SYNTHESIS AND CHARACTERIZATION OF LITHIUM TETRABORATE AND LITHIUM TRIBORATE PHOSPHORS DOPED WITH METALS AND THEIR THERMOLUMINESCENCE PROPERTIES

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF LITHIUM TETRABORATE AND LITHIUM TRIBORATE PHOSPHORS DOPED WITH METALS AND THEIR THERMOLUMINESCENCE PROPERTIES

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The phenomenon of thermoluminescence (TL) has been interested in the measurement of radiation dose over the past few decades. Thermoluminescence property of a material can be used in surface acoustic wave apparatus, sensor sector and non-linear optics (LASER). Moreover, in dosimetry TL concept has been utilized. Thermoluminescence dosimetry is interested in the fields of environmental, personnel, and clinical radiation applications.

In this thesis, dosimetric phosphors lithium tetraborate (Li₂B₄O₇: LTB) [1] and lithium triborate (LiB₃O₅: LBO) [2] which have been synthesized and doped with metals (Cu, Mn, Ag, Al, In, Eu) and thermoluminescence characteristics of synthesized lithium tetraborate (LTB) and lithium triborate (LBO) were analyzed. Un-doped and doped LTB samples were prepared with solution-assisted method (SAM) and microwave-assisted method (MAM). Synthesized LTB and LBO phosphors were characterized with X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR),

Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Differential Thermal Analysis (DTA) to determine structural and morphological properties.

Thermoluminescence (TL) properties of the LTB and LBO samples doped with various doping systems such as single dopant, double-dopant, and three dopant systems were studied. TL results demonstrated that 0.08% Cu and 0.04% Ag doped LTB synthesized with SAM has the highest dosimetric sensitivity among the LTB samples produced with SAM and MAM. According to TL results of LBO samples, 1% Al doped LBO sample gave the best TL properties in terms of peak shape and intensity among the synthesized LBO samples.

Keywords: Lithium Tetraborate, Lithium Triborate, Doping with metals, Characterization Techniques, Thermoluminescence Dosimetry.

LİTYUM TRİBORAT VE LİTYUM TETRABORAT FOSFORLARININ SENTEZİ, TERMOLÜMİNESANS ÖZELLİKLERİ VE KARAKTERİZASYONU

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Termolüminesans son yıllarda alınan radyasyon dozunu ölçmede ilgi çeken bir olay haline gelmiştir. Bir maddenin termolüminesan özelliği yüzey akustik dalga cihazlarında, duyar sektöründe ve doğrusal olmayan optik cihazlarında (LAZER) kullanılabilmektedir. Ayrıca termolüminesans özellik gösteren maddeler dozimetre cihazlarında kullanım alanı bulmaktadır. Termolüminesans dozimetreler çevresel, kişisel ve medikal uygulama alanlarında kullanılmaktadır.

Bu tez çalışmasında lityum tetraborat (Li₂B₄O₇: LTB) ve lityum triborat (LiB₃O₅: LBO) bileşikleri sentezlenmiş ve metaller (Cu, Mn, Ag, Al, In, Eu) kullanılarak katkılamaları yapılmıştır. Ayrıca sentezlenen lityum tetraborat (Li₂B₄O₇: LTB) [1] ve lityum triborat (LiB₃O₅: LBO) [2] bileşiklerinin termolüminesans özellikleri analiz edilmiştir. Katkısız ve katkılı LTB örnekleri çözelti yardımlı sentez tekniği ve mikrodalga yardımlı sentez tekniği kullanılarak yapılmıştır. Sentezlenen LTB ve LBO fosforları X-ışınları kırınım cihazı, FTIR, taramalı electron mikroskopu, geçirgenli electron mikroskopu, DTA analizleri ile sentezlenen örneklerin yapısal doğruluğu ve morfolojik özellikleri belirlenmiştir. Sentezlenen ve çeşitli katkılama sistemleri (tekli, ikili ve üçlü katkılama) ile katkılanan LTB ve LBO örnelerinin termolüminesans özellikleri araştırılmışır. Termolüminesans sonuçlarına göre %0,08 çözelti yardımlı sentez yöntemi ile sentezlenen Cu ve %0,04 Ag katkılı LTB örneğinin bütün sentezlenen LTB örnekleri içinde iyi TL hassasiyetine sahip olduğunu ispatlamıştır. TL sonuçlarına göre, %1,0 Al katkılı LBO örneği sentezlenen LBO örnekleri arasında en iyi şiddet ve ışıldama eğrisi şekline sahiptir.

Anahtar Kelimeler: Lityum Tetraborat, Lityum Triborat, Metal Katkılaması, Karakterizasyon Teknikleri, Termolüminesans Dozimetre.

To my parents Zehra and Faruk Çelik

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LIST OF SYMBOLS AND ABBREVIATIONS

A.u. : Arbitrary Unit

- Zeff: Effective Atomic Number
- **DTA:** Differential Thermal Analysis
- **ENDOR:** Electron Double Resonance
- **EPR:** Electron Paramagnetic Resonance
- FTIR: Fourier Transformation Infrared
- **Gy:** Gray (Joule per kilogram)
- ICP-OES: Inductively Coupled Plasma Optical Emission Spectroscopy
- **ICRP:** International Commission on Radiation Protection
- JCPDS: Joint Committee on Powder Diffraction Standards
- **LTB:** Lithium Tetraborate
- **LBO:** Lithium Triborate
- MAM: Microwave Assisted Method
- NLO: Non-Linear Optic
- **SEM:** Scanning Electron Microscopy
- SAM: Solution Assisted Method
- SAW: Surface Acoustic Wave
- **TEM:** Transmission Electron Microscopy
- TL: Thermoluminescence
- TLD: Thermoluminescence Dosimeter

CHAPTER 1

INTRODUCTION

1.1 Borates

Borate compounds possess diverse crystallinities due to three-fold (trigonal) or fourfold (tetrahedral) coordination of boron atoms in boron-oxide compounds. Basic structural unit of borates, which contains various anionic groups, facilitates occurrence of borates with different crystal structures [3]. Hence, it provides outstanding properties such as large electronic band gaps, attractive nonlinear optical (NLO) properties, mechanical strength, and resistance for chemical and environmental conditions [4]. As a result, borate compounds are utilized in technology materials.

Some borate compounds, which are composed of anionic groups illustrated in **Figure 1**, can be defined as followings:

- LiBO₂ crystal consists of trigonal BO₃³⁻ and tetrahedral groups BO₄⁵⁻ [5].
- Bi-trigonal and di-tetrahedral groups B₂O₅⁴⁻ and B₂O₇⁸⁻.
- Six membered ring structure with a mixed coordination B₃O₆³⁻, B₃O₇⁵⁻, B₃O₈⁷⁻ and B₃O₉⁹⁻ which form the basis for the structure of LiB₃O₅ crystals [2].

 Basis of Li₂B₄O₇ crystal system are coupled double six-membered rings B₅O₁₀⁵⁻ and B₄O₉⁶⁻ [6].



Figure 1. Fragments of boron-oxide compound structures [7].○ O atom, ●, B atom.

Borate compounds find widespread application areas such as surface acoustic wave (SAW) devices of electric circuits to convert electric signals to acoustic wave or vice versa due to crystal and electronic structures [7–9]. Besides, borates are used in sensors that detect pressure and pyroelectricity [11]. Borates having planar BO₃ unit are materials of the interest for ultraviolet converter in lasers due to their nonlinear optical properties such as high polarizability and excellent transparency in ultraviolet region. Therefore, borates have been interested in non-linear optical (NLO) materials that are utilized to produce new laser sources of frequencies are smaller than conventional laser since first NLO borate KB₅O₈.4H₂O was identified [12]. On the other hand, extensive research for borate crystals started with advent of low temperature β -BaB₂O₄ [13]. Likewise, many borate compounds were synthesized up to now. For example, LiB₃O₅,

 CsB_3O_5 , $KBe_2BO_3F_2$, $CsLiB_6O_{10}$, $Sr_2B_2Be_2O_7$, Ca_4LnO (BO₃)₃, $K_2Al_2B_2O_7$ and BiB_3O_6 .

1.2 Luminescence

When incident radiation encounters with a material, some part of its energy may be absorbed, scattered or re-emitted as longer wavelength (lower energy). This re emitted light is called luminescence. Wavelength of re emitted light is longer than incident light's (Stoke's Law), which is characteristic of a material showing luminescence property. Re emitted light is independent from wavelength of the incident light. Generally, luminescence phenomenon is associated with visible light but other wavelengths such as ultra-violet, infrared are also emitted. Furthermore, luminescence can occur by different stimulus. Hence, the name of luminescence is given upon the type of the stimulus. For instance, photoluminescence (excitation by optical e.g. ultra-violet light), sono-luminescence (by sound waves), radio-luminescence (by nuclear radiations), cathode-luminescence (by electron beam) and thermoluminescence (by ionizing radiation, ultra-violet) [14].

Luminescence is classified into fluorescence and phosphorescence by characteristic relaxation time (τ_c) which is defined as time between absorption of incident light and emission of light. If characteristic time is greater than 10⁻⁸ s, this relaxation is called phosphorescence. If this time is shorter than 10⁻⁸ s, the process of luminescence is called fluorescence. Phosphorescence time is seen a bit longer than fluorescence time since metastable level give rise to slow down relaxation process. This process is illustrated in **Figure 2**. Excited electrons in Figure 1a are trapped by metastable level (see Figure 1b) which is arise from defects in the crystal. Furthermore, phosphorescence is subdivided into two main relaxations that are short period $\tau_c < 10^{-4}$ s and long period $\tau_c > 10^{-4}$ s [14].



Figure 2. Energy transitions of (a) fluorescence, (b) phosphorescence. g is denoted to ground state, e is denoted to excitation state, m is denoted to metastable level. E is trap depth.

However, it is difficult to distinguish fluorescence and phosphorescence due to delay of much shorter time. The way to distinguish fluorescence from phosphorescence is the examination of temperature dependent relaxation processes. Fluorescence process is independent from temperature. On the other hand, phosphorescence is temperature dependent. According to the **equation 1**, phosphorescence time is exponentially dependent upon temperature. S is constant (frequency factor), E is energy difference between metastable level and excited energy level, T is temperature, k is Boltzman constant.

$$\tau = S^{-1} exp^{(\Delta E/kT)}$$
 (Arrhenius Equation) Eq. 1

1.3 Thermoluminescence

Thermoluminescence (TL) is simply defined as the emission of light generated by heating of previously irradiated TL material [15]. TL concept might be confused with incandescence that is spontaneous emission of light when luminescence material is heated. There are three fundamental principles of TL. Firstly, luminescence material have to be semiconductor or insulator. However, metals are unable to exhibit

luminescence properties. Secondly, the material must absorb some of the radiation to create charge carriers that are free electrons and holes in a crystal structure. Traps defined as defects in a crystal structure can capture the charge carriers. Therefore, two principle defect types that are traps and luminescence or recombination center are important for TL [14]. These traps are located between conduction band and valence band and the amount of filled traps depends on applied radiation [10, 16]. The term 'valence band' is used to define outermost energy band that contains electrons in ground state energy level. In conduction band, electrons are moving and they are able to generate a net electric current. Thirdly, upon applied heat, electrons are back to ground state and released from traps. Released electrons and trapped holes might recombine to generate luminescence emission [14]. Energy as heat serve to jump activation barrier for the charge carriers. Besides, holes might be energetically ascended to the band and make recombination to give luminescence during the heating process. Figure 3 illustrates basic TL process. Ionizing radiation causes the ionization (a) and creates electrons (b) and hole (e) pairs in the insulators or semiconductors. Without heating the material, some of created electrons and holes might recombine directly (h) or indirectly (d and g). Rest of the electrons and holes can be trapped by defects between valence band and conduction band. Under the applied heat, trapped electrons (c) and holes (f) are released and recombine each other, which causes emission of light.

Generally, TL data is interpreted as a plot of luminescence intensity vs temperature known as thermal glow curve. TL intensity is directly related with concentrations of recombination center and trapped charge. Hence, if the recombination center concentration is smaller and it stays constant, glow peak intensity does not change with thermal treatment in spite of fact that the concentration of the traps are associated with the peak that might be varying [14].



Figure 3. Basic model of thermoluminescence process [14].



Figure 4. TL glow curve from Cu, Ag doped-lithium tetraborate (LTB).

Typical TL glow curve of lithium tetraborate is shown in **Figure 4**. The peaks appear in the glow curves related to the trap depth that affect the peaks temperature and peak shape. Two peaks are clearly shown in **Figure 4** indicating two different type of traps activated when they are appeared at various temperatures [14]. Peak 1 is not used in measurement of absorbed dose due to the fact that it loses stored radiation in short time. Peak 2, called main peak or dosimetric peak, gives us information about the TL properties of a material. Each peak has its value of E_a (activation energy) and *s* (frequency factor), which define TL intensity and peak shape of peak 1 and 2 in **Figure** 4. Furthermore, glow curve shape, activation energy give us information about absorbed X- ray, gamma or Beta radiations [17].

1.4 Trapping and Defects

Defect structures of materials have strong relationships with qualities of dosimeters. Therefore, it is worthy to discuss the concept of defects in TL materials. At the absolute zero temperature, all atoms would be on ideal lattice positions in a perfect crystal. Above 0 K, atoms vibrate due to temperature. Hence, defects occur in a crystal. This type of defects called extended defects such as dislocation, affects the strength of the materials. Besides, defects might be at isolated atomic positions, which is called a point defects. It occurs due to the presence of a foreign atom at a particular site of a material or atomic vacancy. Point defects are of importance for the chemical and physical properties of the materials. For the TL characters of a material, point defects play a significant role due to the fact that defects act as a trap for electrons and holes that are generated by ionizing radiation. Defects are classified into two main categories: intrinsic or native defects and extrinsic defects. Intrinsic defects, which is called Schottky defects, consist of vacancies in lattice due to missing of positive and negative ions. Frenkel or interstitial defects defined as an atom or ion moving into an interstitial position creates a vacancy. On the other hand, extrinsic or impurity defects occurs when impurity or dopant is added into a crystal structure. These foreign materials might be added into crystal structure from melt or they diffuse into host material at later stages. Such defects might be either substitutional or interstitial [18].

Furthermore, ionizing radiation is able to produce further defects called luminescence centers or absorption centers of the materials. The radiation leads to displace the atom from their lattice positions and it creates vacancies and interstitials. Irradiation time and flux of a radiation are of importance on the amount of the defects [19]. To illustrate, probability of negative ion vacancies are higher near localized positive charge. Since negative ion that naturally exist at the vacancies. Thus, anions are not paired by cations at the place. Ionizing radiation generates electrons that wander in the crystal and electrons may be attracted by localized positive charges due to Columbic force, which is explained in **Figure 5**. Therefore, they are trapped in the vacancy. This center is called in literature F center. Likewise, the term V center is used for positive ion vacancy as hole traps [19].

+ - + - +	- + - + -	+ - + - +
- + - + -	+ - + - +	- + - , <u>+</u>
+ - + - +	- + /-7+ -	$+ - + (-0)^{4}$
- + - + -	+ <u>/-</u> /+ - +	- + - + -
+ - + <u>-</u> +	- + - + -	+ - + - +
- + - + -	+ + - +	- + - + -
V Center	Vk Center	V3 Center

Figure 5. V, V_k, and V₃ centers in real crystals [19].

