Luminescent Response of Lithium Tetraborate Nanocrystals

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Abstract– ***In this paper lithium tetraborate ($Li_2B_4O_7$) was produced by water/solution assisted synthesis method. Transition metals, such as Cu and Ag were used to dope $Li_2B_4O_7$ in order to enhance its thermoluminescent properties. The heating temperature parameters for synthesis were 750°C for 2 h and 150°C for another 2 h. The samples produced were doped at doping percentages of 0.08%, 0.12%, 0.5%, 0.1% and 1% of Cu and Ag. Pellets of samples were prepared and there were irradiated with different doses (58 mGy, 100 mGy, 500 mGy and 945 mGy) by using an X-ray source. The morphological and structural characteristics of undoped and doped $Li_2B_4O_7$ were determined by X-ray diffraction (XRD), Scanning electron microscope (SEM), Photoluminescence (PL) and Ultraviolet-visible spectroscopy (UV-Vis). The chemical composition and their morphologies of the obtained pure $Li_2B_4O_7$ and $Li_2B_4O_7$:Cu,Ag was confirmed by XRD and SEM results. The most intense peak of the XRD patterns were compared to the reference data and was found to have a tetragonal structure. The thermoluminescent glow curves of the pellets exposed to different doses exhibited a clear response to X-ray irradiation. Especially $Li_2B_4O_7$:Cu presented a good glow curve at all doses***.

Keywords-- Nanocrystals; Lithium tetraborate; Luminescence.

I. INTRODUCTION

$Li_2B_4O_7$ is a material that has been study in some details for its luminescent properties and technological applications [1]. Also, several studies have highlighted the linearity of the thermoluminescent (TL) response of $Li_2B_4O_7$ in a very wide range of doses as high as 10^3 Gy, from a minimum of a few μGy [2,3], as also a low fading [4]. On the other hand, special mention has also been given to the possibility of using this material for the detection of neutrons [5].

The importance of TL for radiation dosimetry is due to the fact that the amount of light emitted is proportional to the absorbed dose by the irradiated material, which requires sensitive detection and accurate measurements of ionizing radiation. Under favorable conditions, emitted TL light intensity by a solid is proportional to the absorbed dose, and thus, using an appropriate calibration, one can evaluate the applied dose in the radiation field. Then, TL is an established method for radiation dosimetry as well as for retrospective dosimetry. The use of radiation dosimetry in medical practice is needed in a wide variety of applications, such as to optimize X-ray equipment and radiological techniques [6]. TL provides very useful information about the charges trapped and energy transfer processes in a crystalline lattice resulting in light emission. So the main purpose of this paper is to determine the effect of synthesis on the TL properties of Cu and Ag doped $Li_2B_4O_7$.

II. MATERIALS AND METHODS

For the production of $Li_2B_4O_7$ a high temperature water/solution assisted synthesis method was used. Stoichiometric amounts of Li_2CO_3 and $H_3\ BO_3$ were mixed and put in a beaker into which 15 ml of water was added for production of 1 g of $Li_2B_4O_7$. The solid-liquid mixture was stirred in a heating magnetic stirrer until the constituents were sufficiently dispersed at temperatures lower than 100 ^{0}C. The heating action provided by the stirrer evaporated the water included to a certain level in 15–20 min without disrupting dispersion action. This mixing step was followed by heating in a furnace. The mixture containing residual water was exposed to 150 ^{0}C for 3 h in order to guarantee total evaporation of water. An intermittent grinding and mixing was not required in water/solution assisted production since the constituents were dispersed to a reliable level by the stirrer. Therefore the drying and heating was directly followed by the increase of the temperature from 150 ^{0}C to 750 ^{0}C.

For the preparation, the reaction given below was followed

$$Li_2CO_3\ (s) + 4H_3BO_3\ (s) \rightarrow Li_2B_4O_7\ (s) + CO_2\ (g) + 6H_2O\ (g), \quad (1)$$

where all the precursor materials were of high purity reagent grade.

II.1. Doping of the samples

In solution assisted doping, the dopant was dissolved in water to form a master solution from which required amount of dopant was obtained. Solution assisted doping was applied by heating the doped matrix at 150 ^{0}C for two hours and at 750 ^{0}C for 2 h.

The concentration range for copper and silver dopant in the form of water soluble $CuCl_2$ and $AgNO_3$ was 0.1–1% [0.1, 0.02, 0.04, 0.06, 0.08, 0.5, 0.12 and 1%].

