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Production and characterization of H_3BO_3–Li_2CO_3-K_2CO_3-MgO for dosimetry

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ABSTRACT

This work examines a borate glass produced with oxides of potassium and lithium, known as LKB. The suitability of borate glasses for thermoluminescent (TL) dosimetry has been reported in previous studies. In particular, borate glasses doped with different elements showed good characteristics in terms of linearity, sensitivity and effective atomic number. However, borate glasses are also known to have high hygroscopicity, which can reduce the sensitivity of a dosimeter. Contrary to previous studies, in this work, Mg was used as one of the main components of the glass composition. Mg is known to improve the stability of the glass, since it reduces the mobility of the alkali ions and can thus reduce the hygroscopicity of the LKB glass. Three compositions containing 0, 5 and 11 mol% of magnesium oxide were examined in order to determine the effect of magnesium specifically on luminescence, high-temperature resistance and hygroscopicity of LKB glass. The LKB glass with 11 mol% of Mg showed favorable characteristics for the production of dosimeters.

Keywords: borate glass, dosimetry, hygroscopicity

1. INTRODUCTION

The possibility to use glass thermoluminescent dosimeters (TLD) has been investigated in various studies [1-6]. A borate glass made from lithium carbonate, potassium carbonate and boric acid (LKB) doped with different elements showed good characteristics in term of linearity, sensitivity and effective atomic number Ze_{ff} equivalent to tissue [1,2,6]. However, to the best of our knowledge, its suitability for the OSL technique was never investigated before. Optically stimulated luminescence presents many advantages over thermal stimulation, among which the fast non-annealing read-out process and absence of thermal quenching can be mentioned [7].

Although LKB has shown good characteristics for use as a dosimeter, borate glasses are known to have high hygroscopicity, and phenomena like dilution in water or moisture adsorption can reduce the sensitivity of a dosimeter. Magnesium oxide is known to be a modifier of the glass network, enhancing the stability of glasses, since it reduces ion mobility [8]. In the present, work a new borate glass composition was studied in order to obtain a new sensitive OSL borate glass dosimeter less hygroscopic than LKB. MgO was added to LKB as a major component of the glass network rather than a dopant, trying to improve some of the LKB physical and optical characteristics. Some luminescent properties of this new composition were investigated and compared to the glass prepared without magnesium oxide.

2. MATERIALS AND METHODS

Three glass formulations were tested in order to make a comparative analysis of the effect of magnesium oxide on some key features of the glass, particularly on luminescence, resistance to high temperature and hygroscopicity. Only crystalline samples were produced with contents higher than 11% of MgO. Thus, the samples were prepared containing 0, 5, and 11% molarity of magnesium oxide. We will refer to them as LKB, LKBMg5% and LKBMg11%, respectively. The molar compositions of the three glasses are presented in Table 1.

Table 1: Glass molar compositions.

	Reagents			
Glass	**Li2CO3 (%)**	**K2CO3 (%)**	**H3BO3 (%)**	**MgO (%)**
LKB	19.96	10	70.04	0
LKBMg5%	19.1	10	65.9	5
LKBMg11%	14.25	10	64.75	11

A wet quenching method was utilized to synthetize the glasses. This consists in melting the reagents in a furnace at 950 °C for one hour and then rapidly cooling the molten glass to room temperature. A fast cooling ensures the amorphous structure of the sample.

To verify that our melting method produced an amorphous material, a comparison between the X-ray pattern of the reagents in powder form and of the material achieved after the melting procedure was done with a Rigaku RINT 2000/PC X-ray diffractometer, using CuKα radiation (λ=1.5418 Å), operated at 40 kV/40 mA with a *continuous scan* mode between 10 and 80 degrees. The results were compared with reference X-ray powder pattern of the *Inorganic crystal structure database* (ICSD), with the help of the *X'Pert Highscore Plus* software.

Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) on the glasses were performed with a TA Instrument SDT 2960 Simultaneous DSC-TGA equipment from room temperature up to 950 °C.

A first hygroscopicity test was performed by immersing pieces of glass directly in distilled water. Their masses were checked with a high-accuracy balance after 1, 24, 48, 72 and 168 hours.

