Radiation Measurements xxx (2017) 1–4

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Dosimetric properties of MgB_4O_7:Dy,Li and MgB_4O_7:Ce,Li for optically stimulated luminescence applications

L.F. Souza [a], A.M.B. Silva [a], P.L. Antonio [b], L.V.E. Caldas [b], S.O. Souza [a, *], F. d'Errico [c, d], D.N. Souza [a]

[a] Departamento de Física, Universidade Federal de Sergipe, Av. Marechal Rondon, S/N, 49.100-000, São Cristóvão, SE, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, IPEN/CNEN-SP, Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, Brazil
[c] Yale University School of Medicine, 333 Cedar Street, New Haven, CT 06511, USA
[d] Scuola di Ingegneria, Università di Pisa, Largo L. Lazzarino 2, Pisa I-56125, Italy

HIGHLIGHTS

- OSL signals from MgB_4O_7:Ce,Li and MgB_4O_7:Dy,Li were evaluated.
- The radioluminescence emission from the samples showed transitions from Ce^{3+} and Dy^{3+}.
- The OSL signal from MgB_4O_7:Ce,Li showed good stability along the time.
- Promising materials for OSL dosimetry.

ARTICLE INFO

Article history:
Received 30 September 2016
Received in revised form
3 February 2017
Accepted 9 February 2017
Available online xxx

Keywords:
OSL dosimetry
Magnesium tetraborate
Radioluminescence emission

ABSTRACT

The present work describes the optically stimulated luminescence (OSL) of a tissue equivalent crystal, the magnesium tetraborate, doped with dysprosium or cerium and co-doped with lithium due to the lack of materials with characteristics suitable for several dosimetric applications. In the present work, MgB_4O_7:Dy,Li and MgB_4O_7:Ce,Li were characterized through their OSL and radioluminescence emissions. Our results indicate that MgB_4O_7:Ce,Li has a strong emission peaked at 420 nm that is connected to the Ce^{3+} electronic transitions, while the emission of MgB_4O_7:Dy,Li has several peaks connected to the Dy^{3+} transitions. The OSL decay curves from both materials are composed by two components: a slow one and a fast one. MgB_4O_7:Ce,Li is 10 times more sensitive than MgB_4O_7:Dy,Li, especially due to the wavelengths of the emission peaks. The dose response for both materials were sublinear from 0.2 Gy to 100 Gy, for MgB_4O_7:Ce,Li, and from 0.2 Gy to 40 Gy, for the MgB_4O_7:Dy,Li. The OSL signal from MgB_4O_7:Ce,Li showed good stability over 40 days (with a fading < 1%), while MgB_4O_7:Dy,Li presented a complete fading of the signal after 40 days. These results suggest a clear potential of MgB_4O7:Ce,Li for radiation dosimetry purposes using OSL technique.

1. Introduction

Optically Stimulated Luminescence (OSL) nowadays is a very well established technique in personal dosimetry and is available commercially since almost two decades (Yukihara and Mckeever, 2011; Akselrod and Akselrod, 2006). The all-optical nature of the OSL technique has several advantages over conventional Thermoluminescence (TL), which explains its increasing acceptance. The main challenge for OSL technique has been the scarcity of materials suitable for medical applications. Al_2O_3:C (aluminum oxide) and the BeO (beryllium oxide) are the commercially available OSL dosimeters (Sommer *et al.*, 2008; Jahn *et al.*, 2010; Yukihara *et al.*, 2014a and 2014b), but they are not suitable for all radiations types (e.g. neutrons) (Akselrod and Akselrod, 2006; Patra *et al.*, 2016), and thus several research groups are investigating different OSL materials.

