



SYNTHESIS AND CHARACTERIZATION OF LITHIUM TETRABORATE  
DOPED WITH METALS

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DOPED WITH METALS

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# ABSTRACT

## SYNTHESIS AND CHARACTERIZATION OF LITHIUM TETRABORATE DOPED WITH METALS

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Lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) has aroused interest of scientists since 1960s by the courtesy of the thermoluminescence (TL) property it possesses. Over and above, it found widespread use in surface acoustic wave apparatuses, in sensor sector and in laser technology due to its non linear optical characteristics. For the uses in thermoluminescence dosimetry lithium tetraborate is activated by addition of a variety of metals as dopants.

This study comprises the synthesis of lithium tetraborate by two methods (high temperature solid state synthesis and water/solution assisted synthesis) as well as doping and characterization of the material. Lithium tetraborate is readily commercially available in TL dosimetry; hence, the main aim is to specify practical production conditions to pioneer domestic production.

In high temperature synthesis, the initial heating was performed at  $400^\circ\text{C}$  for 3 hours. Then the samples were heated at  $750^\circ\text{C}$  for two hours, intermittently mixed to enhance diffusion and exposed to the same temperature for another two hours. In

water/solution assisted synthesis, stoichiometric quantities of reactants were mixed in water by heating and agitating in order to achieve homogenous mixing and good dispersion of the material. The remnant of water was removed from the system by 3 hours initial heating at 150°C. The synthesis stage is followed by doping step where the metals Cu, Ag and In in different proportions were doped in lithium tetraborate by solid state and solution assisted synthesis techniques.

Powder X-ray diffraction method was employed for the characterization of the material. The thermal properties of doped and un-doped materials were studied by DTA (Differential Thermal Analyses). Besides, FT-IR (Fourier Transform Infra red) spectrometry analyses were performed in order to detect differences in the bond structure caused by doping

The XRD patterns obtained showed that lithium tetraborate production was successful by both high temperature solid state synthesis and solution assisted synthesis. Moreover, it was inferred from the XRD results that addition of dopants did not have a sound effect on the crystal structure. Furthermore, the DTA results displayed that addition of different dopants to the structure of lithium tetraborate did not cause any noticeable difference. The extensive TL measurements showed that the TL response of the material produced is affected by production and doping methods.

Keywords: Lithium tetraborate, inorganic synthesis methods, material characterization techniques, thermoluminescence

# ÖZ

## METAL KATKILI LİTYUM TETRABORAT SENTEZİ VE KARAKTERİZASYONU

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Lityum tetraborat ( $\text{Li}_2\text{B}_4\text{O}_7$ ) termoluminesan (TL) özelliğinden dolayı 1960'lardan beri araştırmacıların dikkatini çekmektedir. Bunun yanında lityum tetraborat yüzey akustik dalga araçlarında, sensor sektöründe ve non-lineer optik özelliklerinden dolayı da lazer teknolojilerinde geniş kullanım alanı bulmaktadır. Termoluminesan dozimetre alanındaki kullanımını için malzeme belli metallerin içine katılanmasıyla aktifleştirilmektedir.

Bu çalışma lityum tetraboratın iki teknikle (katı hal tepkimeleri ve sulu tepkime) sentezlenmesi, katılanması ve karakterizasyonu konularını içermektedir. Lityum tetraborat dozimetreler hali hazırda piyasada bulunmaktadır. Bu nedenle bu çalışmanın asıl amacı malzemenin TL özelliğini iyileştirmek ve pratik üretim yöntemlerinin koşullarını belirleyerek dozimetrelerin yerel üretimi için bir ilk adım atmaktır.

Yüksek sıcaklıkta katı hal yönteminde malzeme öncelikle 3 saat  $400^\circ\text{C}$  de ilk ısıtmaya maruz bırakılmıştır. Daha sonra  $750^\circ\text{C}$ 'de 2 saat tutulmuş ,difüzyonun daha iyi gerçekleşmesi için ara karıştırma yapılmış ve 2 saat daha  $750^\circ\text{C}$ 'sıcaklığa maruz bırakılmıştır.Sulu tepkimede ise kimyasal oranlarda alınan tepkenler homojen ve iyi

dağılımlı bir karışım elde etmek amacıyla su içerisinde ısıtıcı karıştırıcılarda karıştırılmıştır. Bu esnada eklenen suyun büyük kısmı buharlaşarak sistemden uzaklaşmıştır. Ancak malzeme su kalıntılarında tamamen kurtulmak için 150 °C de 3 saat fırınlanmıştır. Sentezleme sürecini yine katı hal ve sulu tepkimelerle gerçekleştirilen Cu, Ag ve In katkılama süreci takip etmiştir.

Malzemenin karakterizasyonu XRD metoduyla gerçekleştirilmiş, katılanmış ve katılanmamış malzemenin ısı özellikleri DTA metodu ile belirlenmiştir. Bunun yanında, katkılamadan kaynaklanabilecek bağ yapısı değişiklikleri olup olmadığını belirlemek amacıyla FT-IR spektrometresi çekimleri yapılmıştır

XRD analizlerinden elde edilen sonuçlara göre, lityum tetraborat hem katı hal yöntemi ile hem sulu tepkimeler ile gerçekleştirilen sentez çalışmaları ile elde edilebilmiştir. Ayrıca, XRD sonuçları göstermiştir ki katkılama prosedürü, uygulanan ikinci bir ısıtmadan dolayı lityum tetraborat piklerinin daha iyi konumlanmasını sağlamış, bir başka deyişle safsızlıklarda azalma sağlamıştır. Fakat, katılanan metalden kaynaklanan farklı kristal oluşumu gözlenmemiştir. Bunun yanında, katılanan metallerin malzemenin termal özellikleri üzerinde dikkate değer bir etkisi olmadığı DTA sonuçları ile belirlenmiştir. Ancak, TL sonuçları incelendiğinde maddenin TL özelliklerinin hem sentez hem de katkılama prosedüründen önemli derecede etkilendiği gözlenmiştir.

Anahtar Sözcükler: Lityum tetraborat, anorganik sentez yöntemleri, madde karakterizasyon, termoluminesans

*To my family and friends*

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# CHAPTER 1

## INTRODUCTION

### 1.1 General Remarks

The luminescence characteristic of materials has been the focus of attention for human beings since very old times. Men, observing the bioluminescence displayed by organisms such as; bacteria in the sea or in decaying organic matter, glow-worms i.e. fire-flies have been bewildered and confused [34]. This very initial concern about luminosity grew into an enormous curiosity resulting in incalculable investigations regarding light emission of materials. The results of research on such light emitting materials revealed that luminescence of organisms and objects may be triggered by various factors, for instance; chemical activity, crystallization, electrical energy, sound, stress applied on a crystal. There are more than ten types of luminescence induced by different mechanisms. The kind of luminescence displayed by the objects that release the energy, stored from irradiation, in the form of light when exposed to heat is defined as *thermoluminescence (TL)*.

There are several groups of materials on which investigations are conducted in order to determine their suitability to TL dosimetry. Among these, LiF and CaF<sub>2</sub> stand for alkali and alkali-earth haloid group; MgSO<sub>4</sub>, CaSO<sub>4</sub> belong to sulfates; MgS, SrS, CaS, BaS are of sulfides and Al<sub>2</sub>O<sub>3</sub>, BeO, SiO<sub>2</sub> go with the oxides [31]. Added to these borates have considerable importance both for TL studies and for production of high technology materials owing to their unique combination of large electronic band gaps, strong nonlinear optical (NLO) properties, chemical and environmental stability, and mechanical robustness [17]. Concerning high technology; borates are particularly used as phosphors in applications such as plasma displays, where their strong absorption in the VUV can be used to generate very bright emission [30]. On

the other hand they are used in TL dosimeters for medical and personnel radiation monitoring especially because of their soft tissue equivalency. Hence, the synthesis and characterization studies of borates have grabbed extensive notice in these past twenty years due to the extremely wide variability of borate crystal chemistry that makes the creation of very different structure types possible [47]. Therefore, borates are both academically and commercially important.

Lithium tetraborate, one of the significant high technology borates satisfies the required characteristics of a TL dosimeter when doped with a number of different metals at certain ratios. The most important features that make lithium tetraborate an attractive alternative for dosimetry are: its linear dose response which is a rarely encountered property, good sensitivity, low fading, low dose threshold and simple annealing procedure. Other uses of lithium tetraborate include applications in surface acoustic wave devices, ultraviolet frequency conversion, including fourth and fifth harmonic generation of Nd:YAG laser [53], frequency converters of YAG laser light [19] [22] [29] [51].

Certainly, Turkey is a very significant borate supplier for the world and there is a variety of boron bearing products provided for the sector by Turkey. However, it is essential that boron, which enhances certain characteristics of the material it is added, should be searched intensely for new utilization areas. Previously another lithium borate namely lithium triborate was studied by Ardiçoğlu [2] and Özdemir [43]. Furthermore, it is of essential significance that such high technology products be produced domestically in Turkey so that the added value of the reserves possessed is increased.

## **1.2 Statement of the Problem and the Purpose of the Study**

Lithium tetraborate is known to be extensively used in several different areas of high technology. Thermoluminescence (TL) dosimetry has been one of the major high technology utilization areas for lithium tetraborate since decades. Furthermore it has proved to have great advantages in this sector owing to very specific properties of

borate crystals. During the long years that lithium tetraborate has been studied for perfection as a TL dosimeter, a variety of activator metals are added as dopants to further enhance the TL properties. However, the complexity of the TL concept as well as search for a practical production method for the material caused numerous studies to be devoted to synthesis, characterization and TL properties of lithium tetraborate. As a result, a number of production procedures and different TL properties are reported for lithium tetraborate in the literature.

On the other hand, although there are a variety of laboratory studies conducted, patents taken, and articles published in literature for lithium tetraborate synthesis, no appreciable sound procedure could be formulated for production in powder form. Besides, hitherto, no literal work dealing with the effect of synthesis and doping methods on TL properties has been encountered. Hence lithium tetraborate production is still preserving its place as an attractive playground to be adopted by researchers.

Since boron is an essential asset to Turkey, the initial major aim of the thesis study is to search new utilization areas for boron in high technology and encourage domestic production of such materials. Therefore, the study firstly aimed at determining a practical procedure for production of lithium tetraborate and characterization of the material. Secondly, on the technological use point of view, the material was searched for its TL properties since lithium tetraborate based TL dosimeters used commercially are imported from foreign countries

### **1.3 Methodology of Thesis**

The start point of the study included determination of synthesis conditions and comparison of two methods of synthesis. The initial characterization steps are taken by XRD for different cases. Structurally confirmed lithium tetraborate samples are doped with metals and passed through a second stage of characterization for the determination of whether the dopants interfered with the crystals structure or not.

Secondly, the samples produced by different techniques are tested for their TL properties. After deciding on the material that displayed the best TL response, experiments were performed to enhance the TL property by changing the doping temperature and retention time for the material during doping stage. This secondary enhancement step is followed by TL measurements as well.

## **1.4 Organization of Thesis**

Chapter 1 embraces the general remarks about the subject studied. In this section the objectives and methodology followed are presented.

Chapter 2 includes the literature review about thermoluminescence concept and lithium tetraborate. The first portion of chapter 2 comprises detailed information about the TL mechanism and how it is used. The properties that a dosimeter is supposed to possess and commercial dosimeters in the industry are also discussed. The second part devoted to lithium tetraborate embodies sound information about the physical, chemical properties of the material, utilization of lithium tetraborate in different areas, synthesis and doping methods for dosimetric use. The up to date studies on TL properties of lithium tetraborate and characterization results in the literature are also included.

Chapter 3 is dedicated to the materials and methods adopted for the experimental studies conducted. The details of synthesis and doping procedures as well as the analyses methods and conditions employed for characterization and determination of TL response are included at this part.

Chapter 4 covers the results of the experiments stated in chapter 3. These results include the outputs from characterization analyses as well as TL measurements.

Finally, Chapter 5 is devoted to the conclusions to be drawn from this study and recommendations.

## **CHAPTER 2**

### **LITERATURE SURVEY**

#### **2.1 Thermoluminescence**

It is possible to define the phenomenon of thermoluminescence (TL) or thermally stimulated luminescence (TSL) in several different ways, the simplest of which is emission of light when a material is heated. However, in the details of the mechanism the definition gets a bit more complicated. Mahesh et al. [34] defined the thermoluminescent phosphors as materials that keep the energy given by a pre-excitation by an appropriate type of radiation, ultraviolet, nuclear or cosmic waves, within itself. Then, when the luminescent object is subjected to heat up to a certain temperature that triggers the release of energy, it is possible to observe emission of this energy as visible light. Thermoluminescent materials are available for the use in radiation dosimetry, (clinical, radiotherapy, personnel) [9], and are functional in archeological and geological dating. It is for sure that there are numerous properties that a TL dosimeter should have and some requirements that it should satisfy so that it can be used in these areas. Not all the dosimeters fulfill all the desired properties; hence different dosimeters have different levels of advantages with respect to the others. Certainly these variations in characteristics of the dosimeters result from differing defect distributions.

##### **2.1.1 History of Thermoluminescence**

It is beneficial to touch on the brief history of thermoluminescence before passing to the technical details. The discovery of thermoluminescence can be traced back to Robert Boyle who observed this property in diamond in the year 1663. Although, exploration of the concept dates back to 1600s, a real understanding of the

phenomenon could not be achieved for more than 2 centuries of experiments on the subject [34] [40]. The credit of discovery of the dosimetric use of thermoluminescence goes to E. Wiedemann (1895) who detected that synthetically prepared  $\text{CaSO}_4$  activated by manganese displayed thermoluminescence properties in detection of radiation resulting from an electrical discharge. After 40 years, Lyman applied the same technique for the ultraviolet range. In the following years a solid understanding of the concept was accomplished with the experimental studies of Randall, Wilkins, Gibson and Garlick. Kortov [31], declares that thermoluminescence dosimetry could be analyzed deeply only in the last 3 decades i.e. almost 3 decades after the discovery of thermoluminescence.

### **2.1.2 TL Mechanism**

The investigation on thermoluminescence in some sense can accomplish with a sound study of the imperfections in a crystal lattice. This is because it is the imperfections that form the traps and luminescent centers. Although thermoluminescence is studied in the ordered crystal it is possible to observe this property in amorphous materials in the form of glass [7].

A closer look at the mechanism of thermoluminescence reveals that a radiation applied to the thermoluminophore causes the occurrence of mobile holes and electrons in the crystal structure of the material. Besides, there are hole traps and electron traps by which the holes and electrons are captured. The amount of occupied traps is directly related to the radiation applied [34] [40]. These traps lie within in two bands energy namely “conduction band” and “valence band”. In conduction band electrons are freely mobile and can produce a net electric current. The valence band can be defined as the outermost energy band that contains electrons when a solid is in the ground state. Upon radiation, pairs of electrons and holes are produced. The first excitation brings about that one of the imperfections captures the electron and the other imprisons a hole. These imperfections possess different metastable trapping states and energies related to the energy bands they are in. After the irradiation, heating of the samples thermally releases the electrons to the conduction band and may recombine with the trapped holes which results in emission of

photons. At this stage the hole traps are named as the “luminescent” or “recombination center”[7].Moreover, according to Chen [7], in some cases the electron traps and hole traps may be far away from each other, former being close to the valence band and the latter being far away from the conduction band. In such a case during the heating process the holes are energetically raised into the band and makes recombination and resultant light emission possible.

A functional means of analyzing the characteristics of these traps passes through a sound realization of the glow curves that are plotted as thermoluminescence intensity versus the constantly increasing temperature. These curves show off one or more peaks named glow peaks that provide information about: the trap depths (thermal activation energy) electron/trap densities, carrier mobility, frequency factor and capture cross section of traps.

Thermoluminescence mechanism and the glow curve can be understood better by evaluating figure 2.1.The very first diagram exhibits the process where the material is exposed to the radiation. When such energy is applied to a thermoluminescent material, electrons are liberated from the valence band to the conduction band leaving the hole trap in the valence band as a positively charged site. Both the electrons and the holes are free to wander within the crystal until they recombine or be trapped at a metastable state which has a strong relationship with the defect distribution and the impurities of the material. When the thermoluminophore is heated there are two possibilities for it to emit a photon. The second illustration in figure 2.1 shows the instability of the electron trap which results from the heating custom. The electron may be provided with the adequate amount of energy and may get rid of the trap to rise up to the conduction band. As a result the photon emission takes place due to the transfer of electron from the electron trap to the hole trap i.e. hole trap is the emitting center. The last drawing shows the reverse case. In other words, the case where the hole trap is less stable during heating and the electron trap is the emitting center [34].

In fact the temperature required to observe the thermoluminescence which is specific to the material is determined by the energy gap between the bands. Application of increased temperature increases the possibility that an electron leaves a trap. At higher temperatures glow peaks to be taken into account are obtained. [34]

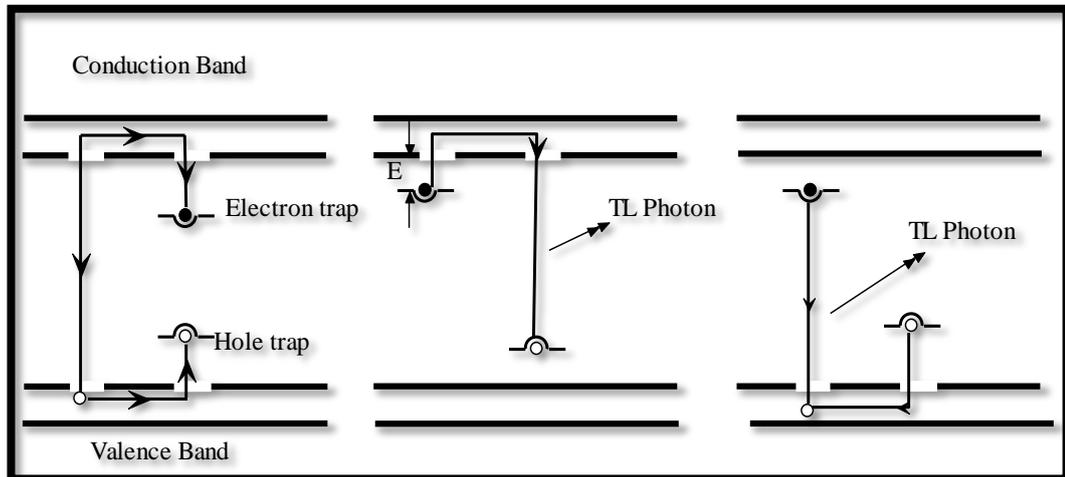


Figure 2.1 Schematic energy level diagram of a thermoluminescent phosphor

However, finally the light emitted diminishes with the further increase in temperature since all of the traps are gradually evacuated.