The V_k center is observed when a pair of negative ions capture a hole. The V_3 is obtained when the material contains neutral halogen that exists at halogen site of halogen ions. Therefore, two halogens traps two holes in the crystal.

1.5 Applications of Thermoluminescence

1.5.1 Thermoluminescence Dosimetry (TLD)

The phenomenon of TL has been interested in the measurement of absorbed dose since initial work of Daniels and colleagues [20]. Various thermoluminescence phosphors are in use for particular radiation measurements. The phosphors for TL dosimetry are selected to measure doses that are important for medical, environmental etc. applications.

1.5.2 TL Dosimeters and TL concept in various application areas

1.5.2.1 Personal Dosimetry

Personal dosimeters are used to control and restrict absorbed dose delivered to individuals during the occupation. A person is required to be exposed to absorbed dose that must be below International Commission on Radiological Protection (ICRP) recommended limits [14]. Recommended limits are based on the doses that are unable to cause any injury to individuals in course of work-life. But low dose might be cancerogenic in long-term [14]. The corresponding dose range is from 10⁻⁵ Gy to 10⁻¹ Gy. Gray (Gy) is IS unit of ionizing radiation, which is defined by absorbed dose of one joule of energy per one kilogram of a matter.

Especially, tissues including skin, organs such as the gonads, lung, bone marrow cells, thyroid and breasts in females are at risk when they are exposed to ionizing radiation. By using personal dosimeters, a depth of penetration of ionizing radiation might be estimated. For practice, absorbed dose by body dosimeters is estimated at a depth of 300-1000 mg/cm² [14].

Personal dosimeters are classified into body and skin type dosimeters according to their main functions. Both skin and body dosimeters are worn on body for detecting of electrons and photons on skin and whole body respectively. Skin dosimeters are able to measure absorbed dose at a depth 7 mg/cm². For body dosimeters, absorbed dose is

measured at a depth between 300 and 1000 mg/cm². Corresponding energy of absorbed dose is between X-ray and Gamma ray (15 kev). Furthermore, those dosimeters are unable to work at higher dose of ionizing radiation. For reliable information, neutron dosimeters might be required to measure extreme dose. On the other hand, the measurement of low energy photons might be problematic due to detector energy response, thickness, and self-absorption in the badge. Besides, materials have low effective atomic number (Z_{eff}), which represents elemental composition and density of a material, used for detection of the low energy photons. Moreover, tissue equivalency might be obtained with arranging thickness of detectors that is required to be about 3 mg/cm², which is crucial to get correct energy response [14].

1.5.2.2 Environmental Monitoring

Environmental dosimetry is interested in measurement of manmade or natural radioactivity in surroundings or it may be arise from cosmic rays consisting of 92 % proton, 7 % α -rays, 1 % heavy nuclei when rays, coming from solar system enter the atmosphere. Those types of radioactivity is monitored by environmental dosimeters. The detectors used in environmental dosimeters are required to have high sensitivity due to low dose level (~10⁻⁵) they have to resist high moisture, sun light, and chemicals in course of long measurement periods (from months to years) [14].

1.5.2.3 Medical Dosimetry

TL dosimeters are utilized to measure the dose taken by the patients during the diagnostic radiology and radiotherapy (e.g. cancer therapy). The dose applied in radiology applications is between 10^{-5} to 1 Gy. For radiotherapy, the dose increases up to 10 Gy. In radiotherapy, dosimeters are crucial to measure the dose applied to target volume as prescribed, which minimizes the dose absorbed by surrounding tissues. The treatment can be effective when the dose is given the target area with 5% accuracy or better in special cases [21]. A material used in TLDs for medical applications is required to have tissue equivalence, non-toxic and high sensitive *in vivo*. If those requirements are considered, LiF and Li₂B₄O₇ (especially) are appropriate for clinical dose assessments [14]. Since Z_{eff} values of Li₂B₄O₇ (especially) are close enough to

human tissue values (7.42) [17]. In **table 1**, the types of applications and corresponding dose range are given. According to this table, tissue equivalency is highly recommended for radiotherapy due to control the dose taken by patients. Furthermore, their dose range covers the doses applied in radiology and radiotherapy. Energy response of them is arranged according to types of dopant in host materials such as LiF and $Li_2B_4O_7$ [14].

Table 1 Requirements for TLDs for medical applications [21].

Task	Dose Range (mSv)	Uncertainty (SD)	Tissue Equivalency
Whole Dosimetry	0.01–0.5	± 50	Important
Radiotherapy	0.1-100	±3.5	Very Important
Diagnostic radiology	0.001-10	±3.5	Important

1.5.2.4 High Dose applications of TLDs

TLDs are crucial to measure the radiation doses (10^2 Gy to 10^6 Gy) which are applied to testing of materials and food sterilizations etc.

1.5.2.5 Thermoluminescence Dating

TL is an important tool to determine the age of archeological and geological specimens. Moreover, it is useful to get information about the formation of the materials such as lava. The simplest formula is given below for age determination.

$$Age = \frac{Natural Thermoluminescen}{(Themoluminescence per unit dose) \times (Natural Dose Rate)} Eq. 2$$

Where natural TL is defined as TL occurs on specimen during lifetime, TL per unit dose is defined as sensitivity of the material [14].

1.5.2.6 Commercial TL Dosimeters

Today, bunch of TL dosimeters are available to monitor different radiation doses in various application areas. TL characters of each dosimeter show differences and similarities. That is, it makes them outstanding or disadvantageous for particular radiation measurement.

The commercial dosimeters are represented by codes such as TLD100, TLD100H, TLD600, TLD600H, TLD700, TLD700H TLD200, TLD400, and TLD500. For instance, the commercial name of LiF based dosimeters are TLD100, TLD100H, TLD600, TLD600H, TLD700 and, TLD700H. Those codes are given the dosimeters based on the type of dopants activating host materials. LiF based dosimeters, commonly used in USA, have reasonably high sensitivity, small fading rate and inertness. On the other hand, complicated glow curve structure and lack of tissue equivalency are drawback of those type dosimeters [16].

Calcium sulfate (CaSO₄) and calcium fluoride (CaF₂) based dosimeters are generally used in environmental radiation monitoring. Those phosphors lose stored radiations in short time (approximately 25% of absorbed dose lost in a month), which is undesirable property for TLDs. CaF₂ is activated with Thulium (Tm) and Manganese (Mn). However, CaF₂: Mn is higher sensitivity than Tm doped CaF₂ phosphors [22]. CaSO₄ is phosphor is doped with Dysprosium (Dy), Thulium (Tm) or Manganese (Mn) metals separately. Among them, Mn doped CaSO₄ has highest TL sensitivity[23].

The other type dosimeters are TLD-500 Aluminum oxide (Al_2O_3) which is activated by Ca, Cr, Ti, Ni, Mg, Na, and Fe. Moreover, Beryllium oxide (BeO) and Magnesium tetraborate (MgB₄O₇) are TL materials in use for TLDs [23]. Abovementioned TL dosimeters are listed in **Table-2**.

Lithium tetraborate (TLD-800) is commercially available. However, TL properties of TLD-800 should be enhanced due to low TL emission, low dose range etc. On the other hand, lithium triborate (LiB_3O_5) is new TLD phosphor having properties tissue equivalency, inertness and nontoxic.

Phosphor	Glow Peak	Zeff	Sensitivity	Linear Dose Range	Thermal Fading
	(°C)			Gy	
LiF:Mg,Ti	210	8 20	1.0	$5x10^{-3} - 10^{2}$	5-10%
(TLD-100)	210	0.20	1.0	5A10 10	per year
LiF:Mg,Cu,P	232	8.14	25	$10^{-4} - 10^{3}$	NA
(TLD-100H)	202	0.11	20	10 10	
Li2B4O7:Mn (TLD-800)	210	7.40	0.4	10 ⁻² - 300	10% per month
Li ₂ B ₄ O ₇ :Cu	205	7.40	8.0	10 ⁻² - 10 ⁵	25% in 60days
Li2B4O7:Cu,Ag	185	7.40	-	-	10% per month
CaSO4:Tm	220	15.30	60	$10^{-5} - 3x10^3$	10% per month
CaSO4:Dy	220	15.30	30	$10^{-4} - 3x10^{3}$	3% per month
CaF ₂ (Natural)	260	16.30	20 to 30	$10^{-3} - 5 \times 10^{3}$	NA
CaF ₂ :Dy	200	16.30	16	$10^{-3} - 10^3$	12% per month
BeO	180-220	7.13	3.0	10 ⁻² - 50	5% per month
Al ₂ O ₃	250	10.20	5.0	10 ⁻² - 100	5% in 14 days
Mg ₂ SiO ₄ .:Tb	195	11.00	40-100	$10^{-3}-4x10^{2}$	3% per month

Table 2 Commercial TLD materials and their characteristics [23].

1.5.3 Essential TL properties for TLD materials

General requirements of a material to be used as TL dosimeter depend on particular applications commonly covered by *personal dosimetry* (dose measured in body) and *environmental dosimetry* (dose measured in the air). They are considered for medical applications and reactor dosimetry. However, each application area may be overlap each other.

Some basic properties for all dosimeters are listed below [22, 32].

- 1. The dosimeters need to have batch homogeneity which is a method controlling the quality of newly produced dosimeters. In this process, all new dosimeters are irradiated with a known dose. If the values are out of tolerance limits, those TL materials are rejected [21].
- 2. The dosimeters need to be free from energy dependence. Dosimeter have to give the same response at high and low energy of the radiation.
- 3. It is expected to a dosimeter give simple glow curve (dosimetric peak around 200°C). If the peak is seen at higher temperature, infrared emissions from sample holder or sample interfere with results.
- 4. The dosimeters have to show gamma ray sensitivity. Besides it is required that dosimeter must have high signal per unit-absorbed dose.

5. The dosimeters must be durable for environmental conditions such as humidity, sunlight and organic solvents. Moreover, they must be chemically inert.

6. The dosimeters for personal and medical applications must have effective atomic number very close to soft biological tissue value.

7. The dosimeter should be non-toxic in body testing, cheap and easy postal service.

Furthermore, some properties such as linearity, dose range, energy response, reproducibility, stability of absorbed radiation, and others determine the performance of a dosimeter. Detailed discussions of these properties are given below.

1.5.3.1 Dose Response

It is expected for a TLD detector to show linear relation between absorbed dose and TL intensity. Linearity is required for TL dosimeters to use them in the region where they show linear TL response versus absorbed dose. Linearity is generally depend on the type of a material and TL reader. When the TL dosimeter is used out of linearity zone, a correction is necessary for the signal coming from TL glow curve [21]. The dose response function of a TL material should be linear in broad scale if it is possible. However, most of the TL materials have limited linear dose response range. Supralinearity and sublinear growth, which are pictured in **Figure 6** (Here, in high

dose saturation of all traps leads to supralinearity), might lead to errors while TL dosimeter is read. The correction for region where it is out of linear range is needed by calibration [14]. Nevertheless, lithium borate compounds have wide linear dose range. They preserve linearity when absorbed dose is applied up to 10³ Gy [35, 36].

Furthermore, dopants are crucial to expand linear dose response for host materials. Park et al. demonstrated that the effects of the dopants on linear dose response by comparing manganese, copper and magnesium doped lithium borate [26]. According to the study, copper-doped lithium borate shows linear response up to 100 Gy absorbed dose. Beyond 100 Gy dose it shows supralinear deviation. However, manganese doped lithium borate conserves linearity up to 10 Gy dose [38, 39].



Figure 6. Dose-response graph shows linearity, subralinear, and sublinear regions.

1.5.3.2 Thermoluminescent Sensitivity

TL sensitivity is defined as the amount of the energy in the form of light from a TL material per unit of radiation exposure [21]. TL sensitivity of dosimeters may change

upon the concentration and the amount of the activator. Corresponding formula is given below.

Sensitivity =
$$\frac{TL intensity}{incident doseXMass of TLD}$$
 (TL.Gy⁻¹. mg⁻¹) Eq. 3

1.5.3.3 The reproducibility of TL Materials

The reproducibility of TLD system, which are detector, reader, annealing-irradiation, can be thought as kind of the sensitivity of a TL material after each cycle of irradiation and annealing process at the same condition. For ideal situation, it is thought that dosimetric materials release all absorbed dose during reading process. However, some of the absorbed radiation is stored in the materials. This residual radiation causes positive errors. The residual radiation has to be erased by annealing process which consists of heating the materials up to certain temperature at certain time and cooling to room temperature. Annealing conditions may change and depend on the TL dosimeters. For instance, LiF: Mg, Ti (TLD-100) has complex annealing process required for two steps. Initially high temperature annealing is applied to dosimetric traps and residual signals. Afterwards, low temperature annealing is needed for stabilization and aggregation of low temperature traps [19].

1.5.3.4 Fading

The fading is defined as the decrease in the TL response of irradiated materials after a certain time. For a TL material, the stability of the signal is essential to be a choice of TL dosimeter. It is expected from the TL materials to keep the absorbed radiation under the conditions such as heat, light and any other factor for years. Nevertheless, TL materials in use lose part of the signal. That is why the assessment of loss of absorbed radiation is necessary before the readout [21].
1.6 Lithium Tetraborate (LTB) and Lithium Triborate (LBO)

1.6.1 General Properties of LTB and LBO

The physical and chemical properties that lithium borates possess play a significant role on the optical characteristics of these materials. Especially crystal structure and inherent defects are unique for borate compounds.

Lithium tetraborate and lithium triborate, a white powder, are a congruently and incongruently melting compound respectively. When LTB materials melt congruently, they have the composition that is the same as solid phase. Otherwise, they would go through phase transition, decomposition or incongruently melting below their melting temperature in air [29]. Density and melting point of LTB are 915±2 °C and $\rho = 2.45$ g/cm³ [41, 42]. LBO melts incongruently at 824±2 °C and it is proposed as following;

 $LiB_3O_5 \rightarrow Li_2B_4O_7 + L$

 $LiB_{3}O_{5} \rightarrow Li_{4}B_{10}O_{17} + L$

Where L represents Lithium borate a compounds. Density of LBO is 2.43g/cc and solubility of that is 184 g/100mL [32].

1.6.2 Uses of LTB and LBO

Lithium borate compounds possess varied crystallinities due to three-fold (trigonal) or four-fold (tetrahedral) coordination of boron atoms in boron-oxide compounds. The members of basic structural units of borates have various anionic groups showing crucial physical properties, which make these materials noteworthy for the scholars. That is why LTB and LBO crystals find many possible application areas such as piezo technology, surface acoustic wave (SAW) devices converting electric signals to acoustic wave or vice versa, and laser converter (for LTB) for the Nd:YAG laser [7, 44]. Moreover, especially LTB (Li₂B₄O₇) based dosimeters have been recently introduced borates that measure ionizing radiations for thermoluminescence dosimetry. LTB and LBO have the effective atomic numbers $Z_{eff} = 7.4$ and $Z_{eff} = 7.3$ respectively, which is very close to soft biological tissue value (7.42) [15]. Hence, tissue equivalency makes LTB and LBO as candidate for personal and medical dosimetry purposes compared to phosphor that does not have tissue equivalency. Another important application area of these crystals are neutron detection. Because two isotopes of ⁶Li and ¹⁰B have large cross-sections for thermal neutrons [34].

