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Structural and optical studies of Er^{3+}-doped alkali/alkaline oxide containing zinc boro-aluminosilicate glasses for 1.5 μm optical amplifier applications

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ABSTRACT

In the present work, we report on the optical spectral properties of Er^{3+}-doped zinc boro-aluminosilicate glasses with an addition of 10 mol % alkali/alkaline modifier regarding the fabrication of new optical materials for optical amplifiers. A total of 10 glasses were prepared using melt–quenching technique with the compositions $(40\text{-}x)B_2O_3 - 10SiO_2 - 10Al_2O_3 - 30ZnO - 10Li_2O - xEr_2O_3$ and $(40\text{-}x)B_2O_3 - 10SiO_2 - 10Al_2O_3 - 30ZnO - 10MgO - xEr_2O_3$ ($x = 0.1, 0.25, 0.5, 1.0,$ and 2.0 mol %). We confirm the amorphous-like structure for all the prepared glasses using X-ray diffraction (XRD). To study the functional groups of the glass composition after the melt–quenching process, Raman spectroscopy was used, and various structural units such as triangular and tetrahedral-borates (BO_3 and BO_4) have been identified. All the samples were characterized using optical absorption for UV, visible and NIR regions. Judd-Ofelt (JO) intensity parameters (Ω_λ, $\lambda = 2, 4$ and 6) were calculated from the optical absorption spectra of two glasses LiEr 2.0 and MgEr 2.0 (doped with 2 mol % of Er^{3+}). JO parameters for LiEr 2.0 and MgEr 2.0 glasses follow the trend as $\Omega_6 > \Omega_2 > \Omega_4$. Using Judd–Ofelt intensity parameters, we obtained radiative probability A (S^{-1}), branching ratios (β), radiative decay lifetimes τ_{rad} (μs) of emissions from excited Er^{+3} ions in LiEr 2.0 and MgEr 2.0 to all lower levels. Quantum efficiency (η) of $^4I_{13/2}$ and $^4S_{3/2}$ levels for LiEr 2.0 and MgEr 2.0 with and without $^4D_{7/2}$ level was calculated using the radiative decay lifetimes $\tau_{rad.}$ (μs) and measured lifetimes $\tau_{exp.}$ (μs). We measured the visible photoluminescence under 377 nm excitation for both LiEr and MgEr glass series within the region 390–580 nm. Three bands were observed in the visible region at 407 nm, 530 nm, and 554 nm, as a result of $^2H_{9/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. Decay lifetimes for emissions at 407 nm, 530 nm, and 554 nm were measured and they show single exponential behavior for all the LiEr and MgEr glass series. From the photoluminescence and radiative decay lifetimes (τ_{rad}), we calculated the full-width at half-maximum (FWHM), emission cross-section (σ_P^E) and bandwidth gain (FWHM × σ_P^E) parameters. Near-infrared photoluminescence under 980 nm excitation was measured for all the LiEr and MgEr glass series in the region 1420–1620 nm. NIR emissions show a broadband centered at ~1530 nm due to the transition of Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$. Decay lifetimes for NIR emission at ~1530 nm were measured and they show a quite exponential nature for all the LiEr and MgEr glass series. From the NIR emission spectra and decay lifetimes, we calculated the full-width at half-maximum (FWHM), the emission cross-section (σ_P^E) and the bandwidth gain (FWHM × σ_P^E) for the NIR emission and it shows FWHM of 50–70 nm for prepared glasses, emission cross-section of $(\sim 3.5) \times 10^{-20}$ cm^2, while bandwidth gain was $(\sim 25) \times 10^{-26}$ cm^3.