II.2. Stoichiometric calculation for doping

For the sample $Li_2B_4O_7$:Ag at 1%, using the molar mass of silver nitrate ($AgNO_3$) of 167.87 g/mol and a molar mass of Ag of 107.86 g/mol, a ratio of 0.63 g of Ag is obtained. Hence,

the required stoichiometric amount of 1% Ag for a 5 g of final sample gives 0.078 g of Ag.

On the other hand, for the sample $Li_2B_4O_7$:Cu at 1% using the molar mass of copper chloride ($CuCl_2$) of 134.45 g/mol and a molar mass of Cu of 63.54 g/mol, a ratio of 0.47 g of Cu is obtained. Hence, the required stoichiometric amount of 1% Cu for a 5 g of final sample gives 0.011 g of Cu.

III. CHACARTERIZATION OF THE MATERIAL

The characterization of undoped and doped $Li_2B_4O_7$ synthesized by water/solution assisted method was evaluated by XRD, SEM, UV-Vis and PL methods. The characterization studies aimed at detection of any structural difference caused by doping operation besides confirmation of lithium borate in the correct form namely $Li_2B_4O_7$.

III.1. XRD analyses

The XRD properties of the samples were obtained using a Bruker D2 Phaser (Coventry, United Kingdom) difractometer with CuKα radiation, which can measure a range of 2θ from 3^0 to140^0, using a voltage of 30 kV and a current of 10 mA.

The XRD patterns obtained for the material produced showed that production of $Li_2B_4O_7$ was successful since all of the main peaks of $Li_2B_4O_7$ matches with those of the material produced. Most intense peaks of the XRD pattern of $Li_2B_4O_7$ sample allowed to determine a tetragonal structure. Moreover, it was seen that the dopant added did not interfere with the crystal structure. Fig. 1 displays the XRD results for $Li_2B_4O_7$.

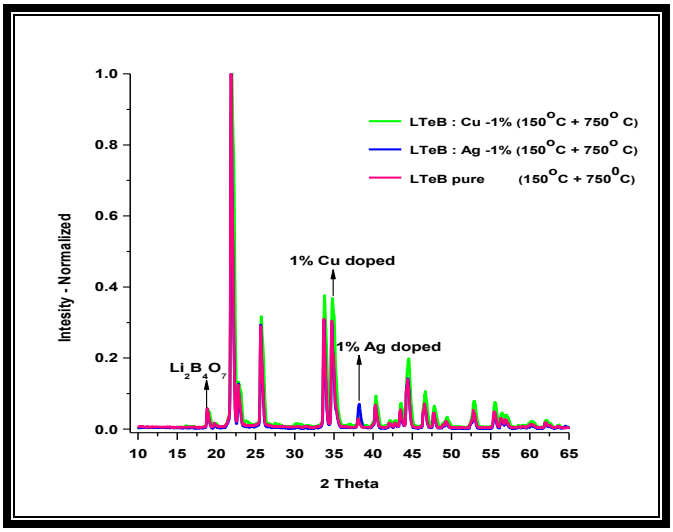

Fig. 1 (a) Undoped $Li_2B_4O_7$ produced by water assisted method and (b) solution assisted doping of $Li_2B_4O_7$:Cu, and $Li_2B_4O_7$:Ag.

III.2. SEM analyses

SEM analyses were performed using a scanning electron microscope Zeiss, EVOHD15LS (Germany). Before analysis, samples were metalized by gold sputtering in a Fine Coat Ion Sputter Jeol JFC-1100. The morphology of the samples was observed using secondary electron flux. The accelerating voltage was in the range 5–11 kV and the magnification was 1.00 kX. Particle size distribution was obtained by SEM image analysis using the ImageJ software.

Scanning electron microscopy was basically used to compare the morphologies of materials. SEM micrographs of undoped $Li_2B_4O_7$ and Cu & Ag-doped $Li_2B_4O_7$ are given in Figs. 2a, 2b and 2c.

