Original Article

Single step thermal treatment synthesis and characterization of lithium tetraborate nanophosphor

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ABSTRACT

This study includes the synthesis of nano-sized lithium tetraborate by an innovative single step thermal treatment method and characterization of the products. The heating temperature for the synthesis was varied between 200 and 850°C with the retention time of 2 h. Polyvinyl pyrrolidone (PVP) with different concentrations was used as surfactant. Characterization of the samples was achieved by thermogravimetric analysis (TGA), derivative thermogravimetry analysis (DTG), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM) techniques and UV–vis spectroscopy. Thermal analysis of initial solution allowed the optimization of the heat treatment program and showed that the thermal stability of samples is started at 460 °C. FT-IR, XRD and TEM results proved the formation of pure nano-crystalline lithium tetraborate at temperature between 460 and 750 °C. Furthermore, the band gap investigation was performed using UV–vis spectra in the presence of different concentrations of PVP and in variety of calcination temperatures. The estimated optical bandgap was found to be between 5.2 and 6.2 eV.

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1. Introduction

Lithium tetraborate (LTB) has been a scientific focus since 1960s by its courtesy of the thermoluminescence property and potential application as versatile radiation detectors and dosimeters. In addition to X-ray and γ-ray radiation, lithium borate based dosimeters have an additional advantage of being sensitive to neutron radiation due to the presence of 6Li and 10B nuclei with large capture cross-sections for thermal neutrons [1–3]. Moreover, lithium tetraborate is an acousto-optical and optoelectronic material widely used in surface acoustic wave apparatuses, in sensor sectors and in laser technology owing to its non-linear optical characteristics in the ultraviolet region and its transparency down to 160 nm [1,4,5].

Even though, LTB was studied as an interesting material over the few past decades, the topic is open for extensive research to obtain this material in nano-scale size. The ultrafine structures containing 10⁻⁹ m grain size or an average phase are categorized as nanostructured materials (NSMs) [6]. At the moment, in a wider context of the phrase, any material that having grains or clusters less than 100 nm, or layers or filaments of that dimension, can be characterized as “nanostructured” [7]. The consideration to these substances has been motivated by the concept that, containing the small size of particle, grain, or phase and the high surface-to-volume ratio, these materials are assumed to display unrivaled optical, mechanical, magnetic, and electronic properties [8]. The properties of NSMs related to the consecutive four widespread microstructural features; (1) ultrafine grain size and size distribution (<100 nm), (2) the chemical compound of the fundamental phases, (3) the existence of interfaces, more particularly, grain boundaries, heterophase interfaces, or the free surface, and (4) interplay between the basic domains. The existence and interaction of these four features principally assign the unique properties of NSMs.

In nanoscale materials, a diversity of size-related factors can be integrated by controlling the sizes of the basic components during synthetic procedure [9].

Since, nanoparticles are small and thermodynamically tend to minimize their energy by formation of agglomerates in order to reach stable state, wherein the surface to volume ratio is minimized [10], so it is very important to prevent the nanoparticles from aggregation with other nanoparticles to make use of their properties in nanoscale. There are several capping materials for avoiding agglomeration such as organic ligand or inorganic surfactant reagents that can be used during synthesis process. Different types of polymers such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyvinyl chloride (PVC) can be effectively applied to stabilize nanoparticles. Besides the type of the stabilizer as capping material, its concentration has also an important impact on their stability during their synthesis procedure [11]. Other important factors of a polymer to act as a good capping material are their molecular weight, their ability to produce large chain ions in solution, and their solubility in water [12].

The present study reports synthesis of LTB nanophosphors by innovative single step thermal treatment method in the presence of PVP (MW = 58,000) as a capping agent. Regarding the thermal method selected for synthesizing nanoparticles, thermal stability of the sample was considered. So, the influence of the PVP concentration and various calcination temperatures on the thermal stability, phase transition, size, morphology and optical bandgap of LTB nanophosphor are investigated.

2. Experimental

The starting materials for synthesis of LTB nanoparticles was lithium carbonate (Li₂CO₃) and boric acid (H₃BO₃) as lithium and boron sources respectively, and 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 used without further purification.