### 2.1.3 Uses of Thermoluminescence

Allowing the mechanisms described above, thermoluminescent materials find wide spread use in industry in two different areas which are further divided into subgroups.

First major utilization area of thermoluminescence is the “radiation dosimetry”. Radiation dosimetry is simply the measurement and/or calculation of the absorbed dose from an exposure to ionizing radiation in tissue and in matter. When a dosimeter is employed to measure the radiation in a tissue it is used either in personnel dosimetry or medical dosimetry. In personnel dosimetry, as the name implies, the dosimeter stores the radiation that the employees experience at the radiation constituting working environment (nuclear reactors and hospital

radiotherapy). The readouts of such dosimeters are performed periodically to monitor radiation exposure of the employee and to take the required precautions on time. On the other hand, medical dosimetry is applicable when it is desired to determine the radiation that the patients receive in diagnostic radiology and radiotherapy. In the other case, thermoluminescence dosimetry is used due to environmental concerns to monitor radiation released to the surrounding.

Secondly, thermoluminescence properties of materials are beneficial in dating of archeological and geological samples which includes complications compared to radiation dosimetry. The natural thermoluminescence output obtained by the read out is related to sensitivity, dose and time from the formation of the sample. Therefore, from an equation including these parameters one may easily calculate the age of the sample [7] [34] [40].

#### **2.1.4 Required TL Properties of a Dosimeter**

It is natural that the sector that uses thermoluminescent dosimeters imposes that they have some characteristic features specific to the usage area. In other words the dosimeter used in personnel dosimetry and medical dosimetry may differ in certain characteristics. However, there are a quantity of basic requirements that all TL dosimeters are expected to fulfill. Below given is a list of the features that a TL material is desired to have to be a TL dosimeter [16] [31] [40].

- 1- A TL dosimeter should give a simple isolated glow curve preferably; with a single glow peak around 200°C (180-250 °C). When the peak is observed at higher temperatures, there is a risk that infrared emissions from the sample and/or sample holder may interfere with the results causing errors in interpretations.
- 2- The dosimeter ought to have high gamma ray sensitivity.
- 3- Fading, loss of TL signal, must be insignificant in a few months in room temperature. More specifically, the dosimetric information should be kept in the dosimeter for sufficiently long time at a stable level.

- 4- The response should be directly proportional to the dose applied in a wide range.
- 5- The pre-radiational information ought to be erased with an easy procedure when desired, for instance in case of successive readouts.
- 6- The TL dosimeter must be resistive to extreme climatic conditions and chemically inert. Dosimeter should be resistant against humidity, gases, moisture, organic solvents.
- 7- The sunlight should not affect the dosimeter to a serious level
- 8- The dosimeter is expected to have high signal per unit of absorbed dose i.e. it should have high sensitivity.
- 9- For the use in personnel and medical dosimetry, it is severely important that the dosimeter have effective atomic number close to that of the human tissue.

Added to these features it is advantageous that the dosimeter be appropriate for postal service and be cheap. It is vital that it is not toxic in case of in-vivo i.e. in the body testing. High accuracy and precision are other critical properties. Yet, no TL material has been synthesized to satisfy all of the properties listed above in a perfect way.

### **2.1.5 Defect Structure of TL Materials**

It is an unquestionable fact that the disparities in the qualities of dosimeters are a consequence of the differences in the defect structures of materials. Therefore, it is of importance to cite a few words about the defects in thermoluminescent materials. The defects in a material's structure may be either intrinsic or extrinsic. The intrinsic defects are native defects like vacancies due to missing atoms, "interstitial defects" where an atom of the crystal is located at a site expected to be vacancy or "substitutional defects" in which atoms change locations oppositely and/or a combination of these. Nonetheless, extrinsic defects occur due to an impurity forced into the material. Such defects may again be substitutional or interstitial.

The defects described above are generally due to absence of totally perfect crystals by nature and addition of impurities. Nevertheless, there are defects that directly take

root from ionizing irradiation. These types of defects are called “*luminescence centers*” or “*absorption centers*” of materials. For instance, lack of a cation at the expected site causes negative ion vacancy and a balance of charges disappears resultantly. An electron free to move in crystal due to the ionizing radiation may possibly be attracted to a site lacking a cation due to the positive charge concentrated here by the Coulomb forces. This system is cited in literature as F center. When just the reverse process occurs i.e. when the hole trap is a positive ion vacancy than the system is defined as a V center. The effect of radiation in formation of these defects is that, radiation removes atoms from their actual locations in the crystal giving rise to vacancies and interstitials [31] [50].

Consequently, having a closer look at the brief history, main mechanism of thermoluminescence and paying more attention to the trap system in a thermoluminescent material it can be concluded that thermoluminescence studies date back to 16<sup>th</sup> century and this property of materials’ is strongly related to the imperfections in a crystal which hosts a complicated mechanism based on trapping and releasing of electrons that result in emission of light. The materials that display this system obviously are called thermoluminescent materials. However, there are numerous constraints for a thermoluminescent material to be an attractive candidate of a thermoluminescent dosimeter.

#### **2.1.6 Commercially Used TL Materials**

The intensive studies carried out by researchers and groups brought its fruits as a bunch of different dosimeters. Each of these objects display various characteristics which make them either advantageous or disadvantageous compared to another.

Among such materials, some of them are readily available in dosimeter sector. The commercial codes given to them are TLD100, TLD100H, TLD600, TLD600H, TLD700, TLD700H TLD200, TLD400, and TLD500. Table 2.1 includes the details of first six (LiF based) dosimeters [14] [31].

Opposite to lithium fluoride based dosimeters, calcium sulfate or calcium fluoride dosimeters produced by Yamashita [34] have undesirably high fading. As a matter of fact, the Tm doped CaF<sub>2</sub> doped dosimeters are rather more sensitive than the ones activated with Mn. The natural CaF<sub>2</sub> is found in the crystal form however the product activated by Mn may be in powder, bulb, chip or microrod form. Approximately 25% of the signal is lost in a month in CaF<sub>2</sub> dosimeters. However these dosimeters, besides having simple glow curves, display sufficiently high sensitivity [31]. Among the CaSO<sub>4</sub> dosimeters doped with Tm, Dy or Mn separately, one with manganese activator possessed the highest sensitivity although it was the first to lose the thermoluminescent. Manganese doped CaSO<sub>4</sub> is in powder form in the sector. Nevertheless, one doped with Dy is used in powder, disc or chip form

Table 2.1 LiF based commercial dosimeters

Dosimeter Code	Dopant	<sup>6</sup> Li Percentage	<sup>7</sup> Li Percentage
TLD100	Mg,Ti	7.5	92.5
TLD100H	Mg,Cu,P	7.5	92.5
TLD600	Mg,Ti	95.6	4.4
TLD600H	Mg,Cu,P	95.6	4.4
TLD700	Mg,Ti	99.9	0.01
TLD700H	Mg,Cu,P	99.9	0.01

Dosimeters made up of lithium fluoride are well known for their noticeably high sensitivity and are very commonly used in USA. The other merits of this dosimeter include its small fading rate, inertness and commercial availability [34]. The major demerit of LiF based dosimeters is that they have considerably complex structure of glow curve which is not a desired property for an ideal dosimeter since they require complicated preheating procedures.

The alumina based dosimeters i.e. TLD500 are obtained by doping Al<sub>2</sub>O<sub>3</sub> with Ca, Cr, Ti, Ni, Mg, Na, and Fe. There are other TLD phosphors like beryllium oxide, magnesium orthosilicate, magnesium tetraborate and calcium sulfate doped both with

dysprosium and thulium available in disc form. Consequently developed up to now and used commercially possess varying characteristics Table 2.2 is devoted to significant characteristics namely the glow peak temperature, effective atomic number and fading of a number of commercial dosimeters (Pradhan, 1981) [31].

Lithium tetraborate being an important material for TL dosimetry has been a matter of curiosity for scientists for years. Therefore the following sections are devoted to the recognition and understanding of TL properties of lithium tetraborate.

Table 2.2 Commercial Dosimeters

TLD phosphor	Dosimetric peak temperature(°C)	Effective atomic number	TL Fading
LiF:Mg,Ti	195	8.2	10% per month
MgB <sub>4</sub> O <sub>7</sub> :Dy	210	8.4	10% per two month
Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> :Mn	210	7.4	10% per month
Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> :Cu,Ag	185	7.4	10% per month
Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> :Cu	205	7.4	9% per two month
CaSO <sub>4</sub> :Tm	210	1.0	10% per month
CaSO <sub>4</sub> :Dy	210	15.0	3% per month
CaSO <sub>4</sub> :Mn	110	15.0	60% per day
CaF <sub>2</sub> :Dy	200	16.0	12% per month
CaF <sub>2</sub> :Mn	260	16.0	10% per month
CaF <sub>2</sub> (natural)	260	16.0	
MgSiO <sub>4</sub> :Tb	195	11.0	3% per month
BeO	180-220	7.2	5% per month
Al <sub>2</sub> O <sub>3</sub>	250	10.2	5% per two weeks

## 2.2 Lithium Tetraborate

### 2.2.1 Properties of Lithium Tetraborate

It is obvious that the physical and chemical as well as structural properties of lithium tetraborate play a major role on its possibility to be used in thermoluminescence dosimetry. Certainly, the crystal structure and defect distribution are the most vital properties, but still characteristics like solubility and thermal behavior are determining factors for the production procedure. At this point it is beneficial to evaluate the physical-chemical properties of lithium tetraborate prior to the examination of structural properties that give rise to thermoluminescence properties.

Initially, lithium tetraborate is a white powder. It does not have a distinctive odor. The melting point of lithium tetraborate is  $917^{\circ}\text{C}$  [49] and it possesses moderate solubility (1-10 %). The density of lithium tetraborate powder is  $2.45\text{g}/\text{cm}^3$ . As soon as the thermal behavior is concerned, lithium tetraborate is called to be a congruently melting material. When a material melts congruently it forms a composition same as that of its solid. On the other hand, the other lithium borates go through phase transition, decomposition or incongruent melting below their liquidus temperatures in air [36]. Lithium tetraborate possesses numerous technological properties such as; pyroelectricity and piezoelectricity which means that it may generate heat induced electricity or may produce electricity under mechanical stress. [18]

Definitely, there are other technological features of lithium tetraborate which led researchers to investigate candidacy for thermoluminescence industry. For instance, it has been discovered that lithium tetraborate acquired interesting optical properties. Hence, scientists directed their research on the investigation of linear and nonlinear optical properties of lithium tetraborate. Sugawara [51] made research to characterize the nonlinear optical properties of this material and came into the decision that this sample is an exceptional nonlinear material for frequency conversion in the UV range. Excellent transparency and low scattering are other superior characteristics of  $\text{Li}_2\text{B}_4\text{O}_7$ . Lithium tetraborate is also known to have a high radiation resistivity and a

wide operation dose range. Before continuing with the crystal and structural properties of lithium tetraborate, it is of assistance to go into the details of non linear opticity. A number of interesting materials which have crystal structures without a center of symmetry modify the light that passes through them [8]. Nonlinear optical (NLO) materials are used to generate new laser sources of frequencies that cannot be obtained directly from available in available lasers [3] [32]. For a material to be used in NLO industries it should have an ease in production procedure and good chemical and mechanical stability besides being resistant to damages.

Unquestionably, all of the above properties of lithium tetraborate are attributed to its peculiar crystallization system. Lithium tetraborate is observed to crystallize in tetragonal lattice point group with the cell dimensions of  $a=9.477$ ,  $c=10.86$  and point group of  $4mm$  [5]. Becker [5] has demonstrated the  $B_4O_9$  rings as in figure 2.2.

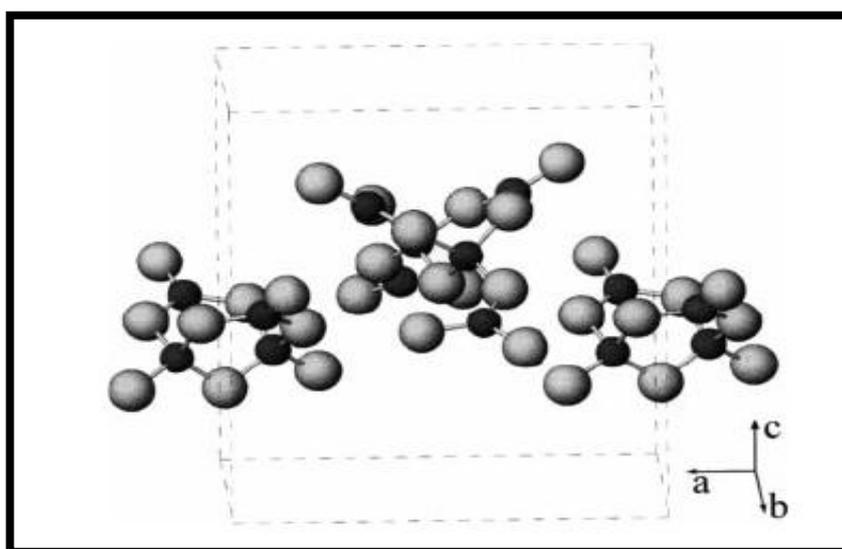


Figure 2.2 Details of the arrangement of  $[BO_3]$  and  $[BO_4]$  groups, condensed to  $[B_4O_9]$  rings, in the crystal structure of  $Li_2B_4O_7$

[Large light gray spheres represent O atoms, smaller dark gray spheres B atoms.

Li atoms are left out ][5]

It is also found out that lithium tetraborate experiences a solid phase transition from triclinic to monoclinic at  $270^\circ C$ . It was discovered that no noticeable change was observed until this temperature apart from shifts in peak locations and their

intensities in XRD patterns [37]. A closer look at the lattice structure of lithium tetraborate shows that lithium tetraborate is formed by two  $\text{BO}_4$  tetrahedra and two  $\text{BO}_3$  triangles [55]. There are two non-planar, six membered rings in the group. The two boron atoms and one oxygen atom of the group are shared by two rings that are twisted. Each diborate unit is linked at corners of four boron atoms with bridging oxygen with identical diborate units to form a three-dimensional network. This structure explored can be seen in the Figure 2.3.

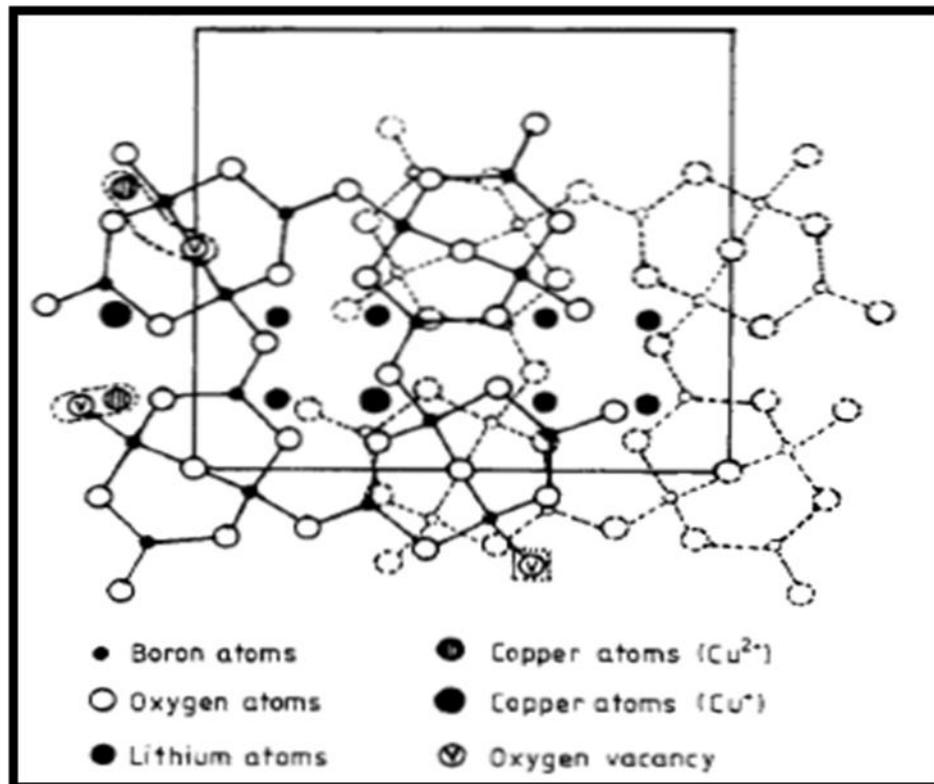


Figure 2.3 Unit cell projection of lithium tetraborate along c-axis and a few lattice defects

(broken lines: separate interlocking twin to first network).[50]

A very all-embracing research has recently been conducted by Natalia [38] who studied the crystal structure of lithium tetraborate at 20, 200, 400 and 500°C and reported the frameworks in great detail. Natalia [38] concluded that the crystal structure enhancement at high temperatures shows that O1 atoms shift apart giving

free space for lithium atom to fall through oxygen atoms along c-axis causing the contraction in this direction and that high asymmetry of Li atomic thermal vibrations is a characteristic feature for NLO lithium tetraborate. Natalia [38] provided a rather detailed figure of the structure (Figure 2.4).

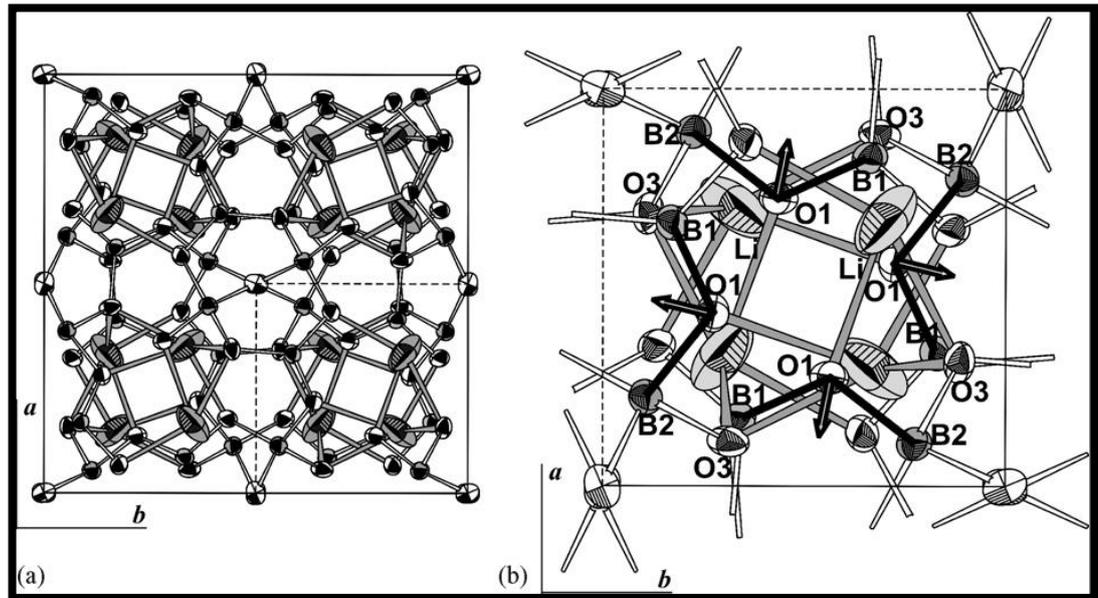


Figure 2.4 Structure projection of  $\text{Li}_2\text{B}_4\text{O}_7$  in  $\mathbf{ab}$  plane (a) full unit cell and (b) a quarter of the unit cell at  $20^\circ\text{C}$

[38]

### 2.2.2 Uses of Lithium tetraborate

The large group of borates is an attractive chemical playground adopted by many researchers and groups. Noteworthy attention is directed towards lithium tetraborate due to the attractive features that its interesting chemical structure provides. These properties of lithium tetraborate opened the gates of different utilization areas for it.

