



Broadband NIR luminescence of Bi-doped $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramics

Nengli Dai^{*}, Huaixun Luan, Zijun Liu, Yubang Sheng, Jinggang Peng, Zuowen Jiang, Haiqing Li, Luyun Yang, Jinyan Li^{*}

Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China
College of Optoelectronic Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

Transparent Bi-doped $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) glass-ceramics are prepared by controlled nucleation and crystallization of glasses with TiO_2 worked as nucleating agents. The presence of β -eucryptite (LiAlSiO_4) crystalline phase can be indicated by X-ray diffraction analyses. Enhanced near infrared luminescence in the range of 1000–1550 nm with FWHM over 270 nm is observed from Bi-doped LiAlSiO_4 glass-ceramics compared with initial glass. Blue emission centered at 425 nm in glass and glass-ceramics could be ascribed to the emission band of the Bi^{3+} ions ($^3\text{P}_1-^1\text{S}_0$). Based on optical basicity theory, the broad infrared luminescence from the Bi-doped LAS glass and glass-ceramics can be derived from low valence Bi ions. The possible mechanism of the enhancement of near infrared (NIR) fluorescence is also discussed in this manuscript.

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1. Introduction

As a new type of functional material, transparent glass-ceramic has attracted more and more attentions because of its combining the advantages of glasses and crystals. Glass-ceramics with microstructures comprised of uniformly dispersed crystals <100 nm in size offer promise for many potential new applications including optical amplifiers, solar collectors, and upconversion emitting devices for laser application [1,2]. Due to its easy fabrication and good optical properties, transparent glass-ceramics possess luminescence characteristics that are significantly different from those of glasses and have been widely used to study the broadband infrared luminescence from doped transition metal ions (Ni^{2+} , Cr^{3+} or Cr^{4+}) in previous reports [3–8].

In recent years, bismuth doped optical materials have drawn much attention for their potential application in optical fiber amplifiers. The near infrared (NIR) optical properties of bismuth were investigated in lots of host materials, mainly including silicate, germanate, phosphate, borate, chalcogenide glasses and some other medium, such as crystals [9–14]. Although many researchers have investigated the nature of the NIR luminescence, the origin of the IR luminescence was not clear yet. Several proposals on the mechanism of Bi NIR emission have been made tentatively, assigning the role of emission center to Bi^{5+} , Bi^+ , Bi metal clusters or negatively charged bismuth dimers [11,13,15–17], but unfortunately, the origin of NIR emission still remains highly debated.

To our knowledge, there were many researches focusing on the mechanism of NIR luminescence from Bi in glass and crystal hosts [11–16], but little attention was drawn on the study of spectroscopic properties and

mechanism of NIR fluorescence from bismuth in glass-ceramics [18]. In this work, we study the effects of the heat-treatment conditions on the broadband infrared luminescence property of Bi-doped $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system glass and glass-ceramics, not only the PL broadband peak position from Bi doped LAS glass ceramics but also the FWHM that depends on the exciting wavelength was researched, and the mechanism of the enhanced near infrared luminescence in the glass-ceramics was discussed in this paper.

2. Experimental

The LAS glass series with compositions of $59\text{SiO}_2-19\text{Al}_2\text{O}_3-6\text{MgO}-6\text{Li}_2\text{O}-10\text{TiO}_2-0.5\text{Bi}_2\text{O}_3$ were prepared by a conventional melting method. Analytical pure reagent commercial oxides (>99.5%) were selected as the raw materials. TiO_2 was added to the batch to promote phase separation and internal nucleation [19]. The nucleating agents melt homogeneously into the glass but promote very-fine-scale phase separation on reheating. Mixed batch of 30 g was melted in alumina crucible at 1580 °C for 2 h in the high-temperature furnace in air atmosphere, and the accuracy of high-temperature furnace the experiment used is ± 1 °C. Then the liquid melt was poured on the pre-heated steel mold and annealed at 650 °C for 2 h in the annealing furnace to eliminate the internal stress. The obtained glasses were cut into $15 \times 15 \times 2$ mm³ and polished for further thermal treatment processes to obtain transparent glass-ceramics.

