

# Evidence of the influence of phonon density on $\text{Tm}^{3+}$ upconversion luminescence in tellurite and germanate glasses

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Spectral properties of blue upconversion luminescences in  $\text{Tm}^{3+}$  doped tellurite (PWT,  $\text{PbF}_2\text{-WO}_3\text{-TeO}_2$ ) glasses and germanate (PWG,  $\text{PbF}_2\text{-WO}_3\text{-GeO}_2$ ) glasses pumped by a tunable dye laser were studied at room temperature. Two emission bands centered at 453 and 477 nm, corresponding to the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  and  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transitions of  $\text{Tm}^{3+}$  ions respectively, were observed. The two-photon absorption mechanism responsible for the 477 nm luminescence was confirmed by a quadratic dependence of luminescent intensities on the excitation power. Tellurite glasses showed a weaker upconversion luminescence than germanate glasses. This observation was inconsistent with the prediction from the phonon sideband measurement. In this article, Raman spectroscopy and transmittance measurement were employed to investigate the origin of the difference in upconversion luminescences in the two glasses. Compared with phonon sideband spectroscopy, Raman spectroscopy extracts more information, including both phonon energy and phonon density, and therefore, is a more effective analytical tool for understanding upconversion luminescence. Our results showed that the phonon energy as well as phonon density of the host glass is important in determining the upconversion efficiency. © 2002 American Institute of Physics.

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## I. INTRODUCTION

The study of blue lasers for use in color display, optical recording, biomedical diagnostics and optical communication applications has become a focus of research in recent years. The search for compact and efficient solid-state blue lasers has stimulated renewed interest in upconversion phenomena.<sup>1</sup> Upconversion involves the absorption of two or more photons by a rare-earth ion followed by emission of a photon of higher energy.  $\text{Tm}^{3+}$  doped in many host materials is known to exhibit upconversion behavior. Among different host materials, glass is the most attractive one. It is transparent over a wide optical range and a relatively large amount of rare-earth ions can be easily and homogeneously incorporated into its matrix. Furthermore, glass has good mechanical properties and can be used to fabricate even fibers. In a recent paper, Kishimoto and Hirao<sup>2</sup> reported that phonon sideband spectroscopy could be used to study the efficiency of upconversion luminescence in these doped glasses. They showed that glass matrix with higher phonon energy usually has a lower upconversion efficiency resulting in a weaker upconversion luminescence. However, germanate glass has a higher phonon energy than that of tellurite glass and yet it possesses a better upconversion efficiency.<sup>2</sup> In fact, the phonon energies of these two glasses are very close to each other. Hence, the consideration of phonon energies alone may not be sufficient to explain the upconversion efficiencies.

Raman scattering, which studies the interaction between photons and high frequency optical phonons caused by vibration of molecules and atoms in matter, is a nondestructive and convenient diagnostic tool for material characterization and analysis. Recently, Chen *et al.* reported the Raman and upconversion luminescence spectra of  $\text{Tm}^{3+}$  doped in germanate glass.<sup>3</sup> The Raman peaks of the glass matrix were quite distinguishable. However, the researchers did not correlate the Raman spectra with the upconversion luminescence spectra. In this article, upconversion luminescences of  $\text{Tm}^{3+}$  doped tellurite (PWT,  $\text{PbF}_2\text{-WO}_3\text{-TeO}_2$ ) glasses and germanate (PWG,  $\text{PbF}_2\text{-WO}_3\text{-GeO}_2$ ) glasses were measured. Previous phonon sideband measurements<sup>2</sup> predicted that germanate glasses should have a weaker upconversion luminescence than that of tellurite glasses. Our results, however, revealed the opposite. In order to better understand the efficiency of upconversion luminescence in these two glasses, Raman spectroscopy and transmittance measurement were employed. The upconversion luminescent intensities of these two glasses were correlated with the results of Raman spectroscopy and transmittance measurements. By comparing the Raman peaks of germanium oxide and tellurium oxide, the effects of phonon density of the host matrix on the upconversion efficiency can then be determined. Since the Raman spectroscopic studies can extract more information than phonon sideband measurement, we have shown that Raman spectroscopy is a superior technique than phonon sideband spectroscopy in studying the upconversion luminescence of these glasses.

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TABLE I. Composition of the glasses prepared.