Since the 1980s, magnesium tetraborate (MgB_4O_7) has been frequently used as host matrix for thermoluminescent dosimetry

* Corresponding author.
E-mail address: sosouza@ufs.br (S.O. Souza).

http://dx.doi.org/10.1016/j.radmeas.2017.02.009
1350-4487/

(Prokic, 1980) and for temperature sensing applications (Prokic, 2007; Souza *et al.*, 2014; Souza *et al.*, 2015; Yukihara *et al.*, 2015). This material is attractive for dosimetric applications due characteristics such as being an insulator with wide band gap of approximately 9.5 eV (Oliveira *et al.*, 2016), and having a low effective atomic number ($Z_{eff} = 8.4$). The material presents a high sensitivity, 15 times higher than conventional TLD-100 (Prokic, 2000) and a boron content which is useful in neutron dosimetry, especially if dosimeters are made with ^{10}B (Fernandes *et al.*, 2008).

Some borates (LiB_4O_7) were recently investigated for OSL dosimetry applications, such as 2D dosimetry (Oliveira *et al.*, 2013; Patra *et al.*, 2016; Oliveira *et al.*, 2016), but the OSL properties of MgB_4O_7 doped with lanthanides have not been reported so far.

Early studies of MgB_4O_7 with only one lanthanide as dopant showed weak OSL emissions, not useful for dosimetric applications. In other studies, co-doping with Li showed an increase in the thermoluminescent (TL) intensity of different host matrices, such as MgO:Ce, MgO:Eu, MgO:Nd, $CaSO_4$:Dy, $CaSO_4$,Tm, CaF_2:Mn, MgB_4O_7:Dy, MgB_4O_7:Tm, MgB_4O_7:Tb, MgB_4O_7:Mn, MgB_4O_7:Ce,Ca-B_4O_7:Dy, and CaB_4O_7, due to a better incorporation of activator ions and to improved energy transfer processes (Prokic, 2000; Orante-Barrón *et al.*, 2011).

In this work, we examined the radioluminescence (RL) and optically stimulated luminescence MgB_4O_7:Ce,Li and MgB_4O_7:Dy,Li, in particular we investigated some important parameters for the application of materials in OSL dosimetry including dose response curve, OSL decay curve and fading.

2. Materials and methods

Undoped and doped MgB_4O_7 were synthesized using solid-state synthesis. This route has been described previously for the synthesis of MgB_4O_7 doped with Dy and Nd (Subanakov *et al.*, 2014; Souza *et al.*, 2014; Souza *et al.*, 2015). In this work, for the production of MgB_4O_7, MgB_4O_7:Ce,Li, and MgB_4O_7:Dy,Li we used analytical grade of MgO (Merck, 99.9% purity), H_3BO_3 (Merck, 99.9% purity), cerium carbonate ($Ce_2(CO_3)_3xH_2O$ Sigma-Aldrich, 99.9% purity), dysprosium oxide (Dy_2O_3); lithium carbonate ($LiCO_3$ - Sigma-Aldrich, 99.9% purity) was used for co-doping of the samples.

The compounds were uniformly homogenized using an agate mortar and pestle. The mixtures were calcined in a muffle furnace (EDG-1800) at 900 °C for 7 h, followed by slow cooling to room temperature (25 °C) for crystallization. The resulting powders were granulated; the grain size selected for pellet production was between 75 and 180 μm. All the analyses were performed using samples in pellet format that were produced by cold compaction in a hydraulic press, with 50 kg f/cm^2. Each pellet had a final mass of 10.0 mg, 3.0 mm of diameter, and 2.0 mm of thickness.

For the RL measurements, the samples were exposed to X-rays from a 40 kV/25 mA X-ray tube (X-ray diffractometer Rigaku, RINT, 2000/PC, with a Co target). The RL emission was collected using an optical fiber connected to an Ocean Optics HR2000 spectrometer (transmission between 200 and 1000 nm). Data were collected during the irradiation of the samples using the Spectra Suite software (Ocean Optics).

