CONF-961202--4 SAND97-0238C

OPTICAL PROPERTIES OF LANTHANIDE -CONTAINING
HALIDE-MODIFIED ZINC TELLURITE GLASSES

D.L. SIDEBOTTOM*, MICHAEL A. HRUSCHKA*, B.G. POTTER**, RICHARD K. BROW**, JAMES J. HUDGENS***

*University of New Mexico, AML Suite 100, 1001 University Blvd. SE, Albuquerque, New Mexico, 87106.

**Sandia National Labs, AML Suite 100, 1001 University Blvd. SE, Albuquerque, New Mexico, 87106.

***presently at Texas Instruments, Plano, Texas.

RECEIVED

JAN 31 1997

OSTI

ABSTRACT

As part of an ongoing investigation to characterize the properties and structure of zinc halide-tellurium oxide glasses, we report preliminary measurements of the optical properties of several Nd- and Er-doped tellurites. Measurements include fluorescence lifetimes and estimates of the theoretical radiative lifetimes (as obtained by traditional Judd-Ofelt analysis of optical absorption spectra) as well as phonon sideband studies sensitive to vibrational characteristics near the rare earth ion. The response of these optical features to the substitution of alternative halides is examined.

INTRODUCTION

MASTER

A variety of commercially important photonic devices have inherited their special functionality from the unique optical behavior of rare-earth ions doped into materials[1]. Common examples include lasers and optical amplifiers (e.g., Nd:YAG) as well as phosphor materials (e.g., Eu:Y₂O₃). The optical properties of these materials result from electronic transitions occurring within the partially filled 4f energy shell of the lanthanide series[2,3]. Although normally forbidden by Laporte's selection rule ($\Delta l = \pm 1$), these intrashell, "forced" electric dipole transitions are allowed by virtue of an overlap of the 4f energy levels with nearby 5d levels. This overlap leads to admixing of electron configurations of opposite parity resulting in several optical transitions within the 4f level which are of practical importance for device applications.

Since these transitions are the result of subtle mixing of opposite parity states with pure 4f electron states, they are generally much weaker than normal Laporte-allowed dipole transitions[2]. Given the sensitivity of the forced dipole transition probability to the orbital overlap of 4f and 5d levels, the process of excited state decay is sensitive to certain aspects of the ion local environment. The local crystal field symmetry produces a Stark splitting of the individual 4f levels and thus contributes to the intrinsic 4f-4f transition linewidth and the radiative lifetime, τ_R . The local vibrational density of states of the host lattice can, in addition, provide an alternative, non-radiative pathway for excited state decay, characterized by a rate Γ_{NR} . This non-radiative process can be particularly detrimental to the performance of amplifying devices where a population inversion is required.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

dy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

It is with regard to non-radiative losses that glasses appear to offer several advantages for hosting rare earth ions[4,5]. Unlike many of their crystalline counterparts, glasses possess a wide range of compositions with correspondingly diverse structural features. In principle, this allows one to adjust host properties in a continuous manner, with the potential to select desired optical and mechanical behaviors. Particularly important is the enhanced control this provides over the bulk vibrational characteristics of the host matrix. Not surprisingly this feature has led to several recent examinations of network forming glasses[6,7] in terms of their suitability as rare-earth doped devices. Tellurite glasses[5] appear to possess a suitable compromise of needed properties: (1) low maximum phonon energy ($\leq 800 \text{ cm}^{-1}$) which is a prominent factor determining the degree of non-radiative losses, (2) high refractive index and low UV edge, required in many optical component applications, and (3) low glass transition temperatures. These properties can be modified by the substitution of alkali or alkali-earth oxides which convert bridging Te-O-Te bonds to non-bridging oxygens to depolymerize the network.

In this paper, we report measurements of the optical properties of Zn-tellurite glasses doped with Nd^{3+} and Er^{3+} . The novelty of our study is the substitution of zinc halides (ZnCl_2 , ZnF_2) for ZnO which significantly extends the glass forming range of the zinc tellurite system. Our experimental probes include Raman scattering, optical absorption, and fluorescence lifetime techniques designed to evaluate variations in the radiative and non-radiative contributions to the total decay rate upon halide substitution. We also report some intriguing preliminary phonon sideband results which provide clues about the local vibrational environment of the rare earth ion.

