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Luminescence features of dysprosium and phosphorus oxide co-doped lithium magnesium borate glass

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ABSTRACT

Lithium magnesium borate (LMB) glass system co-doped with the oxides of dysprosium (Dy_2O_3) and phosphorus (P_2O_5) were synthesized using melt-quenching method. Prepared samples were characterized using various techniques to determine the effects of co-dopants concentration variation on their thermoluminescence (TL) and photoluminescence (PL) properties. TL glow curves of LMB:0.5Dy sample revealed a single prominent peak at T_m=190 °C, where TL intensity was enhanced by a factor of 2.5 with the increase of P_2O_5 concentration up to 1 mol%. This enhancement was accompanied by a shift in T_m towards higher temperature. Good linearity in the range of 1–100 Gy with linear correlation coefficient of 0.998 was achieved. PL spectra displayed two significant peaks centred at 481 nm and 573 nm. These attractive luminescence features of the proposed glass system may be useful for the development of radiation dosimetry.

1. Introduction

Luminescence is the light emission process from a material upon excitation and such light emitting materials are called phosphors. According to the kind of radiation used to excite the emission, different names are given to luminescence phenomena such as Thermoluminescence (the process where certain crystalline materials emit lights when heated) and Photoluminescence (electrons moved to energetically higher levels through absorption of photons).

Borates are an attractive dosimeter host due to their tissue equivalence, good linearity, high sensitivity to external dose, low cost, and easy preparation (Prokic, 2007; El-Adawy et al., 2010; Elkholy, 2010; Mhareb et al., 2015). Conversely, the hygroscopic nature of borate glass negatively affects its performance. Intensive researches have been dedicated to improving the stability and enhancing the sensitivity by adding different types of metals (alkali/alkaline earth) as modifiers and transition metals and rare earth(s) as dopants (co-dopants) (Liu et al., 2007; Jiang et al., 2010; Alajerami et al., 2012a, 2012b; Aboud et al., 2012). The addition of a second modifier reagent improved the intensity, created disruption in the lattice, opened the network structure, weakened the bond strength, and lowered the viscosity of glass (Jiang et al., 2010; Ayta et al., 2011; Alajerami et al., 2013; Hashim et al., 2014). The co-dopant techniques were used to overcome the quenching state and to enhance the sensitivity for dopant (Elkholy, 2010; Jiang et al., 2010; Alajerami et al., 2013; Hashim et al., 2014; Mhareb et al., 2015; Hashim et al., 2015).

In the current study, lithium carbonate (Li_2CO_3) and magnesium oxide (MgO) were used as the first and second modifier, respectively. Lithium was added to reduce the hygroscopic properties and improve the strength of the host (borate). The addition of magnesium oxide increases the strength of the glass and enhances the electron emission. Dysprosium oxide was utilized as a dopant. Dysprosium oxide, being one of the most efficient rare earths, is exploited to improve the TL properties of borate glasses (Anishia et al., 2011). Phosphorus oxide (P_2O_5) was involved as a co-dopant to overcome the quenching state. In this view, we scrutinize luminescence efficacy of lithium magnesium borate (LMB) glass doped with Dy_2O_3 and co-doped with different concentration of P_2O_5.

2. Materials and methods

The proposed glass compositions were prepared using the conventional melt-quenching technique. Boron oxide (B_2O_3), lithium carbonate (Li_2CO_3), magnesium oxide (MgO), dysprosium oxide (Dy_2O_3)

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and phosphorus oxide (P_2O_5) with 99% analytical grade purity (Sigma Aldrich Company) were used to prepare the glass samples. The above-mentioned materials are weighted and the powders were well mixed for half hour in an alumina crucible before being melted in an electric furnace at 1200 °C for 60 min. The molten mixture was stirred frequently to ensure the homogeneity before being poured on a pre-heated steel mould at 350 °C (Alajerami et al., 2012a, 2012b; Mhareb et al., 2014). The prepared glass was annealed for three hours to avoid any mechanical stress that cause embrittlement. Finally, the temperature was gradually reduced with a cooling rate of 10 °C min^{-1}. Table 1 enlists the proposed compositions ratios and the samples code.

The amorphous nature of the prepared samples was confirmed using X-ray diffraction (XRD) measurement. A PANalytical XRD diffractometer model PW 3040 MPD attached to an Xpert Data Viewer is used with λ=1.54 Å operated at 40 kV and 30 mA, where 2θ was varied from 10° to 90°. The structural properties (bonding vibrations) were determined via Fourier Transform Infrared (FTIR) measurement. The PL spectra were recorded at room temperature using a Perkin Elmer LS55 spectrofluorometer consisting of a 150 W Xenon lamp, monochromator and detector.

The TL properties are determined by exposing the synthesized samples to ^{60}Co source at a dose rate of 15.31 Gy min^{-1}. The reading process was conducted in the Malaysian Nuclear Agency using a Harshaw TLD reader (4500) with a linear heating rate of 5 °C s^{-1}. The dosimetric glow peaks were monitored within the range of 50–400 °C. TLD reader calibration was performed by the Read Calibration Factor (RCF) of a standard dosimeter (TLD-100) to estimate the sensitivity of the proposed dosimeters. Readings were acquired after 24 h of irradiation to eliminate the spurious TL signals. Samples were stored in a dark place at ambient temperature to avoid any influence of background light. Three samples were used to obtain each experimental data point with improved statistics.