For the OSL measurements, we used a reader developed by the Nuclear Energy Department of the Federal University of Pernambuco (DEN-UFPE). This reader is suitable for materials that have luminescent emission in the UV region of the electromagnetic spectrum. The device is equipped with 20 blue light emitting diodes (LEDs) for stimulation (peak emission at 470 nm) and a shutter in front of a photomultiplier tube with a maximum detection peak at 420 nm (EMI 9635 B). The system blocks emissions above the blue region and thus permits a good separation of the stimulation light from the emission light of the samples.

The OSL measurements were performed in the continuous-wave (CW) mode of operation. All readings were performed at room temperature (27 °C). For all tests, the pellets were irradiated with a beta source of $^{90}Sr/^{90}Y$ delivering an absorbed dose rate of 0.35 Gy/min.

For fading analyses, the samples were irradiated with doses of 5 Gy and stored in the dark; the readout of the samples was performed from 1 to 40 days after irradiation. The background or zero dose reading was determined through the OSL reading of each pellet without exposure to radiation. This background value was subtracted from the OSL intensity values obtained after irradiation. In this work, the term OSL intensity refers to the area under the OSL curve during the stimulation of samples from 0 to 40 s.

3. Results and discussion

The RL emission spectra of undoped and doped samples of MgB_4O_7 synthesized are shown in Fig. 1a and b. For undoped samples no luminescence emission was observed between the ultraviolet (UV) and infrared (IR) regions.

The RL spectrum of MgB_4O_7:Ce,Li (Fig. 1(a)) is characterized by a double band due to the splitting of the 4f ground state into $^2F_{7/2}$ and $^2F_{5/2}$ from the ion Ce^{3+}. The bands are located from the UV to the visible region (UV–vis), with the main peak centered at 412 nm and a weaker peak centered at 600 nm that is associated with the electronic transitions. The wavelength position of the emission band from the Ce^{3+} ion is strongly affected by the crystal field of the surrounding anions, and thus the emission of Ce^{3+} can be placed in a different position ranging in the UV-IR region, depending on the host lattice (Dorenbos, 2000).

The emission wavelength found for the borates doped with Ce in the present work is in agreement with the results by Twardak *et al.*

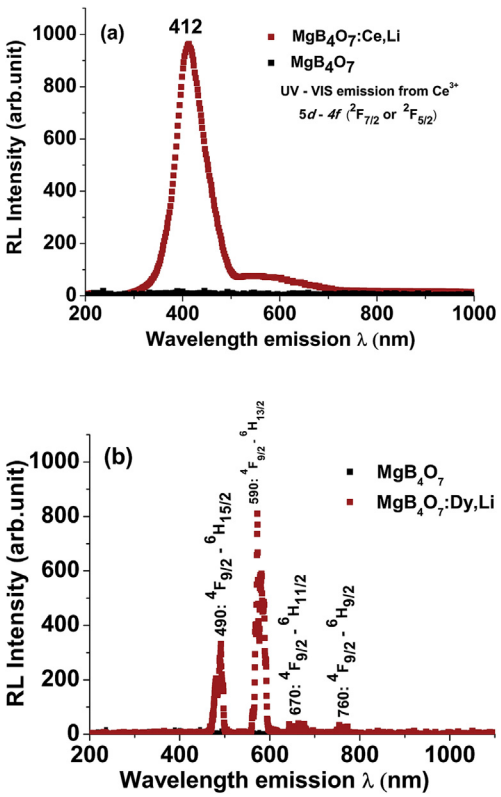

Fig. 1. RL emission from MgB_4O_7, MgB_4O_7:Ce,Li (a) and MgB_4O_7:Dy,Li (b).

Please cite this article in press as: Souza, L.F., et al., Dosimetric properties of MgB_4O_7:Dy,Li and MgB_4O_7:Ce,Li for optically stimulated luminescence applications, Radiation Measurements (2017), http://dx.doi.org/10.1016/j.radmeas.2017.02.009

(2014) who investigated the luminescent properties of lutetium orthosilicates doped with Ce (Lu_2SiO_5:Ce). They observed a broad emission peak between 350 nm and 500 nm (maximum at 430 nm).

