Original Article

Formation and characterization of ultrafine nanophosphors of lithium tetraborate \((\text{Li}_2\text{B}_4\text{O}_7)\) for personnel and medical dosimetry

Nasrin Khalilzadeh\textsuperscript{a,}\textsuperscript{*}, Elias Bin Saion\textsuperscript{b}, Hamed Mirabolghasemi\textsuperscript{c}, Nayereh Soltani\textsuperscript{d}, Abdul Halim Bin Shaari\textsuperscript{b}, Mansor Bin Hashim\textsuperscript{e}, Noriah Mod Ali\textsuperscript{f}, Arash Dehzangi\textsuperscript{g}

\textsuperscript{a} Nuclear Science and Technology Research Institute, Karaj, Iran
\textsuperscript{b} Department of Physics, Faculty of Science, University Putra Malaysia, Selangor, Malaysia
\textsuperscript{c} Department of Materials Science & Engineering, National University of Singapore, Singapore, Singapore
\textsuperscript{d} Young Researchers and Elite Club, Shahr-e-Qods Branch, Islamic Azad University, Tehran, Iran
\textsuperscript{e} Institute of Advanced Technology, University Putra Malaysia, Selangor, Malaysia
\textsuperscript{f} Health Physics Group, Malaysian Nuclear Agency, Bangi, Selangor, Malaysia
\textsuperscript{g} Center for Quantum Devices, Department of Electrical and Computer Engineering, North Western University, Evanston, IL, USA

Abstract

The present study demonstrates an innovative single-step thermal synthesis of nanosized lithium tetraborate dosimeter and its characterization. The optimum calcination temperature and time for the synthesis of the nanoparticles material was 750 °C and 2 h, respectively. Characterization of the samples was carried out using X-ray diffractometry (XRD), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), and thermoluminescence (TL). FT-IR, XRD and TEM results confirmed the formation of pure nano-crystalline lithium tetraborate. The product showed a linear response over a wide range of doses from \(10^{-1}\) to \(1.5 \times 10^2\) Gy. Moreover, the samples illustrate non-energy dependence among a wide range energy interval from 24 keV up to 1250 keV and almost no fading during one month storage.

© 2015 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda.

1. Introduction

Ever since Daniels et al. reported for the first time on the TL as a technique in radiation dosimetry \cite{1}, the TL has been attracted tremendous attention in science, industry and medicine for radiation dose monitoring. They showed that the irradiated material contains stored energy, which could be thermally released. The first introducing material in radiation dosimetry was \(\text{Li}_2\text{B}_4\text{O}_7\): \(\text{Mn}\) phosphor \cite{2} which shows several drawbacks such as poor TL intensity, limited dose linearity, loss information (fading) and energy dependence. However, because there

\* Corresponding author.
E-mail: nikhalilzadeh40@gmail.com (N. Khalilzadeh).
http://dx.doi.org/10.1016/j.jmrt.2015.11.002
2238-7854/© 2015 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda.
are only a few tissue equivalent TL materials for radiation dosimetry particularly in clinical applications and radiation therapy, lithium tetraborate Li$_2$B$_4$O$_7$ (LTB) is one of the most popular materials for personal thermoluminescence dosimetry (TLD). The effective atomic number ($Z_{\text{eff}}$) of LTB is 7.4, which closely matches with the $Z_{\text{eff}}$ of human tissue (7.42) [3]. Furthermore, LTB is an almost stable chemical compound and can be easily doped with TL sensitizers such as rare earth elements, copper or manganese ions. The resultant materials show some desirable features for TL in terms of high sensitivity [4]. Takenaga et al. successfully improved the sensitivity of LTB by replacing Mn with Cu [5]. They also found that TL emission spectra at 365 nm for LTB: Cu, In pellets and LTB: Cu, In, Ag pellets improved the linearity of dosimeter. However, those TL were sensitive to light and had high fading [6]. Doping of LTB crystals have also received attention as a promising method to produce neutron scintillator with large cross section for neutron capturing by lithium and boron isotopes [7] in surface acoustic wave devices for intermediate frequency (IF) filters [8,9]. Recently, prepared Cu doped LTB crystals modified TL response but supralinearity has been seen [10]. The single crystal growth of non-doped and Cu doped LTB improved linearity, though fading was 85% and 6% after 6 days, respectively [11].

