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Increased radiative lifetime of rare earth-doped zinc oxyhalide tellurite glasses

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We have investigated the structural and optical properties of rare earth-doped zinc tellurite glasses modified by the substitution of ZnF_2 . Raman and phonon sideband spectroscopies were employed to characterize changes in the glass structure as well as to probe vibrational behavior in the immediate vicinity of the rare earth ion. These measurements are combined with photoluminescence and optical absorption to monitor the effect of halide substitution upon the optical behavior of the rare earth dopant. A substantial increase in the intrinsic radiative lifetime of Nd^{3+} is observed with increasing halide concentration. © 1997 American Institute of Physics. [S0003-6951(97)00240-4]

As knowledge about the structure and properties of novel glass forming materials continues to increase, so does their potential for applications as hosts for optically active devices.¹ The incorporation of rare earth ions into a variety of materials has been key to the development of optical amplifiers, phosphors, and other devices that operate using intrashell or “forced” electric dipole transitions occurring within the $4f$ electron level.² These transitions are considerably weaker than Laporte-allowed intershell transitions and are also sensitive to variations in the local environment of the rare earth ion produced by the host material.^{2,3}

Since the success of many optical devices depends upon the decay lifetime (τ_M) of a given excited state, significant research efforts have focused on the manipulation of this optical parameter. The decay rate for an excited state population, $\Gamma_M = 1/\tau_M$, is comprised of two processes: the intrinsic radiative decay rate (Γ_R), stemming from the local electrostatic environment of the dopant, and the nonradiative decay rate (Γ_{NR}), primarily due to multiphonon deexcitation of the excited state. In the absence of concentration quenching effects,⁴ the total decay rate is then

$$\Gamma_M = \Gamma_R + \Gamma_{NR}. \quad (1)$$

The radiative decay rate is influenced by variations in the host matrix via changes in the local crystal field symmetry at the rare earth site. In addition to the field symmetry, the local phonons in the host can couple with electron orbitals of the ion (electron–phonon coupling) allowing the excited rare earth ion to decay nonradiatively via the production of lattice vibrations.⁵

The probability for nonradiative decay to occur decreases exponentially with the number of phonons required to bridge the energy gap, E_g .⁵ Consequently it is desirable to surround the ion with a matrix that possesses a low maximum phonon energy. Silica possesses a reasonable large phonon energy (1100 cm^{-1}) while fluoride containing glasses exhibit much lower (500 cm^{-1}) phonon energies.⁶

Unfortunately, fluoride-based glasses lack many of the desirable features of silica-based glasses such as chemical durability and fiberization.

In this regard, tellurite glasses represent something of a compromise between the requirement for both a low phonon energy (700 cm^{-1}) as well as good mechanical characteristics. They also provide the benefits of low optical absorption at visible and infrared wavelengths and a high index of refraction ($1.8 < n < 2.3$).^{6–8} In this letter, we report measurements (Raman scattering, optical absorption, phonon sideband spectroscopy, and emission lifetime spectroscopy) of the optical properties of rare earth-doped zinc oxyhalide tellurite glasses. Our goal is to develop insight into the manipulation of the local structural environment and its influence on both radiative and nonradiative deexcitation of the rare earth dopant population. In addition to studying the effects of structural depolymerization of the tellurite network via ZnO addition, we have also investigated the influence of halide substitution (ZnF_2). We find that the inclusion of ZnF_2 significantly expands the glass forming range of the zinc tellurite system and substantially increases the radiative lifetime of the rare earth ion.

