Influence of Microwave Heating and Thermal Auxiliaries on Synthesis of Lithium Triborate and Thermo luminescent Response

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ABSTRACT

Microwave treatment is used to decrease power inputs and synthesis duration for the production of lithium triborate (LiB3O5). Sucrose, urea and water as thermal auxiliaries were added to the starting materials. The effect of amount of thermal auxiliaries against the duration of heating and synthesis temperature of the target material LiB3O5 was investigated. The synthesis stages were followed by doping of Al2O3 into LiB3O5 to enhance its thermo luminescent (TL) properties. Identification and characterization of the obtained compounds were investigated by XRD, FTIR, DTA, SEM and particle size analyzer. The glow curves were obtained by using a TL reader. Characterization studies showed that the best crystallinity of LiB3O5 can be done with 40 % sucrose, 20 % urea and 0.1 ml water addition to initial mixture. The TL results indicate that the particle size and phase purity of host compound affect TL intensities of glow curves.

Keywords: Lithium Triborate, Microwave Synthesis, Sucrose, Urea, Luminescence

1. INTRODUCTION

Lithium triborate (LiB3O5) is one of the most known lithium borate compound. It has remarkable advantages in relation to medical and radiotherapy applications. It is chemically inert to body fluids, nontoxic and tissue equivalent. LiB3O5 has been synthesized by various methods, including solid state reaction, single crystal growth technique. These methods need larger processing time and high power input [1-5]. These are the most important problems of modern material science. Microwave treatment is a promising method to decrease power inputs and synthesis duration [6]. There are many advantages of microwave processing over conventional processing methods such as energy savings, improved product uniformity and shorter processing times [7].

Microwave energy as a heat source has been used for a number of applications in chemical and ceramic processing such as nano-materials, thin films, porous ceramics [8, 9] and synthesis of borate and some metal borate compounds [5, 10, 11]. Microwave is also used as an assisting equipment to synthesize chemical compounds. In this kind of process, synthesis procedure consists of two heating steps. While the first one is performed in a microwave oven; the second is performed in an electrical furnace. This technique has been effectively used to produce powders in shorter times in comparison with the conventional synthesis methods [11, 12].

Contrary to common belief, microwaves cannot break any chemical bond [13]. The actual mechanism of microwave heating does involve molecular rotational energy induced by microwave. Therefore, in order to use the microwave energy, it needs at least one of the reactants which should be a microwave susceptible. Materials with a low dielectric loss factor and insulators can be heated after adding compounds that absorb microwave, for example, water, magnetite, silicon carbide, or graphite [7, 14]. These materials are used as thermal auxiliary for heating up the raw materials until they start to absorb microwave energy by themselves.

Two aims are accomplished in the present research: One is to synthesize LiB3O5 by microwave assisted high temperature solid state method using thermal auxiliaries in a shorter time and to investigate the effect of thermal auxilarities on LiB3O5 structure. Distilled water, urea and sucrose were used as thermal auxilarities in the preheating step. Second purpose is to dope LiB3O5 with Al2O3 to gain thermo luminescent property and to investigate the particle size effect and more pure phase on TL intensities of compounds.

2. EXPERIMENTAL PROCEDURE

2.1 Microwave Solid State Synthesis

Stochiometric quantities of the starting materials, Li2CO3 and H3BO3, were weighed separately (according to Li2O:3B2O3 ratio), then mixed and ground in agate mortar. Homogenized mixture was transferred into convenient porcelain crucible and heated in the domestic microwave oven. The reaction was performed under microwave irradiation (2450 MHz) at 1000 W for various time intervals (30 min. - 120 min.). The same experimental conditions were applied using four binary compounds, LiBO2 – H3BO3, LiBO2–B2O3, LiOH–H3BO3, LiOH–B2O3 respectively for the preparation of LiB3O5.

