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Lithium diborate glass for high-dose dosimetry using the UV-Vis and FTIR spectrophotometry techniques



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HIGHLIGHTS

• Lithium diborate glass investigations were prepared for high-dose dosimetry.

- UV-Vis and FTIR spectrophotometry techniques can be used for the evaluation of glass dosimeters.
- Glass samples change their colors proportional to the absorbed doses.

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ABSTRACT

Glass has been used in radiation dosimetry mainly for its linear response with absorbed dose, low cost and easy evaluation. The lithium diborate glasses were irradiated with doses from 200 Gy to 10 kGy using a⁶⁰Co Gamma-Cell system 220 and evaluated with the UV-Vis and FTIR techniques. The results indicate that the samples present lithium diborate, linearity with the absorbed dose, usefulness as YES/NO radiation detectors (due to their color change), low fading for time periods up to 60 days and a good response reproducibility. In conclusion, the lithium diborate glass may be promising for dosimetry in high doses of radiation.

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1. Introduction

The borosilicate glasses when exposed to gamma radiation exhibit changes in their optical absorption spectra. Numerous papers have tried to explain the mechanism by which amber glasses become colored or even ash in the presence of gamma radiation (Baydogan and Tugrul, 2012; Rojas et al., 2006; Kaur et al., 2014; Abbas and Ezz-Eldin, 1994; Maeder, 2013).

In crystalline materials, it is possible to correlate the optical absorption bands with the structural defects of the crystal lattice and which are due to matrix ions. The existence of structural defects, such as gaps, vacancies, and other lattice defects, occurs due to the necessity of minimizing the free energy that requires a

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certain amount of the structural disorder (increase in entropy) (Abbas and Ezz-Eldin, 1994). Single crystals of zirconia stabilized with yttria (ZrO₂: Y₂O₃) were widely studied in the last 20 years, in regard to the production of structural defects and damage when exposed to gamma radiation. By optical absorption spectroscopy it can be shown that color centers originate from the paramagnetic deviances (called T-type centers). A ZR³⁺ ion is produced in the yttria stabilized zirconia through electronic excitation due to the interaction with energy photons such as gamma radiation. The main advantages of glasses are their chemical inertness, insolubility, rigidity, small size, and very low cost. They may be used for dosimetry in the main radiation processes of simple disinfection (10–100 Gy), water purification (1–10 kGy), pasteurization (1–10 kGy) and may be applied in medical sterilization (10-100 kGy). They also may be used as Yes/No irradiation indicators, because the visual observation of glasses and their color provide immediate confirmation of irradiation (Caldas and Teixeira, 2002).



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Fig. 1. Spectra for glasses irradiated with 200 up to 10 kGy absorbed dose. (a) UV-Vis spectra of lithium diborate glass: absorbance *versus* wavelength, (b) FTIR spectra of lithium diborate glass: absorbance *versus* wave number. The average of 3 samples was evaluated for each curve, and the uncertainty obtained was lower than 1%.

The FTIR and UV-Vis techniques are extensively studied in low and high doses of radiation with applications in dosimetry as: PMMA (Galante et al., 2004), Fluoropolymers (Liz et al., 2011), Fricke Gel (Pirani et al., 2013; Oliveira et al., 2014), Rubber nanopowder (Abadchi and Jalali-Arani, 2014). The TL technique is widely used for the evaluation of glasses irradiated with high doses (Prokic, 2001; Rojas et al., 2006, Son et al., 2013; Teixeira et al., 2008). There are papers in the literature specifically for irradiated glasses (Caldas and Teixeira, 2002; Rodrigues and Caldas, 2002; Teixeira and Caldas, 2008). The techniques FTIR and UV-Vis for high doses can also be useful with lithium diborate glass which is investigated for the first time with these applications in the present work.

One explanation for the formation of color centers is credited to the production of electron-hole pairs, which then may be individually trapped in numerous local defects in the glass structure (Abbas and Ezz-Eldin, 1994). However, the increase in optical density with increasing gamma radiation dose is also attributed to the presence of impurities inherent in the glass as the ratio $Fe^{3+}/$ Fe^{2+} . Therefore, the full understanding of the real effect of the gamma radiation exposure of the glass is still the subject of studies, and it remains without a definitive explanation (Bahri et al., 2014; Maeder, 2013; Son et al., 2013).

The ionizing radiation induces characteristic absorption bands



Fig. 2. Integral area *versus*: (a) wavelength - UV-Vis; (b) wave number - FTIR. Both cases: irradiation from 200 Gy up to 10 kGy absorbed doses.

in the glass samples depending on the irradiation conditions (Quezada and Caldas, 1999). There is a variation in color due to the exposure to radiation. The color change is due to the oxidation mechanism which may create color centers that can absorb light. The UV-Vis spectrophotometry is considered a low-cost technique, and specifically in this study, the color centers of the glass samples will not be destroyed. The objective of this study was to expose the lithium diborate glass samples to high doses, and to use the techniques of UV-Vis and FTIR spectrophotometry for the evaluation of the samples.

