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Technical note

Effects of thermal treatment on broadband near-infrared emission from Bi-doped chalcohalide glasses

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Abstract

GeGaSKBr glass with Bi ions as emission centers were fabricated. An intense emission centered at around 1230 nm with the width of more than 175 nm was observed by 808 nm photo-excitation of the glass. Lower quenching rate and thermal treatment promote micro-crystallization process, thus strengthening the emission.

Keywords: X-ray method; Optical properties; Glass; Functional applications; Bismuth-doped

The demand to increase the transmission capacity of wavelength division multiplexing (WDM) system is indispensable for satisfying the rapid development of telecommunications industry. Much effort has been devoted on broadening and flattening of gain from rare-earth-doped fiber amplifier (RDFAs) to fiber Raman amplifiers (FRAs).[1–3] However, the gain bandwidths of RDFAs are limited at most to 100 nm due to narrow *f*–*f* transitions and multiwavelength pumping FRAs have complicated system structures and require high power excitation sources. Recently, bismuth-doped oxide glasses have been attracted much attention for their broadband near-infrared emission.[4–9] In particular, Razdobreev *et al.* reported a high efficient all-fiber bismuth-doped laser in the 1150–1225 nm regions.[10]

We have presented for the first time bismuth-doped chalcohalide glasses as broadband optical amplification media by single wavelength pumping[11] and especially investigated the effect of melting temperature on infrared luminescence of these glasses.[12] In this letter, we will present our further work on effects of post-thermal treatment on near-infrared emission of the Bi-doped chalcohalide glasses.

Glasses for the investigation are with composition (mol %) of $70GeS_2$–$9.5Ga_2S_3$–20KBr–$0.5Bi_2S_3$ (GGKB). High-purity elements Ge, Ga, Bi, and S (5N-purity) and reagent-grade KBr (3N-purity) were used as raw materials. Glass samples were melted at fixed temperature (MT = 850 °C) for 10 h in sealed quartz tube, and then quenched in air or water. Different heating conditions were used to treat the as-prepared sample. The obtained glasses were cut into tablet-like pieces with a size of 2.0 mm × Ø10 mm, and well polished for optical measurements. The absorption spectra of samples were measured by a Jasco V-570 spectrophotometer and the infrared luminescence spectra were recorded by a Zolix SBP300 spectrofluorometer with an InGaAs detector at 850–1650 nm and excited with an 808-nm laser diode (LD). X-ray diffraction (XRD) measurements were carried out using Mo Ka radiation to identify crystalline phases and the average sizes of the crystals in the sample.

The absorption and luminescence spectra of GGKB glass samples quenched in air or water are shown in Figs. 1 and 2. A band centered at 1925 nm is observed in absorption spectra (Fig. 1) and is due to impurity absorption (–OH).[12] But several weak absorption bands of Bi ions at 700, 800 and 1000 nm are not visible. Similar phenomenon was also observed in Bi-doped soda-lime–silicate glass.[13] This is most likely attributed to the fairly broad energy bands of the lower valent Bi ions which make glasses less sensitive to the weak absorptions in

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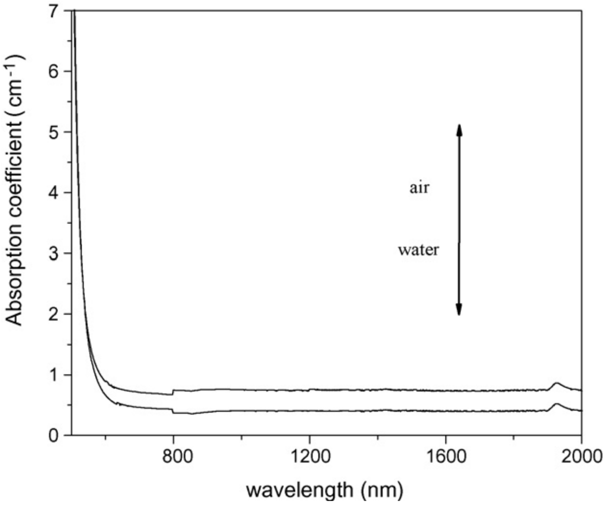

Fig. 1. Absorption spectra of GGKB glasses quenched at water or air.

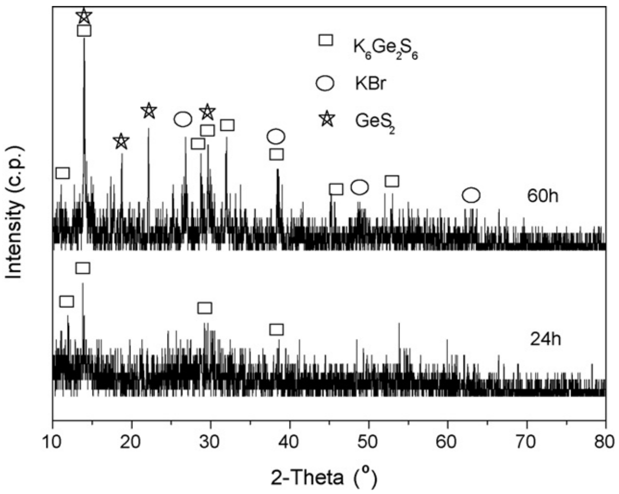

Fig. 3. XRD spectra of GGKB glasses recorded after different thermal treatment.

