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LUMINESCENCE AND FLUORESCENCE LINE NARROWING STUDIES OF CHROMIUM DOPED GLASS

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Abstract - The technique of fluorescence line narrowing is applied to the \(2E - 4A_2\) transition on \(\text{Cr}^{3+}\) ions in ED-2 glass. The resultant sharp zero-phonon line is accompanied by a vibrational sideband which carries information about the range of vibrational modes of the glass. The homogeneous broadening of the zero-phonon line is measured as a function of temperature.

I - INTRODUCTION

Dopant ions have been employed successfully as probes of the internal ionic arrangement of crystals using the techniques of EPR and optical spectroscopy. This is made possible by the fact that in general all the ions occupy identical sites and, particularly at low temperatures, sharp signals are obtained. A difficulty with applying these techniques to amorphous materials is that the ions occupy a range of sites with different energy level structures and the resultant signal from these materials is broad, obscuring the fine structure of the individual lines. The technique of fluorescence line narrowing (FLN), however, should in principle overcome some of these difficulties. In FLN a narrowband laser is used to excite a small subset of ions whose absorptions are in resonance with the laser and the resultant emission from these ions can be very narrow. There have been many studies of FLN of rare earth-doped glasses /1/ which aimed to probe the symmetry and range of sites encountered in glasses. Because of their stronger coupling to neighbouring ions transition metal ions are much more sensitive probes of the ionic environment. This greater sensitivity, allied to the range of crystal fields encountered in a glass, results in exceedingly broad emission from transition metal-doped glasses. When doped in crystalline hosts the optical transitions on such ions appear as phonon-assisted bands which may be accompanied by sharp zero-phonon lines. In this study we report on FLN experiments carried out on the zero-phonon \(2E - 4A_2\) transition of \(\text{Cr}^{3+}\) in a silicate glass.

II - EXPERIMENTAL DETAILS

We chose ED-2 glass, a silicate glass with \(\text{Li}_2\text{O}, \text{CaO}\) and other oxides acting as
network modifiers, and doped with $0.05 \% \text{Cr}_2\text{O}_3$. Luminescence spectra were recorded using an argon ion laser for excitation, a SPEX 14018 double monochromator, and either an EMI 9865B or an RCA 31034 photomultiplier with photon counting electronics. For phase-sensitive detection the pumping light was chopped and a Brookdeal 9501 lock-in amplifier was used to analyse the signal. For resonant FLN measurements a single wheel chopping system was used to chop the output from a Coherent 590 cw dye laser and to block the spectrometer from scattered laser light while the sample was being excited. The system was designed such that the luminescence was detected approximately one millisecond after the laser was fired. A variable temperature cryostat was used to obtain data between 4 K and 300 K.

III - SPECTROSCOPIC MEASUREMENTS

The luminescence from chromium doped ED-2 glass at low temperatures consists of a peak, whose half width is approximately 180 cm$^{-1}$, and a very broad band stretching from 14500 cm$^{-1}$ to below 10,000 cm$^{-1}$. The sharp feature at 14600 cm$^{-1}$, shown in detail in Fig. 1(a), is due to emission from ions in high-field sites; ions in these sites have $^4E$ levels below $^4T_2$ levels and at low temperatures the luminescence is emitted from the $^4E$ levels. The emission consists of zero-phonon R lines and their accompanying sidebands. This feature, at 14600 cm$^{-1}$, is the composite of all the zero-phonon R lines from chromium ions in different crystal fields. The decay is not a single exponential and is of millisecond duration. The broader luminescence at longer wavelength is due to emission from ions in low field sites.

Fig. 1. (a) The part of the luminescence spectrum of Cr$^{3+}$-doped ED-2 glass due to emission from $^4E$ levels.