2. Materials and methods

The glass samples were produced by the splat cooling technique (nominal melting temperature of 1250 °C). The melt composition was prepared using the molar proportion of Li₂O - 2 B₂O₃. No intentional metal transition or any other dopant was added to the glass composition. The lithium diborate glass samples used in this work were composed by small rectangular pieces, with dimensions of $1 \times 1 \times 4$ mm³. The glass samples were irradiated with absorbed doses between 200 Gy and 10 kGy using a⁶⁰Co Gamma Cell-220 system (dose rate of 1.089 kGy/h); then each sample was evaluated, and it presented an absorbance spectrum acquired on a UV-Visible (UV-Vis) Spectrophotometer (Genesys 10S/Thermo Scientific) and on a Fourier Transform Infrared (FTIR) Spectrometer



Fig. 3. Integral area versus absorbed dose: (a) UV-Vis and (b) FTIR. Both cases: irradiation from 200 Gy up to 10 kGy absorbed doses (uncertainties lower than 0.1%).

(Frontier/Perkin Elmer). The spectra were collected on the wavelength range from 190 to 400 nm, spectral bandwidth of 1.8 nm, scan interval of 1 nm, for the 6 doses plus the blank, all in triplicate (total of 21 acquisitions) for UV-Vis; for the FTIR technique, the spectra were collected on the range of 450–4000 cm⁻¹, resolution of 4 cm⁻¹, scan interval of 1 cm⁻¹, 16 acquisitions, absorbance mode and using the samples directly on Universal Attenuated Total Reflectance Accessory (UATR) for the acquisition of all spectra. The absorbance peaks were observed for each glass sample for both techniques.

3. Results and discussion

The spectra present a baseline variation (and maximum absorbance values) proportional to the absorbed dose received by the samples in Fig. 1. These results show that it is possible to use the techniques of UV-Vis and FTIR to determine if the glass samples were irradiated or not.

The total area under the curves from 190 to 400 nm and 450 to 4000 cm⁻¹ is presented in Fig. 2; their responses show a linear growth on 190–200 nm and a linear decrease on 450-1000 cm⁻¹, for the UV-Vis and FITR analyses respectively.

A linear relationship between integrated area and the absorbed



Fig. 4. Absorbance *versus* number of measument. (a) UV-Vis (220 nm) and (b) FTIR (880 cm⁻¹). Samples of lithium diborate glass irradiated with 5 kGy (absorbed dose).

dose of the samples can be observed in Fig. 3 for both techniques. The results obtained were $R^2 = 0.9972$ and $R^2 = 0.9983$ for UV-Vis and FTIR techniques respectively. The sensitivity value for samples evaluated in the UV-Vis technique was different than that evaluated in FTIR technique, because their absorption coefficients are different. Both spectral bands at each technique (shown in Fig. 1) obey the Beer-Lambert Law, where the absorption coefficients, which are characteristic for each technique.

The response reproducibility to the detectors instrument associated to the number of measurements for just one sample is shown in Fig. 4. In the first case, the measurements were taken through the UV-Vis technique (220 nm), and the relative standard deviation was less that 1.9%, for the maximum absorbance. In the second case, the measurements were taken using the FTIR technique (880 cm⁻¹), and the relative standard deviation was less that 3%, for the maximum absorbance.

Fig. 5 presents the color change for lithium diborate glass irradiated with absorbed doses from 0 up to 10 kGy. This color variation in relation to absorbed dose indicates that the glasses may be used as YES/NO dosimeters (Caldas and Teixeira, 2002; Rodrigues and Caldas, 2002).

The fading of the sample signals shows evidence of its action in the early days post-irradiation in Fig. 6; approximately 20% of the



Fig. 5. Color intensity in relation to the increase in absorbed dose, for lithium diborate glasses, showing possibility of their use as YES/NO radiation detectors.



Fig. 6. Fading of the response using the UV-Vis (220 nm) and FTIR (880 $\rm cm^{-1})$ techniques (uncertainties lower than 0.1%).

signal is lost due to fading when samples are stored during 60 days, for both techniques used in this study. The samples were stored protected from light and heat throughout this period, the results are in agreement with literature (Annalakshmi et al., 2011; El-Adawy et al., 2010; Narayan et al., 2007).

4. Conclusions

The UV-Vis and FTIR spectra of the lithium diborate glass samples were obtained. For the analyses, the results obtained were: (1) The area under each spectrum showed an increase with the absorbed dose; they present good reproducibility for absorbance; (2) The dose-response curve showed a linear relationship in a defined range; (3) The proportionality of the absorbance with the dose was also checked with the FTIR analysis; (4) The glass samples changed their coloration proportional to the absorbed doses; (5) They may be used as Yes/No detectors and possibly as high-dose dosimeters; (6) They presented 20% fading in their signals after 60 days post-irradiation. These results show that lithium diborate glass is promising as radiation detectors in high doses.

