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Optical Transitions of Mn^{2+} in Fluoride Glasses

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The optical properties of Mn^{2+} ions have been extensively investigated in numerous host materials. The $3d^5$ electrons associated with the manganese ion are sensitive to crystal field and the optical transitions yield valuable information on the local environment. Thus, the Mn^{2+} ion optical spectra in fluorozirconate and fluorohafnate glasses suggest that these ions are in positions of low crystal field. Most likely Mn^{2+} substitutes for Ba^{2+} ions in these glasses. As the glass undergoes devitrification the Mn^{2+} ion spectrum changes suggesting that optical methods can be used for studying the temperature dependence of glass transitions.

I. Introduction

The potential use of heavy-metal fluoride glasses in fiber optic communication systems has sparked considerable interest (*1*–*6*). These halide glass materials have promise as ultratransparent, low-loss fibers for infrared communication systems, and laser hosts. Two of the most promising new glasses are composed of $57ZrF_4$, $36BaF_2$, $3LaF_3$, and $4AlF_3$ (designated ZBLA) and $58HfF_4$, $33BaF_2$, and $9LaF_3$ (referred to hereafter as HBL). These glasses are especially suited for fiber optics and laser use since the infrared absorption (multiphonon absorption edge) occurs at wavelengths longer than 6 μm (*7*). The HBL and ZBLA materials have roughly similar compositions, glass transition (T_g) and crystallization temperatures (T_X).

The optical properties of the transition metal ion Mn^{2+} have been extensively studied in numerous crystalline materials (*8*–*11*). The purpose of this paper is to utilize Mn^{2+} ions as probes to compare the optical properties of crystals and the two host glasses, ZLBA and HBL. Broadband optical excitation is employed which results in optical absorption and emission bands composed of the sum of the transitions of the individual ions in various sites within the glass. This inhomogeneous broadening of the optical bands limits the information that can be obtained. Nonetheless, it is still possible to obtain data on the oscillator strengths and crystal field of the various transitions of the Mn^{2+} ion. In crystalline systems Mn^{2+} can change valence state when exposed to ionizing radiation. This possibility is investigated for glass hosts.

As the ligands of the Mn^{2+} ions change position the luminescence is also altered. This makes it possible to investigate the devitrification of glass as a function of temperature. A comparison of the optical properties of the Mn^{2+} ion in these glasses and in

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crystalline hosts such as $RbMgF_3$ (*10*), and CdF_2 (*11*), can be made. From such comparisons, general conclusions regarding the relative strength of the crystal field in the vicinity of the Mn^{2+} ion can be drawn. For simplicity the energy levels of Mn^{2+} will be labeled with the O_h symmetry nomenclature, even though it is known the sites have lower symmetry.

II. Experimental Methods

The samples used in this study were prepared using methods described earlier (*3, 12*). The ZLBA glass, formed with 2 at.% MnF_2 in the melt, was obtained from RADC, Hanscom AFB, Massachusetts. The HBL samples, doped with 1 at.% MnF_2 in the melt, were acquired from Hughes Research Laboratories. While detailed composition analysis for these particular samples is not available, measurements on other samples indicate that the final composition of these fluoride glasses is within 1 and 2 mol.% of the starting composition (*13*). Also, the Mn concentration in these glasses was determined by EDAX and found it to be 1 at.% in HBL and 2 at.% in ZBLA.

Low-temperature measurements were made with a liquid-nitrogen cryostat, or a CTI Cryodyne Cryocooler Model 2ISC. The Cryocooler incorporates a resistance heater which allows temperature control within 2 K over the range from 14 to 300 K. For measurements above room temperature the sample was enclosed in a copper holder with small windows for the entrance of excitation light and the exit of the fluorescence. A copper–constantan thermocouple was mounted directly on the sample. The temperature was controlled to within ±5 K with a resistance heater.

Emission and excitation spectra were taken by exciting the samples with light from a 75-W xenon-arc lamp passed through a 0.22-m Spex monochromator. The fluorescence was focused into a 0.8-m Spex monochromator and a mirror was used to route the light emerging from the exit slit to a cooled RCA C31034 photomultiplier tube. The photomultiplier signal was preamplified and passed to a lock-in amplifier synchronized with a variable-speed light chopper in the excitation beam. The output of the lock-in amplifier was displayed on an x–y recorder or stored on tape or disk by a Hewlett–Packard HP-85 minicomputer. The intensity of the exciting light at the sample position was measured with a Photo-Research Model 310 photometer/radiometer. The excitation spectra have been corrected accordingly.