For magnesium oxide doped with Ce and co-doped with Li (MgO:Ce,Li), the main peak is centered at 525 nm; for other systems such as CaO:Ce, CaS:Ce and MgS:Ce, the emission is very similar to that of MgO, being centered at 556 nm, 505 nm, and 525 nm, respectively, which are also related with the Ce^{3+} transitions (Orante-Barrón *et al.*, 2011; Dorenbos, 2000; Yukihara *et al.*, 2013).

The RL emission spectrum of MgB_4O_7:Dy,Li showed several well-defined emission peaks at 490, 590, 670, and 760 nm, as can be seen in Fig. 1 (b). These emissions are related to the typical electronic transition of Dy^{3+} ion ($^4F_{9/2} - {}^6H_J$) (Dieke, 1968; Yukihara *et al.*, 2013; Yukihara *et al.*, 2014a and 2014b).

MgB_4O_7:Ce,Li presented an OSL signal 10 times higher than MgB_4O_7:Dy,Li, as can be seen in Fig. 2(a). It is noteworthy that the main emissions of MgB_4O_7:Dy,Li are peaked at 490 nm and 590 nm, while the OSL emission of MgB_4O_7:Ce,Li, at 412 nm, is exactly in the range of the transmission used in the OSL reader, that is from 200 to 490 nm. Thus, only a small fraction of the signal of MgB_4O_7:Dy,Li is transmitted through the filters; therefore, the OSL signal from Dy^{3+} is not optimal for this system, while Ce^{3+} perfectly matches it. This underlines that the right choice of a filter is crucial for an optimal OSL detection.

The measured OSL decay curves of both samples are well fitted by a double exponential decay described in Equation (1).

$$I = I_0 + A_1 e^{\left(\frac{-x}{\tau_1}\right)} + A_2 e^{\left(\frac{-x}{\tau_2}\right)} \quad (1)$$

Equation (1) comprises three terms, where I is the luminescent intensity as function of time, I_0 is a constant background, A_1 and A_2 are constants and τ_1 and τ_2 are the characteristic lifetime decay of the processes. In Fig. 2 (b), the main components of the fitted OSL curve for the MgB_4O_7:Ce,Li are shown, which is the most sensitive from both evaluated materials. The fitted curve indicates two components with lifetimes of 0.8 and 6 s. The first exponential is related to a fast component, which is assigned to the electrons that recombine directly with holes. The second exponential term is connected with a slow component, due to the presence of shallow traps in the structure, where electrons are re-trapped during several seconds before being recombined with holes. For MgB_4O_7:Dy,Li, lifetimes of approximately 1 and 8 s were obtained. (D'Amorim *et al.*, 2014; Marini *et al.*, 2015; Yukihara *et al.*, 2004).

Fig. 3(a) shows the OSL dose response of MgB_4O_7:Ce,Li and MgB_4O_7:Dy,Li. Each point corresponds to the average response of 5 samples to a given dose. The experimental standard deviations are represented by error bars, barely visible, showing that the behavior of these samples is very reproducible.

In the OSL dose response curve, the deviations from linearity are predicted to occur as a result of the dynamics of the process of charge capture between different defects in the material (Yukihara *et al.*, 2004; Yukihara and McKeever, 2011). The dose response for MgB_4O_7:Ce,Li is sublinear from 0.2 to 100 Gy and for MgB_4O_7:Dy,Li the sublinear behavior can be seen approximately from 0.2 to 40 Gy. Above these values both curves show a saturation tendency. Although the materials presented sublinear dose response curves, they can still be used by applying calibration factors.

In other Ce-doped materials irradiated with a beta source, such as Lu_2SiO_5:Ce, the dose response is linear from 100 mGy to 1 Gy (Twardak *et al.*, 2014), and for magnesium oxide, such as MgO:Nd,Li and for borates ($Li_2B_4O_7$:Ag), linear behavior is presented from 0.01 Gy up to 100 Gy and from 0.1 Gy to 500 Gy, respectively (Patra *et al.*, 2016; Oliveira *et al.*, 2013).