Sample code	Composition (mol %)
PWT 2	49.9TeO <sub>2</sub> -39.92PbF <sub>2</sub> - 9.98WO <sub>3</sub> -0.2Tm <sub>2</sub> O <sub>3</sub>
PWG2	46GeO <sub>2</sub> -49PbF <sub>2</sub> - 4.8WO <sub>3</sub> -0.2Tm <sub>2</sub> O <sub>3</sub>
PWT 1	52TeO <sub>2</sub> -42PbF <sub>2</sub> - 5.9WO <sub>3</sub> -0.1Tm <sub>2</sub> O <sub>3</sub>
PWG 1	50GeO <sub>2</sub> -40PbF <sub>2</sub> - 9.9WO <sub>3</sub> -0.1Tm <sub>2</sub> O <sub>3</sub>

## II. EXPERIMENT

The starting materials for preparing the Tm<sup>3+</sup> doped PWT and PWG glasses were TeO<sub>2</sub>, GeO<sub>2</sub>, PbF<sub>2</sub>, WO<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub>. The composition of the glasses is listed in Table I. The oxides were first mixed thoroughly by ball milling for 2 h with ethyl alcohol. The mixtures were then sintered in an alumina crucible at 1200 °C for 15 (PWT glasses) or 20 (PWG glasses) min. Throughout the sintering processing, the crucibles were covered with alumina lids to reduce volatilization loss. The molten PWT and PWG glasses were quenched by being pressed rapidly between two stainless steel molds which were preheated in a furnace at 350 °C for 15 min. The glasses were subsequently annealed for 1 h at just below the glass transition temperatures of 350 and 400 °C for PWT and PWG glasses, respectively. Finally, the samples were allowed to cool to room temperature in air.

The room temperature Raman spectra were measured at a backscattering geometry using an Ar-ion laser (Coherent Innova 70) operating at 488 nm as the excitation source. Spectra were recorded by a double grating spectrometer (Spex 1403) equipped with standard photon counting equipment. A 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran dye laser pumped by the same Ar-ion laser was used in our upconversion luminescence study. Three different dye laser wavelengths (648, 650 and 652 nm) were used and their output powers were monitored with a power meter (Ophir 10A). The transmittance measurement was obtained by an UV-VIS scanning spectrophotometer (Shimadzu, UV-2101).

## III. RESULTS AND DISCUSSION

The room temperature blue upconversion emission spectra of PWT2 and PWG2 glasses excited with 200 mW laser light of different wavelengths are presented in Fig. 1. Two emission bands at 453 and 477 nm, corresponding to the <sup>1</sup>D<sub>2</sub>→<sup>3</sup>H<sub>4</sub> and <sup>1</sup>G<sub>4</sub>→<sup>3</sup>H<sub>6</sub> transitions, respectively, were observed. It is noticed that the 477 nm upconversion luminescent intensity maximizes at the pump wavelength of 650 nm, demonstrating a resonance effect for both glasses. The 453 nm luminescent peaks of germanate glasses show a similar resonance phenomenon. This, however, is not observed in tellurite glasses. Apart from the 453 and 477 nm emission bands, a weak emission at ~457 nm is also detected. This peak has not been reported in similar glass systems.<sup>2,3</sup> Since the energy of this emission band does not match any transition within the energy levels of Tm<sup>3+</sup> ion, we believe that this emission band is not due to intra-ion transition of Tm<sup>3+</sup> ion. PWT and PWG glasses of lower Tm<sup>3+</sup> doping concentration (PWT1 and PWG1) show similar emission profiles.

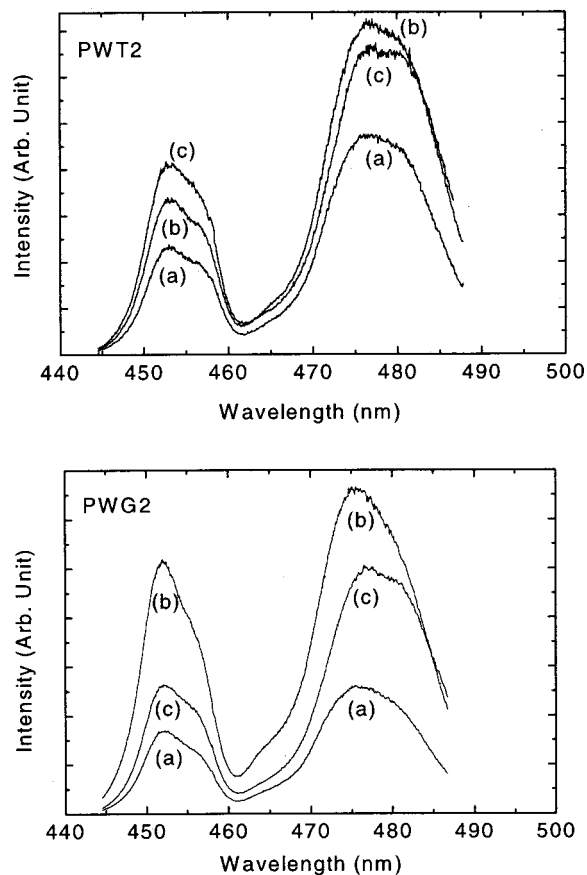


FIG. 1. Upconversion luminescence of PWT2 and PWG2 glasses measured with excited wavelength of (a) 648 nm, (b) 650 nm and (c) 652 nm.