The optical absorption spectrum in the range of 200–1100 nm is measured on PerkinElmer-Lambda35 spectrophotometer. The NIR luminescence spectra are obtained by ZOLIX SBP300 spectrophotometer, detected by InGaAs photo-detector with excitation of 808 nm. The excitation and emission spectra in the ultraviolet and visible region are measured by Jasco FP-6500 fluorescence spectrophotometer. X-ray

^{*} Corresponding authors at: Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China. Tel./fax: +86 27 87559463. E-mail address: ljj@mail.hust.edu.cn (J. Li).

diffraction (XRD) measurements are performed by using Cu K α 1 as radiation to identify crystalline phases.

3. Results and discussion

3.1. The choice of glass-ceramic system

Excellent transparency required glass-ceramics holding low light-scattering in the process of nucleation and crystallization. A scattering model developed by Andreev and Hopper described interfering fields from the individual particles that produced a large compensating effect [20,21]. Formula of this model is presented as follows:

$$\sigma_c \approx \left[\left(\frac{2}{3} \times 10^{-3} \right) k^4 \theta^3 \right] (n \Delta n)^2 \quad (1)$$

where θ is the mean phase width, $k = 2\pi/\lambda$ (where λ is the wavelength of light), n is the refractive index of the crystal, and Δn is the index difference between the crystal and the glass host. In this case, good transparency is achieved with particle radii smaller than 30 nm and a refractive index difference of less than 0.3.

To choose an applicable glass-ceramic system which could not only hold good transparency but also provide nice optical capabilities, we explored different kinds of compositions. One system of glasses contained the basic oxides SiO₂–Al₂O₃–Li₂O–MgO with nucleating oxide TiO₂ was investigated primarily in our experiment. The crystalline β -eucryptite (LiAlSiO₄) might precipitate after thermal treatment and phase separation.

3.2. Nucleation and crystallization

According to the classic diagram of Tamann [22], the optimal nucleation temperatures occur often between 50 °C and 100 °C above the glass-transition temperature (T_g) and the rate of crystal growth should be kept low to minimize particle size. Since annealed at 650 °C, the glass samples were heat-treated at 725 °C, 750 °C, 775 °C and 800 °C for 3 h with the rate of 5 °C/min, respectively. Heat-treatment leads to the nucleating and crystallization in the glass hosts, and the color of glasses darken from orange to dull brown, while the treatment temperature increased to 800 °C, which is shown in Fig. 1. This change of appearance is possibly due to the increased absorption of the oxide-rich member of the phase separated glasses. Further heating resulted in the development of slight haze due to scattering caused by the increasing difference of refractive index of the initial glass (sample treated at 800 °C).

As we know, LAS glass-ceramics are obtained via the precipitation of β -quartz partly stuffed by other network modifier ions as the basic crystalline phase. Distorted tetrahedral cavities, capable of accepting small cations with ionic radii of 0.06–0.08 nm, are created in the idealized β -quartz structure. The LiAlSiO₄ phase derives from the solid solution wherein Al³⁺ replaces Si⁴⁺ in the quartz tetrahedral positions, the charge balance being maintained by Li⁺ that stuff the tetrahedral cavities. The Li⁺-stuffed derivative of β -quartz is the β -eucryptite (LiAlSiO₄), where nearly one-half of the silicon is replaced by aluminum and lithium that preferably occupy tetrahedral cavities on the [SiO₄] tetrahedral plane of alternating [SiO₄] and [AlO₄] tetrahedrons [1]. The addition of alkali earth oxides such as MgO acting as fluxes can lower the melting temperature and the glass-transition temperature (T_g) and first crystallization temperature (T_x) of LAS glasses.

