The study on Er$^{3+}$ doped lithium bismuth aluminium borate glass for infrared medium applications

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Abstract. In this work, lithium bismuth aluminium borate glasses doped with different concentration of Er$_2$O$_3$ were prepared to investigate the physical, chemical group, optical and luminescence properties. All glasses were prepared by melt-quenching method. Glass density is in a range of $3.20 - 3.27$ g/cm$^3$ with no obvious relation to Er$_2$O$_3$ concentration. The FTIR spectra confirm the trigonal BO$_3$ and tetrahedra BO$_4$ borate unit appearing in glass network. This BO$_4$ unit and non-bridging oxygen tend to increase with increment of Er$_2$O$_3$ content. Er$^{3+}$ in glass absorb photon in visible light and near-infrared region, confirmed by the absorption spectra. The emission and excitation spectra perform the infrared emission of Er$^{3+}$ under 523 and 977 nm excitation. The strongest emission with 1536 nm belongs to 1.00 mol% Er$_2$O$_3$ doped glass that was excited by photon with 523 nm. This developed glass possesses the good potential for using as the source and medium material for infrared emitting and communication device.

Keywords: Borate glass; Erbium ion; infrared emission

1. Introduction

In presents, luminescence materials have an important role in human daily life, especially bulk luminescence materials. They have been the component in several optical devices for example laser, (light emitting diode; LED), radiation detector, display and imaging devices. The bulk luminescence materials in the laser device, called laser gain medium, are the single crystal material with luminescence center, such as lanthanide ion (Ln$^{3+}$). But the synthesis process of crystal materials is complicated and takes long-time duration. This results to an expensive price of both devices. There is the optional material which can be used as luminesce bulk similarly to crystal, but easier to prepare and cheaper. It is a glass material. Lithium borate glass doped with Ln$^{3+}$ is very interesting to develop for using as luminescence material. Lithium borate can form to be glass in a wide range of chemical stoichiometry. It owns the high strength of atomic bonding, high transparency, low temperature preparation, high thermal stability and good ion solubility for Ln$^{3+}$ [1-3]. However, borate glass possesses the high phonon energy [4-6] that can degrade the luminescence efficiency of Ln$^{3+}$ dopant. Therefore, lithium borate glass should be added with a heavy or high-density element such as bismuth.
[7-9] to dampen the phonon vibration and reduce the phonon energy in glass. Moreover, the concentration quenching effect is another phenomenon which decreases the emission intensity of glass with high Ln$^{3+}$ concentration. It was found that adding aluminium into Ln$^{3+}$ doped glass can reduce the effect of concentration quenching [10,11] because it extends the Ln – O distance and de-clusters of Ln$^{3+}$. For erbium ion (Er$^{3+}$), it is one of Ln$^{3+}$ group emitting the strong visible light (VIS) and near infrared (NIR) radiation. Then, it has been doped into various glasses for photonic applications especially, optical fiber for communication [12-14] and infrared laser device in LIDAR system [15-18]. LIDAR, light detection and ranging, is a remote inspection by imaging from infrared laser. It is very useful for explorer the topography, buildings or events from a distance. The strong infrared emission of Er$^{3+}$ is around 1.5 μm wavelength that is very suitable for C and L band of communication window [19] in optical fiber with low signal loss. As all mentions, it is very attractive to research in the Er$^{3+}$ doped lithium bismuth aluminium borate (LiBiAlB:Er) glass for infrared medium application.

In this work, LiBiAlB:Er glasses were prepared to study in the physical, chemical group, optical and luminescence properties. The influence of Er$_2$O$_3$ concentration on these properties were also investigated to evaluated the optimum chemical composition of glass for infrared medium application.