Lifetime measurements were made utilizing a Nicholet Model 1070 signal averager. For lifetime measurements, the overlapping ^4E, $^4A_1$ bands at 390 nm were excited and fluorescence measured from the $^4T_1 \rightarrow {}^6A_1$ transition which emits at 595 nm. Since the nonradiative transition from ^4E, $^4A_1$ degenerate levels to the $^4T_1$ level is much faster than the radiative transition $^4T_1 \rightarrow {}^6A_1$, the lifetime value reflects the radiative transition rate.

Optical absorption measurements were made with a Perkin–Elmer 330 spectrophotometer. The spectral resolution utilized was always less than the observed linewidths. Integrated intensities were calculated by numerical integration.

Devitrification was accomplished by placing the sample in a small electric furnace and maintaining a uniform temperature for 15 min. Temperature was measured with a platinum vs platinum-10%–rhodium thermocouple placed next to the sample and was maintained to ±5 K.

A typical irradiation consisted of a beam of 1.7 MeV electrons with a current of 7 μA impinging on a sample placed 10 cm from a control gate. A dose rate of 3.7×10^{13} MeV/cm^3 sec was measured using Ag–glass dosimeters.

III. Experimental Results

A comparison of the absorption and excitation spectra for Mn^{2+} in ZBLA glass is shown in Fig. 1. The absorption data were taken with a specimen 16.0 mm thick. Ten wavelength scans were averaged to improve the signal-to-noise ratio. The resolution of the spectrophotometer was 2 nm, compared to a resolution of 5 nm for the excitation curve. This is evidenced by the instrument broadened excitation band at 400 nm in Fig. 1. If Fig. 1 were corrected for instrument broadening as well as wavelength dependence, the peak of the excitation spectrum at 400 nm would be increased by a factor of 3 or so. In the figure this would take the peak shown in the excitation spectrum at 350 nm into the noise level. However, since excitation spectra are much more sensitive than absorption it is easily possible to detect the peak using this technique. Similar bands, at the same wavelength positions, were observed for the HBL : Mn samples. In the case of the HBL glass the maximum sample thickness was 4.0 mm and the Mn^{2+} concentration was only 1 at.% in the melt; therefore, the optical absorption was significantly weaker than for the ZBLA specimens. The excitation spectrum of the HBL specimen was reduced in intensity compared to that for ZBLA, reflecting the lower Mn concentration of the sample. No temperature dependence of the excitation spectra was observed between 15 and 300 K.

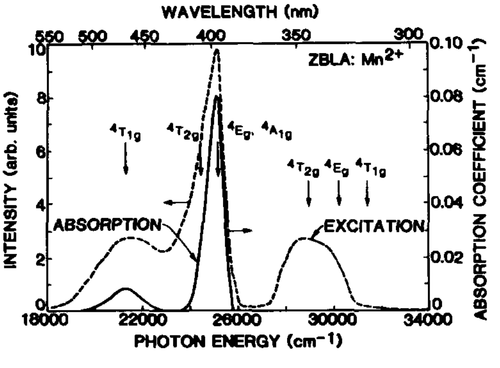

FIG. 1. Absorption and excitation spectra for Mn^{2+} in ZBLA glass.

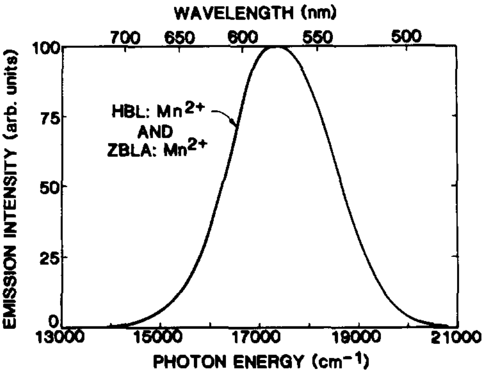

FIG. 2. Room-temperature emission spectra for Mn^{2+} in HBL and ZBLA glasses.

The inhomogeneous broadening of the Mn^{2+} bands due to the glass host is apparent. Nonetheless, the glass spectra do have essentially the same position and half-width as the excitation spectra reported for CdF_2 : Mn (*11*). The emission spectra of ZBLA : Mn and HBL : Mn taken at room temperature are shown in Fig. 2. For both glasses the maximum emission is at 17,400 cm^{-1}, and the half-width of the band is 2400 cm^{-1}. Compared to $CdF_2 : Mn^{2+}$, the emission in the glass is shifted to lower energy by about 2100 cm^{-1}, but the half-width is similar. Figure 3 portrays the temperature dependence of the fluorescence decay lifetime in HBL : Mn. The lifetime of the same Mn^{2+} transition in ZBLA glass is shown at two temperatures by the full triangles.

