

On the near-infrared luminescence from TeO₂ containing borate glasses

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The effects of melting temperature and glass composition on the Near-infrared (NIR) luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works. Three absorption bands are detected at around ~370 nm, ~430 nm and ~530 nm, however, the absorption band at around ~600 nm could not be detected in all borate glasses. And no NIR luminescence was observed under the excitation of a 974 nm laser diode. The NIR luminescence was observed in Te-green and Te-purple glasses, which showed the absorption band at around ~600 nm. This absorption band was ascribed to $^2\Pi_g \rightarrow ^2\Pi_u$ transition of Te_2^- . Consequently, it is suggested that the origin of NIR luminescence of Te-containing green and purple glass is likely to be caused by Te_2^- center. (Not to sure of the meaning of this sentence...)

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1. Introduction

Among non-silicate glasses, such as heavy metal oxide and non-oxide glasses, high TeO₂ containing glasses are promising candidate materials for photonics applications, unifying the following features (1) wide transmission window, (2) good glass stability and durability and (3) high refractive index, better non-linear optical properties and relatively low phonon energy. Broad band erbium doped fiber amplifiers (EDFAs) have been demonstrated using TeO₂-based fibers as erbium hosts.^{1,2)}

However, high TeO₂ containing glasses often show coloration, pale green, brilliant purple to dark red, depending on glass composition and melting conditions.^{3,4)} The color centers of these glasses have already been reported.^{4,5)} According to their reports, the color centers of pale green glasses are clusters of Te_2 and Te_2^- species⁵⁾ and those of brilliant purple glasses are Te metallic colloids.⁴⁾

Recently, the authors have found near-infrared (NIR) luminescence centered at 1250 nm with 250 nm of half width from pale green and purple TeO₂-containing glasses for the first time to our knowledge.^{6,7)} We concluded that NIR luminescent centers might be Te_2 or Te_2^- species. Thus, the valence state of Te may change depending on glass composition and melting conditions, which produce color center and luminescent center in the glasses. In this study, the effects of melting temperature and glass compositions on the NIR luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works.^{6,7)}

2. Experimental

2.1 Sample preparation

Two series of glasses were prepared. Glasses of Series I are the composition of $62\text{B}_2\text{O}_3 \cdot 9\text{Al}_2\text{O}_3 \cdot 9\text{ZnO} \cdot 9\text{K}_2\text{O} \cdot 10\text{TeO}_2$ (mol%),

those of Series II are $90[(80-X)\text{B}_2\text{O}_3 \cdot 10\text{Al}_2\text{O}_3 \cdot 10\text{ZnO} \cdot X\text{K}_2\text{O}] \cdot 10\text{TeO}_2$ (mol%, $X = 0, 10, 20$ and 30). Reagent grade chemicals of H_3BO_3 , Al_2O_3 , ZnO , K_2CO_3 and TeO_2 were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucibles under various conditions (850°–1300°C for 15–60 min) in an electric furnace in air for Series I glasses. Glasses of Series II were melted in 50 cc alumina crucibles at 1200°C for 20 min in an electric furnace in air. After melting they were poured onto iron plate and pressed by another iron plate. Then, they were annealed at 450°C for 30 min and cooled slowly to room temperature in the furnace. All glasses were polished optically into about 1.5–2.0 mm in thickness for optical measurement. Hereafter, these glasses are referred to as Te-850, Te-1000, Te-1100, Te-1200, Te-1300, $X = 0$, $X = 10$, $X = 20$ and $X = 30$, respectively.

2.2 Optical measurement

The absorption spectra (300–800 nm) were measured using a Cary 1E ultraviolet-visible (UV-VIS) spectrometer at room temperature.

The NIR luminescence spectra (1000–1700 nm) were measured under the excitation of a 974 nm laser diode at room temperature. The optical setup for NIR luminescence measurement is shown in Fig. 1. Emission from the samples was dispersed by a single monochromator (blaze, 1.0 mm; grating, 600 grooves/mm; resolution 3 nm) and detected by InGaAs photodiode.

3. Results and discussion

3.1 Appearance and absorption spectra

The colors of Series I glasses change from colorless (Te-850) to brown (Te-1300) with increase in melting temperature. In glasses of Series II, color changes from reddish orange ($X = 10$) to colorless ($X = 30$) with increase in X (increasing amount of

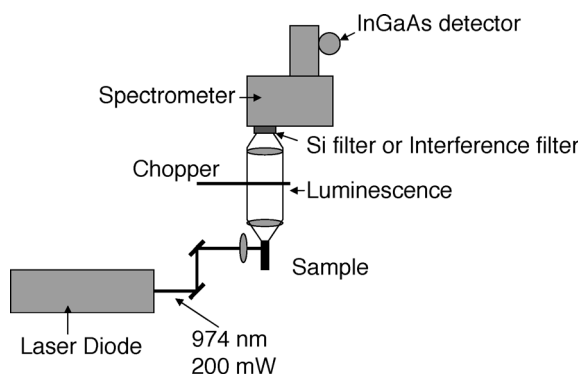


Fig. 1. Optical setup for NIR luminescence measurement.

