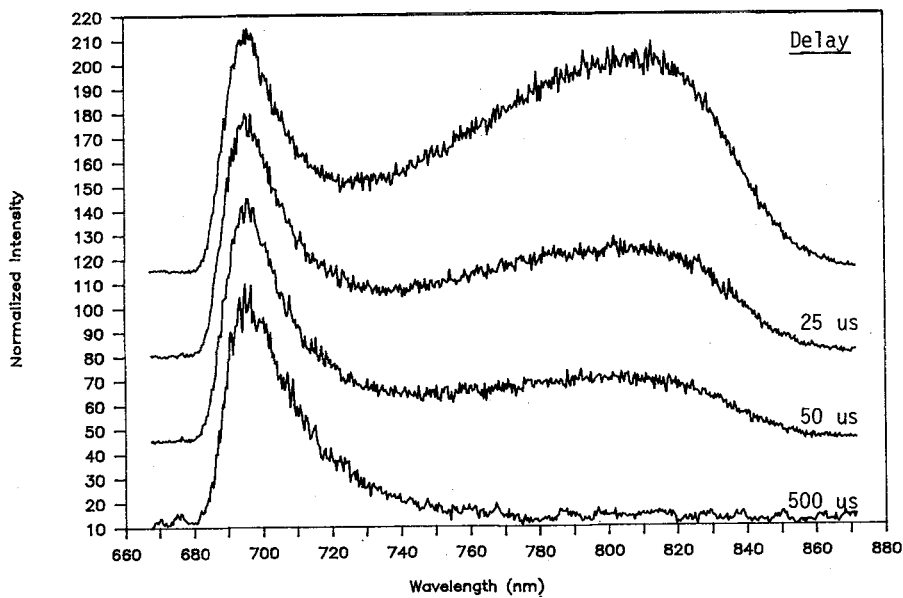


FIGURE 1. Time Resolved Spectra of LaCaZrSiBorate Glass at 4^oK, Excitation 460 nm.

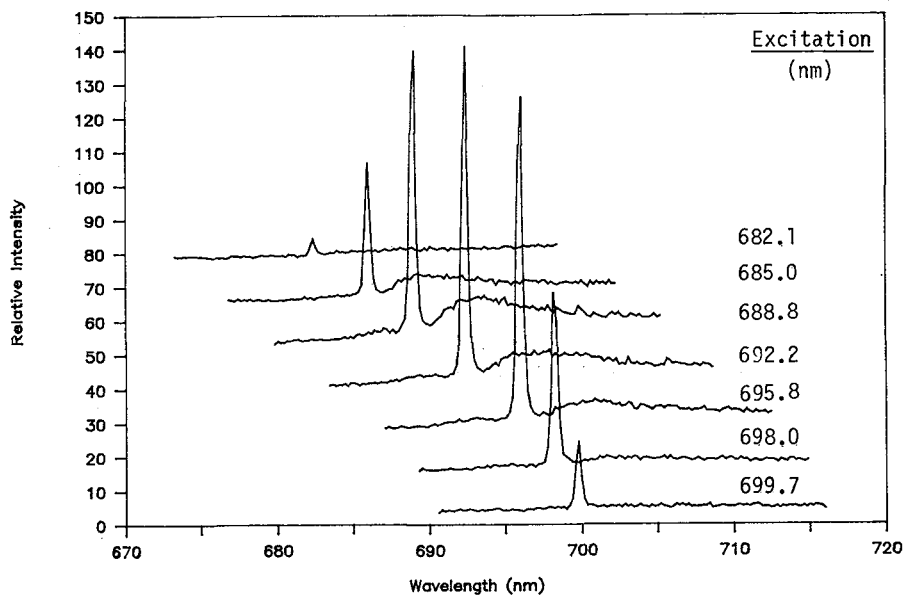


FIGURE 2. Details of the Emission in the ${}^2E \rightarrow {}^4A_2$ Emission Range When Exciting in the 4E Level at 70^oK.