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Optically stimulated luminescence of borate glasses containing magnesia, quicklime, lithium and potassium carbonates

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ABSTRACT

The OSL characteristics of three different borate glass matrices containing magnesia (LMB), quicklime (LCB) or potassium carbonate (LKB) were examined. Five different formulations for each composition were produced using a melt-quenching method and analyzed in terms of both dose-response curves and OSL shape decay. The samples were irradiated using a ⁹⁰Sr/⁹⁰Y beta source with doses up to 30 Gy. Dose-response curves were plotted using the initial OSL intensity as the chosen parameter. The OSL analysis showed that LKB glasses are the most sensitive to beta irradiation. For the most sensitive LKB composition, the irradiation process was also done using a ⁶⁰Co gamma source in a dose range from 200 to 800 Gy. In all cases, no saturation was observed. A fitting process using a three-term exponential function was performed for the most sensitive formulations of each composition, which suggested a similar behavior in the OSL decay.

1. Introduction

The use of glass in the dosimetry of ionizing radiation has been amply investigated, particularly when high radiation doses are involved. Radiation detection applications are pointed out as one of the emerging research areas in glass science (Mauro et al., 2014). In particular, over the past decade, borate glasses have been studied as thermoluminescent dosimeters (TL) (Rojas et al., 2006; Aytá et al., 2010, 2011).

Borate glass matrices based on lithium carbonate, potassium carbonate and boric acid (LKB), doped or co-doped with different materials, have shown good thermoluminescence characteristics in terms of response linearity and sensitivity; moreover, their effective atomic number (Z_{eff}) is similar to that of biological soft tissue (Alajerami et al., 2013a, 2013b; Hashim et al., 2014). Optically stimulated luminescence (OSL), also known as photostimulated luminescence, was also observed in some borate glasses (Qiu et al., 1997), and opened new possibilities for radiation dosimetry (Nanto et al., 2015; Marini et al., 2015). However, borate glasses present high hygroscopicity, which can significantly limit their practical applicability as dosimeters.

The only two OSL dosimeters that are commercially available are

both crystalline ($\text{Al}_2\text{O}_3:\text{C}$ and BeO). To the best of our knowledge, no vitreous matrices are currently in use as OSL dosimeters. Glass matrices can be appealing compared to crystalline materials due to characteristics as easy preparation, inexpensive production, possibility to cast large and uniform pieces, and high transparency. These matrices are focus of our research, and we hereby present a comparison between the OSL characteristics of various formulations of three borate glasses: $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-B}_2\text{O}_3$ [LKB], $\text{Li}_2\text{CO}_3\text{-MgO-B}_2\text{O}_3$ [LMB], and $\text{Li}_2\text{CO}_3\text{-CaO-B}_2\text{O}_3$ [LCB].

In this work, we investigated the effect of adding MgO in high molar ratios to borate glasses. Magnesia (MgO) has been proposed as a dopant increasing the luminescent signal of glass matrices (Alajerami et al., 2013b, 2013c). In our case, we added magnesia also because it is known to reduce glass hygroscopicity, as confirmed by Marini et al. (2015).

Quicklime was added because it is used in glass production for increasing the final product durability and chemical wear resistance. Since Ca and Mg have similar valence characteristics, we also tried this oxide to our formulations in view of investigate its impact on the OSL signal, which is not reported in the literature.

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Table 1
Produced glasses and purity level of the reagents.

Reagents (purity level)	Li ₂ CO ₃ –K ₂ CO ₃ –B ₂ O ₃ [LKB] mol%	Li ₂ CO ₃ –MgO–B ₂ O ₃ [LMB] mol%	Li ₂ CO ₃ –CaO–B ₂ O ₃ [LCB] mol%
B ₂ O ₃	20Li ₂ CO ₃ . 10K ₂ CO ₃ . 70B ₂ O ₃	20Li ₂ CO ₃ . 10MgO. 70B ₂ O ₃	20Li ₂ CO ₃ . 10CaO. 70B ₂ O ₃
(> 98%)	(L10KB)	(L10MB)	(L10CB)
Li ₂ CO ₃	20Li ₂ CO ₃ . 15K ₂ CO ₃ . 65B ₂ O ₃	20Li ₂ CO ₃ . 15MgO. 65B ₂ O ₃	20Li ₂ CO ₃ . 15CaO. 65B ₂ O ₃
(> 99%)	(L15KB)	(L15MB)	(L15CB)
K ₂ CO ₃	20Li ₂ CO ₃ . 20K ₂ CO ₃ . 60B ₂ O ₃	20Li ₂ CO ₃ . 20MgO. 60B ₂ O ₃	20Li ₂ CO ₃ . 20CaO. 60B ₂ O ₃
(99%)	(L20KB)	(L20MB)	(L20CB)
MgO	20Li ₂ CO ₃ . 25K ₂ CO ₃ . 55B ₂ O ₃	20Li ₂ CO ₃ . 25MgO. 55B ₂ O ₃	20Li ₂ CO ₃ . 25CaO. 55B ₂ O ₃
(97%)	(L25KB)	(L25MB)	(L25CB)
CaO	20Li ₂ CO ₃ . 30K ₂ CO ₃ . 50B ₂ O ₃	20Li ₂ CO ₃ . 30MgO. 50B ₂ O ₃	20Li ₂ CO ₃ . 30CaO. 50B ₂ O ₃
(98%)	(L30KB)	(L30MB)	(L30CB)