1.6.3 Synthesis studies of lithium tetraborate

Single crystal and polycrystalline forms of LTB can be prepared using different synthesis methods. Powder form of LTB was synthesized by Sangeeta *et al.* who used solid-state sintering method by which Li₂CO₃ and B₂O₃ precursors are taken by stoichiometric ratio and sintered at 700°C for 48 h [30]. Lithium rare earth borates were produced by Jubera *et al.* using solid-state synthesis method [35]. Furthermore, microwave (wavelength range from 1mm to 300 mm) irradiation was employed solid state sintering method to energy savings, improved product uniformity, shorter processing times and very rapid processing [36]. Microwave can be absorbed, reflected or transmitted by a material. Insulators, effectively transparent, are unable to store energy as heat. Conductors such as metals reflects the microwave, which heats the material on a molecular level. Hence, it leads to uniform heating, however, in heating without microwave the material is heated from outer surface to interior, which results into steep thermal gradients [37].

Prokic in 2001 was employed wet synthesis method for the synthesis of LTB powders. According to this method, starting materials Li₂CO₃ and H₃BO₃ powders were mixed in the solvent, which was followed by heating in a furnace [38].

Another method for nano-scaled powder LTB production is combustion synthesis method used firstly by Singh *et al.* In combustion method, urea and ammonium nitrate work as fuel and oxidizer, respectively. The starting mixture containing Li(NO₃),H₃BO₃, NH₄NO₃, NH₂CONH₂. Then, the mixture was put in a quartz crucible and preheated in a muffle furnace at 580°C. The mixture underwent flameless combustion to produce nanocrystalline LTB [39].

The production of semiconductor as single crystal can be performed with Bridgman and Czochralski methods.

In this study, wet synthesis method and microwave assisted method were used to compare the effect of preparation technique on TL properties.

1.6.4 Synthesis studies of lithium triborate

The synthesis techniques such as solid state sintering method, microwave method assisted synthesis method, wet synthesis method, hydrothermal method are employed for the production of the polycrystalline LBO. Moreover, single crystal LBO can be produced with Bridgman and Czochralski methods.

Konig and Hoppe synthesized first LBO crystals using solid-state sintering method. According to corresponding method, the glass form of B_2O_3 was covered with LiF powder at 750°C for 10 hours [2].

In addition, in the study of Moryc and Ptak polycrystalline form of LBO was obtained with solid-state synthesis method. In this method boric acid (containing isotopes of ¹⁰B (94.4%) and ¹¹B (98.4%)) and lithium carbonate or lithium hydroxide (containing isotope of ⁶Li isotope), which are starting materials, were mixed and heated in the furnace [40].

Özdemir *et al.* synthesized powder LBO with solid-state sintering method from Li_2CO_3 and H_3BO_3 mixture as precursor. These starting materials were taken and mixed upon stoichiometric ratio and heated at 750°C for 7, 14, 21 hours. The optimum duration was found as 14 hours in the furnace at that temperature according to XRD patterns [41].

Microwave-assisted solid-state synthesis technique was used to decrease power consumption and synthesis time interval [42]. In this technique, the microwave radiation, which was used as heat source, absorbed by the microwave susceptible materials. It was used in bunch of application areas such as nano-materials, thin films

and porous ceramics [43] and also used in synthesis of some metal borate compounds. Microwave-assisted synthesis method was employed in two steps. Firstly, the reactants were exposed to microwave radiations in a microwave oven. In this stage, it was required to one of the reactants be microwave susceptible. If none of the reactants was able to absorb microwave radiation, some materials, which absorb microwave, could be used as fuel. For example, water, magnetite, silicon carbide, or graphite [44]. Secondly, high temperature heating was applied.

In wet synthesis method or solution-assisted method, the starting materials are mixed in solvent (especially water). Mixing the starting materials in water medium makes advantage to homogenize the initial mixture thoroughly. Furetta *et al.*[45], and Ege *et al.* [46] to synthesize lithium triborate used this synthesis method.

1.6.5 Crystal Structure of Lithium Tetraborate

LTB crystals have tetragonal crystal structure determined by Krogh-Moe [6]. In **Figure 7**, crystallographic unit cell of LTB shown consists of two BO₄ tetrahedral units and two BO₃ triangles. Two boron atoms and an oxygen atom in tetragonal group are shared by two six membered rings that are two non-planar. The Li atoms are placed in interstices [47]. Three-dimensional form of lithium tetraborate (LTB) is constructed by the basic repeating structural block (B₄O₉)⁶⁻. In this structure, crystallographic ally, two inequivalent boron sites and four inequivalent oxygen sites exist. All of the lithium sites are identical [48]. Hence, LTB crystallizes in tetragonal system (space group is I4₁cd and point group is 4mm) with unit cell parameters a =b = 9.47 Å, and c = 10.28 Å and α = β = γ =90°.



Figure 7. (a) Two $B_{(1)}O_3$ and two $B_{(2)}O_4$ units are linked by oxygen bridges to yield an anion group $[B_4O_9]^{6-}$, (b) unit cell of LTB and the lithium atoms lie in a channel of very distorted tetrahedra [49].

1.6.6 Crystal Structure of Lithium Triborate

A small LBO crystal was firstly produced by Konig and Hoppe (1978) using solidstate synthesis method. According to their study, LBO crystallizes in orthorhombic system with the space group Pna₂₁-C_{2v} and the unit cell parameters were calculated as a = 8.456 Å, b = 5.133 Å and c = 7.386 Å [2]. LBO is formed by anionic (B₃O₇)⁵⁻ group, shown in **Figure 8**, consists of one BO₄ tetrahedron and two BO₃ triangles. These groups linked to yield a six-membered ring where two of the B atoms are threefold coordinated and the rest of "B" atom is four-fold coordinated by "O" atoms [50].



Figure 8. The structural unit of LBO, \circ O atom, \bullet , B atom [50].

1.6.7 TL Property of LTB

Li₂B₄O₇ crystals naturally show TL emission even if it is low. Electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) study was done by Swinney et al.[51], which explained that of the reason for TL emission due to large concentrations of oxygen and lithium vacancies in LTB crystal. They behave as charge compensators for each other. During irradiation of the matter at 77 K, these inherent vacancies become electron and hole traps. The electron trapped center (an oxygen traps one electron is thermally stable at room temperature, however, the amount of trapped hole center (a lithium vacancy act as a hole trap on an adjacent oxygen ion) is rapidly decrease above 100 K. The decrease of trapped hole centers and lack of recombination of initially created electrons and holes effectively, which explains the reason of no strong TL intensity above room temperature for un-doped LTB crystal.

1.6.7.1 Dopants and their effects on TL properties of lithium tetraborate

When adding dopants into Li₂B₄O₇ crystals, they creates external defects in the host material. Mainly, the addition of activators into LTB is done with two methods. The dopants can be added either during or after the synthesis of LTB.

TL character of LTB phosphor is not only affected by the dopant type but also affected by dopant amount. The choice of suitable dopant is determined upon the match with atomic radius of dopants and elements in host material. Otherwise, the formation of LTB solid solution would be distorted. The dopant type might also change effective atomic number of LTB, which is important criteria for the choice of the suitable dopants. After the suitable dopant was found, the other parameter, the amounts of the dopants, affects TL properties of LTB.

Copper (Cu) and Manganese (Mn) are main activators added into LTB crystals. Both of these dopants are effective to increase TL intensity of LTB dramatically. Ionic radius of Li ions in LTB and the dopants (Cu and Mn) are close to each other. Moreover, they can either replace with Li ions or fill interstitial sites in LTB [31]. In addition, LTB can preserve tissue equivalency after doping of LTB with Cu and Mn upon the amount of those dopants.

Schulman *et al.* were the first to synthesize Mn doped LTB, which is promising material for TL dosimetry [1]. However, TL emission of Mn doped LTB is observed in the red region, which is out of spectral response region of photomultiplier tubes (400-500 nm) used in TL readers and hence this material is affected to low TL sensitivity [52]. The characteristic TL emission of the host material is estimated 380 nm, which can be changed upon the type and the concentration of a dopant. In addition, the local environment in the crystal can affect TL emission wavelength. For example, TL emission wavelength for Mn doped LTB is estimated 580 nm, which is characteristic of the emission band of Mn²⁺ [53]. According to EPR study done by Danilkin *et al.*, in LTB crystal structure Mn²⁺ ions, which occupy two different sites, are responsible for electron and hole trapping [54]. Mn²⁺ ions are likely found by substituting for a Li⁺ or breaking the boron-oxide network in LTB crystals and

substituting for a B^{3+} in a four-fold coordinated site. Trapped-holes by Mn^{2+} at a B^{3+} site are released at 213°C, which is followed by the release of electrons from Mn^{2+} localized at a Li⁺ site. As a result, recombination of released electrons and holes give TL emission at 270 °C [55].

Copper is another important activator for LTB phosphors. Copper-doped LTB crystals, which were firstly investigated by Tekanage *et al.*, show higher TL sensitivity than Mn-doped LTB crystals. Cu^+ ions either substitute for Li⁺ or occupy interstitial sites. It means that Cu^+ ions act as electron and hole traps, which reduce the concentrations of the isolated oxygen and lithium vacancies in un-doped LTB in order to have intense TL peak at 200°C above room temperature [56].

Silver (Ag) can be used as main activator or second activator (co-dopant). In our study Ag was used as co-dopant near the Cu and Mn main dopants. Ag ions can enhance the TL sensitivity of LTB crystals. When silver is added into LTB crystals, either main dopant or co-dopant, a portion of the silver ions that are existing in the host material as non-paramagnetic Ag^+ ions ([Kr] $4d^{10}$) replacing Li⁺ before irradiation. During the irradiation, these replaced Ag^+ ions act as hole trap and turn out Ag^{2+} ions at low temperature. Interstitial Ag^+ ions trap electrons and become Ag. Therefore, they contribute to increase TL emission with increasing electron and hole traps in the crystal [48].

In addition to these dopants, many scientist have been searching for new dopants such as Fe, Co, Mo, Eu, Dy, Tm, In, P or Mg to enhance the TL properties of the LTB phosphor. For example, Prokic used triple dopant system using metals, Cu, Ag and P [38]. In the same way, Pekpak *et al.* investigated triple-dopant (Cu, Ag and In) system in LTB crystals [23].

1.6.8 TL Property of LBO

Ogorodnikov *et al.* can explain TL mechanism of LBO phosphors. They built a model that is two competing trapping centers. According to their study, there are three

relevant trapping centers which are the shallow trapped electron center B^{2+} and two trapped hole centers O^{2-} . The recombination of trapped electrons and hole from electron center B^{2+} and hole center O^{-} give luminescence emission [57].

1.6.8.1 Dopants and their effects on TL properties of lithium triborate

Thermally stimulated luminescence (TSL) emission of LBO can be enhanced with the addition of activators. Previously, in our research group, Özdemir (2005) used various activators to add LBO such as CuO, MnO₂, Fe₂O₃, CoCO₃, MgO and Al₂O₃ [58]. It was observed that Al₂O₃ (1 wt%.) doped LBO showed better TL properties than the others did. The main dosimetric peak of Al₂O₃ (1 wt%.) doped LBO appeared at 195°C. Ardiçoğlu et al. carried out the following studies, which were enhancement of TL properties of LBO and the effects of the activators [59]. Moreover, oxide form of rare earth metals, Gd₂O₃, La₂O₃ and Y₂O₃, were used as the activators. Ardiçoğlu concluded that Gd₂O₃ (5 %) doped LBO has the maximum TL responses observed using the peaks at 110 and 190°C. In addition to Ardiçoğlu's study, Depçi (2009) doped LBO with rare earth metals Y₂O₃, La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, Al₂O₃, CuO. According to Depçi, Cu doped LBO gave highest TL intensity but dosimetric peak located at 117 °C [60].

CHAPTER 2

AIM OF THE STUDY

Lithium tetraborate and lithium triborate compounds, TLD materials, have significant dosimetric properties such as tissue equivalence, reasonable sensitivity, excellent stability, and the simple glow curve structure etc. Although these materials (especially LTB) are used in TLDs, they do not meet all of the essential dosimetric properties. Therefore, the studies to enhance their TL properties was aimed. Additionally, it was planned to examine the effects of varying amounts of the dopants (Cu, Mn, Al, Ag, In, Eu) and different dopant systems (co-dopant and tri-dopant) on TL properties of LTB and LBO phosphors. In literature, copper and manganese are known activator for LTB. However, the amounts of copper and manganese in the range from 0.02 to 0.1 wt% was not investigated. Copper and Manganese were used as main activators for LTB with varying amounts (from 0.02 to 0.1 wt%). By this way, the effect of varying amounts of the main dopants, in single, co-dopant and triple dopant systems, on TL properties of LTB was investigated. On the other hand, LBO is the newer TLD material than LTB. Depci used aluminum as main dopant for LBO samples[60]. In this study, we want to survey the effect of second dopant, Eu and Cu was used as co-dopant for LBO, on TL properties of LBO samples. Especially Eu²⁺ was firstly investigated in LBO. Moreover, the effects of the synthesis methods, wet synthesis method [38] and microwave assisted method [36], on TL characters of LTB were investigated. Furthermore, TL characterization of produced LTB phosphor was determined using TL measurements including glow curve structure, TL sensitivity, linear range, and dark fading.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

All materials and chemicals used in the experimental studies are analytical grade. The following chemicals were used for production and doping of LTB and LBO phosphors. The powder forms of Li₂CO₃ and H₃BO₃ were used as starting materials for synthesis of LTB and LBO compounds. CuCl_{2.}2H₂O, MnCl₂.4H₂O, AgNO₃, and In₂(SO₄)₃ compounds, which are metal sources, were utilized for doping of synthesized LTB phosphors. In addition, Al₂O₃ and EuCl₂ compounds were used for doping produced LBO samples.

3.2 Instrumentation

3.2.1 Powder X-Ray Diffractometer (XRD)

The samples were characterized by a Rigaku Mini-Flex X-ray powder Diffractometer (XRD) with a radiation source of Cu-K α line (λ =1,54056 Å) to confirm phase purity. The scanning rate within a 2 θ range of 3 to 90° is 2 °/min. The XRD patterns of produced LTB and LBO samples were matched with standard data JCPDS card no: 18-0717 and JCDPS No: 70-0735, respectively.

3.2.2 Furnace

The samples were heated in Protherm furnaces that are able to heat the samples up to 1500° C and they have heating rate control parameters.

3.2.3 Fourier Transform Infrared Spectrometer (FT-IR)

The vibrational modes of the produced materials were studied by VARIAN 1000 FTIR spectrometer between wavenumbers 500 to 4000 cm⁻¹ with 128 scans. FTIR spectrometer is equipped with attenuated total reflectance (ATR). Resolution were chosen as 8 cm^{-1} .

3.2.4 Transmission Electron Microscope (TEM)

The particle size and morphology of polycrystalline samples were investigated using transmission electron microscope (TEM) operating (JEOL 2100F electron microscope) at 200 kV and pictures were taken by GATAN Orios 2 camera. The samples were prepared for TEM with suspending the particles in ethanol by ultra sonification and drying a drop of the suspension on a carbon-coated copper grid.

