Journal of Thermal Analysis and Calorimetry (2018) 133:1327–1333
https://doi.org/10.1007/s10973-018-7200-4

Investigation of neutron sensitivity of un-doped and Dy-doped CaB_4O_7 for thermoluminescence applications

Sera İflazoğlu[1,2] · Ayşen Yılmaz[2] · Vural E. Kafadar[1] · A. Necmeddin Yazıcı[1]

Received: 6 November 2017 / Accepted: 12 March 2018 / Published online: 23 March 2018

Abstract
In this study, thermoluminescence characteristics of un-doped and Dy-doped calcium tetraborate (CaB_4O_7) compounds are reported. The polycrystalline powder samples of un-doped and Dy-doped CaB_4O_7 were prepared by a solid-state reaction at high-temperature method. The identification and characteristics of the obtained compounds were determined by X-ray diffraction, Fourier transform infrared analysis, differential thermal analysis, thermogravimetric analysis, and scanning electron microscopy. The glow curves were obtained using a thermoluminescent reader. Neutron sensitivity, dose–response, and heating rate of CaB_4O_7 compounds were determined by using a bare ^{252}Cf mixed neutron + gamma (n + γ) source, and dose response results are compared to those of Harshaw TLD-600 and TLD-700 neutron dosimeters (^{6}LiF:Mg,Ti and ^{7}LiF:Mg,Ti). The sensitivity of CaB_4O_7:Dy (0.5%) sample is approximately 4.35 and 3.36 times higher than that of TLD-600 and TLD-700, respectively.

Keywords CaB_4O_7 · CaB_4O_7:Dy · Thermoluminescence · Neutron dosimetry

Introduction

Nowadays, in the increasing artificial radiation environment, development of neutron dosimeter is a needed study against the nuclear industry. The detection of neutrons is a very significant and special subject of the dosimeter. In radiation oncology and nuclear fuel cycle industry, the neutron dosimeter holds an important place. Personal neutron dosimeter is a very difficult area, and although few studies have been made on this subject in the world, there has not been such a study in Turkey yet. Therefore, the development of sensitive neutron dosimeter thermoluminescent constitutes a great importance for the measurement of neutron dose. Neutron dosimetry is especially difficult due to the unavoidable presence of gamma rays and the fact that most detection systems respond to both gamma rays and neutrons. In the medical and biological sciences, a popular method used to determine the neutron and gamma-ray component in mixed n-γ radiation fields has been paired ionization chambers, i.e., a hydrogenous ionization chamber to detect neutrons and an additional non-hydrogenous chamber designed to be as neutron insensitive as possible [1, 2]. Calcium borate compounds have an effective atomic number 12.5, and they are promising materials to develop in order to use them in environmental applications [3]. Thermally stimulated luminescence studies of borate compounds were started in 1974 by the work of Kazanskaya [4]. Since then, detailed TL studies on various alkali and alkaline earth tetraborates were reported. Thermoluminescence characteristics of sintered CaB_4O_7-containing activators such as Cu, Pb, Eu, or Dy have been first investigated by Fukuda et al. [5]. It was found that the TL intensity depends not merely on the concentration of dopant, but also on the type of dopant and the preparation methods. Thereafter, Manam and Sharma [6] reported TL of un-doped and Cu- and Mn-doped CaB_4O_7. TL of Dy-doped CaB_4O_7 phosphors has been investigated, and the material was found suitable for ionizing radiation dosimeter.

CaB_4O_7:Dy is a relatively unstudied TL phosphor, which is suggested as an alternative to LiF (TLD-100) for

✉ Sera İflazoğlu
sera_iflazoglu@hotmail.com

[1] Department of Engineering Physics, University of Gaziantep, 27310 Gaziantep, Turkey

[2] Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

the dosimetry of ionizing radiation using thermoluminescence because of its linear response dose, negligible fading, and excellent reusability [7–9]. During the last few years, CaB_4O_7:Dy TL phosphor material has been produced by Dr. Prokic in Belgrade, which shows high sensitivity and good TL characteristics. The glow curve of this material shows one prominent TL peak at about 220 °C, and its sensitivity is approximately eight times higher than that of LiF (TLD-100). There was no fading of the emitted thermoluminescence for a storage period of months in the dark at ambient temperature [10]. Doped alkaline earth borates are among the most promising materials suitable for personal dosimetry due to their high sensitivity and, in some cases, their TL tissue-like properties for radiation absorption. CaB_4O_7 is particularly advantageous because of its high mechanical strength and non-hygroscopicity [11].