In a typical preparation, 0.0058 mol of lithium carbonate and 0.024 mol of boric acid were added to 20 ml deionized water including PVP. In order to find the optimum concentration of PVP, a variety of its molar ratios of 0.009, 0.018, and 0.027 were examined. The master mixture was stirred for 1 h at 60 °C. To control the structure and size of nanoparticles, the stoichiometry and solubility of the precursors were considered [13]. The solution had a pH of 8.09 measured by means of a glass electrode. To achieve homogenous and monodisperse nanoparticles the temperature was optimized through the main stages of the synthesis process. The final solution was assigned to slow separation nucleation based on single step thermal treatment method, which is basically credited of Pechini method [14]. Besides particle size and morphology control, this method leads to a more precise stoichiometry [14–16]. Before the heat treatment, no precipitation was observed. The solution was sintered at different temperatures from 200 to 850 °C for 2 h to let the removing of organic content, crystallization of nanoparticles, and determining the optimum sintering temperature. The obtained solid cake was ground and sieved through 200 and 100 micron mesh to reduce the particle sizes close to the crystalline sizes.

The characterization of the prepared LTB nanoparticles were conducted using various techniques to explore parameters of interest. Thermal analysis of LTB was investigated by thermogravimetric analysis (TGA), derivative thermogravimetry analysis (DTG) and differential scanning calorimetry (DSC) using a Perkin Elmer Thermal Analyzer model TGA7/DTA7 and a Mettler-Toledo DSC 822e model differential scanning calorimeter in the presence of N₂ with 10°C/min heating rate from room temperature to 1000 °C to optimize the heat treatment program and determine the thermal stability of samples. Fourier transform infrared spectroscopy (FT-IR) was used to study the chemical composition of calcined samples at different temperatures using Perkin Elmer Spectrum 1650. The crystal phase and cell parameters of prepared samples were determined by X-ray diffraction (XRD) technique using Shimadzu 6000 diffractometer utilizing Cu Kα (0.154 nm) radiation. The morphology and average particle size of the nanocrystalline powder were evaluated using transmission electron microscopy (TEM) by JEOL 2010F UHR operating at an accelerating voltage of 200 kV. The average size and size distribution of nanoparticles were determined by Java-based image processing program image J. The optical properties of
3. Results and discussion

3.1. TGA, DTG, and DSC studies

Thermal analysis of LTB nanoparticles is depicted in Fig. 1(a) and (b). The weight loss of samples occurred through three phases, which can be seen on TGA and DTG curves. The greatest part of the weight loss occurs up to 400 °C through phase (I) and (II), which is almost 54%. The remaining ~4% mass loss on the tail of the curve may come from the breaking of chemical bonds in the sample, that is bond decomposition. The first phase of the weight loss, at about 60 °C can be attributed to the loss of water. The second phase is ascribed to the loss of some gases and organic matter such as CO₂ because of carbonate based precursor and PVP as capping agent accompanied by exothermic peaks can be seen in the DSC curve. This curve exhibits an exothermic peak starting at almost 400 °C followed by an endothermic peak which can be ascribed to the burn out of the organic material. The last exo–endothermic peak around 917 °C in the third phase can be due to the melting point of LTB that is compromised with literatures [17]. The majority of the mass loss occurs under 460 °C so, it can be emphasized that the thermal stability of samples is started at 460 °C, which allows for optimization of the heat treatment program.

3.2. FT-IR spectra investigation

The infrared spectroscopy provided important information about the vibration frequency of functional groups and network structures of the samples. Fig. 2 shows the FT-IR spectra of LTB nanoparticles calcinated at (a) 200, (b) 330, (c) 460, (d) 650, (e) 700 and (f) 750 °C in the range of 200–4000 cm⁻¹. At 220 and 330 °C, there is still a trace of absorption peaks of hydroxyl group and PVP compound but at higher temperature, the FT-IR results only exemplify the absorption bands of LTB nanoparticles. According to Table 1, the absorption bands of B–O and B–O(B) in BO₃ structure can be seen at 1600–1200 cm⁻¹ [18]. The bands in the range of 1500–700 cm⁻¹ can be related to the B–O(B) stretching vibrations of BO₄ tetrahedral [19]. The absorption bands in the region of 700–4000 cm⁻¹ is connected to the O–B–O deforming vibrations of BO₄ tetrahedral [19], and the peak appearing in the range of 400–200 cm⁻¹ can be attributed to Li–O [20]. The observed peaks in 418–688 cm⁻¹ appear in Fig. 2 at calcination temperatures of 650–750 °C can be designated to O–B–O deformation mode of BO₄ tetrahedral in Li₂B₄O₇ [19–21].

3.3. XRD investigation

The XRD patterns of synthesized lithium tetra borate under different calcination temperatures are shown in Figs. 3 and 4. The calcined samples at lower temperatures showed incompletely crystallization (Fig. 3) while the full crystallinity of LTB occurred at 650–750 °C (Fig. 4).