3.2.5 Differential Thermal Analyzer (DTA)

Thermal stabilities of two differently synthesized lithium tetraborate compounds were evaluated with differential thermal analysis (TA Instrument DTA 1600). The samples were heated in atmospheric condition. Heating interval was chosen from 25°C and 1100°C with heating rate employed was 10 °C/min.

3.2.6 Scanning Electron Microscope (SEM)

The SEM analyses were performed by using Zeiss SUPRA 50 VP with which has magnification range between 12-900000, variable pressure between 2 and 133 Pa, and acceleration voltage of 0.1-30 kV.

3.2.7 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)

Perkin Elmer Optima 4300DV Inductively Coupled Plasma Optical Emission Spectrometer was used to determine the actual amounts of the dopant in the host material. 1.0 gram of the samples were dissolved in 8.0 mL of HNO₃. Subsequently, the mixture was placed in Anton Paar Multiwave 3000 microwave oven. The power of the oven was set 800 Watt and ramp of the oven was 5 °C/min. The samples were kept in the oven for 1 min.

3.2.8 Beta Radiation Generator

 90 Sr/ 90 Y source was used for the production of pure Beta radiations. The source gives 0.04 Gy Beta radiation per second. 10 mg of the samples were exposed to Beta, 90 Sr/ 90 Y radiations at room temperature for 5 minutes.

3.2.9 Thermoluminescence Reader

The dosimetric properties of the samples were investigated by using Harshaw TLD Reader Model 3500. Schematic representation of TL reader is shown in **Figure 9**. Glow curve readout was performed at linear heating rate of 1°C/s up to 400 °C. To eliminate unwanted infrared lights emitted from heater, a standard clean glass filter always installed in the reader between sample and photomultiplier tube, which has the peak sensitivity of wavelength at \approx 400 nm.



Figure 9. Harshaw TLD Reader Model 3500 and schematic representation of a TLD reader [61].

3.3 Experimental Procedure

3.3.1 Synthesis of Lithium Tetraborate

The powder samples of un-doped lithium tetraborate were synthesized with water/solution assisted method (SAM) and microwave assisted method (MAM). Each synthesis method was employed to determine the most appropriate procedure for the production of LTB.

3.3.1.1 Wet/Solution Assisted Method (SAM)

The powder samples of un-doped Li₂B₄O₇ were synthesized with wet/solution assisted method (SAM) [23]. In SAM, Li₂CO₃ (98.5% pure, Merck) and H₃BO₃ (99.5% pure, Merck) were mixed with stoichiometric amounts and 15.0 ml of distilled water was added to obtain 1.0 g of lithium tetraborate product. The mixture was heated and stirred on magnetic stirrer around 90°C until a homogeneous mixture was obtained. The heating and stirring of the mixture continued till three four parts of water was evaporated. Then, highly viscous mixture was preheated in a muffle furnace up to 150°C with 6.6 °C/min heating rate. It was kept at this temperature for 3 h in order to get rid of residual water in the mixture. After the preheating stage, the cooled sample

re-grinded in agate mortar. Afterwards, the furnace was adjusted to heat the sample up to 750°C with 4.0 °C/min heating rate and retention time was 1 h at this temperature. Intermittent grinding of the mixture facilitates discharge of gases properly while heating solid mixture.

The expected reaction is given below.

$$Li_2CO_3(s) + 4H_3BO_3(s) \rightarrow Li_2B_4O_7(s) + CO_2(g) + 6H_2O(g)$$
 Eq. 4

3.3.1.2 Doping Procedure for LTB based on SAM

All samples were doped with metals according to wt/wt percentage. Water-soluble CuCl₂.2H₂O, MnCl₂.4H₂O, AgNO₃, In₂(SO₄)₃ were used as metal sources. Copper and Manganese were used as chief dopant. Initially, synthesized lithium tetraborate samples were doped with copper and manganese separately. Copper and manganese were used as main dopants individually. Their amounts were within the range from 0.1 to 0.02 wt%. In addition single dopant procedure, silver was added to lithium tetraborate as co-dopant. In co-doping process, concentration of the main dopants (Cu and Mn) were added with varying amounts (from 0.02 wt% to 0.1 wt%) and constant amount of silver (0.04 wt%) was used as co-dopant. Furthermore, indium was served as third dopant. In triple doping process, likewise co-doping process the concentration of the main dopants (Cu and Mn) were added with varying amounts (from 0.02 wt% to 0.1 wt%) and constant amount of indium (0.04 wt%) metal was used as third dopant. Hence, we produced metal doped LTB phosphors such as Li₂B₄O₇:Cu, Li₂B₄O₇:Mn, Li₂B₄O₇:Cu, Ag, Li₂B₄O₇:Cu, Ag, Li₂B₄O₇:Cu, Ag, In, and Li₂B₄O₇:Mn, Ag, Li₂B₄O₇:Cu, Ag, In.

1.0 g of LTB and the dopants (chosen upon doping combination) were stirred in 15.0 ml of distilled water to form suspension by heating and stirring with magnetic stirrer at 90 °C for 30 min. The suspension in a crucible was put into the furnace to heat up to 150° C with heating rate 6.6 °C/min and kept at this temperature for 3 h. After intermittent grinding of the mixture was performed, the furnace was adjusted to heat the sample up to 700°C with 4.0 °C/min heating rate and the retention time was 2 h at

this temperature. Dopants and their amounts used in doping system (single doping, codoping and triple dopant system) are given tables 3, 4, 5, 6, 7, 8.

3.3.1.3 Microwave Assisted Method (MAM)

In microwave-assisted method, synthesis of Li₂B₄O₇ and doping procedure were performed at the same time. All reagents and dopant amounts used in accordance with weight ratio. Dopants (CuCl₂.2H₂O, MnCl₂.4H₂O, AgNO₃, In₂(SO₄)₃) and their amounts used in doping system (single doping, co-doping and triple dopant system) are given tables 3, 4, 5, 6, 7, 8. Weight ratio and metal combination are the same as SAM doping procedure. Additional to these reagents, (1:3.33 mole ratio) glycine (98.5% pure, Merck) was added as fuel. Final mixture was heated and stirred on magnetic stirrer at 90°C until homogeneous mixture was obtained. Heating was continued until viscous mixture was obtained. Subsequently, the mixture was held in the microwave oven at 1200 w for 10 min. Further heating was performed at 750°C for 1 h in muffle furnace. As a result, un-doped and doped LTB powders were obtained.

In addition to glycine, urea and citric acid were tried as fuel. According to XRD results, it was determined that glycine is the most effective fuel among them.

LBO Weight (g)	Cu wt%	CuCl _{2.} 2H ₂ O (g)
1.0	0.10	0.0026
1.0	0.09	0.0024
1.0	0.08	0.0021
1.0	0.07	0.0018
1.0	0.06	0.0016
1.0	0.05	0.0013
1.0	0.04	0.0010
1.0	0.03	0.0008
1.0	0.02	0.0005

Table 3 Weight Percentages of Cu as single dopant for SAM and MAM

LTB Weight (g)	Cu wt%	CuCl _{2.} 2H ₂ O (g)	Ag wt%	AgNO ₃ (g)
1.0	0.10	0.0026	0.04	0.0006
1.0	0.09	0.0024	0.04	0.0006
1.0	0.08	0.0021	0.04	0.0006
1.0	0.07	0.0018	0.04	0.0006
1.0	0.06	0.0016	0.04	0.0006
1.0	0.05	0.0013	0.04	0.0006
1.0	0.04	0.0010	0.04	0.0006
1.0	0.03	0.0008	0.04	0.0006
1.0	0.02	0.0005	0.04	0.0006

Table 4 Weight Percentages of co-doping study for SAM and MAM

Table 5 Weight Percentages of triple-doping study for SAM and MAM

LTB Weight	Cu wt0/	CuCl ₂ .2H ₂ O	A a wt9/	AgNO ₃	In w/ 0/	In ₂ (SO ₄) ₃
(g)		(g)	Ag wt70	(g)	111 WL 70	(g)
1.0	0.10	0.0026	0.04	0.0006	0.04	0.0009
1.0	0.09	0.0024	0.04	0.0006	0.04	0.0009
1.0	0.08	0.0021	0.04	0.0006	0.04	0.0009
1.0	0.07	0.0018	0.04	0.0006	0.04	0.0009
1.0	0.06	0.0016	0.04	0.0006	0.04	0.0009
1.0	0.05	0.0013	0.04	0.0006	0.04	0.0009
1.0	0.04	0.0010	0.04	0.0006	0.04	0.0009
1.0	0.03	0.0008	0.04	0.0006	0.04	0.0009
1.0	0.02	0.0005	0.04	0.0006	0.04	0.0009

LTB Weight (g)	Mn wt%	MnCl ₂ .4H ₂ O (g)
1.0	0.10	0.0036
1.0	0.09	0.0032
1.0	0.08	0.0028
1.0	0.07	0.0025
1.0	0.06	0.0021
1.0	0.05	0.0018
1.0	0.04	0.0014
1.0	0.03	0.0010
1.0	0.02	0.0007

 Table 6 Weight Percentages of Mn as single dopant for SAM and MAM

Table 7 Weight Percentages of co-doping study for SAM and MAM

LTB Weight (g)	Mn wt%	MnCl _{2.} 4H ₂ O (g)	Ag wt%	AgNO ₃ (g)
1.0	0.10	0.0036	0.04	0.0006
1.0	0.09	0.0032	0.04	0.0006
1.0	0.08	0.0028	0.04	0.0006
1.0	0.07	0.0025	0.04	0.0006
1.0	0.06	0.0021	0.04	0.0006
1.0	0.05	0.0018	0.04	0.0006
1.0	0.04	0.0014	0.04	0.0006
1.0	0.03	0.0010	0.04	0.0006
1.0	0.02	0.0007	0.04	0.0006

LTB	Mn wt%	MnCl ₂ .4H ₂ O	A a wt0/	AgNO ₃	In wt %	In ₂ (SO ₄) ₃
Weight (g)	IVIII WU70	(g)	Ag wi /o	(g)	111 wt 70	(g)
1.0	0.10	0.0036	0.04	0.0006	0.04	0.0009
1.0	0.09	0.0032	0.04	0.0006	0.04	0.0009
1.0	0.08	0.0028	0.04	0.0006	0.04	0.0009
1.0	0.07	0.0025	0.04	0.0006	0.04	0.0009
1.0	0.06	0.0021	0.04	0.0006	0.04	0.0009
1.0	0.05	0.0018	0.04	0.0006	0.04	0.0009
1.0	0.04	0.0014	0.04	0.0006	0.04	0.0009
1.0	0.03	0.0010	0.04	0.0006	0.04	0.0009
1.0	0.02	0.0007	0.04	0.0006	0.04	0.0009

Table 8 Weight Percentages of triple-doping study for SAM and MAM

3.3.2 Synthesis of Lithium Triborate

Powder form of lithium triborate samples synthesized by the reaction of Li₂CO₃ (98.5% pure, Merck) and H₃BO₃ (99.5% pure, Merck) in an aqueous media. The synthesis procedure is based on the method used by Depci [60]. Starting materials were mixed with stoichiometric amounts in 15.0 ml distilled water. The mixture was heated and stirred at 90 °C until viscous gel form was obtained. Then, the viscous mixture was placed into porcelain crucible and preheating stage was employed in a muffle furnace at 200°C for 4 h with 6.6 °C/min heating rate to get rid of the residual water in the mixture. After the preheating stage, the sample in crucible re- ground in an agate mortar. Afterwards, ground sample was heated in the furnace adjusted to heat the sample up to 700°C with 4.0 °C/min heating rate and retention time was at this temperature 4 hour.

The expected reaction is given below.

$$Li_2CO_3(s) + 6H_3BO_3(s) \rightarrow 2LiB_3O_5(s) + CO_2(g) + 9H_2O(g)$$
 Eq. 5

3.3.2.1 Doping Procedure of Lithium Triborate

Synthesized lithium triborate samples were doped with Al₂O₃, AgNO₃, CuCl_{2.}2H₂O, and EuCl₂. 1.0 gram of lithium triborate and certain amounts of dopants were blended in agate mortar. Subsequently, powder form of mixture was placed in porcelain crucible and it was heated up to 750°C with 4.0 °C/min heating rate in furnace. The retention time was 10 h at that temperature. After heating stage, sample was slowly cooled down room temperature.

Metal concentrations and dopant combinations are given in the tables 9, 10 and 11.

Table 9 Aluminum	Doping	Scheme
--------------------	--------	--------

LBO Weight (g)	Aluminum (Al) wt %	Al ₂ O ₃ (g)
1.0	1	0.0188
1.0	5	0.0940

Table 10 Europium Doping Scheme

LBO (g)	Europium (Eu) wt %	EuCl ₂ (g)
1.0	1.00	0.0146
1.0	0.75	0.0110
1.0	0.50	0.0073

Table 11 Multiple Dopant Concentrations Chart

LiB ₃ O ₅	A1 xx+ 0/	Al ₂ O ₃	Fn n/ 0/	EuCl ₂	Cu wt	CuCl ₂
(gr)	AI WU 70	(g)	Euwi 70	(g)	%	(g)
1.0	1	0.0188	1.00	0.0146	-	-
1.0	1	0.0188	0.50	0.0073	-	-
1.0	1	0.0188	0.25	0.0036	-	-
1.0	1	0.0188	-	-	0.08	0.0021
1.0	1	0.0188	0.25	0.0036	0.08	0.0021
1.0	5	0.9400	0.25	0.0036	-	-
1.0	5	0.0940	-	-	0.08	0.0021
1.0	5	0.0940	0.25	0.0036	0.08	0.0021
1.0	5	0.0940	0.10	0.0014	0.08	0.0021

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization

Synthesized lithium tetraborate/triborate phosphors were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Differential Thermal Analysis (DTA) to determine structural and morphological properties. Thermoluminescence (TL) properties of lithium tetraborate/triborate samples were studied to examine the dosimetric properties of them.

4.1.1 X-Ray Diffraction (XRD) results

4.1.1.1 XRD results for LTB

Powder X-ray diffraction method was employed to determine whether the host materials (lithium tetraborate and lithium triborate) is correctly produced. Besides, the method help us to examine the effects of dopants on the crystal structure of host materials.



Figure 10. XRD Pattern of LTB (JCDPS No: 18-0717).

LTB crystals consist of two BO₄ tetrahedral units and two BO₃ triangles. Two boron atoms and an oxygen atom in tetragonal group are shared by two six membered rings that are two non-planar. Three-dimensional form of lithium tetraborate (LTB) is constructed by the basic repeating structural block $(B_4O_9)^{6-}$. In this structure, crystallographically, two inequivalent boron sites and four inequivalent oxygen sites exist. All of the lithium sites are identical [48].



Figure 11. Powder XRD patterns of metal-doped LTB samples produced with SAM and MAM.



Figure 12. Powder XRD patterns of metal-doped LTB samples produced with SAM and MAM.

