Journal of Alloys and Compounds 751 (2018) 159–169

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Optically Stimulated Luminescence (OSL) dosimetric properties of $Li_2B_4O_7$:Ag,Gd and its relationship with thermoluminescence (TL) glow-curves

A. Ozdemir [a], N. Can [b, c], K. Kurt [d], Z. Yegingil [a, *]

[a] Çukurova University, Art Sciences Faculty, Physics Department, 01330, Sarıçam Adana, Turkey
[b] Celal Bayar University, Faculty of Arts and Sciences, Department of Physics, Manisa, Turkey
[c] Physics Department, Jazan University, P.O. Box 114, 45142, Jazan, Saudi Arabia
[d] Mersin University, Art Sciences Faculty, Physics Department, Mersin, Turkey

ARTICLE INFO

Article history:
Received 29 January 2018
Received in revised form
6 April 2018
Accepted 7 April 2018
Available online 9 April 2018

Keywords:
Lithium tetraborate
X-ray Luminescence
Thermoluminescence
Optically Stimulated Luminescence
Correlation between TL and OSL

ABSTRACT

The aim of this work was to develop a new lithium tetraborate luminophore with impurities that are strong co-activators for Optically Stimulated Luminescence (OSL) and to investigate its dosimetric properties using OSL method. $Li_2B_4O_7$:Ag,Gd phosphor consisting of polycrystalline powder was synthesized using Solution Combustion Synthesis method. The structural characterization of the synthesized phosphor was performed using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) methods. OSL dosimetry properties as a function of step-annealing procedure, radiation dose response, reproducibility of response and loss of stored signal in dark were investigated. Thermoluminescence (TL) glow curve of $Li_2B_4O_7$:Ag,Gd phosphor consists of two separated glow peaks located at ~80 and ~210 °C with a heating rate of 2 °C/s. The traps responsible for these two TL peaks in $Li_2B_4O_7$:Ag,Gd phosphor were found to be optically sensitive. $Li_2B_4O_7$:Ag,Gd exhibits high OSL sensitivity and a good OSL signal reproducibility to ionizing radiation. The beta dose-response was performed in the range from 0.1 Gy to 500 Gy. The time-integrated total OSL signal intensity increases linearly with increasing dose from ~6 Gy to 500 Gy. The minimum detectable dose was found to be ~17.1 ± 0.9 μGy. The stored energy increased ~6 % within 4 weeks following a strong fading value of 27 % of the initial OSL intensity after 24 h. Indeed, the X-ray Luminescence (XL) emission spectra are the characteristic of the expected f-f transitions. Luminescence spectrum of Gd doped $Li_2B_4O_7$ exhibits major red emissions (590 nm, 607 nm, 621 nm) and a weak blue emission (450 nm) along with the emission bands from undoped $Li_2B_4O_7$. These results strongly suggest that the luminescence properties of $Li_2B_4O_7$:Ag,Gd deserves more attention as possible dosimeter material. Explanations of many TL/OSL phenomena observed in the study of $Li_2B_4O_7$:Ag,Gd phosphor and improvements based on the better knowledge in the mechanism of TL/OSL in $Li_2B_4O_7$:Ag,Gd, a boron-based compound were achieved by this study.

1. Introduction

Optically Stimulated Luminescence (OSL) and Thermoluminescence (TL) technique have been widely used in radiation dosimetry applications. The OSL technique was first proposed for radiation dosimetry in 1956 by Antonov-Romanovski et al. [1]. The technique has gained importance with its implementation to determine the age of quartz extracted from sediment [2]. This technique in the dosimetry application has gained popularity in the 1990s. The main reason was non-availability of high-sensitive OSL materials until the development of Al_2O_3:C was reported first in mid 1990s by Akselrod et al. [3]. Since then, OSL properties of the Al_2O_3:C material have been extensively studied by many researchers [4–13]. There are many commercially available TL dosimeters, but the number of commercially available OSL phosphors is still limited to two materials, Al_2O_3:C and BeO. Al_2O_3:C phosphor exhibits excellent OSL properties, but the disadvantage is its high-Z_{eff} atomic number. Because of its high atomic number, it gives over response for low energy ionizing radiation. In clinical and personal dosimetry applications, in the mixed environment with gamma and