2. Materials and methods

Table 1 shows our borate glass formulations and the purity level of our reagents. The glasses were produced using a fixed amount of lithium carbonate (Li₂CO₃; 20 mol%) and various amounts of the glass former boron oxide (B₂O₃) as well as various percentages of three additives (K₂CO₃, MgO, and CaO).

All glass formulations were produced using a melt-quenching method. The mixtures were first kept at 1100 °C for 30 min in a platinum crucible, and then cooled down by placing them between two bronze sheets at 0 °C. After vitrification, the compositions were thermally treated at 350 °C for 24 h to reduce residual stresses.

The final sample structure was investigated by X-ray diffraction (XRD) scanning grains below 75 μm with a Rigaku diffractometer RINT-Ultima Plus 2000/PC unit from 10° to 80° (2θ), with a scan rate of 1°/min, at ambient temperature. A thermal characterization was done by differential thermal analysis (DTA) with a DTA – 50 Shimadzu unit, placing grains below 53 μm in an alumine crucible and a nitrogen atmosphere and using a heating rate of 20 °C/min from 30 °C to 800 °C.

For each formulations, twelve pellets were prepared according to the procedures described by Marini et al. (2015) and their optically stimulated luminescence (OSL) was examined. A minimum of three cycles of irradiation/reading/bleaching were done on each batch using a fixed dose. Only pellets presenting a standard deviation within 10% of the mean were selected.

The dosimetric analysis was done using a Risø TL/OSL reader. A ⁹⁰Sr/⁹⁰Y beta source built into the reader, producing a dose rate of 0.1 Gy/s, and a ⁶⁰Co gamma source producing a dose rate of 0.933 kGy/h, were used for the sample irradiations. A blue LED with a peak emission at 470 nm (FWHM=20 nm) was used as stimulation light and a Hoya U-340 filter (transmission between 290 and 390 nm) was used for the emitted luminescence. The OSL measurements were performed with continuous wave stimulation (CW-OSL) applied right after the irradiations. The initial OSL intensity (the integral over the first 0.16 s of the OSL emission curve) was the parameter chosen for the dose-

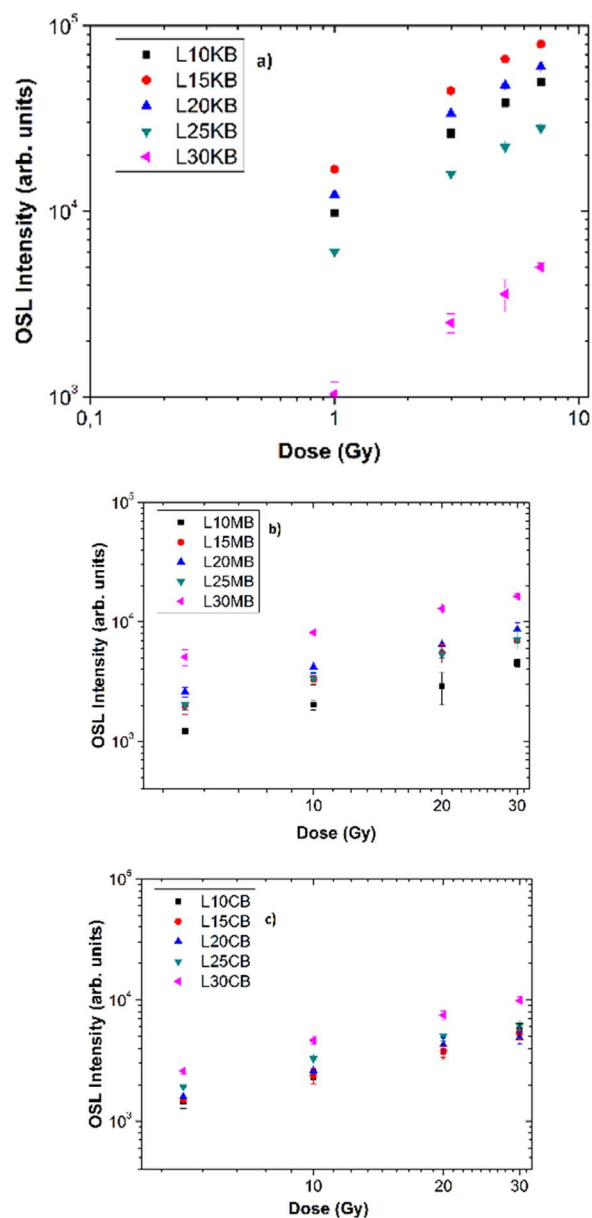


Fig. 1. Pellet dose-response curves. Samples of a) LKB, b) LMB, and c) LCB.