Hence, LTB crystallizes in tetragonal structure with $I4_1cd$ space group having unit cell parameters a =b = 9.47 Å, and c = 10.28 Å and α = β = γ =90°. Corresponding reference XRD data of LTB is shown in Figure 10. XRD patterns of synthesized materials (undoped Li₂B₄O₇ and doped Li₂B₄O₇) are indicated in Figures 11 and 12. X-ray diffraction patterns shown with Miller indices (h k l) of synthesized materials matched with corresponding reference data given as the Joint Committee on Powder Diffraction Standards (JCDPS) No: 18-0717 in Figure 10. Moreover, the peak intensities of LTB samples produced with SAM illustrated in Figures 11 and 12 are higher than LTB produced with MAM. Since second heating stage applied during doping LTB led to increase the crystallinity of LTB XRD patterns of LTB produced using both methods indicate that there is no second phase and no additional peaks due to dopants. However, peak intensities of LTB samples synthesized with MAM decreased. Furthermore, Replacement of Cu and Ag ions with Li site in oxygenic octahedrons and tetrahedrons structures of LTB give rise to deviation of cell parameters from reference data (JCDPS No: 18-0717). Besides, it led to the shift in the peak positions of the materials synthesized using two different methods towards lower theta degree because of the mismatch in ionic radius of Li⁺ (0.06 nm) and dopants; Cu⁺(0.096 nm) and Ag⁺ (0.0126 nm) [73, 74]. This case was not obviously observed for Mn²⁺ (0.07 nm) doped LTB samples due to closeness of ionic radius of Li⁺ and Mn²⁺ ions. The corresponding effects of dopants on XRD patterns were shown in Figure 13. As can be noticed from this figure, the peaks shifted to lower angle for the samples doped with Cu and Ag due to mismatch of ionic radius of Li⁺ (0.06 nm) and dopants; Cu⁺(0.096 nm) and Ag⁺ (0.0126 nm).



Figure 13. XRD patterns show the effect of dopants on the peak positions.

4.1.1.2 XRD results for LBO

XRD patterns of LiB₃O₅ and metal doped LiB₃O₅ compounds are given in **Figures 15-16**. X-ray diffraction patterns shown with Miller indices (h k l) of synthesized materials are well matched with corresponding reference data (JCDPS No: 70-0735) which is shown **Figure 14**. Crystal structure of LBO is orthorhombic crystal system with space group *Pna2*₁, unit cell parameters are: a = 8.456 Å, b = 5.133 Å and c = 7.386 Å [64]. However, some reflections in XRD patterns were identified the reflections of Li₂B₄O₇ (JCDPS No: 18-0717) and Li₃B₇O₁₂, which were denoted by the symbols (*) and (₀) respectively. Those reflections aroused from decomposition of lithium triborate for Li₂B₄O₇ above 773 K and Li₃B₇O₁₂ occurs above 923 K [29]. The peaks associated with Li₃B₇O₁₂ was only observed in XRD patterns of 5% Al doped LBO and Al and Eu doped LBO samples.

When the peak positions of XRD patterns of un-doped and doped LBO samples in **Figures 15** and **16** was compared to each other, no extra peak due to the dopants was detected except small shifts in the peak positions. Additionally, the peak intensities of

doped LBO samples generally decreased with respect to peak intensity of un-doped LBO.



Figure 14. XRD Pattern of LBO (JCDPS No: 70-0735).



Figure 15. Powder XRD patterns of Al and Eu-doped LBO samples. The reflections that belongs to $Li_2B_4O_7$ and $Li_3B_7O_{12}$ are marked by (*) and (₀) respectively.



Figure 16. Powder XRD patterns of co-doped and triple-doped LBO samples. The reflections that belongs to $Li_2B_4O_7$ and $Li_3B_7O_{12}$ are marked by (*) and (o) respectively.

4.1.2 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) results

ICP-OES elemental analysis utilized to determine the amounts of the dopants in LTB samples to compare experimental and theoretical dopant amounts. The samples produced three times to determine whether synthesis method is reproducible. 0.08% Cu and 0.04% Ag doped LTB samples synthesized with SAM were analyzed using ICP-OES. This sample, which contains 0.08% Cu and 0.04% Ag doped, was chosen for ICP-OES measurement since they showed the proper TL characters for TL dosimetry. According to ICP-OES results, the mean value of copper and silver amounts are 0.075 ± 0.01 wt% and 0.017 ± 0.01 wt% respectively in LTB samples. Measured silver amount is nearly half of the theoretical value (0.04 wt%), which is due to difficulty of preparation silver standard for low concentration of the solutions.

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR) results

4.1.3.1 FTIR results for LTB

Fourier transform infrared spectroscopy was employed to determine chemical bonding of synthesized LTB and LBO samples. Besides, FTIR was utilized to see the spectra differences of differently synthesized lithium tetraborate samples and metal doped lithium tetraborate/triborate samples after the dopant addition.



Figure 17. FTIR spectra of synthesized and doped LTB samples.



Figure 18. FTIR spectra of synthesized and doped LTB samples.

Fourier transform infrared spectroscopy (FTIR) of LTB samples shown in **Figures 17** and **18** was performed to determine chemical bonding of LTB. FTIR spectra were fitted with the literature values for BO₃ and BO₄ ring structure vibrations between 600 cm⁻¹ and 1600 cm⁻¹ [49]. The same FTIR spectra were obtained by using two different methods. In addition, the formation of new vibrational band was not detected after the addition of dopants into LTB. The characteristic vibrational modes of LTB could be given as follows: the asymmetric stretching vibration band of B-O in BO₃ unit at 1432 and 1344 cm⁻¹, an asymmetric stretching band of B-O in BO₄ unit assigned at 1130 cm⁻¹, the broad bands at 944 and 826 cm⁻¹ assigned as symmetric stretching of B-O in BO₄ and BO₃ rings respectively. The weak band observed at 710 cm⁻¹ is assigned as out of plane bending of B-O in BO₃ unit [65].

4.1.3.2 FTIR results for LBO

FTIR spectra of synthesized LBO compounds are indicated in **Figure 19**. Boron atoms in LiB₃O₅ compound have three- and four-fold coordinations, which were identified by FTIR spectroscopy. FTIR spectra were fitted with the literature values for BO₃ and BO₄ ring structural vibrations [40]. Moreover, IR spectra of un-doped LBO and doped LBO samples are in good agreement with each other. B-O stretching band in BO₃ trigonal unit is at 1200-1500 cm⁻¹, B-O stretching of tetrahedral BO₄ is assigned at 850-1200 cm⁻¹, and 600-800 cm⁻¹ is associated with bending vibrations of various borate segments. A band at 700 cm⁻¹ is associated with bond bending of B-O-B bridges in the boron-oxygen network.



Figure 19. FTIR spectra of synthesized and doped LBO samples.



4.1.4 Differential Thermal Analysis (DTA)

Figure 20. DTA curves of LTB samples. (a) Un-doped LTB, (b) 0.08% Cu and 0.04% Ag doped LTB with SAM, (c) 0.08% Cu and 0.04% Ag doped LTB with MAM.

Thermal behavior of LTB samples was assessed by using differential thermal analysis (DTA). From DTA curve shown in **Figure 20**, there was a sharp melting peak of undoped LTB at 916°C, which is close to melting point (915°C) of LTB obtained by Sangeeta et al. [30]. DTA curves of materials synthesized with SAM and MAM were quite similar although it was observed that there is slight decrease on melting point of the materials due to dopant. Moreover, the broad peak between 400°C and 600°C since exit of organic substance (glycine), used in the synthesis process, was detected in DTA curve of the sample produced with MAM.

4.1.5 Scanning Electron Microscopy (SEM)

Figure 21. SEM images of 0.08% Cu and 0.04% Ag doped LTB sample synthesized with SAM (A), 0.05% Cu and 0.04% Ag doped LTB sample synthesized with SAM (B).

Scanning electron microscopy (SEM) images in **Figures 21** and **22** revealed that the morphological characteristics of Li₂B₄O₇: Cu, Ag samples produced with two different synthesis methods. SEM images A and B in **Figure 21** illustrate morphologies and crystallite size of LTB samples synthesized using SAM. Images A and B in **Figure 22** belong to LTB synthesized with MAM. The morphology of the samples produced with

SAM had sticky characteristic and separate particle shapes were observed. SEM images of the samples produced with MAM revealed the morphologies that are not uniform and form fiber-like architecture due to the usage of organic fuel (glycine) employed during synthesis procedure. During heating the samples, glycine started to decompose at 233°C. With the decomposition and combustion of this organic material, the great amount of the gases exit the reactor, which can change the morphology of LTB samples.



Figure 22. SEM images of 0.08% Cu and 0.04% Ag doped LTB sample synthesized with MAM (A), 0.05% Cu and 0.04% Ag doped LTB sample synthesized with MAM (B).

4.1.6 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) gives significant information about polycrystallinity and microstructural morphology of the samples. TEM imaging was taken for the samples showing the optimum TL characters according to TL glow curve structure. Namely, the main peak of this sample is located at around 210°C with the highest TL intensity in the other produced LTB samples. TEM micrograms A and B in **Figure 23** belong to the samples have the same amount of activators 0.08% Cu and

0.04% Ag. However, the preparation methods of the samples are different. Crystallite size of the sample A produced by using SAM is smaller than the sample B produced with MAM. These differences may affect the TL intensity of the samples that have the same amount of activators 0.08% Cu and 0.04% Ag. In addition, TEM micrograms of sample C and D belong to the same amount of activators (0.05% Cu and 0.04% Ag). The crystallite size of samples is nearly the same.



Figure 23. TEM images of 0.08% Cu and 0.04% Ag doped LTB synthesized with SAM (a), 0.08% Cu and 0.04% Ag doped LTB synthesized with MAM (b), 0.05% Cu and 0.04% Ag doped with synthesized with SAM (c), 0.05% Cu and 0.04% Ag doped LTB synthesized with MAM (d).

4.1.7 Thermoluminescence Results

The radiation dosimetric performance of a TL material is highly depend upon shape of its glow curve, intensity and peak temperatures of the glow peaks. As mentioned in chapter 1, lithium tetraborate and lithium triborate phosphors have proper dosimetric
properties in sense of thermoluminescence characteristic. Thermoluminesce glow curves of synthesized lithium tetraborate and lithium triborate samples were utilized to determine whether those samples show ideal TL glow curve structure and TL intensity. The samples that have sufficient TL intensity and proper TL structure were analyzed for further dosimetric measurements such as dose-response, annealing and fading.

4.1.7.1 TL results of LTB

4.1.7.1.1 Effect of dopant

TL glow curves of un-doped Li₂B₄O₇, Cu doped and Cu, Ag doped Li₂B₄O₇ and Cu, Ag, In doped Li₂B₄O₇ produced with SAM and MAM are shown in **Figures 24** and **25**. The samples were exposed to Beta ⁹⁰Sr/⁹⁰Y at room temperature for 5 minutes while the radiation given was 1.0 Gy/min. Glow curve of un-doped Li₂B₄O₇ shows one isolated peak at around 240°C and one small peak at around 130°C as shown in **Figures 24** and **25**. TL intensity of un-doped LTB has lower radiation absorption potential than Li₂B₄O₇: Cu and Li₂B₄O₇: Cu, Ag, which is related to the intrinsic and extrinsic defects in the host lattice. However, the predominant peak in the glow curve of Cu doped Li₂B₄O produced with SAM and MAM shifted to 290°C. Nevertheless, there is a small hump around 210°C as shown in **Figure 24**. TL glow curve nature of the samples produced with two different methods are in good agreement with each other in terms of temperature of main peaks. However, TL intensities of the samples produced with MAM showed lower TL intensity. Nevertheless, it is observed that peaks near 90°C have higher TL intensity for Cu-doped LTB produced with SAM.

Majority of copper ions are in the monovalent charge state before β -rays [51]. Cu⁺ ions not only substitute for Li⁺ ions but also occupy interstitial sites in LTB crystals and act as charge compensator [66]. After irradiation of the sample, Cu⁺ ions are able to trap a hole and become Cu²⁺_{active} (trapped-hole center), and also trap an electron and form Cu⁰_A and Cu⁰_B (both trapped-electron centers) [77, 78]. The peaks were observed near 90°C and 290°C might be attributed to the decay process of Cu²⁺_{active} during

thermal annealing. Recombination of electrons (released from unidentified defect) and trapped hole centers gives rise to the peak near 90°C. Another peak near 290°C appeared due to recombination of Cu^{2+}_{active} hole centers and Cu^{0}_{A} and Cu^{0}_{B} electron centers at the same time [66]. The excitation due to β -irradiation and relaxation due to heating of the material consisting of Cu^{+} are given **equation 6**.

$$2\mathrm{Cu}^{+} \xrightarrow{\boldsymbol{\beta}-irradiatio} \mathrm{Cu}^{2+}_{\mathrm{active}} + \mathrm{Cu}^{0}_{\mathrm{A}} \text{ or } \mathrm{Cu}^{0}_{\mathrm{B}} \xrightarrow{\boldsymbol{heating}} (\mathrm{Cu}^{+})^{*} \to \mathrm{Cu}^{+} + h\mu \ [67] \qquad \mathrm{Eq.} \ 6$$

Desired glow curve shape, which is described by Furetta, was achieved by co-doping of Li₂B₄O₇, which was produced with SAM [19]. As illustrated in **Figures 24** and **25**, TL glow curve of Li₂B₄O₇. Cu, Ag containing main peak at around 210°C. According to the TL glow curve results, we obtained the simple glow curve shape and higher TL intensity with respect to Pekpak *et al.* [68]. The differences between TL glow curves of Cu and Ag doped LTB from Cu doped LTB are attributed to the effect of Ag. According to Brant *et al.* intense TL peak for Ag-doped LTB is appeared near 160°C due to recombination of thermally released electron and hole centers. TL emission of Ag doped LTB at 160°C was masked and TL emission corresponding to Cu is more pronounced, which might be the reason of highly intense peak observed near 210°C for Cu and Ag doped LTB sample [48]. The mechanism of corresponding TL peak is described by subsequent events that are given below:

 $Ag^{+}_{s} + hole^{+} \rightarrow Ag^{2+}_{s}$ where Ag^{+}_{s} denotes substitutional Ag ions.

 $Ag^{+}_{i} + e^{-} \rightarrow Ag^{0}_{i}$ where Ag_{i} denotes interstitial Ag ions.

$$Ag^{2+}_{s} + Ag^{0}_{i} \xrightarrow{Heating} Ag^{+}_{s} + Ag^{+}_{i} + h\nu$$
 Eq. 7



Figure 24. Some of the selected glow curves of un-doped Li₂B₄O₇, Li₂B₄O₇: Cu, Li₂B₄O₇: Cu, Ag and Li₂B₄O₇: Cu, Ag, In produced with SAM.



Figure 25. Some of the selected glow curves of un-doped $Li_2B_4O_7$, $Li_2B_4O_7$: Cu, $Li_2B_4O_7$: Cu, Ag and $Li_2B_4O_7$: Cu, Ag, In produced with MAM.

Therefore, TL emission of un-doped sample can be enhanced by the addition of second or third dopants that may increase the amount of defects responsible for TL in the host lattice[69]. In our study, we observed this effect with second dopant and TL intensity of un-doped LTB was increased at least 40 times for the samples as shown in **Figure 24** when we compared peak heights of the main peaks of un-doped and Cu-Ag doped LTB samples.