To begin with, lithium tetraborate finds usage in surface acoustic wave (SAW) devices used in electric circuits. Such devices convert acoustic wave to electrical signal and vice versa utilizing the piezoelectric effect of certain materials. Usually quartz, lithium niobate, lithium tantalate, lanthanum gallium silicate are used in this

area and lithium tetraborate is proved to be a pretty logical alternative [19] [22] [29] [51] [53]. Moreover, lithium tetraborate is known to be used in sensors like pressure sensors and pyroelectric sensors [19]. Owing to its non linear optical properties this material finds use in major application areas of nonlinear opticity as ultraviolet frequency converter in lasers optical communication and signal processing.

Recently lithium tetraborate has been important for thermoluminescence dosimetric purposes. The thermoluminescent characteristics of lithium tetraborate are explained in great detail at the related section hence this subject is not discussed here. Nonetheless, it is essential to mention that the most grave problem with the use of lithium tetraborate in dosimetry is the difficulty of reproduction of the material.

### **2.2.3 Synthesis of Lithium Tetraborate**

There are numerous studies devoted to the understanding of optimal synthesis conditions of lithium tetraborate. Although they suggest different methods of production, they do have certain common tendencies. Indeed, lithium tetraborate produced for the use in thermoluminescence dosimetry can be in five different forms: powder form, pellet form, in glass or polycrystalline form or it can be melted and recrystallized to obtain a single crystal.

The lithium tetraborate in powder form can be used for thermoluminescence dosimetry purposes. In spite of the fact that powder lithium tetraborate is claimed to be inconvenient for the use in this area, Panasonic utilizes this product in TLD badges [41]. Hence, it is obvious that the problems faced during laboratory period can easily be overcome during the commercial stage, since the main difficulty is to get exactly the same weight of the powder during thermoluminescence measurements. Pradhan [40] emphasizes the possibility of contamination of the powder as a demerit of this form. However, once the powder product is placed on badges, they are covered with a thin, translucent layer of film which protects the dosimeter from getting polluted. The main advantage of powder production against other types is that the energy consumed during the process is noticeably less than that

for glass and crystal formation since in each case higher temperatures are employed to melt material first.

There are a few techniques to obtain lithium tetraborate as powder. It can be produced by heating of a hydrated precursor of lithium tetraborate which is  $\text{LiB}_5\text{O}_6(\text{OH})_4 \cdot \text{H}_2\text{O}$  at  $600^\circ\text{C}$ . Another alternative is starting with a mixture of lithium borates such as  $\text{LiB}_2\text{O}_3(\text{OH}) \cdot 3\text{H}_2\text{O}$  and  $2\text{LiB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$  or a mixture of  $\text{LiB}_2\text{O}_3(\text{OH}) \cdot \text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$ . [6]. The second technique applied to produce lithium tetraborate as powder is the wet reaction. This method was applied by Furetta [15] who performed wet reaction with stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$ . The same method was applied by Prokic in 2001 [41]. Thirdly, solid state synthesis option was performed by Sangeeta [45] whose production procedure followed was milling and homogenizing  $\text{Li}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$  powders and sintering the mixture at  $700^\circ\text{C}$  for 48 hours. Solid state synthesis was employed also by Jubera [28] who aimed at producing lithium rare earth borates with initial reactants of  $\text{H}_3\text{BO}_3$  and  $\text{LiBO}_2$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ . The heating route tracked was keeping the mixture at  $400^\circ\text{C}$  for 2 hours and at  $700^\circ\text{C}$  for a time span during which all the nitric vapors in the system, due to dissolving the constituents in nitric acid, could be evaporated. Then after, different sintering temperatures are chosen for different products.  $\text{Li}_2\text{B}_4\text{O}_7$ : Cu in form of powder was prepared to study thermally stimulated luminescence materials in the radiotherapy [9]. The product in the powder form can be pelletized for a better practicability and ease in laboratory measurements. On the other hand, the final products in pellet form are quite fragile and are vulnerable against breakage [40].

The second method of lithium tetraborate production commonly used is synthesis of lithium tetraborate in glass form. This technique lies at a place between powder product and single crystal when the ease in production procedure is concerned. Cautious control of the temperature and rapid cooling would be sufficient to obtain the product in glass form. Jaychandran [27], produced lithium borate glasses by pouring molten lithium borate into a stainless steel dish at room temperature followed by cooling in air. In 2001, lithium tetraborate glass was synthesized by melting Li B O with the molar ratio B/Li of 2.00 in a Bridgman type furnace. And

finally the doped (to be explained in the following sections) dry material was maintained at 980°C for 1 hour to avoid bubbles [53]. Another procedure applied for lithium tetraborate production in this form is starting the reaction of  $\text{Li}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$  at 950°C in a platinum crucible and then increasing the temperature up to 1150°C for the system to relieve from even small traces of water and carbon dioxide. [29]. Manam [35] who followed Schulman method [48] by mixing  $\text{Li}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$  in stoichiometric ratios, melting the mixture at 950°C in a silica crucible and allowing rapid cooling of the material to room temperature. Manam [35] reheated the glassy mass that has formed to 650°C and kept the material at this temperature for half an hour which is followed by cooling again. The sample is then powdered by grinding and sieving. Certainly when the cooling time is increased after melting the reactants, the resultant material comes into being in polycrystalline form.

The final and the most tedious technique to achieve the production of lithium tetraborate as a TL dosimeter candidate is single crystal growth. There are two basic methods to produce lithium tetraborate as single crystal namely; Bridgman method and Czochralski method named after Percy Williams Bridgman and Jan Czochralski respectively. Both of these methods require special systems which work on molten material cooled slowly in presence of a seed crystal.

#### **2.2.4 Doping of Lithium tetraborate with Metals**

When doping of the lithium tetraborate produced, as a TL dosimeter candidate is concerned, it can be observed that there are a variety of metallic elements from alkali metals to rare earth metals [44] that are forced into the lithium tetraborate structure. A bunch of research has been conducted in order to determine the optimum amount of doping material to be used and the ideal method to accomplish the most promising results. An effective overview of the doping procedure can be based on the classification of the diversity of elements, forms and amounts of dopants as well as the doping technique adopted.

The choice of dopants is based on numerous factors. Initially, a main constraint that affects the dopant preference is the suitability of the atomic radii of the dopants and

the elements in the matrix material. It is especially the lithium sites for lithium tetraborate due to the extremely small size of boron. For instance, Cerium doped by Senguttuvan [49] and Ishii [25] caused a problem related to solid solution formation with lithium tetraborate single crystal and hence the dopant mostly segregated out of lithium tetraborate phase making the crystal opaque which is not favorable although the other three dopants studied did not give rise to such kind of drawbacks owing to their ionic radii closer to that of lithium. On the other hand, a very significant criterion that affects the choice of dopant is the effective atomic number of the final product. A number of metals, though yielding promising results are not preferable due to their high atomic numbers which increases the effective atomic number of the dosimeter which is unfavorable for the use in personnel dosimetry.

Researchers up to this date have not stucked to a group of elements but they have studied on multifarious metals. Table 2.3 summarized a number of dopants studied.

Beyond these, two most important major activators used for lithium tetraborate are Manganese and Copper. They are essential due to their several attractive features against other TL dosimeters such as biological tissue equivalency and high sensitivity accompanied by a number of merits and/or demerits with respect to each other.

Table 2.3 List of several dopant metals used for lithium tetraborate

Dopant Metal	Weight % of the matrix	Mole % of the matrix	Form of dopant
Magnesium	0.1	0.1	MgO
Indium	0.07/0.5		Metallic/I <sub>2</sub> O <sub>3</sub>
Nickel	0.5		NiO
Cerium	0.1,1.0,2.0		CeO
Silver			
Europium	0.016-0.008		Eu <sub>2</sub> O <sub>3</sub>
Titanium	0.5		
Praseodymium		0.01,.0.5,0.1, 0.2,0.3,0.5,1.0	
Potassium		0.1-4	
Chromium	0.13 and 2.5		
Cobalt	10		
Dysprosium	2		
Iron		0.1	
Lanthanum		0.1	
Thulium		0.1	
Rare earth metals			
Phosphorus	0.8		

[1] [4] [11] [12] [23] [24] [25] [26] [29] [33] [39] [41] [42] [44] [49] [53]

**Manganese** doped lithium tetraborate is studied by Ignatovych [24], Park [39], Lorrain [33], and Wall [54] in the years 2007, 2002, 1986, 1983, respectively. Park [39], not only worked on copper, magnesium and manganese oxides doped in lithium tetraborate for the first time but also he compared the thermoluminescence results for the three products (Cu, Mn, and Mg doped lithium tetraborate single crystals). However, before Park [39], the critical comparison i.e. comparison of manganese and copper as dopants was performed by Wall [54] including almost all of the thermoluminescence properties.

The main activator in our case, i.e., **Copper** is the most notable metal as dopant. Different compounds of copper such as copper nitrates, chlorides and oxides have been employed as activator depending on the method of doping. For instance, El Faramawy [13] , preferred dissolving different amounts of **Cu(NO<sub>3</sub>)<sub>2</sub>** accompanied by lithium tetraborate in alcohol, then drying the solution and searching for an appropriate sintering temperature. Afterwards, Park [39] , made use of **CuO** for the production of Cu activated lithium tetraborate crystal. In the same year Senguttuvan

[49] added copper oxide as activator to lithium tetraborate in powder form. In 2004, **CuO** was also employed for production of glassy samples for a research on luminescence properties of lithium tetraborate [23]. Most recently, Holovey [21], used **CuO** for single crystal production with its thermoluminescence enhanced by addition of CuO before crystallization procedure. Besides, **CuCl<sub>2</sub>** was used by Manam [35] who added this compound directly to the stoichiometric mixture of lithium carbonate and boric acid followed by melting of the new mixture obtained.

Having discussed the doping procedures and the different compounds of copper used, it is high time to comment on the amount of the activators to be added. The quantity of doping material differs in a narrow range. The decision of the amount metal to be added is made either weight based or molar based with the percentage given for the compound or elements itself. When all of the quantities of dopants in the above mentioned studies are converted to copper weight percentage, the values for the successive experiments turn out to be values like 0.24, 0.40, 0.38, 0.01-1, 0.007-0.05, 0.08-0.37, and 0.03 %. From these values it can be concluded that copper as the main activator is studied from 0.03% up to 0.4 % by weight. It was found that the sample quality decreased quickly with increasing dopant concentration [1]. However, in different research products, different quantities are referred to as the optimum amount.

In a number of studies, copper is assisted by another metal which is named to be the coactivator as afore mentioned. These elements added in a smaller portion down to 10 % of the activator are proved to increase the response intensity. There are a few coactivators utilized with copper. For instance, copper and silver are claimed to be a very effective couple considering the thermoluminescence intensity. Moreover, Indium can be added solely or can serve as a luminescence center together with silver when the activator is copper [12] [41] [54]. Phosphorus is another element allowed to co-work with silver as coactivator studied by Prokic [41].

Certainly, copper came into prominence amongst the other alternatives owing to its numerous merits against other metals. Firstly, it is known that, on its introduction as

an impurity in lithium tetraborate, Cu may easily occupy one of the interstitial positions. Secondly, copper overcomes the drawback of poor TL sensitivity which is discussed under the thermoluminescence properties subject thoroughly. Indeed it is claimed to increase the material's photon sensitivity by a factor of approximately 50. Another property of copper which makes it a noticeable material for low dose measurements is that, undoped lithium tetraborate is approximately 10 times less sensitive than TLD-100 (a commercially used TL dosimeter) whereas LTB: Cu, is 5 times more sensitive than TLD-100 [14]. Furthermore, lithium tetraborate doped with copper has very important TL properties such as linear dose response, low fading, high sensitivity etc.

### **2.2.5 TL Properties of Lithium Tetraborate**

Once a candidate for TL dosimetry is obtained, a crucial step is faced for the specification of thermoluminescence characteristics of the material. Sensitivity, linear dose response, minimum detectable dose, shape of the glow curves, the occurrence temperature and intensity of TL peaks, fading, sunlight susceptibility, and vulnerability against humidity. It is beneficial to touch the definitions of some of these properties before providing related research on each of the characteristics.

#### **2.2.5.1 Sensitivity**

TL sensitivity can be expressed in different units and can be determined via different ways. Prokic [42] described sensitivity as the area under the glow curve per unit weight of the dosimeter and per unit dose of gamma rays applied. As result of this research Prokic has found out that lithium tetraborate doped with copper, silver and phosphor is 5 times more sensitive compared to a commercial TL dosimeter. On the other hand, formerly Pradhan [40] defined sensitivity as the quantity of light that the material emits per unit radiation dose which is in complete compliance with the definition in the "Handbook of Thermoluminescence" [16] which expresses sensitivity in terms of TL response per unit dose and unit mass of sample. According to the research of Wall [54], the sensitivity of the home made  $\text{Li}_2\text{B}_4\text{O}_7$ : Cu was approximately twice that of LiF:Mg, Ti. Earlier, Jayachandran [27] discovered that the sensitivities of manganese doped lithium borate and of LiF (commercially TLD-

100) were approximately equal [14] who studied sensitivity extensively made relative sensitivity comparisons between dosimeters TLD100, TLD700H, D-3-2, lithium tetraborate and lithium tetraborate with copper and claimed that lithium tetraborate had gamma sensitivity that is 5 times that of TLD100 and TLD700.

### 2.2.5.2 Linear dose response

Linear dose response, as the name implies, means that the response displayed by the material is directly proportional to the dose of radiation that it is exposed to. It is a known fact that in contrast to commonly used TL materials, lithium borate possesses perfect linearity as a particularly useful TL property, when doses up to  $10^3$  Gy are applied. Linearity can be observed rarely over 10 Gy which makes lithium borates rather distinct amongst others. (Figure 2.5) [15] [42] [56]. The other TL materials usually display supralinear characteristics

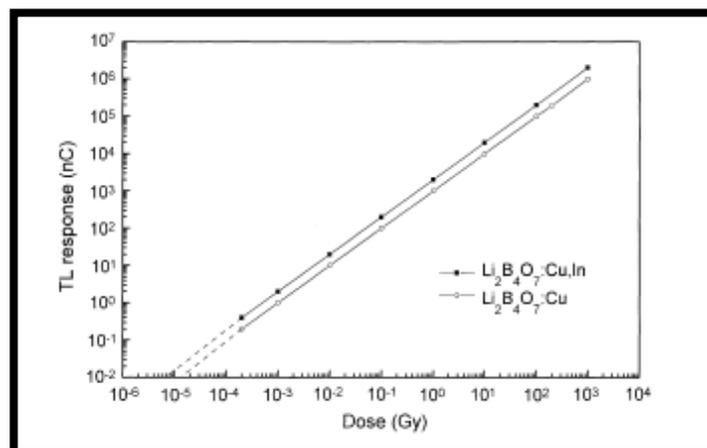


Figure 2.5 TL response vs. dose of lithium borate sintered TL dosimeters.

[15]

Undoubtedly, like all TL properties the dopants added play a major role in linear dose response as it is obvious is in Figure 2.5. The product of Park's [39] study displays another aspect of this effect by comparing the linearity for manganese, copper and magnesium activated lithium tetraborate in Figure 2.6 in the following page.

This feature of lithium borates is assigned to the activator effect of copper doped in the material [50]. Linearity measurements performed on copper doped and manganese doped lithium tetraborate exhibit that copper doped sample has tendency to show supralinearity (deviation from linearity) for 100Gy dose while manganese doped sample is superlinear at about 10Gy (Figure 2.7) [10] [33] [54]. It is possible to observe that supralinearity in case of copper is lower.

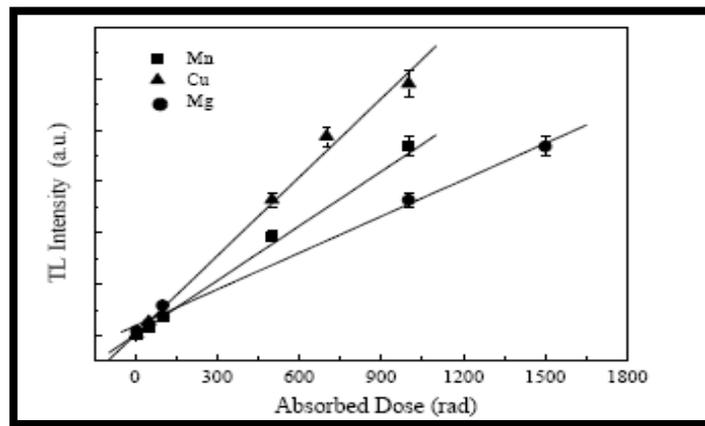


Figure 2.6 TL intensity as a function of X-ray dose for different dopants.

[39]

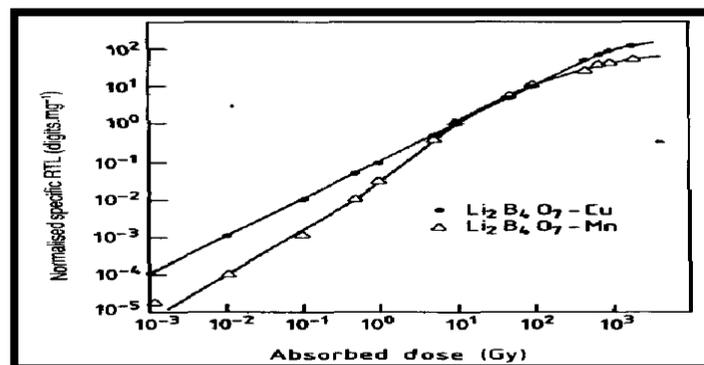


Figure 2.7 Absorbed dose response of lithium borate doped with copper or manganese.