The relative intensities of these emission bands for PWG and PWT glasses are shown in Fig. 2. The PWG glasses, in general, have stronger upconversion emission intensities ( $\geq$  one order of magnitude) compared with PWT glasses. This observation is similar to results obtained in tellurite- and germanate-based oxide glasses.<sup>2</sup>

Figure 3 shows the intensity of the 477 nm emission band as a function of excitation power. We see that the upconversion emission intensity varies quadratically with exci-

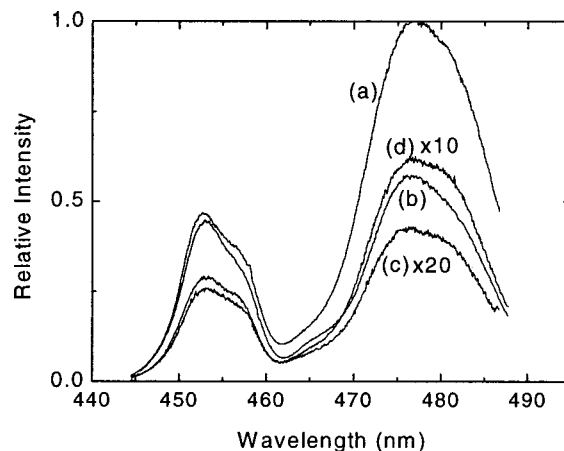


FIG. 2. The relative intensities of (a) PWG1, (b) PWG2, (c) PWT1 and (d) PWT2 glasses excited by 200 mW at 650 nm.

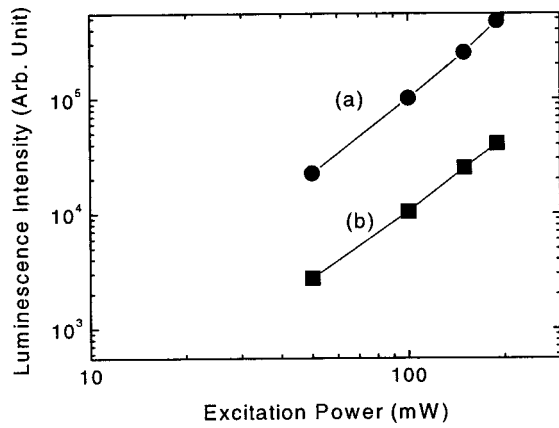


FIG. 3. Relationship between intensity of 477 nm emission band vs excitation power for (a) PWG2 and (b) PWT2 glasses. The excitation wavelength is 650 nm. The slopes of curves (a) and (b) are equal to 2.

tation intensity for both PWT and PWG glasses. This result suggests that the  $^1G_4$  level is populated through a two-photon process.<sup>4,5</sup> The energy levels of  $Tm^{3+}$  ions and the two-step upconversion process are shown in Fig. 4. The mechanism is a multi-step excitation by the excited state absorption process.<sup>6</sup> An excited  $Tm^{3+}$  ion in the  $^3F_2$  level with 650 nm excitation relaxes to the  $^3F_4$  level via nonradiative transitions. The excited  $Tm^{3+}$  ion in the  $^3F_4$  level is then raised to  $^1D_2$  level by the absorption of a second excitation photon. Blue emission centered at 453 nm then results from relaxation to  $^3H_4$  level. On the other hand, the ion in the  $^3F_4$  level may also relax to the  $^3H_4$  level via nonradiative transitions or cross-relaxation process. If the ion is in the  $^3H_4$  level and a second excitation photon is absorbed, another blue emission from  $^1G_4$  level centered at 477 nm is generated. Here, the strong resonance effect observed in 477 nm emission band is due to the energy difference between the  $^3H_4$  and  $^1G_4$  levels ( $=15\,392\text{ cm}^{-1}$ ), which is strongly resonant to 650 nm. A similar resonance effect for the 453 nm emission band in germanate glasses is expected since the difference of energies between the level  $^3F_4$  and  $^1D_2$  is  $15\,225\text{ cm}^{-1}$  (657 nm), very close to the 650 nm excitation