Samples of ZnO–TeO_2 glass were prepared by melting ZnO and TeO_2 powders in a gold crucible at 800°C . Halide-substituted samples prepared using ZnF_2 powder required lower melt temperatures ($\approx 650^\circ\text{C}$) but, owing to a tendency for these halides to react with gold, were melted in alumina crucibles. Doped glasses were obtained by addition of the desired rare earth oxide to the melt. Final compositions were determined ($\pm 10\%$ relative) by x-ray photoelectron spectroscopy. Details of the glass forming range and thermal analysis have been presented previously.⁹ For emission lifetime measurements, excitation was provided by a N_2 -pumped dye laser operating at a wavelength of 520 nm which delivered 1 ns pulses of about $150 \mu\text{J}$ at a 10 Hz repetition rate. Further details concerning optical characterization are found elsewhere.¹⁰

Raman spectra collected from a series of $x\text{ZnO}-(1-x)\text{TeO}_2$ are shown in Fig. 1(a). In addition to a deformation (bending) mode at about 420 cm^{-1} , two additional

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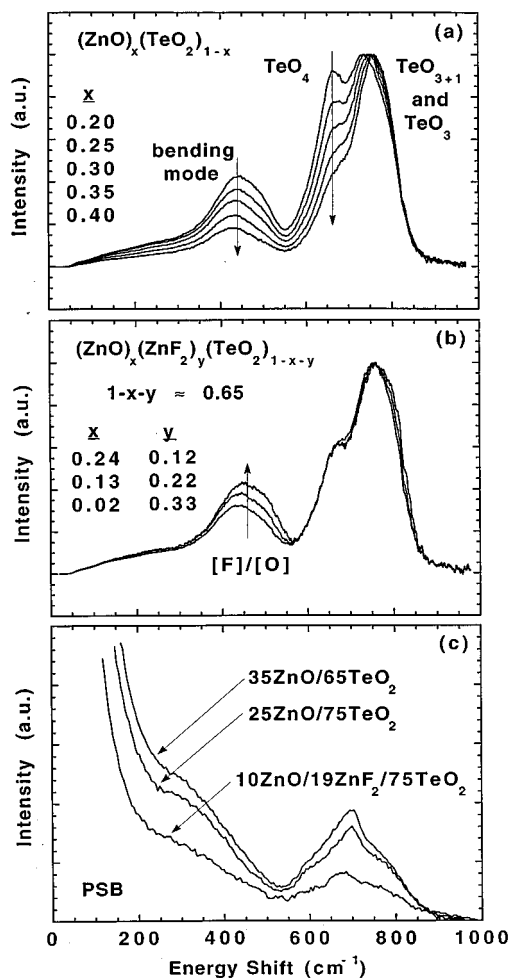


FIG. 1. (a) Raman intensity for a series of zinc tellurite glasses of varying batch compositions. The arrows indicate the direction of change for increasing ZnO. (b) Raman intensity for zinc oxyfluoride tellurite glass with approximately 65 mol % TeO₂. The arrow indicates the direction of change for increasing [F]/[O] ratio. (c) Phonon sideband spectra for two zinc tellurite glasses (approximately 25 and 35 mol % ZnO) and one oxyfluoride (10ZnO–19ZnF₂–71TeO₂) doped with Eu³⁺. The intensity shown is normalized to the intensity of the direct electronic transition at zero energy shift.

modes are observed, one occurring at 670 cm⁻¹ which has been previously assigned to the symmetric stretch of Te–O bonds in trigonal bipyramidal TeO₄ units, and the other occurring at 740 cm⁻¹ which is due to the Te–O symmetric stretch of the so-called TeO₃₊₁ unit which resembles the TeO₄ unit except that one axial Te–O bond length is larger.¹¹ Also included in this second peak, toward the high energy side, is the Te–O stretch of TeO₃ trigonal pyramids. With the addition of ZnO the Te–O–Te network becomes increasingly more depolymerized as TeO₄ is converted to TeO₃, and these structural changes are indicated by changes in the relative Raman intensities in Fig. 1(a). Also evident is a slight shift of the peak at 740 cm⁻¹ to higher energy which is consistent with the conversion of TeO₃₊₁ to TeO₃ units with increasing [ZnO].