3. Results and discussion

The typical XRD patterns as shown in Fig. 1 in the absence of any sharp peaks confirm the amorphous nature of prepared samples at different concentrations of P_2O_5.

Fig. 2 shows the FTIR spectra for the LMB: Dy,P glass series. The occurrence of prominent bands around 700 cm^{-1}, 800–1200 cm^{-1}, 920 cm^{-1} and 1200–1600 cm^{-1} are allocated to the vibration of B–O–B bonds, B–O stretching of tetrahedral BO_4 units, the asymmetric vibrations of P–O–P of oxygen bridging in phosphate chains, and the asymmetric stretching relaxation of B–O in trigonal BO_3 units, respectively.

Table 2 summarizes the FTIR band assignments. The bending vibration of B–O–B reveals peaks in the range of 685–700 cm^{-1}, a BO_4 band appears at 1037–1040 cm^{-1}, the asymmetric P–O–P vibrations reveal peaks around 920 cm^{-1} and the asymmetric stretching vibration of BO_3 is assigned in the range of 1350–1356 cm^{-1}. With increasing P_2O_5 and decreasing B_2O_3 content, the high frequency BO_4 bands corresponding to stretching vibrations became broader, less distinct and overlapped between the boron and phosphorus bands (Tho, et al., 2012).

The intensity of the BO_3 band increases with increase of the P_2O_5 content, which indicates an increase of the vibration. In addition, the intensity of the BO_4 band decreases with increased P_2O_5 content, which indicates an overlap of the BO_4 with P–O–P. The effect of P_2O_5 is shown in Fig. 2 and Table 2. The phosphorus band isn't available in S2. Although the phosphorus band is clear in S5, S6, S7 and S8 that indicate the P_2O_5 has special band because it is one of glass former.

Fig. 3 shows the glow curve of LMB glass co-doped at different concentrations of Dy_2O_3 and P_2O_5 irradiated with 3 Gy of ^{60}Co source. A simple glow curve with single prominent peak is evidenced at 190 °C, where the optimal intensity was obtained at 0.5 mol% (S2 sample). The effect of co-dopant P_2O_5 concentration variation on the glow curve was also shown in the same figure. Almost two and half-fold enhancement in the TL peak intensity accompanied by a shift towards higher temperatures (~220 °C) is observed at 1 mol% of P_2O_5 (sample S6). This observation is ascribed to the ability of P ions to create deeper traps in the host matrix. The TL mechanisms in the proposed dosimeters are explained according to Porwal et al. (2005) and Annalakshmi et al. (2014) and reported elsewhere (Mhareb et al., 2015). They identified the defect centers such as borate radicals $(BO_3)^{2-}$ and oxygen vacancies (O_V^-) which are formed during gamma irradiation and established a mechanism for the TL process. Following their explanations, the current TL glow curves can be interpreted via the following processes:

(i) irradiation yields

$$\text{LMB: } Dy^{3+} \rightarrow (BO_3)^{2-}, (O_V^-)$$

and

(ii) heating causes

$$(BO_3)^{2-} \rightarrow (BO_3)^{3-} + h,$$

$$[O_v]^- + h \rightarrow [O_v]^* \rightarrow Dy^{3+*} \rightarrow Dy^{3+} + h\upsilon.$$

As mentioned, for Dy^{3+} doped LMB, phosphors $(BO_3)^{2-}$ and (O_V^-) radicals are formed upon gamma irradiation. Upon heating, the borate radical releases the hole (h) which in turn recombines with the electron trapped at the oxygen vacancy, resulting in the release of recombination energy. Then the energy released from the Dy^{3+} recombination essentially excites the Dy ions and originates the characteristic light emission. The addition of P_2O_5 as co-dopant acts as an activator for dysprosium oxide sensitization. Two explanations have been put forward in the quest to understand the behavior of P_2O_5 as a co-dopant with Dy_2O_3. Firstly, the energy transferred from the Dy^{3+} ions causes the phosphor to be in an excited state, upon which the energy may be transferred from the P ions to the Dy^{3+} ions, thus bringing it to the ground state. Secondly, the continuous increase of phosphorus creates a reverse effect on the intensity of the peaks, which results from the effect of the saturation quenching (Hashim et al., 2014; Mhareb et al., 2015).

Fig. 4 depicts the ^{60}Co dose (1–100 Gy) dependent TL intensity response of LMB:Dy and LMB: Dy,P glasses. Presence of small amount of P_2O_5 impurity (1 mol%) enhanced the TL intensity by two and half times higher than the Dy_2O_3 activation. These observation manifested the profound role of the co-dopants in LMB:Dy glass system. In addition, excellent dose linearity with a good linear correlation coefficient equal to 0.998 was obtained.

The linear property of the dose response is further verified by theoretically calculating the linearity index *f(D)* (Furetta and Weng, 1998), where *f(D)* is a measure of deviation from linearity given by Eq. (1):

Table 1
Compositions of prepared glass samples.

Glass code	Composition (mol%)				
	Li_2O	B_2O_3	MgO	Dy_2O_3	P_2O_5
S1	20%	69.7%	10%	0.3%	–
S2	20%	69.5%	10%	0.5%	–
S3	20%	69.3%	10%	0.7%	–
S4	20%	69.0%	10%	1.0%	–
S5	20%	69.0%	10%	0.5%	0.5%
S6	20%	68.5%	10%	0.5%	1.0%
S7	20%	68.0%	10%	0.5%	1.5%
S8	20%	67.5%	10%	0.5%	2.0%