response. The LMB and LCB batches were irradiated with doses ranging from 5 to 30 Gy, while LKB was irradiated with doses ranging from 1 to 7 Gy, in all cases using the ⁹⁰Sr/⁹⁰Y source. The L15KB samples were also irradiated to doses ranging from 200 to 800 Gy with the ⁶⁰Co source; in this case, a collimator with a 1 cm opening was used in front of the photomultiplier to avoid saturation damage.

3. Results and discussion

The XRD analysis showed the presence of broad bands instead of

Table 2
Glass transition temperature (T_g), crystallization temperature (T_c), and a measure of glass stability (T_s) for each produced composition.

Sample	T _g (°C)	T _x (°C)	T _s (°C)	Sample	T _g (°C)	T _x (°C)	T _s (°C)	Sample	T _g (°C)	T _x (°C)	T _s (°C)
L10KB	456.9	481.6	24.7	L10MB	516.9	546.2	29.3	L10CB	516.7	542.0	25.3
L15KB	432.7	459.1	26.4	L15MB	507.2	539.1	31.9	L15CB	519.2	546.3	27.1
L20KB	418.4	439.3	20.9	L20MB	522.3	550.1	27.8	L20CB	526.3	551.2	24.9
L25KB	407.0	422.4	15.4	L25MB	516.4	545.3	28.9	L25CB	513.5	538.1	24.6
L30KB	394.7	409.5	14.8	L30MB	504.0	536.5	32.5	L30CB	509.7	535.1	25.4

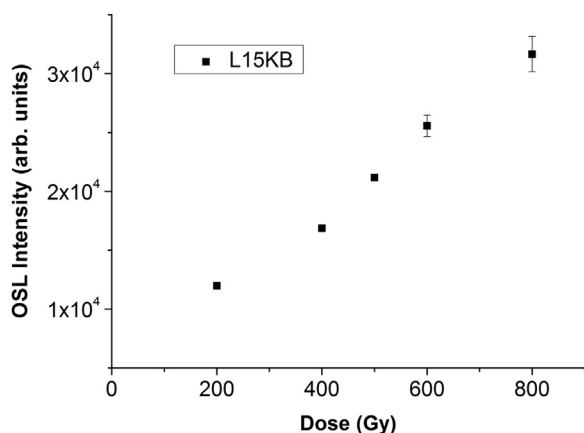


Fig. 2. Dose-response curve for L15KB using gamma irradiation.

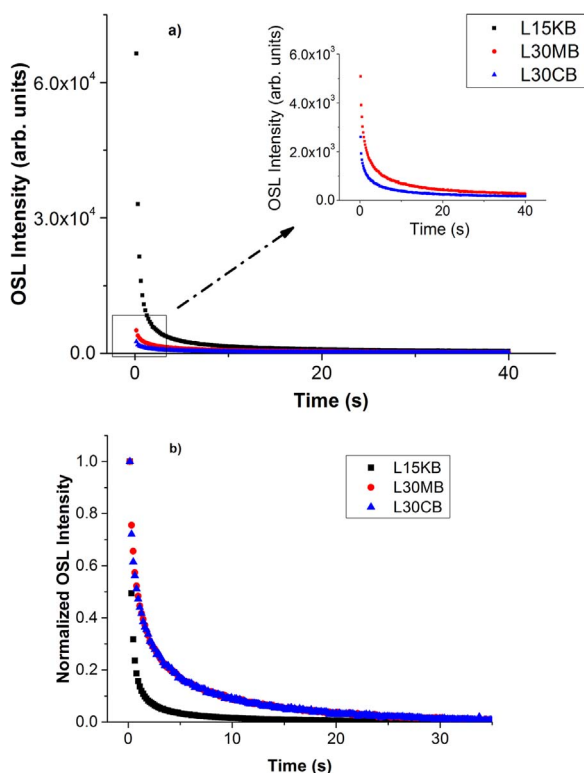


Fig. 3. a) OSL curves for the most sensitive compositions of each batch irradiated with 5 Gy ($^{90}\text{Sr}/^{90}\text{Y}$); b) Normalized OSL curves.

sharp peaks in all compositions, and confirmed the amorphous nature of the prepared samples. Table 2 reports the glass transition temperature (T_g), the first crystallization temperature (T_x), and $T_s=T_x-T_g$ (an

indicator of the thermal stability of the glasses), all of which were obtained by differential thermal analysis.