2. Experimental method
2.1 Glass preparation
The LiBiAlB:Er glasses with different concentration of Er$_2$O$_3$ as 0.05, 0.50, 1.00, 2.00, 3.00 and 4.00 mol% (referred as Er0.05, Er0.50, Er1.00, Er2.00, Er3.00 and Er4.00 sample, respectively) were prepared by the melt-quenching method. The high-purity chemicals consisting of lithium carbonate (Li$_2$CO$_3$), bismuth oxide (Bi$_2$O$_3$), aluminium oxide (Al$_2$O$_3$), boric acid (H$_3$BO$_3$) and erbium oxide (Er$_2$O$_3$) were mixed thoroughly under stoichiometry in a 25Li$_2$O – 10Bi$_2$O$_3$ – 15Al$_2$O$_3$ – (50-x)B$_2$O$_3$ – xEr$_2$O$_3$ system. All batch samples were put into the alumina crucible and taken into an electrical furnace for melting at 1,200 °C for 3 h. Then, melts were poured onto the pre-heated graphite mould for quenching. The quenched glasses were sequentially annealed at 500 for 3 h to reduce the thermal strain. The obtained glasses were cut in the rectangular shape and polished for good transparency.

2.2 Characterization
The density (ρ) of all LiBiAlB:Er glasses were measured under Archimedes’ principle using 4-digit microbalance (Sartorius, BSA224S-CW). The mass of glasses in air (m$_a$) and in water (m$_i$) were used to evaluate the density by equation,

$$\rho = \frac{m_a \rho_i}{(m_a - m_i)} \quad (1)$$

where $\rho_i$ is the water density at room temperature. The molar volume (V$_M$) of glasses were identified by relation,

$$V_M = \frac{M_p}{\rho} \quad (2)$$

where $M_p$ is the total molecular weight of chemical composition in glass [20]. Glasses refractive index (n) were measured by Abbe refractometer (ATAGO, NAR-1T SOLID). The chemical bonding vibration and structure unit in glasses network were monitored via Fourier transform infrared (FTIR) spectrometer (Shimadzu, IRPrestige-21). The absorption spectra of glasses were investigated using UV-VIS-NIR spectrometer (Shimadzu, UV-3600). The infrared emission and visible light excitation spectra of glasses were studied by the setup of PTI QM-300 (HORIBA CANADA) machine using Xe-flash lamp as a light source.

3. Results and discussions
3.1 Density, molar volume and refractive index
Table 1. The density and refractive index of LiBiAlB:Er glasses

| Glass | Density (g/cm$^3$) | Refractive index |
|-------|-------------------|-----------------|
| Er0.05 | 3.20 | 1.6540 |
| Er0.50 | 3.21 | 1.6542 |
| Er1.00 | 3.26 | 1.6536 |
| Er2.00 | 3.24 | 1.6539 |
| Er3.00 | 3.27 | 1.6545 |
| Er4.00 | 3.20 | 1.6542 |

Figure 1. The molar volume as a function of Er$_2$O$_3$ concentration for LiBiAlB:Er glasses

The density and refractive index of LiBiAlB:Er glasses don’t represent the trend of relation to the Er$_2$O$_3$ concentration as shown in table 1. These are possibly a result of the inhomogeneity or the very small bubble existence in glass samples. For glass molar volume, it increases with increment of Er$_2$O$_3$ concentration as shown figure 1. It can represent a glass modifier role of Er$^{3+}$ that destroys the bridging oxygen in LiBiAlB glass network. The addition of non-bridging oxygen (NBO) number creates the interstitial space in glass structure leading to the expansion of glass volume per mole.

3.2 FTIR

Figure 2. The FTIR spectra of LiBiAlB:Er glasses

The FTIR spectra of LiBiAlB:Er glasses shown in figure in 2 represent the obvious 3 vibrations and a weak vibration of chemical units in glass network. The absorbed infrared with 693 cm$^{-1}$ wavenumber was used to bending vibrate the B-O-B linkage of trigonal BO$_3$ borate groups [21,22].
The stretching vibrations of B-O bonds of tetrahedra BO₄ units and NBO vibrations in glass network own the infrared absorption at 971 cm⁻¹ wavenumber [23]. This vibration tends to have more strength with rising of Er₂O₃ concentration which corresponds to the increment of glass molar volume explained about the NBO number addition. The more strength of 971 cm⁻¹ vibration also exhibits the enhancement of BO₄ unit following Er₂O₃ content in glass. The vibration with 1,259 cm⁻¹ infrared represents the B-O stretching of BO₃ units in pentaborate, pyroborate, orthoborate groups [24] while the very small vibration around 3,750 cm⁻¹ belongs to O-H stretching of OH groups [25]. All FTIR results point out that the BO₃ and BO₄ borate groups are the main structure unit in LiBiAlB:Er glass network.

