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Effect of carbon addition and TeO_2 concentration on NIR luminescent characteristics of TeO_2-doped soda-lime–silicate glasses

Penprapa Punpai [a,*], Shigeki Morimoto [a], Sasithorn Khonthon [a], Yusuke Arai [b], Takenobu Suzuki [b], Yasutake Ohishi [b]

[a] *School of Ceramic Engineering, Institute of Engineering, Suranaree University of Technology, 111, University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand*
[b] *Research Center for Advanced Photon Technology, Toyota Technological Institute, 2-12-1, Hisakata, Tempaku-ku, Nagoya-shi 468-8511, Japan*

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ABSTRACT

The effects of carbon addition and TeO_2 concentration on the near-infrared (NIR) luminescent characteristics of Te-doped soda-lime–silicate glasses are investigated. Three absorption bands were detected in all glasses at around 330–380 nm, ~430 nm and ~630 nm, respectively. The last absorption band (~630 nm) has been ascribed to $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^-. The broad NIR luminescence centered at 1200 nm was detected under the excitation of 974 nm laser diode except for glasses of lower carbon addition. The NIR luminescence was found to be strongly affected by melting atmosphere and TeO_2 concentration. It is considered that the absorption band, ~630 nm, is related strongly to the NIR luminescence of Te-doped soda-lime–silicate glasses. Consequently, it is suggested that the origin of NIR luminescence detected in Te-doped soda-lime–silicate glasses is likely to be caused by Te_2^-.

1. Introduction

Tellurite glasses (high TeO_2-containing glasses) have received much attention as promising candidates for new glass because of their special properties [1–5], high nonlinear refractive indices [6], large nonlinear optical sensibility [6–9], relatively low phonon energy in the blue [10] and green band emission [11], wide transmission window and good stability and durability [3,4,12,13]. In addition these glasses are well known to be good hosts for some rare earth and heavy metal ions with small multi-phonon decay rate [6,14,15], and they are potential materials for up-conversion lasers [16,17], optical fiber amplifiers [18], such as tellurite-base Er-doped fiber amplifier [19], nonlinear optical devices, such as optical switching [6], optical memory, etc. [6].

However, high TeO_2-containing glasses often show the coloration, pale green to brilliant purple, depending on glass compositions and melting conditions [20,21]. Few research [20,22] has been reported on the coloration and color centers of TeO_2-containing glasses, their coloration change from pale green to brilliant purple depending on melting conditions and glass compositions. The color center of pale green TeO_2-containing glasses is clusters of $Te{:}Te_2$ and Te_2^- [22], that of brilliant purple TeO_2 glasses is Te–metallic colloids [20].

Recently, the authors have found near-infrared (NIR) luminescence centered at 1250 nm with 250 nm of half width from pale green and purple TeO_2-containing glasses for the first time to our knowledge [23–25], and we concluded that the NIR luminescent center might be Te_2 and Te_2^-. In this paper, the effects of carbon addition and TeO_2 concentration on NIR luminescent characteristics of TeO_2-doped soda-lime–silicate glasses are investigated and compared with previous work [23].

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* Corresponding author. Tel.: +66 44 22 4475; fax: +66 44 22 4612.
E-mail address: shigeki@sut.ac.th (P. Punpai).

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2. Experimental

2.1. Sample preparation

Two series of glasses were prepared. In series (I) glasses, compositions was $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot 1TeO_2 \cdot$ Xcarbon (X = 0–1, wt%). Series (II) glasses, compositions was $72SiO_2 \cdot 2Al_2O_3 \cdot 4MgO \cdot 8CaO \cdot 13Na_2O \cdot 1K_2O \cdot XTeO_2 \cdot 0.3$carbon (X = 0.2–2, wt%).

High purity silica sand, alumina and reagent grade chemicals of MgO, $CaCO_3$, Na_2CO_3, K_2CO_3, TeO_2 and carbon were used as raw materials. Batches corresponding to 25 g of glass were mixed thoroughly and melted in 50 cc alumina crucible at 1450 °C for 1 h 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 600 °C for 30 min and cooled slowly in the furnace.

The glasses were cut and polished optically into about 2 mm in thickness for optical measurements. Hereafter, these glasses are referred to as C-0, C-0.1, C-0.2, C-0.3, C-0.5, C-1.0 and Te-0.2, Te-0.5, Te-0.7, Te-1.0, Te-2.0, respectively.

2.2. Absorption and luminescence measurement

The absorption spectra were measured with Cary 1E ultraviolet-visible (UV–Vis) spectrometer in the range of 300 nm to 800 nm at room temperature.

The luminescence spectra in the NIR region (1000–1700 nm) were measured under the excitation of 974 nm laser diode at room temperature. Emission from the sample were dispersed by a single monochromator (blaze, 1.0 nm; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode.