Experimental

CaB_4O_7 as a powder form was synthesized by high-temperature solid-state reaction method. $CaCO_3$ (98.5% pure, Merck) and $H_3(^{10}B)\ O_3$ (96% pure, Nukem Isotopes) were mixed with stoichiometric amounts, and 15.0 mL of distilled water was added to obtain calcium tetraborate product. The mixture was heated and stirred on magnetic stirrer around 90 °C until a homogeneous mixture was obtained. The heating and stirring of the mixture continued till three/four parts of water was evaporated. Then, highly viscous mixture was preheated in a muffle furnace up to 750 °C with 4 °C min^{-1} heating rate. It was kept at this temperature for 4 h in order to get rid of residual water in the mixture. After the preheating stage, the cooled sample re-grinded in agate mortar. Afterward, the furnace was adjusted to heat the sample up to 850 °C with 4 °C min^{-1} heating rate and retention time was 10 h at this temperature. Intermittent grinding of the mixture facilitates discharge of gases properly while heating solid mixture.

The expected reaction is given below:

$$CaCO_3(s) + 4H_3BO_3(s) \rightarrow CaB_4O_7(s) + CO_2(g) + 6H_2O(g) \quad (1)$$

The Dy-doped CaB_4O_7 sample was prepared in a similar manner by taking the starting material in stoichiometric ratio and adding desired (0.5% Dy) amount of Dy_2O_3 in the mixture. The metal ion doping of the calcium tetraborate compound was carried out by the calcium tetraborate synthesis described above.

The un-doped and Dy-doped CaB_4O_7 samples produced were characterized by XRD, FTIR, DTA/TGA, and SEM methods. The X-ray diffractometer employed for the crystal structure investigations was a Rigaku MiniFlex X-ray diffractometer with a radiation source of Cu-Kα line (λ = 1.54056 Å) to confirm phase purity. The scanning rate within a 2θ range of 3°–90° is 2° min^{-1}. The XRD patterns of produced un-doped and Dy-doped CaB_4O_7 samples were matched with standard data JCPDS (Card No: 31-0253). The vibrational modes of the produced materials were studied by VARIAN 1000 FTIR spectrometer between wave numbers 500 and 4000 cm^{-1} with 128 scans. FTIR spectrometer is equipped with attenuated total reflectance (ATR). Resolution was chosen as 8 cm^{-1}.

In order to assess the thermal behavior of the samples as well as their chemical stability, differential thermal analysis was carried out in an aluminum crucible at a heating rate of 10 °C min^{-1} in atmospheric condition using a Perkin Elmer TGA/DTA simultaneous thermogravimetric analyzer and a differential thermal analyzer. Heating interval was chosen from 30 and 930 °C. The SEM analyses were performed by using JEOL 6390 LV, which has magnification range between 12 and 900,000, variable pressure between 2 and 133 Pa, and acceleration voltage of 0.1–30 kV. ^{252}Cf source was used for the production of neutron radiations. The samples were irradiated for 1 min at room temperature with a ^{252}Cf neutron + gamma source delivering about 0.08 Gy min^{-1} radiation. The all samples were exposed to neutron, ^{252}Cf radiations at room temperature. The average energy of the neutron source is around 2.3 MeV. The neutron source was purchased from Eckert and Ziegler Isotope Products GmbH, and its calibration was also done by the manufacturer on March 01, 2015. Thermoluminescence glow curves of un-doped and Dy-doped calcium tetraborate compounds were obtained by using a Harshaw QS 3500 Manual type TL reader. The reader was interfaced to a PC in which the TL signals were studied and analyzed. Glow curves were measured using a platinum planchet at a linear heating rate of 1 °C s^{-1} from 50 up to 400 °C.