[33]

### **2.2.5.3 Minimum detectable dose**

Studies on threshold dose are applied in case the minimum dose that can be detected by the dosimeter is desired to be determined. Another name in the nomenclature of thermoluminescence for dose threshold is lowest level of detection. El-Faramawy [13] determined this value as 20Gy. However this value went down to 6Gy in the investigation executed by Prokic [42].

### **2.2.5.4 Glow curve**

The glow curve is plotted by software connected to TL measurement systems and illustrates the thermoluminescence intensity versus temperature that increases up to a certain value with a definite rate during the read out. The peaks observed on this curve correspond to the ionization of traps at various energy levels. The intensity axis of the plot gives a clue about the relative populations of electrons in different traps [34]. The glow curves are particularly important in the sense that they are the main indicators of whether a material can be used for TL dosimetry purposes or not. Generally it is desired that the glow curve gives a simple, if possible single, peak around 200°C. The peaks observed at low temperatures in the proximity of 100 °C fade away quickly hence they do not yield any information about the radiation content. In general, this maximum is not symmetric and the half-width of this peak is wide. These properties of the shoulder peak imply that it has a complicated nature. Such maxima are claimed to result from superposition of a number of local trapping levels [22]. In a similar way, peaks observed around 300 °C are not assigned to good TL properties. Sangeeta [46] recorded major peak at 210°C for undoped lithium tetraborate. Copper activated lithium tetraborate was recorded to give two peaks at 120 and 178°C. Certainly the low temperature peak encountered rapid fading. In order to avoid such unnecessary peaks it is a common practice to apply pre-readout annealing or perform readings after 24 hours from the irradiation process.[13].Table 2.4 exemplifies a variety of glow curve results from different research studies.

Table 2.4 The temperatures of the main and shoulder glow peaks for lithium tetra borate doped with different metals

Dopant	Researcher	Temperature For the main peak(°C)	Temperature for the shoulder peak(s) (°C)
Cu-In	Furetta [15]	210	125
Cu	Manam [35]	175	290,325
Cu-Ag-In	Prokic [41]	190	125,225
Cu	Prokic [42]	185	
Ag	Prokic [42]	190	
P	Prokic [42]	135	
Cu	Cuong [9]	230	

The intensities of these peaks provided in literature are given in arbitrary units. Hence, mainly they can be used in comparative manner. Indeed, in all cases there are several parameters that affect the shape, size and location of the glow curve. These parameters may be listed as: heating rate, radiation dose, pre- and post-irradiation heat treatments and activator used [40]. Certainly preparation method,  $\text{Li}_2\text{O-B}_2\text{O}_3$  system, basic chemicals used, concentrations are other major factors influencing glow curve and the TL intensity [42].

#### 2.2.5.5 Fading

Fading in the thermoluminescence terminology refers to the reduction in radiation induced signal i.e. intensity of a peak in a time span. Certainly, material to be used for TL dosimetry purposes is required to have low or no fading so that accredited results can be obtained. Thus, fading can be regarded as a quality indicator for the dosimeter. The product of El-Faramawy [13] is declared to fade 11% at the end of the third month. The sample of Furetta's [15] study displayed similar fading with a percentage of 10 % in three months. Prokic [42] obtained samples for which the main peaks faded 10% in the first three months which is a quite slow rate of fading. In this study the peak at the low temperature region faded in 48 hours as it may be expected.

An important factor that affects the fading characteristics of lithium tetraborate is whether it is exposed to light or not. Lithium tetraborate doped with copper is

generally quite sensitive to light. This subject is worked by Furetta [15] who proved that copper activated lithium tetraborate loses its TL intensity about 5 times when it was kept at sunlight for 3 hours. When the sample was exposed to the room light only, the fading resulted was less than 10% in 6 hours. According to the research of Wall [54], fading is quite attention taking when the samples are exposed to tungsten or fluorescent light Figure 2.8.

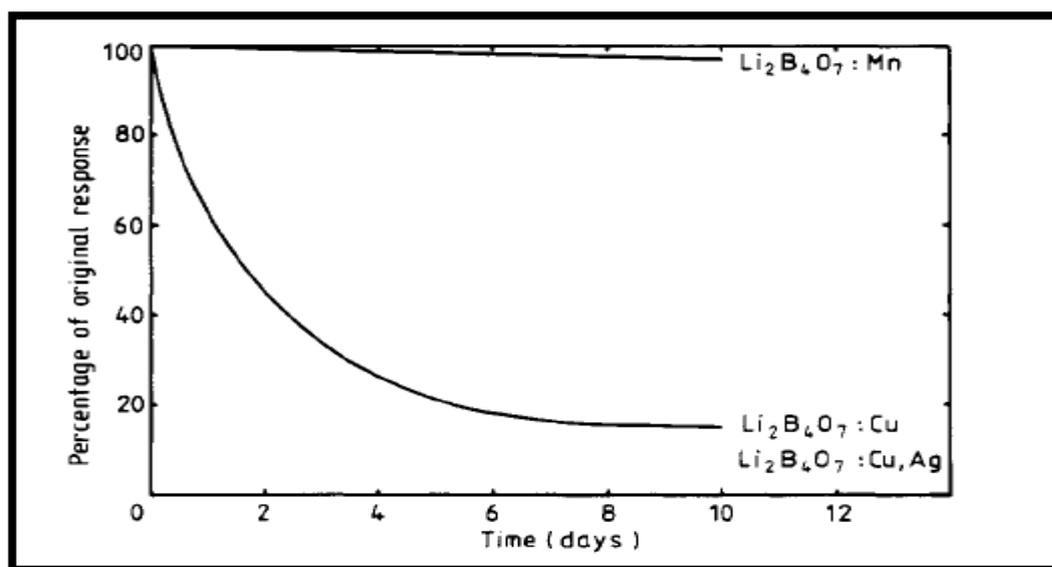


Figure 2.8 Fading of dose signal when phosphors are exposed to fluorescent and tungsten light

[54]

Another condition that should be taken into account during thermoluminescence studies is the humidity. However, for lithium tetraborate this is not severely serious. Wall [54] has declared that a loss of 10 to 25 % in 2-3 months in an environment where the relative humidity is 95% is a comparably small effect. Hence, copper doped lithium tetraborate is only slightly affected by humidity. The research conducted by Prokic [42] revealed that when two samples of copper, silver and phosphor doped lithium tetraborate are maintained in a humid condition (90% relative humidity) and in dry atmosphere (15% humidity) and when the TL responses

are compared no significant difference due to humidity is observed. In such cases the main peak is not affected by the moisture conditions.

Consequently there is expanded research on the TL properties of lithium tetraborate performed by prestigious researchers. As a result of these studies it is found that lithium tetraborate doped with copper and in some cases a coactivator is a sensitive dosimeter when compared to the commercial dosimeters. Furthermore, it has a very distinctive and significant property which is linear dose response. Linearity is quite a rare property among dosimeters. The glow curves obtained from TL measurements display resemblance. Generally the first peak around 100°C easily fades away and the main peak is around 200°C which stays steady under normal conditions for a period of time.

Certainly the TL signal cannot be stored in dosimeter forever. And this span determines the fading property of the material. Fading of lithium tetraborate is in acceptable limits and can even be claimed to have low fading. It is not severely affected by humidity of the environment although exposure to direct sunlight may fasten the loss of TL signal. This is why lithium tetraborate based dosimeters should be protected from direct sunlight until the TL measurement.

### **2.2.6 Defect Structure of Lithium Tetraborate**

The interaction of lithium oxide and boron oxide causes attachment of an additional oxygen atom to the boron- oxygen triangle to produce boron oxygen tetrahedron. It is a fact that crystals are not always in perfect shape but they usually possess imperfections in their structure. These imperfections are responsible for the unusual properties of materials. The boron-oxygen tetrahedron has excessive negative charge compensated by lithium cation which is located in the vicinity of the tetrahedron. The complex acts as a negative point defect forming hole traps in the absence of the lithium atom that balances the negative charge in normal conditions. Conversely, a positively charged point defect results when oxygen vacancies take place. These positively charged traps may trap electrons in the first place.

### **2.2.7 Effective Atomic Number**

Lithium tetraborate is used especially in personnel dosimetry. Thus, it is crucial that the dosimeter gives the exact amount of radiation that the user is exposed to [15]. In order to obtain the best result, certainly the dosimeter is supposed to possess nearly the same atomic composition as that of the human tissue. This concept can be evaluated by the parameter called effective atomic number ( $Z_{\text{eff}}$ ). The dosimeters to be used in personnel dosimetry should have an effective atomic number that is closest to that of biological tissue which is known to be 7.42. Such materials display similar elemental composition and density with the human tissue [11] which in advance brings about the interpretation that the dose responses they reflect would be more reliable than those that do not have this property.

When a dosimeter shows the same  $Z_{\text{eff}}$  with human tissue i.e. soft tissue, it is called to be a tissue equivalent dosimeter. And such a characteristic is quite rare among the dosimeters and the dosimeter which satisfies this requirement the best is lithium tetraborate with the value closest to 7.42

### **2.2.8 TL Measurement of Lithium Tetraborate**

The TL measurement procedure adopted varies from material to material for which there are differing annealing systems. The heating rates as well as the radiation dose that the sample is exposed are important factors to be decided.

Annealing can be defined as the preliminary heating procedure applied before irradiating the material, in order to relieve the sample from possible former radiations. Annealing (especially in case of successive readings) is important in the sense that the measurement results obtained are exact consequences of the dose applied during irradiation. The radiation temperature and exposure time may show variety depending on the material. Annealing can also be referred to as thermal cleaning of the samples. For the case of lithium tetraborate, researchers worked on a diversity of procedures. Table 2.5 a number of annealing procedures followed by various scientists.

Table 2.5 Annealing procedures for lithium tetraborate

Scientist	Annealing Temperature(°C)	Annealing Time
Giesber [17]	352	100sec
Xiong [56]	450	Not specified
Furetta [15]	700	30 min
Lorrain [33]	120	Not specified
Prokic [41]	650-700	15 min
Prokic [41]	110	5 sec

The second step (first step in absence of annealing) in TL measurement is the radiation of sample at a certain dose level. For the case of powder product, the weight of the sample to be measured possesses crucial importance. This is because the resultant response is directly related to the quantity of material. El-Faramawy [13], determined the optimum weight interval as 5-10mg to gather the best glow curve illustrations depending on the study of Wall [54] which displays the effect of sample weight on the TL signal.

The doses to be applied vary in a range depending on the objective of the measurement. In order to detect the dose threshold i.e. the minimum detectable dose, which gives a clue about the sensitivity of the material (important for medical cases especially) low doses are preferred. On the other hand, in order to determine the linearity of the response of the sample with respect to the radiation given, a wide range of doses must be applied successively upon annealing. High radiation doses are preferable in order to analyze the glow curves in more detail. Srivastava [50] founded his studies on a radiation dose of 100Gy. Xiong [56] irradiated the samples from low doses as 0.1 – 1Gy up to 2000Gy. Holovey [20] [21] who based his studies on different annealing conditions worked on a moderate dose of 1.7Gy.

Following the irradiation is the measurement of the response of the material. At this stage, the most significant issue is the heating rate. Generally the heating rate for which the best resolved glow peaks are obtained is preferable. This rate is proved to be the lowest possible value. Ege [12] who studied on lithium tetraborate doped with Cu, Ag, and P investigated the TL results for heating rates of 1, 2, 5, 10, 20 and 40

**K/s**. It was observed that TL peaks shifted towards higher temperature regions accompanied by a decrease in the intensity of the main peak with an increase in heating rate although the shapes of the glow curves did not display any change as a function of the heating rate. The other common heating rates employed for lithium tetraborate are **0.5° K/s** [17] [20] [21], **5°C/s** [15], **6°C/s** [13], **2.90 ± 0.03 ° K/s** [22]. In all of the TL research made on lithium tetraborate the maximum temperature reached is around 400 °C since the main peak is expected around 200°C.

As a consequence, the thermoluminescence measurement procedure is performed by annealing, radiation exposure and finally dose measurement with a definite heating system. Annealing is employed to erase the effect of former exposures to radiation and generally used in case of a number read outs made on one sample. In the case of lithium tetraborate, annealing at a low temperature, as low as 110 °C for 5 seconds may be enough. This is because the thermoluminescence signal is almost totally cleaned during the measurement stage. When the radiation exposure is concerned lithium tetraborate doses from 0.1Gy to 2000Gy are applied depending on the focus of the study. For conventional thermoluminescence measurement practices an appropriate dosage can be decided in a range between 1Gy to 5Gy. Then after, the thermoluminescence measurement is followed and this is as a tradition applied up to 400 °C although there are different heating rates in literature the lowest possible being the best choice.

### **2.2.9 TL Mechanism in Copper Doped Lithium Tetraborate**

The mechanism which gives rise to the above mentioned significant thermoluminescent properties is explained on the basis of release of trapped electrons. As an impurity, copper exists both in  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  states. The dominant band of traps with energy  $1.65 \pm 0.08$  eV may be ascribed to the presence of intrinsic lattice defects or complexes linked to positively charged copper ions (preferably  $\text{Cu}^{2+}$ ). Normally, the lattice of the material does not appreciably shift the emission from the excited state of  $\text{Cu}^+$  ions, which is mainly due to a  $3d^9 4s \rightarrow 3d^{10}$  transitions invariably in the range 3.4-3.5 eV [50].

### 2.2.10 Characterization of Lithium Tetraborate

It is essential to apply the material characterization techniques after synthesis of lithium tetraborate in order to check the phase of material. There are several methods utilized to investigate the crystal structure of samples obtained. Among these the one that is most commonly used is the x-ray diffraction (XRD) method. A differential thermal analysis (DTA) is performed by heating the sample and a reference to detect transitions, crystallization, melting and sublimation during heating procedure from the endotherm and exotherm dents and eaves on the DTA curves. Scanning electron microscopy which has practically been used only since 1965 is a very significant characterization instrument in material science. This instrument images surface of the sample by scanning it with a high-energy beam of electrons which interact with the surface atoms of the sample and signal the surface topography of it.

XRD resolves the crystallographic structure, chemical composition, and physical properties of materials. After the required measurement of the sample in powder form is made, the pattern obtained from the product is compared to the ICDD (International Center for Diffraction Data) cards. The first three peaks i.e. the ones having the highest intensities successively are expected to match in order to make sure that the product is in right form. The characteristic peaks of lithium tetraborate are at 14,664; 21,628 and 22,270 2theta values. The XRD measurements can be performed accordingly.

Manam [35] used Fourier Transform Infrared Spectroscopy (FTIR) in order to characterize lithium tetraborate activated by copper. For this measurement it is a common practice to mix 2-3 mg of the sample with 80mg of potassium bromide to obtain a sturdy sample since FTIR may exclude the signs from potassium bromide by taking it as the background. The so called spectrum was obtained in the 4000–400  $\text{cm}^{-1}$  interval. Figure 2.9 displays the FTIR recorded by Manam [35]. Moreover Vdovin has detailed studies on the vibrational spectrum of lithium tetraborate [52].

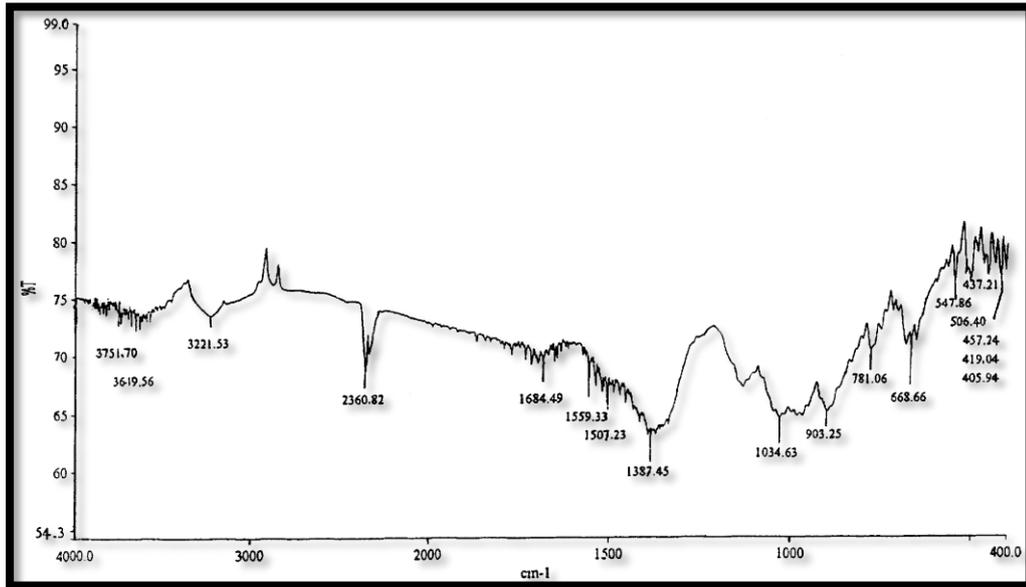


Figure 2.9 FTIR spectra of  $Li_2B_4O_7:Cu$  sample at room temperature [35]

The common bands seen in FTIR results of Lithium tetraborate can be listed as:

- 580 ( $cm^{-1}$ ) : Borate deformation, plane bending of boron oxygen triangles
- 900-865 ( $cm^{-1}$ ) : Stretching vibrations of tetrahedral  $BO_4^-$
- 1000 ( $cm^{-1}$ ) : Diborate Groups
- 1080 ( $cm^{-1}$ ) : Pentaborate
- 1246-1807 ( $cm^{-1}$ ) : Stretching vibration  $(BO_3)^{3-}$
- 1343-1248( $cm^{-1}$ ) : Stretching vibrations of B-O of trigonal  $(BO_3)^{3-}$  units

In the extensive study of Matthews [36] [37], DTA curves of lithium borates up to 1293°K are obtained and interpreted thoroughly. The results revealed that lithium tetraborate exhibited an endotherm at 1188° K which is attributed to the congruent melting of the material which accepts energy about 94.5 cal/gr. Sangeeta is another scientist who published a report on the solidification behavior of lithium tetraborate and hence required DTA measurements. According to the research of Sangeeta [45], lithium tetraborate shows a sharp melting peak at 915 °C Figure 2.10.

