https://doi.org/10.15415/jnp.2017.51016

Radio-Optically- and Thermally Stimulated Luminescence of $Zn(BO_2)_2:Tb^{3+}$ exposed to Ionizing Radiation

E CRUZ-ZARAGOZA[1*], G CEDILLO DEL ROSARIO[1,2], M GARCÍA HIPÓLITO[2], J MARCAZZÓ[3], J M HERNÁNDEZ A[4], E CAMARILLO[4] AND H MURRIETA S[4]

[1]Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, A. P. 70-543, 04510 Ciudad de México, México

[2]Posgrado en Ciencia e Ingeniería de Materiales, Instituto de Investigaciones en Materiales-UNAM, A. P. 70-360, 04510 Ciudad de México, México

[3]Instituto de Física Arroyo Seco-CIFICEN, CONICET-UNCPBA, Pinto 399, 7000 Tandil, Argentina

[4]Instituto de Física, Universidad Nacional Autónoma de México, A. P. 20-364, 01000 Ciudad de México, México

***Email: ecruz@nucleares.unam.mx**

Published online: August 07, 2017

Abstract The optical absorption of zinc tetraborate at different concentrations of the terbium impurity (0, 0.5, 1, 2, 4, 8 mol%) was analyzed. The radioluminescence (RL) emission spectra was obtained after beta irradiation of a $^{90}Sr/^{90}Y$ source. The RL spectrum showed the characteristics bands of Tb^{3+} with two main emissions at 489 nm and 546 nm which corresponding to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions respectively in this ion. The OSL and TL characteristics have been analyzed. The stimulation blue light (497 nm) of a diode laser at 500 mA was used to bleach the thermoluminescent (TL) signals obtained with 5Gy of ^{60}Co source. The two main glow peaks (79 and 161 °C) are sensitives under 497 nm stimulation, and they were shifted to higher temperature values and faded their TL intensities. Similar behavior of TL glow curves before and after OSL stimulation with blue light was observed when the samples were exposed to 30 Gy gamma dose of ^{137}Cs irradiator. The OSL signal response was linear with the dose range of 1-10 Gy and increased their response up to 200 Gy gamma dose. The OSL shows a bleaching sensitive shallow traps and diminishing the intensity of the TL glow curves remaining a complex traps distribution. The RL, TL and OSL properties were investigated in $Zn(BO_2)_2:Tb^{3+}$ phosphor.

Journal of Nuclear Physics, Material Sciences, Radiation and Applications
Vol-5, No-1, August 2017
pp. 169–178

Cruz-Zaragoza, E
Del Rosario, GC
Hipólito, MG
Marcazzó, J
Hernández A, JM
Camarillo, E
Murrieta S, H

Keywords: Optically Stimulated Luminescence; Radioluminescence; Thermoluminescence; Radiation effects; Zinc borate

1. INTRODUCTION

The thermoluminescence (TL) and photoluminescence properties, using various alkaline earth ions (Li, Ca, Mg, Ba, Sr, Zn) based on tetraborate and various dopants, have been analyzed [Schulman et al., 1967; Takenaga et al., 1980; Sabharwal & Sangeeta, 1998; Furetta et al., 1999; Santiago et al., 2001; Li et al., 2007; Cruz-Zaragoza et al., 2016; Cedillo Del Rosario et al., 2017]. Important features of borate material such as near soft tissue, high TL sensitivity and its good performances for gamma, beta and neutron dosimetry have been the base for enhancement of this TL phosphor [Kazanskaya et al., 1974; Prokic, 1980; Li et al., 2008]. In this case, the zinc tetraborate has a high effective atomic number (Z_{eff} = 22.4) close to that of CaF_2 (16.90) and it last is near to the compact bone (13.59) [Bos, 2001]. However, the thulium-doped zinc tetraborate showed a TL intensity peak at ~300 °C and it was more higher than that of LiF:Mg,Ti dosimeter [Annalakshmi et al., 2014]. In the case of $Zn(BO_2)_2$ borate doped with terbium, the photoluminescence emission bands (490, 543, 584 and 620 nm) were ascribed to Tb^{3+} impurity when the borate were excited with wavelength 261 nm [Li et al., 2007]. It is well known that an important property of some phosphors is the radioluminescence (RL) [Santiago et al., 1998; Krbetschek & Trautmann, 2000], and in our Tb^{3+} doped zinc borate is present too.