Result and discussions

XRD analyses

The XRD patterns obtained for the material produced showed that production of calcium tetraborate was successful since all of the main peaks of calcium tetraborate coincide with those of the material produced. Most intense peaks of the XRD pattern of calcium tetraborate sample were assigned with the help of JCPDS card no: 31-0253 data of calcium tetraborate with monoclinic structure and cell parameters a = 12.264 Å, b = 9.895 Å, and c = 7.796 Å. Moreover, it was seen that the dopant added did not interfere with the crystal structure. Figure 1 displays the XRD results

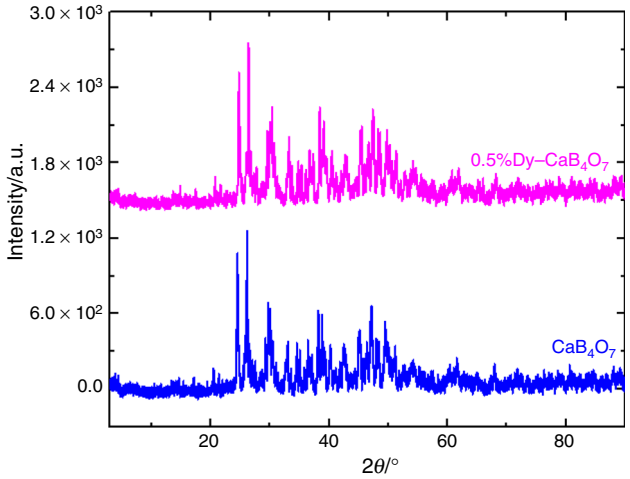

Fig. 1 XRD patterns of un-doped and 0.5% Dy-doped CaB_4O_7 samples

for calcium tetraborate produced by high-temperature solid-state synthesis and doped by solid-state doping.

FTIR analyses

Fourier transform infrared spectroscopy (FTIR) was employed as an auxiliary characterization alternative. Figure 2 displays the spectral resemblance between un-doped calcium tetraborates and %0.5 Dy-doped calcium tetraborate produced by high-temperature synthesis. The existence of characteristic B–O trigonals and tetragonals in the spectrum confirmed the structure. According to the results of FTIR spectroscopy measurements, the locations of the vibration bands of borate compounds before and after doping are the same. No new bond formation has been observed due to the added metals. FTIR spectra were fitted

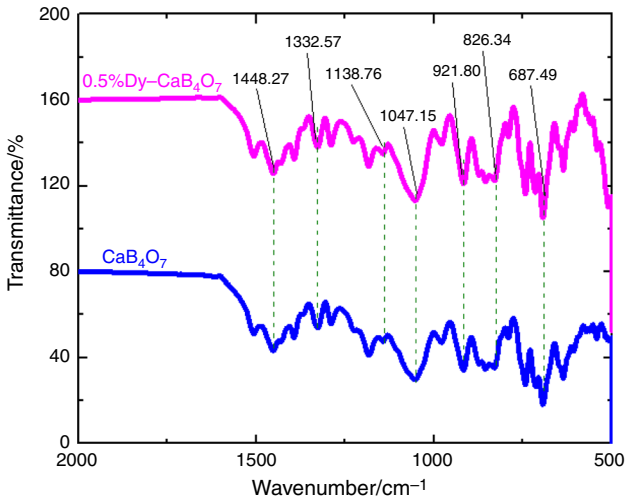

Fig. 2 FTIR spectra of un-doped and 0.5% Dy-doped CaB_4O_7 samples

with the literature values for BO_3 and BO_4 ring structure vibrations between 600 and 1600 cm^{-1} [12–16]. In addition, the formation of new vibrational band was not detected after the addition of dopants into borate samples. The characteristic vibrational modes of borate compounds could be given as follows: the asymmetric stretching vibration band of B–O in BO_3 unit at ~ 1448.27 and ~ 1332.57 cm^{-1}, an asymmetric stretching band of B–O in BO_4 unit assigned at ~ 1138.76 cm^{-1}, the broad bands at ~ 921.80 and ~ 826.34 cm^{-1} assigned as symmetric stretching of B–O in BO_4 and BO_3 rings, respectively. The weak band observed at ~ 687.49 cm^{-1} is assigned as out-of-plane bending of B–O in BO_3 unit [16]. The absorption peaks attribute to borate network according to Table 1.