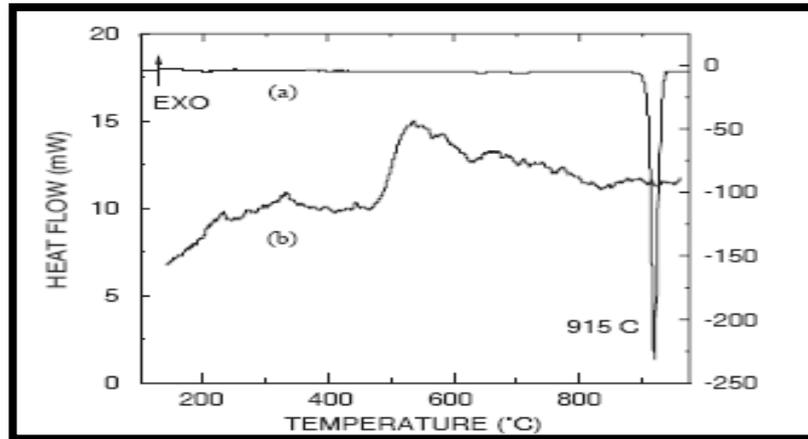


Figure 2.10 DTA Result for lithium tetraborate a) DTA curve b) TGA curve  
[45]

An essential auxiliary tool to evaluate the characterization results is the binary phase diagram since it displays the relative concentrations of two substances in a mixture against temperature. Figure 2.12 gives this diagram for  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  system. In this figure the regions represented by  $\text{L}^*2\text{B}$  are the regions that include lithium tetraborate.

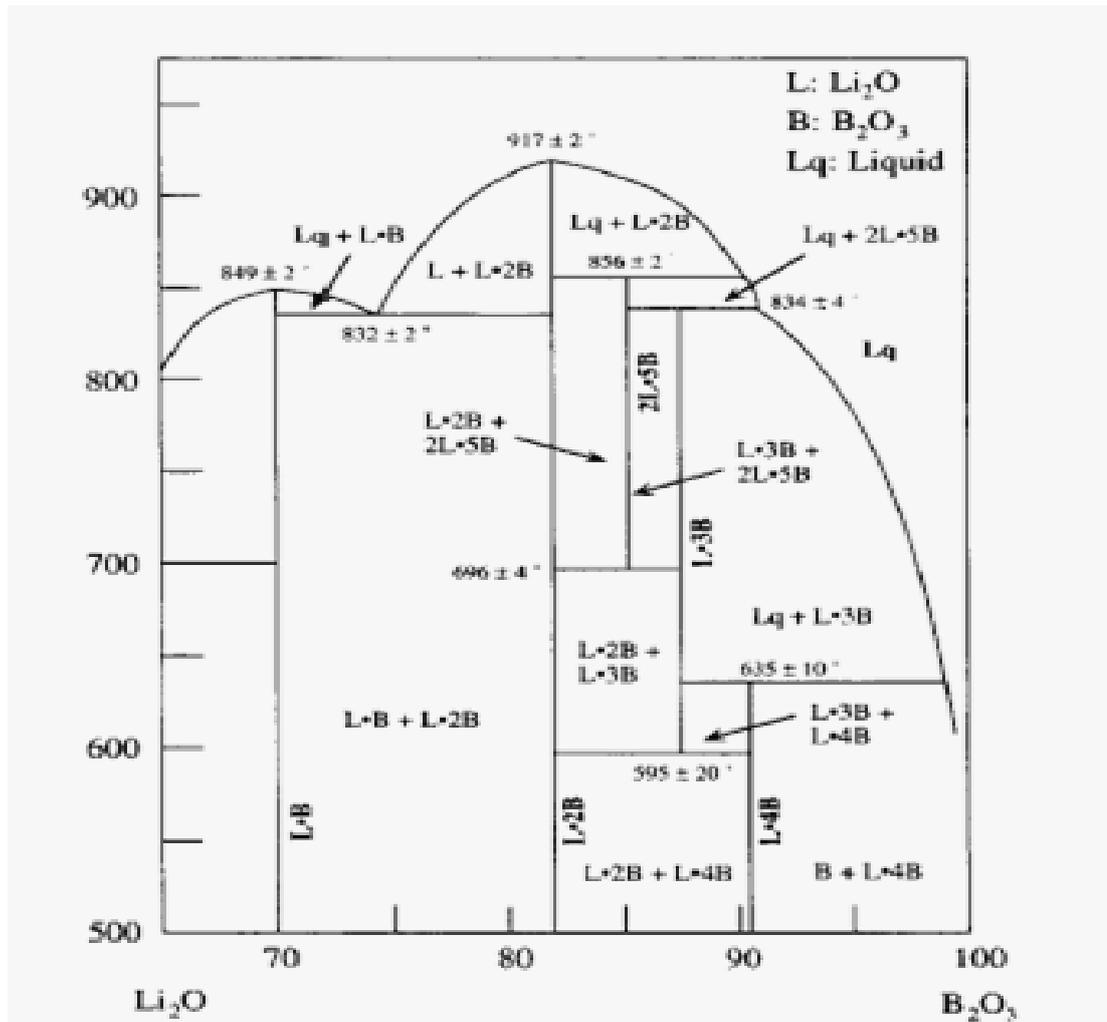


Figure 2.11 Phase Diagram of  $\text{Li}_2\text{O}$ - $\text{B}_2\text{O}_3$  system

Scanning electron microscopy which provides microphotographs of materials was used by Wall [54]. Wall has pictured lithium tetraborate doped with copper and with both copper and silver to image the morphology of the materials produced. (Figure 2.12)

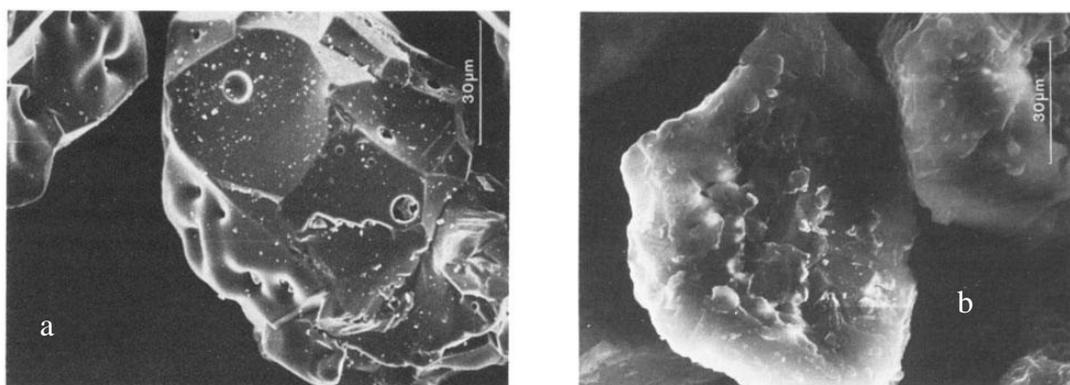


Figure 2.12 a) Lithium tetraborate:Cu, b) Lithium tetraborate:Cu, Ag  
[54]

On the whole, it is vital to perform the XRD analyses of the material produced. The other analyses techniques like IR, FTIR Spectrometry may be applied to have further information on the bonding structure and framework. Moreover, there are two basic thermal analyses namely DTA and TGA having been used in characterization of lithium tetraborate.

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Materials

There are a number of compounds used in the experiments. All of the materials used apart from distilled water were in powder form. The following list gives the names solid powders used in synthesis and doping of lithium tetraborate.

Material Used	Utilization Purpose
$\text{Li}_2\text{CO}_3$	Lithium tetraborate production
$\text{H}_3\text{BO}_3$	Lithium tetraborate production
$\text{CuCl}_2$	Doping
$\text{Cu}_2\text{O}$	Doping
$\text{AgNO}_3$	Doping
$\text{In}_2(\text{SO}_4)_3$	Doping

#### 3.2 Instrumentation

##### 3.2.1 Furnace

Solid-state reactions have been carried out in air by using Protherm furnace with heating ability up to 1300°C and the heating procedure control option.

##### 3.2.2 Powder X-Ray Diffractometer

The crystal structures of the lithium tetraborate were recorded by the powder X ray diffraction (XRD) measurements. The 2 theta range adopted for the XRD examinations were determined to be 5° and 80° with reference to the literature and

the 2 theta values for which this materials displays the characteristic peaks. The scan speed adopted was 1 degree /minute. The X ray Diffractometer employed for these investigations is a Rigaku MiniFlex X-ray Diffractometer with a radiation source of  $\text{CuK}\alpha$ .

The XRD patterns and d-values obtained for the produced material were compared to International Centre for Diffraction Data (ICDD) card numbered 18-0717.

### **3.2.3 Differential Thermal Analyzer**

Thermal characterization of the material was achieved by Setaram Simultaneous TG/DTA equipment. The temperature range adopted was between room temperature ( $25^{\circ}\text{C}$ ) and  $1100^{\circ}\text{C}$  since the melting temperature of pure lithium tetraborate is  $917^{\circ}\text{C}$ . The heating rate employed was  $10^{\circ}\text{C}/\text{min}$  and measurements were performed under normal atmosphere.

### **3.2.4 Fourier Transform Infrared Spectrometer**

The vibrational modes of the materials produced were studied by VARIAN 1000 FTIR spectrometer between wave numbers 400 to  $4000\text{cm}^{-1}$ . The pellets were prepared with a sample to KBr ratio of 100mg: 2mg

### **3.2.5 Scanning Electron Microscope**

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

### **3.2.6 Thermoluminescence Reader**

The dosimetric properties of the samples were determined by using Harshaw TLD Reader Model 3500. The heating rate was chosen as the lowest possible for the measurements to be most reliable. As a result, the heating rate of  $1^{\circ}\text{C}/\text{sec}$  was adopted from  $50^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ . The examined dosimeters were exposed to Beta,  $^{90}\text{Sr}$ - $^{90}\text{Y}$  radiations at room temperature for 5 minutes while the radiation given was

0.5Gy/min. The sample amount was 10 mg which is within the reliable range determined by Wall [54].

### **3.3 Experimental Procedure**

#### **3.3.1 Synthesis and Doping of Lithium Tetraborate**

The major aim of the study was to determine the most practical method to produce and dope powder lithium tetraborate that can be used for dosimetric purposes. Therefore, three convenient techniques were applied to reach the best product.

Firstly, the high temperature solid state production and doping technique was employed. Then, lithium tetraborate was produced by solution assisted synthesis and doping was also performed with in assistance of water. Finally, lithium tetraborate was synthesized by high temperature solid state synthesis and doped by solution assisted method.

For the production of lithium tetraborate, in both cases namely, solid state and solution assisted techniques, the amounts of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ) in powder form were mixed in stoichiometric amounts weighing 0.4369g and 1.4622 g respectively for 1 g of product. The powder mixture was homogenized thoroughly in the agate mortar before passing to the next stage of production. The further steps of the procedure differ depending on the production method.

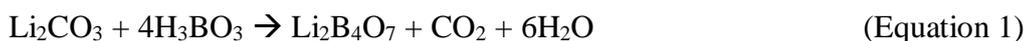
#### **3.3.2 Production Of Lithium Tetraborate By High Temperature Solid State Synthesis**

The afore given quantities (per 1 gram of product) of  $\text{Li}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$ , after mixing homogenously were put into furnace in porcelain crucible and heated up to  $400^\circ\text{C}$  from room temperature with a heating rate of  $400^\circ\text{C/hr}$  . Retention time at this temperature was selected as three hours to remove volatiles like  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from the system. After this preliminary heating stage, the sample in crucible was

transferred to the agate mortar for re-blending and pounding the dry sample back to powder form. This regrinding stage was adopted to enhance the diffusion potential of atoms. Afterwards, the furnace was adjusted to heat the sample up to 750 °C and keep it at this temperature for 2 hours. An additional regrinding stage was added at this step to improve the diffusion ability of atoms. Finally, the mixture was re-heated at the same temperature for another 2 hours to reach the best quality lithium tetraborate with minimum energy consumption.

Upon the completion of the heating cycle and cooling followed, the sample was grinded and stored in desiccators. The equation given below was the expected reaction from the stoichiometric amounts of the reactants.

The expected reaction is given below.



### **3.3.3 Production of Lithium Tetraborate by Water/Solution Assisted Synthesis Method**

For water/solution assisted synthesis 0.4369g of  $\text{Li}_2\text{CO}_3$  and 1.4622g of  $\text{H}_3\text{BO}_3$  were mixed, and put in a beaker into which 15 ml of water was added for production of 1g of lithium tetraborate. The solid liquid mixture was stirred in a heating magnetic stirrer until the constituents were dispersed sufficiently. The heating action provided by the stirrer evaporates the water to a certain level in 15-20 minutes included without disrupting dispersion action. This mixing step was followed by heating in the furnace. The mixture containing residual water was exposed to 150 °C for 3 hours in order to guarantee total evaporation of water. An intermittent grinding and mixing was not required in water/solution assisted production since the constituents were dispersed to a reliable level by the stirrer. Therefore the drying heating was directly followed by the increase of the temperature from 150°C to 750° C. The reaction given in Equation 1 is valid also for this case.

### 3.3.4 Doping Procedure

As mentioned before, two main doping techniques were followed namely, the solid state doping and doping by solution assisted method. These two methods were applied in three variations that resulted in three types of products as i) solid state produced lithium tetraborate doped by high temperature solid state method, ii) solid state produced doped via solution assisted technique and iii) lithium tetraborate generated via water/solution assisted method and doped the same way. Initially the same doping amount was adopted for all cases to determine the best production combination, Hence, copper which is proved to be a very effective activator for lithium tetraborate was added to the lithium tetraborates produced by two different techniques via two different doping procedures. Then after, chosen a specific procedure was based on the results from thermoluminescence measurements.

### 3.3.5 High Temperature Solid State Doping

Solid state doping was solely applied to the lithium tetraborate obtained from the solid state production. The copper was doped in  $\text{Cu}_2\text{O}$  form in the weight ratio given in the Table 3.1

Table 3.1 Copper Doping Scheme

$\text{Li}_2\text{B}_4\text{O}_7$ Weight	Cu % of $\text{Li}_2\text{B}_4\text{O}_7$	$\text{Cu}_2\text{O}$ (g)	$\text{CuCl}_2$ (g)
1	0.1	0.0023	0,0021
1	0.2	0.0045	0,0042
1	0.3	0.0068	0,0063
1	0.4	0.0090	0,0085
1	0.5	0.0113	0,0106
1	0.6	0.0135	0,0127
1	0.7	0.0158	0,0148
1	0.8	0.0180	0,0169
1	0.9	0.0203	0,0190
1	1	0.0225	0,0212

The lithium tetraborate copper mixture was homogenized in an agate mortar. The level of homogenization could directly be detected by the color of the solid mixture. Blending should be continued until no red spot can be detected and the powder color is totally pale pink.

The next step was heating the sample from the room temperature to 750°C by 400°C/hr. The material is kept at this temperature for 3 hours. No initial heating was required since the sample produced did not have tendency to be affected by humidity. And finally the sample was cooled, grinded and stored in desiccators being ready for TL measurements and analysis.

### **3.3.6 Solution Assisted Doping**

Solution assisted doping was applied to both lithium tetraborates produced by high temperature solid state synthesis or solution assisted synthesis. However in both cases the same procedure was followed.

Initially, 1 gram of lithium tetraborate was stirred with 15 ml of water in presence of copper in the ratios given in Table 3.1. However, for this procedure  $\text{CuCl}_2$  was used since it is a water soluble copper compound. After the sample had been completely dispersed and the dopant material was homogenously mixed with the host material the heating stage was started. The sample was allowed to evaporate its water at 150°C for three hours. The reaction temperature was chosen as 700°C for the dopant to perforate into the vacancies of structure of lithium tetraborate. The retention time for the secondary heating stage was 2 hours.

The lithium tetraborate produced by high temperature solid state synthesis was doped by this method with different concentrations of Ag and In addition to Cu to observe the effect of co-activator. Although the proportions of Cu used were 0.1 and 0.3% of lithium tetraborate when accompanied by a co-activator. The ratio for Ag and In was as low as 0.01%-0.05% for varying amounts of Cu. This was because the coactivators were added about one tenth of the main activator to the host material

and to preserve the effective atomic number at its ideal value. Table 3.2 gives the details for the doping concentrations for the solid state produced solution assisted doped lithium tetraborate. The compounds used for coactivator doping were  $\text{Ag}(\text{NO})_3$  and  $\text{In}_2(\text{SO}_4)_3$  since they were available and cheap compared to other sources of these elements. Major solutions for all three dopants are prepared since the quantities of dopants were quite difficult to weigh. And, required amounts of dopants are taken from this main source as solution. These solutions were so arranged that the percentage of the dopants correspond to an appropriate volume of the solution. For instance in order to dope 1g of lithium tetraborate with 0.1% Cu 1ml of  $\text{CuCl}_2$  solution would be sufficient. Likely if one is to dope 0.04% Ag it suffices to take 4ml of  $\text{AgNO}_3$  solution. According to the calculations made, 0.1164 g  $\text{CuCl}_2$  was dissolved in 55ml water, 0.0135 g  $\text{In}_2(\text{SO}_4)_3$  was dissolved in 30ml water. Since the case is rather severe in case of  $\text{AgNO}_3$ , its solution is diluted to  $1/10^{\text{th}}$  from the concentrated solution of 0.0944 g of  $\text{AgNO}_3$  in 60ml water.

Moreover, triple dopant experiments were performed Cu being the chief activator and Ag and In being co-activators. For such experiments the Cu concentrations experimented were 0.1 and 0.3 % of lithium tetraborate. Two major percentages of Ag were adopted with varying In concentrations. Table 3.3 displays the related values.

Table 3.2 Double Dopant Concentration Chart

Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> Weight	Cu % of Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	CuCl <sub>2</sub> (g)	Ag % of Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	AgNO <sub>3</sub> (g)	In % of Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (g)
1	0.1	0,0021	0.01	0.000157		
1	0.1	0,0021	0.02	0.000314		
1	0.1	0,0021	0.03	0.000472		
1	0.1	0,0021	0.04	0.000626		
1	0.1	0,0021	0.05	0.000780		
1	0.3	0,0063	0.01	0.000157		
1	0.3	0,0063	0.02	0.000314		
1	0.3	0,0063	0.03	0.000472		
1	0.3	0,0063	0.04	0.000626		
1	0.3	0,0063	0.05	0.00078		
1	0.1	0,0021			0.01	0.000451
1	0.1	0,0021			0.02	0.000902
1	0.1	0,0021			0.03	0.001353
1	0.1	0,0021			0.04	0.001804
1	0.1	0,0021			0.05	0.002255
1	0.3	0,0063			0.01	0.000451
1	0.3	0,0063			0.02	0.000902
1	0.3	0,0063			0.03	0.001353
1	0.3	0,0063			0.04	0.001804
1	0.3	0,0063			0.05	0.002255

### 3.3.7 Experiments on Doping Temperatures and Heat Exposure Times

Upon the promising results from the first TL measurements a series of temperature and retention time experiments were performed on two samples produced by high temperature solid state synthesis and doped by solution assisted procedure. The first of these samples contained 0.1 % copper and 0.04% Ag and the second one included 0.5% Ag with 0.1% Cu. Initially, both of these samples were heated at 750°C for 4 and 6 hours. Then the better of the two was subjected to the same temperature for 8 and 10 hours. The different doping temperatures experimented were 800 °C, 850 °C and 900°C applied for 4 hours Hence the comparison of different doping temperatures as well as exposure times for the product of 700 °C could be made in order to reach the best production procedure.

