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Synthesis and characterisation of dysprosium-doped borate glasses for use in radiation dosimeters

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Abstract:

This paper reports on the synthesis and characterisation of Dy_2O_3-doped magnesium borate (MB) glasses containing different modifiers, lithium, calcium, and sodium oxides. Glasses composed of $(70\text{-}z)B_2O_3\text{-}20Li_2O$; CaO; $Na_2O\text{-}10MgO\text{-}zDy_2O_3$ (where $0.05 \leq z \leq 0.7$ mol%) were prepared using the melt-quenching method. X-ray diffraction (XRD) pattern of the as-quenched samples verified their amorphous character. Differential thermal analysis (DTA) confirmed excellent glass-forming ability and thermal stability in the range of 0.60-0.67 and 0.18-0.82, respectively. The energy dispersive X-ray (EDX) spectra verified the precise elemental traces in the studied glasses. Furthermore, MB glasses doped with 0.1 mol% of Dy_2O_3 and modified with lithium oxide were found to have the best soft tissue equivalence ($Z_{eff} \approx 8.13$). In short, the proposed MB glass system doped with dysprosium ions (Dy^{3+}) was established as effective for accurate radiation detection in emergency situations.

Keywords: **dysprosium, MB glass, melt-quenching, radiation detection.**

Classification number: **2.1**

Introduction

The scientific interest in glassy systems began a few decades ago with the pioneering works of Anderson and Mott on disordered solids as examples of non-crystalline solids [1]. Due to the notable physical and optical properties of borate compounds, new uses of these compounds have gradually emerged [2-4]. Oxide glasses have gained attention due to their structural features [5-7]. The borates containing the isolated planer $[BO_3]^{3-}$ group in their structure have been shown to be good birefringent materials [8]. The distinguishing feature of the melt-quenching technique used to produce amorphous material is that the amorphous solid can be formed by continuous hardening (increase in viscosity) of the melt [9]. The existence of alkaline metal ions, which act as modifiers in glass systems, build up vacancies and create ionic bonds instead of covalent bonds with the oxygen atoms. This gives the glassy chemical a well-defined shape. The fact that alkaline metal ions have the properties of being small and mobile means these materials are commonly used in thermoluminescent (TL) glass systems. This is because the occurrence of these materials in glass systems introduces a degree of electrical conductivity, particularly in a molten state or at a high temperature. Moreover, the addition of alkaline metal ions creates non-bridging oxygen, the concentration of which increases linearly as the alkaline content increases. Lithium, sodium and calcium are all alkali earth metals and are commonly used in glass systems due to their resistance to corrosion and easier processing. Rare earth elements such as samarium (Sm), europium (Eu), terbium (Tb), dysprosium (Dy) and thulium (Tm) are generally introduced as the doping elements or doping salts, especially in TL dosimetry applications. These lanthanide elements can modify the structure of the glass, as well as its electrical, optical and TL properties. Environmental and personnel monitoring for radiation exposure requires a sensitive TL detector; it should

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be cost effective, have good reproducibility, high sensitivity and tissue equivalence. All of these criteria can be met with the addition of Dy ions to the glass system.