The RL phenomenon is the luminescence emission *in situ* and in real-time during irradiation from some natural and synthetic material. It has been analyzed mainly for dating purposes and the RL has been also proposed to be uses for radiation dosimetry [Petö, 1996; Petö & Kelemen, 1996; Aznar; 2005]. Because the RL measurement of the phosphors is possible to carry out in real-time while the TL is obtained post-irradiation of the samples, then RL has an important advantage to TL dosimetry. It is accepted that to produce the TL response which is come from the recombination of charges mainly electron-hole in the band gap of the solid phosphor previously irradiated. Similar phenomenon occurred when the phosphor was stimulated by light of an appropriate wavelength and it is known as optically stimulated luminescence (OSL). The OSL is ascribed to the transitions of charge carriers at different trapping levels associated with impurities and point defects present in the lattice of the crystalline solid [Chen & Pagonis, 2011]. Various efforts [Huntley et al., 1985; McKeever & Chen, 1997; Olko, 2010] have been dedicated to analyze the TL and OSL properties related to the common traps in the luminescent phosphors material, then there are interesting features to investigate in the material with both TL and OSL properties. The aim of this paper is to study the thermoluminescent and optically stimulated luminescence properties, including the RL emission, of the $Zn(BO_2)_2$ doped with terbium ion.

2. EXPERIMENTAL PROCEDURE

2.1 Samples preparation

The terbium-doped zinc borate phosphor was synthesized by the solvent evaporation method as reported in a recent paper [Cedillo Del Rosario et al., 2017] obtaining a higher TL sensitivity under gamma and beta radiation. All zinc borate samples were sintered at 800 °C for 18 h or at 900 °C during 16 h, in both cases the single $Zn(BO_2)_2$ phase was obtained. The XRD patterns for crystal structure and phase **of the** $Zn(BO_2)_2$ were identified and they previously were reported [Cedillo Del Rosario et al., 2017]. Samples of undoped and terbium-doped $Zn(BO_2)_2$ were selected in powder form with less than 74 μm particle sizes. For absorption measurements some pellets of thickness 1 mm and diameter 6mm were used. These particles sizes were selected to obtain the well-defined TL and OSL signals.

2.2 Irradiation samples

Beta-^{90}S/^{90}Y irradiations using a 0.017 Gy/min dose rate for radioluminescence emission, and gamma-^{60}Co Gammacell-200 Nordion with 0.1689 Gy/min and from ^{137}Cs Gammacell-3000 Elan Best Theratronics (9.42 Gy/min) self-irradiators were used to carried out the irradiations for TL and OSL measurements. The samples were placed in acrylic plates with 3 mm thickness to have the electronic equilibrium condition during the irradiations. Previously to irradiation the samples received the annealing with 400 °C for 30 min in the oven. Samples were irradiated at room temperature. The TL and OSL measurements were done on double samples of 12.00±0.01 mg. Glow curves were obtained in a Harshaw model 3500 TLD reader, and the OSL and RL signals were measured by the same photon counting in an OSL equipment made in our Luminescence and Dosimetry Laboratory at the Nuclear Science Institute (ICN-UNAM). The glow curves were obtained at the same heating rate (2 °C s^{-1}) from room temperature up to 450 °C and with nitrogen atmosphere in order to avoid the spurious TL signals. The optical absorption of the pellets samples was carried out in a UV-VIS spectrophotometer Cary 5000 at Optical Property of Solids Laboratory at Physics Institute (IF-UNAM).