2.2 Microwave Assisted High Temperature Solid State Synthesis

In microwave application, to synthesis new compounds, at least one of the reactants should be a microwave susceptible to store some of the energy in the form of heat. If not, some compounds are added to initial reactants to absorb microwave, for example, water,
magnetite, silicon carbide, or graphite [7]. In the present study, the starting materials were not enough to absorb adequate microwave radiation to start the reaction, so sucrose, urea and water were added to the starting materials as thermal auxiliaries.

Microwave assisted high temperature solid state reaction method consists of two heating steps. While the first heating step was performed in a microwave oven; the second one was performed in an electrical furnace [5, 11]. Stochiometric quantities of the starting materials, Li$_2$CO$_3$ and H$_3$BO$_3$, were weighed separately according to Li$_2$O:3B$_2$O$_3$ ratio and 20% by weight sucrose was added. The mixture was ground in an agate mortar and transferred into porcelain crucible and exposed by microwave at 1000 W for 10 minutes [14]. Then reground mixture was heated in an electrical furnace at different temperatures for different time intervals. The procedure was repeated by adding different amounts of sucrose, urea (10 to 50 % of total weight of initial reactants) and water (0.05 ml to 0.25 ml) into the starting materials.

2.3 Synthesis of Al$_2$O$_3$ Doped Lithium Triborate

Lithium triborates synthesized by microwave assisted high temperature solid state reaction were used as host lattices and Al$_2$O$_3$ was doped into them. 1 gram lithium triborate and 0.1 gram Al$_2$O$_3$ (1 wt. %) were mixed in an agate mortar and the mixture put into porcelain crucible and heated at 750 °C for 7 hours.

2.4 Characterization of the Obtained Materials

In order to characterize and identify the phase compositions and crystallinity of the compounds, X-ray Powder Diffraction was used. The XRD data were collected using Rigaku X-ray Diffractometer (Model, Miniflex) with Cu Kα (30 kV, 15 mA, λ=1.54051 Å) radiation at room temperature. Scanning was generally done between 5°<2θ<70°. The measurements were made with 0.01 and 0.05 degree steps and 1 degree/ minute rate. The divergence slit was variable and scattering and receiving slit were 4.2 degree and 0.3 mm, respectively.

The vibrational modes of functional groups of the undoped and doped lithium triborate compounds were measured in the range of the 400 to 2000 cm$^{-1}$ by using KBr pellet method and VARIAN 1000FTIR Spectrometer. Spectroscopic grade KBr was used for making IR pellets (KBr:Sample ratio of 100mg:3mg).

Differential thermal analysis was carried out to assess the thermal behavior of lithium triborate as well as their chemical stability in an aluminum crucible at a heating rate of 283 K (Celsius)/min in N2 by using Setaram Labsys TGA/DTA simultaneous thermo gravimetric analyzer and differential thermal analyzer.

In order to investigate the morphology and the particle size of the synthesized materials, scanning electron microscopes, JSM-6400 Electron Microscope (JEOL), equipped with NORAN System 6 X-ray Microanalysis System & Semafore Digitizer (for pellet form sample) and Fei Quanta 400 D (for powder form sample), were used.

Malvern Mastersizer 2000 particle size analyzer was used to determine the particle size of lithium triborate compounds obtained using sucrose, urea and water. Uniformity of particle size distribution and surface area of the samples could be also determined by this analyzer.

In thermo luminescence (TL) analysis, the prepared samples were irradiated at room temperature with beta rays emitted from a 90Sr-90Y source for 5 min. Then the glow curves (GCs) were immediately recorded, so that there was no significant fading of the TL peaks at room temperature. GCs were obtained using a Harshaw Q8 3500 manual type reader interfaced to a PC where TL signals were analyzed. GC readout was carried out on platinum planchet at linear heating rate 2 oC s$^{-1}$ up to 400 oC. Fifteen milligrams of powder were used for each measurement.