Questions remain regarding the structure of substances, and solving them will facilitate accurate predetermination of the properties of synthetic materials under development. The properties of the glass samples properties are affected by the composition and the various modifying agents of the materials. The very few TL materials (TL dosimeters) appear to be the most attractive due to the fact that they are amorphous materials [10-13]. The most common approach for producing amorphous solid materials (notably, oxide glasses and organic polymers) is to cool the molten form of the material using a melt-quenching technique [14, 15]. Borate glass is relatively chemically stable and does not present any serious problems for doping with impurities such as rare earth, copper, and manganese ions. This study may be useful for future researchers to understand the effects of lithium, calcium, and sodium as modifiers in borate glasses with the presence of dysprosium. The present work attempts to provide new fundamental knowledge about various properties of the proposed glass composition for new TL glass dosimeter applications. In this work, Dy^{3+}-doped magnesium borate (MB) glasses with three different modifiers (Na_2O, Li_2O, and CaO) were prepared using a melt-quenching method. The physical properties of the as-quenched samples, including their amorphous state and their glass-forming abilities, were determined. Generally, pure borate glass has certain shortcomings for radiation dosimeter applications due to its highly hygroscopic nature and weak TL glow peak at low temperatures. However, the addition of alkali oxides into borate can overcome these drawbacks as the inclusion of a modifier such as Ca can ensure low hygroscopicity and high chemical stability. The amorphous nature of all the as-quenched samples was verified by X-ray diffraction (XRD) analysis. Differential thermal analysis showed that all the studied glasses obey Kauzmann criterion with excellent *Trg* values and good glass-forming ability. Elemental analyses of glasses were performed using energy dispersive x-ray (EDX) spectroscopy, whereby all the data were used to calculate the effective atomic number (*Zeff*). The obtained results on the proposed glasses may contribute to the study of the TL properties for radiation dosimetry in general and personnel monitoring in particular.

Materials and methods

A brief description of the glass preparation method is presented. A series of Dy_2O_3-doped LMB glasses of nominal composition $(70\text{-}z)B_2O_3\text{-}20Li_2O$; CaO; $Na_2O\text{-}10MgO\text{-}zDy_2O_3$ (where $0.05 \leq z \leq 0.7$ mol%) were prepared using the melt-quenching method. Analytical grade chemical reagents (in powder form and 99.9% pure) of boron oxide (B_2O_3), magnesium oxide (MgO), lithium oxide (Li_2O), calcium oxide (CaO), sodium oxide (Na_2O) and dysprosium (III) oxide (Dy_2O_3) were used as glass constituents. These chemicals were supplied by Acros Organic and QReC (reagent grade) and were 99.9% pure. Powdered constituents for each batch of 10 g were mixed thoroughly using a milling machine to obtain a homogenous mixture. For each sample, the mixture was placed in a porcelain crucible before being melted inside an electronic furnace (Nabertherm GmbH:SN 299205) at 1100^0C for 1 hour and was stirred frequently to ensure complete homogeneity. The resultant melt was annealed at 350^0C for 4 hours and allowed to cool gradually (at a rate of 10^0C min^{-1}) to room temperature. Finally, the frozen solid was cut into the preferred size and polished for additional spectroscopic analyses. Six samples were prepared and are listed in Table 1. In the case of CMB doped with 0.50 Dy, this concentration was chosen for its optimum concentration at 0.5 mol%, revealed a TL glow curve at a single broad peak, and its *Tm* was around 211^0C and it meets the requirements of the ideal TL dosimeter when exposed to such radiation (Cobalt-60 gamma ray). The sample exhibited a stable state when analysed with 0.5 mol% of Dy concentration.

Table 1. Nominal composition of the studied glasses.

Glass Code	Composition (mol%)					
	B_2O_3	MgO	Li_2O	CaO	Na_2O	Dy_2O_3
LMBDy0	70.00	10.00	20.00	-	-	0.00
LMBDy0.10	69.90	10.00	20.00	-	-	0.10
CMBDy0	70.00	10.00	-	20.00	-	0.00
CMBDy0.50	69.50	10.00	-	20.00	-	0.50
NMBDy0	70.00	10.00	-	-	20.00	0.00
NMBDy0.10	69.90	10.00	-	-	20.00	0.10

The XRD analysis was performed using micro-sized powdered glasses in order to check the amorphous phase of the studied samples. The samples were scanned by mean of the XRD method using an X-ray diffractometer (Siemens Diffractometer D5000 model) with CuK_α radiation operating at 40 kV and 30 mA in Bragg-Brentano geometry at room temperature. The diffraction patterns were measured in steps of 0.05 degree (^{0}) for 1 s counting time per step, with 2θ ranging from 10^0 to 90^0. The inbuilt software in