In recent years, intensive research focuses on the development of nanosized phosphors due to some positive findings including better radiation resistance, wide range linearity [12], less fading and detection of high energy ionizing radiations [13] unobtainable with conventional macroscopic materials. The peculiar properties of nanomaterials are arising from their increased surface to volume ratio and changes in their electronic structure due to quantum confinement. Consideration of these substances has been motivated by the understanding that small size particle, grain, or phase and high surface-to-volume ratio give these materials unrivalled optical, mechanical, magnetic, and electronic properties [14]. Nanophosphor LTB and LTB-Cu were prepared by combustion method showed good improvement on TL characteristics of this dosimeter [14], but sublinearity and serious fading have seen. Anyway, some luminescence features of LTB were improved by synthesis in micro and nano scales with adding different activators. The present study reports remarkable improvement on some properties of undoped LTB nanophosphors for the first time by an innovative single step thermal treatment method. The ultrafine nanoparticle LTB has showed considerable performance on linearity, energy storage ability, and energy dependence as comparison with the samples that newly prepared in micro and nano scales. This article provides a detail on the preparation and characterization of undoped LTB nanophosphors.

2. Experimental

2.1. Synthesis of LTB nanoparticles

The starting materials for synthesis of LTB nanoparticles are lithium carbonate (Li$_2$CO$_3$) and boric acid (H$_3$BO$_3$) as lithium and boron sources respectively, and polyvinylpyrrolidone (PVP) (MW = 58,000) as a surfactant agent. Lithium carbonate, boric acid, and PVP were purchased from Sigma–Aldrich. All chemicals are analytical grade products and were used without further purification.

In a typical preparation, 0.0058 mol of Li$_2$CO$_3$ and 0.024 mol of H$_3$BO$_3$ were added to 20 ml deionized water include 0.027 mol PVP. The master mixture was stirred for 1 h at 60 °C. The final solution was assigned to slow separation nucleation based on single step thermal treatment method, which is basically credited of Pechini method [15]. The solution was stirred at 750 °C for 2 h undergone fast cooling regime to allow crystallization of nanoparticles [16]. The solid cake was ground and sieved through 200 and 100 µm mesh to ensure that the particles were close to crystalline size.

2.2. Characterization

The characterization of the prepared LTB nanoparticles was conducted using various techniques to explore parameters of interest. The structural characteristics of the nanocrystalline powder were determined by X-ray diffraction (XRD) technique using Shimadzu 6000 diffractometer utilizing Cu Kα (0.154 nm). A Perkin Elmer 1650 FTIR Spectrometer was used to identify the chemical composition of calcined samples. The average particle size and size distribution of nanoparticles were evaluated by transmission electron microscopy (TEM) images using JEOL 2010F HR version electron microscope operating at an accelerating voltage of 200 kV. The average size and size distribution of nanoparticles were determined by Java-based image processing programme image J. Thermally stimulated luminescence (TSL) investigation of the pellet LTB nanoparticles was done to determine TL intensity, energy storage ability, and energy dependence using Harshaw TLD reader model 4500.

2.3. TL investigation

The LTB chips were prepared by 0.0320 g substance with 0.48 cm diameter and 0.089 cm thickness, which were calcined at 750 °C. Annealing of the chips was performed to eliminate all previous exposure effects in pre-irradiation and post-irradiation process for obtaining the nil samples. The chips were annealed at different temperatures of 250, 300, and 400 °C for time intervals of 15, 30, 60 min in TLD annealing furnace (model A134307) with a heating rate of 1 °C/min to get optimum annealing programme. The optimum pre-heating annealing schedule was found at 300 °C for 30 min. The chips were assigned for very fast cooling regime by 20 °C/min. The nanophosphors were subjected to different Time Temperature Profile (TTP) plans to optimize the best fitted acquire area. In this matter, different pre-heating temperatures were applied to the samples of 50, 60, 120, and 160 °C with time intervals of 5, 6, 20, and 60 s. The best TTP schedule was found at 50 °C for 60 s. The chips were exposed to the Gamma dose radiation in personnel and medical ranges from 0.1 to 1.5 × 10$^2$ Gy at room temperature at 59.7% humidity by two different calibrated sources. Eldorado 8 $^{60}$Co for 0.1, 0.5, and 1 Gy doses and Gamma cell (GC220 Excel) for 5, 10, 100, and 150 Gy doses with dose rates of
0.049 Gy/min and 2.189 kGy/h, respectively. All samples were kept in a plexy glass container to achieve electron equilibrium during irradiation [17]. All nanophosphor chips were stored at room temperature in a dark room for 24 h to remove all shallow peaks before TL measurements. The TL glow curves of exposed samples were recorded by a Harshaw TLD Reader, with a heating rate of 5 °C/s under a nitrogen atmosphere to prevent any spurious signals and remove effects of induced oxygen. Energy dependence property of synthesized LTB nanoparticles was investigated using a calibrated X-ray source from 40 up to 150 kV, 60Co, and 137Cs reference sources. The chips were exposed to a test dose of 500 mGy at room temperature in almost 64% humidity. The X-ray filtration was done by Aluminium attenuation layers. The samples were read-out under the same TTP programme and same situation, which were employed in other parts of characterization.