3. RESULT AND DISCUSSION

3.1 Characterization of Undoped Compounds

XRD patterns of the samples synthesized by microwave solid state method using Li$_2$CO$_3$ and H$_3$BO$_3$, are given in Fig. 1. They show that microwave irradiation at 1000 W cannot supply the required energy to start the synthesis process, because the reflections do not confirm the new phase or LiB$_3$O$_5$ compound. The peaks belonging to Li$_2$CO$_3$ (JCPDS Card No:87-0729) and H$_3$BO$_3$ (JCPDS Card No:23-1034) are observed for all time intervals which means that the synthesis of lithium triborate is not possible in these conditions. The same results were obtained for four binary compounds, LiBO$_2$–H$_3$BO$_3$, LiBO$_2$–B$_2$O$_3$, LiOH–H$_3$BO$_3$, LiOH–B$_2$O$_3$ (XRD patterns were not given in the text). As known, in microwave application at least one of the reactants must be a microwave susceptible. Therefore the chemical compositions of the reagents are important. Previous studies show that the presence of chemically bound water is necessary for the absorption of microwaves since the main acceptor in salts is water for microwave [7, 14]. Among the starting materials, lithium compounds do not contain chemically bound water. It is transparent to microwave and it does not store energy in the form of heat. On the other hand, boric acid contains chemically bound water [15], but this bound water was not enough to absorb adequate microwave radiation to start the reaction.
Fig 1: XRD patterns recorded for the materials synthesized by microwave 2.45 GHz frequency, 1000 W for various time intervals. The reflections marked by (*) has been identified with Li$_2$CO$_3$ and the reflections marked by (+) has been identified with H$_3$BO$_3$.

In the literature Li$_2$CO$_3$ and H$_3$BO$_3$ powders were ground and pre-heated at 300 °C for 4 hours to remove water and then the mixture was heated at 750°C for different time intervals [4, 16] for the synthesis of LiB$_3$O$_5$. In order to decrease energy consumption in the preheating step, microwave oven was used as preheating equipment.

Materials with a low dielectric loss factor and insulators can be heated after adding compounds such as water, magnetite, silicon carbide, or graphite [7] that absorb microwave. In salt systems, molecular water may act as an “additive.” [14]. These materials are used as thermal auxiliaries for heating up the raw materials until they start to absorb microwave energy by themselves. In the present study, distilled water, sucrose and urea were added to the starting materials as thermal auxiliaries. Microwave radiation is expected to activate the rotational degrees of freedom in H$_2$O molecules in the sample and the water molecules escape from the medium by heating up the raw materials. When a mixture (starting materials and water) is exposed to microwave radiation, heat generation take place in the microwave oven on account of constant rotation of dipolar water molecules. Therefore, the water molecules are heated up and driven off by phase change and creating heat in the system. Reactions involved in urea and sucrose combustion process are exothermic. Since significant amount of heat is generated, it can cause decomposition of starting material. The exothermic decomposition of thermal auxiliaries are accompanied by gassing (such as CO, CO$_2$, NH$_3$ and water vapor). The gassing does not only help the products to disintegrate, but also dissipate the heat of combustion [8, 17 – 19]. In the present study, the mixture (starting materials and sucrose and urea) was exposed by microwave irradiation. After about 5 or 6 minutes, scorching smell arose from the mixture with sucrose and the smell of ammonia evolved from the mixture with urea. These indicated that sucrose and urea were affected by microwave irradiation and they were decomposed [19, 20].

XRD patterns (not given in text) showed that after microwave irradiation (10 min), amorphous structure was observed due to the completed decomposition of the mixtures. During the microwave heating, metal ions can be uniformly distributed in molecular scale through polyfunctional groups (e.g. –COOH, -NH$_2$, -OH etc) from chelating agent ligands (sucrose, urea, water etc.). Literature survey shows that during heating, this metal ion-chelated complex is decomposed into carbon dioxide, ammonia and water and a large amount of heat is generated due to the exothermic reaction [17, 21 – 23].