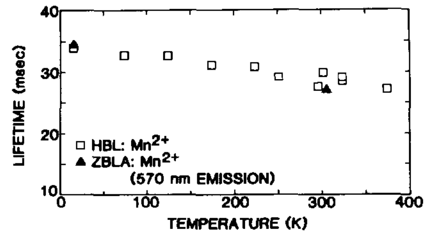

FIG. 3. Temperature dependence of the Mn^{2+} emission lifetimes in HBL and ZBLA glasses.

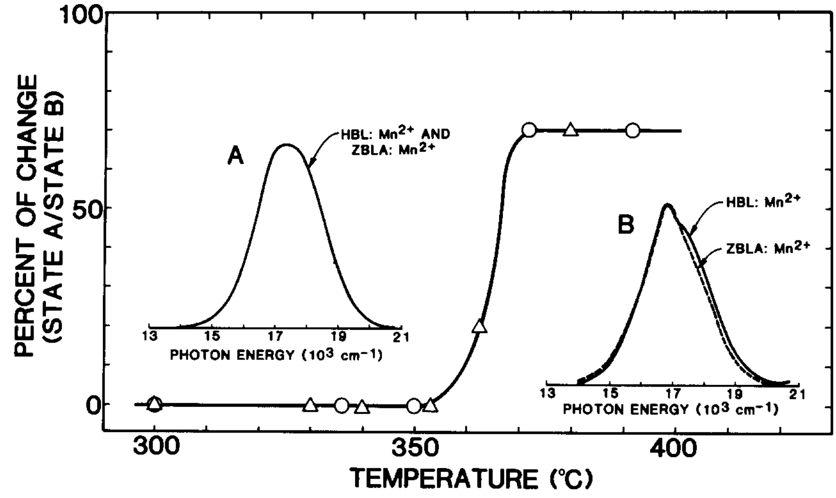

FIG. 4. Relative change of Mn^{2+} emission in HBL and ZBLA glasses as a function of heat-treatment temperature. The insets show the emission spectra before and after heat treatment. The triangles represent data from ZBLA samples and the circles data for HBL.

In this research a simple optical technique to observe devitrification of the sample was found. The optical emission of a sample was monitored during a series of heat treatments. In Fig. 4 the spectrum shown in A (state A) was taken at 300 K for an untreated specimen. The sample was then heated in air to a specified temperature for 15 min, quenched to a room temperature and then the emission spectrum recorded at 300 K. State B in Fig. 4 illustrates the change in the Mn^{2+} emission spectrum for temperatures above 370 K. The percent of the sample remaining vitreous can be determined by the fraction of state A present and an indication of the approximate transition temperature can be found. It should be noted that the change in the shape of the emission band occurs rapidly around a temperature of 360°C for both HBL and ZBLA. For both glasses, the emission from the devitrified glass is the same just as the Mn^{2+} emission before heat treatment was identical for the two glasses. A similar experiment utilizing the rare-earth Er^{3+} ion spectra in ZBLA glass, produced the same results (*14*).

A final experiment involved the effect of electron irradiation on the Mn^{2+} transitions. After irradiation with 1.7 MeV electrons for 30 sec, the Mn^{2+} emission intensity is reduced to about 20% of its initial value. Further irradiation does not reduce the emission intensity significantly more. A new broad absorption band appears near 500 nm. The band shifts toward lower energy as temperature increases. The rapid saturation of the absorption coefficient with irradiation suggests that it is the result of a valence change of the Mn. The optical data are consistent with the $^5E \rightarrow {}^5T_2$ transition for Mn^{3+} (*15, 16*). If it is assumed that 50% or so of the Mn^{2+} changes to Mn^{3+} as suggested by the emission decrease, then the oscillator strength for this transition is about $\sim 10^{-4}$.

IV. Discussion

The oscillator strengths of the Mn^{2+} transitions between the ground and excited states are very low due to spin forbiddenness. If the concentration of ions is known, the oscillator strength, f, of a particular transition can be calculated from the integrated absorption with the use of Smakula's equation (*17, 18*), which for bands with an assumed Gaussian shape, is

$$fN = \frac{mc}{\pi e^2}\frac{9n}{(n^2+2)^2}\int \sigma(\nu)\,d\nu$$
$$= 0.87 \times 10^{17}\frac{n}{(n^2+2)^2}\alpha_m W. \quad (1)$$