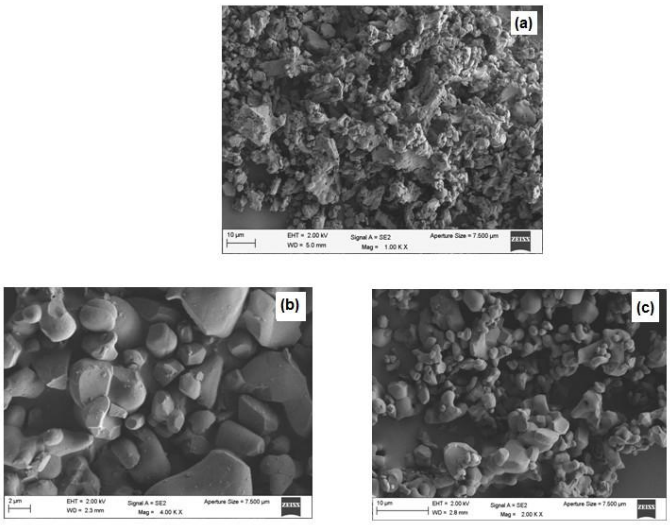

Fig. 2 SEM micrographs of undoped $Li_2B_4O_7$ and Cu,Ag-doped $Li_2B_4O_7$. (a) Undoped $Li_2B_4O_7$ using a 1.00 kX magnification, (b) $Li_2B_4O_7$:Cu and (c) $Li_2B_4O_7$:Ag.

III.3. UV-Vis spectroscopy analyses

The optical absorption spectra of Cu and Ag-doped $Li_2B_4O_7$ and undoped and doped samples were measured by using Carry 500 series UV-Vis spectrophotometer. All optical spectra were taken at room temperature. Fig. 3 shows the absorption spectra for both $Li_2B_4O_7$:Cu and $Li_2B_4O_7$:Ag for different percentage of doping amounts.

As it is evidence from the absorption spectrum, the presence of copper and silver in the matrix was confirmed. Also, any change in the spectral shape with the addition of any doping amount is observed.

The wavelength of UV-vis absorption used was from about 200 nm to 800 nm. The samples absorbed the light from 220 nm to 600 nm.

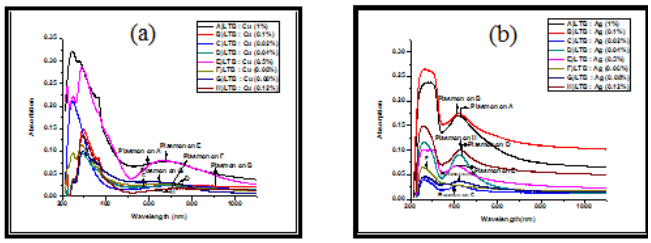

Fig. 3 Absorption spectra for both (a) $Li_2B_4O_7$:Cu and (b) $Li_2B_4O_7$:Ag for different percentage of doping amounts.

III.4. PL Analyses

PL spectra of the studied samples are presented in Figures 4a, 4b and 4c, respectively. The spectral investigation under study state excitation and emission of photoluminescence. The PL spectra were corrected by the xenon lamp emission spectrum. $Li_2B_4O_7$ with various copper content exhibit two UV bands at 240 and 260 nm in the excitation spectrum and a single emission band at about 370 nm. The emission intensity increasing Cu content in the sample without any change in the spectral shape.

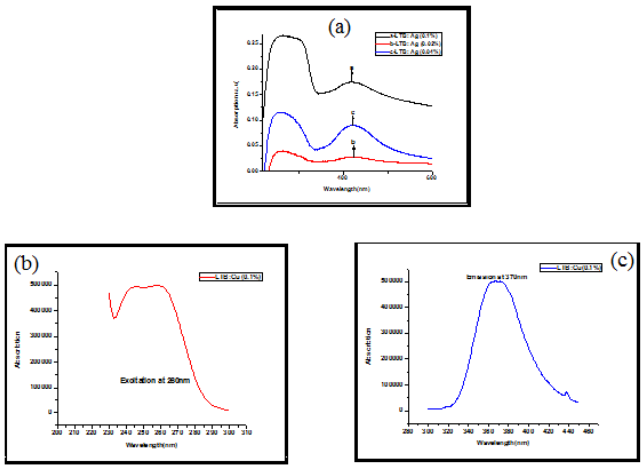

Fig. 4 PL spectra of the studied samples.

III.5. Annealing process

The annealing process is necessary to reuse the dosimeters and be able to eliminate the effects of previous irradiations without affecting the sensitivity. The annealing was carried out at different temperatures for different time period, so before irradiation, the samples were annealed at 400 ^{0}C h, followed by 100 ^{0}C by 2 h. After that the samples were cooled to room temperature for 24 h.