3. RESULTS AND DISCUSSION

3.1 Optical Absorption and Radioluminescence

The optical absorption of undoped and terbium-doped $Zn(BO_2)_2$ samples at different concentrations (0-8 mol%) were obtained before gamma irradiation (Figure 1). Two main bands observed around 234 and at 278 nm were related to the structure of the material, and they were sensible and increased with the terbium dopant concentration in the lattice of the zinc tetraborate. However, in the samples with higher terbium concentration (8 mol%) fourth optical absorption bands were observed at: 487, 547, 589 and 620 nm, which were related to the $^5D_4 \rightarrow {}^7F_J$ (J = 3, 4, 5, 6) electronic transitions of the Tb^{3+} ion [Çetin et al., 2007]. Following the samples were exposed to gamma radiation from ^{60}Co at 3 and 6 kGy doses and not apparent change in the optical absorption was observed, i.e., absent bands associated to the color centers and to the Tb^{4+} ion, in this last case the finding is in agreements to those found by others authors [Li et al., 2007].

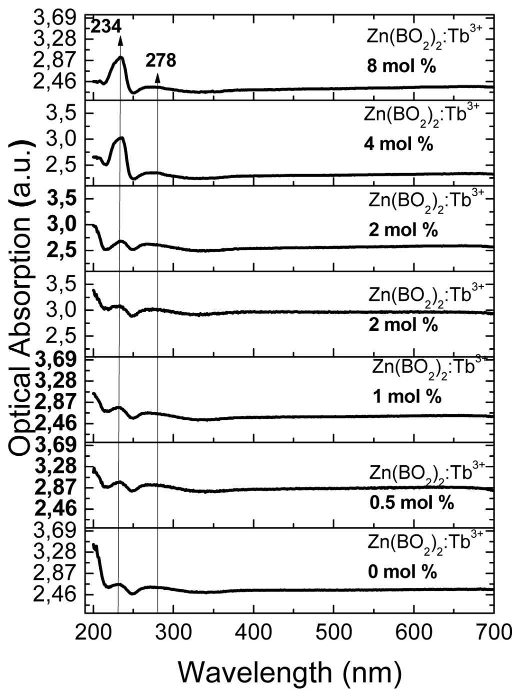

Figure 1: Optical absorption of undoped $Zn(BO_2)_2$ and $Zn(BO_2)_2:Tb^{3+}$ [0.5-8 mol%].

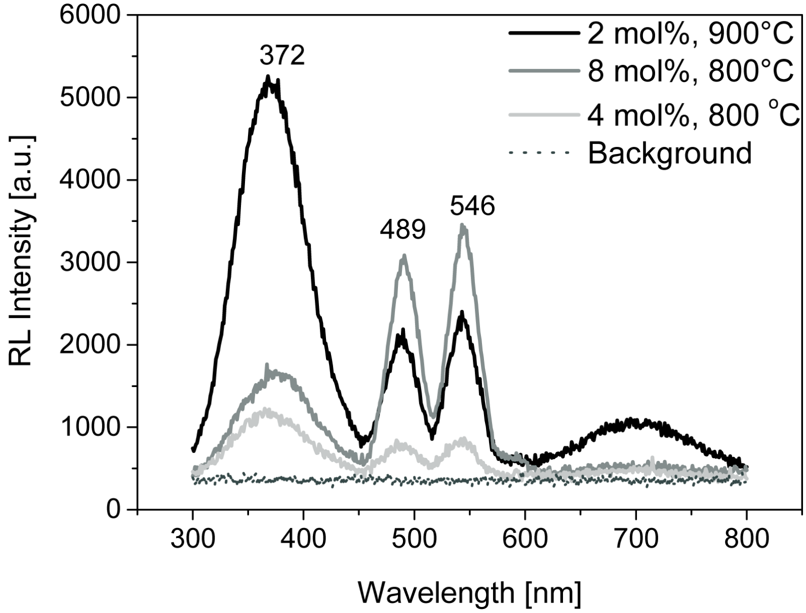

Figure 2: Radioluminescence (RL) spectra of $Zn(BO_2)_2$:Tb^{3+} with the main emissions at 489 and 546 nm belonging to the terbium impurity. The samples were exposed to $^{90}Sr/^{90}Y$ source

The RL emission was obtained from the samples during beta irradiation. It can be seen in figure 2 three bands peaked at 372, 489 and 546 nm for all terbium-doped samples. The first band (372 nm) and a broad band at 700 nm were observed too in the undoped sample. These bands should be assigned to the intrinsic emission of the structure of the zinc tetraborate or some phase present in the material. It seems that the sample with higher sintered temperature (900 °C) presents a highest RL intensity of their first emission band. In particular, the peaks centered at 489 and 546 nm can be ascribed to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+}.