DTA/TGA analyses

Temperature dependence to mass change and thermal stability of the synthesized compounds have been studied by using Pyris 1 Perkin Elmer DTA/TGA Analyzer. The measurement was carried out at nitrogen atmosphere at the range of 30 and 930 °C. The heating rate was 10 °C s^{-1}. DTA and TGA results of un-doped and 0.5% Dy-doped CaB_4O_7 compounds are illustrated in Fig. 3. In figures, it is observed that two samples were thermally stable in the particular desired range.

SEM results

Scanning electron microscopy was basically used to compare the morphologies of products of high-temperature solid-state synthesis methods. In the given study, the SEM images of developed samples are shown in Figs. 4 and 5. As seen, it could be said that the particles size are in the range of ~ 5 to 100 μm, and there is homogeneous distribution among particles. These SEM images show that the compounds are not exactly crystalline. The compounds are thought to be molten. It can be said that the particles are 'agglomerate' because they appear to be attached.

TL results

The radiation dosimetric performance of thermoluminescence (TL) materials is highly dependent upon shape of its glow curve intensity and peak temperatures of the glow peaks. Thermoluminescence glow curves of synthesized un-doped and Dy-doped calcium tetraborate samples were utilized to determine whether those samples show ideal TL glow curve structure and TL intensity for neutron measurements or not. The samples that have sufficient TL intensity and proper TL structure were analyzed for further dosimetric measurements such as dose–response and heating rate. ^{252}Cf neutron source

Table 1 Frequencies and their assignments for FTIR spectra of borate compounds

Frequencies/cm^{-1}	Assignment	References
~ 685	B–O–B bending vibration	[10]
~ 700	B–O–B bending vibration in borate ring	[10–12]
850–1100	B–O stretching of tetrahedral BO_4^-	[10–12]
600–800	Bending vibrations of various borate	[11, 12]
~ 907	B–O stretching vibration of BO_4 units in tri-, tetra-, and pentaborate groups	[10, 13]
~ 1400	B–O stretching trigonal BO_3 units	[10–14]