The glass was milled in an agate mortar, obtaining a fine powder sieved between 150 and 75 μm. Three lots of pellets were produced with the three kinds of glass by pressing a mix of glass powder and Teflon into a mold at 10 MPa during 1 minute with a hydraulic press. The pellets were then sintered in 1800-EDF furnace. Over a period of 30 minutes, the pellets were heated up to 300 °C with a heating rate of 25 °C/s, then the temperature was raised and held at 400 °C for 90 min. The process was completed by a free-rate cooling until room temperature. A 3:1 mass ratio between glass powder and Teflon (37.5 mg of glass and 12.5 of Teflon) was selected to produce pellets of 6 mm diameter, 1 mm thickness and approximately 50 mg weight.

For the OSL measurements, the pellets were irradiated with a $^{90}Sr/^{90}Y$ source at a dose rate of (7.5 ± 2.1) mGy/s. The OSL reader we used was developed by LMRI at the Federal University of Pernambuco and comprises a stimulating light source consisting of 20 LEDs emitting blue light at 470 nm, a shutter, an electronic control system and a photomultiplier tube. The measurements were performed with pulsed wave mode, with stimulation and reading time of 20,000 ms and a rate of 100 ms per channel.

3. RESULTS AND DISCUSSION

The X-ray pattern of the reagents in powder form before the melting procedure presented some sharp peaks indicating the presence of crystalline phases. The peaks were compared with the reference X-ray powder pattern of the ICSD database, confirming that they correspond to the reagents. The sintered glass, on the other hand, showed a smooth X-ray powder pattern that is

typical of the amorphous structure of glasses. Therefore we confirmed that our synthesis process correctly produced a glass for each of the three compositions we examined.

Some characteristic temperatures for each glass composition are reported in Table 2. These temperatures were found by means of a differential thermal analysis. No significant differences are encountered among the melting temperature of the three compositions. The glass transition temperature, on the other hand, was found to increase with increasing magnesium oxide contents. The 5 and 11% glasses present a T_g which is 30 degrees centigrade higher than the 0% one.

Table 2: Reference Temperatures.

	LKB	**LKBMg5%**	**LKBMg11%**
Glass transition temperature T_g (°C)	19.1	10	65.9
Melting temperature T_m (°C)	14.25	10	64.75

Useful information on the mass loss due to rise in temperature can be obtained by thermo-gravimetric analysis. The results we obtained are presented in Fig. 1. Both the 0% and the 5% compositions experience a significant weight loss if heated up to 400 °C. From 120 to 300 °C the 0% magnesium composition loses about the 12,5% of its mass, while the 5% magnesium loses the 16%. In the interval between 300 and 400 °C, they both lose about another 1,7% of their total mass. Usually, the procedures used to anneal TL dosimeter include temperature cycles that range up to about 300-400 °C, depending on the material. Therefore, the analysis of the mass lost in this temperature range is particularly important. The TGA analysis of the LKBMg11% glass, on the other hand, reveals that a very small mass loss is experienced by this composition. The mass loss for the LKBMg11% glass is limited to about 0.7% for temperatures up to 300 °C and to 1.1% for temperature up to 400 °C. The glass composition containing 11% of magnesium oxide appears to be significantly more resistant to high temperatures, and then, at least for this aspect, more suitable for TL dosimetry.