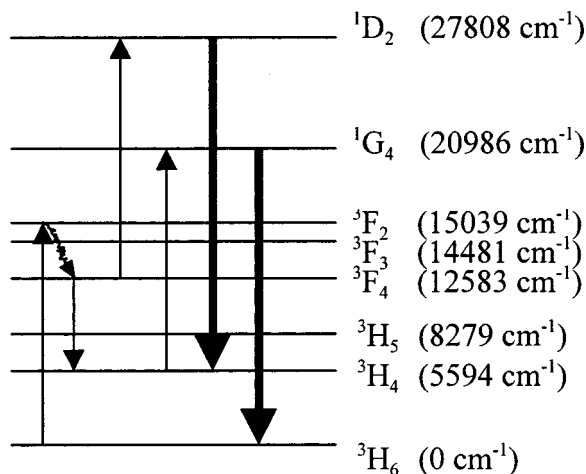


FIG. 4. Energy level diagram and the upconversion mechanism of  $Tm^{3+}$  ion. The energy values are obtained from Ref. 11.

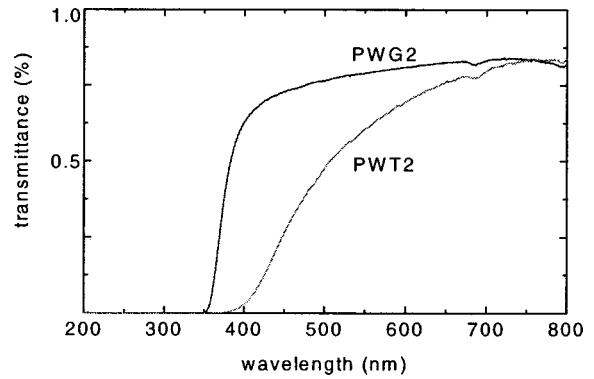


FIG. 5. Transmittance curves of PWG2 and PWT2 glasses.

energy. However, the absence of resonance effect in the 453 nm luminescence band in tellurite glasses needs further investigation.

The efficiency of this upconversion emission depends on the lifetime of the intermediate excited state,  $\tau$ , whose magnitude is governed by the radiative and nonradiative decay processes as<sup>7</sup>

$$\frac{1}{\tau} = W_{RD} + W_P + W_E, \tag{1}$$

where  $W_{RD}$  is the radiative decay rate,  $W_P$  is the multi-phonon relaxation rate and  $W_E$  is the energy transfer rate due to the cross-relaxation process between ions. In the weak-coupling case of rare-earth luminescence centers,  $W_P$  follows an exponential gap law given by<sup>7</sup>

$$W_P = C \left[ \frac{\exp(\hbar\omega_p/kT)}{\exp(\hbar\omega_p/kT) - 1} \right]^p e^{-\alpha\Delta E} \tag{2}$$

In Eq. (2),  $p = \Delta E/\hbar\omega_p$  is the phonon order,  $\alpha = -\ln(\epsilon)/\hbar\omega_p$  where  $\epsilon$  accounts for the exact nature of the ion-phonon coupling and is insensitive as the log dependence in the formula, and  $C$  is a constant dependent on the host. This multi-phonon decay of rare-earth ions in glass, in general, depends on the maximum phonon energy of the host glass as we observe its exponential dependence in Eq. (2). As a result, the lifetime of the intermediate excited state, and thus the intensity of the luminescence, decreases with increasing phonon energy. Based on phonon sideband measurement,<sup>2</sup> germanium-based oxide glasses with larger phonon energies should suffer a lower efficiency, i.e., a weaker luminescence. However, this prediction is inconsistent with our measurement as shown in Fig. 2. Kishimoto *et al.* also observed a similar effect in their glass systems,<sup>2</sup> suggesting that this disagreement was due to the difference in the absorption profiles of these glasses. Figure 5 shows the transmittance spectra of the PWT2 and PWG2 glasses with absorption edges at  $\sim 400$  nm and 350 nm, respectively. At 477 nm, the PWG glass has a transmittance of only about twice that of PWT glass. Therefore, we believe that the difference in the absorption profiles of the two glasses cannot completely account for their difference in their luminescent intensities.