Figure 1(b) demonstrates the changes that occur upon substitution of ZnF₂ into the matrix. The ratio of [Zn]/[Te] has been kept fixed and, as can be seen, the features of the high energy Raman bands are unaffected by increases in the

[F]/[O] ratio while the relative intensity of the bending mode is increased. This suggests that F is readily dissolved into the tellurite network and directly replaces O without producing any further depolymerization of the network. The increase in the bending mode is consistent with the conversion of TeO₃ units to Te(O,F)₃₊₁ units. (Note that such a conversion will have little effect on the relative intensities of the two stretching modes at 670 and 740 cm⁻¹.)⁹

These Raman measurements provide a picture of the vibrational density of states in the glass averaged over its entirety. In order to examine the local vibrational density of states (DOS) encountered by a rare earth ion, we have used phonon sideband (PSB) spectroscopy¹² to study zinc oxide and oxyfluoride glasses doped with Eu³⁺. In the experiment, the excitation energy is varied in the vicinity of the Eu³⁺ ⁵D₂ absorption band (occurring at 465 nm) and the emission between the ⁵D₀ to ⁷F₀ levels (615 nm) is monitored.

In Fig. 1(c) we compare the local vibrational density of states as obtained from the PSB intensity with the global DOS obtained from Raman scattering [Figs. 1(a) and 1(b)]. In Fig. 1(c), two sidebands are visible as a peak at about 700 cm⁻¹ and a shoulder at about 300 cm⁻¹ that rests atop the tail of the direct absorption line. The energies of these features compare favorably with those observed by Raman scattering. The major difference is that the peak of the low energy band has an energy 40% lower than that of the Raman bending mode. Even though the Raman spectra indicate that addition of ZnO changes the overall vibrational character of the matrix by decreasing the numbers of TeO₄ units, these statistical changes do not extend to the vibrational features in the vicinity of the rare earth ion. This is evident in Fig. 1(c), where no significant differences in the PSB features are detectable for samples containing either 25 or 35 mol % ZnO. We speculate that by virtue of its large size, the rare earth ion to some degree dictates the features of its coordination shell and in so doing does not experience the statistical changes occurring for the glass matrix as a whole. Results for a sample containing fluorine exhibit similar sideband features, albeit with a weaker overall intensity, suggest-

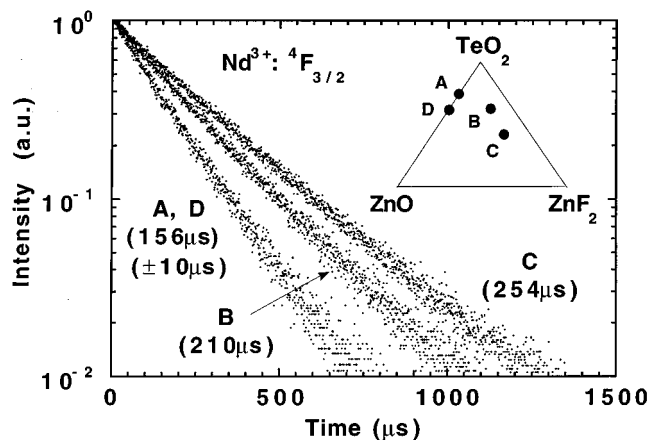


FIG. 2. The measured emission decay from the ⁴F_{3/2} state for three glasses of varying fluorine contents (A: 28ZnO–72TeO₂–0.1Nd₂O₃, B: 15ZnO–23ZnF₂–62TeO₂–0.1Nd₂O₃, and C: 17ZnO–38ZnF₂–45TeO₂–0.1Nd₂O₃). The measured emission lifetime is given in Table I.

TABLE I. Summary of Judd–Ofelt analysis. The JO parameters have units of 10^{-20} cm² and the lifetimes have units of 10^{-6} s.

Sample	[Zn]/[Te]	[F]/[O]	Ω_2	Ω_4	Ω_6	τ_R	τ_M
A	0.39	...	2.78	4.56	3.39	164	152
D	0.47	...	2.74	5.18	3.36	153	159
B	0.62	0.34	2.68	3.50	2.89	203	210
C	1.23	0.71	1.24	2.87	2.29	252	254

ing a reduced electron–phonon coupling accompanies halide substitution.