EXPERIMENT

Samples of ZnO-TeO_2 glass were prepared by melting ZnO and TeO_2 powers in a gold crucible for approximately 1 hour at about 800°C . Halide-substituted samples prepared using ZnCl_2 and ZnF_2 powders required lower melt temperatures ($\approx 650^\circ\text{C}$) but, owing to a tendency for these halides to react with gold, were melted in silica crucibles. Final compositions were determined ($\pm 10\%$ relative) by X-ray photoelectron spectroscopy. The glassforming range was determined by visual inspection and X-ray powder diffraction analysis. The glass samples were generally transparent at visible wavelengths with a UV cutoff exhibited at around 380 nm. Glass transition and crystallization temperatures were determined using differential thermal analysis[8]. The $x\text{ZnO-(1-x)TeO}_2$ glassforming range[9] was determined to be $0.2 \leq x \leq 0.35$, and could be increased to $x \approx 0.6$ by halide substitution. Doped glasses were obtained by addition of the desired rare earth oxide to the melt. For optical investigations, the doping levels were varied in an isostructural manner by adding optically inactive lutetium together with the optically active ion so as to maintain 1 mol% total rare earth.

Optical characterization included UV-VIS-NIR absorption, Raman scattering, spectral and temporal photoluminescence, and photoluminescence excitation (phonon sideband) measurements. Absorption measurements were performed in transmission mode at wavelengths from 200 nm to 3000 nm (Perkin-Elmer Lambda 900). Raman scattering was performed with an Ar^+ laser (514.5 nm, approx. 200mW) and a Spex 1877 Triplemate spectrometer with a typical spectral resolution of about 2 cm^{-1} . Fluorescence spectra were collected using an Ar^+ laser (488 nm) focussed to an approximately 100 μm incident spot size and a 0.275 m grating spectrometer (ARC) with a 2 nm resolution. The emitted light intensity was detected by either a cooled photomultiplier tube (Hamamatsu R2658) or a LN_2 -cooled, Ge detector (North Coast). For

measurements of the fluorescence lifetime the excitation intensity was modulated by a mechanical chopper to provide a temporal resolution of approximately 10 μ s. Signal averaging of the emission decay was achieved using a box car integrator (SRS). Phonon sideband measurements were performed using a tunable source comprised of a 400 W Xe lamp and 0.15m monochromator (ARC) with a spectral resolution of 1nm. The emitted intensity was measured using the 0.275 m spectrometer described previously.

The total measured fluorescent decay rate of the excited state of a rare earth ion can be expressed as the sum of three independent processes[10]: radiative (Γ_R), non-radiative (Γ_{NR}) and interion energy transfer (Γ_Q), such that $\Gamma_M = \Gamma_R + \Gamma_{NR} + \Gamma_Q$. Interion energy transfer, or "quenching", is a non-radiative decay mode in which the excited ion's energy migrates from ion to ion, via multipolar electrostatic interactions, to trap sites in the material where the energy is lost non-radiatively[11]. While this process plays a dominant role at high ion concentrations, Γ_Q becomes vanishingly small at concentrations below some critical threshold.

Determination of the intrinsic radiative decay rate, Γ_R , was accomplished through a Judd-Ofelt[3,12] analysis of the absorption spectra. The Judd-Ofelt theory involves a parameterization of the rare earth absorption intensities and provides estimates of the radiative decay rate of all excited states as well as predictions for oscillator strengths and branching ratios. Briefly, the experimentally determined oscillator strengths, P_{if} , of observed transitions (integrated area under corresponding absorption peaks) can be expressed under certain simplifying conditions by a linear sum of standard transition matrix elements, U_{if} , of the form $P_{if} = C \sum_{q=2,4,6} \Omega_q |U_{if}^{(q)}|^2$. The Ω_q ($q = 2, 4, 6$) are the so-called Judd-Ofelt (JO) parameters whose values 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].

Measurements of the total fluorescence rate at low ion concentration ($\Gamma_Q = 0$) together with Γ_R determined by Judd-Ofelt analysis of the absorption, allow for determination of the non-radiative decay rate Γ_{NR} ($\Gamma_{NR} = \Gamma_M - \Gamma_R$). This non-radiative decay occurs through the generation of lattice vibrations (optical phonons) which carry away the excited state energy. The probability for this process to occur is determined by the strength of the electron-phonon coupling and number of phonons required to bridge the energy gap, E_g , to the next lowest available electronic energy level. A phenomenological theory of multiphonon decay has been developed[13,14], which predicts an energy gap dependence of the form

$$\Gamma_{NR} = Ae^{-\alpha E_g}, \quad (1)$$

where α and A are phenomenological parameters which indicate the sensitivity of Γ_{NR} to E_g , and the value of Γ_{NR} in the limit of vanishing E_g , respectively. The parameters α and A are specific to a given host and can be compared with those obtained from other glass matrices to evaluate the relative contribution of multiphonon decay in the deexcitation of 4f energy levels.