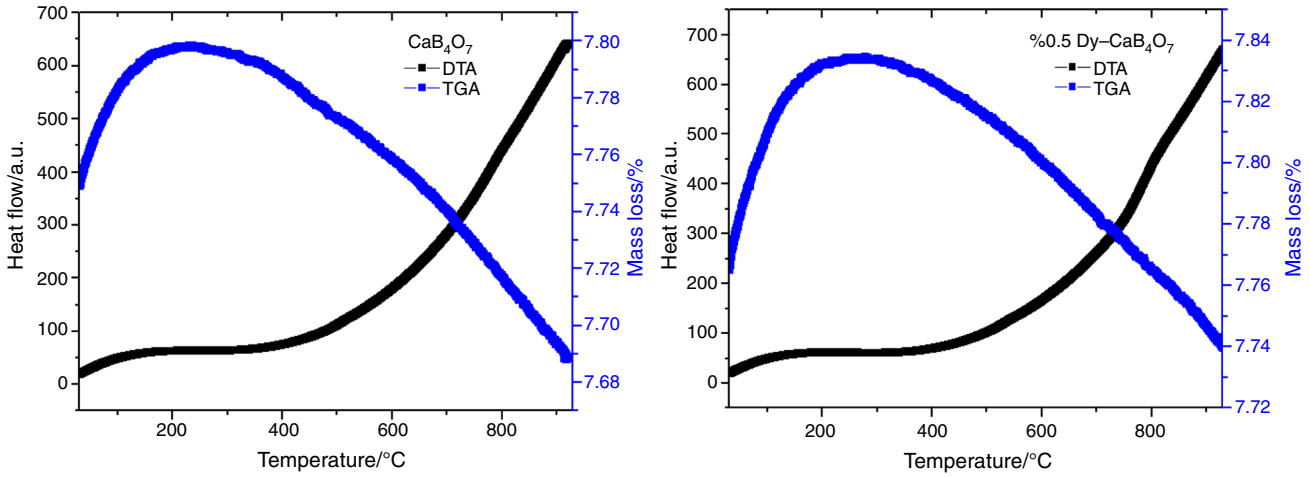

Fig. 3 DTA/TGA curves of un-doped and 0.5% Dy-doped CaB_4O_7 samples

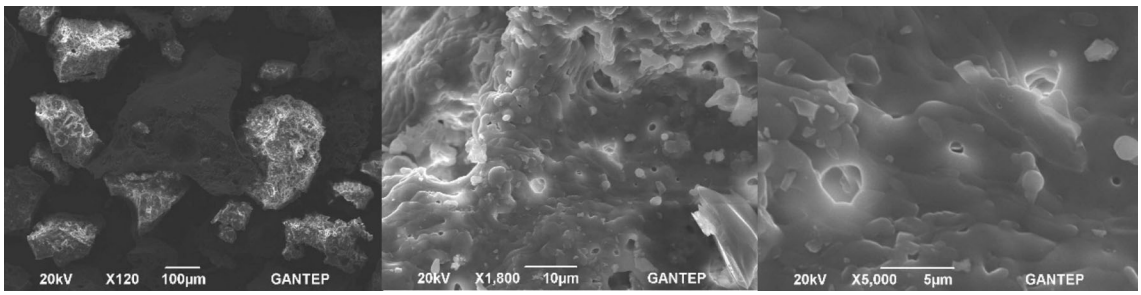

Fig. 4 SEM images of un-doped CaB_4O_7 sample

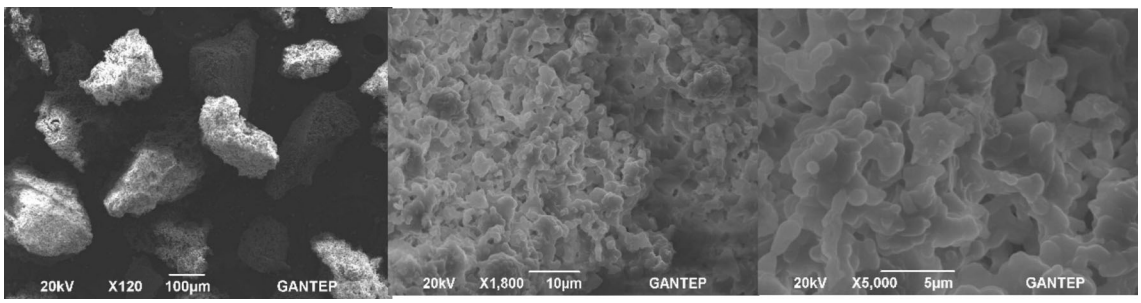

Fig. 5 SEM images of 0.5% Dy-doped CaB_4O_7 sample

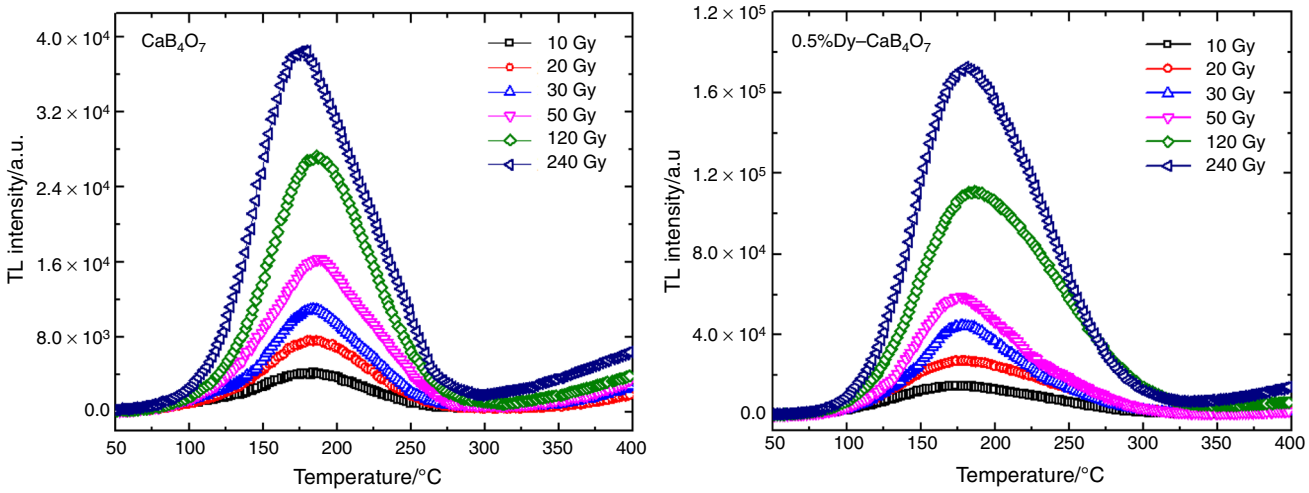

Fig. 6 Glow curves of un-doped and 0.5% Dy-doped calcium tetraborate compound corresponding to various radiation doses using ^{252}Cf neutron source with a heating rate of 1 °C s^{-1}

was used for thermoluminescence measurements made with the aim of developing neutron dosimetry. The average energy of the neutron source is around 2 MeV. Background TL measurements were taken for each borate compound before each irradiation. Measurements were made at a heating rate of 1 °C s^{-1} at 50–400 °C. After thermoluminescence measurements, it was observed that borate compounds were not sensitive to neutron. After annealing the compound for 1 h at 600 °C, neutron-sensitive borate compounds were obtained. Before each thermoluminescence measurement, each compound was annealed at 600 °C for 1 h. The XRD measurements of the annealed compounds were taken after annealing. According to the XRD measurement results, no change in the structure of the compounds was observed after annealing. Dose–response and heating rate measurements of the obtained borate compounds were performed.