3.2 Thermoluminescence and OSL Properties

Because the zinc tetraborate presents a broad optical absorption band, it was decided to use a blue light (467.5 nm) from LED to carried out the optical bleaching of the glow curves. At least three glow peaks (Figure 3) were observed: 80, 160 and 282 °C, in the glow curves obtained at 5 Gy of ^{60}Co. At the end of 60 min of illumination samples irradiated, the first two glow peaks were shifted at higher temperature: 85 and 189 °C. The glow peaks seem very

Cruz-Zaragoza, E
Del Rosario, GC
Hipólito, MG
Marcazzó, J
Hernández A, JM
Camarillo, E
Murrieta S, H

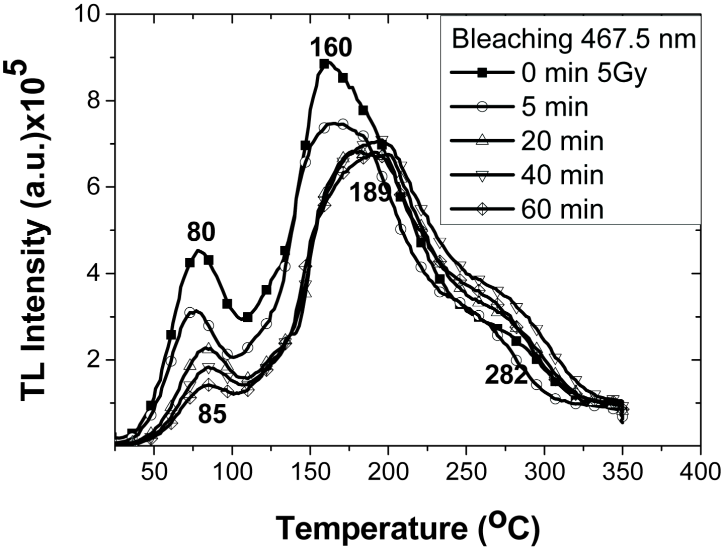

Figure 3: Optical bleaching by blue light of LED (467.5 nm) effect on TL glow curves obtained between 0 and 60 min from zinc tetraborate doped with Tb^{3+} [0.5 mol%]. The gamma-^{60}Co dose was 5 Gy.

sensible to the blue light, and possible some traps are in relationship with the optically stimulated luminescence. The broad glow curves seem a traps distribution are in the band gap of zinc tetraborate phosphor and overlapping of glow peaks remaining under the whole glow curve. The glow peak at 80 °C was partially bleaching and may related to the terbium impurity in the sample, while the bleached peak at 189 °C may influenced by the blue light on the structure of the material. A single glow peak at that position temperature (190 °C) was observed in dysprosium and sodium co-doped MgB_4O_7 phosphor [Furetta et al., 2000], and that peak can be in relation with the structure of tetraborate.

The terbium-doped tetraborate samples at different concentrations were irradiated with 30 Gy in order to fill the traps for OSL signals detection (Figure 4). At lower terbium concentration, 0.5 and 1 mol%, the OSL intensity signal was very weak and it was increased as the concentration increases. At higher concentration, 8 mol%, the OSL presents very high intensity, this behavior was similar for RL emission where the 489 and 546 nm were the most higher bands intensity. Furthermore, the OSL response was investigated between 1 and 200 Gy using gamma radiation from ^{137}Cs. The linear dose response was from 1 to 10 Gy and the OSL response was proportional to the