Figure 1: *TGA analysis results.*

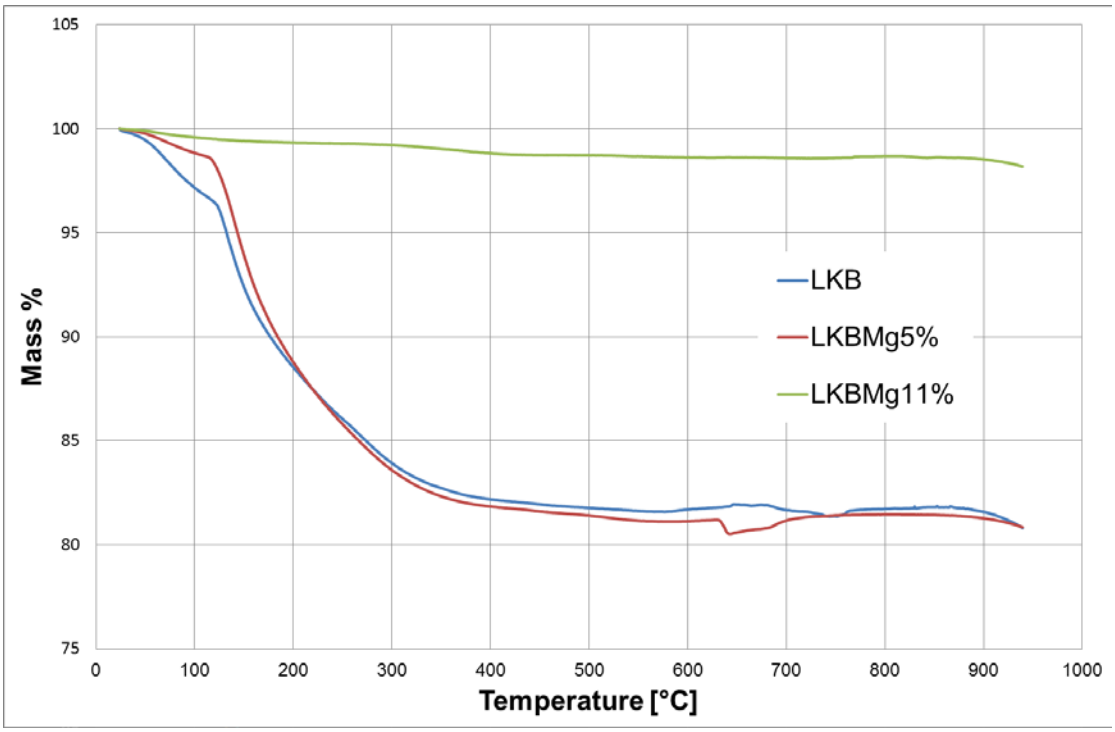


Fig. 2 shows the mass loss experienced by three pieces of glass immersed in distilled water for a week. Each of the three compositions shows a significant mass reduction. As expected, the LKBMg11% glass exhibited a higher resistance against the action of water if compared with the formulation without magnesium, which shows a drastic initial dilution, with a mass loss of about 65% during the first 24 hours. After this fast drop, the dilution appears to slow down, although it never reaches equilibrium and after a week the sample was fully dissolved. Both formulations with magnesium lose less mass during the entire experiment, and the 11% formula appears to be the most stable.

LKB experienced a massive and fast dilution upon contact with liquid water. The glasses that contain magnesium also experienced dilution, indicating that our current formulations do not present sufficient resistance yet. However, the LKBMg5% and LKBMg11% glasses showed a significantly slower dilution. After a week, LKBMg11% was the only glass that was not completely dissolved.

The glow curves we obtained for the glass pellets at different doses are presented in Fig. 3. The curves were determined with the continuous wavelength reading method. As can been seen, the curves present a decaying trend, that is typical of the continuous wave method. All three compositions exhibit the same decay pattern.