In **Figures 24** and **25**, the effects of triple doping LTB is illustrated. Indium was used as third dopant and lead to decrease in TL intensity of main peak around 210°C. When Indium is added to LTB crystals, they replace with Li⁺ ions near the oxygenic octahedrons and tetrahedrons, which effects oxygen atoms composing octahedrons and tetrahedrons. Hence, LBO lattice will probably be distorted due to huge difference between valance electrons of In³⁺ and Li⁺. Therefore, it influences TL emission of Cu ions, which lead to shift in TL emission and lose in TL intensity [65]. On the other hand, TL glow curve shapes of triple-doped LTB were conserved. They show similar TL glow curve shape to co-doped LTB samples. Moreover, even if their TL intensities of triple-doped LTB is lower than Cu and Ag doped samples, they are clearly enhanced with respect to un-doped LTB samples. Therefore, TL emission of un-doped sample can be increased by the addition of small quantities of activators that may increase the amount of defects in the host lattice.



Figure 26. Some of the selected glow of un-doped Li₂B₄O₇, Li₂B₄O₇: Mn, Li₂B₄O₇: Mn, Ag and Li₂B₄O₇: Mn, Ag, In produced with SAM.



Figure 27. Some of the selected glow curves of un-doped $Li_2B_4O_7$, $Li_2B_4O_7$: Mn, $Li_2B_4O_7$: Mn, Ag and $Li_2B_4O_7$: Mn, Ag, In produced with MAM.

As illustrated in **Figures 26** and **27**, TL glow curves of un-doped Li₂B₄O₇, Mn doped and Mn, Ag doped Li₂B₄O₇ and Mn, Ag, In doped Li₂B₄O₇ produced with SAM and MAM. Un-doped Li₂B₄O₇ has one isolated peak at around 240°C and one small peak at around 130°C in **Figures 26** and **27**. The effects of Mn doping into LTB is obviously seen in these figures. TL mechanism of Mn is given in **equation 8** by subsequent events. After irradiation of the sample, Mn²⁺, which can substitute for Li⁺ and acts as hole trap, captures hole and becomes Mn³⁺. Upon the heating, trapped electrons and holes are released and recombine with each other. As a result, it gives emission at 600 nm.

$$\mathrm{Mn}^{2+} \xrightarrow{\boldsymbol{\beta}-irradiatio} \mathrm{Mn}^{3+} + \mathrm{e}^{-} \xrightarrow{heating} (\mathrm{Mn}^{2+})^* \to \mathrm{Mn}^{2+} + \mathrm{h}_{\mathcal{P}} (600 \ nm) [67] \qquad \text{Eq. 8}$$

For Mn-doped LTB samples produced with SAM and MAM main peak shifted to higher temperature (320°C). The release of trapped electrons and holes started after 250°C, which can be inferred from these glow peaks in **Figures 26** and **27**. This results are in good agreement with the findings of Annalakshmi *et al.* [53]. They observed TL peak for Mn-doped LTB at around 270°C. According to their study, main peak temperature increases with decreasing Mn concentrations, which can explain why the main peaks in **Figures 26** and **27** shifted to 320°C. Furthermore, there was no change in peak shape of Mn-doped LTB samples. When TL intensities of Mn doped LTB samples produced with SAM and MAM were compared to each other, it was decided that SAM is better than MAM by assessing TL peak intensities.

Co-dopant (Mn-Ag) effects on glow curves of LTB samples produced by SAM and MAM are illustrated in **Figures 26** and **27**. In TL glow curve as shown in **Figure 26** Mn and Ag doped LTB sample produced with SAM gave barely TL intensity in comparison to un-doped LTB and Mn-doped LTB samples. Similarly, **in Figure 27** there was no remarkable contribution of dopants for the main peak of Mn and Ag LTB sample produced with MAM. However, the temperature of the main peaks of these samples shifted to lower value due to TL emission of Ag. This case is clearly noticed in **Figure 26** for the sample produced with SAM.

Indium was used as third dopant and its effect on TL glow curves is clearly seen in **Figure 26**. Indium enhanced the TL intensity of the main peak of un-doped LTB produced with SAM. The peak position of the main peak is acceptable. Because main peak temperature (T_m) is at around 220°C when we compared the triple-doped LTB. Nevertheless, **in Figure 27** the main peak of triple-doped LTB nearly disappeared. We attributed that the production technique and batch inhomogeneity may be responsible for this lost.

We investigated the effects of copper concentrations and synthesis differences on the TL sensitivity of LTB. **Figures 28** and **29** present the glow curves of Cu-doped LTB samples produced with SAM and MAM method with varying concentrations of copper from 0.02% to 0.1%. As it is indicated in **Figure 28**, the TL glow curves of Cu-doped LTB samples produced with SAM consist of two separate peaks except 0.09% Cu-doped LTB sample that contains three separate peaks at different temperatures. The predominant peaks of Li₂B₄O₇: Cu samples locate at around 275°C and another peak at 100°C with lower intensity. The highest TL intensity was obtained by adding 0.08% Cu into LTB. On the other hand, 0.02-0.04% Cu-doped samples did not show remarkable TL response. In general, the TL intensity increased after high Cu-doping concentrations. However, there is no linear relation between TL intensity and the amount of dopants. Although Cu-doped Li₂B₄O₇ samples produced with MAM have



Figure 28. TL glow curves of $Li_2B_4O_7$: Cu (varying amounts of Cu from 0.02 to 0.1%) produced with SAM.



Figure 29. TL glow curves of $Li_2B_4O_7$: Cu (varying amounts of Cu from 0.02 to 0.1%) produced with MAM.

similar glow curves in terms of the peak positions (especially peaks are around 275° C) in **Figure 29**, the peak intensities at 100°C increased significantly. This situation can be explained by the effect of background radiation which leads to increase the TL intensity peaks. However, peaks at 100°C in **Figure 29** are inappropriate for the radiation measurements for TLD since lifetime of the peak is nearly shorter than 24 h [70]. In addition, as **Figure 29** shows the TL intensity of 0.1 % Cu doped sample is the highest among samples in range of 0.1 % and 0.02 % Cu concentrations.

We investigated the effects of copper concentrations and synthesis differences on the TL sensitivity of LTB. Figures 28 and 29 present the glow curves of Cu-doped LTB samples produced with SAM and MAM method with varying concentrations of copper from 0.02 % to 0.1 %. As it is indicated in Figure 28, the TL glow curves of Cu-doped LTB samples produced with SAM consist of two separate peaks except 0.09 % Cudoped LTB sample that contains three separate peaks at different temperatures. The predominant peaks of Li₂B₄O₇. Cu samples locate at around 275 °C and another peak at 100° C with lower intensity. The highest TL intensity was obtained by adding 0.08 % Cu into LTB. On the other hand, 0.02-0.04 % Cu-doped samples did not show remarkable TL response. In general, the TL intensity increased after high Cu-doping concentrations. However, there is no linear relation between TL intensity and the amount of dopants. Although Cu-doped Li₂B₄O₇ samples produced with MAM have similar glow curves in terms of the peak positions (especially peaks are around 275°C) as shown in **Figure 29**, the peak intensities at 100°C increased significantly. However, peaks at 100°C as shown in Figure 29 are inappropriate for radiation measurements for TLD since lifetime of the peak is nearly shorter than 24 h [70]. In addition, as illustrated in Figure 29, the TL intensity of 0.1 % Cu doped sample is the highest among samples in range of 0.1 % and 0.02 % Cu concentrations.

The glow curves of Cu and Ag-doped LTB samples produced using two different methods at different copper concentrations from 0.02 and 0.1 % and constant silver amount 0.04 % are indicated in **Figures 30** and **31**. As can be noticed from **Figure 30**, the TL glow curves of co-doped LTB samples synthesized with SAM consist of one predominant peak at around 210°C. The intensity of peaks at 100°C is quite low with

respect to TL peaks at higher temperature. Nevertheless, $Li_2B_4O_7$: Cu, Ag samples produced with MAM have low TL intensities that samples produced with SAM. Especially, the peak temperature of highest TL peak observed at around 275°C in only Cu-doped LTB samples shifts to low temperature side ($T_m \approx 210^{\circ}$ C) after the addition of second activator (0.04% Ag) (see **Figures 30** and **31**). Again, no remarkable TL intensity was observed after adding low copper concentrations (0.02 % and 0.04 %) for the samples produced using two different methods. As a result, it is obvious that 0.08 % Cu-activator and 0.04 % Ag co-activator concentrations exhibited significant effect on TL glow curve shape and leads to highest TL intensity of LTB phosphor produced with SAM and MAM.



Figure 30. TL glow curves of co-doped $Li_2B_4O_7$ produced with SAM. (Varying Cu content from 0.02 wt% to 0.1 wt% and 0.04 wt% Ag).



Figure 31. TL glow curves of co-doped $Li_2B_4O_7$ produced with MAM. (Varying Cu content from 0.02 wt% to 0.1 wt% and 0.04 wt% Ag).

The glow curves of Cu and Ag-doped LTB samples produced using two different methods at different copper concentrations from 0.02 and 0.1 % and constant silver amount 0.04 % are indicated in **Figures 30** and **31**. As can be noticed from **Figure 30**, the TL glow curves of co-doped LTB samples synthesized with SAM consist of one predominant peak at around 210°C. The intensity of peaks at 100°C is quite low with respect to TL peaks at higher temperature. Nevertheless, Li₂B₄O₇. Cu, Ag samples produced with MAM have low TL intensities that samples produced with SAM. Especially, the peak temperature of highest TL peak observed at around 275°C in only Cu-doped LTB samples shifts to low temperature side (T_m \approx 210°C) after the addition of second activator (0.04 % Ag) (see **Figures 30** and **31**). Again, no remarkable TL intensity was observed after adding low copper concentrations (0.02 % and 0.04 %) for the samples produced using two different methods. As a result, it is obvious that 0.08 % Cu-activator and 0.04 % Ag co-activator concentrations exhibited significant effect on TL glow curve shape and leads to highest TL intensity of LTB phosphor produced with SAM.



Figure 32. TL glow curves of triple-doped $Li_2B_4O_7$ produced with SAM. (Varying Cu content from 0.02 wt% to 0.1 wt %, 0.04 wt% Ag and 0.04 wt% In).



Figure 33. TL glow curves of triple-doped $Li_2B_4O_7$ produced with MAM. (Varying Cu content from 0.02 wt% to 0.1 wt %, 0.04 wt% Ag and 0.04 wt% In).

When Indium was added with Cu and Ag into LTB, it influenced the peak intensities and peak shapes illustrated in Figures 32 and 33. In the presence of three dopants (Cu, Ag and In) the samples synthesized using both methods gave TL emissions with lower intensities than only co-doped LTB samples. The reason of declines in TL intensities can be explained by huge difference between valence electrons of In³⁺ and Li⁺, which can distort the crystal lattice of LTB [71]. Moreover, in Figure 32 the addition of In changed LTB sample with the highest TL intensity, which is 0.09 % Cu, 0.04 % Ag and 0.04 % In doped LTB sample. When we compared glow curves of co-doped and triple-doped LTB samples produced with SAM, third dopant changed the sample having the highest TL intensity. Among the co-doped samples, 0.08 % Cu and 0.04 % Ag doped LTB sample exhibited remarkable TL intensity and proper glow peak at around 210°C. Nevertheless, TL intensity of this sample, whose main peak located the same temperature, sharply decreased in the presence of third dopant. In addition, As shown in Figure 32, TL intensity of 0.1 % Cu, 0.04 % Ag doped sample increased by adding In with content of 0.04%. However, new peak was detected at around 280°C. As a result, the effect of third dopant was observed for abovementioned LTB samples produced with SAM. There was no noteworthy changes in TL glow curves of the rest of the samples.

In **Figure 33**, the effects of synthesis method and third dopant on glow curves is given. As can be seen from **Figure 33**, generally main peak intensities decreased compare to the samples produced with SAM have. However, the intensities of the peaks at about 100°C increased when we compared to triple doped samples produced with SAM. Additionally, new peak constitutions were observed beyond the main peak near 300°C. This case was evidently noted for 0.06 % Cu, 0.04 % Ag and 0.04 % In doped sample having the highest TL intensity among the triple doped LTB samples produced with MAM, which is not proper for TL dosimetry. Nevertheless, if we looked at the glow curve of 0.09 % Cu, 0.04 % Ag and 0.04 % In doped sample and other samples, the peaks near 300°C tend to decrease as TL intensity of the main peak decreased. In **Figures 34** and **35** it was investigated that variation of TL intensity with manganese content from 0.02 % to 0.1 %. Moreover, the effect of synthesis methods on glow curves of Mn-doped LTB samples was illustrated in these figures. Generally, TL intensities of Mn-doped LTB samples produced with SAM showed low absorption character for applied- β radiation (Figure 34). TL glow curve of the sample, containing 0.7 % Mn, consists of two separated peaks. The peak with low intensity located at about 90°C. Another peak appeared near 325°C with 9x10⁵ intensity. Glow curve shape of this sample is inappropriate for dosimetric measurements due to peak temperature of main peak. Rest of the samples did not give remarkable TL intensity and glow curve shape. When we compared glow curves of Mn-doped samples produced with SAM and the samples produced with MAM, TL signal of the sample with the highest intensity decreased to 2x10⁵. Additionally, the temperature of the peak at 325°C remained at the same position. On the other hand, if we focused on TL signals of other samples in **Figure 35**, TL peaks at around 300°C of the samples except 0.08 % and



Figure 34. TL glow curves of $Li_2B_4O_7$: Mn (Varying amounts of Mn from 0.02 to 0.1%) produced with SAM.



Figure 35. TL glow curves of $Li_2B_4O_7$: Mn (Varying amounts of Mn from 0.02 to 0.1%) produced with MAM.

0.09 % Mn doped LTB samples significantly increased. T_m values of these peaks shifted to lower temperatures. However, there was no detectable linear relation between TL intensity and Mn contents in LTB.

Silver was added as co-dopant with varying amounts of Mn into LTB samples synthesized with SAM and MAM and their representative data are given in **Figures 36** and **37**. It was expected for silver to shift T_m to lower temperature due to characteristic TL peak of Ag⁺ at °C 170 [48]. As can be noticed from **Figure 36**, the main peaks of glow curves of Mn and Ag doped LTB samples produced with SAM were seen at around 220°C. When we look at glow curves of Mn-doped LTB samples (see Figure 34), main peaks appeared at 320°C. However, the peak intensities of co-doped samples dramatically decreased, which is illustrated in **Figure 36**. In **Figure 37**, it is unable to notice silver effects on TL glow curves of co-doped LTB samples produced with MAM. The intensities of peaks at 90°C did not change when we compared to Mn doped samples produced with MAM (see Figure 35). On the other

hand, main peaks of glow curves lost much of TL signals. Nevertheless, 0.1%, 0.08%, and 0.04% Mn doped LTB samples gave TL signal at 300°C.



Figure 36. TL glow curves of co-doped $Li_2B_4O_7$ produced with SAM. (Varying Mn content from 0.02 wt% to 0.1 wt% and 0.04 wt% Ag).



Figure 37. TL glow curves of co-doped $Li_2B_4O_7$ produced with MAM. (Varying Mn content from 0.02 wt% to 0.1 wt% and 0.04 wt% Ag).