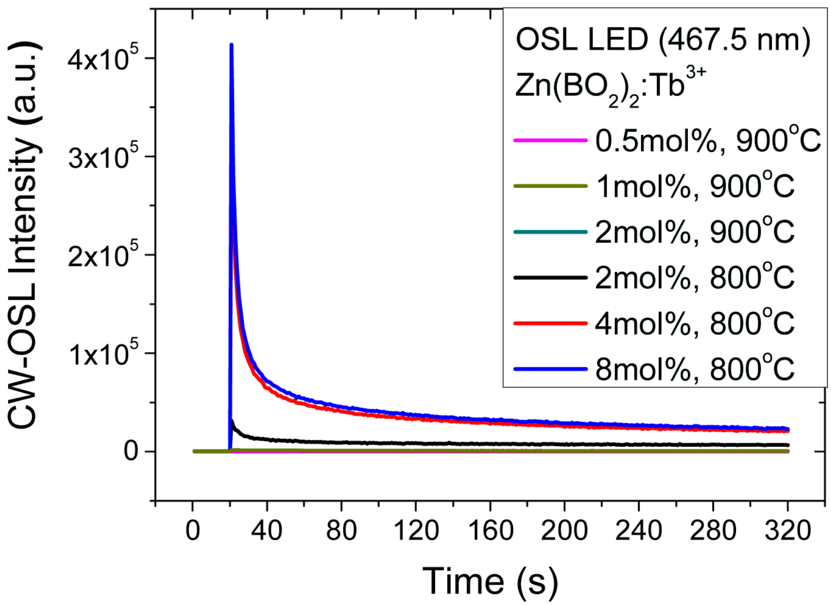

Figure 4: Continuous-wave optically stimulated luminescence (CW-OSL) of zinc tetraborate doped with Tb^{3+} [0.5-8 mol%] stimulated with blue light of diode laser (LED). Samples were irradiated with ^{137}Cs at 30 Gy.

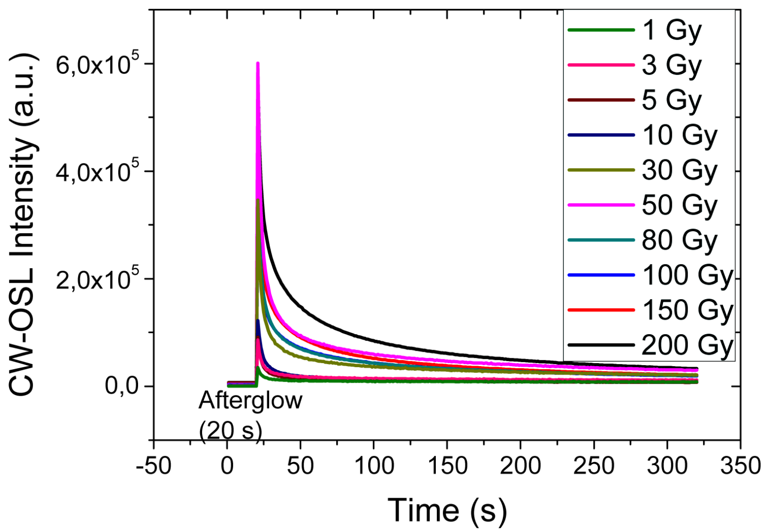

Figure 5: OSL signals response of terbium-doped zinc tetraborate [4 mol%] exposed between 1 and 200 Gy gamma doses of ^{137}Cs Gammacell-3000 Elan self-irradiator.

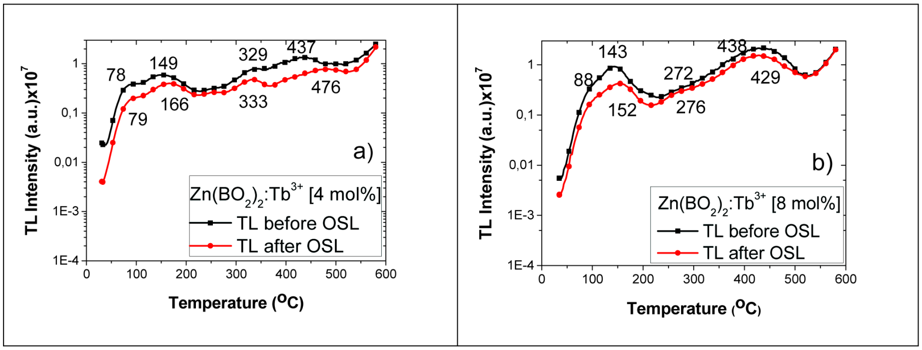

Figure 6: TL glow curves before and after OSL read out of the samples with Tb^{3+}, a) 4 mol% and b) 8 mol%, using blue light (497 nm) during stimulation. The gamma-^{137}Cs dose was 10 Gy.