RESULTS

Fluorescence lifetime measurements were performed on 25ZnO-74TeO₂-xNd₂O₃-(1-x)Lu₂O₃ glass for 0.01 $\leq x \leq 1$. Luminescence decay from the ⁴F_{3/2} state was monitored and the observed rate, Γ_M , was reasonably constant for $x \leq 0.3$ but increased significantly for $x=1$. This

concentration dependence indicates a quenching threshold in the vicinity of $x \approx 0.3$, and so by restricting our optical studies to $x \leq 0.1$, we can safely ignore Γ_Q in the determination of Γ_{NR} .

The absorption spectrum of 25ZnO-74TeO₂-0.1Nd₂O₃-0.9Lu₂O₃ is presented in Fig.(1). Approximately eight identifiable absorption lines are observed and a UV edge occurs near 360nm. Values of the calculated JO parameters (Ω_q) and the Γ_R for the decay from the $^4F_{3/2}$ state are presented in the inset.

Also included in the figure, are values of Ω_q for two halide substituted base tellurite glasses, with approximate molar compositions of 5ZnF₂-25ZnO-70TeO₂ and 15ZnCl₂-15ZnO-70TeO₂. These parameters do exhibit consistent trends upon halide substitution with Ω_2 increasing and Ω_4 decreasing as we go from oxide to fluoride to chloride, while Γ_R increases slightly and Ω_6 remains reasonably unaffected. Thus replacement of oxide by halide anions appears to produce significant changes in the local crystal field asymmetry.

Using the values of Γ_R determined from JO analysis, the non-radiative or multiphonon decay rate, $\Gamma_{NR} = \Gamma_M - \Gamma_R$, was determined. We have determined Γ_{NR} for 25ZnO-74TeO₂-0.1Re₂O₃-0.9Lu₂O₃ (Re = Nd or Er) for the decay of a variety of electronic states. In this manner we are able to evaluate the

dependence of Γ_{NR} upon the energy gap to the next nearest electron energy level. Results of this analysis are provided in Fig. (2). Fits of the phenomenological expression Eq.(1) yield $\alpha = 2.0 \times 10^{-3} \text{ cm}$ and $A = 3 \times 10^6 \text{ s}^{-1}$. We have also included in the figure results of a similar analysis performed by Reisfield[2] for a silicate glass. Silicate glasses possess higher maximum phonon energy ($\approx 1200 \text{ cm}^{-1}$) than that exhibited by the zinc-tellurite composition ($\approx 750 \text{ cm}^{-1}$). As expected the non-radiative decay rate due to multiphonon emission is much lower for the zinc-tellurite glass. What is interesting is the much smaller value for α . This value is about half of that commonly observed in other glassformers (even those with smaller maximum phonon energy[5]). This implies that non-radiative decay in zinc-tellurite is less sensitive to decreasing energy gap and remains low even in the limit of vanishingly small energy steps.

Fig. 1 Absorptivity of 25ZnO-74TeO₂-0.1Nd₂O₃-0.9Lu₂O₃. Inset shows trends in the JO parameters with anion substitution.

Fig. 2 Non-radiative decay rate vs. energy gap to next nearest level. Closed circles: 25ZnO-74TeO₂-0.1Re₂O₃-0.9Lu₂O₃ of the present study, Open circles: a silicate glass [2].

To better understand the vibrational behavior of the lattice in the immediate vicinity of the rare earth ion, we have also performed phonon sideband (PSB) measurements of several zinc tellurite hosts doped with 1 mole % Eu_2O_3 . In this experiment[15] the excitation wavelength is varied near the $^5\text{D}_2$ absorption band while the 615 nm emission resulting from the $^5\text{D}_0$ to $^7\text{F}_0$ transition is monitored. Maximum emission occurs when the incident wavelength is coincident (at 465 nm) with direct absorption into the $^5\text{D}_2$ level.

Our results are shown in Fig. (3). In addition to the peak at 451 nm an additional shoulder is evident at 458 nm. These bands correspond to an absorption process wherein excess energy from the incident photon is transferred into the lattice in the form of phonons. These phonons can only be generated in the immediate vicinity of the rare earth ion, and so these spectra reflect only the local vibrational environment.