3. Result and discussion

3.1. Absorption spectra

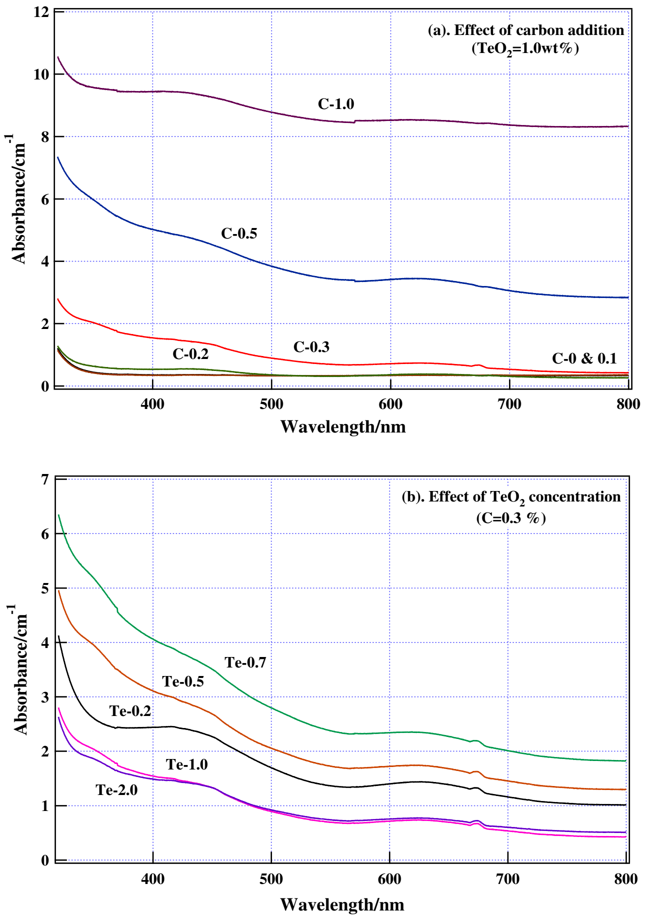

Fig. 1. Absorption spectra of TeO_2-doped glasses. (a) Effect of carbon addition (TeO_2 = 1.0 wt%).(b)Effect of TeO_2 concentration (Carbon = 0.3 wt%).

The appearances of glasses in series I change from colorless (C-0) to dark green–black (C-1.0) with increase in the amount of carbon addition. In series II, color of glasses change from green (Te-0.2) to pale green (Te-2.0) with increase in TeO_2 concentration. Fig. 1 shows absorption spectra of TeO_2-doped soda-lime–silicate glasses of series I and II glasses. Appearances and absorption bands of glasses are summarized in Table 1.

Three absorption bands can be observed in all glasses, 330–380 nm, ~430 nm, ~630 nm, respectively. In series I glasses, weak absorption bands can be detected even in C-0 glass, the absorbance increases with increase in the amount of carbon, and the absorbance is very high in whole wavelength region in C-0.5 and C-1.0 glasses.

On the other hand, the absorbance of series II glasses increases with increase in the amount of TeO_2 (0.2–1.0 wt%) and decreases again. However, the absorption band owing to Te–metallic colloids (~530 nm) cannot be observed in all glasses discussed here.

The assignment of these absorption bands has been already known that absorption band (I) is due to exciton transition, band (II) $^3\Sigma g^- \rightarrow {}^3\Sigma u^-$ transition of Te_2, band (III) Te metallic colloids and band (IV) $^2\Pi g \rightarrow {}^2\Pi u$ transition of Te_2^- [20,21], respectively.

Table 1
Melting conditions, appearance and absorption bands of glasses studied

No.	Melting condition (°C min)	Appearance	Absorption bands/nm			
			I	II	III	IV
C-0	1450-60	Colorless	~380[a]	432	–	638[a]
C-0.1	1450-60	Pale green	~380[a]	432	–	638[a]
C-0.2	1450-60	Green	377[a]	432	–	638[a]
C-0.3	1450-60	Green	327	435	–	633
C-0.5	1450-60	Dark green	355	436	–	638
C-1.0	1450-60	Dark green-black	375	438	–	634
Te-0.2	1450-60	Green	367	437	–	635
Te-0.5	1450-60	Green, partly brownish green	344	432	–	633
Te-0.7	1450-60	Green, partly brownish green	349	435	–	634
Te-1.0	1450-60	Green	327	435	–	633
Te-2.0	1450-60	Green	331	436	–	633
Te-1200[b]	1200-20	Reddish orange	370	430	530	–

[a] Very weak.
[b] $63B_2O_3 \cdot 9Al_2O_3 \cdot 9ZnO \cdot 9K_2O \cdot 10TeO_2$ (mol%) melted in alumina crucible [25].