* Corresponding author.
E-mail address: zehra@cu.edu.tr (Z. Yegingil).

https://doi.org/10.1016/j.jallcom.2018.04.078
0925-8388/© 2018 Published by Elsevier B.V.

neutron radiation, accurate estimation of the radiation dose absorbed by the tissue with high sensitivity is important for human health. This requires dosimetric material with a human tissue equivalence, which is soft biological tissue ($Z_{eff} = 7.4$). Some of the most commonly used host materials in the radiation dosimetry are lithium tetraborate ($Li_2B_4O_7$), magnesium tetraborate (MgB_4O_7), sodium tetraborate ($Na_2B_4O_7$), beryllium oxide (BeO), calcium sulphate ($CaSO_4$), aluminum oxide (Al_2O_3), lithium fluoride (LiF), magnesium oxide (MgO), etc. Among these host materials, the closest phosphor to human tissue is $Li_2B_4O_7$ with Zeff = 7.3. Because of this reason, the researchers paid adequate attention to $Li_2B_4O_7$. To improve the dosimetric characteristics of the $Li_2B_4O_7$, researchers have investigated powder [14,15], glass [16] and single crystal [16–20] forms of the material doped with various ions. TL and OSL mechanisms, basically based on the same physical principles, have been studied. The correlation between TL and OSL studies on this synthetic material has been reported in the literature [21–24].

To date, there are no appropriate requirements for optimum TL and OSL in $Li_2B_4O_7$ in the literature. The data are so scattered that a statistical correlation is generally not applicable. Notwithstanding this difficulty, there is sufficient evidence supporting several arguments including the following: 1. Some impurities are useful for doping into $Li_2B_4O_7$ for optimum TL and OSL such as Ag, Cu, Li, Ce, In, Ni, Ti, Mn, P, Mg, Eu, Pr, K, Cr, Co, Dy, Fe, La, Th [25–29]; 2. Silver and copper are the important impurities for TL and OSL in $Li_2B_4O_7$ to be used for dosimetry. The effect of Ag and Cu ions is enhanced both in sensitivity and temperature of TL when used with various co-activators.

In the present study, $Li_2B_4O_7$:Ag,Gd phosphor was synthesized using solution combustion synthesis method. The structural characterization of the synthesized phosphor was performed using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) methods. Its basic luminescence dosimetric characteristics, such as preheating procedure, dose-response, reproducibility and dark fading were investigated under blue light stimulation (using 470 nm light from blue light emitting diodes-LEDs). Besides these, the effect of various stimulation duration on both residual TL (R-TL) and bleached TL obtained from the same TL data was also demonstrated with the Continuous Wave-Optically Stimulated Luminescence (CW-OSL) technique. These results may be helpful in the development of tissue equivalent TL/OSL detectors best suited for wide high range of radiation exposures.

