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Journal of Non-Crystalline Solids



journal homepage: www.elsevier.com/locate/jnoncrysol

## Near-infrared luminescence property of Te-doped zinc phosphate glasses



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#### ARTICLE INFO

Article history: Received 12 October 2016 Received in revised form 27 November 2016 Accepted 28 November 2016 Available online xxxx

Keywords: Broadband NIR emission NIR property Te<sub>2</sub> clusters Glass

## 1. Introduction

The rapid development of optical communication technique has a great demand for the speed and capacity of optical fiber transmission system. However, traditional rare earth ions-doped optical fiber amplifiers and lasers cannot satisfy the demand due to the narrow emission band of rare earth ions. Thus, ultrabroad band NIR luminescent materials have been widely studied in the past decades because of their promising applications in broadband optical amplifiers and tunable lasers.

Until now, broadband NIR luminescence has been observed in glasses doped with various elements. In particular, Bi-doped optical materials have been extensively studied since NIR luminescence was discovered in aluminosilicate glass [1–3]. Besides, broadband NIR emission was also found in Te-doped glasses and glass ceramics [4], and it was pointed out that NIR emission exists not only in Bi-doped and Te-doped glasses but also in other 6p-elements (Pb)-and 5p-elements (Sb, Sn)-doped glasses [5]. Bi-doped glasses have attracted most attention among them, and fiber laser based on bismuth-doped aluminosilicate glass fiber has been demonstrated [6]. Though the modulation of NIR luminescence was put forward thanks to extensive investigations of Bi-doped glasses with different chemical compositions, the nature of the bismuth active luminescent centers is still controversial [7,8]. At present, it is widely accepted that bismuth with low valence state is responsible for the NIR emission [3].

Different from Bi-doped optical materials, the broad NIR emission centers in Te-doped glasses were ascribed to elemental clustering,

#### ABSTRACT

Broadband near-infrared (NIR) emission has been observed from Te-containing glasses melted under reduced conditions in recent years. However, it has not been paid great attention compared with Bi-containing glasses, and there are few reports on the NIR emission property of Te-containing glasses. In this paper, we report tunable broadband NIR emission from 900 to 1500 nm in Te-doped zinc phosphate glasses. The emission intensity increases with increasing melting temperature, indicating the temperature-dependent formation of the related luminescent center. A red shift is observed when increasing the wavelength of excitation. The NIR emission intensity increases linearly with the increase of excitation power. Based on absorption, emission and Raman spectra of the glasses melt at various temperatures, Te<sub>2</sub> clusters are suggested to be responsible for the NIR emission. © 2016 Elsevier B.V. All rights reserved.

especially Te<sub>2</sub> [4,9–13]. Ohishi et al. firstly reported the observation of NIR emission in Te-doped glasses and glass-ceramics, and they considered Te clusters to be the luminescent centers [4]. The influences of carbon addition and the concentration of TeO2 on the emission intensity of Te-doped silicate glasses were investigated [10], which showed that addition of carbon and an appropriate concentration of TeO2 are beneficial to NIR emission. Besides, the NIR emission was also observed in Tedoped silica-based optical fiber [11], based on which fiber laser is demonstrated [12]. Study on the influence of different redox conditions during the fiber drawing process [13] indicated that reducing condition was important for the NIR luminescence, which is consistent with previous study. Theoretically, the formation of lower valence states of Te, e.g. Te<sub>2</sub>, depends on melting condition and optical basicity of glass matrix [10]. However, there are few reports about the effect of melting temperature on the NIR emission of Te-doped glasses. In this paper, absorption and Raman spectra are used to characterize the temperature dependent formation of NIR luminescent center. The NIR luminescence property of the Te-doped zinc phosphate glasses is also investigated.

#### 2. Experimental

#### 2.1. Sample preparation

The glass sample with the composition of  $50ZnO-10TeO_2-50P_2O_5$  (mol%) was prepared by conventional melt-quenching technique using analytical pure ZnO, TeO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> reagents as raw materials. Mixed batches about 20 g in weight were mixed homogenously in an agate mortar, and each batch was transferred into alumina crucible with a lid and melted at 800 °C, 1000 °C, 1200 °C for 20 min, respectively. Melts were poured onto a stainless steel and the volatilization losses

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Fig. 1. Absorption spectra of the glasses melted at different temperature. Inset shows their photographs.

were checked by weighting to confirm that actual glass composition was close to the batch. Finally the glasses were cut into the size of  $10 \times 10 \times 1$  mm and then well polished to meet the requirements for measurements.

#### 2.2. Measurements

The absorption spectra of the glass samples were measured with a Perkin-Elmer Lambda-900 UV/VIS/NIR spectrophotometer (Perkin Elmer, Waltham, MA). Raman spectra were acquired on a Raman spectrometer (Renishaw inVia, Gloucestershire, UK) with a laser excitation source of 532 nm. The emission spectra were measured with an iHR320 spectrofluorometer (Jobin-Yvon, France) equipped with 808, 980 nm laser diodes as excitation sources. The fluorescent lifetimes were collected with an iHR320 spectrometer quipped with a TDS 3012B digital oscilloscope (Tektronix, USA) and pulse LDs of 808, 980 (LEO Photoelectric, China). All the measurements were performed at room temperature.

#### 3. Results and discussion

As shown in the inset of Fig. 1, the appearance of the glasses change from purplish red to deep purple as the melting temperature increases from 800 °C to 1200 °C. This tendency is consistent with the investigation of the coloration in this glass system [14]. Two absorption bands at 537 and 420 nm are observed from the absorption spectra, which can be assigned to Te metallic colloids and the  ${}^3\sum g^- \rightarrow {}^3\sum u^-$  transition of Te<sub>2</sub> clusters [4], respectively. Moreover, these two bands enhance greatly with increasing melting temperature. Usually, a higher melting temperature promotes the reduction in redox equilibrium of glass melt, thus a part of TeO<sub>2</sub> will be reduced to Te, which subsequently form Te<sub>2</sub> clusters or further gather together to precipitate Te metallic colloids. As a result, the absorption of these two bands increases and the glass shows a deeper color with increasing melting temperature.

Fig. 2 shows the emission spectra (a) and the peak intensity (b) of the glasses excited by a laser diode at 808 nm. A broad NIR emission peaking at 1100 nm with a full width at half maximum about 280 nm is observed. Similar to the results of the absorption spectra, the emission intensity increases with increasing melting temperature. There are some fluctuations of the intensity mainly due to the homogeneity of glass and polished glass surface state. Even so, the average peak



Fig. 2. Luminescence spectra (a) and emission intensity (b) of the glasses excited by laser diodes at 808 nm (average intensity of the glass melted at 800 °C is intended to be 1).



Fig. 3. (a) Raman spectra of the glasses melted at different temperature. (b) Variation trends of emission intensity at 1100 nm, absorptivity at 420 nm, Raman intensity at 213 cm<sup>-1</sup> and temperature.

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