this region. In fact, several weak absorptions from Dy^{3+} ions in the same region were also overcovered in the Bi–Dy-co-doped chalcohalide glasses.[11,12] The possible oxidation state of Bi ions in the present glasses will be discussed later. Luminescence spectra (Fig. 2) show an emission band centered at 1230 nm for the sample prepared at the relatively lower quenching rate (in air). As discussed in our previous work, the band at 1230 nm could be attributed to Bi ions emission.[11,12] It is very interesting to find that quenching procedure exerted a remarkable effect on infrared luminescence of sample. Bi ions emission was almost totally quenched when the glass was cooled in water, which was also characterized by the much lowered baseline in absorption spectra (Fig. 1). It is known from our previous work that the lower baseline of absorption spectrum co-exists with the lower intensity of Bi emission in chalcohalide glasses.[11,12] From above observations it can be concluded that the higher quenching rate weakened luminescence of the present glasses.

In order to confirm the positive role of crystallization, further post-thermal treatment on the sample quenched in water was carried out at 330 °C for 24 h, 60 h and 70 h, respectively. XRD patterns of two samples are shown in Fig. 3 from which the average crystallite size was evaluated by using Scherrer's equation as about 35 nm (GeS_2), 15 nm ($K_6Ge_2S_6$) and 20 nm (KBr) for the samples treated for 60 h, and about 10 nm ($K_6Ge_2S_6$) for 24 h.[14] Fig. 4 presents the emission spectra of these thermally treated samples and the untreated sample for comparison. As our expectation, infrared emission of Bi in the present chalcohalide glass was much enhanced by the post-thermal treatment, which is generally proportional to the heating time. Although treating for 60 h obtained the highest emission intensity, the treated sample showed the poor stability in air. On the other hand, the sample treated for 24 h exhibited the moderate emission intensity and fairly good stability. Explanations may be due to formation of different crystalline phases in glass matrix. As shown in XRD patterns of treated samples in Fig. 3, thermal treating for the longer time favors the growth of halide crystallites (KBr) besides GeS_2 and $K_6Ge_2S_6$ crystalline phases, while in the case of the shorter time treating, $K_6Ge_2S_6$ crystals dominate over others.[15–17]

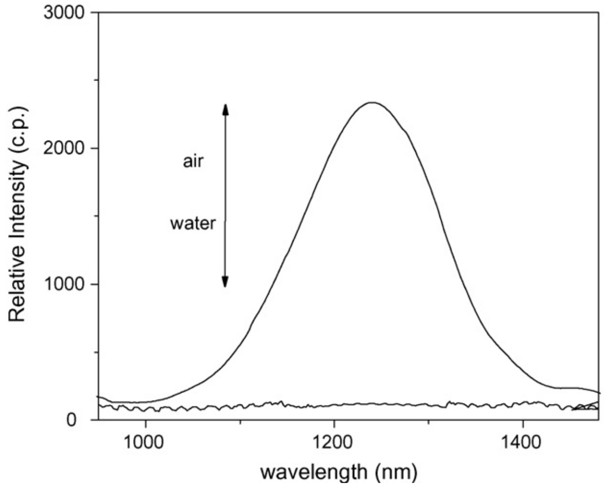

Fig. 2. Fluorescence spectra of GGKB glasses quenched in water or air, pumped by 808 nm LD.

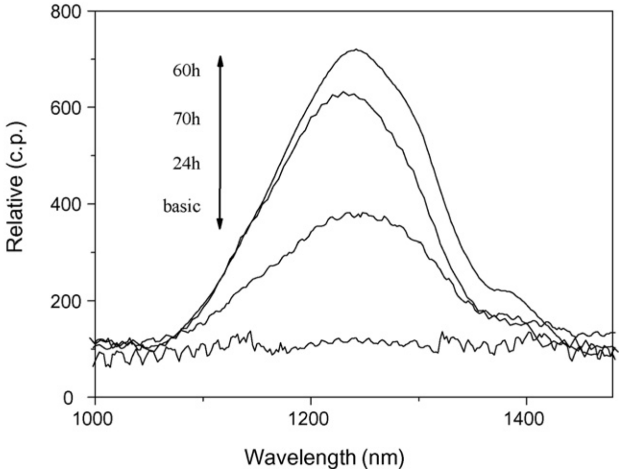

Fig. 4. Florescence spectra of GGKB glasses recorded before and after thermal treatment.

As for the valence state of bismuth ion contributes to the infrared emission in oxide glasses there have been several controversial suggested origins, such as Bi^{5+}, and low valence states of Bi.[4,13,18] Since there is no oxidation circumstance in the course of preparation of chalcohalide glasses and the high concentration of Br and S components are involved, we attributed the observed infrared emission from Bi ions of the low valence state (Bi^{2+} or Bi^{+}).[19,20] Although there are no direct data to identify the low valence state of Bi ions due to lack of effective method, this suggestion is supported by the reported work on BiBr and BiO molecules that showed broadband infrared emissions peaking at about 1300 nm.[21]

In summary, we synthesized GeGaSKBr chalcohalide glass doped with Bi ions as emission centers. By 800 nm photoexcitation at the room temperature, a near-infrared emission centered at about 1230 nm with the width of more than 175 nm was observed from the sample quenched in air but almost totally disappeared when quenched in water. Formation of crystallites in glass matrix due to the slower quenching rate is the possible reason. Results of further post-thermal treatment on the sample quenched in water are in consistent with the explanation.

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