number of trapped charges taking place in the OSL process. Followed an increasing stage of the dose response up to 200 Gy, implying that the trapped charge concentration should also grow with dose. Finally, the relationship between OSL and TL traps were analyzed for 4 and 8 mol% of terbium concentration which have the most higher TL and OSL intensities. Figures 6 a, b, shown the TL glow curves before and after OSL measurement was carried out in the samples using blue light (497 nm). All TL peaks (Figure 6 a, b) shifted at higher temperature suggesting some traps were sensitive to OSL stimulation but remain the complex distribution of traps for TL glow curves in the band gap of zinc tetraborate phosphor.

CONCLUSIONS

The optical absorption, radioluminescence (RL), TL and OSL properties of the $Zn(BO_2)_2:Tb^{3+}$ were investigated. The bands of the RL spectra at 372 and 700 nm can be attribute to the intrinsic emission of the structure of the zinc tetraborate. The RL peaks centered at 489 and 546 nm were ascribed to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+} impurity in the lattice of the phosphor. These bands growth as the impurity concentration increases. The TL and OSL properties by using gamma and beta radiation, respectively, shown that the zinc tetraborate doped with terbium present these properties and it is an interesting material deserving further study. The TL traps are in relation to the those of OSL property of this zinc tetraborate. The OSL linear dose-response was between 1 and 10 Gy gamma dose. A good reproducibility and fading of the OSL signals was found. Also the RL and OSL response at different impurity concentration was analyzed and it was found that zinc tetraborate at higher concentrations of terbium makes more intensity the RL emission and TL intensity and OSL linear response during irradiation.

ACKNOWLEDGEMENTS

We want to acknowledge the technical work from staff: Adriana Tejeda, Omar Novelo and Josué Romero (IIM-UNAM) for characterizing our samples using XRD, SEM and EDS. Also thanks Dr. Jesus Roman Lopez (CONACYT and ICN-UNAM) for help in RL measurements. The first author (Guillermina Cedillo) acknowledges the financial support from CONACYT Mexico for the doctoral fellowship number 202043. This work was partially supported by PAPIIT-DGAPA UNAM under project number IN112617.

REFERENCES

[1] Annalakshmi, O., Jose, M.T., Madhusoodanan, U., Subramanian, J., Venkatraman, B., Amarendra, G., Mandal, A.B. (2014). Thermoluminescence dosimetric characteristics of thulium doped ZnB_2O_4 phosphor. J. Lumin. **146**, 295–301.

[2] Aznar, M.C. (2005). Real-time in vivo luminescence dosimetry in radiotherapy and mammography using Al_2O_3:C. Risø-PhD-12(EN), Denmark.

[3] Bos, A.J.J. High sensitivity thermoluminescence dosimetry. Nucl. Instrum. Methods B 184, 3-28 (2001).

[4] Cedillo Del Rosario, G., Cruz-Zaragoza, E., García Hipólito, M., Marcazzó, J., Hernández, J.M.A., Murrieta H.S. (2017). Synthesis and stimulated luminescence properties of $Zn(BO_2)_2:Tb^{3+}$. Applied Radiation and Isotopes **127,** 103–108.

[5] Çetin, A., Kibar, R., Ayvacikli, M., Tuncer, Y., Buchal, Ch., Townsed, P.D., Karali, T., Selvi, S., Can, N. (2007). Optical properties of Tb implantation into ZnO. Surface & Coatings Technology **201**, 8534–8538.

[6] Chen, R., & Pagonis, V. (2011). Thermally and Optically Stimulated Luminescence: A Simulation Approach. United Kingdom: John Wiley & Sons Ltd.

