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Optical and erbium ion concentration correlation in lithium magnesium borate glass

M.H.A. Mhareb[a,b,*], S. Hashim[a], S.K. Ghoshal[a], Y.S.M. Alajerami[c], M.A. Saleh[d], M.M.A. Maqableh[a], N. Tamchek[e]

[a] Department of Physics, Faculty of Science, Universiti Teknnologi Malaysia, UTM, 81310 Skudai, Johor, Malaysia
[b] Radiation Protection Directorate, Energy and Minerals Regulatory Commission, 11183 Amma, Jordan
[c] Department of Medical Radiography, Al-Azhar University, Gaza Strip, Palestine
[d] Nuclear Engineering Programme, Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, UTM, 81310 Skudai, Johor, Malaysia
[e] Department of Physics, Faculty of Science, Universiti Putra Malaysia, UPM, 43400 Serdang, Selangor, Malaysia

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ABSTRACT

Tuning the optical response of lithium magnesium borate glass via controlled doping of rare earth ions is the key issue in photonic devices. Glasses with composition $30Li_2O–(60−x)B_2O_3–10MgO-xEr_2O_3$, where $0 \leq x \leq 1$ are prepared by conventional melt-quenching technique. The X-ray diffraction (XRD) pattern confirms the amorphous nature of all samples. Fourier transform infrared (FTIR) spectra reveal the presence of BO_3 and BO_4 local structure unit. The physical parameters, such as the direct and indirect optical energy band gap, oscillator strength, refractive index, ion concentration, Polaron radius, molar volume and inter-nuclear distance are calculated and analyzed. The room temperature UV–vis–IR spectra comprised of ten absorption bands centered at 1523, 973, 796, 650, 550, 522, 486, 447, 406, 373 nm corresponding to the transitions from the ground state to $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $(^4F_{5/2} + {}^4F_{3/2})$, $^2G(1)_{9/2}$, $^4G_{11/2}$ excited states, respectively. The peak evidenced at 522 nm is due to hypersensitive transition. The up-conversion spectra exhibits three emission peaks centered at 509, 547 and 656 nm. All the emission bands (green and red) at 0.5 mol% of Er^{3+} shows a significant enhancement in the intensity attributed to the energy transfer from Mg^{2+} to the Er^{3+} ion. Our results suggest that these glasses can be nominated for solid state lasers.

1. Introduction

In the past, borate glasses are commonly used in industrial and medical fields [1–3]. They possess several attractive features including ease of preparation, very good host for rare earth ions, higher relative stability and most importantly inexpensive [4,5]. However, the hygroscopic nature detrimental for device fabrication needs to be inhibited. Many efforts are dedicated to reduce and control this property. One way to modify the hygroscopic nature is through the addition of different modifiers (alkali and alkaline) that interrupt the glassy network and reduce the viscosity of the glass. The other alternative is the incorporation of dopants (rare earths, alkali and alkaline) as activators that enhances the emission properties of lithium borate glass (LMB) decisive for applications [6–8]. These improvements earn additional advantages such as elevated transparency and stability at higher temperatures and low melting point.

Lately, MgO is widely used as an excellent modifier. Wu et al. [9] studied the phase relation of LMB, Balaji Rao et al. [10] analyzed the role of titanium on optical and physical properties of LMB, Anishia et al. [11] and Ramasamy et al. [12] reported the thermo-luminescence from rare earth doped LMB. Alajerami et al. [2] analyzed in detail the optical properties of Dy^{3+} and Sm^{3+} doped with LMB. Varieties of optical properties of LMB can be used in the laser field provided the rare earth contents are optimized [13–19]. Rare earth (RE) elements are capable of converting infrared to visible light with improved efficiency via the process of up-conversion. Er^{3+} in particular are attractive in laser applications [20]. Despite extensive effort the mechanism of optical and rare earth concentration correlation in LMB glasses is far from being understood.

We report the impact of Er_2O_3 concentration on the optical, structural and physical properties of LMB glasses. Glasses are prepared with varying concentration of erbium and detail characterizations are made. The structural and optical properties are

* Corresponding author. Tel.: +60 1121739004.
E-mail address: mmhareb@hotmail.com (M.H.A. Mhareb).

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Table 1
Chemical compositions and glass codes.

Glass no.	Composition mol			
	Li_2O (%)	B_2O_3 (%)	MgO (%)	Er_2O_3 (%)
S0	30	60.0	10	0.0
S1	30	59.7	10	0.3
S2	30	59.5	10	0.5
S3	30	59.3	10	0.7
S4	30	59.0	10	1.0

considerably improved by controlling the erbium ion concentration in the glass host. The noteworthy enrichment in the absorption and emission intensities is analyzed to compare and understand.