Figure 2: *Mass loss due to water corrosion.*

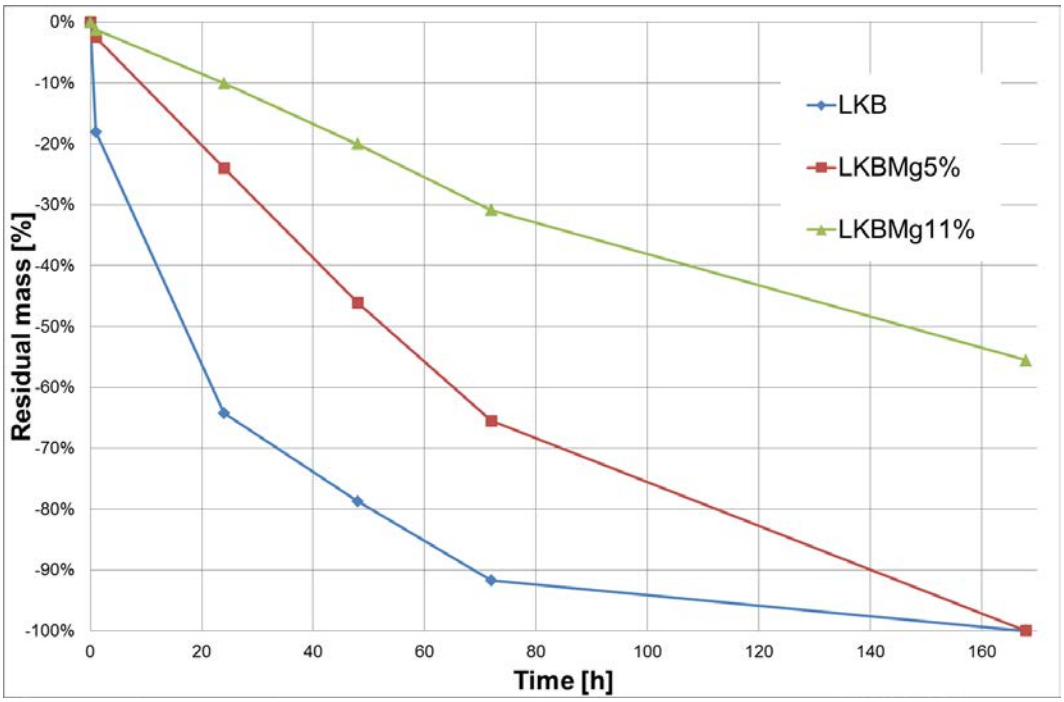
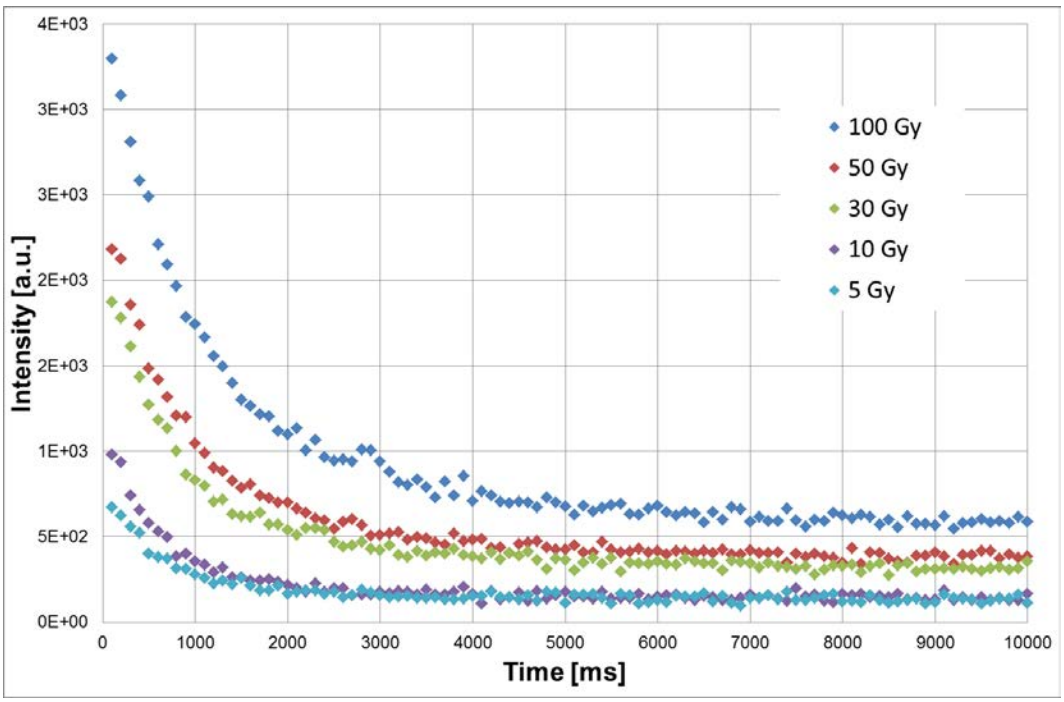