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References

- Abadchi, M.R., Jalali-Arani, A., 2014. The use of gamma irradiation in preparation of polybutadiene rubber nanopowder; its effect on particle size, morphology and crosslink structure of the powder. Nucl. Instr. Meth. B 320, 1–5.
- Abbas, A.F., Ezz-Eldin, F.M., 1994. Optical absorption of some gamma-irradiated lithium-boro-silicate glasses doped with some rare-earth metal oxides. Nucl. Instr. Meth. 93, 457–463.
- Annalakshmi, O., Jose, M.T., Amarendra, G., 2011. Dosimetric characteristics of manganese doped lithium tetradiborate - an improved TL phosphor. Radiat. Meas. 46, 669–675.
- Bahri, T.N.H.T.K.H., Wagiran, R., Hussin, I., Hossain, T., Kadni, 2014. Thermoluminescence properties of CaO-B₂O₃ glass system doped with GeO₂. Radiat. Phys. Chem. 102, 103–107.
- Baydogan, N., Tugrul, A.B., 2012. Borosilicate glass for gamma irradiation fields. Solid State Sci. 14, 1692–1697.
- Caldas, L.V.E., Teixeira, M.I., 2002. Commercial glass for high doses using different dosimetric techniques. Radiat. Prot. Dosim. 101, 149–152.
- El-Adawy, A., Khaled, N.E., El-Sersy, A.R., Hussein, A., Donya, H., 2010. TL dosimetric properties of Li2O-B2O3 glasses for gamma dosimetry. Appl. Radiat. Isot. 68, 1132–1136.
- Galante, A.M.S., Villavicencio, A.L.C.H., Campos, L.L., 2004. Preliminary investigations of several new dyed PMMA dosimeters. Radiat. Phys. Chem. 71, 391–394.
- Kaur, R., Singh, S., Pandey, O.P., 2014. UV-vis spectroscopic studies of gamma irradiated lead sodium borosilicate glasses. J. Mol. Struct. 1060, 251–255.
- Liz, O.S.R., Medeiros, A.S., Faria, L.O., 2011. FTIR and DSC studies on gamma irradiated P(VdF-HFP) fluoropolymers applied to dosimetry. Nucl. Instr. Meth. B 269, 2819–2823.
- Maeder, T., 2013. Review of Bi_2O_3 based glasses for electronics and related applications. Int. Mat. Rev. 58, 3–40.
- Narayan, P., Senwar, K.R., Vaijaourkar, S.G., Bhatnagar, P.K., 2007. Application of commercial glasses for high dose measurement using the thermoluminescent technique. Appl. Radiat. Isot. 66, 86–89.
- Oliveira, L.N., de Almeida, A., Caldas, L.V.E., 2014. Fricke gel diffusion coefficient measurements for applications in radiotherapy level dosimetry. Radiat. Phys. Chem. 98, 42–45.
- Pirani, L.F., Moreira, M.V., Costa, J.J., Oliveira, L.N., Caldas, L.V.E., de Almeida, A., 2013. Fricke dosimeter gel measurements of the profiles of shielded fields. Appl. Radiat. Isot. 82, 239–241.
- Prokic, M., 2001. Lithium diborate solid TL detectors. Radiat. Meas. 33, 393–396.
- Quezada, V.A.C., Caldas, L.V.E., 1999. Glass detectors for dose determination in a flower irradiation process. Radiat. Prot. Dosim. 85, 473–475.
- Rodrigues Jr., A.A., Caldas, L.V.E., 2002. Commercial plate window glass tested as routine dosimeter at a gamma irradiation facility. Radiat. Phys. Chem. 63, 765–767.
- Rojas, S.S., Yukimitu, K., de Camargo, A.S.S., Nunes, L.A.O., Hernandes, A.C., 2006. Undoped and calcium doped diborate glass system for thermoluminescent dosimeter. J. Non-Cryst Solids 352, 3608–3612.
- Son, K., Ji, Y.H., Kim, K.B., Kim, M.S., Jung, H., 2013. The analysis of readout values according to reading methods: glass dosimeter reader. Radiat. Meas 59, 214–217.
- Teixeira, M.I., Caldas, L.V.E., 2008. Dosimetric properties of various colored commercial glasses. Appl. Radiat. Isot. 57, 407–413.
- Teixeira, M.I., Costa, Z.M., Pontuschka, W.M., Caldas, L.V.E., 2008. Study of the gamma radiation response of watch glasses. Radiat. Meas. 43, 480–482.

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