TL dose–response results of un-doped and 0.5% Dy-doped CaB_4O_7

The characterization dose–response graphs of the synthesized calcium tetraborate compounds are given in Fig. 6. The un-doped calcium tetraborate and 0.5% Dy-doped calcium tetraborate are exhibiting sensitivity to neutron radiation. Calcium tetraborate compounds, which are sensitive to neutron, show a linear increase in two compounds compared to increasing doses relative to the dose–response results. No significant change in peak temperatures versus increasing dose amount of calcium tetraborate compounds has been observed. Figure 6 shows that the un-doped

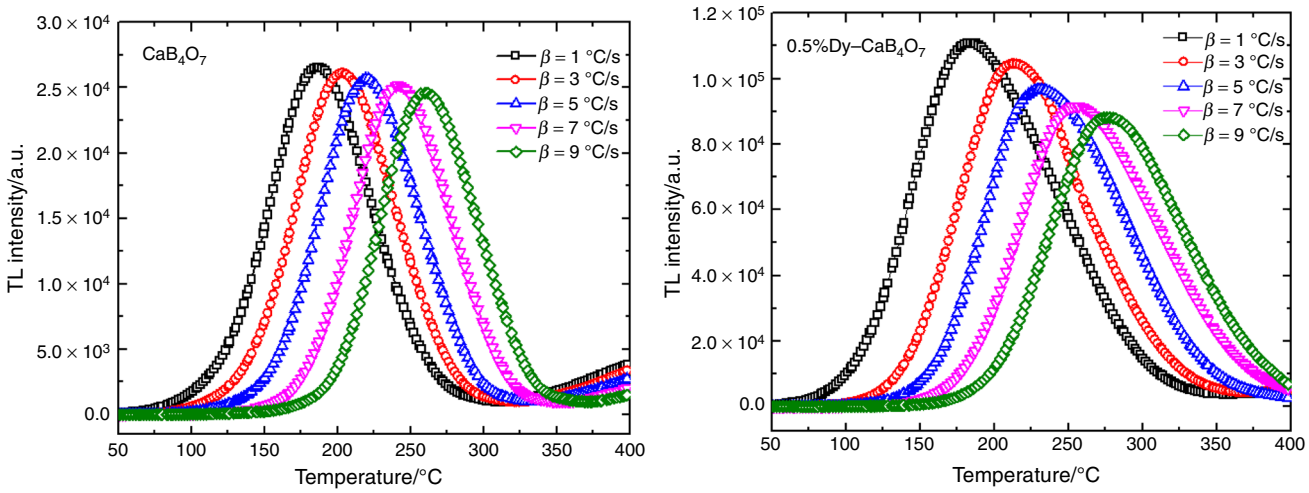

Fig. 7 Glow curves of un-doped and 0.5% Dy-doped calcium tetraborate compound measured after various heating rates between 11 and 91 °C s^{-1}. Measurements are taken after irradiation of 120 Gy using ^{252}Cf neutron source

calcium tetraborate and 0.5% Dy-doped calcium tetraborate compounds have a single peak compared to the dose–response graphs. The maximum peak temperatures of un-doped calcium tetraborate and 0.5% Dy-doped calcium tetraborate were determined to be 178 and 180 °C, respectively.