3.3. Absorption spectra

![Absorption spectra](image)

**Figure 3.** The absorption spectra of LiBiAlB:Er glasses in (a) visible light and (b) near-infrared region

Er³⁺ ions in LiBiAlB:Er glasses absorb the photons in VIS and NIR region as shown in figure 3 (a) and (b), respectively. The absorption of light with 450, 489, 523, 543, 653 nm and infrared with 803, 977, 1530 nm wavelength corresponds to the Er³⁺ transition from ¹I₁₃/₂ ground state to ⁴F₅/₂, ⁴F₇/₂, ²H₁₁/₂, ⁴S₃/₂, ⁴F₉/₂, ⁴I₁₃/₂, ⁴I₁₁/₂ and ⁴I₉/₂ excited state, respectively [26,27]. The strong absorption at 523 nm belongs to the hypersensitive ⁴I₁₅/₂ → ²H₁₁/₂ transition of Er³⁺ following the rules, |ΔS| = 0, |ΔL| ≤ 2 and |ΔJ| ≤ 2 [28]. The strength of this transition is very sensitive to the asymmetric level of ligands around Er³⁺. Glass absorption ability for these photons increase with addition of Er₂O₃ concentration.

3.4 The emission and excitation spectra

Since, LiBiAlB:Er glass performs the strongest absorption at 523 nm and the Er³⁺ ions are practically pumped by laser diode around 980 nm in applications, glasses were studied the emission spectra under 523 and 977 nm excitation as shown in figure 4 (a) and (b). The emission spectra under both excitation wavelengths perform the similar emission peak at 1536 nm wavelength corresponding to the ¹I₁₃/₂ → ¹I₁₅/₂ transition of Er³⁺ [29]. The emission strength under 523 nm excitation is higher than one under 977 nm excitation due to the stronger absorption. The emission intensity increases with increment of Er₂O₃ concentration since 0.05 mol% until 1.00 mol% (for 523 nm excitation) and until 2.00 mol% (for 977 nm excitation), over than that the intensity decreases because of the concentration quenching effect.
To confirm and check the excitation wavelengths for 1536 nm emission, the excitation spectra were monitored and shown in figure 5 (a). There are 8 excitation wavelengths those can make an emission at 1536 nm of LiBiAlB:Er glasses. The excitation wavelengths such as 302, 375, 450, 489, 523, 653, 803 and 977 nm assign to the $^4I_{15/2} \rightarrow ^2K_{13/2}$, $^4G_{11/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ transition, respectively [30]. Some excitation transitions are confirmed by the transitions from absorption spectra. The mechanism of Er$^{3+}$ transitions for emission and excitation spectra are shown in figure 5 (b). All excitations pumped Er$^{3+}$ from $^4I_{15/2}$ ground state to those excited states. After that, Er$^{3+}$ all decay down by non-radiative relaxation (NR) to the luminescence level, $^4I_{13/2}$. The $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition then occur resulting to the emission with 1536 nm wavelength. The strong emission at 1536 nm indicates that LiBiAlB:Er glasses with 1.0 and 2.0 mol% of Er$_2$O$_3$ possess the potential for infrared medium applications in laser device and optical fiber.
4. Conclusion

LiBiAlB:Er glasses were successfully prepared by melt-quenching technique. Glass density is in a range of 3.20 - 3.27 g/cm$^3$ with no obvious relation to Er$_2$O$_3$ concentration. The FTIR results represent the trigonal BO$_3$ and tetrahedra BO$_4$ borate groups are the main structure unit in glass network. The consistency between molar volume and FTIR results confirm the addition of non-bridging oxygen with increment of Er$_2$O$_3$ concentration. The developed glasses absorb some of visible light and infrared radiation. The absorbed visible light with 523 nm and absorbed infrared with 977 nm can excite the glasses to emit the 1536 nm infrared under $^4$I$^3/2 \rightarrow ^4$I$^1/2$ transition of Er$^{3+}$. The strongest emission with 1536 nm belongs to 1.00 mol% Er$_2$O$_3$ doped glass that was excited by photon with 523 nm. LiBiAlB:Er glass own the potential for using as an infrared medium in the infrared laser device and optical fiber.

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