The results were corrected with consideration of temperature, pressure, and humidity according to standard protocols of Secondary Standard Dosimetry Laboratory (SSDL) [18].

3. Results and discussion

3.1. XRD investigation

The XRD pattern of synthesized lithium tetra borate is depicted in Fig. 1. The diffraction peaks observed in the XRD patterns match with the (2 0 0), (1 1 2), (3 1 0), (2 0 2), (2 1 3), (3 1 2), (4 1 1), and (3 3 2) crystalline planes of the tetragonal structure of lithium tetraborate (LTB) [19].

Fig. 1 – (a) XRD pattern [1 1 2] of LTB nanoparticles and (b) the standard pattern of ICDD PDF 00-018-0717.

3.2. FT-IR spectral investigation

Infrared spectroscopy provided essential information about functional groups and network structures in the samples. Fig. 2 shows the peaks corresponding to the frequencies of stretches vibrations of the bonds between atoms in LTB. Detailed assignment of the observed IR bands is listed in Table 1. Absorption bands of LTB nanoparticles can be seen without any trace of bending vibration of organic compounds (such as; C–H, –CH₃ and –CH₂ coming from methylene groups in polymeric precursor). The absorption bands of B–O and B–O(B) of BO₃ triangle appear at 1600–1200 cm⁻¹ [20]. The range of 1500–700 cm⁻¹ is connected with the B–O(B) stretching vibrations of BO₄ tetrahedral [21]. Absorption bands between 700 and 400 cm⁻¹ are related to O–B–O deforming vibrations of BO₄ tetrahedral [21] and the peaks between 400 and 200 cm⁻¹ can be attributed to Li–O [22]. The peaks from 688 to 418 cm⁻¹ are assigned to O–B–O deformation mode of tetrahedral BO₄ in Li₂B₄O₇ [21–23].

3.3. TEM investigation

The average size and size distribution of nanophosphor powders were calculated from TEM images based upon at least 150 nanoparticles for each sample. The size distribution histograms fitted to the Gaussian distribution using OriginPro9 are given in Fig. 3. Morphological evaluation of the TEM images (Fig. 3) shows that the nanoparticles are generally spherical in shape and approximate monodisperse. LTB nanoparticles have relatively narrow size distributions in the range from 1.0 to 7.0 nm with estimated average size of ~3.3 nm [24], which has meaningful effect on energy dependence of TL dosimeters [25].

Table 1 – Major peaks in FT-IR spectra of LTB nanoparticles.

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Assign structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600–1200</td>
<td>Asymmetric stretching vibrations of B–O in BO₃</td>
<td>[20]</td>
</tr>
<tr>
<td>1500–700</td>
<td>B–O–H in plane bending of BO₄ tetrahedral</td>
<td>[21]</td>
</tr>
<tr>
<td>950–870</td>
<td>Stretching of tetrahedral BO₄</td>
<td>[21]</td>
</tr>
<tr>
<td>870–415</td>
<td>O–B–O deformation mode of BO₄ tetrahedral</td>
<td>[21–23]</td>
</tr>
<tr>
<td>400–200</td>
<td>Li–O</td>
<td>[22]</td>
</tr>
</tbody>
</table>
3.4. Thermally stimulated luminescence (TSL)