Finally, we examine the effect of halide substitution upon the excited state decay rate. We have performed emission lifetime measurements for the $^4F_{3/2}$ to $^4I_{9/2}$ decay in four glasses doped with 0.1 mol % Nd₂O₃. These include two glasses containing no fluorine but for which the [Zn]/[Te] ratio is changed (A:28ZnO–72TeO₂:0.1Nd₂O₃ and D:35ZnO–65TeO₂:0.1Nd₂O₃) and two containing fluorine (B:15ZnO–23ZnF₂–62TeO₂:0.1Nd₂O₃ and C:17ZnO–38ZnF₂–45TeO₂:0.1Nd₂O₃). The emission decay for samples A, B, and C are shown in Fig. 2. Figure 2 shows that the measured lifetime increases substantially with the introduction of fluorine into the tellurite matrix, increasing from about 150 μ s in sample A to more than 250 μ s in sample C. The measured lifetime of sample D (159 \pm 10 μ s) was unchanged from that determined for sample A, indicating that the increased lifetimes seen for samples B and C are indeed due to the presence of fluorine and not merely a result of changes occurring in the [Zn]/[Te] ratio.

Determination of the intrinsic radiative lifetime, τ_R , was accomplished through a Judd–Ofelt^{3,13} analysis of the absorption spectra. The Judd–Ofelt theory models the experimentally observed oscillator strengths as a linear sum of standard transition matrix elements involving so-called Judd–Ofelt (JO) parameters [Ω_q ($q=2,4,6$)]. These JO parameters are directly influenced by the host matrix and provide a qualitative measure of the asymmetry of the local crystal field near the rare earth ion.³ Errors in the determination of Γ_R are no larger than about 20%.¹⁴

Results of the JO analysis are provided in Table I together with experimentally observed total emission lifetimes. All three of the JO parameters decrease with increasing fluorine content, whereas τ_R increases. Furthermore, the values of τ_R obtained from the JO analysis are all within 5% of τ_M and appear to account for the increase in the total emission lifetime that we observe. We conclude that halide substitution does significantly modify the local crystal field symmetry of the rare earth ion and produces a substantial enhancement of the intrinsic radiative lifetime. For this particular transition, multiphonon losses are negligible since the energy gap ($E_g \approx 5000$ cm⁻¹) would require more than seven phonons of the 700 cm⁻¹ variety for nonradiative decay to occur. Thus it is not yet clear to what extent the addition of F might also affect the nonradiative decay rate, although our PSB results [see Fig. 1(c)] indicate a decrease in the electron–phonon coupling from which a decrease in multiphonon decay would be anticipated.

One alternative explanation for the increased τ_M with fluorine substitution involves variation in the hydroxyl concentration. Infrared (IR) transmission studies of the oxide

and fluorine containing glasses indicated the presence of hydroxyl groups. With fluorine substitution, the concentration of the OH groups (indicated by IR absorption at 3100 cm⁻¹) was found to decrease by as much as 70% compared with the oxide glasses. These hydroxyl groups can serve as efficient nonradiative energy trap states when in the immediate environment of the rare earth dopant ion. However, examination of the emission lifetime of Nd³⁺ in 25ZnO/75TeO₂ indicated that significant reduction in the 1.06 μ m radiative emission lifetime (due to concentration quenching effects) only became evident at concentrations above 0.3 mol % rare earth. Thus, even in the oxide glasses, in which the probability for nonradiative energy losses due to the presence of OH groups is a maximum, quenching of the majority of the excited rare earth population through Nd–Nd energy transfer to the OH trap sites remains negligible for the 0.1 mol % Nd³⁺ doping level chosen in the present study.

These arguments, coupled with the low multiphonon relaxation probability anticipated for the large energy gap characteristic of the Nd³⁺ $^4F_{3/2}$ level and the close correlation between the JO radiative lifetimes and those measured experimentally over a range of sample compositions, consistently indicate that the substitution of fluorine serves to modify the local electrostatic environment surrounding the rare earth dopant.

In summary, we have demonstrated that substitution of halide ions into the zinc tellurite matrix produces dramatic increases in the emission lifetime. Furthermore, JO analysis indicates this increase results from modification of the local electrostatic field symmetry around a rare earth dopant ion. Despite global variations in the glass structure caused by depolymerization of the tellurite network when zinc oxide is added, phonon sideband measurements reveal that the vibrational character of the coordination shell near the rare earth ion appears to be largely unaffected.

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