Fig. 3 (b) shows the results of the stability study of the OSL signal

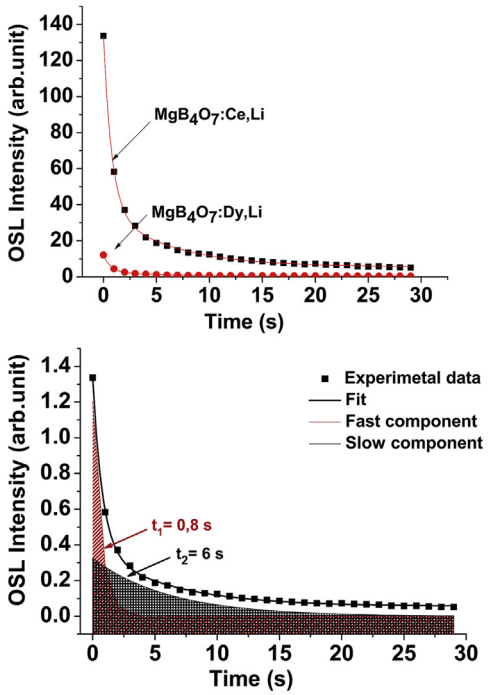

Fig. 2. (a) OSL decay curves from pellets of MgB_4O_7:Ce,Li and MgB_4O_7:Dy,Li when irradiated with 1 Gy of absorbed dose of $^{90}Sr/^{90}Y$. (b) The fitting of the OSL decay curve from the MgB_4O_7:Ce,Li and the contribution of fast and slow component is showed in filled area.

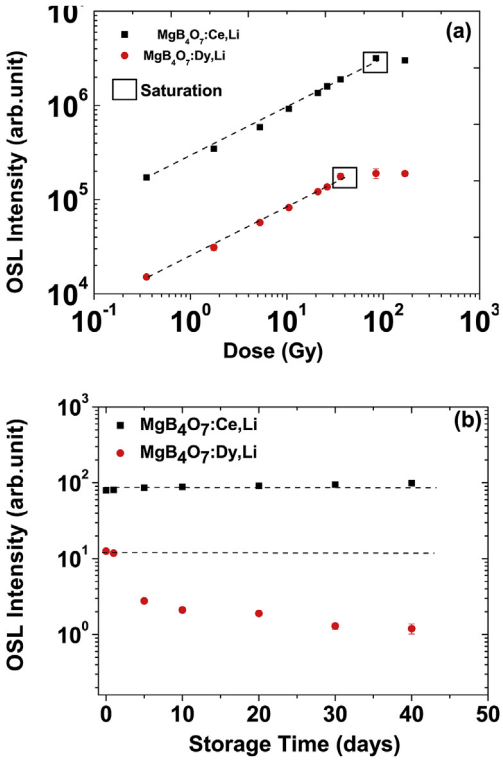

Fig. 3. (a) Dose response of MgB_4O_7:Ce,Li and MgB_4O_7:Dy,Li when irradiated with doses from 0.2 to 200 Gy of $^{90}Sr/^{90}Y$.; (b) Fading characteristic of samples when irradiated with 5 Gy of $^{90}Sr/^{90}Y$.

Please cite this article in press as: Souza, L.F., et al., Dosimetric properties of MgB_4O_7:Dy,Li and MgB_4O_7:Ce,Li for optically stimulated luminescence applications, Radiation Measurements (2017), http://dx.doi.org/10.1016/j.radmeas.2017.02.009

for both materials over 40 days. Although the samples were kept in the dark, the OSL signal from MgB_4O_7:Dy,Li faded by about 80% during three days following irradiation. The observed instability is probably due to the signal lost from the shallow traps. After 40 days, the OSL signal of MgB_4O_7:Dy,Li had completely faded. The instability of the OSL signal is a limiting factor for dosimetric applications, especially for personal monitoring (McKeever *et al.*, 1995; Chen, 2016). The OSL signal from MgB_4O_7:Ce,Li remains constant during the period of 40 days, indicating that the traps responsible for the OSL signal are very stable and the material can be used for personal monitoring.