Thermally stimulated approaches are a category of physical processes in which a definite property of the material under investigation is measured as a function of temperature. Typically, the property in question is measured during the heating of the sample. The process of excitation may be done by irradiation samples by ionizing radiation. The characteristic property of the sample according heating is not repeated during cooling. Re-excitation of the material is necessary due to repeat the measurement [16]. The most widely considered and applied of all thermally stimulated experiences is the emission of light during the heating of an excited sample, which is called TL. The TL technique is a powerful tool for evaluation of a material as a dosimeter [26] and is the main subject of our study in the present research. The investigation was performed for nanophosphor LTB chips in different annealing conditions and TTP situations and their glow curve shapes, linearity, energy dependence, and energy storage ability were studied in detail.

3.4.1. Glow curve

Glow curves of the samples are shown in Figs. 4–6. The samples were exposed by 60Co gamma radiation under 0.1, 0.5, 1, 5, 10, 100, and 150 Gy. The trend of glow curves depicts two shoulders at all doses except 0.1 Gy. All obtained glow curves in dose range of 1–150 Gy show a predominant peak at 150 °C and two shoulders at 110 and 200 °C. It should be underlined the shoulders are the outcome of capping effect during nanoparticles preparation [27].

Fig. 5 shows the glow curves of synthesized nanocrystalline LTB exposed to 10, 5, and 1 Gy doses. The result shows the predominant peak in the named doses has been the same as above. The TL glow curves of nanophosphor in 0.5 and 0.1 Gy have a predominant peak at 200 °C, and two shoulders at 140,
285 °C for 0.5 Gy and also 290 °C for 0.1 Gy. Table 2 illustrates the peak position data of LTB nanophosphors irradiated in different dose ranges of Co-60 gamma ray. Moreover, Table 3 depicts the comparison of the TL properties of the present study with other researchers (undoped and Cu doped LTB).

Due to Figs. 4–6 and Tables 2 and 3 it should be emphasized the peak position of undoped LTB nanoparticle appeared at 200 and 150 °C, which are resulted of ultrafine nanoparticle size and almost monodisperse LTB nanophosphors with nearly 3 nm in diameter. The 10% fading of LTB nanoparticles after one month is a noticeable result that is less than the outcome of other researchers as comparison in Table 3. Furthermore, all glow curves show same characteristic shoulders. On the other hand, nanophosphors of LTB were exposed by maximum 150 Gy. Their intensity was 10 times higher than newly reported samples, which has been irradiated with 1000 Gy [14].

3.4.2. TL response of LTB nanophosphor
Fig. 7 depicts TL response changes of irradiated Li2B4O7 with variety of doses for nanophosphors chips. It was found LTB nanophosphor pellets showed noticeable linear response without any supralinearity or sub linearity from 0.1 to 1.5 × 10² Gy. It should be emphasized the linearity of LTB is in the range of medical and personal dosimetry [17]. These results illustrate an excellent trend comparable to the doped samples in other researches [29], that are depicted in Table 3.

3.4.3. Energy dependence of LTB nanophosphor chips
The energy dependence of LTB is seen in Fig. 8. The response was normalized by 137Cs response at the same irradiation condition. Regarding non-doped LTB are spherical ultrafine monodisperse nanoparticles, the trend of its energy dependence [25] among a wide range of 24–1250 keV is almost constant.

3.4.4. Energy storage ability (fading)
A desirable TL material, for the dosimetric purposes, is stable without serious fading in room temperature during long period of time. To investigate the energy storage ability of LTBs, they were exposed to 100 Gy dose by a 60Co reference source. The chips were read-out in 1st, 2nd, 7th, 10th, 14th and 31st days from irradiation date. The read-out plan was performed under the same TTP programme and condition, which had been employed in other parts of the characterization. Moreover, the nanophosphors particles were kept in the dark at ambient temperature during the measurement. As depicted in Fig. 9, TLDs show no changes in TL response after one month. Furthermore, the fading was 10% after one month.

![Figure 7](image1)
**Fig. 7** – The changes of TL response of Li2B4O7 nanophosphor with irradiation doses.

![Figure 8](image2)
**Fig. 8** – Energy response of LTB chips (relative to 137Cs) versus photon energy.