K₂O). However, $X = 0$ glass revealed phase separation during casting. The melting conditions and appearance of these glasses are summarized in Table 1.

Figure 2 shows the absorption spectra of Te-containing borate glasses. The absorption spectra were analyzed and separated into three bands using peak fitting with Gaussian distribution. The results are shown in Table 1. Basically, three absorption bands can be observed, ~370 nm (Band I), ~430 nm (Band II) and ~530 nm (Band III), respectively. The assignment of these absorption bands are already known that Band I is the exciton transition, Band II $^3\Sigma_g^- \rightarrow ^3\Sigma_u^-$ transition of Te₂ and Band III Te metallic colloids.^{4,5} In Series I glasses, the UV absorption increases with an increase in melting temperature. It seems that the melting temperature affects the change in valence of Te. According to redox equilibrium, the higher melting temperature provides a lower valence state of metal ions, and hence the increase in UV absorption might be due to the Te species of a lower valence state.

However, these spectral patterns are different from those reported previously (ZTP, Te-SL and Te-Spinel in Table 1).⁶ The former three absorption bands are the same, but Band IV cannot be detected in all borate glasses discussed in this study. The assignment of Band IV has already been done and is ascribed to $^2\Pi_g \rightarrow ^2\Pi_u$ transition of Te₂.⁵ It is considered that the color cen-

ter of Te₂⁻ is lacking in all borate glasses from these results. Lindner et al.⁵ reported that the absorption band due to Te₂⁻ appeared at 606 nm in Te-doped blue and green sodalite crystal. This position is nearly the same as those in ZTP, Te-SL and Te-Spinel glasses. Thus, the absorption band due to Te₂⁻ center appeared at around 600 nm in many host materials. If Te₂⁻ centers are present in borate glasses, the absorption band should appear at around 600 nm. However, this band could not be detected in all borate glasses, and therefore, it is concluded that Te₂⁻ center is lacking or of a very low concentration in borate glasses.

Te₂ or Te₂⁻ species may be formed during reduction process of TeO₂ to metallic colloids (Te)_n in glasses and they gather together and precipitate Te metallic colloids.⁴ Zinc tellurium phosphate glass (ZTP) appeared to be brilliant purple and many small particles were observed by scanning electron microscope (SEM) observation in this glass.⁶ These particles were confirmed to be Te-metallic colloids and the strong absorption at around 537 nm was derived from the surface plasmon resonance absorption of Te-metallic colloids.⁴ This glass contained the same amount of TeO₂ (10 mol%) as that in borate glasses and was melted at nearly the same temperature (1200°C-2 h). This indicates that ZTP glass was prepared under higher reducing condition than borate glasses. According to Duffy's optical basicity concept,⁸ Λ values for both glasses were calculated without TeO₂: ZTP: 0.43 and $X = 0$: 0.46, $X = 10$: 0.50, $X = 20$: 0.55 and $X = 30$, respectively. The Λ value of ZTP is smaller than those of borate glasses. The smaller Λ value provides higher reducing condition, and therefore, a large amount of Te metallic colloids (Te)_n was formed in ZTP glass compared with borate glasses. This tendency can be clearly seen in Series II glasses. Thus, the reduction process did not proceed enough in borate glasses and the amount of Te₂ or Te₂⁻ species seems to be very low. This implies the lacking or very weak absorption of Band IV in borate glasses.

3.2 NIR luminescence

No NIR luminescence can be detected in all borate glasses under the excitation of 974 nm laser diode at room temperature.

Table 1. Melting Conditions, Appearances and Absorption Bands of Te-containing Glasses

Glass No.	Melting conditions °C-min.	Appearance	Absorption bands/nm			
			I	I	III	IV
Te-850	850-60	Colorless	—	—	—	—
Te-1000	1000-20	Pale orange	370	430**	530**	
Te-1100	1100-20	Orange brown	370	430**	530**	
Te-1200	1200-20	Reddish orange	370	430**	530	
Te-1300	1300-15	Reddish brown	370	430**	530	
$X = 0$	1200-20	Phase separation	—	—	—	—
$X = 10$	1200-20	Reddish orange	370	430**	530**	
$X = 20$	1200-20	Pale orange	370	430**	530**	
$X = 30$	1200-20	Colorless	—	—	—	—
ZTP*	1200-60	Brilliant purple	375	417	537	600
Te-SL*	1450-60	Pale green	374	444	526**	625
Te-Spinel*	1600-60	Brownish pink	—	420	556	599
				488**		

*: Reference 6), **: very weak.