4. Conclusions

In this work, relevant luminescent and dosimetric properties of our synthesized OSL materials MgB_4O_7:Ce,Li and MgB_4O_7:Dy,Li were determined and examined. The luminescent emissions are due to the Ce^{3+} ions, in the UV–vis region, and to the Dy^{3+} ions, in the UV-IR region.

The emission of the MgB_4O_7:Ce,Li matches well the spectral window of the OSL device we used, and thus we could observed a signal 10 times higher than that of MgB_4O_7:Dy,Li, emitting mainly outside of the spectral window.

The OSL decay curves from both materials are composed of a slow and a fast component.

Of the two materials we investigated, MgB_4O_7:Ce,Li presented the most interesting properties for OSL dosimetry, such as signal stability over 40 days after exposure to ionizing radiation or low fading and wide dynamic range or linearity of the dose response (0.2–100 Gy). In summary, this new phosphor shows suitable dosimetric properties.

Acknowledgments

The authors gratefully acknowledge the support received from the Brazilian agencies FAPITEC-SE, CAPES, CNPq, FAPESP, and Project INCT Radiation Metrology in Medicine (INCT/RMM).

References

Akselrod, M.S., Akselrod, A.E., 2006. New Al_2O_3:C,Mg crystals for radio-photoluminescent dosimetry and optical imaging. Radiat. Prot. Dosim. 119, 218–221.
Chen, J., 2016. OSL point dosimeters for in vivo patient dosimetry. Scintill. Dosim. 329 (Abreviar título do periódico).
D'Amorim, R.A.P.O., Vasconcelos, D.A.A., Barros, V.S.M., Khoury, H.J., Souza, S.O., 2014. Characterization of α-spodumene to OSL dosimetry. Radiat. Phys. Chem. 95, 141–144.
Dieke, G.H., 1968. Spectra and Energy Levels of Rare Earth Ions in Crystals. Interscience Publishers, New York.
Dorenbos, P., 2000. The 5d level positions of the trivalent lanthanides in inorganic compounds. J. Lumin 91, 155–176.
Fernandes, A.C., Osvay, M., Santos, J.P., Holovey, V., Ignatovych, M., 2008. TL properties of newly developed lithium tetraborate single crystals. Radiat. Meas. 43, 476–479.
Jahn, A., Sommer, M., Henniger, J., 2010. 2D-OSL- Dosimetry with beryllium oxide. Radiat. Meas. 45, 674–676.
Marini, A., Valença, J.V.B., Passos, R.A., Souza, S.O., Ciolini, R., d'Errico, F., 2015. Production and characterization of H_3BO_3–Li_2CO_3–K_2CO_3–MgO glass. Radiat. Phys. Chem. 116, 92–94.
McKeever, S.W.S., Moscovitch, M., Townsend, P.D., 1995. Thermoluminescent Dosimetry Materials: Properties and Uses. Nuclear Technology Publishing, Kent.
Oliveira, L.C., Milliken, E.D., Yukihara, E.G., 2013. Development and characterization of MgO: Nd,Li synthesized by solution combustion synthesis for 2D optically stimulated luminescence dosimet. J. Lumin 133, 211–216.
Oliveira, T.M., Lima, A.F., Brik, M.G., Souza, S.O., Lalic, M.V., 2016. Electronic structure and optical properties of magnesium tetraborate: an ab initio study. Comput. Mat. Sci. 124, 1–7.
Orante-Barrón, V.R., Oliveira, L.C., Kelly, J.B., Milliken, E.D., Denis, G., Jacobsohn, L.G., Yukihara, E.G., 2011. Luminescence properties of MgO produced by solution combustion synthesis and doped with lanthanides and Li. J. Lumin 131, 1058–1065.