![Figure 9](image3)
**Fig. 9** – TL response of nanoparticle LTB chips exposed to 100 Gy 60Co reference source during one month.
Table 3 – The comparison of TL properties of undoped and Cu doped LTB dosimeters.

<table>
<thead>
<tr>
<th>Author</th>
<th>Phase</th>
<th>Material</th>
<th>Peak position (°C)</th>
<th>Maximum exposure dose (Gy)</th>
<th>Linearity (Gy)</th>
<th>Energy dependence</th>
<th>Storage time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Khalilzadeh et al. [12]</td>
<td>Nanocrystal (3.5 nm)</td>
<td>Li$_2$B$_4$O$_7$</td>
<td>150</td>
<td>150</td>
<td>$10^{-1}$–$0.15 	imes 10^3$</td>
<td>Independent (24–1250 keV)</td>
<td>10% after one month</td>
</tr>
<tr>
<td>Kelemen et al. [11]</td>
<td>Single crystal</td>
<td>Li$_2$B$_4$O$_7$</td>
<td>210</td>
<td>1</td>
<td>$10^{-3}$–1</td>
<td></td>
<td>80% after 10 days</td>
</tr>
<tr>
<td>Singh et al. [14]</td>
<td>Nanocrystal (30 nm)</td>
<td>Li$_2$B$_4$O$_7$:Cu</td>
<td>270</td>
<td>10,000</td>
<td>$0.3 	imes 10^{-3}$–$10 	imes 10^3$</td>
<td>-</td>
<td>6% after 10 days</td>
</tr>
<tr>
<td>Singh et al. [14]</td>
<td>Nanocrystal (30 nm)</td>
<td>Li$_2$B$_4$O$_7$:Cu</td>
<td>108</td>
<td>1000</td>
<td>-</td>
<td>Sublinear below $1 \times 10^2$ and linear response from $10^2$ to $5 \times 10^3$</td>
<td>18% after one month</td>
</tr>
<tr>
<td>Pekpak et al. [10]</td>
<td>Crystal</td>
<td>Li$_2$B$_4$O$_7$:Cu</td>
<td>100</td>
<td>-</td>
<td>Supralinearity up to 100</td>
<td>-</td>
<td>10% after three months</td>
</tr>
<tr>
<td>El-Adawy et al. [28]</td>
<td>Glass</td>
<td>Li$_2$B$_4$O$_7$</td>
<td>200</td>
<td>Almost 68</td>
<td>0–70</td>
<td>-</td>
<td>40% after about one month</td>
</tr>
<tr>
<td>Furetta et al. [3]</td>
<td>Crystal</td>
<td>Li$_2$B$_4$O$_7$:Cu</td>
<td>210</td>
<td>1000</td>
<td>Supralinearity up to 100</td>
<td>Dependent</td>
<td>10% after three months</td>
</tr>
</tbody>
</table>


4. Conclusions

An innovative single-step thermal treatment procedure using a slow separation nucleation regime has resulted in the first-time preparation of pure nano-crystalline lithium tetraborate. The successful synthesis of this nanoparticle material has been confirmed by XRD, FT-IR, TEM, and TL analyses. The specific objective of the present study is the named method can prepare remarkable nanophasor LTB dosimeter without adding any activator. The unique feature of the current research is obtaining linearity response over a wider range, without any supralinearity and sublinearity, as a comparison to the results of the other researchers. It should be emphasized that interesting properties can be seen in non-doped lithium tetraborate nanoparticles. The LTB nanophasors demonstrate excellent thermoluminescence properties such as simple glow curve, non-energy dependence and almost no fading. It is worth noting that nanophasor LTB can be suggested as a thermoluminescence dosimeter material for evaluating the absorbed dose for personnel and medical dosimetry purposes.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This work was granted by the Ministry of Higher Education of Malaysia under the FRGS and RUGS grants. The authors would be appreciated for attention and collaboration of the staff of the Physics Department Faculty of Science, Faculty of Engineering, and Bioscience Institute of University Putra Malaysia. Moreover, we also would like to thank to the staff of the Nuclear Agency of Malaysia for allowing the use of their facilities. Furthermore, so many thanks to the staff of school of Applied Physics of University Kebangsaan Malaysia for their good cooperation.

References