[7] Cruz-Zaragoza, E., Furetta, C., Marcazzó, J., Santiago, M., Guarneros, C., Pacio, M., Palomino, R. (2016). Beta radiation induced luminescence of polycrystalline Cu-doped $Li_2B_4O_7$. J. Lumin. **179,** 260–264.

[8] Furetta, C., Kitis, G., Weng, P.S., Chu, T.S. (1999) Thermoluminescence characteristics of MgB_4O_7:Dy,Na. Nucl. Instrum. Methods A **420,** 441–445.

[9] Furetta, C., Prokic, M., Salamon, R., Kitis, G. (2000). Dosimetric characterization of a new production of MgB_4O_7:Dy,Na thermoluminescent material. Applied Radiation and Isotopes **51,** 243–250.

[10] Huntley, D.J., Godfrey-Smith, D.I., Thewalt, M.L.W. (1985). Optical dating of sediments. Nature **313**, 105–107.

[11] Kazanskaya, V.A., Kuzmin, V.V., Minaeva, E.E., Sokolov, A.D. (1974). Magnesium borate radiothermoluminescent detectors. In Proc. 4th Int. Conf. Luminescence Dosimetry (pp. 581-592). Krakow, Poland.

[12] Krbetschek, M.R., Trautmann, T. A (2000). spectral radioluminescence study for dating and dosimetry. Radiat. Meas. **32**, 853–857.

[13] Li, J; Zhang, C.X., Tang, Q., Zhang, Y.L., Hao, J,Q., Su, Q., Wang, S.B. (2007). Synthesis, photoluminescence, thermoluminescence and dosimetry properties of novel phosphor $Zn(BO_2)_2$:Tb. J. Phys. Chem. Solids **68**,143-147.

[14] Li, J., Zhang, C., Tang, Q., Hao, J., Zhang, Y., Su, Q., Wang, S. (2008). Photoluminescence and thermoluminescence properties of dysprosium doped zinc metaborate phosphors. J. Rare Earths **26**, 203–206.

[15] McKeever, S.W.S., & Chen R. (1997). Luminescence models. Rad. Meas. **27**(5/6), 625-661.

[16] Olko, P. Advantages and disadvantages of luminescence dosimetry (2010). Rad. Meas. **45**, 506–511.

[17] Petö, Á. (1996). Relative yields of radioluminescence and thermoluminescence in several TL phosphors. Radiat. Prot. Dosim. **65(1/4),** 123–126.

[18] Petö, Á., Kelemen, A. (1996). Radioluminescence properties of alpha-Al_2O_3 TL dosemeters. Radiat. Prot. Dosim. **65,** 139–142.

[19] Prokic, M. (1980). Development of highly sensitive $CaSO_4$:Dy/Tm and MgB_4O_7:Dy/Tm sintered thermoluminescent dosimeters. Nucl. Instrum. Methods **175,** 83–86.

[20] Sabharwal, S.C., (1998). Sangeeta. Effect of sodium doping on TL and optical properties of barium borate (BaB_2O_4) single crystals. J. Crystal Growth **187**, 253-258.

[21] Schulman, J.H., Kirk, R.D., West, E.J. (1967). Use of lithium borate for thermoluminescence dosimetry. In Proc. Int. Conf. on Luminescence Dosimetry, US AEC Symposium series CONF-650637 (pp. 113-117). Stanford University, USA.

[22] Santiago, M., Graseli, C., Caseli, E., Lester, M., Lavat, A., Spano, F. (2001). Thermoluminescence of SrB_4O_7:Dy. Phys. Stat. Sol. (a) **185(2),** 285–289.

[23] Santiago, M., Lester, M., Caseli, E., Lavat, A., Ges, A., Spano, F., Kessler, C. (1998). Thermoluminescence of sodium borates compounds containing copper. J. Mater. Sci. Letters **17,** 1293–1296.

[24] Takenaga, M., Yamamoto, O., Yamashita, T. (1980). Preparation and characteristics of $Li_2B_4O_7$:Cu phosphor. Nucl. Instrum. Methods **175**, 77–78.