2. Experimental

The Er^{3+} ions doped LMB glasses are prepared by following conventional melt quenching technique. The chemicals used are boron oxide (B_2O_3), lithium oxide (Li_2O), magnesium oxide (MgO) and erbium oxide (Er_2O_3) of 99.99% analytical grade purity. These materials are weighted and mixed for an hour to achieve a homogeneous mixture and then placed in an alumina crucible inside the electric furnace for 90 min at 1100 °C. The molten mixture stirred frequently to ensure homogeneity before pouring on a steel plate at 350 °C for three hours to avoid mechanical stress. Finally, the temperature is gradually reduced at the rate of 10 °C/min. This chemical compositions and glass codes are summarized in Table 1.

The amorphous nature of the samples is examined by PANalytical XRD diffractometer model PW 3040 MPD attached with XPert Data Viewer using Cu$K\alpha$ radiations (λ = 1.54 Å) at 40 kV and 30 mA, with 2θ varying from 10° to 90°. The Fourier transform infrared (FTIR) with Attenuated Total Reflectance (ATR) measurement is used to investigate the functional group within the range of 2000–400 cm^{-1}. The thermal parameters are recorded via differential thermal analyzer (DTA) by Perkin Elmer equipped with Cu target and nickel filter. The room temperature UV–vis measurement is carried out using Shimadzu 3101 in the range of 200–2000 nm. Perkin Elmer LS55 Luminescence Spectrophotometer is used for emission measurements attached with a xenon lamp of Monk–Gillieson type in the range 200–800 nm.

The optical band gap (E_g) is calculated from the absorption edge using Davis and Mott relation [21]:

$$h\nu\alpha(\omega) = A\left(h\nu - E_g\right)^n \quad (1)$$

where $\alpha(\omega)$ is the absorption coefficient, ω angular frequency and A is a constant. The refractive index (n) is calculated following [22]:

$$\frac{\left(n^2-1\right)}{\left(n^2+2\right)} = 1 - \sqrt{\frac{E_g}{20}} \quad (2)$$

The density (ρ) is measured using Archimedes' principle with toluene (99.99% purity) as immersion liquid.

$$\rho = \frac{a}{(a-b)} \times 0.865\ \mathrm{g/cm^3} \quad (3)$$

where α represent the weight of the glass in the air, b represents the weight the glass in the toluene of room temperature density 0.865 g/cm^3. The molar volume (V_m) yield,

$$V_m = \frac{M}{\rho} \quad (4)$$

where M is the molecular weight of glass samples.

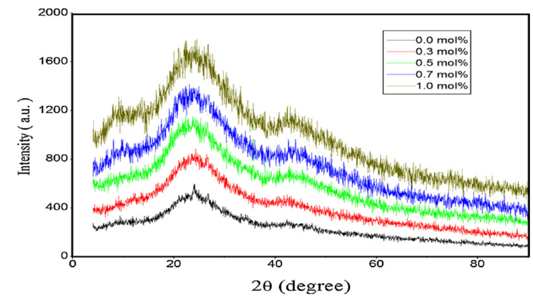

Fig. 1. The XRD patterns of all samples.

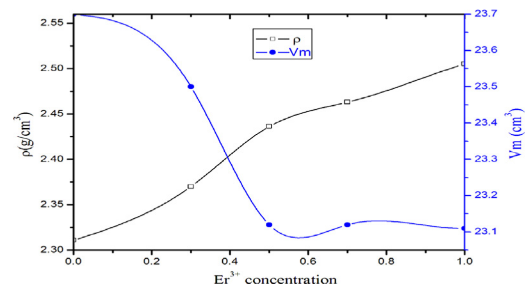

Fig. 2. The Er_2O_3 concentration dependent density and molar volume.

The average boron–boron separation $\langle d_{B-B}\rangle$ is determined using equations [23].

$$\left\langle d_{B-B}\right\rangle = \left[\frac{V_m^B}{N_A}\right]^{1/3} \quad (5)$$

$$V_m^B = \frac{V_m}{2(1-X_B)} \quad (6)$$

where, N_A is the Avogadro number, V_m^B the volume of boron atoms per mole and X_B is the mole fraction. Ion concentration for Er^{3+} inside glass is calculated following the expression,

$$N = \frac{\text{mol\% of doped} \times \rho \times N_A}{\text{Average molecular weight of glass}}\left(\mathrm{ions/cm^3}\right) \quad (7)$$

The Polaron radius of Er^{3+} yield,

$$r_p\left(\text{Å}\right) = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{1/3} \quad (8)$$

Inter-nuclear distance of Er^{3+} given by,

$$r_i\left(\text{Å}\right) = \left(\frac{1}{N}\right)^{1/3} \quad (9)$$

The field strength of Er^{3+} yields,

$$F(\mathrm{cm^2}) = \left[\frac{Z}{r_p^2}\right] \quad (10)$$

Oscillator strengths are calculated from the absorption peak following [24]:

$$f_{\exp} = 4.32 \times 10^{-9} \int \Delta\nu \quad (11)$$

where $\Delta\nu$ (cm^{-1}) is the width of absorption band.

3. Results and discussion

The XRD patterns of all glass samples as shown in Fig. 1 in the absence of any sharp peak confirm the amorphous nature. Calculated physical properties for LMB samples at different concentration of Er_2O_3 are summarized in Table 2. The Er_2O_3 concentration