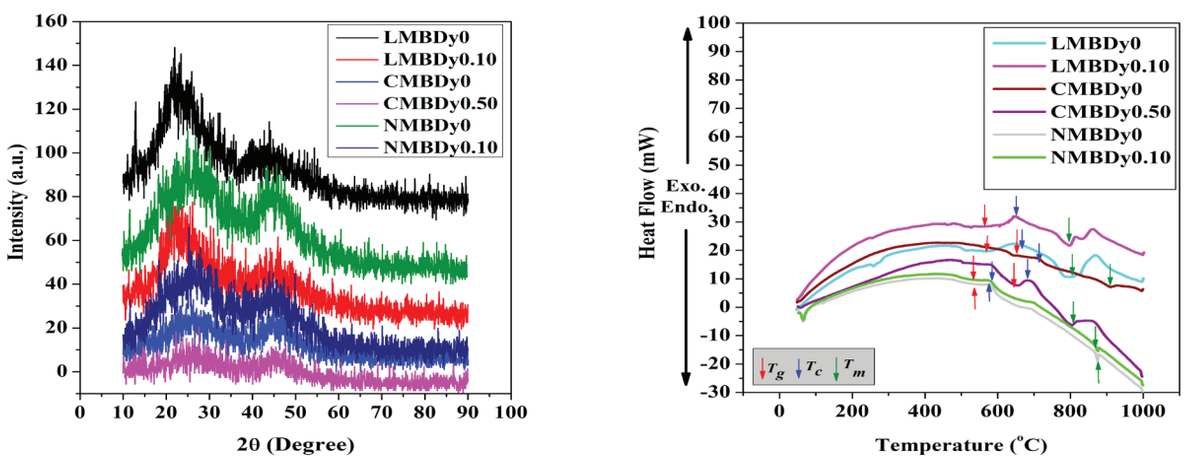
the diffractogram provided information on atomic pair correlations and bond lengths of the MgO, Li_2O, CaO, Na_2O, B_2O_3 or Dy_2O_3 compounds used as glass constituents.

Supplementary differential thermal analysis (DTA) was used to analyse the heat flows in the glass system as a function of temperature. Thermal behaviour, including the glass transition temperature (T_g), crystallisation temperature (T_c) and melting temperature (T_m), was measured using TG-DTA (Perkin Elmer Pyris Diamond Thermogravimetry - Differential Thermal Analyzer model). This was also used to evaluate glass-forming ability (T_{rg}) and thermal stability in terms of the Hruby parameter (H_R). The TG-DTA was conducting on fine and micro-sized powdered glasses at a temperature range of 50-1000^{0}C (accuracy ±0.1^{0}C) with a heating rate of 10^{0}C min^{-1}. The glass-forming ability or thermal stability range was determined from the difference between T_c and T_g. The powder (5 mg) was ground from the bulk glass sample and added to the pan. The sample weight was determined to ensure that the total weight of both sample and pan was within 0.1 mg. The low heating rate was chosen to increase the resolution of the system.

The composition of elements present in the prepared glass samples was determined using EDX analysis, which enabled the effective atomic number (Z_{eff}) of the studied samples to be determined. This was achieved using a ZEISS Supra 35 VP scanning electron microscope (SEM) coupled with EDX spectroscopy. Samples were coated with gold using a BIO-RAD Polaron E5400 SEM sputter coating system to ensure good electrical connectivity with the sample holder. The data recorded consisted of spectra presenting peaks corresponding to the elements making up the composition of the sample being examined.