In the equation N is the concentration of manganese ions, n the index of refraction, α_m the maximum absorption coefficient of the band, and W the full width at half maximum, in electron-volts. This formula simplifies for the ZBLA and HBL glasses, to the expression

$$fN = 0.7 \times 10^{16}\, W\alpha_m. \quad (2)$$

For the $^6A_1 \rightarrow {}^4T_1$ Mn^{2+} transition in ZBLA glasses, $\alpha_m = 7.9 \times 10^{-3}\ cm^{-1}$ and $W = 0.16$ eV. When the measured value of $N = 3.4 \times 10^{20}\ cm^{-3}$ is used this yields a value $f = 3 \times 10^{-8}$. In order to check on this oscillator strength an expression from DiBartolo (*19*) relating the oscillator strength and radiative lifetime for electric dipole transitions can be used. The appropriate expression is

$$f\tau = (1.51 \times 10^4)\lambda_0^2\frac{9}{n(n^2+2)^2}, \quad (3)$$

where τ is the radiative lifetime in seconds, and λ_0 is the wavelength of the peak position of the band in meters. For the $^4T_1 \rightarrow {}^6A_1$ emission, $\tau = 33$ msec and $\lambda_0 = 570$ nm. This yields an oscillator strength $f = 4 \times 10^{-8}$ which is consistent with the oscillator strength calculated using Smakula's equation.

The oscillator strength of the ^4E, $^4A_1$ absorption band in both ZBLA and HBL has been computed to be 2×10^{-7} in the two hosts, respectively. Since these levels decay by nonradiative transitions to the $^4T_1$ level, it is not possible to use the lifetime formula to check the consistency of the oscillator strength value.

Because of the valence and size of the manganese ion it is expected to substitute for Ba^{2+} in both the ZBLA and HBL glass structures. Almeida and MacKenzie (*20*) indicate that barium is a network modifier. As such it occupies relatively open positions in the glass network. Therefore, when the Mn^{2+} ion replaces Ba^{2+}, the crystal field at the ion site is somewhat lower than would be found in most crystalline structures. In fact, the crystal field should be similar to that found in open lattices such as CaF_2 and CdF_2 (*11*). Some years ago Tanabe and Sugano (*21, 22*) developed a graph depicting energy level changes with crystal field for d^n electrons which is useful in identifying the energy levels associated with optical absorption and emission bands. For example, the lowest $^4T_1$ level decreases in energy relative to the $^6A_1$ ground state as the crystal field increases. Thus the greater the crystal field Dq the lower the absorption and emission energy. This is portrayed clearly in Fig. 5. Other levels can be independent of field strength, Dq. The ^4E, $^4A_1$, levels are constant with respect to the ground state and the absorption occurs at virtually the same energy (25,000 cm^{-1}) in the glass as well as in the crystalline host. Thus, the Mn^{2+} ion can be a useful optical probe for examining materials. The emission and excitation data illustrated in Figs. 1 and 2 are very similar to those found for CaF_2 and CdF_2 (*11*). From the Tanabe–Sugano diagram (*21, 22*) in Fig. 5 and the data presented in this paper it is evident the Mn^{2+} ions reside in rather open sites. Other experiments provide supporting evidence for the Mn^{2+} ions being in Ba^{2+} modifier sites. The optical excitation and emission as well as the lifetimes of the radiative transitions are the same for both HBL and ZBLA hosts. This is an indication that the Mn^{2+} ion levels are not effected by Hf^{4+} or Zr^{4+} ions.

The devitrification study is interesting. From Fig. 4, it is apparent that a shift of the emission spectra to longer wavelength occurs. The shift is small in comparison to the

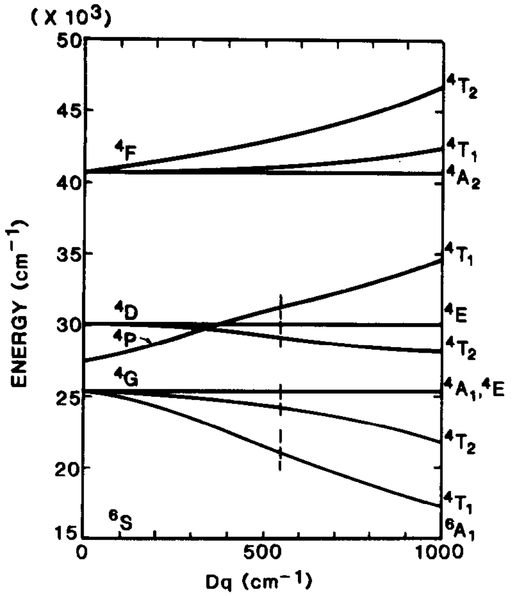

FIG. 5. Tanabe–Sugano energy level diagram for Mn^{2+}, with $B = 960\ cm^{-1}$.

emission bandwidth. A review of Fig. 5 as discussed above suggests that the crystal field at the Mn^{2+} site is increased by devitrification. A small component of the original emission, some 30% of the total emission intensity, remains after the sample has changed. The lifetime of the transition changes from 33 to 27 msec. Although the devitrification temperature observed by this method agrees with the previously determined glass-transition temperature, for quantative results the experiment should be repeated in a controlled atmosphere. In fact, this method lends itself to measurements made *"in situ"* in various atmospheres.

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