Table 3.3 Triple Dopant Concentration Chart

Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> Weight	Cu % of Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	CuCl <sub>2</sub> (g)	Cu <sub>2</sub> O (g)	Ag % of Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	AgNO <sub>3</sub> (g)	In % of Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (g)
1	0.1	0,0021	0.0023	0.04	0.000629	0.01	0.000451
1	0.1	0,0021	0.0023	0.04	0.000629	0.03	0.001353
1	0.1	0,0021	0.0023	0.04	0.000629	0.05	0.002255
1	0.1	0,0063	0.0023	0.05	0.000787	0.01	0.000451
1	0.1	0,0063	0.0023	0.05	0.000787	0.03	0.001353
1	0.1	0,0063	0.0023	0.05	0.000787	0.05	0.002255
1	0.3	0,0021	0.0068	0.04	0.000629	0.01	0.000451
1	0.3	0,0021	0.0068	0.04	0.000629	0.03	0.001353
1	0.3	0,0021	0.0068	0.04	0.000629	0.05	0.002255
1	0.3	0,0063	0.0068	0.05	0.000787	0.01	0.000451
1	0.3	0,0063	0.0068	0.05	0.000787	0.03	0.001353
1	0.3	0,0063	0.0068	0.05	0.000787	0.05	0.002255

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Characterization and TL Measurement

Lithium tetraborate produced was characterized for the control of the crystal structure after production and after doping. The samples obtained from different methods were exposed to radiation for determination of TL responses. After determination of the best quality material, 5 samples were analyzed further to distinguish the effect of dopants.

The techniques utilized to characterize the product were: Powder X-Ray Diffraction, Fourier Transform Infrared Spectrometry, Differential Thermal Analysis, Scanning Electron Microscopy, and Thermoluminescence studies were used for the characterization of compounds.

##### 4.1.1 Powder X-Ray Diffraction

Powder X-ray diffraction was the major characterization method employed in order to detect whether the matrix material is in the correct form and to notice if the dopant metals added caused any change in the crystal structure of the material produced.

Figure 4.1 demonstrates the XRD pattern for the ICDD card coded 18-0717 which gives the XRD peaks for lithium tetraborate

As seen in Figure 4.2, the XRD pattern obtained for lithium tetraborate synthesized by high temperature solid state synthesis are almost in complete compliance with that

of ICDD card 18-0717 of lithium tetraborate. Figure 4.3 belongs to the lithium tetraborate samples produced by water/solution assisted synthesis. In these XRD patterns it is quite easy to detect characteristic lithium tetraborate peaks.

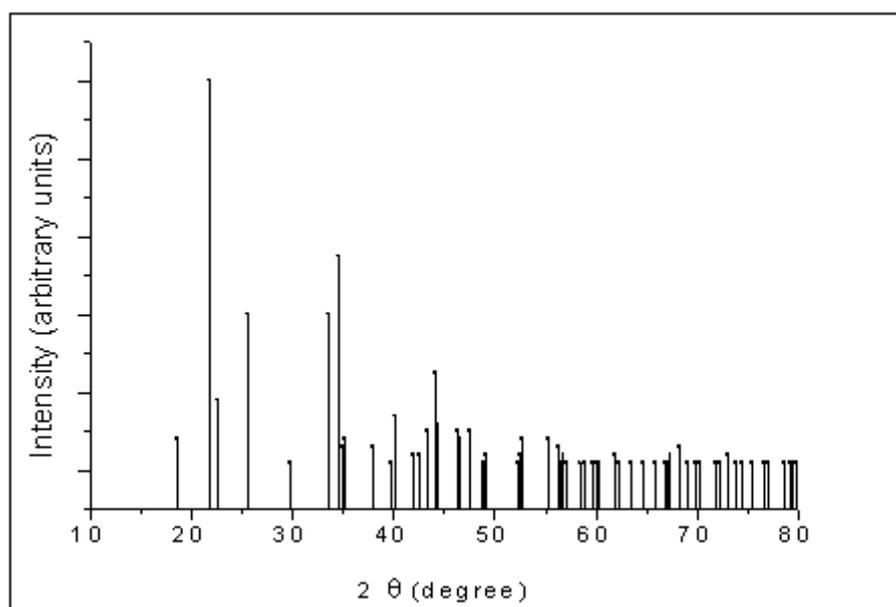


Figure 4.1 XRD Pattern of Lithium Tetraborate  
(ICDD-18-0717)

Upon ensuring the correct matrix formation, the interference of doping material was searched. Following three figures (Figure 4.4, 4.5, 4.6) belong to the doped lithium tetraborate powders.

To provide ease in comparison, the bold bottommost plot will represent undoped sample. Figure 4.4 displays the undoped lithium tetraborate synthesized by high temperature solid state synthesis at the bottom and solid state synthesized and solid state doped samples along to the top. Figure 4.5 refers to solid state synthesized solution assisted doped samples while Figure 4.6 illustrates the XRD plots for water/solution assisted produced and doped materials.

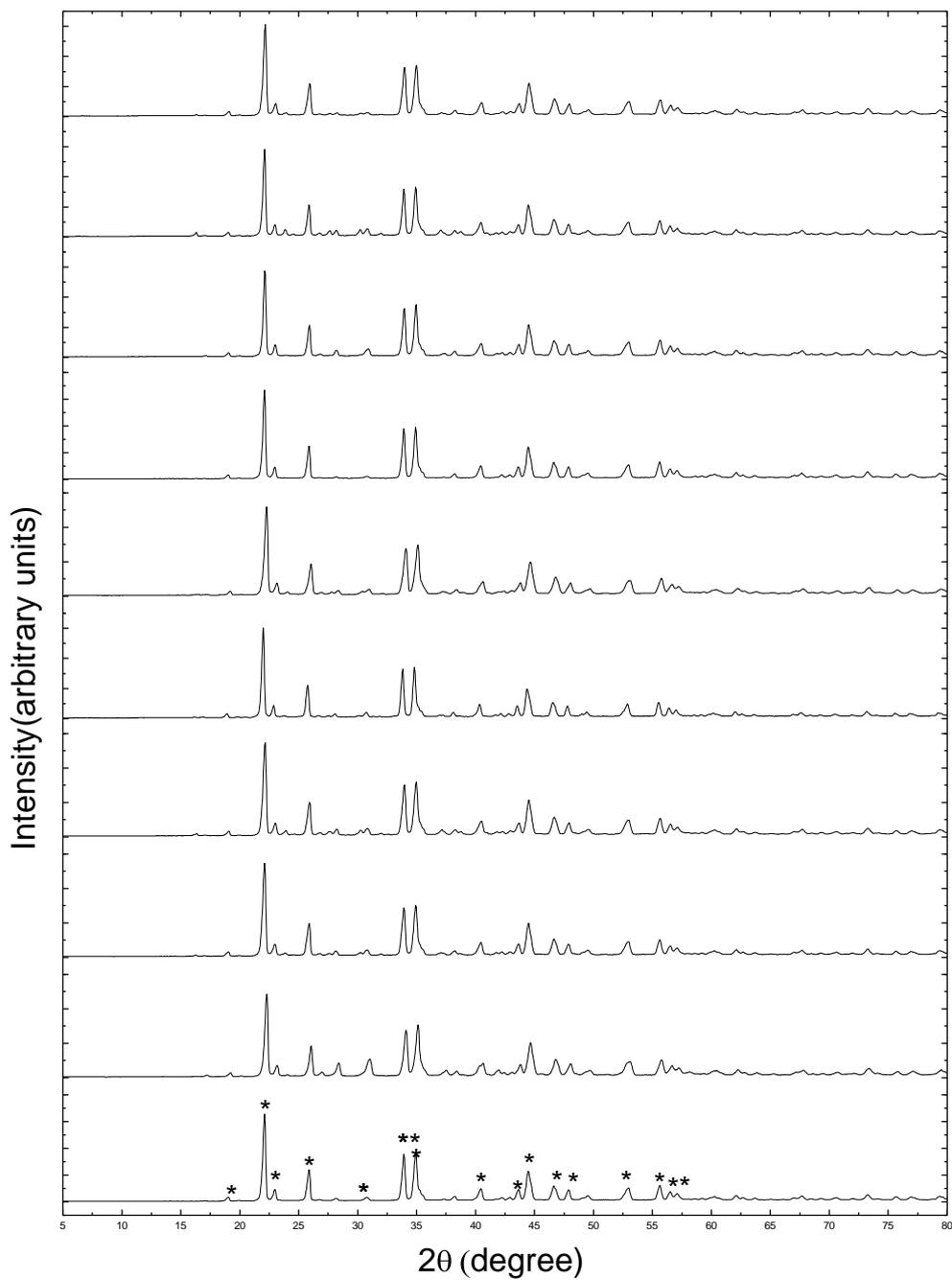


Figure 4.2 XRD Pattern diagram for lithium tetraborate samples produced by high temperature solid state synthesis

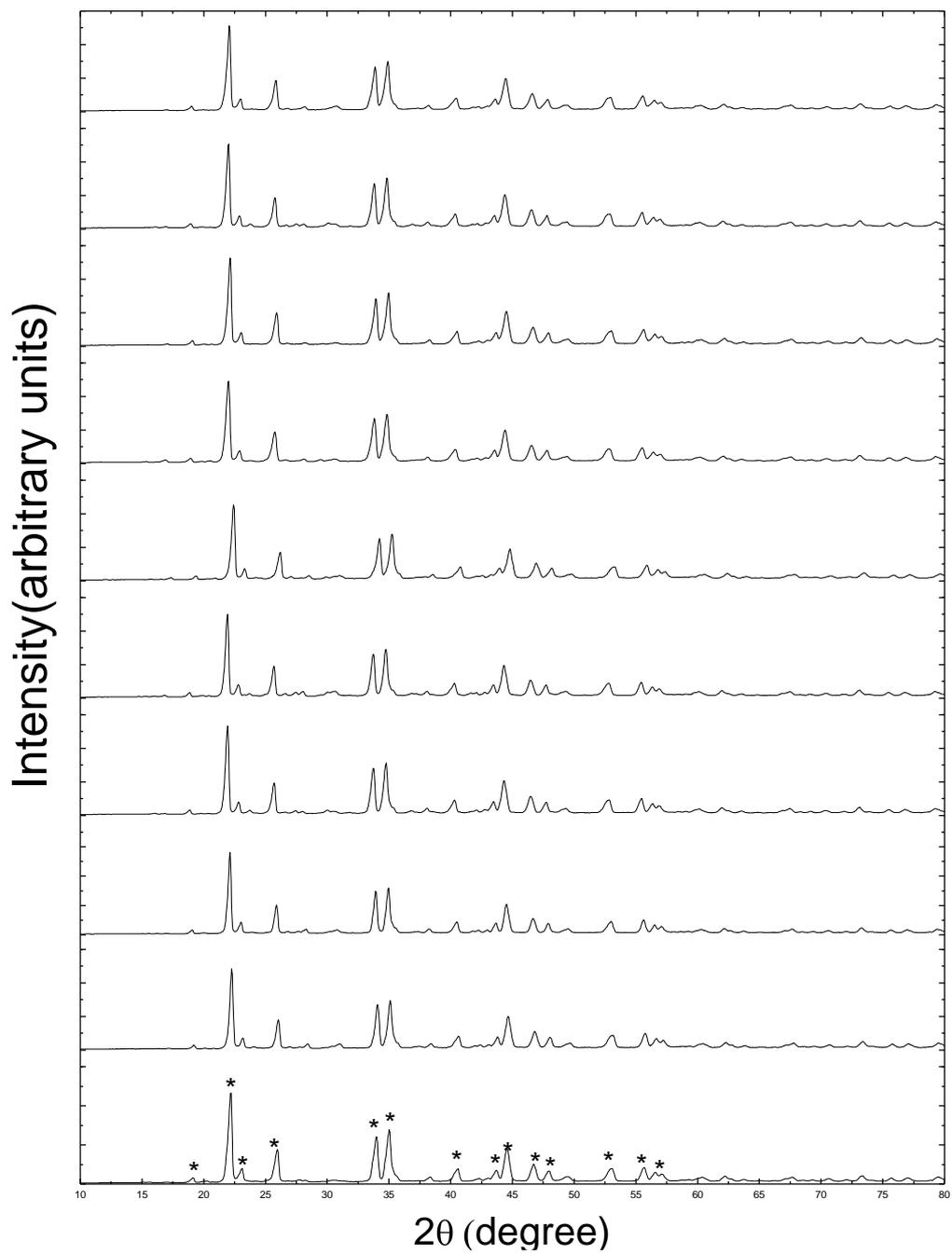


Figure 4.3 XRD Pattern diagram for 10 lithium tetraborate samples produced by water/solution assisted synthesis

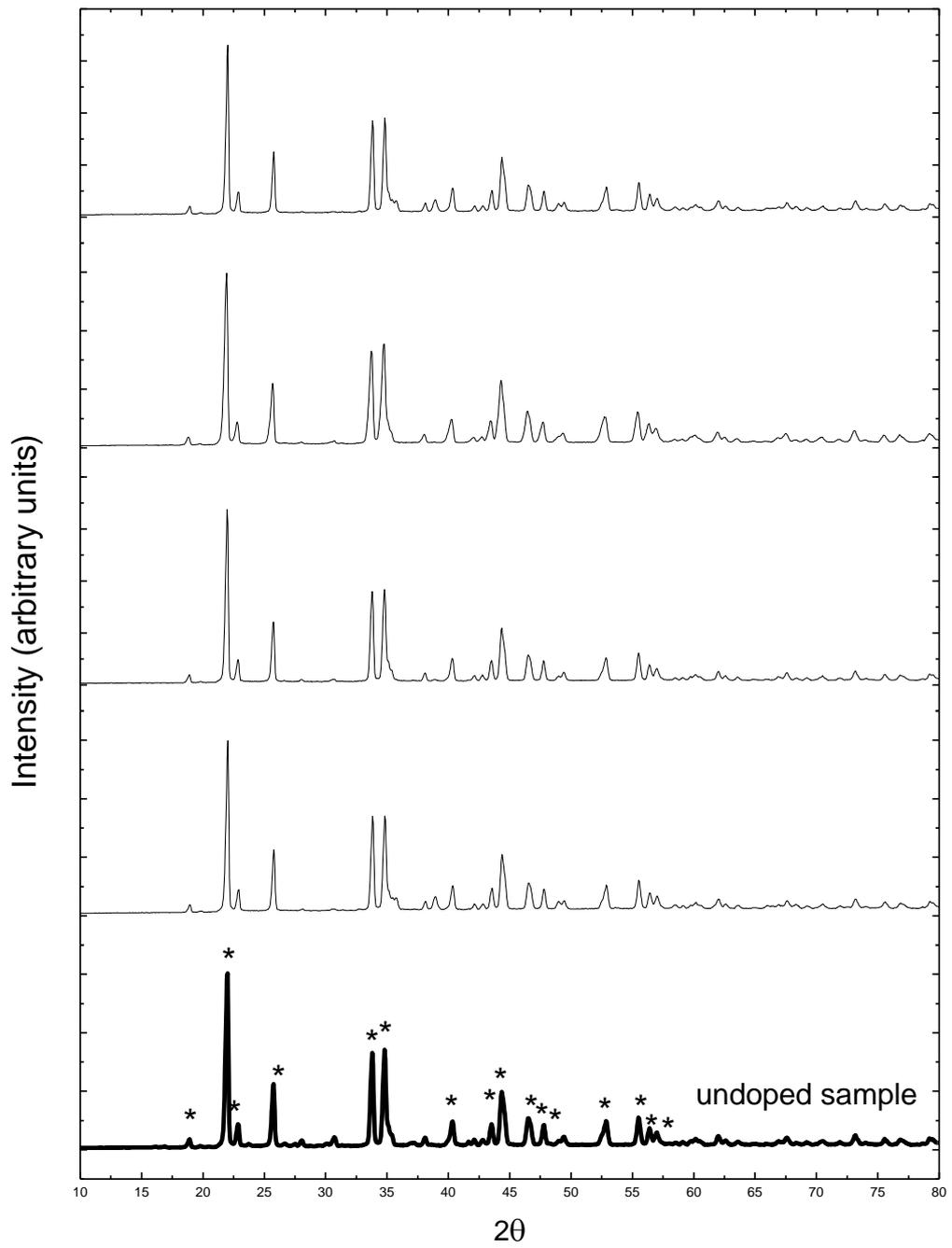


Figure 4.4 XRD Pattern of solid state synthesized solid state doped samples

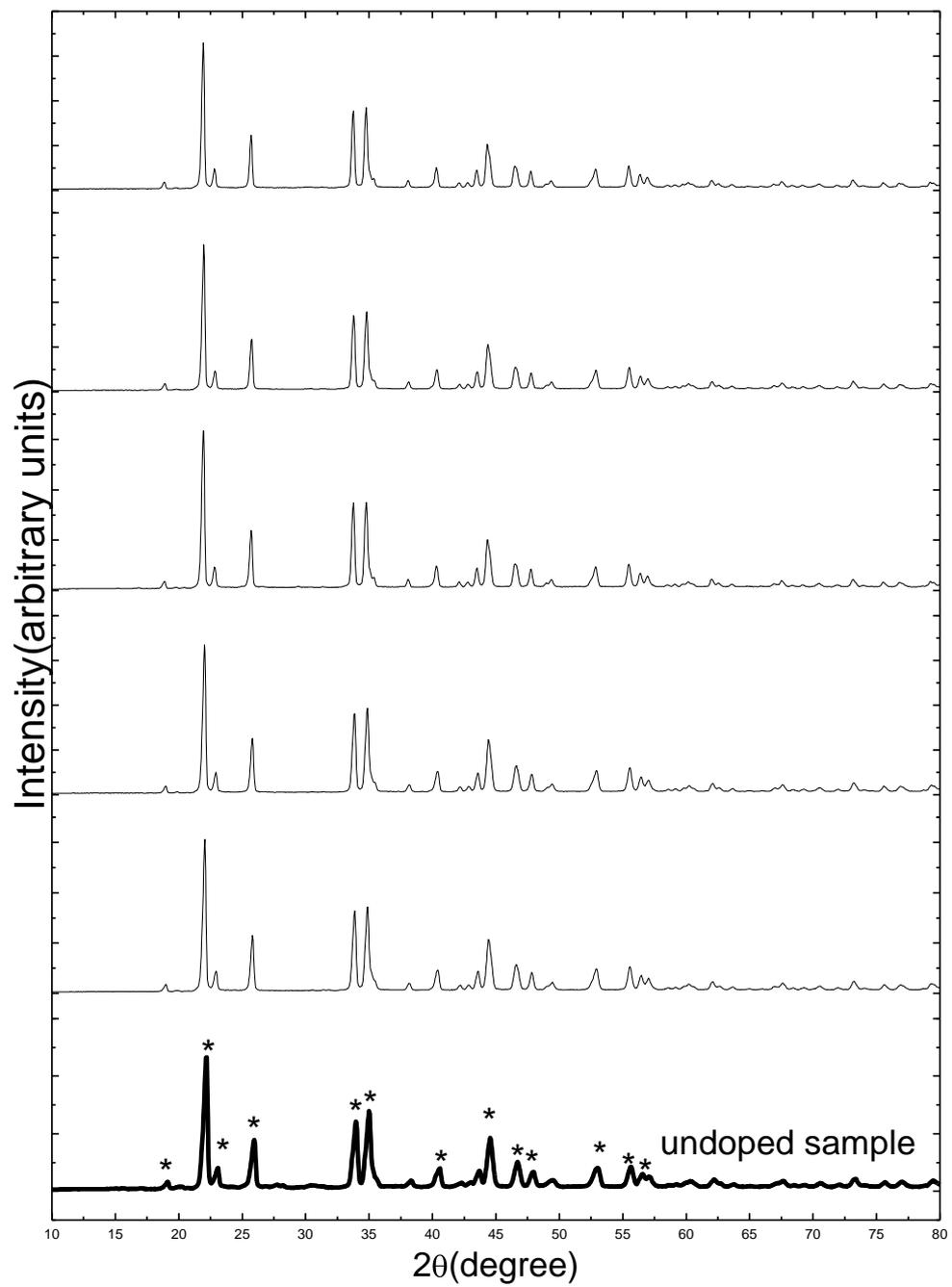


Figure 4.5 XRD Pattern of water/solution assisted synthesized solution assisted doped samples