2. Materials and methods

2.1. Synthesis of $Li_2B_4O_7$:Ag,Gd polycrystalline powder

Polycrystalline powder samples of lithium tetraborate doped with silver and gadolinium $Li_2B_4O_7$:Ag(1 % wt),Gd(1 % wt) were synthesized by using solution combustion synthesis method. The details of the method were already reported in an early work [15]. High purity raw materials were used during synthesis. Oxidizer lithium nitrate ($LiNO_3$, Sigma- Bioultra ≥99.0%), boric acid (H_3BO_3, Sigma ≥99.5%) and urea as a fuel (N_2H_4CO, Sigma- Bioreagent) were used as starting materials. Silver nitrate ($AgNO_3$, trace metals basis, 99.9999%) and gadolinium nitrate hexahydrate ($GdN_3O_9 \cdot 6H_2O$, trace metals basis 99.99%) were also used as the dopant sources of Ag^+ and Gd^{+3} ions. Lithium nitrate, boric acid and urea were mixed in stoichiometric ratios and dissolved in double distilled water by stirring continuously for 2 h at 300 °C, and the dopant ions were added to the solution as a percentage by mass at the same time. The resultant solution was allowed to powder form by keeping the solution on the hot plate for 30 min at 500 °C. The amorphous structure obtained was sintered at 800 °C for 2 h to obtain the polycrystalline form of the samples in an ash furnace (Nabertherm Model P330) in air. Afterwards, it was left in the furnace for cooling down to room temperature. Finally, it was grounded to get a uniform finish with high transfer efficiency of both light and heating.

2.2. Structure characterization methods

X-Ray Diffraction (XRD) measurements of $Li_2B_4O_7$:Ag,Gd phosphor were performed using a PANalytical EMPYREAN XRD with a copper (Cu) and cobalt (Co) X-ray tube operated at 60 kV and 40 mA and using CuKα radiation of wavelength $\lambda = 0.1541$ nm. The Phase identification was performed using the International Center for Diffraction Data (ICDD) Database.

The surface morphology of the $Li_2B_4O_7$:Ag,Gd phosphor was investigated using FE-SEM with EDX, Zeiss, Supra55 with a spectral slit width of 1.5 nm at room temperature.

2.3. TL/OSL readout system and measurements

TL and OSL properties of the material were demonstrated using the automated Riso TL/OSL reader Model DA-20 with a beta irradiator $^{90}Sr/^{90}Y$ plaque (40 mCi@2007) in calibrated geometry and delivering a dose rate of 6.689 Gy/min. The standard PMT in the Riso TL/OSL reader is a bialkali EMI 9235QB PMT, which has maximum detection efficiency between 200 and 400 nm. Hoya U-340 filter (340 ± 40 nm @ 7.5 mm thickness) with maximum transmission at ~340 nm was used for detection of TL glow curve and OSL signal. The OSL decay curves of the material were recorded using blue light emitting diodes for stimulation at room temperature. The TL/OSL reader is equipped with 28 blue LEDs arranged in 4 clusters and their emission spectrum has a peak at 470 nm (FWHM = 20 nm). The total power from these 28 LEDs is ~80 mW/cm^2 at the sample position [30].

In this study, ~10 mg of samples with 90–140 μm particle size were spread out uniformly on at least three thin planchettes to carry out TL and OSL measurements. Before all the powder samples were used in TL/OSL investigations, the samples were annealed in an ash oven at 350 °C for 25 min to eliminate the luminescence effects of any prior excitation. The phosphors were always waited at least 30 min on an aluminum block to cool down. Unless otherwise stated, the synthesized samples were irradiated with 0.2 Gy beta dose for TL/OSL measurements. TL measurements were recorded at a heating rate of 2 °C/s from room temperature to 450 °C. The CW-OSL signals of the $Li_2B_4O_7$:Ag,Gd phosphor were recorded during 200 s blue light stimulation at the room temperature after preheating samples at 120 °C for 10 s to remove the unstable signals and it was recorded 0.1 counts/s for each stimulation duration. After each dose exposure, the samples were waited for 5 min (300 s) then the TL/OSL measurements were achieved.

2.4. X-ray luminescence measurements

The X-ray Luminescence (XL) spectra of the material was carried out with a homemade radioluminescence system which has an attached Ocean Optics model QE Pro (Ocean Optics USB-2000, Inc., Dunedin, FL, USA) by f/2 collimator in front of fiber optic cable (1 mm core diameter, transmission between 200 and 1100 nm) throughout the CCD detector while irradiating by mini x-ray tube operated at from 4 kV up to 40 kV for stimulating the phosphors. XL measurements were performed by placing ~5 mg powder samples in stainless steel cups.