For the LMB and LCB formulations, we observed that T_g increases up to a certain ratio between MgO and B_2O_3 and then decreases. This variation in T_g may be ascribed to the structural transition from BO_3 triangles to BO_4 tetrahedra, which is followed by an inversion in the process known as boron oxide anomaly (Konijnendijk and Stevels, 1975). This phenomenon does not occur in LKB, where the addition of potassium carbonate always leads to a reduction of T_g .

Qiu et al. (1997) showed that when potassium is added as glass modifier to cerium-doped borate glass a more intense OSL signal is produced compared to glass containing lithium or sodium. In our research, we confirmed that glass modified with potassium, LKB, is more sensitive to radiation compared with samples produced with magnesium and calcium. For this reason, the LKB samples were analyzed in a lower dose range than the LMB and LCB samples. Our dose-response curves are shown in Fig. 1. In terms of initial OSL intensity, L15KB was the most sensitive of the LKB formulations. The LMB and LCB formulations have a similar behavior: they present overlapping dose response curves for intermediate amounts of glass modifiers, and a higher intensity of the dose response with larger amounts of modifiers (i.e. L30MB and L30CB). No saturation effect of the signal was detected for any of our formulations in the examined dose range.

Fig. 2 shows the L15KB dose-response curve for ^{60}Co gamma irradiations in the 200–800 Gy dose range: once again no saturation effect was observed.

Fig. 3a shows the OSL curve for the most sensitive formulations of each glass type irradiated to 5 Gy with the $^{90}\text{Sr}/^{90}\text{Y}$ beta particle source. L15KB clearly presents a higher intensity in comparison with the other formulations. In order to compare the OSL intensity decay characteristics of the three compositions, OSL curves normalized to their initial intensity are shown in Fig. 3b. Although the initial intensity of light emitted by L30MB is considerably higher than that from L30CB, the normalized OSL curves have similar shapes.

In a preliminary analysis of the electron de-trapping kinetics of our glass formulations, we fitted the OSL intensity curves with a three-term exponential function:

$$I_{OSL} = A_1 * e^{-t/\tau_1} + A_2 * e^{-t/\tau_2} + A_3 * e^{-t/\tau_3}$$

where A_1 , A_2 , and A_3 are constant coefficients, τ_1 , τ_2 , and τ_3 are the decay constants and I_{OSL} is OSL intensity. A_1 , A_2 , and A_3 correspond to the fast, medium, and slow CW-OSL component, respectively.

The fitting constants and the coefficient of determination (R^2) are shown in Table 3. The R^2 values are very close to unity, indicating a close agreement between the measured OSL decay curves and the three-term exponential functions. The decay constants for the L30MB and L30CB glasses are similar, mainly in terms of medium and slow decay components. This suggests that the average electron detrapping time after stimulation is similar, although the concentration of traps is different. The L15KB composition presents lower decay constants for

Table 3

OSL parameters for the compositions L15KB, L30MB, and L30CB.

Glass type	Coefficient of determination (R^2)	CW-OSL component	Coefficient (A)	Decay constant (s)
L15KB	0,99975	Fast	$1,36 \times 10^5$ (A_1)	0,14 (τ_1)
		Medium	$2,04 \times 10^4$ (A_2)	0,85 (τ_2)
		Slow	$4,31 \times 10^3$ (A_3)	6,91 (τ_3)
L30MB	0,99947	Fast	$3,52 \times 10^3$ (A_1)	0,21 (τ_1)
		Medium	$2,24 \times 10^3$ (A_2)	1,54 (τ_2)
		Slow	$1,18 \times 10^3$ (A_3)	10,13 (τ_3)
L30CB	0,99924	Fast	$2,42 \times 10^3$ (A_1)	0,15 (τ_1)
		Medium	$1,10 \times 10^3$ (A_2)	1,56 (τ_2)
		Slow	$6,13 \times 10^2$ (A_3)	9,71 (τ_3)

all decay components, suggesting a faster release of the electrons from the traps compared to the other batches.

4. Conclusions

The structural and OSL characteristics of three different borate glasses containing magnesia, quicklime, lithium and potassium carbonates were studied, as well as some characteristics of the OSL decay curve. The XRD and DTA analyses confirmed the effectiveness of our glass manufacturing methodology. The OSL analysis showed that LKB glasses are the most sensitive to beta irradiation. In terms of initial OSL signal intensity, the L15KB, L30MB, and L30CB formulations presented the highest sensitivities for their respective glass types. The OSL curves for these most sensitive formulations may be accurately fitted with a three-term exponential function. L30MB and L30CB presented similar OSL decay, suggesting similarities in detrapping kinetics, even though the concentration of traps is different. L15KB presented lower values of decay constants for all components of the exponential fitting of its OSL curve.

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