The intermediate amorphous solids subsequently decompose and thermally react to form complex oxide phases in a furnace [24, 25]. Therefore, after microwave pre-heating step, the second heating step was performed in an electrical furnace. In this part, the effect of amount of thermal auxiliaries (water, sucrose and urea) against duration of heating and synthesis temperature of target
material, lithium triborate, were investigated. The comparison of XRD patterns indicate that the crystallinities of LiB$_3$O$_5$ are at maximum during 0.1 ml of water (WMAS), 20 % urea (UMAS) and 40 % sucrose (SMAS) addition to the initial mixture at 750 °C for 3 hours in an oven, so only their XRD patterns are given in Fig. 2.

![Figure 2: Powder X-ray diffraction patterns of lithium triborate.](image)

XRD patterns of LiB$_3$O$_5$ are analyzed and it can be seen that all peaks matched very well with the data reported in JCPDS Card File No: 77-0774. Although the predominant phase formed is lithium triborate, some reflections of lithium tetraborate as an impurity phase are observed (JCPDS Card File No: 18-717). The peaks belonging to lithium tetraborate were denoted by lozenge “♦”. The presence of another impurity phase, Li$_3$B$_7$O$_{12}$ (JCPDS Card No: 80-0672), occurred in lithium triborate in 20 % urea. Therefore, lithium triborates which were synthesized by addition of sucrose and water into starting materials were much pure than lithium triborate which was synthesized by adding urea into starting materials. In addition, it can be seen in Fig. 2 that the purity of the final powder was not affected due to the thermal auxiliaries. This shows that the thermal auxiliaries are chelating agent and template material and elements (other than Li, B and O) such as C, H, and N can be easily removed during heating step in a furnace [21, 23, 26].

Analysis of the IR spectra (Fig. 3) shows that on changing the thermal auxiliaries, vibrations of boron-oxygen bonds of lithium triborate do not change. Approximately 19 clear bands are observed and three IR spectral regions, 1200–1500 cm$^{-1}$ associated with the B-O stretching trigonal BO$_3$ units, 850–1200 cm$^{-1}$ associated to the B-O stretching of tetrahedral BO$_4$ units, and 600 - 800 cm$^{-1}$ associated with bending vibrations of various borate segments, are mainly active. These are close to literature values [2, 5].

Under the light of XRD and IR analyses, it can be concluded that LiB$_3$O$_5$ is synthesized by microwave assisted synthesis method at 1000 watt power level for 10 minutes exposure time followed by heating at 750°C for 3 hours in an oven. With the use of combination of microwave oven and conventional oven together, the reaction time is shortened when compared with the literature [1, 4, 27]. However, the amount of impurity in lithium triborate cannot be decreased by using different thermal auxiliaries.
Thermal behaviors of lithium triborates show same property and have nearly same DTA curve. Therefore only one DTA curve are given in Fig. 4, indicating the DTA curve of lithium triborate and its melting points identified by using phase diagram [28]. Three distinct endothermic peaks are observed on DTA curve and they can be attributed to the incongruent melting points. These peaks prove transformation of lithium triborate to other lithium borate compounds according to temperature. They are also in agreement with the literature data [5, 29].
SEM images of lithium triborates which were obtained in pellet form (left side of figure) and powder form (right side of figure) are given in Fig. 5. When SEM images of lithium triborate are examined, the sizes of irregularly shaped particles are detected as between 1-125 μm. Comparing different SEM micrographs of lithium triborate compounds, the particle size of UMAS (adding 20 % urea) is smaller than WMAS (0.1 ml water) and SMAS (adding 40 % sucrose). On the other hand, SEM images of LiB3O5 with 40 % wt. sucrose as in Fig. 5-f shows that actually this material has spherical morphology and small size but agglomeration is observed because of binding property of sucrose [17, 30]. Small particle size (in the range of 1 – 40 μm) may be explained by evolved gases during activation of organic materials in microwave oven. In the literature, it was reported that during organic materials combustion, great amount of gas evolved. For that reason powders have high surface area and also show a very narrow particle size distribution [8, 17].