Fig. 2 – FT-IR spectra of LTB nanoparticles calcinated at (a) 200, (b) 330, (c) 460, (d) 650, (e) 700 and (f) 750 °C with 0.027 mol PVP in the range of 200–4000 cm⁻¹.

Fig. 1 – Thermal analysis of nanoparticulate LTB (a) TGA–DTG and (b) DSC.
As can be seen in the patterns in Fig. 4, the diffraction peaks are matched 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 [22]. It is to be noted that at higher calcination temperature of 800 and 850 °C, the substances fused in crucibles.

Fig. 5 shows the XRD patterns [1 1 2] of LTB nanoparticles synthesized with different molar ratios at calcination temperature of 750 °C. As can be observed, there is neither extra peak shifting. It can be concluded that there is not a considerable amount of impurity in the samples [23–25].

### 3.4. TEM investigation

To investigate the role of PVP as well as the effects of calcination temperature on the characteristics of LTB nanoparticles, various PVP concentrations of 0.009, 0.018 and 0.027 mol under calcination temperatures of 650 and 750 °C were studied by TEM (Figs. 6 and 7). The average size and size distribution of

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

<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>Ge et al., 2007 [18]</td>
</tr>
<tr>
<td>1500–700</td>
<td>B—O—H in plane bending of BO₄ tetrahedral</td>
<td>Ramesh, 2012 [19]</td>
</tr>
<tr>
<td>950–870</td>
<td>Stretching of tetrahedral BO₄</td>
<td>Ramesh, 2012 [19]</td>
</tr>
<tr>
<td>400–200</td>
<td>Li—O</td>
<td>Povarennykh, 1978 [20]</td>
</tr>
</tbody>
</table>

---

**Fig. 3 – XRD patterns of synthesized LTB nanoparticles under different calcination temperatures (a) 200, (b) 330, and (c) 460 °C with 0.027 mol of PVP.**

**Fig. 4 – XRD patterns [1 1 2] of synthesized lithium tetraborate under different calcination temperatures (a) 650, (b) 700, and (c) 750 °C with 0.027 mol of PVP.**

**Fig. 5 – XRD patterns [1 1 2] of synthesized lithium tetraborate with different molar ratios of PVP (a) 0.009, (b) 0.018, and (c) 0.027 calcinated at 750 °C.**
nanophosphorous powders were calculated from TEM images considering at least 150 nanoparticles for each sample. The size distribution histograms were fitted to the Gaussian distribution using OriginPro9 program to interpret the value of particle numbers (frequency %) versus particle sizes in nm. As can be seen in these figures, the small spherical LTB nanoparticles are formed when a proper amount of PVP was used. The optimum amount of PVP varies with calcination temperature as shown in Table 2. Although, the small size of nanoparticles (4.17 nm) is obtained using 0.0018 mol PVP at 650 °C, but the presence of 0.027 mol of PVP at 750 °C results in the smallest nanoparticles of 3.34 nm. Moreover, the best particle size distribution occurs with 0.018 and 0.027 mol of PVP calcined at 750 °C as can be seen in Fig. 7.

**Fig. 6** – TEM images of LTB nanoparticles with concentrations of (a) 0.009, (b) 0.018, and (c) 0.027 mol PVP calcinated at 650 °C.

**Fig. 7** – TEM images of LTB nanoparticles with concentrations of (a) 0.009, (b) 0.018, and (c) 0.027 mol PVP calcinated at 750 °C.
3.5. UV–vis spectra investigation

The optical bandgaps of the obtained LTB nanoparticles were also investigated in this research using UV–vis absorption spectra. The UV–vis absorption spectra of LTB prepared with different molar ratios of PVP at calcination temperature of 750 °C are shown in Fig. 8 and the estimated bandgaps are listed in Table 3. As can be seen in this figure, the absorption edges for all samples are below 240 nm. With increasing the PVP concentration, the absorption edge slightly moves to shorter wavelength due to the decrease of the nanoparticle size (Tables 2 and 3), hence the quantum confinement phenomenon is likely to happen resulting in larger bandgaps. The UV–vis spectra are plotted in Tauc region for absorption, which corresponds to the transitions through extended states in both valence and conduction band for indirect transitions [26]. The optical bandgap of LTB can be determined from the derivative Tauc plot of the UV–vis absorption spectra and extrapolating of the linear portions of the curves to the energy axis according to:

\[ a(hv) = A(hv - E_g)^n \]  
\[ \alpha(hv) = A(hv - E_g + E_p)^2 \]  

where; \( a \) is the absorption coefficient, \( hv \) is the photon energy, \( E_g \) represents the optical band gap, \( A \) is a constant, and \( n \) depends on the nature of the transition which has values of 1/2, 3/2, 2, and 3 for allowing direct transitions, forbidden direct transitions, allowed indirect transitions, and forbidden indirect transitions, respectively [27].