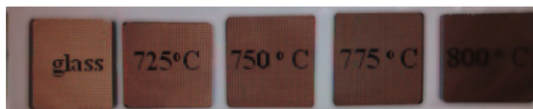


Fig. 1. Photograph of Bi-doped LAS glass and glass-ceramics heat-treated at various temperatures for 3 h.

X-ray diffraction patterns of Bi-doped GCs and untreated glass sample are represented in Fig. 2. No apparent diffraction peaks can be observed from the as-made glass, except a large gibbosity between 20°–30°. The results show that the parent glass is amorphous. Sharp diffraction peaks appear in the XRD patterns of the glass-ceramics heat-treated at 725 °C and 750 °C for 3 h. The peak positions agree well with that of LiAlSiO₄ crystal (ICDD, No.73-0254). Powder diffraction patterns yield lattice parameters identical for single crystals of β -eucryptite ($a = b = 10.3562$ Å; $c = 10.7677$ Å). According to the XRD patterns, the sizes of precipitated phase are calculated by using the Scherrer equation.

$$D_{hkl} = \frac{K \lambda}{\beta \cos \theta} \quad (2)$$

where D_{hkl} is the crystal size at the vertical direction of ($h k l$), λ is the wavelength of X-ray, θ is the angle of diffraction, β is the full width at half maximum (FWHM) of the diffraction peak and the constant $K = 0.89$. The calculated mean nanocrystal size was about 24.3 nm, which is much smaller than 30 nm, as a result, scattering in this glass-ceramics is negligible and the glass-ceramics would keep good transparency.

3.3. Bi-doped glass-ceramics containing LiAlSiO₄ crystal phase

Transparent glass-ceramics have been studied as host media for doped luminescent ions, particularly transition metal ions. Since Fujimoto and Nakatsuka reported a novel infrared luminescence from Bi-doped silicate glass in 2001, this VA group element is considered a key luminescent ion for potential use in tunable lasers and fiber amplifiers, because, in certain ligand field environments, the ion absorbs broadly in the visible wavelength range yet fluoresces in the near infrared [17,23]. In this work, we investigated the NIR fluorescence in Bi-doped LAS glass-ceramics, and transparent glass-ceramics possess luminescence characteristics that are significantly different from those of glasses.

Absorption spectra of Bi-doped LAS glass and glass-ceramics treated at various temperatures are shown in Fig. 3. For the samples before and after heat-treatment, absorption band centered at ~470 nm is observed obviously, which should be attributed to Bi-related NIR active centers, in accord with the results reported previously [8–14,18,23]. However, there is no obvious absorption peak at ~700 nm; the possible reason of this phenomenon may be due to the intense and wide absorption at ~470 nm covering the weak absorption band at ~700 nm. The similar phenomenon can also be found in other reports [18,24,25]. Evident red-shift of ultraviolet absorption band can be found in the figure. Compared with their parent glass, glass-ceramics show enhanced absorption at 470 nm band when were given 725 °C and 750 °C heat-treatment. No absorption peaks could be found when the sample was thermal

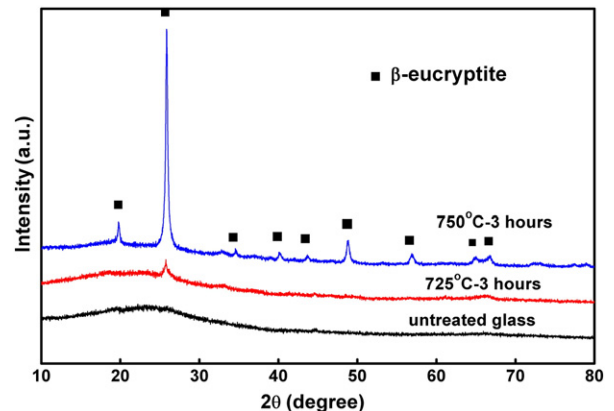


Fig. 2. X-ray diffraction patterns of Bi-doped original glass and LAS glass-ceramics heat-treated at various temperatures for 3 h.

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