

# Enhancement of upconversion luminescence due to the formation of nanocrystals in Er<sup>3+</sup>-doped tellurite glasses

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Optically transparent Er<sup>3+</sup>-doped tellurite-based nanocrystallized glasses with the composition of 70TeO<sub>2</sub>·15Li<sub>2</sub>O·15Nb<sub>2</sub>O<sub>5</sub>·0.5Er<sub>2</sub>O<sub>3</sub> (mol) have been prepared by a conventional melting quenching and the subsequent heat treatment processes. The sizes of grown nanocrystals in glass matrix appear to be 35–50 nm from the X-ray diffraction (XRD) measurement. The microhardness measurement shows that the Vickers hardness values of the nanocrystallized tellurite glasses are larger (33%–62%) than those in the base glass. The Raman spectra imply that the maximum phonon energy of the based glass decreases and shifts from 668 to 638 cm<sup>-1</sup> after heat-treatment. Visible upconversion luminescence and infrared luminescence of the base glass and heat-treated glasses under 980-nm laser diode (LD) excitation are investigated. The 524-, 546- and 656-nm upconversion intensities by 980-nm pumping increase significantly.

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Recently, erbium-doped oxyfluoride and heavy metal oxide glasses have received great attention due to their optical and fluorescence properties and potential application in fibre amplifiers, upconversion lasers, and three-dimensional displays<sup>[1–3]</sup>. Tellurium oxide (TeO<sub>2</sub>) glass, as a kind of heavy metal glasses, possesses relative low phonon energy (650–750 cm<sup>-1</sup>) compared with other oxide and this reduces the multiphonon loss which is critical in determining the upconversion efficiency<sup>[4]</sup>. Different methods were also proposed to enhance the upconversion efficiency of Er<sup>3+</sup>-doped tellurite glass<sup>[3,5,6]</sup>. One of most popular methods was based on the introduction of fluoride<sup>[3]</sup> or halide<sup>[5]</sup> components into tellurite glass. However, some issues such as low chemical and mechanical stabilities along with the fiberizability are frequently encountered. In 1999, Komatsu *et al.*<sup>[7]</sup> reported a new transparent Er<sup>3+</sup> and Eu<sup>3+</sup> TeO<sub>2</sub>-based ceramic glass containing nanocrystallized phase, which is a high potential as new optical functional materials. However, few reports dealt with the upconversion emission of Er<sup>3+</sup> ions are excited at about 980 nm in tellurite-based ceramic glass. In this letter we investigate the visible upconversion and infrared emission in the Er<sup>3+</sup>-doped 70TeO<sub>2</sub>·15Li<sub>2</sub>O·15Nb<sub>2</sub>O<sub>5</sub>·0.5Er<sub>2</sub>O<sub>3</sub> base glass and heat-treated samples, excited by the 980-nm laser diode (LD). The different values of Vickers microhardness ( $H_V$ ) between the base glass and heat-treated samples are also compared.

Er<sup>3+</sup>-doped 70TeO<sub>2</sub>·15Li<sub>2</sub>O·15Nb<sub>2</sub>O<sub>5</sub>·0.5Er<sub>2</sub>O<sub>3</sub> (mol) glass was prepared by using the conventional melt quenching. The anhydrous powders of TeO<sub>2</sub>, Li<sub>2</sub>CO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, and Er<sub>2</sub>O<sub>3</sub> with more than 99.9 % purity were used as raw materials. Batches of 100-g powders were melted in platinum crucibles at 850 °C in an electrically heated furnace in air atmosphere. After the stirring and refining process, the glass was cast into a heated copper mold, and then it took at least 64 h to finish the fine

annealing process. An undoped glass was prepared for measuring the Raman spectrum. The glass obtained was cut into pieces of 10 × 10 × 2 (mm) size, and the samples were polished for optical measurements. The glass transition temperature ( $T_g$ ) and onset crystallization temperature ( $T_x$ ) were decided with different thermal analyses (NETZSCH, DTA) methods at a heating rate of 5 °C/min. The measured  $T_g$  and  $T_x$  were 375 and 440 °C, respectively. The X-ray diffraction (XRD) measurements (Rigaku Inc.D\max-2550X, Japan) of the crushed powers of the as quenched and heat-treated samples at different temperatures (420 °C for 5 h, 440 °C for 5 h) were carried out with  $2\theta$  from 10° to 70°. The surface hardness of the glass samples was determined on the basis of Vickers hardness. The Vickers microhardness ( $H_V$ ) measurements were performed with a Shimadzu microhardness tester. For each sample the values of  $H_V$  were determined on the basis of at least five indentation measurements on the flat surface of the specimen. The indentations were made with a 100-g load applied for 5 s. Ultraviolet/visible (UV/V) transmission spectra were recorded between 300 and 700 nm using a spectrophotometer. The upconversion luminescence spectra in the range of 500–700 nm were measured with a JOBIN-YVON TRIAX550 fluorescence spectrometer upon excitation at 980 nm. Raman scattering spectra for the glass and glass-ceramics were measured at room temperature in the wave number range from 100 to 900 cm<sup>-1</sup> using an Ar<sup>+</sup> laser with a wavelength of 514.5 nm (SPEX 1877 0.6-m Triple spectrometer). All measurements were performed in the same configuration, fluorescence signal is collected in a direction perpendicular to the exciting beam, and all the samples were located at the same site in the process of measuring fluorescence properties.