III.6. Irradiation process and TL measurements

he pellets of Li_2B_4O:Cu and Li_2B_4O:Ag were exposed to a different level of X-ray sources. The doses were 58 mGy, 100 mGy, 500 mGy, 945 mGy. The thermoluminescence glow curves of the synthesized Li_2B_4O:Cu and Li_2B_4O:Ag were obtained by using a Harshaw TLD model 3500. Irradiation at room temperature was done by using X-ray. Initially 1% and 0.1% of $Li_2B_4O_7$:Cu and $Li_2B_4O_7$:Ag were only studied.

Figures 5a - 5d display the glow curve sets of different doped samples. The glow curves of pellet samples exposed to different doses exhibited a low temperature peak at about 100 ^{0}C and a high temperature peak at about 160 ^{0}C. A heating rate of 1 C/s was used from 50 ^{0}C to 400 ^{0}C. Among these TL results the best result was obtained with 0.1% of Cu concentration.

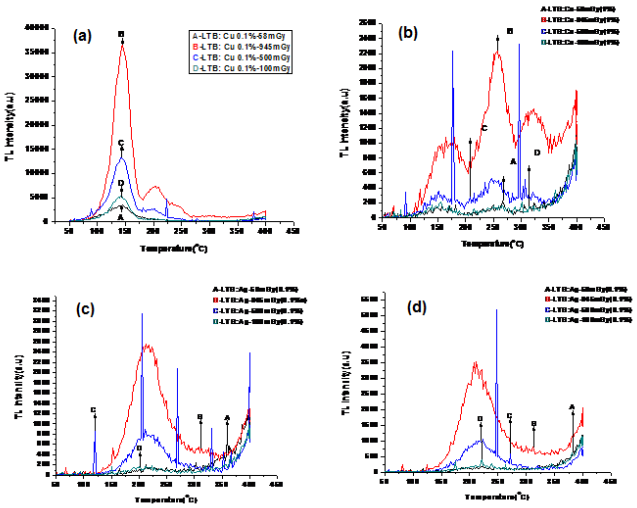

Fig. 5 Glow curve sets of different doped samples. (a) $Li_2B_4O_7$:Cu at 1% Cu, (b) $Li_2B_4O_7$:Cu at 0.1% Cu, (c) $Li_2B_4O_7$:Ag at 1% Ag and (d) $Li_2B_4O_7$:Ag at 0.1% Ag.

IV. DISCUSSION AND CONCLUSIONS

This work investigated the TL dosimetric properties of Li_2B_4O doped with Cu and Ag synthesized by using water/solution assisted method. The powder XRD results indicated that the basic lattice parameters were not changed with the addition of dopants. The morphology of the Li_2B_4O produced showed to have a tetragonal symmetry

The TL results obtained showed that the material produced showed a good TL response. In this case where solely copper was added as a dopant, sample with 0.1% Cu dopant gave the best results among the concentration levels. Also, the obtained result showed that the maximum temperature of the glow peak increased with increasing heating rate.

Further analyzes are necessary to characterize this material dosimetrically. Further, much more study is needed to evaluate the use of this material in neutron dosimetry, as suggested in the literature.

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REFERENCES

[1] E. Pekpak, A. Yilmaz, and G. Ozbayoglu, "The effect of synthesis and doping procedures on thermoluminescent response of lithium tetraborate," J. Alloys and Compounds 509, pp 2466-2472, 2010.

[2] C. Furetta, M. Prokic, R. Salamon, V. Prokic, and G. Kitis, "Dosimetric characteristics of tissue equivalent thermoluminescent solid TL detectors

based on lithium borate," Nucl. Instr. Methods Phys. A456, pp 411-417, 2001.
[3] M. Prokic, "Lithium borate solid TL detectors," Rad. Meas. 33, pp 393-396, 2001.
[4] N.A. El-Faramawya, S.U. El-Kameesya, A. El-Agramyb, and G. Metwallyb, "The dosimetric properties of in-house prepared copper doped lithium borate examined using the TL-technique," Rad. Phys. Chem. 58, pp 9-13, 2000.
[5] M. Ishii, Y. Kuwano, S. Asaba, T. Asai, M. Kawamura, N. Senguttuvan, T. Hayashi, M. Koboyashi, M. Nikl, S. Hosoya, K. Sakai, T. Adachi, T. Oku, and H.M. Shimizu, "Luminescence of doped lithium tetraborate single crystals and glass," Rad. Meas. 38, pp 571-574, 2004.
[6] T. Rivera, "Thermoluminescence in medical dosimetry," Applied Rad. Isotopes 71, pp 30-34, 2012.