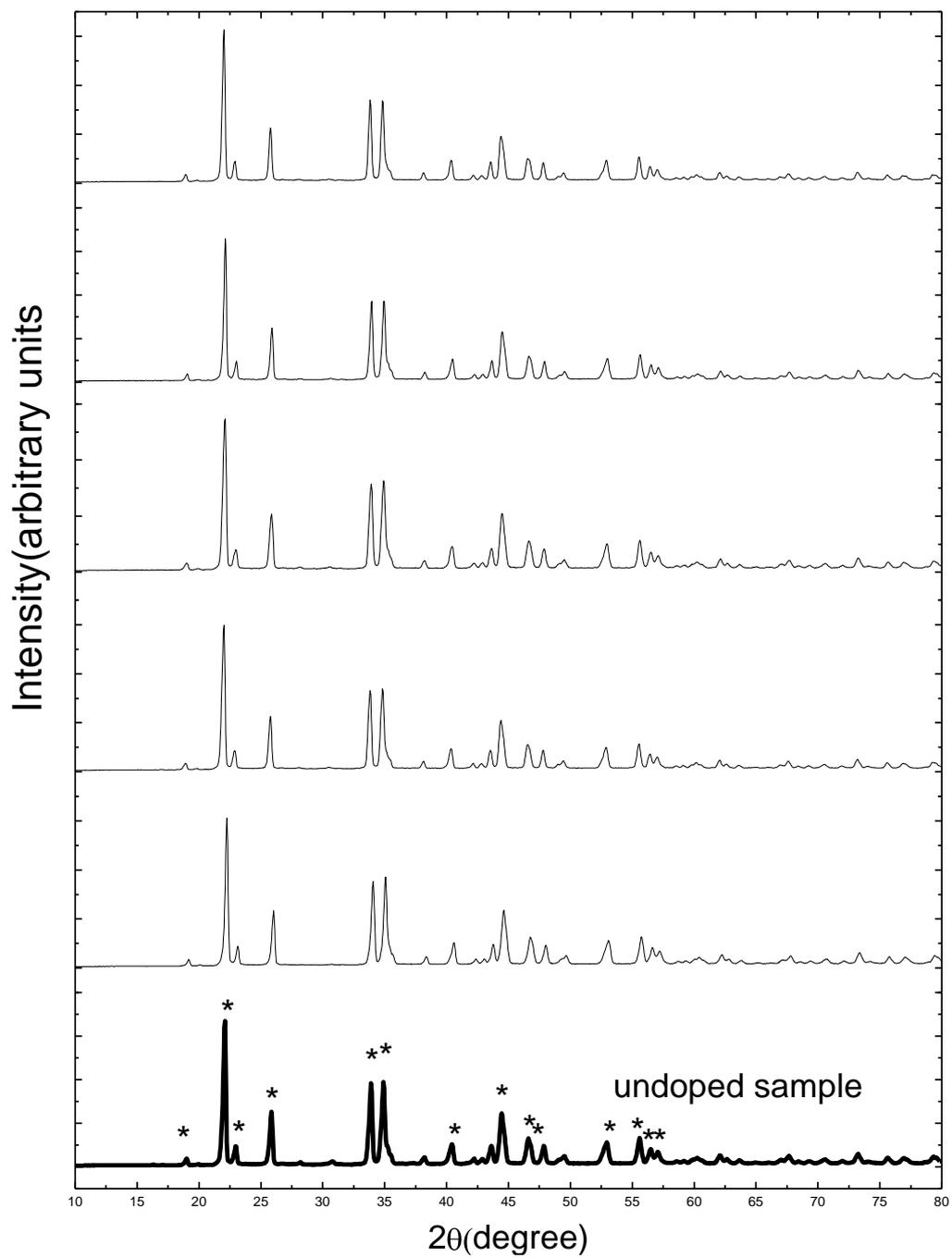


Figure 4.6 XRD Pattern of high temperature synthesized solution assisted doped samples

### 4.1.2 Fourier Transform Infrared Spectrometry

Fourier transform infrared spectrometry (FTIR) is employed as an auxiliary characterization alternative. Figure 4.7 displays the spectral resemblance between lithium tetraborates produced by solution assisted method and high temperature synthesis. It is a characteristic of lithium tetraborate that a concentration of absorption bands is observed between  $1400\text{-}900\text{cm}^{-1}$  [35] since they are indicators of presence of borate anions. Moreover, the peak distribution obtained is in compliance with the source in literature confirming the formation of lithium tetraborates. Although there are slight differences between the curves obtained for solution assisted produced product and that synthesized by high temperature method the overall appearance signs existence of borate units. Besides, Figure 4.8 is devoted to the investigation of effect of doping on vibrational modes of lithium tetraborate. The bottom most plot belongs to the undoped sample while the others include copper, silver and indium in either solely or double and triple combination.

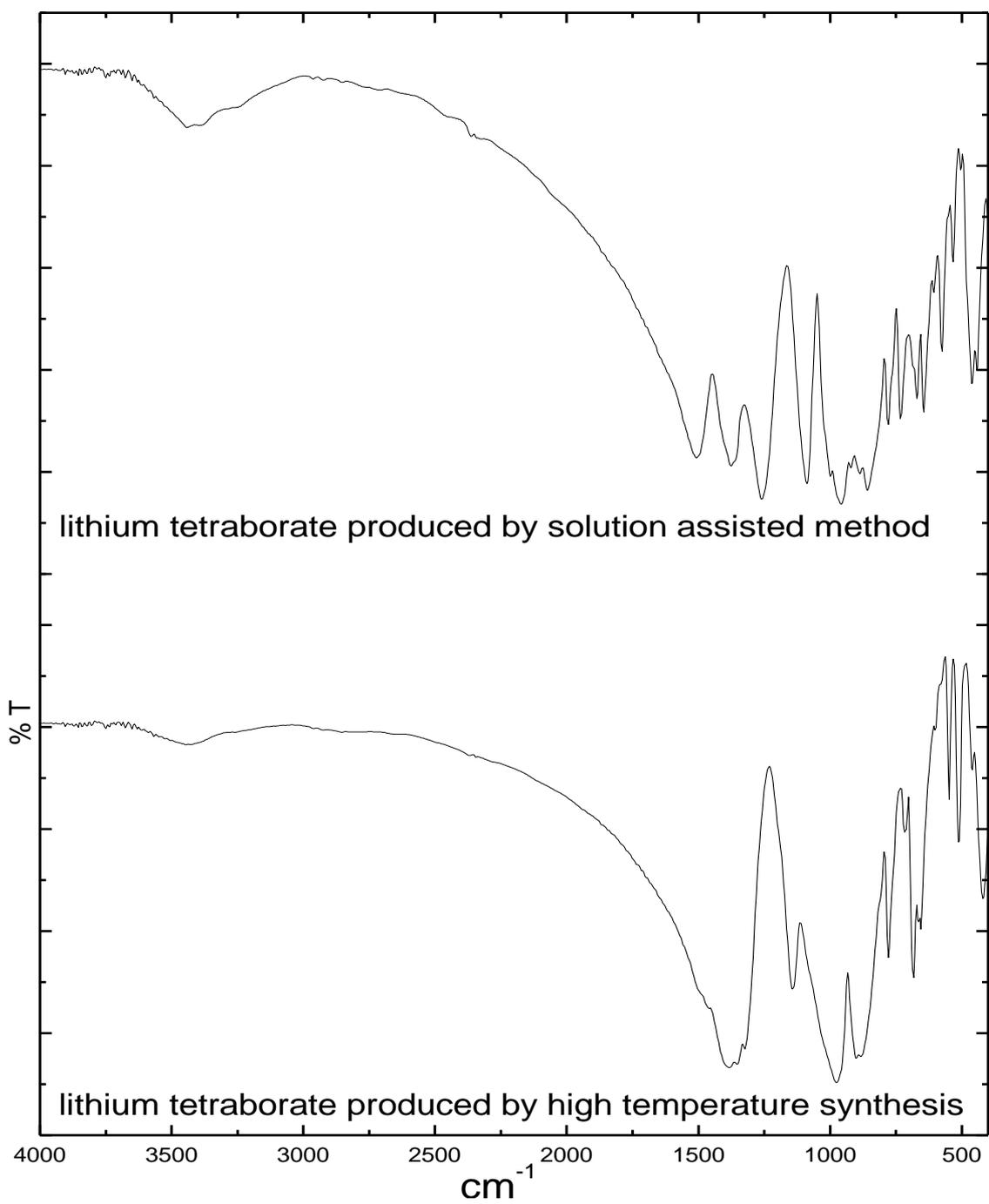


Figure 4.7 FT-IR result comparison for lithium tetraborate doped by two different methods

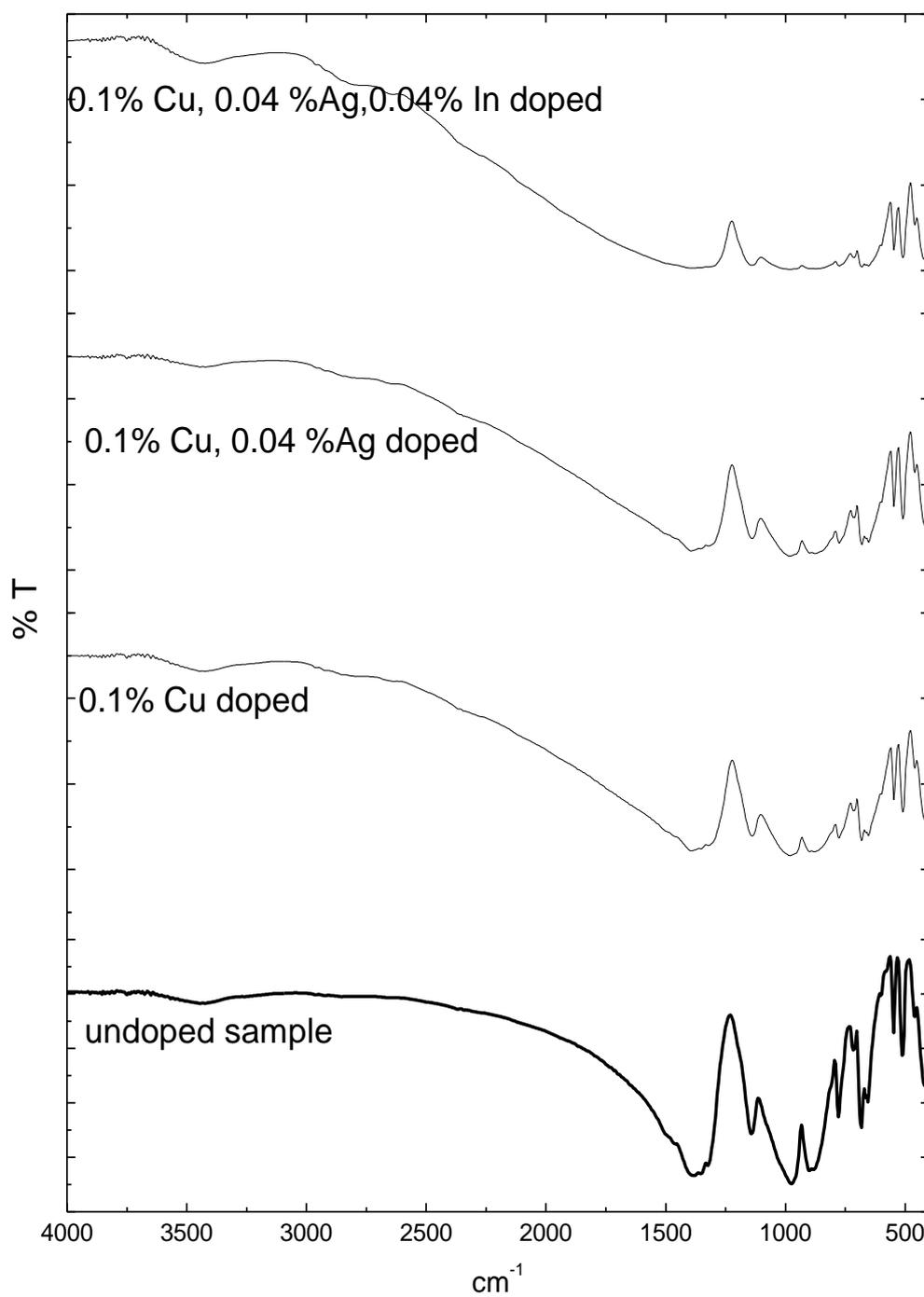


Figure 4.8 FT-IR result for doped and undoped lithium tetraborates

### 4.1.3 Differential Thermal Analyses

The results of the DTA showed that lithium tetraborate produced included impurities since the melting point is observed to decrease to 828-865°C although this value is around 917 °C for pure lithium tetraborate. When referred to the phase diagram (Figure 2.11), it can be seen that these two products lie on different sides of the eutectic point 832°C. Figure 4.9 and 4.10 are devoted to undoped solid state and water/solution assisted produced lithium tetraborate. In these figures it is noticed that although there is a slight difference between the melting points of the materials synthesized by high temperature solid state synthesis and water assisted method the DTA curves are quite similar. Figures 4.11, 4.12, 4.13 show the DTA records for the samples synthesized by solid state method and doped by solution assisted doping. The effect of doping can be observed as secondary peaks at lower temperatures and lowered melting points..

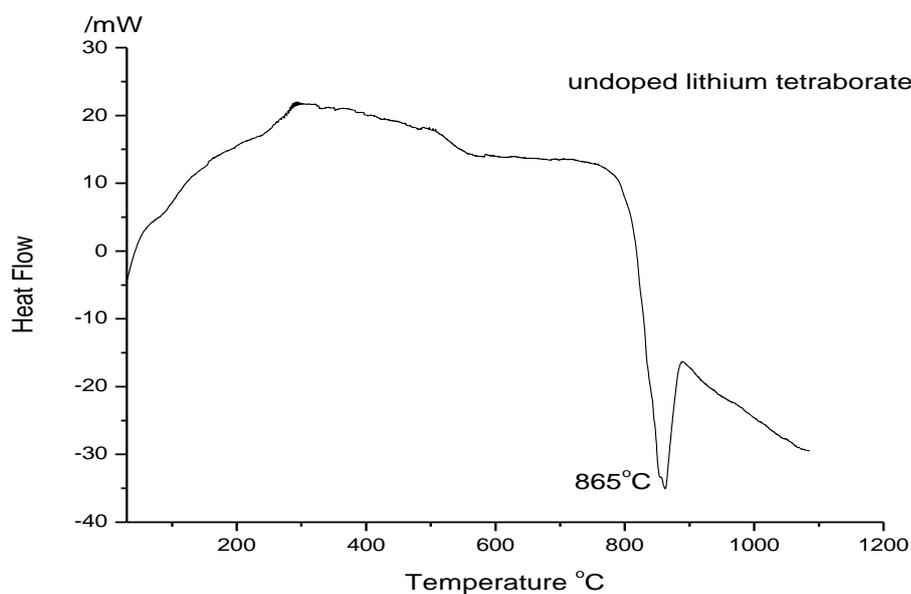


Figure 4.9 DTA result for lithium tetraborate produced by solid state synthesis

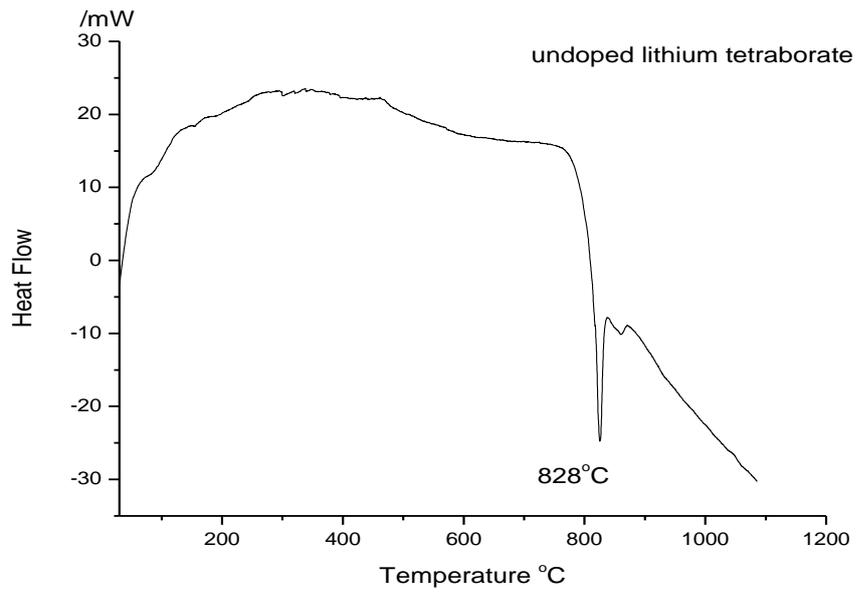


Figure 4.10 DTA result for lithium tetraborate produced by water/solution assisted synthesis