The power XRD patterns for the glass and heat-treated crystallized samples are shown in Fig. 1. The peaks are attributed to the pyrochlore-type cubic compounds such

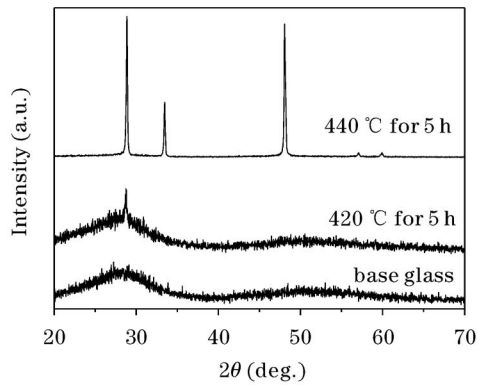


Fig. 1. Power XRD pattern at room temperature for the base glass and heat-treated samples.

**Table 1. The Vickers Hardness Values of the Base Glass and Transparent Crystallized Glasses**

$H_V$ (Gpa)	Base Glass	Crystallized (420 °C, 5 h) Glass	Crystallized (440 °C, 5 h) Glass
		2.1	2.8

as  $\text{Li}_{1.75}\text{Nb}_{1.75}\text{Te}_{0.25}\text{O}_6$ [2]. The diameters of the crystalline particles were estimated from the full width at the half maximum of a XRD peak at around  $2\theta = 28.8^\circ$  by using Scherrer's equation. The samples heat-treated at 420 °C for 5 h and 440 °C for 5 h have particles of approximately 35- and 50-nm size, respectively. The Vickers microhardness ( $H_V$ ) values of three different samples are listed in Table 1. The transparent nanocrystallized glass has much higher  $H_V$  values (33%–62 %) than the base glass, and the  $H_V$  values in higher heat-treated temperature are usually higher than those in the lower temperature. It is known that  $\text{TeO}_2$ -based glasses have extremely low fracture toughness  $K_{IC}$  of about 0.23  $\text{MPam}^{1/2}$  and are mechanically fragile[8,9]. Therefore, it is demonstrated from Table 1 that the tellurite-based nanocrystallized glass has high resistance against deformation compared with the base glass. The optical transmission spectra of three samples are shown in Fig. 2. As shown in Fig. 2, there are no change in the absorption

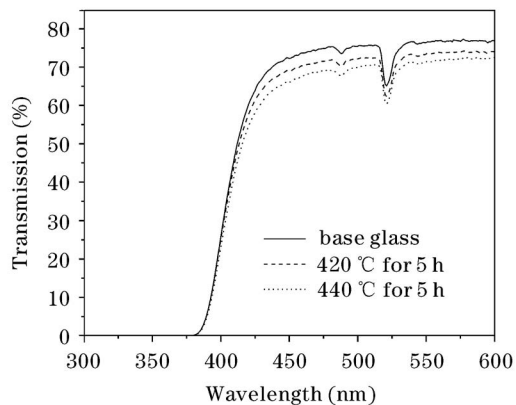


Fig. 2. Optical transmittance spectra for the base glass and heat-treated samples.

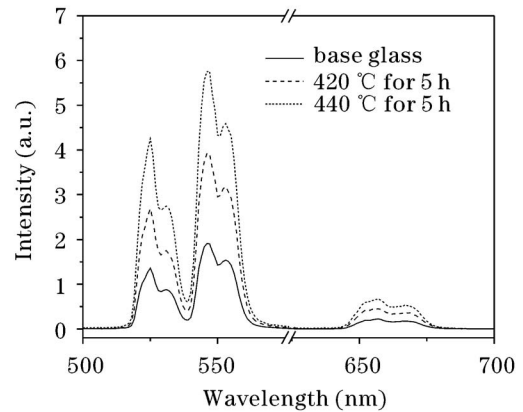


Fig. 3. Upconversion fluorescence spectra of  $\text{Er}^{3+}$ -doped base glass and heat-treated samples.

edge due to the formation of nanocrystals and the decrease in the transmission in the range of 425–600 nm is relatively small.