Figure 38. TL glow curves of triple-doped Li₂B₄O₇ produced with SAM. (Varying Mn content from 0.02 wt% to 0.1 wt%, 0.04 wt% Ag and 0.04 wt% In).



Figure 39. TL glow curves of triple-doped $Li_2B_4O_7$ produced with MAM. (Varying Mn content from 0.02 wt% to 0.1 wt%, 0.04 wt% Ag and 0.04 wt% In).

In the presence of a third activator, it was aimed to see whether the addition of indium increases the intensity of Mn and Ag doped LTB samples. It can be inferred from Figures 38 and 39 that the TL intensities and peak temperatures of triple doped LTB samples produced with SAM and MAM were different from each other. As can be noticed from Figure 38, there was no serious change in TL glow curves with the addition of In with Mn and Ag activators when we compared the TL glow curves of co-doped the samples . However, we observed that 0.02 % Mn, 0.04% Ag and 0.04% In doped LTB produced with SAM gave three peaks at the temperatures 90°C, 230°C and 280°C, respectively. The peak near 280°C was unexpectedly observed. Moreover, peak intensity at 225-230°C of 0.02 % Mn, 0.04 % Ag and 0.04 % In doped LTB increased significantly with adding In. In the same way, the addition of 0.04 % In with Mn and Ag activators into LTB samples produced with MAM did not change the TL characters. Namely, TL intensities and peak temperatures generally remained constant, which is illustrated in Figure 39. Especially 0.08 % Mn, 0.04 % Ag and 0.04 % In doped sample produced with SAM gave the same TL glow curve as the sample without In did.

4.1.7.1.2 Effect of dose

The dose response of 0.08 % Cu and 0.04 % Ag doped Li₂B₄O₇ samples were studied as a function of beta doses between 40 mGy to \approx 1.7 kGy. Some of the selected TL glow curves after different dose levels are shown in **Figure 40**. Samples were read immediately after irradiation and it is seen that there are no great differences in the glow curve structures of samples with increasing dose levels. **Figure 41** shows the resulting dose response curves obtained by peak height and peak area methods. In peak area method, integrated area of each main peak was measured after various dose irradiations of the sample. As seen from **Figure 41**, the dose response curves of obtained by both methods showed different behaviors. According to peak area measurements, a linear dose response curve was detected between 300 and 1.3 kGy

and then a saturation effect starts with increasing beta doses. However, peak height of glow curves shown in Figure 41 have narrower linearity range than peak area measurements of main peaks. In this case, a deviation starts from linearity after 576 Gy and a supralinearity is seen in the dose response curve which is obtained by peak height method [69]. There are a number of ways to explain the disagreement between the dose response curves obtained peak height and peak area methods. One of them might be that the dosimetric peak of this material is due to continuous distribution of traps and not a single trap. If a glow peak is the overlapping of many glow peaks, its dose response curves obtained after both methods are different. The other might be the thermal quenching effect which explains the decrease of the thermoluminescence (TL) intensity with increasing temperature [72]. In general, the thermal quenching is no sufficient effect on the TL intensity of materials below 150°C. However, it is established that the process of thermal quenching is most effective for temperatures greater than 150°C in many materials, i.e, in quartz. If the thermal quenching exists in a given material, it is expected that the TL sensitivity of this material decreases with increasing heating rate, which was observed in the studied material. As a result, the peak area method is better than the other method to obtained absorbed dose in this material.



Figure 40. TL glow curves of 0.08 % Cu and 0.04 % Ag doped Li₂B₄O₇ sample produced with SAM after irradiation to 1.73 kGy.



Figure 41. TL response of 0.08 % Cu and 0.04 % Ag doped Li₂B₄O₇ sample produced with SAM.

4.1.7.1.2 Reproducibility

In order to determine the optimum annealing procedures for eliminating the effects of previous irradiations, the sample (0.08 % Cu and 0.04 % Ag doped $Li_2B_4O_7$) was firstly exposed to 12 Gy with β -rays before each measurement. After the read out, an annealing treatment at 250°C for 15 min was carried out before the next irradiation and measurement. The results of reproducibility experiment are shown in **Figure 42**. After nine repeated cycles of read and annealing, TL intensities of the main peak at 210°C remain almost the same within less than 5% based on standard deviation. Therefore, the annealing procedure at 250°C for 15 min is sufficient to erase residual TL signal completely.



Figure 42. Reproducibility of peak area of main dosimetric peak of 0.08 % Cu and 0.04 % Ag doped $Li_2B_4O_7$ sample produced with SAM after 9 repeated cycles of read-anneal.

4.1.7.1.3 Fading

In order to determine dark fading of synthesized 0.08 % Cu and 0.04 % Ag doped $Li_2B_4O_7$ produced with SAM, the sample was firstly irradiated to β -rays at room temperature. Then the samples were stored in a dark place at room temperature. The TL measurements were performed after a desired time intervals during the period of 40 days. The glow curves showed that lower temperature peak at 90°C disappeared in 12 h storage period. Moreover, the TL intensity of main peak at 210°C stayed nearly constant during a period of 2 weeks storage. Then there was a sharp decrease in intensity after two weeks period. The sample had a fading of 40 % in 40 days storage period.



Figure 43. Fading of 0.08 % Cu and 0.04 % Ag doped $Li_2B_4O_7$ sample produced with SAM during 40 days storage in dark place at room temperature.

4.1.7.2 TL results of LBO

4.1.7.2.1 Effect of Dopant

Figure 44 shows comparative study of un-doped LBO and Al doped LBO samples in terms of TL properties. As can be seen from Figure 44, un-doped LBO did not give separated peak at around 220°C. However, dopant effect can be easily noticed in this figure. Al doped LBO showed remarkable glow peak at around 220°C and TL intensity of this peak is highly depended on the concentration of Al added into LBO. It was observed that TL intensity decreased with increasing Al concentration. While TL intensity of 1 % Al doped LBO was estimated 3.0×10^6 , intensity of 5 % Al doped LBO was obtained as approximately 1.0×10^6 . Both Al doped sample showed similar TL glow shape. TL glow curve Al doped LBO samples gave characteristic two glow peaks with main peak at 220°C and small peak seen as hump at around 160°C. Furthermore, TL mechanism of Al doped sample can be described by function of Al ions in LBO crystals. Al⁺ and Al³⁺, which are states in most natural samples according to electron paramagnetic resonance (EPR) studies, are responsible for corresponding TL signals. Monovalent Al^+ ions tends to enter Li^+ sites to compensate charge equilibrium in LBO lattice. Here, there is a limitation to be considered, which is lattice distortions in the local region of lattice because of ionic size differences in ions. Nevertheless, the ionic size of Al^+ (0.075 nm) differs from substituted Li^+ (0.06 nm) ions by 1.1 times, which cannot engender distortions in LBO lattice. As a result, Al⁺ ions substitutes for Li⁺ ions and Al³⁺ ions occupies interstitial sites in LBO crystal. Al³⁺ ions can captures holes and turns out Al⁴⁺ form upon irradiation. On the other hand, released electrons after irradiation trapped by oxygen defects in LBO crystal. Upon the heating trapped electrons are liberated from corresponding defects and recombine with Al⁴⁺ ions reduced to Al^{3+} in excited state. Therefore, the characteristic TL emission of $(Al^{3+})^*$ is obtained when excited $A1^{3+}$ returned to ground state [73].



Figure 44. Glow curves of un-doped LiB_3O_5 and Al doped LiB_3O_5 samples. The samples were exposed to Beta ${}^{90}Sr/{}^{90}Y$ at room temperature for 5 minutes while the radiation given was 1.0 Gy/min.



Figure 45. Glow curves of un-doped LiB₃O₅ and Eu doped LiB₃O₅ samples. The samples were exposed to Beta 90 Sr/ 90 Y at room temperature for 5 minutes while the radiation given was 1.0 Gy/min.

Figure 45 illustrates the effects of Eu^{2+} ions on TL properties of LBO samples. Generally, the glow curves of Eu-doped LBO samples had the peak at about 325°C. Nevertheless, the glow curve of 1 % Eu doped LBO consists of two extra peaks with respect to 0.5 % Eu and 0.75 % Eu doped LBO samples. When TL intensities were considered in terms of Eu content in LBO, there was no linear relation between TL intensity and the amount of dopants. The highest TL intensity (approx. $3.5x10^4$) among Eu doped samples was achieved with adding 1 % Eu into LBO. However, TL glow curve shape of these samples are not suitable for TL dosimetry due to inappropriate glow curve shape and low TL sensitivity.



Figure 46. Glow curves of Al doped LBO, Al - Eu doped LBO and Al, Eu and Cu doped LBO samples.

In this study, it was aimed to examine the effects of second and third activators on TL properties of Al-doped LBO samples and representative data was given in **Figure 46**.

The addition of Eu into LBO with 1 % Al generally decreased the TL intensity of main peak near 220°C from 3.0x10⁶ to 1.4x10⁶ for 1% Al and 0.25 % Eu doped LBO sample. On the contrary, it contributed to increase TL intensity of peak at lower temperature (estimated 160°C). Nevertheless, the peak temperatures at highest intensity barely changed. Furthermore, copper (0.08 %) was used as third activator with Al and Eu. With the addition of Cu, TL glow curve shape changed drastically with respect to glow curve shape of Al and Eu doped LBO samples, which is illustrated in **Figure 46**. Triple-doped LBO had one prominent peak at around 120°C instead of peak near 220°C. Similar result was reported by Depci with adding 0.7 % wt CuO into LBO [60]. According to his study, Cu doped LBO sample gave TL peak at 117°C, which is in agreement with the results given in **Figure 46**.



Figure 47. Glow curves of Al doped LBO, Al - Eu doped LBO and Al, Eu and Cu doped LBO samples.

The effects of co-dopant and third dopant on TL glow curve of 5 % Al doped LBO samples are shown in **Figure 47.** The addition of Eu (0.25%) as co-dopant with 5 %

Al led to decreased TL intensity of the peak at about 220°C by approximately 5 times. Moreover, Cu (0.08 %) was used as co-dopant with 5 % Al, which changed the glow curve shape in the way of glow curve of 1% Al and 0.08% Cu doped sample. In **Figure 47**, Al and Cu doped sample has two peaks with higher intensity at approximately 120°C and lower intensity at approximately 190 °C. Second peak at approximately 190°C is different from 1 % Al and 0.08 % Cu doped LBO sample. Additionally, Eu (0.25 %) was used as third dopant with Al and Cu. Again, Eu caused decrease in TL intensity of the sample. On the other hand, it had no the effects on the peak positions of these peaks depicted in **Figure 47**.

CHAPTER 5

CONCLUSIONS

In this study, lithium tetraborate and lithium triborate phosphors were successfully synthesized and they were doped with metal activators. For the production of LTB, solution assisted method and microwave assisted method were employed, which were demonstrated by XRD results. Both methods work to obtain single-phase LTB polycrystalline products. Moreover, LBO samples were synthesized based on solution-assisted method. With this method maximum phase purity for LBO was obtained according to XRD results of un-doped and doped LBO samples Furthermore, in heating stage, it was noticed that heating rate (especially at final heating stage) has dramatic effects on obtaining pure LTB and LBO products. Hence, it was determined that temperature should be increased by 4 °C/min during the final heating procedure.

TL results were firstly studied for LTB samples produced with SAM and MAM. According to the results, there are high influences of production technique, types of activators and concentration of them on the shape of glow curve, intensity and peak temperature of glow peaks of LTB. The samples produced with SAM showed better TL glow curve shape and intensity. Therefore, the glow curves of samples doped with SAM were more suitable for the potential use in TL dosimetry than the samples doped with MAM.

In the case of single dopant systems for LTB samples, 0.08 % Cu doped LTB sample produced with SAM showed highest TL intensity peak at around 275°C. However, peak shape of this sample is not suitable for TL dosimetry.

When the co-doping system is concerned for LTB samples, 0.08 % Cu and 0.04 % Ag doped sample produced with SAM gave the best results among the double-doped LTB samples. In addition, in literature, copper and silver are used in co-dopant system for LTB. However, TL intensity of the main peak of Cu-Ag doped LTB was increased with decreasing copper amount (0.08 wt)% in this study.

In triple dopant systems for LTB samples, TL intensities of the samples generally decreased upon adding of In with Cu and Ag or Mn and Ag.

When TL results of single, double and triple doped LTB samples were concerned, 0.08 % Cu and 0.04 % Ag doped sample produced with SAM gave the best results. The sample shows nearly ideal TL properties such as simple glow curve shape that has main TL peak around 200°C and linear dose response curve for personal dosimetric applications.

TL results of LBO samples showed that 1 % Al doped LBO sample gave the best TL properties in terms of peak shape and intensity. The addition of extra Al led to decrease TL intensity. Moreover, Eu was used as main dopant or co-dopant with Al, which caused to decrease TL intensity of the main peak at about 220°C. Besides, the addition of Cu (0.08%) with Al or Al and Eu changed the glow curve structure of Al doped LBO or Al and Eu doped LBO samples. It caused to shift the main peaks (220°C) of these samples to lower temperature (120°C).

REFERENCES

- [1] E. J. J. H. Schulman, Kirk, R. D. , West, "Use of lithium borate for thermoluminescence dosimetry," in *Proceeding of the USAEC Symposium Series* 650637, 1965, pp. 113–118.
- [2] R. H. Von H. König, "Zur Kenntnis von LiBO₃O₅," Z. anorg. allg. Chem., vol. 439, pp. 71–79, 1978.
- [3] A. Majchrowskia, T. Lukasiewiczb, Z. Mierczykc, and M. Malinowskid, "International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane," 2000.
- [4] V. S. Gorelik, A. V. Vdovin, and V. N. Moiseenko, "Raman and hyper-Rayleigh scattering in lithium tetraborate crystals," *J. Russ. Laser Res.*, vol. 24, no. 6, pp. 553–605, 2003.
- [5] W. H. Zachariasen, "The crystal structure of lithium metaborate," *Acta Crystallogr.*, vol. 17, pp. 749–751, 1964.
- [6] J. Krogh-Moe, "The crystal structure of lithium diborate, Li₂O.2B₂O₃," *Acta Crystallogr.*, vol. 15, no. 3, pp. 190–193, 1962.
- [7] N. I. Leonyuk, "Structural aspects in crystal growth of anhydrous borates," J. Cryst. Growth, vol. 174, no. 1–4, pp. 301–307, 1997.
- [8] M. Voda, R. Balda, M. Al-Saleh, I. S. de Ocariz, M. Cano, G. Lobera, and J. Fernandez, "Optical properties of Pr-doped lithium tetraborate glasses '," J. Alloys Compd., vol. 323–324, pp. 250–254, 2001.
- [9] S. M. Kaczmarek, "Li₂B₄O₇ glasses doped with Cr, Co, Eu and Dy," *Opt. Mater.* (*Amst*)., vol. 19, no. 1, pp. 189–194, 2002.
- [10] R. K. and S. U. Tamotsu Sugawara, "Linear and Nonlinear Optical Properties of Lithium Tetraborate," *Solid Slate Commun.*, vol. 107, no. 5, pp. 233–237,

1998.