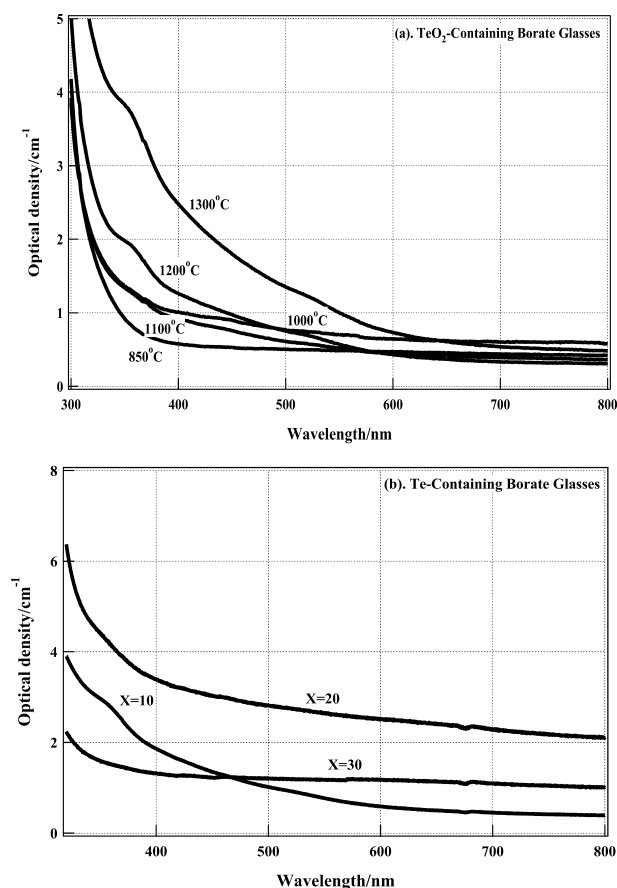


Fig. 2. Absorption spectra of Te-containing borate glasses. (a) Effect of melting temperature, (b) Effect of glass composition.

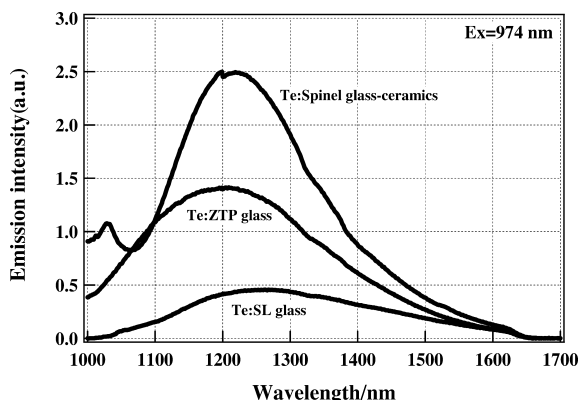


Fig. 3. NIR luminescence spectra of Te-containing glasses and glass-ceramics.⁶⁾

However, as reported previously,^{6,7)} ZTP, Te-SL and Te-Spinel glasses and glass-ceramics exhibited NIR luminescence centered at around 1200–1250 nm (Fig. 3).

In Table 1, the color center of borate glasses is different from those of ZTP, Te-SL and Te-Spinel glass and glass-ceramics. Especially, the band IV (~600 nm) is lacking in all borate glasses. This color center has been ascribed to Te_2^- . Murata et al.⁹⁾ discussed the NIR luminescence characteristics of various

Bi-doped glasses based on optical basicity concept without any reducing agents, and they reported that the generation of NIR luminescence was affected strongly by optical basicity of base glass. They concluded that Λ of 0.4 was the critical point (above 0.4 no NIR luminescence was observed). As discussed in the previous section, the concentration of the color center due to Te_2 or Te_2^- species might be very low, resulting in the lacking of absorption bands and NIR luminescence in all borate glasses. On the contrary, the Λ values for Te-SL and Te-Spinel are 0.58 and 0.47. These values are much larger than that of ZTP glass. However, a small amount of carbon was added into Te-SL glass, which was melted at a higher temperature (1450°C), and Te-Spinel glass was melted at a much higher temperature (1600°C). The reducing agent and higher melting temperature enhance the reducing condition, and hence it seems that Te-SL and Te-Spinel glass and glass-ceramics exhibited NIR luminescence.

Consequently, it is suggested that the origin of NIR luminescence of Te-containing glasses is likely to be caused by Te_2^- .

4. Conclusion

The effects of the melting temperature and glass composition on the Near-infrared (NIR) luminescent characteristics of Te-containing borate glasses are investigated and compared with previous works.

Three absorption bands are detected at around ~370 nm, ~430 nm and ~530 nm, however, the absorption band at around ~600 nm cannot be detected in all borate glasses. Also, no NIR luminescence was observed under the excitation of a 974 nm laser diode. The NIR luminescence was observed in Te-green and Te-purple glasses, which showed the absorption band at around ~600 nm. This absorption band was derived from $^2\Pi_g \rightarrow ^2\Pi_u$ transition of Te_2^- .

Consequently, it is suggested that the origin of NIR luminescence of Te-containing green and purple glass is likely to be caused by Te_2^- center. (As with abstract, not sure of the real meaning of the sentence...)

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