Results and discussion

Figure 1A illustrates the typical XRD patterns of the six studied samples, which consisted of two amorphous halos (broad hump) without any sharp crystalline peaks. These experimental patterns, useful for identification, were obtained using diffractometer methods. The 1976 Interim Report of the National Bureau of Standards was referred to in order to verify the overall results [16]. The magnitude of scattering in a given direction (θ or 2θ) is described in units relative to the scattering from a single electron. The intensity is the quantity measured by the diffraction device and is given as the magnitude of the amplitude squared. The scattering magnitudes are expressed in electron scattering units, and diffraction angles refer to CuKα X-rays [17, 18]. These broad humps (at 2θ values around 20-30^0 and 40-50^0) representing the atomic pair correlations of the bond distances of the constituents MgO, Li_2O, CaO, Na_2O, B_2O_3 or Dy_2O_3 confirmed the amorphous nature of the as-quenched sample. However, the intensity of the studied samples gradually decreases with increasing values of 2θ. The scattering factors decrease with increasing 2θ because of destructive interference within the atoms and due to thermal effect. As shown in Fig. 1A, these samples reveal no discrete peaks and a lack of periodicity that is typical for short-range ordered materials, such as glass or liquid that reaches the glassy phase. It is also observed that no sharp peaks were obtained from the XRD analysis. In this case, the broad peaks cannot belong to the glassy phase. The local structure of glass has no long-range order and, therefore, generates only broad features in the diffraction pattern. Therefore, all the glass systems reveal that the samples are glass in nature.



(A) (B)

Fig. 1. XRD patterns of LMBDy0, LMBDy0.10, CMBDy0, CMBDy0.50, NMBDy0, and NMBDy0.10 (A); DTA traces of LMBDy0, LMBDy0.10, CMBDy0, CMBDy0.50, NMBDy0, and NMBDy0.10 (B).

Figure 1B shows the DTA curves of LMBDy0, LMBDy0.10, CMBDy0, CMBDy0.50, NMBDy0, and NMBDy0.10 samples with their respective endothermic peaks of T_g at 519.25, 548.87, 626.01, 509.91, 517.01, and 529.68^{0}C, respectively. The exothermic peak of T_c for LMBDy0 and LMBDy0.10 samples appeared at 644.18^{0}C and 670.30^{0}C. Whereas, the exothermic peak of T_c for CMBDy0, CMBDy0.50, NMBDy0, and NMBDy0.10 samples appeared at 744.99, 638.59, 578.99, and 582.75^{0}C, respectively. Meanwhile, the endothermic peak of T_m for the samples occurred at 797.002^{0}C (LMBDy0), 823.12^{0}C (LMBDy0.10), 934.99^{0}C (CMBDy0), 803.77^{0}C (CMBDy0.50), 860.72^{0}C (NMBDy0), and 874.71^{0}C (NMBDy0.10).

The values of T_g, T_c and T_m were found to be sensitive to concentrations of Dy^{3+} ions, as shown in Table 2. Each DTA trace was recorded three times to obtain the average peak value. The estimated values of T_{rg} were found to obey the Kauzmann assumption ($0.5 \leq T_{rg} \leq 0.66$), indicating good glass-forming ability or a lower devitrification tendency [19]. According to Hruby's assumption, a glass system is said to be thermally stable if $H_R \sim 0.5$ and unstable if $H_R \leq 0.1$ [20]. The large values of H_R and T_{rg} obtained clearly indicate excellent thermal stability and glass-forming ability, respectively (Table 2). However, Table 2 shows that the NMBDy0 and NMBDy0.10 samples were found not to meet the glass thermal stability requirement and, therefore, cannot be considered good glass formers. Hence, the glass samples require higher cooling rates.

Table 2. DTA thermal analysis of the studied glasses.

Glass code	T_{rg} value	H_R value
LMBDy0	0.65	0.82
LMBDy0.10	0.67	0.79
CMBDy0	0.67	0.62
CMBDy0.50	0.63	0.78
NMBDy0	0.60	0.22
NMBDy0.10	0.61	0.18

EDX emissions of the LMBDy0, LMBDy0.10, CMBDy0, CMBDy0.50, NMBDy0, and NMBDy0.10 samples are shown in Fig. 2 (A, B, C, D, E, F). The peak height of the spectra represents the abundance of each element in the glass samples, with the x-axis representing the X-ray energy (keV). In this case, lithium (Li) was not easy to detect (Fig. 2A and 2B), due to the very low energy of characteristic radiation. The data from the EDX analysis were used to calculate the effective atomic number (Z_{eff}). The value of the experimental fractional weights, W_{iE} (from the EDX analysis), is compared with the nominal fractional weights, W_{iT}, for all the glass samples (Table 3). All these values were compared to calculate the effective atomic number (Z_{eff}), as shown in Table 4.