- [11] A.S.Pradhan, "Thermoluminescence Dosimetry and Its Applications," *Radiat. Prot. Dosimetry*, vol. 1, no. 3, pp. 153–167, 1985.
- [12] C. F. Dewey, W. R. Cook, R. T. Hodgson, and J. J. Wynne, "Frequency doubling in KB₅O₈4H₂O and NH₄B₅O₈4H₂O to 217.3 nm," *Appl. Phys. Lett.*, vol. 26, no. 12, pp. 714–716, 1975.
- [13] C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, and S. Lin, "New nonlinearoptical crystal: LiB₃O₅," *J. Opt. Soc. Am. B*, vol. 6, no. 4, p. 616, 1989.
- [14] S.W.S. McKeever, *Thermoluminescence of Solids*. London: Cambridge University Press, 1988.
- [15] E. Pekpak, A. Yılmaz, and G. Özbayoglu, "An Overview on Preparation and TL Characterization of Lithium Borates for Dosimetric Use," *Open Miner*. *Process. J.*, vol. 3, pp. 14–24, 2010.
- [16] C. F. Mahesh, K. Pao-shan Weng, *Thermoluminescence in solids and its applications*, First. Kent: Nuclear Technology Publisher, 1989.
- [17] M. P. A. Ege, E.Ekdal, T.Karali, N. Can, "Effect of heating rate on kinetic parameters of β-irradiated Li₂B₄O₇ :Cu,Ag,P in TSL measurements," *Meas. Sci. Technol.*, vol. 20, no. 5, p. 58002, 2009.
- [18] L. M. E. Smart, Solid State Chemistry : An introduction. 2005.
- [19] C.Furetta, Handbook of Thermoluminescence. 2003.
- [20] F. Daniels, C. A. Boyd, and D. F. Saunders, "Thermoluminescence as a research tool," *Sci. Transl. Med.*, vol. 117, pp. 343–349, 1953.
- [21] T. Rivera, "Thermoluminescence in medical dosimetry," *Appl. Radiat. Isot.*, vol. 71, pp. 30–34, 2012.
- [22] V. Kortov, "Materials for thermoluminescent dosimetry: Current status and future trends," *Radiat. Meas.*, vol. 42, no. 4–5, pp. 576–581, 2007.

- [23] E. Pekpak, "Synthesis And Characterization Of Lithium Tetraborate Doped With Metals," M.S. thesis, Mine Engineering, Middle East Technical University, Ankara, 2009.
- [24] C. Furetta, M. Prokic, R. Salamon, and G. Kitis, "Dosimetric characterisation of a new production of MgB₄O₇:Dy,Na Thermoluminescent Material," *Appl. Radiat. Isot.*, vol. 52, no. 2, pp. 243–250, 2000.
- [25] M. Prokic, "Dosimetric Characteristics Of Li₂B₄O₇: Cu, Ag, P Solid," vol. 100, pp. 265–268, 2002.
- [26] K. S. Park, J. K. Ahn, D. J. Kim, H. K. Kim, Y. H. Hwang, D. S. Kim, M. H. Park, Y. Park, J. J. Yoon, and J. Y. Leem, "Growth and properties of Li₂B₄O₇ single crystals doped with Cu, Mn and Mg," *J. Cryst. Growth*, vol. 249, no. 3–4, pp. 483–486, 2003.
- [27] S. Lorrain, "A study of new preparations of radiothermoluminescence LTB with various activators," *Radiat. Prot. Dosimetry*, vol. 17, pp. 385–392, 1986.
- [28] B. F. Wall, C. M. Driscoll, J. C. Strong, and E. S. Fisher, "The suitability of different preparations of thermoluminescent lithium borate for medical dosimetry.," *Phys. Med. Biol.*, vol. 27, no. 8, pp. 1023–1034, 1982.
- [29] M. Mathews, A. Tyagi, and P. Moorthy, "High-temperature behaviour of lithium borates," *Thermochim. Acta*, vol. 319, no. 1–2, pp. 113–121, 1998.
- [30] Sangeeta, B. Tiwari, and S. C. Sabharwal, "Investigations on the solidification behavior of Li₂B₄O₇," *J. Cryst. Growth*, vol. 273, no. 1–2, pp. 167–171, 2004.
- [31] 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," *Radiat. Meas.*, vol. 38, no. 4–6, pp. 571–574, 2004.
- [32] A. B. Kaplun and A. B. Meshalkin, "Phase equilibria in the binary systems Li₂O-B₂O₃ and Cs₂O-B₂O₃," J. Cryst. Growth, vol. 209, no. 4, pp. 890–894,

2000.

- [33] J. Manam and S. K. Sharma, "Evaluation of trapping parameters of thermally stimulated luminescence glow curves in Cu-doped Li₂B₄O₇ phosphor," vol. 72, pp. 423–427, 2005.
- [34] Y. V. Burak, V. T. Adamiv, I. M. Teslyuk, "Optical absorption of isotopically enriched Li₂B₄O₇ single crystals irradiated by thermal neutrons," *Radiat. Meas.*, vol. 38, pp. 681–684, 2004.
- [35] V. Jubera, J. P. Chaminade, A. Garcia, F. Guillen, and C. Fouassier, "Luminescent properties of Eu³⁺-activated lithium rare earth borates and oxyborates," *J. Lumin*, vol. 101, pp. 1–10, 2003.
- [36] W. H. Sutton, "Microwave Processing for Ceramic Materials," Ceram. Soc. Bull., vol. 68, pp. 376–386, 1989.
- [37] B. P. Saha, R. Johnson, I. Ganesh, and Y. R., G.V.N. Rao, S. Bhattacharjee, and Mahajan, "Thermal anisotropy in sintered cordierite monoliths," *Mater. Chem. Phys.*, vol. 67, no. 1–3, pp. 140–145, 2001.
- [38] M. Prokic, "Lithium borate solid TL detectors," *Radiat. Meas.*, vol. 33, no. 4, pp. 393–396, 2001.
- [39] L. Singh, V. Chopra, and S. P. Lochab, "Synthesis and characterization of thermoluminescent Li₂B₄O₇ nanophosphor," *J. Lumin.*, vol. 131, no. 6, pp. 1177–1183, 2011.
- [40] W. S. Moryc, "Infrared spectra of BaB₂O₄ and LiB₃O₅: new nonlinear optical materials.," *Appl. Phys. B*, vol. 511–512, pp. 241–249, 1999.
- [41] M. Kızılkaya. Z. Özdemir, G. Özbayoğlu, "Synthesis and characterization of lithium tetraborate doped metals," *Physicochem. Probl. Miner. Process.*, vol. 38, pp. 321–327, 2004.
- [42] C. N. Rao, Chemical Approaches to The Synthesis of Inorganic Materials. New

Delhi: Wiley, 1994.

- [43] M. L. Occelli, Synthesis of Microporous Materials, First. New York, 1992.
- [44] K. E. Haque, "Microwave energy for mineral treatment processes—a brief review," Int. J. Miner. Process., vol. 57, no. 1, pp. 1–24, 1999.
- [45] 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. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, vol. 456, no. 3, pp. 411–417, 2001.
- [46] A. (Türkler) Ege, E. Ekdal, T. Karali, and N. Can, "Determination of thermoluminescence kinetic parameters of Li₂B₄O₇: Cu, Ag, P," *Radiat. Meas.*, vol. 42, no. 8, pp. 1280–1284, 2007.
- [47] M. M. Islam, V. V Maslyuk, T. Bredow, and C. Minot, "Structural and electronic properties of Li₂B₄O₇," *J. Phys. Chem. B*, vol. 109, no. 28, pp. 13597– 604, 2005.
- [48] A. T. Brant, B. E. Kananan, M. K. Murari, J. W. McClory, J. C. Petrosky, V. T. Adamiv, Y. V. Burak, P. A. Dowben, and L. E. Halliburton, "Electron and hole traps in Ag-doped lithium tetraborate (Li₂B₄O₇) crystals," *J. Appl. Phys.*, vol. 110, no. 9, 2011.
- [49] E. K. Zhigadlo, M. Zhang, "An infrared spectroscopic study of sealants.," Scand. J. Dent. Res., vol. 84, no. 6, pp. 396–400, 1976.
- [50] W. Zhong and D. Tang, "Growth units and morphology of lithium triborate (LBO) crystals," J. Cryst. Growth, vol. 166, no. 95, pp. 91–98, 1996.
- [51] M. W. Swinney, J. W. McClory, J. C. Petrosky, S. Yang, T. Brant, V. T. Adamiv, Y. V. Burak, P. a. Dowben, and L. E. Halliburton, "Identification of electron and hole traps in lithium tetraborate (Li₂B₄O₇) crystals: Oxygen vacancies and lithium vacancies," *J. Appl. Phys.*, vol. 107, no. 11, p. 113715, 2010.

- [52] S. M. Alotham, T. Ahamad, M. Naushad, "Preparation of new thermoluminescent material (100-x)B₂O₃-xLi₂O: Cu²⁺ for sensing and detection of radiation," *Bull. Mater. Sci.*, vol. 39, no. 1, pp. 331–336, 2016.
- [53] O. Annalakshmi, M. T. Jose, U. Madhusoodanan, J. Sridevi, B. Venkatraman, and G. Amarendra, "Radiation-Induced Defects In Manganese-Doped Lithium Tetraborate Phosphor," vol. 163, no. 1, pp. 14–21, 2015.
- [54] A. Ratas, M. Danilkin, M. Kerikmäe, A. Lust, and H. Mändar, "Li₂B₄O₇: Mn for dosimetry applications : traps and mechanisms," *Proc. Est. Acad. Sci.*, vol. 61, no. 4, pp. 279–295, 2012.
- [55] O. Annalakshmi, M. T. Jose, U. Madhusoodanan, J. Sridevi, B. Venkatraman, G. Amarendra, and a B. Mandal, "Radiation-Induced Defects in Manganese-Doped Lithium Tetraborate Phosphor.," *Radiat. Prot. Dosimetry*, pp. 1–8, 2014.
- [56] O. Y. and T. Y. Mutsuo Takenaga, "Preparation And Characteristics of Li₂B₄O₇: Cu Phosphor," *Nucl. Instruments Methods*, vol. 175, pp. 77–78, 1980.
- [57] I. N. Ogorodnikov, A. V Kruzhalov, and A. V Porotnikov, "Dynamics of electronic excitations and localized states in LiB₃0₅," *J. Lumin.* 76&77, vol. 76, no. 97, pp. 464–466, 1998.
- [58] Z. Özdemir, "Synthesis and Characterization of Metal Doped Lithium Triborate As a Thermoluminescence Material," Ph.D. dissertation, Mine Engineering, Middle East Technical University, Ankara, 2005.
- [59] B. Ardic and Z. Ozdemir, "Production and identification of rare-earth doped lithium triborate," vol. 418, pp. 77–79, 2006.
- [60] T. Depçi, "Synthesis And Characterization Of Lithium Triborate By Different Synthesis Methods And Their Thermoluminescent Properties," Ph.D. dissertation, Mine Engineering, Middle East Technical University, Ankara, 2009.
- [61] A. Savva, "Personnel TLD monitors, their calibration and response," no.
September, pp. 3–12, 2010.

- [62] N. Can, T. Karali, P. D. Townsend, and F. Yildiz, "TL and EPR studies of Cu, Ag and P Doped Li₂B₄O₇ Phosphor," vol. 2038, 2006.
- [63] G. D. Patra, S. G. Singh, B. Tiwari, S. Sen, D. G. Desai, and S. C. Gadkari, "Thermally stimulated luminescence process in copper and silver co-doped lithium tetraborate single crystals and its implication to dosimetry," *J. Lumin.*, vol. 137, pp. 28–31, 2013.
- [64] E. Bétourné and M. Touboul, "Synthesis of lithium borates (B/Li≥3) as LiB₃O₅ by dehydration of hydrated precursors," *J. Alloys Compd.*, vol. 255, no. 1–2, pp. 91–97, 1997.
- [65] Z. Y. Xiong, P. Ding, Q. Tang, J. M. Chen, and W. Q. Shi, "Thermoluminescence Spectra of Lithium Tetraborate Single Crystal," Adv. Mater. Res., vol. 160–162, pp. 252–255, 2010.
- [66] A. T. Brant, D. A. Buchanan, J. W. McClory, P. A. Dowben, V. T. Adamiv, Y. V. Burak, and L. E. Halliburton, "EPR identification of defects responsible for thermoluminescence in Cu-doped lithium tetraborate (Li₂B₄O₇) crystals," *J. Lumin.*, vol. 139, pp. 125–131, 2013.
- [67] O. Annalakshmi, M. T. Jose, U. Madhusoodanan, B. Venkatraman, and G. Amarendra, "Kinetic parameters of lithium tetraborate based TL materials," J. Lumin., vol. 141, pp. 60–66, 2013.
- [68] E. Pekpak, A. Yilmaz, and G. Özbayolu, "The effect of synthesis and doping procedures on thermoluminescent response of lithium tetraborate," J. Alloys Compd., vol. 509, no. 5, pp. 2466–2472, 2011.
- [69] S. J. Dhoble, S. C. Gedam, I. M. Nagpure, S. V. Godbole, M. K. Bhide, and S. V. Moharil, "Luminescence of Cu⁺ in halosulphate phosphor," *J. Mater. Sci.*, vol. 43, no. 9, pp. 3189–3196, 2008.
- [70] C. Furetta, Handbook of Thermoluminescence. London: World Scientific, 2003.

- [71] Z. Xiong, Q. Tang, X. Xiong, D. Luo, and P. Ding, "The roles of Ag, in and P in the thermoluminescence emission of Li₂B₄O₇ phosphors," *Radiat. Meas.*, vol. 46, no. 3, pp. 323–328, 2011.
- [72] S. W. S. Mckeewer, R. Chen, *Theory of Thermoluminescence and Related Phenomena*. World Scientifc, Singapore, 1997.
- [73] T. Depçi, G, Özbayoğlu, A. Yılmaz, N. Yazıcı, "The thermoluminescent properties of lithium triborate (LiB₃O₅) activated by aluminium," *Nucl. Instruments Methods Phys. Res.*, vol. 266, pp. 755–762, 2008.

APPENDIX

XRD PATTERNS OF LTB SAMPLES



X-ray patterns of the prepared materials are given in the following figures.

Figure 48. XRD Patterns of Cu doped LTB produced with SAM.



Figure 49. XRD Patterns of Cu doped LTB produced with MAM.



Figure 50. XRD Patterns of Cu-Ag doped LTB produced with SAM.



Figure 51. XRD Patterns of Cu-Ag doped LTB produced with MAM.



Figure 52. XRD Patterns of Cu-Ag-In doped LTB produced with SAM.



Figure 53. XRD Patterns of Cu-Ag-In doped LTB produced with MAM.



Figure 54. XRD Patterns of Mn doped LTB produced with SAM.



Figure 55. XRD Patterns of Mn doped LTB produced with MAM.



Figure 56. XRD Patterns of Mn-Ag doped LTB produced with SAM.



Figure 57. XRD Patterns of Mn-Ag doped LTB produced with MAM.



Figure 58. XRD Patterns of Mn-Ag-In doped LTB produced with SAM.



Figure 59. XRD Patterns of Mn-Ag-In doped LTB produced with MAM.