Among indirect transitions, momentum is conserved in double-step processes, because the photon cannot provide a change in momentum. So, the absorption for such transition is:

\[ \alpha(hv) = A(hv - E_g + E_p)^2 \]  

where \( A \) is a constant, \( E_g \) and \( E_p \) represent the optical band gap and the phonon energy, respectively. In this condition, the extrapolation to \( \alpha = 0 \) gives the values of \( E_g + E_p \) [28].

The effect of calcination temperature on the absorption and the bandgap of LTB nanoparticles, under 650, 700 and 750 °C temperatures with 0.027 mol of PVP were investigated by UV–vis as well (Fig. 9; Table 4). It can be observed that with increasing temperature the absorption fluctuated, due to gradually decreasing the optical bandgap which is resulted of red shift [29] (Table 4).

The exact bandgap of LTB was obtained from Eq. (2), with \( n = 2 \), regarding indirect allowed transitions. Furthermore, the gentle inflate of the curve in Fig. 9 (II) can be due to the existence of the defect which comes from carbonate based precursor \((\text{CO}_3^2-)\) and inorganic matter \((\text{PVP})\) in the structure of nanoparticles. Moreover, the bandgap decline of LTB in Table 4 at different calcination temperatures can be because of capping effect, which is likely to be happened in the presence of polymeric precursors for nanoparticle preparation. So, the red

**Table 2 – TEM data of LTB nanoparticles prepared with different concentrations of PVP at various calcination temperatures.**

<table>
<thead>
<tr>
<th>PVP (mol)</th>
<th>650 °C</th>
<th>750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROPS* (nm)</td>
<td>Ave. size (nm)</td>
</tr>
<tr>
<td>0.009</td>
<td>19.0–79.0</td>
<td>45.0</td>
</tr>
<tr>
<td>0.018</td>
<td>1.5–10.0</td>
<td>4.1</td>
</tr>
<tr>
<td>0.027</td>
<td>4–12.0</td>
<td>7.73</td>
</tr>
</tbody>
</table>

* ROPS = range of particle size.
shift can be related to the reduction of bandgap in the current investigation [29].

4. Conclusions

The nanoparticulate lithium tetraborate has been successfully synthesized by an innovative single step thermal treatment method. The effect of calcinations temperature and PVP concentration on physical properties of LTB nanoparticles was carefully examined. Thermal analysis proved the wide range thermal stability of samples from 460 to 750 °C. FT-IR, XRD and TEM results confirmed the formation of pure nano-crystalline LTB with narrow size distribution and small average size of ~3.3 nm at calcinations temperature of 750 °C and in the presence of 0.027 mol of PVP. The estimated optical bandgap in this case was around 5.5 eV.

Table 3 - The obtained values of the optical bandgaps and particle sizes of LTB at different ratios of PVP calcined at 750 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVP (mol)</th>
<th>Calcination (°C)</th>
<th>Band gap (eV)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.009</td>
<td>750</td>
<td>5.2</td>
<td>22.98</td>
</tr>
<tr>
<td>b</td>
<td>0.018</td>
<td>750</td>
<td>5.25</td>
<td>3.68</td>
</tr>
<tr>
<td>c</td>
<td>0.027</td>
<td>750</td>
<td>5.4</td>
<td>3.34</td>
</tr>
</tbody>
</table>

Fig. 9 – (I) UV–vis spectra and (II) (ahv) 1/2/(1/eV) versus hv (eV) plots of the LTB nanoparticulate synthesis with 0.027 mol of PVP calcined at (a) 650, (b) 700, and (c) 750 °C.

Table 4 - The obtained values of the optical bandgap and particle size of LTB at different calcination temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVP (mol)</th>
<th>Calcination (°C)</th>
<th>Bandgap (eV)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.027</td>
<td>650</td>
<td>6.2</td>
<td>7.73</td>
</tr>
<tr>
<td>b</td>
<td>0.027</td>
<td>700</td>
<td>6.1</td>
<td>3.3</td>
</tr>
<tr>
<td>c</td>
<td>0.027</td>
<td>750</td>
<td>5.5</td>
<td>3.34</td>
</tr>
</tbody>
</table>

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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