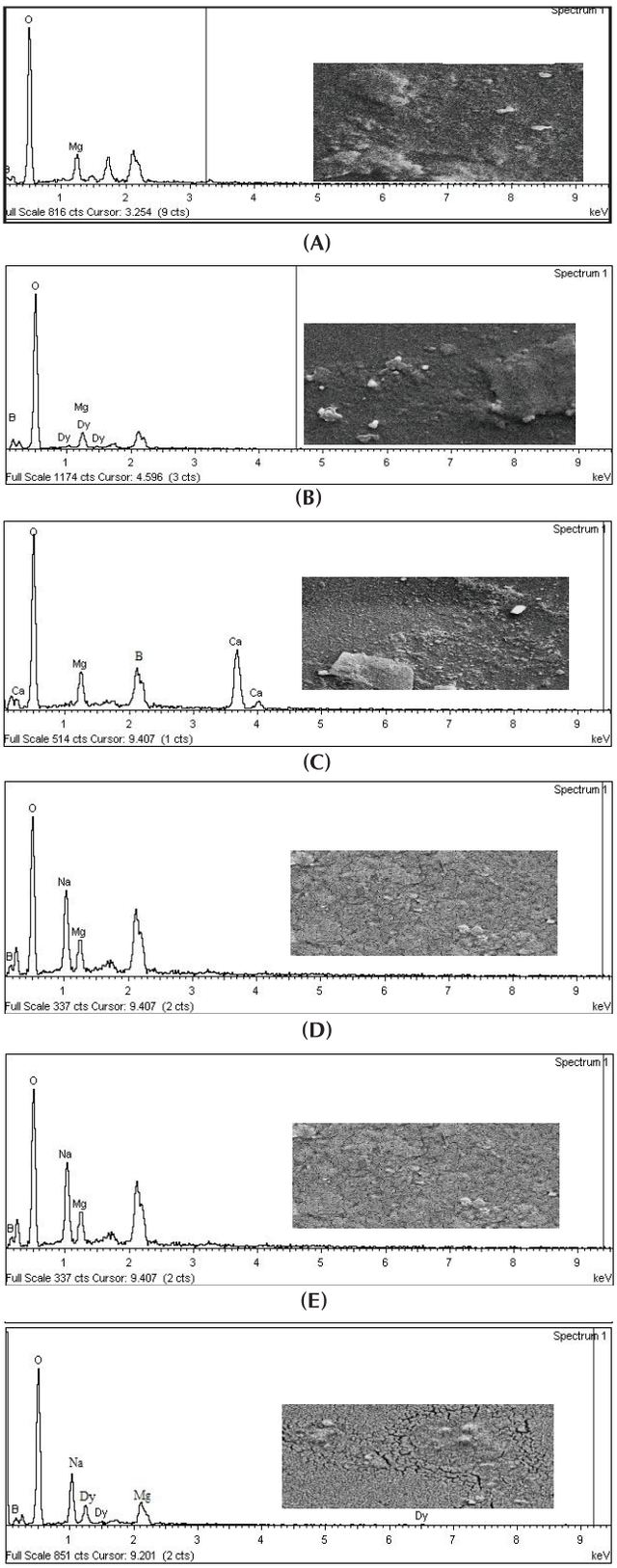


Fig. 2. EDX spectrum of LMBDy0 (A), LMBDy0.10 (B), CMBDy0 (C), CMBDy0.50 (D), NMBDy0 (E), and NMBDy0.10 (F) glass.