Fig 5: SEM images of lithium triborates

The particle size analysis, specific surface area and uniformity of the lithium triborate compounds are given in Table 1. Particle size analysis is also determined by Rosin-Rambler distribution method. By comparing the P80 (80 % passing) values and particle size analysis results of lithium triborate compounds, it can be defined that the particle size, distribution, specific surface area and uniformity of WMAS and SMAS show similarity, but particle size of SMAS is a little bit bigger than others. On the other hand, lithium triborate obtained by microwave assisted synthesis method by adding urea has the smallest particle size. Small particle size and high surface area may be explained with evolved gases during activation of organic materials in microwave oven [5, 8, 17]. Lithium triborate obtained by adding sucrose has also high surface...
area but its particle size is bigger than others, since its particles agglomerated (see also Fig. 5-e and f).

**Table 1:** Particle size analysis results of lithium triborates

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Vol. Weighted Mean (μm)</th>
<th>Specific surface area (m²/g)</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMAS</td>
<td>36.144</td>
<td>0.593</td>
<td>0.641</td>
</tr>
<tr>
<td>UMAS</td>
<td>22.676</td>
<td>0.985</td>
<td>0.919</td>
</tr>
<tr>
<td>SMAS</td>
<td>43.468</td>
<td>0.965</td>
<td>0.711</td>
</tr>
</tbody>
</table>

3.2 Characterization of Al2O3 doped Lithium Triborate

TL properties of materials can be increased by introducing a very low concentration of activators which are known as doped material. The addition of small quantities of activators with another charge number may increase the concentration of imperfections which are important factors affecting thermo luminescent properties of materials in host lattice. In the present study, Al2O3 was doped into lithium triborates to improve TL properties according to the literature [4, 5].

The effect of addition of Al2O3 on the LiB3O5 structure was determined by XRD and FTIR analyses. XRD patterns and infrared spectra of the Al-doped lithium triborate compounds are given in Fig. 6 and Fig. 7, respectively. In XRD patterns of Al-doped lithium triborate compounds indicate that there is no reflection associated with the activator. The patterns of Al-doped lithium triborate show great similarity with that of undoped lithium triborate. However, some slight peaks of another lithium borate, Li3B7O12 (JCPDS Card No: 80-0672), are observed and are denoted by squares on X-ray patterns of Al-doped lithium triborate. This is related with heating process, Li3B7O12 occurs above 650°C [31] and explained using DTA curve which given in the present study.

![XRD Patterns](image)

*Fig 6: Powder XRD patterns of Al-doped lithium triborate*
3.3 Thermo luminescence Response of Al-doped Lithium Triborates

Fig. 8 shows the glow curves of undoped (left side) and Al-doped lithium triborate compounds. Undoped lithium triborate compounds do not show sufficient TL response. By comparison of TL curves, it can be seen that the shape of the TL peaks in the glow curves of SMAS is different and it shows thepoorest TL intensity. Generally, the undoped samples exhibit a poor TL efficiency and emission of these samples may be related to intrinsic defects [32, 33].

Fig 8: The glow curves of undoped (left side) and Al-doped (right side) lithium triborate compounds.
Comparative glow curves of 1 % Al2O3-doped LiB3O5 compounds are given right side of Fig. 8. It can be seen that the shape of the TL peaks in the glow curve structure of all doped samples keep almost constant, showing thermal auxilarities-independent character. But, their intensities are changed. Their glow curves are composed of two well separated TL peaks with the main one at about 206 ºC and the low-temperature peak at about 135 ºC. In general, Al included natural or synthetic thermo luminescent materials reported to give an efficient emission in the violet to blue region of the spectrum and Al acts like very efficient radioactive recombination centre [34, 35]. From Fig. 8, TL glow peak of Al-doped SMAS has the highest thermo luminescent intensity. The first peak intensity at 135 ºC is smaller whereas main peak intensity at 206 ºC is greater than others. By comparing their main peak intensities with each other, Al-doped SMAS is approximately 1.5 times and 6 times more sensitive than Al-doped WMAS and Al-doped UMAS, respectively.