Heating rate results of un-doped and Dy-doped CaB_4O_7

In the variable heating rate (VHR) method, the heating rates were changed between 1 and 91 °C s^{-1}. The effects of heating rate on the glow curves of the synthesized un-doped and Dy-doped calcium tetraborate compounds were irradiated ^{252}Cf neutron source at doses 120 Gy and irradiations to observe the changes in the glow curve structures and to check the glow peak intensities and dose dependence effects of the peak positions as a function of exposed dose levels. It is well known that the then heating rate is an important experimental parameter on the glow peak intensities and peak temperatures of many TL dosimetric materials. In general, the peak intensity decreases with the increasing heating rate due to thermal quenching [17–22]. It is clearly seen from Fig. 7 that the maximum peak temperatures of all glow peaks increase while the corresponding TL intensities and the total areas under the glow curves of calcium tetraborate compounds decrease with the increasing heating rates.

Conclusions

The calcium tetraborate compounds were synthesized by solid-state method in this study. The doping of metal ions was carried out after the synthesis of the compounds. The XRD and FTIR spectra measurements were investigated after synthesis and doping processes. According to XRD results, they are coincided with JCPDS cards. The thermal analyses (DTA-TGA) were carried out after finding the neutron sensitivity of calcium tetraborate compounds that show neutron dosimetric properties. According to the measurement results, the calcium borate compounds maintain their thermal stability with respect to temperature change.

Then, the TL glow curves of calcium tetraborate compounds were measured to investigate its radiation dosimetric properties. The neutron sensitivity of developed samples was found in the thermoluminescence measurements after irradiation by a ^{252}Cf neutron source in this study. The TL glow curve measurements were repeated two times for each sample before and after neutron irradiation. It was seen that the thermoluminescence measurements did not exhibit appropriate results after neutron irradiations. On the other hand, it was observed that the annealing process has probable effects on the TL glow curves of these compounds and they start to exhibit glow curves after annealing processes. Therefore, calcium tetraborate compounds were annealed at 600 °C for 1 h before TL glow curve measurements and then they were exposed to neutron radiation to measure their glow curves. TL neutron sensitivity of the samples was also compared with TLD-600 and TLD-700 by calculating the glow curve area per unit of mass of dosimeter and per unit of dose of neutrons [22]. The CaB_4O_7:Dy (0.5%) samples are more sensitive than un-doped CaB_4O_7 samples for neutron doses. CaB_4O_7:Dy (0.5%) is approximately 4.35 and 3.36 times higher than that of TLD-600 and TLD-700, respectively. The TL neutron sensitivity of the un-doped calcium tetraborate samples is below both TLD-600 and TLD-700. The compounds with positive results are considered to be in accordance with the conditions necessary for their acceptance as an ideal neutron dosimetry.

Acknowledgements This work was supported by TÜBİTAK, and the Project Number is 115F268.