Table 3. Nominal and experimental value of fractional weights of each element of the studied samples.

Element	Nominal, W_{iT}	Experimental, W_{iE}	Nominal, W_{iT}	Experimental, W_{iE}
	LMBDy0		***LMBDy0.10***	
Mg	0.0603	0.0260	0.0603	0.0110
Li	0.0929	0.1667	0.0929	0.1667
B	0.2174	0.1955	0.2171	0.2512
O	0.6293	0.6118	0.6288	0.5703
Dy	-	-	0.0008	0.0008
	CMBDy0		***CMBDy0.50***	
Mg	0.0603	0.0217	0.0603	0.0226
Ca	0.1667	0.1853	0.1667	0.0670
B	0.2174	0.2870	0.2158	0.2580
O	0.5556	0.5060	0.5528	0.6358
Dy	-	-	0.0043	0.0166
	NMBDy0		***NMBDy0.10***	
Mg	0.0603	0.0203	0.0603	0.0168
Na	0.1484	0.0606	0.1484	0.0651
B	0.2174	0.2261	0.2171	0.2288
O	0.5739	0.6930	0.5734	0.6790
Dy	-	-	0.00087	0.0097

A dosimeter material should have a Z_{eff} as close as possible to the Z_{eff} of human tissue and is called a tissue-equivalent material. According to the International Commission on Radiological Protection, for human tissue, Z_{eff}=7.4. For a mixture or composite such as glass, an equation defined by Mayneord (1937) [21] can be used to determine the single index of Z_{eff} number for a given composite of materials. This is adopted in Eq. (1).

$$Z_{eff} = (a_1 Z_1^{\ m} + a_2 Z_2^{\ m} + a_3 Z_3^{\ m} + ... + a_n Z_n^{\ m})^{1/m} \quad (1)$$

where a_1, a_2,... a_n are the weight fraction of each component of the glass material, which depend on the total number of electrons in the mixture, and Z_n is the atomic number of the element *n*. The value of *m* adopted for photon purposes is 2.94.

The experimental and theoretical results for the Z_{eff} of LMBDy0, LMBDy0.10, CMBDy0, CMBDy0.50, NMBDy0, and NMBDy0.10 samples are given in Table 4.

Table 4. $Z_{eff\ (theoretical)}$ and $Z_{eff\ (experimental)}$ of the samples.

Glass Code	$Z_{eff\ (experimental)}$	$Z_{eff\ (theoretical)}$	Percentage deviation (%)
LMBDy0	7.34	7.74	5
LMBDy0.10	8.13	8.67	6
CMBDy0	12.19	12.03	1
CMBDy0.50	16.64	13.92	16
NMBDy0	7.94	8.53	7
NMBDy0.10	13.78	9.32	32

It can clearly be seen that the Z_{eff} of all the glass samples depends on the concentration of dysprosium, which increases with the addition of dysprosium concentrate. Of the three modifiers, lithium, calcium and sodium, the closest tissue-equivalent properties were recorded for LMBDy0, LMBDy0.10 glass samples as these materials had Z_{eff} values near to that of soft tissue. By contrast, calcium magnesium borate and sodium magnesium borate glass systems are considered suitable TL materials with bone-equivalent performance when dopant is added. These results support the study of TL properties for radiation dosimetry in general and personnel monitoring in particular [22].

Conclusions

A series of Dy_2O_3-doped MB glasses modified with lithium, calcium, and sodium oxides were prepared using the melt-quenching method and characterised to determine their feasibility for use in radiation dosimeters. Differential thermal analysis confirmed their excellent glass-forming ability and thermal stability. Energy dispersive X-ray spectra verified the elemental traces in the sample. Furthermore, MB glasses doped with 0.1 mol% of Dy_2O_3 and modified with lithium were found to have the closest soft tissue equivalency (Z_{eff}≈8.13). The proposed MB glasses doped with dysprosium ions (Dy^{3+}) were established as effective for accurate radiation detection in personnel monitoring.

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