(b) The FLN signal at 20 K.
whose $^4T_2$ levels lie lowest. The decay is again not a single exponential and its duration is of the order of tens of microseconds. This difference in lifetimes allows the overlapping $^2E$ and $^4T_2$ emissions to be distinguished using phase-sensitive techniques /[2/. In the separated $^2E$ emission one can now see vibrational sidebands accompanying the composite zero-phonon emission. Since the shape of the sideband is a weighted spectrum of vibrational modes this sideband is of particular interest. However, we cannot observe the sideband due to low frequency vibrations as it is masked by the inhomogeneously broadened emission of the zero-phonon lines.

We set out to obtain a narrow zero-phonon line by employing the technique of FLN. The FLN signal at 20 K is shown in Fig. 1(b). We expect that Cr$^{3+}$ should occupy a somewhat distorted octahedral environment and so the $^2E$ level should be split into an upper $R_2$ and a lower $R_1$ level. As the laser is tuned into the $^2E$ band we excite some ions whose $R_1$ lines are resonant with the laser and other ions whose $R_2$ lines are resonant with the laser and hence the sharp resonant FLN signal contains both $R_1$ and $R_2$ lines, albeit from different ions. This narrow line is accompanied by two broader transitions. The broad transition at lower energy covers the range of $R_1$ lines from ions whose $R_2$ lines are in resonance with the laser, and the weaker transition at higher energy covers the range of $R_2$ lines from ions whose $R_1$ lines are in resonance with the laser. By tuning the laser to the lower energy side of the composite $^2E$ band the $R_1$ lines can be eliminated and a clear sideband spectrum can be observed. Fig. 2(a) shows the shape of the sideband which we could observe to within 15 cm$^{-1}$ of the zero-phonon line, the remainder being masked by the wing of the resonant $R$ line. We note the high density of low frequency modes. For comparison, in Fig. 2(b) we show the sideband of the corresponding transition of Cr$^{3+}$ in crystalline MgO. Such low frequency modes in glasses have been observed using other techniques e.g. Raman scattering, infra-red spectroscopy.

Fig. 2. Comparison of the sideband of the $^2E - ^4A_2$ line of Cr$^{3+}$ in ED-2 glass with the analogous sideband in a crystal.
Because of the width of our laser ($\Delta \nu = 0.8$ cm$^{-1}$) we were unable to observe the ground state splitting. Despite this we measured the width of the FLN signal as a function of temperature from 5 K to 150 K, above which the signal became too weak for accurate measurement. At 100 K the linewidth has a distinct Lorentzian form in contrast to the almost Gaussian lineshape at lower temperatures. As the temperature is raised one expects relaxation mechanisms to cause broadening of the zero-phonon line and these mechanisms result in a Lorentzian lineshape. We separated the Lorentzian component from the residual low temperature width using standard techniques /3/, and the extracted Lorentzian linewidth, divided by two to allow for the resonant excitation /4/, yields the broadening due to relaxation mechanisms. The measured line broadening is shown in Fig. 3. For comparison we also show the analogous broadening of the $R_1$ line of Cr$^{3+}$ in Al$_2$O$_3$ /5,6/ which is typical of that found in Cr-doped crystals. We note that at low temperatures the broadening in the glass is much larger than that found in crystals; being almost two orders of magnitude greater at 30 K. In addition, the temperature dependence of the broadening is different in the two cases. In crystals one expects the temperature dependent broadening at low temperatures to vary as a high power of temperature /5/, much more so than the linear dependence found in the glass up to 70 K. Above 70 K the broadening in the glass tends towards a quadratic dependence on temperature. The larger broadening observed in Cr-doped glass is consistent with measurements made on rare earth-doped glasses, where the broadening is much in excess of that found in crystals /7,8/. In the case of rare earth-doped glasses the temperature-dependent broadening varies from ion to ion, varying from linear in some cases /9/ to almost quadratic in others /8/. More accurate measurements and analyses of the broadening mechanisms in the chromium doped glass are being made.
IV - CONCLUSIONS

We have applied the technique of FLN to Cr$^{3+}$ transitions in glass. The results presented above show that the $2E$ emission from Cr$^{3+}$, in those glasses where it can be observed, carries useful information about the coupling of the Cr$^{3+}$ ion to the vibrating glass host.

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