The upconversion luminescence spectra of the samples at room temperature are shown in Fig. 3. We can see the green up-conversion emission by naked eyes in all samples. There are three upconversion fluorescences in visible band (in Fig. 3), which located at 656, 546, and 524 nm, respectively. They correspond to  $\text{Er}^{3+}:^4F_{9/2} \rightarrow ^4I_{15/2}$ ,  $\text{Er}^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ , and  $\text{Er}^{3+}:^2H_{11/2} \rightarrow ^4I_{15/2}$ , respectively. The intensity of 546-nm peak was much stronger than that of two others. We investigate the pump power dependence of the three bands upconversion signals intensity in log-log plots. The slopes of three emissions of 524, 546, and 656 nm were almost two. This result indicates that two photon steps are involved for the upconversion process[5]. The fluorescence intensity around green 550 nm and red 665 nm for heat treatment samples is strong compared with that in the base glass. What is more, the upconversion intensity increases with heat treatment temperature. Figure 4 shows the fluorescence spectra around 1.55  $\mu\text{m}$  of three samples. Compared with the result of the visible spectra in Fig. 3, the 1.55- $\mu\text{m}$  spectral shape of three samples did not nearly change. These phenomena may be understood by considering the fact that the formation of the crystalline phase in tellurite-based glass ceramics leads to decrease the phonon energy

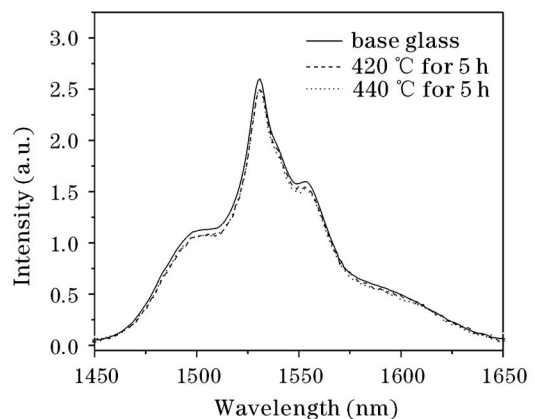


Fig. 4. Fluorescence spectra around 1.55  $\mu\text{m}$  of  $\text{Er}^{3+}$ -doped base glass and heat-treated samples.

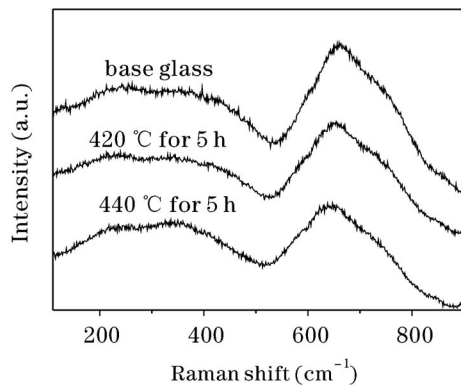


Fig. 5. Raman scattering at room temperature for the glass and heat-treated samples (heat-treated at 420 and 440 °C for 5 h) without doping rare earth.

of host. For example, Oishi *et al.*<sup>[10]</sup> had demonstrated the phonon energy of tellurite based glass ceramics based on MgO-K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>-TeO<sub>2</sub> system change from 726 to 677 cm<sup>-1</sup> due to the formation nanocrystalline phase by heat-treatment of the glass above the glass transition temperature. When the glass ceramics are annealed, some of Er<sup>3+</sup> ions are incorporated into the tellurite nanocrystalline phase. Raman spectra obtained for undoped glass ceramic and base glass are shown in Fig. 5. The maximum phonon energy of the based glass decreases and shifts from 668 to 638 cm<sup>-1</sup> after heat-treatment. The previous study shows that the visible fluorescence under 980-nm excitation on Er<sup>3+</sup>-doped materials results from energy transfer among Er<sup>3+</sup> ions, and is very sensitive to the multiphonon relaxation rate of rare-earth ions which strongly depend on the phonon energy of their matrix. According to Miyakawa and Dexter, the multiphonon relaxation rate  $W_p$  is written as<sup>[11]</sup>

$$W_p = W_0 \exp(-\alpha \Delta E / \hbar \omega), \quad (1)$$

where  $\Delta E$  is the energy gap to the next lower level and  $\hbar \omega$  is the phonon energy. According to Eq. (1), glass host with low phonon energy always has the lower  $W_p$ . For the Er<sup>3+</sup>:<sup>4</sup>S<sub>3/2</sub> and <sup>4</sup>I<sub>13/2</sub> levels,  $\Delta E$  are about 2800

and 6500 cm<sup>-1</sup>, respectively. Therefore, the  $W_p$  for Er<sup>3+</sup>:<sup>4</sup>S<sub>3/2</sub> level is more easily subject to be affected by the change of the phonon energy of glass host.

In conclusion, we have prepared the transparent Er<sup>3+</sup>-doped tellurite-based nanocrystallized glasses with the composition of 70TeO<sub>2</sub>·15Li<sub>2</sub>O·15Nb<sub>2</sub>O<sub>5</sub>·0.5Er<sub>2</sub>O<sub>3</sub>. The increase in the Vickers hardness values of heat-treated samples due to nanocrystallization has high resistance against deformation compared with the base glass. The upconversion intensities around 524, 546 and 656 nm of Er<sup>3+</sup> in nanocrystallized tellurite glass are strong compared with those in the base glass.

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