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1. Introduction

Over the past two decades, the rapid growth of advanced optical communication networks became the hotspot for researchers in order to cover the increasing of information's technology demand, which required to find and improve optical materials extensibility to carry on the high-speed capacity, broadband wavelength division multiplexing (WDM) and dense wavelength division multiplexing (DWDM) for optical amplifier usage where wide and flat gain spectrum became an important key in optical telecommunication [1,2]. Currently, Erbium-doped fiber amplifier (EDFA) based on silicate glasses show a narrow bandwidth about 40 nm only, which is considered as one of the limitations for the EDFA and rare-earth (RE) ions like Er^{3+} [3], Tm^{3+} [4], and Yb^{3+} [5]-doped glasses such as tellurite [6], germanate [7], silicate [8], phosphate [9], and borate [10] started to gain more attention for optical amplifier applications in the communication bands O-, S-, C-, L-, and U [11]. Moreover, RE-doped glasses show a variety of applications in optical amplifiers, lasers, optical switches, and nonlinear devices [12–14]. Generally, Er^{3+} ion exhibits mainly three emissions in ultraviolet, visible and infrared regions, with transitions $^4I_{11/2} \rightarrow {}^4I_{13/2}$ at 3000 nm, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ at 1500 nm, and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ at 550 nm, respectively, and the first transition can be used for medical purpose, while the second transition is applicable for third telecommunication window, and the last transition could be employed in display applications with green emission due to eye safe [15–18]. Recently, many researchers proposed different host glass compositions, considering the host effect on the structural, thermal and optical properties of Er^{3+}. Among many glass formers, B_2O_3 has attractive features between silicate, phosphate, tellurite and germanate as a result of promising properties like cheap cost, high transparency, low melting point, high thermal stability, different coordination numbers, a moderate solubility of RE ions, easy preparation in bulk form and low-cost preparation [19–21]. In fact, borate glasses possess large phonon energy with respect to other glass formers, while additional glass former can reduce the non-radiative transition probability substantially, in addition, the combination of B_2O_3 with other lower phonon energy glass former gives more probability to bridge the energy difference in RE dopant, such as the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I1_{3/2}$ [22]. The high refractive index and low dispersion of combining SiO_2 and B_2O_3 made borosilicate glasses widely used in optical applications [23]. ZnO used widely in borosilicate system due to the ability of break the bonds of B_2O_3 and forming BO_4 [24]. Generally, increasing the RE ion dopant concentration gives higher optical gain and photoluminescence, but in fact, with reaching beyond 2 mol % of RE concentration leads to the formation of a cluster in most of the glasses [25]. Regarding the above matter, it's necessary to employ the combination of Al_2O_3 and ZnO which is excellent to enhance the mechanical strength and chemical durability of glass. Al_2O_3 is remarkable material to improve the geometric distribution of RE-dopants to avoid clustering of the RE ions [26–28]. Boro-aluminosilicate glasses show interesting features such as easy obtainability, a wide variety of structural units, decrease the glass viscosity, delaying crystallization, and better wettability of glasses [29,30]. In our recent publication [31], we have reported the influence of alkali (Li^{+2}, Na^{+2}, K^{+2}) and alkaline (Mg^{+}, Ca^{+}, Sr^{+}, Ba^{+}) content on the structural, thermal and optical properties of zinc boro-aluminosilicate glasses. We synthesized fully transparent colorless glasses, and these glasses were explored with X-ray diffraction (XRD), X-ray dispersive analysis (EDAX), Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, Raman spectroscopy, Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC), and optical absorption. Based on the obtained results, it was difficult to evaluate the optimum host among the 7 glasses from our previous investigation. In the present work, we choose Li_2O from alkali and MgO from alkaline due to a relatively lower cutoff wavelength. We doped Er^{3+} with concentrations of 0.1, 0.25, 0.5, 1.0, and 2.0 mol % into these glasses and their visible and NIR optical features were studied.

2. Experimental

2.1. Synthesis

In order to synthesize two glass series with the molar composition of (40-x)B_2O_3 – 10SiO_2 – 10Al_2O_3 – 30ZnO – 10Li_2O – xEr_2O_3 and (40-x)B_2O_3 – 10SiO_2 – 10Al_2O_3 – 30ZnO – 10MgO – xEr_2O_3 (x = 0.1, 0.25, 0.5, 1.0, and 2.0 mol %), we used melt-quenching technique with similar experimental procedure reported in our previous study [31]. We synthesized the mentioned 10 glasses using the raw materials, which were purchased in high purity powders form, from Sigma-Aldrich: B_2O_3 (339075–99.98%), Al_2O_3 (11028-98%), ZnO (96479-99%), Li_2CO_3 (431559–99.99%), MgO (342793-99%), Fisher Scientific SiO_2 (437151000–99.99%), and Strem Chemicals Er_2O_3 (93-6810- 99.9%). The principal aim of this study is to figure out the optical properties change and effect of adding 10 mol % alkali (Li_2O) or alkaline (MgO) on Zinc-boro-aluminosilicate glasses doped with Er^{+3} ions. The glasses were nominated for convenience as “LiEr 0.1”, “LiEr 0.25”, “LiEr 0.5”, “LiEr 1.0”, “LiEr 2.0” and “MgEr 0.1”, “MgEr 0.25”, “MgEr 0.5”, “MgEr 1.0”, and “MgEr 2.0” as shown in Table 1. Chemicals involved in these compositions were calculated using stoichiometric ratio and weighed carefully in 20 g batch. We mixed the final powder of each composition using agate mortar, then melted in high purity alumina crucibles at 1400 °C for 1 h. The melts were subsequently poured onto a stainless steel plate and then quickly pressed with another steel plate. The obtained glass disks were clear, bubble free with average diameters varying within 3–4 cm. They possessed a thickness of ~0.6 cm and good optical transparency. Due to the rose color of Er_2O_3, we got 10 pink glasses. LiEr 0.1 and MgEr 0.1 show light pink color while they get darker with increasing the

Table 1
Nominal composition for (LiEr and MgEr) synthesized glasses (mol %).

Glass code	B_2O_3	SiO_2	Al_2O_3	ZnO	Li_2O	MgO	Er_2O_3
LiEr 0.1	39.9	10	10	30	10	–	0.1
LiEr 0.25	39.75	10	10	30	10	–	0.25
LiEr 0.5	39.5	10	10	30	10	–	0.5
LiEr 1.0	39	10	10	30	10	–	1.0
LiEr 2.0	38	10	10	30	10	–	2.0
MgEr 0.1	39.9	10	10	30	–	10	0.1
MgEr 0.25	39.75	10	10	30	–	10	0.25
MgEr 0.5	39.5	10	10	30	–	10	0.5
MgEr 1.0	39	10	10	30	–	10	1.0
MgEr 2.0	38	10	10	30	–	10	2.0