TL intensity of glow curve is related with particle size and purity of host compound [36, 37]. In order to clarify these, all lithium triborates which were synthesized in the present study by adding different amount of thermal auxilarities were doped with Al2O3. Their glow curves are given in Fig. 9. XRD and IR spectra results show that the crystallinities of LiB3O5 are at maximum during 0.1 ml of water (WMAS), 20 % urea (UMAS) and 40 % sucrose (SMAS). As seen from Fig. 9, for each experiment set up, the TL intensities of the glow curves belonging to lithium triborates having best cristalinity are higher than others. In addition, this situation can be explained by evaluating the structure of these host material compounds. Ogornikov et al., [38] mentioned that localized boron-oxygen bonds dominate the electronic states of lithium triborate. Electrons are moved from the valance band to the conduction band, when excited by ionized radiation. In case of this phenomenon, thermo luminescence properties of lithium triborate are much related to boron-oxygen bonds in the structure. The specific wave numbers of lithium triborates which were synthesized in this study indicated that some specific vibration belonging to boron-oxygen bonds are missing; so, they have the lowest TL intensity, except the lithium triborate having the best crystallinity. Among the lithium triborates, SMAS shows the highest purity. Therefore, its glow curve has higher intensity than others.

In addition, the other factor to be considered for TL is the effect of particle size of host material. The relationship between the particle size and maximum intensity of glow curve of Al2O3 (1 %) doped lithium triborate samples and their abbreviations are given in Table 2. Main TL peaks of doped lithium triborate compounds (at around 200º) are considered and their sensitivities are investigated depending on particle sizes. The results indicated that the thermo luminescent sensitivities of main peaks decrease with decreasing particle size. The investigation of TL intensity depending on particle size shows that SMAS has highest sensitivity than others due to the larger average particle size.

The difference between the thermo luminescent intensities of materials can be attributed to particle size effect and more pure phase.

### Table 2: Particle size versus maximum TL intensity of doped lithium triborate compounds.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>P(80) (µm)</th>
<th>Vol. Weighted Mean (µm)</th>
<th>Al2O3 doped LiB3O5 Max. TL Intensity of Main Peak (200º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UMAS</td>
<td>35.56</td>
<td>22.676</td>
<td>148994</td>
</tr>
<tr>
<td>WMAS</td>
<td>56.368</td>
<td>36.144</td>
<td>511277</td>
</tr>
<tr>
<td>SMAS</td>
<td>63.246</td>
<td>43.468</td>
<td>579363</td>
</tr>
</tbody>
</table>
4. CONCLUSION

Experimental results showed that lithium triborate cannot be successfully synthesized by using microwave energy. It is found that, LiB$_3$O$_5$ can successfully be synthesized by microwave assisted high temperature solid-state reaction at 1000 watt power level for 10 minutes exposure time followed by heating at 750°C for 3 hours in an oven. With use of combination of microwave and conventional ovens together, the reaction time is shortened. Use of water, urea and sucrose as thermal auxiliary in the preheating step enhance the production of LiB$_3$O$_5$ compound. However, single phase compound could not be obtained by this method and some lithium borate compounds like tetraborate (Li$_2$B$_4$O$_7$)
and lithium octaborate (Li₂B₁₀O₁₉) were detected in the lithium triborate phase like literature data.

The comparison of XRD patterns and IR spectrum show that the crystallinities of LiB₃O₅ are at maximum during 0.1 ml of water (WMAS), 20 % urea (UMAS) and 40 % sucrose (SMAS) addition to the initial mixture. And the results of this study suggest that lithium triborate can be synthesized in shorter times when compared to conventional synthesis methods.

Thermo luminescent properties of lithium triborate were improved by the addition of Al₂O₃ as activator. Characterization studies of doped lithium triborate indicated that there were no indications for the production of new compound by adding activators into lithium triborate. TL part shows that Al₂O₃ doped LiB₃O₅ is a promising TLD material for dosimetric purposes and the difference between the thermo luminescent intensities of same compounds can be attributed to particle size effect and more pure phase.

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REFERENCES


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