Patra, G.D., Singh, S.G., Tiwari, B., Singh, A.K., Desai, D.G., Tyagi, M., Gadkari, S.C., 2016. Optically stimulated luminescence in Ag doped $Li_2B_4O_7$ single crystal and its sensitivity to neutron detection and dosimetry in OSL mode. Radiat. Meas. 88, 14–19.
Prokic, M., 1980. Development of highly sensitive $CaSO_4$:Dy/Tm and MgB_4O_7:Dy/tmsintered thermoluminescent dosimeters. Nucl. Instrum. Meth. 175, 83–85.
Prokic, M., 2000. Effect of lithium co-dopant on the thermoluminescence response of some phosphors. Appl. Radiat. Isot. 52, 97–103.
Prokic, M., 2007. Individual monitoring based on magnesium borate. Radiat. Prot. Dosim. 125, 247–250.
Sommer, M., Jahn, A., Henniger, J., 2008. Beryllium oxide as optically stimulated luminescence dosimeter. Radiat. Meas. 43, 353–356.
Souza, L.F., Antonio, P.L., Caldas, L.V., Souza, D.N., 2015. Neodymium as a magnesium tetraborate matrix dopant and its applicability in dosimetry and as a temperature sensor. Nucl. Instrum. Meth.A 784, 9–13.
Souza, L.F., Vidal, R.M., Souza, S.O., Souza, D.N., 2014. Thermoluminescent dosimetric comparison for two different MgB_4O_7: Dy production routes. Radiat. Phys. Chem. 104, 100–103.
Subanakov, A.K., Bazarova, Z.H.G., Nepomnyshchikh, A.I., Perevalov, A.V., Bazarov, B.G., 2014. Synthesis and characterization of dysprosium doped magnesium tetraborate. Inorg. Mat. 50, 485–488.
Twardak, A., Bilski, P., Zorenko, Y., Gorbenko, V., Sidletskiy, O., 2014. OSL dosimetric properties of cerium doped lutetium orthosilicates. Radiat. Meas. 71, 139–142.
Yukihara, E.G., Whitley, V.H., McKeever, S.W.S., Akselrod, A.E., Akselrod, M.S., 2004. Effect of high-dose irradiation on the optically stimulated luminescence of Al_2O_3:C. Radiat. Meas. 38, 317–330.
Yukihara, E.G., McKeever, S.W.S., 2011. Optically Stimulated Luminescence, Fundamentals and Applications. John Wiley & Sons Ltd.
Yukihara, E.G., Milliken, E.D., Oliveira, L.C., Orante-Barro, V.R., Jacobsohn, L.G., Blair, M.W., 2013. Systematic development of new thermoluminescence and optically stimulated luminescence materials. J. Lumin 133, 203–210.
Yukihara, E.G., Coleman, A.C., Bastani, S., Gustafson, T., Talghader, J.J., Daniels, A., Svingala, F.R., 2015. Particle temperature measurements in closed chamber detonations using thermoluminescence from $Li_2B_4O_7$:Ag,Cu, MgB_4O_7:Dy,Li and $CaSO_4$:Ce,Tb. J. Lumin 165, 145–152.
Yukihara, E.G., Milliken, E., Doull, B., 2014a. Thermally stimulated and recombination processes in MgB_4O_7 investigated by lanthanide doping. J. Lumin 154, 251–259.
Yukihara, E.G., McKeever, S.W.S., Akselrod, M.S., 2014b. State of art: optically stimulated luminescence dosimetry – frontiers of future research. Radiat. Meas. 71, 15–24.

Please cite this article in press as: Souza, L.F., et al., Dosimetric properties of MgB_4O_7:Dy,Li and MgB_4O_7:Ce,Li for optically stimulated luminescence applications, Radiation Measurements (2017), http://dx.doi.org/10.1016/j.radmeas.2017.02.009