Figure 3. *OSL glow curves at different doses.*



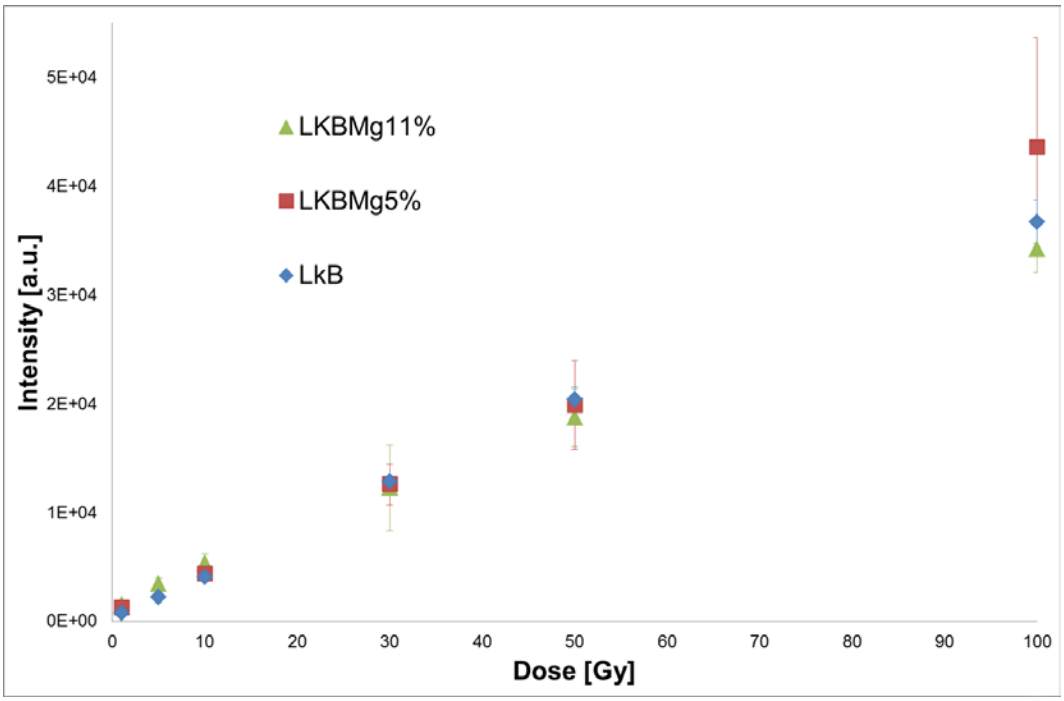
An exponential fitting was implemented to interpolate the readings using the *OriginPro8* software. A two-exponential formula was found to accurately interpolate the experimental data:

$$I = I_0 + A_1 e^{-\frac{t}{T_1}} + A_2 e^{-\frac{t}{T_2}}$$

The fitting function comprises 3 terms, two exponential functions and a constant value I_0. The latter term is due to the noise. The slope of the glow curve is reflected in the T_1 and T_2 constants. At each dose level it is always $T_1 >> T_2$, indicating that the overall decay curve is the sum of a fast component and a slow one. As already pointed out by other authors [9,10], the fast component can be traced to the traps that are located at shallower energy levels. These traps are the first to be filled during the trapping process, and the first that release the charge carriers during the stimulation. On the other hand, the slow component is produced by deeper traps. The analysis of the glow curves shows that both the fast and slow components of the glass without magnesium are constant. Conversely, for the glasses with added magnesium oxide the slow component becomes prominent when the dose increases, determining a change in the overall slope of the glow curve. The addition of magnesium oxide appears to modify the trapping centers, but not the recombination centers, since no differences were encountered in the position of the emission spectrum peaks, evaluated with a spectrofluorimeter.

To evaluate the linearity of the response of our materials with the dose, 3 pellets of each composition were irradiated to different doses between 1 and 100 Gy. The mean of the three readings were then plotted against dose to obtain the dose response curve shown in Figure 4.

Figure 4. *Dose response curves comparison.*



The three compositions showed good linearity over the whole interval between 1 and 100 Gy, with a regression coefficient R^2 always higher than 0.99. A comparison between the dose

response curves of the three compositions is presented in Fig. 4. Accounting for the experimental uncertainties, no significant differences emerge in the response of the three glasses. The presence of magnesium oxide does not appear to modify the sensitivity of the materials.