References

1. Delgado A, Muñiz JL, Gómez Ros JM, Romero AM, Rodríguez R. On the use of LiF TLD-600 in neutron-gamma mixed fields. Radiat Prot Dosimetry. 2007;125(1–4):327–30.
2. Abdel-Zaher Nabawia A, Moselhey Manal T H, Guirguis Osiris W. Effect of fast neutrons on the structure and thermal properties of PVA/HPMC blends. J Therm Anal Calorim. 2016;126:1289–99.
3. Haghiri ME, Saion E, Soltani N, Abdullah Wan WS, Navasery M, Hashim M. Thermoluminescence characteristics of copper activated calcium borate nanocrystals (CaB_4O_7: Cu). J Lumin. 2013;141:177–83.
4. Kazanskaya VA, Kuzmin VV, Minaeva EE, Sokolov AD. In: Proceedings of the fourth international conference on luminescence dosimetry. Krakow; 1974. p. 581.
5. Fukuda Y, Mizuguchi K, Takeuchi N. Thermoluminescence in sintered CaB_4O_7:Dy and CaB_4O_7:Eu//Radiat. Prot Dosim. 1986;17:397–401.
6. Manam J, Sharma SK. Thermally stimulated luminescence studies of undoped and doped CaB_4O_7 compounds. Semicond Phys Quantum Electron Optoelectron. 2003;6(4):465–70.
7. Furetta C, Prokic M, Salamon R, Prokic V, Kitis G. Dosimetric characteristics of tissue equivalent thermoluminescent solid TL detectors based on lithium borate. Nucl Instrum Methods Phys Res Sect A. 2001;456(3):411–7.
8. Dhoble SJ, Shahare DI, Moharil SV. Synthesis of CaB_4O_7:Dy phosphor. Ind J Pure Appl Phys. 2004;42:299–301.
9. Tekin EE, Ege A, Karali T, Townsend PD, Prokic M. Thermoluminescence studies of thermally treated CaB_4O_7:Dy. Radiat Meas. 2010;2010(45):764–7.
10. Prokic M. Effect of lithium co-dopant on the thermoluminescence response of some phosphors. Appl Radiat Isot. 2000;52(1):97–103.
11. Mishra GC, Upadhyay AK, Satapathy KK, Panigrahi AK, Kher RS. Thermoluminescence and mechanoluminescence of gamma-

ray-irradiated CaB_4O_7:Dy phosphors: a comparative study. OPJIT Int J Innov Res. 2012; 1(1): ISSN 2319-4340.
12. Rojas SS, Yukimitu K, de Camargo ASS, Nunes LAO, Hernandes AC. Undoped and calcium doped borate glass system for thermoluminescent dosimeter. J Non-Cryst Solids. 2006;352:3608–12.
13. Depci T, Özbayoğlu G, Yılmaz A. Comparison of different synthesis methods to produce lithium triborate and their effects on its thermoluminescent property. Metall Mater Trans A. 2010;41:2584–94.
14. Özdemir Z, Özbayoğlu G, Yılmaz A. Investigation of thermoluminescence properties of metal oxide doped lithium triborate. J Mater Sci. 2007;42:8501–8.
15. Manam J, Sharma SK. Evaluation of trappingparameters of thermally stimulated luminescence glow curves in Cu-doped $Li_2B_4O_7$ phosphor. J Radiat Phys Chem. 2005;72:423–7.
16. Pekpak E, Yılmaz A, Özbayoğlu G. The effect of synthesis and doping procedures on thermoluminescenct response of lithium tetraborate. J Alloys Compd. 2011;509:2466–72.
17. Kumar M, Chourasiya G, Bhatt BC, Sunta CM. Dependence of peak height of glow curves on heating rate in thermoluminescence. J Lumin. 2010;130(7):1216–20.
18. Yazıcı AN, Hacıibrahimoğlu MY, Bedir M. The effect of various experimental parameters on glow peaks and trapping parameters of CaF_2:Dy (TLD-200) crystals. Turk J Phys. 2000;24(5):623–49.
19. Rasheedy MS, Zahran EM. The effect of the heating rate on the characteristics of some experimental thermoluminescence glow curves. Inst Phys Publ. 2006;73:98–102.
20. Dogan T, Yüksel M, Akça S, Portakal ZG, Yegen SB, Kucuk N, Topaksu M. Normal and anomalous heating rate effects on thermoluminescence of Ce-doped ZnB_2O_4. Appl Radiat Isot. 2017;128:256–62.
21. Kadari A, Kadri D. New numerical model for thermal quenching mechanism in quartz based on two-stage thermal stimulation of thermoluminescence model. Arab J Chem. 2015;8(6):798–802.
22. İflazoğlu S, Kafadar VE, Yazıcı B, Yazıcı AN. Thermoluminescence kinetic parameters of TLD-600 and TLD-700 after 252Cf neutron + gamma and 90Sr–90Y beta radiaions. Chin Phys Lett. 2017;34(1):017801.