

**LASER SPECTROSCOPY AND FLUORESCENCE  
LINE NARROWING OF Cr<sup>3+</sup> IN LaCaZrSiB<sub>2</sub> O<sub>3</sub>  
GLASS AND GLASS-CERAMIC**

A. Bruce, J. Capobianco, G. Cormier, D. Krashkevich, D. Simkin

► **To cite this version:**

A. Bruce, J. Capobianco, G. Cormier, D. Krashkevich, D. Simkin. LASER SPECTROSCOPY AND FLUORESCENCE LINE NARROWING OF Cr<sup>3+</sup> IN LaCaZrSiB<sub>2</sub> O<sub>3</sub> GLASS AND GLASS-CERAMIC. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-459-C7-461. <10.1051/jphyscol:19877109>. <jpa-00226925>

**HAL Id: jpa-00226925**

**<https://hal.archives-ouvertes.fr/jpa-00226925>**

Submitted on 1 Jan 1987

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**LASER SPECTROSCOPY AND FLUORESCENCE LINE NARROWING OF  $\text{Cr}^{3+}$  IN  $\text{LaCaZrSiB}_2\text{O}_3$  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  $\text{LaCaZrSiB}_2\text{O}_3$  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  $\text{Cr}^{3+}$  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  $\text{Cr}^{3+}$  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  $\text{Cr}^{3+}$  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  $\mu\text{s}$  to 1.5 ms generally proved to be sufficient to completely eliminate scattered laser light but still permit detection of the  $\text{Cr}^{3+}$  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  $2726 \text{ cm}^{-1}$ , or  $C/B = 3.94$ . These values are entirely consistent with those reported by Andrews et al. (1) for  $\text{LiAlB}_2\text{O}_3$  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  $0.5 \text{ ms}$  to  $1.5 \text{ ms}$  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  $514 \text{ cm}^{-1}$  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  $\text{Cr}^{3+}$  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  $\text{Cr}^{3+}$  sites. The sidebands, which are observed at about  $75 \text{ cm}^{-1}$  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  $\text{LaKN14}$  glass ( $75 \text{ cm}^{-1}$ ) is larger than that reported in ED2 glass ( $55 \text{ cm}^{-1}$ ) (2) and in magnesium aluminum silicate glass-ceramic (3) ( $70 \text{ cm}^{-1}$ ).

#### REFERENCES

1. L.J. Andrews, A. Lempicki, and B.C. McCollum, *J. Chem. Phys.*, **74**, 5526 (1981).
2. F. Durville, B. Champagnon, E. Duval, and G. Boulon, *J. Phys. Chem. Solids*, **46**, 701 (1985).
3. F.J. Bergin, J.F. Donegan, T.J. Glynn, and G.F. Imbusch, *J. Lumin.*, **34**, 307 (1986).

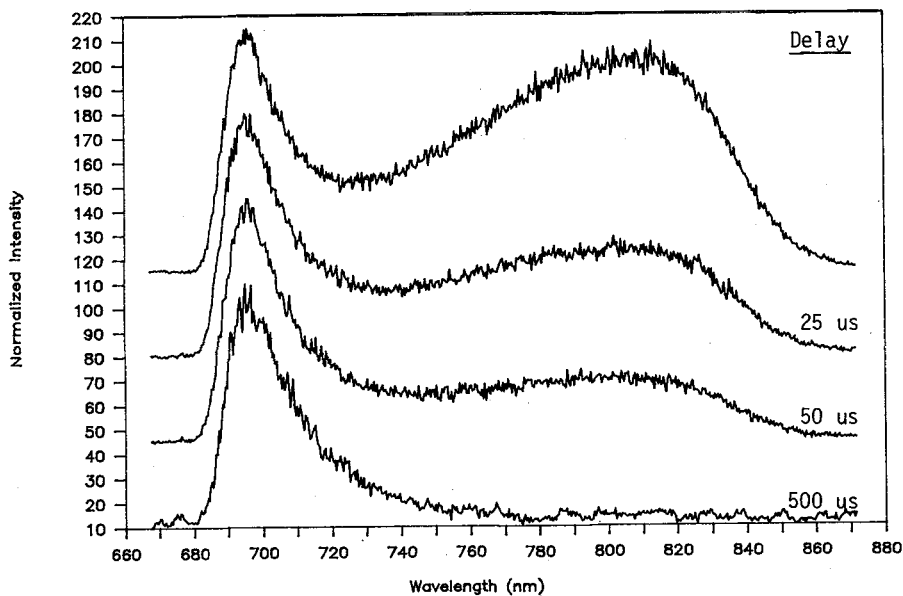


FIGURE 1. Time Resolved Spectra of LaCaZrSiBorate Glass at 4<sup>o</sup>K, Excitation 460 nm.

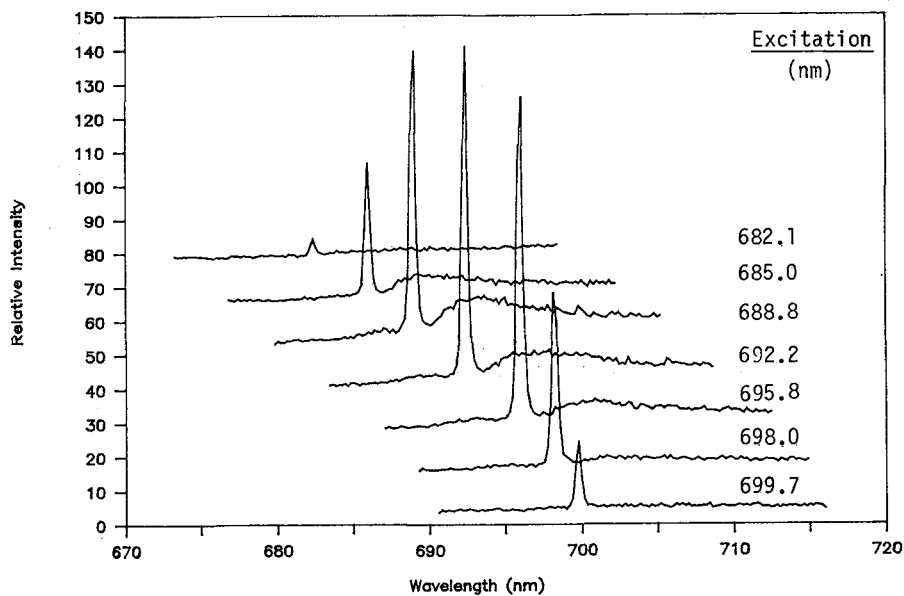


FIGURE 2. Details of the Emission in the  ${}^2E \rightarrow {}^4A_2$  Emission Range When Exciting in the  ${}^4E$  Level at 70<sup>o</sup>K.