4. CONCLUSIONS

In this study we synthesized a variety of new luminescent glasses. X-ray diffraction confirmed that our materials have an amorphous structure, since they have smooth X-ray powder pattern showing no crystalline phases. With a differential thermal analysis, it was found that magnesium oxide slightly affects the melting temperature of the glasses, that is about 645 °C for each composition. The glass transition temperature, on the other hand, shows a difference of about 30 °C, rising from 300 °C for the glass without magnesium to 330-335 °C in the presence of magnesium oxide. Thus, magnesium oxide improves the resistance of the glass to high temperatures, especially in the range of interest for TL dosimetry, between 300 and 400 °C. Concerning the deterioration with water, our tests revealed that the addition of magnesium oxide does improve the resistance of the compositions, but this is not sufficient to yield a truly non-hygroscopic glass.

The OSL glow curves suggest that the presence of MgO appears to modify the trapping centers. The slope of the overall glow curve of the LKB glasses does not change with dose. The glow-curve slope of the glass with MgO, on the other hand, decreases while dose increases: this is due to the slow component that becomes more important at high doses. The dose response curves of the three glasses showed good linearity, with a regression coefficient R^2 always higher than 0.99. The three curves have no significant differences, implying that MgO does not affect the sensitivity of the materials. Linearity at doses above 10 Gy is not a common characteristic of dosimetric materials, thus both LKB and LKBMg seems to be suitable for high-dose measurements.

5. ACKNOWLEDGMENTS

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REFERENCES

1. ALAJERAMI, Y.S.M.; HASHIM, S.; RAMLI, A.T.; SALEH, M.A.; KADNI, T. Thermolum inescence characteristics of the Li2CO3-K2CO3-H3BO3 glass system co-doped with CuO a nd MgO. **J Lumin**, v. 143, p. 1-4, 2013.
2. ALAJERAMI, Y.S.M.; HASHIN, S.; GHOSHAL, S.K.; SALEH, M.A.; KADNI, T.; SARIP AN, M.I.; ALZIMAMI, K.; IBRAHIM, Z.; BRADLEY, D.A. The effect of TiO2 and MgO o n the thermoluminescence properties of a lithium potassium borate glass system. **J Phys Che m Solids**, v. 74, p. 1816-1822, 2013.
3. MOFFATT, J.E.; SPOONER, N.A.; CREIGHTON, D.F.; SMITH, B.W. Luminescence prop erties of common glasses for aplication to retrospective dosimetry. **Rad Meas**, v. 47, p. 851-856, 2012.
4. KALNINS, C.A.G.; EBENDORFF-HEIDEPRIEM, H.; SPOONER, N. A.; MONRO, T.M. Optically stimulated luminescence in fluoride-phosphate glass for radiation dosimetry. **J Am Ceramic Soc**, v. 94, p. 474-477, 2011.
5. JUSTUS, B.L.; RYCHNOVSKY, S.; MILLER, M.A.; PAWLOVICH, K.J.; HUSTON, A.L. Optically stimulated luminescence radiation dosimetry using doped silica glass. **Rad Prot D osim**, v. 74, n. 3, p. 151-154, 1997.
6. ELKHOLY, M.M. Thermoluminescence of B2O3-Li2O glass system doped with MgO. **J Lu min**, v. 130, p. 1881-1892, 2010.
7. MCKEEVER, S.W.; MOSCOVITCH, M. On the advanteges and disvantages of optically sti mulated luminescence dosimetry and thermoluminescence dosimetry. **Rad Prot Dosim**, v. 1 04, n. 3, p. 263-270, 2003.
8. HOLLOWAY, D.G.; TAWNEY, D.A. **The physical properties of glass**. London: Wykeha m Publications (London) Ltd, 1973.
9. D'AMORIM, R.A.P.O.; VASCONCELOS, D.A.A.; BARROS, V. S.M.; KHOURY, H.J.; S OUZA, S.O. Characterization of α-spodumene to OSL dosimetry. **Rad Phys Chem**, v. 95, p. 141-144, 2014.
10. YUKIHARA, E.G. WHITLEY, V.H.; MCKEEVER, S.W.S.; AKSELROD, A.E.; AKSELR OD, M.S. Effect of high-dose irradiation on the optically stimulated luminescence of Al2O3: C. **Rad Meas**, v. 38, p. 317-330, 2004.