In order to explain this discrepancy, Raman spectroscopy was employed to investigate the phonon spectra of PWT and PWG glasses. Figure 6 illustrates the room temperature Ra-

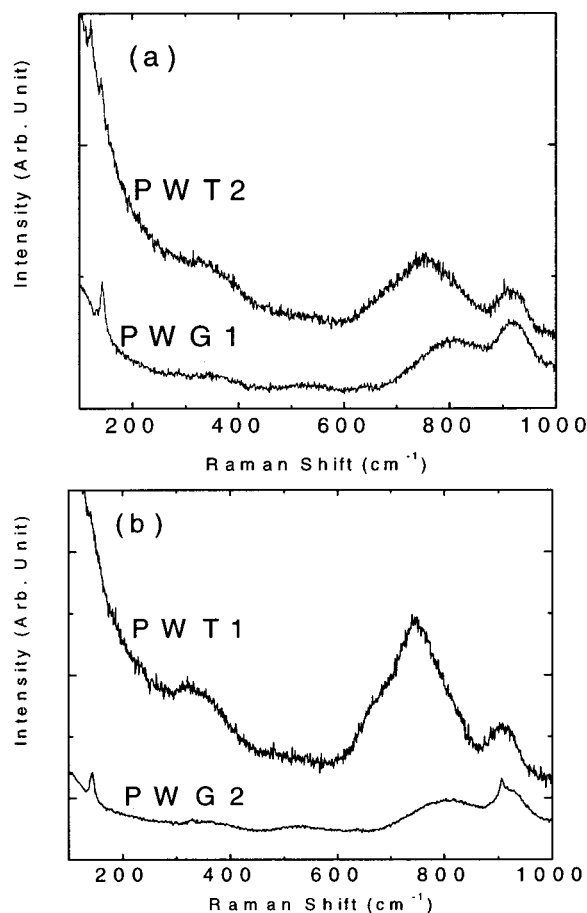


FIG. 6. Raman spectra of (a) PWT2 and PWG1 glasses, (b) PWT1 and PWG2 glasses excited at 488 nm.

man spectra of PWT and PWG glasses. Our Raman spectra of PWG glasses agree well with that reported in a previous study.<sup>3</sup> Three Raman bands at 345, 808 and 920  $\text{cm}^{-1}$ , originated from the Pb–F, Ge–O and W–O vibrational bonds, respectively,<sup>8,9</sup> are observed. Similar spectra are observed in PWT glasses, with the 808  $\text{cm}^{-1}$  peak (Ge–O mode) being replaced by a 741  $\text{cm}^{-1}$  peak that corresponds to a Te–O mode. In fig. 6, the W–O peak is used as an internal reference to obtain a relative Raman spectra. As we have pointed out, the upconversion luminescent lifetime, and thus the luminescent intensity, decreases with increasing energy lost by multi-phonon scattering. However, as the energies of the phonon are very near indicating that the  $p$  in different glass systems are in close proximity to each other, we believe that the phonon density, in this case, might become important in determining  $W_p$ . The constant  $C$ , if we look at it in more detail, also depends on the phonon density of the matrix. Based on Debye approximation,  $C \propto \rho(\omega)^{5/3}$  where  $\rho(\omega)$  is the phonon density of state of the matrix.<sup>10</sup> Therefore a larger phonon density will result in a larger  $C$ , implying a greater  $W_p$  and a weaker upconversion luminescence. As shown in Fig. 6, the Ge–O peak in PWG glasses (808  $\text{cm}^{-1}$ ) has a weaker intensity and smaller area than the Te–O peak (741  $\text{cm}^{-1}$ ) in PWT glasses. This indicates that the phonon den-

sity of the Te–O mode in PWT glasses is much higher than that of Ge–O mode in PWG glasses. On the other hand, the Ge–O mode has a larger energy than the Te–O mode. Although the PWT glass has smaller phonon energy than the PWG glass, it exhibits a lower luminescent intensity because of its increased multi-phonon scattering due to larger phonon density. We expect that this phonon density effect will become more pronounced when the difference in phonon energies is small as in our case. This interpretation based on phonon density has not been used in previous studies.<sup>2,3,7</sup> Analysis of vibrational energy as well as the phonon density through Raman spectroscopy, as a result, is of great significance in understanding upconversion luminescence.

#### IV. CONCLUSION

The blue upconversion luminescences in  $\text{Tm}^{3+}$  doped tellurite and germanate glasses have been studied using of a tunable dye laser as a pumping source. Tellurite glasses have shown a much weaker upconversion luminescence than germanate glasses. This contradicts the prediction by phonon energy consideration. We have correlated the luminescent efficiency of these two glasses with Raman spectroscopy and transmittance measurement. Our results suggest that in these glass systems, not only is the phonon energy of the host glass important in determining the luminescent efficiency, but also the phonon density. Since Raman spectroscopy can extract more information (both phonon energy and phonon density) than phonon sideband spectroscopy, it is a more effective tool for investigating upconversion luminescence.

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