To show how this local vibrational behavior compares with vibrational features obtained from Raman scattering (averaged over all lattice sites), we replot in Fig. (4) our PSB spectra now as a function of energy shift from the pure electronic absorption band (21500 cm^{-1}) together with the Raman spectrum collected from $35\text{ZnO}-65\text{TeO}_2$ glass as well as that obtained from amorphous TeO_2 . The Raman peak at 670 cm^{-1} has been previously assigned[9] to the symmetric Te-O stretch in a TeO_4 bipyramidal tetrahedron and that at 740 cm^{-1} to the symmetric Te-O stretch in a deformed TeO_4 bipyramidal tetrahedron whose axial bond length is much larger. This deformed unit is referred to as TeO_{3+1} . The peak at 420 cm^{-1} is the Te-O-Te bending (deformation) mode. Comparison with our PSB spectra indicates that much of these global vibrational characteristics are reproduced in the vicinity of the rare earth ion. However, it is apparent that the relative ratio of $\text{TeO}_{3+1}/\text{TeO}_4$ is reduced around the rare earth site since the PSB spectra more closely resemble the Raman spectrum from the more polymerized TeO_2 glass. While these results are preliminary, we propose this indicates that the

Fig. 3 Phonon sideband spectrum for $35\text{ZnO}-64\text{TeO}_2-1\text{Eu}_2\text{O}_3$.

Fig. 4 Phonon sideband intensity vs. energy shift from the 465nm transition for $25\text{ZnO}-74\text{TeO}_2-1\text{Eu}_2\text{O}_3$ and $15\text{ZnCl}_2-15\text{ZnO}-69\text{TeO}_2-1\text{Eu}_2\text{O}_3$. Raman intensity of $35\text{ZnO}-65\text{TeO}_2$ and TeO_2 for comparison.

rare earth is preferentially incorporated into the lattice near the TeO_4 units and most likely nearest the two lone pair electrons that constitute the bipyramidal tetrahedral TeO_4 unit.

Included in Fig.(4) are recent measurements for a chlorine-substituted glass ($15\text{ZnCl}_2\text{-}15\text{ZnO-}69\text{TeO}_2\text{-}1\text{Eu}_2\text{O}_3$). While also preliminary, we see evidence of significant changes in the local vibrational features. In particular we observe that the intensity of the bands (relative to the peak electronic transition intensity) have generally decreased implying a corresponding decrease has occurred in the electron-phonon coupling strength[15] upon substitution of chlorine.

CONCLUSIONS

We have examined a series of rare earth-doped zinc-tellurite glasses in an effort to better understand the interplay of dopant and host and its impact on electron decay dynamics. We find that zinc tellurite glasses possess a low phonon energy and a significantly reduced sensitivity (smaller α) of the non-radiative transition probability to the size of energy gap being encountered. We also have shown that halide substitution in these glasses does influence the crystal field symmetry (as determined by Ω_q) and vibrational behavior. Measurements of phonon sideband spectra reveal that the local vibrational environment at the rare earth ion is different from that inferred from Raman spectroscopy. These results are intriguing as they provide clues to the lattice structure around which the rare earth ion prefers to take residence. Tentative evidence suggests the rare earth is coordinated with TeO_4 bipyramidal tetrahedra.

Acknowledgments: Funding for this work was provided by a grant from the National Science Foundation (contract # DMR-940309). B.G.P. and R.K.B. also acknowledge the resources of Sandia National Laboratory supported by the US Department of Energy under contract DE-ACO4-94AL850000.

REFERENCES

1. Optical Fibre Lasers and Amplifiers, ed. by P.W. France (CRC Press, Boca Raton, FL 1991).
2. R. Reisfeld and C.K. Jorgensen in Lasers and Excited States of Rare Earths, (Springer-Verlag, Berlin 1977).
3. R.D. Peacock, *Structure and Bonding* **22**, 83 (1975).
4. M.J. Weber, *J. Non-Cryst. Sol.* **42**, 189 (1980); **47**, 117 (1982).
5. J.S. Wang, E.M. Vogel, and E. Snitzer, *Opt. Mats.* **3**, 187 (1994).
6. C. Brecher, L.A. Riseberg, and M.J. Weber, *Phys. Rev.* **B18**, 5799 (1978).
7. M.J. Weber, *J. Non-Cryst. Sol.* **123**, 208 (1990).
8. M.A. Hruscka, D.L. Sidebottom, R.K. Brow, and B.G. Potter, to be published.
9. H. Burger, et al., *J. Non-Cryst. Sol.* **151**, 134 (1992).
10. R. Reisfeld, *Structure and Bonding* **22**, 123 (1975).
11. W.M. Yen, *Mod. Probs. in Condens. Matt. Sci.* **21**, 185 (1987).
12. B.R. Judd, *Phys. Rev.* **127**, 750 (1962); G.S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).
13. T. Miyakawa and D.L. Dexter, *Phys. Rev.* **B1**, 2961 (1970).
14. L.A. Riseberg, and H.W. Moos, *Phys. Rev.* **174**, 429 (1968).
15. S. Tanabe, K. Hirao, and N. Soga, *J. Non-Cryst. Sol.* **142**, 148 (1992).