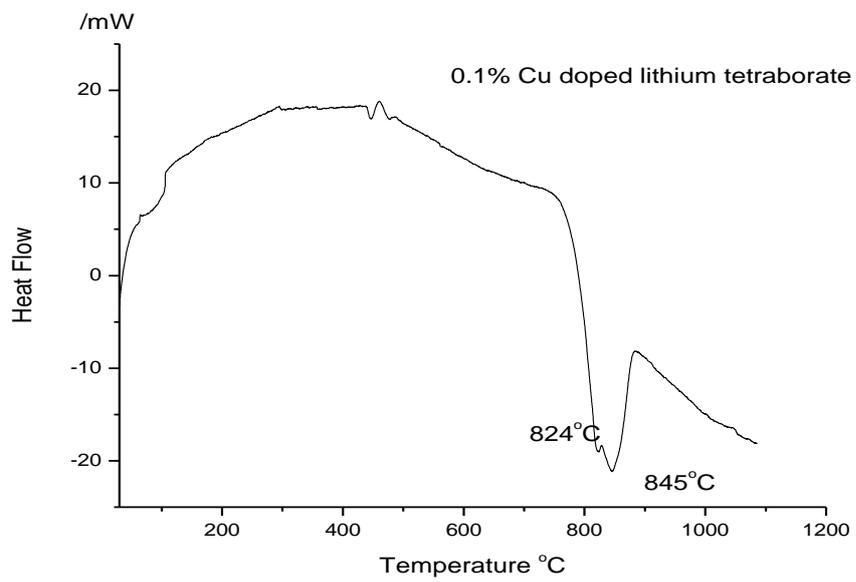


Figure 4.11 DTA result for lithium tetraborate doped with 0.1% Cu by solution assisted doping

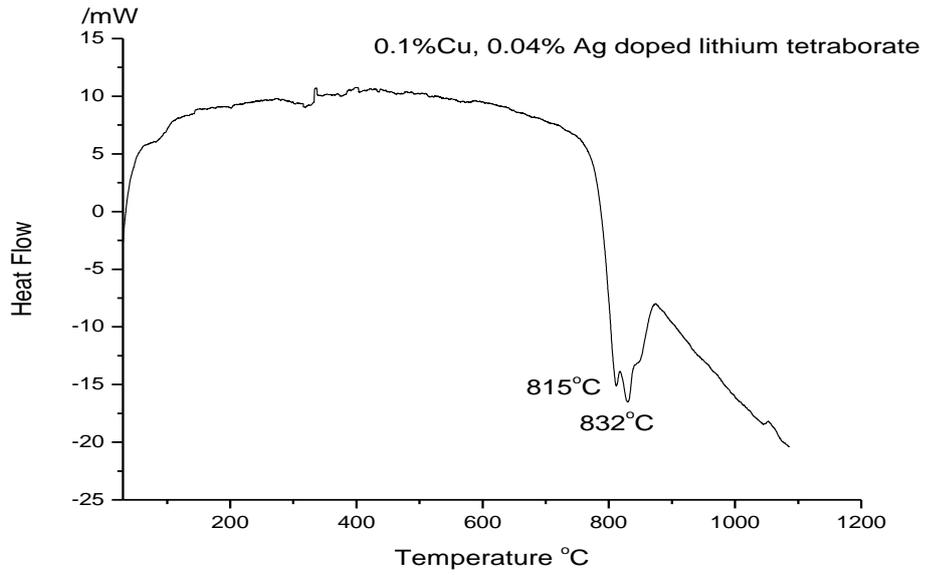


Figure 4.12 DTA result for lithium tetraborate doped with 0.1% Cu, 0.04% Ag

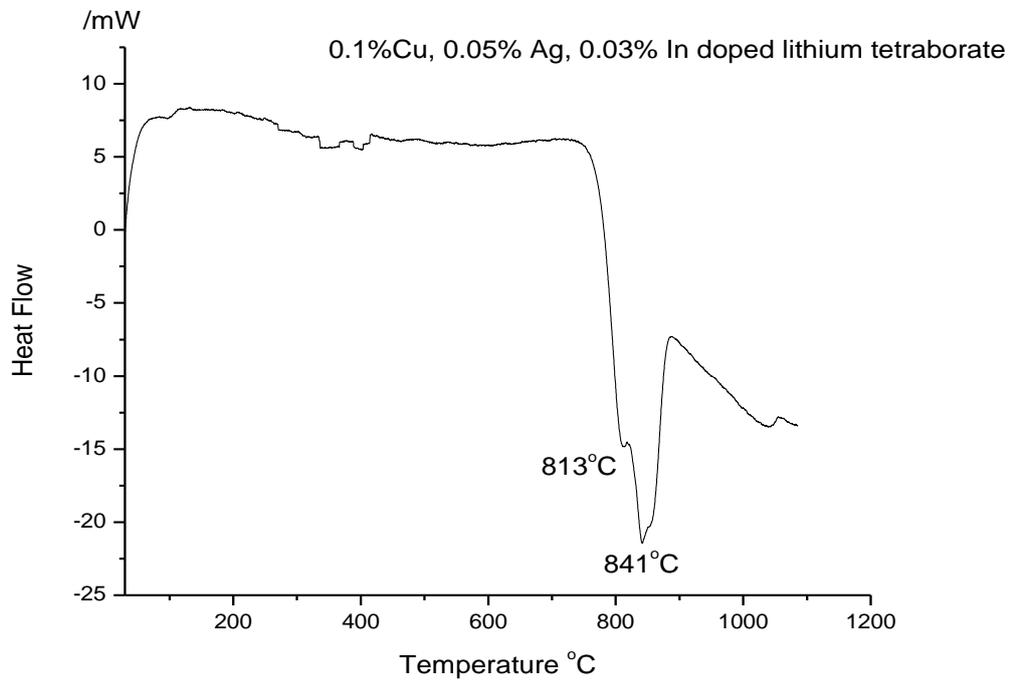


Figure 4.13 DTA result for lithium tetraborate doped with 0.1% Cu, 0.05% Ag, and 0.03 In

#### 4.1.4 Scanning Electron Microscopy

The images obtained from the scanning electron microscope displayed another attention taking difference between the lithium tetraborates synthesized by two different methods. Figures 4.14, 4.15 illustrate the morphologies of lithium tetraborate produced by water/solution synthesis and doped by solution assisted technique with two different magnification and perspective. On the other hand figures 4.16 and 4.17 belong to the material produced by high temperature solid state method doped by solution assisted method.

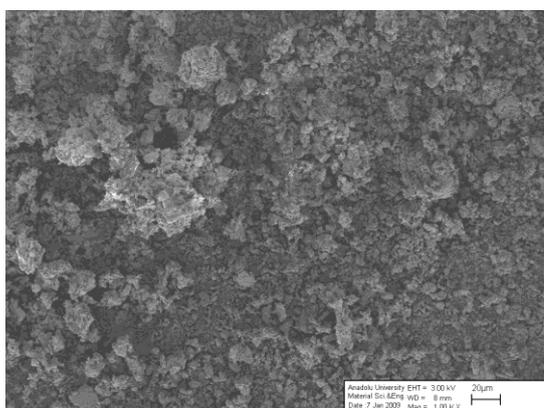


Figure 4.14 Lithium tetraborate produced by water/solution assisted method- magnification=1.00 K X

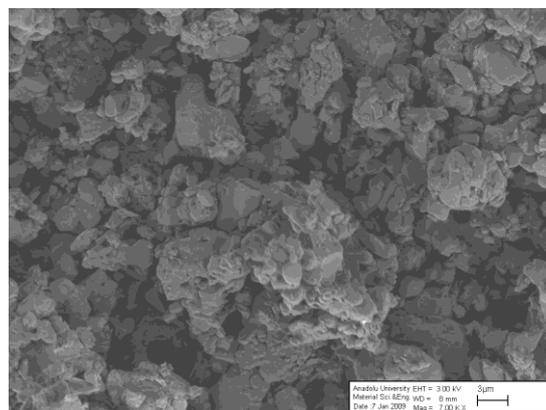


Figure 4.15 Lithium tetraborate produced by water/solution assisted method- magnification=7.00 K X

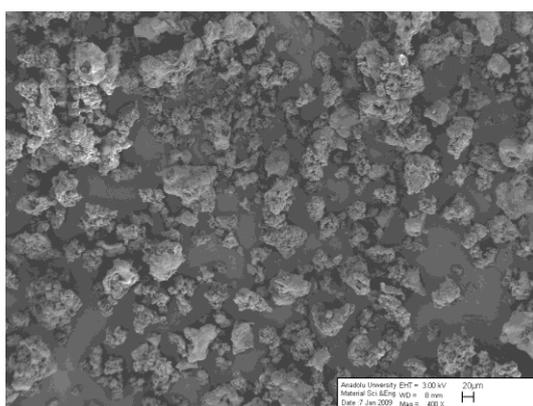


Figure 4.16 Lithium tetraborate produced by high temperature solid state method-magnification=1.00 K X

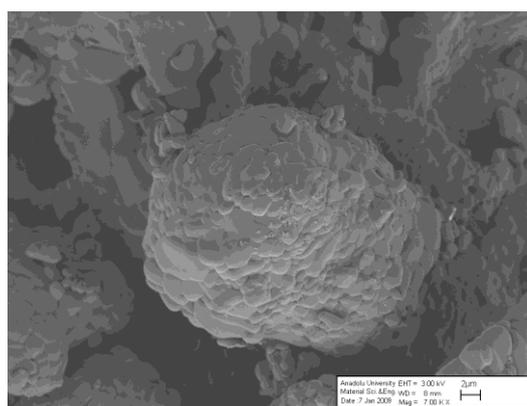


Figure 4.17 Lithium tetraborate produced by high temperature solid state method-magnification=7.00 K X

The comparison of the Figures 4.14 and 4.16 show that the product of water/solution assisted synthesis display sticky characteristics and the morphology of the particles can be analyzed better due to the higher magnification of the microscope. Figure 4.15 shows an undulating particle surface while the image in Figure 4.17 shows a smoother surface.

#### **4.1.5 Thermoluminescence**

As mentioned previously, lithium tetraborate finds extensive use in thermoluminescence area as a radiation dosimeter. This utilization area of lithium tetraborate begot the expansion of the subject to contain the dosimetric properties of lithium tetraborate produced. The output of thermoluminescence evaluations i.e. glow curves are used as the indicators of the dosimetric utilization potential of the material.

Figure 4.18 displays the TL response of lithium tetraborate synthesized by wet reaction and doped by 0.1-1% copper. Although the intensities differ in quantity for different concentrations of the dopant, the glow curves generally tend to have the major peak in the temperature range of 85°C-115°C with a low shoulder which appears around 200°C. Indeed, the low temperature peak was strongly expected to fade away which has no sound meaning considering thermoluminescence dosimetry. On the other hand, although appearance of a peak near 200 °C was encouraging, the intensity offered by this peak is quite low since it gives a maximum lower than  $10^4$  ranges. Besides, the peak at 200°C is quite broad and shallow which is not a desired case in TL dosimetry. When the effect of dopant concentration is concerned, it is apparent that lower concentrations of dopants yield better results. Even though 0.1% copper gives a higher peak than 0.2% copper in the low temperature region, at around 200°C, 0.1% copper doped sample forges ahead which brings us to the conclusion that 0.1-1% copper interval, the lower the dopant concentration the higher the TL peak intensity.

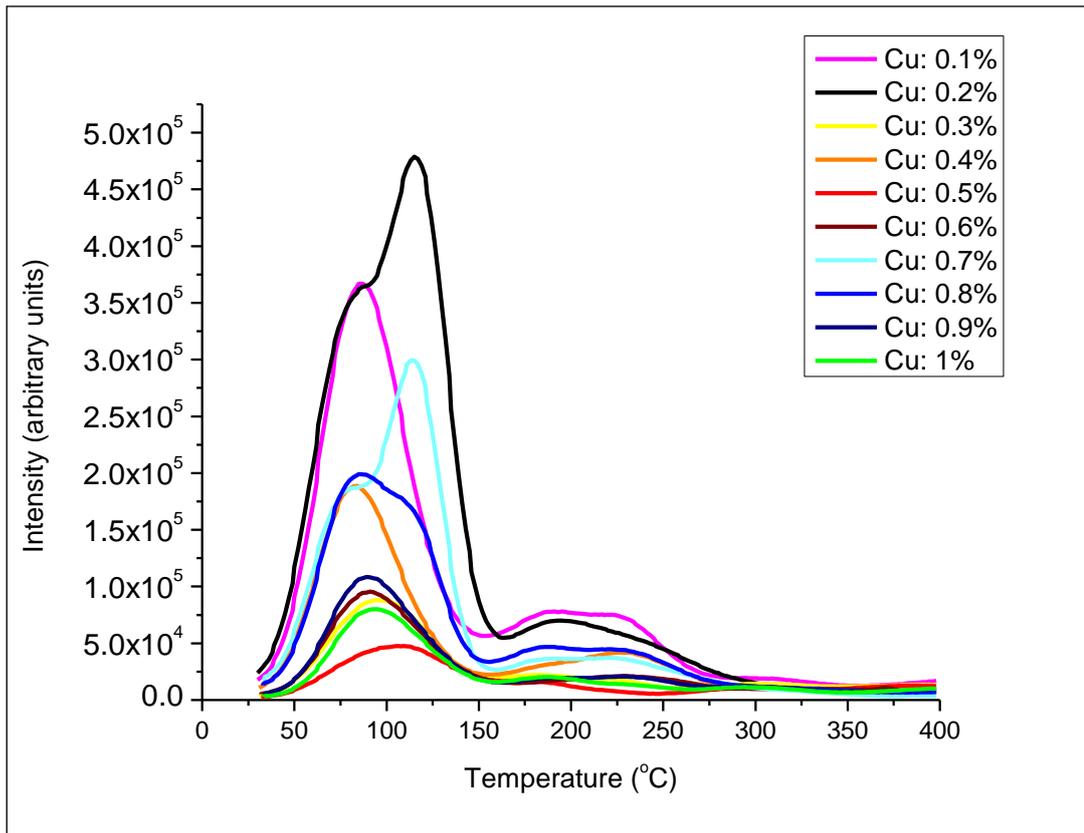


Figure 4.18 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  synthesized by water/solution assisted method and Cu doped by solution assisted doping

The case for the material synthesized by high temperature solid state technique and doped by solution assisted method is noticeably different. Figure 4.19 illustrates the glow curves recorded for the same concentrations of same dopant for solid state synthesis and solution assisted doping. First of all, for these samples, the desired peak i.e. the glow peak around  $200^\circ\text{C}$  exceeds the minor peak observed at temperatures between  $128\text{--}136^\circ\text{C}$ . This trend of the glow curves is in complete compliance with the literature stated in section 2.12 “*TL Properties of Lithium Tetraborate*”. Furthermore, it can be observed from Figure 4.19 that although the succession of the glow curves does not completely follow a regular path that increase or decrease with the dopant concentration, curves for high concentration doped material were accumulated mostly at the lower portion (low intensity) of the plot. Nevertheless, the highest intensities were shared by 0.1, 0.3, 0.4% copper doped

lithium tetraborate 0,1 % copper containing one having the highest intensity peak as for the case in water/solution assisted synthesis.

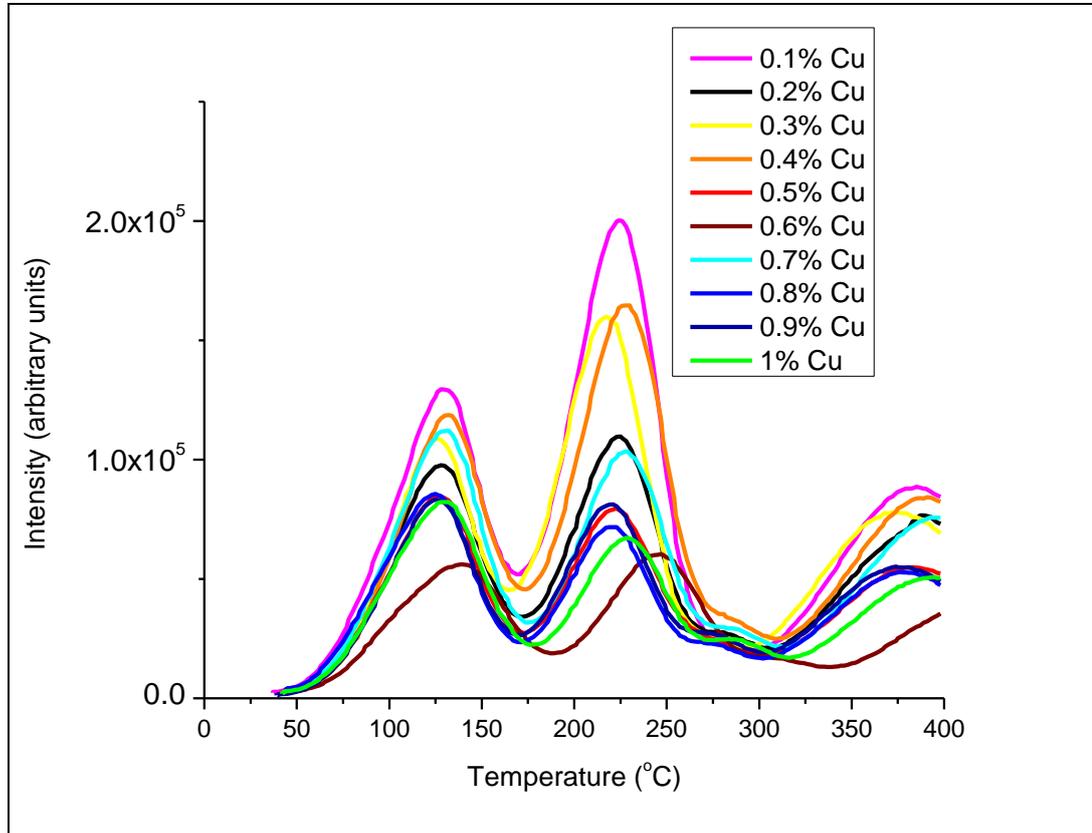


Figure 4.19 Glow curves of  $\text{Li}_2\text{B}_4\text{O}_7$  synthesized by solid state synthesis and Cu doped by solution assisted technique

As it may straightforwardly be detected from the illustrations above, solid state synthesis displayed superior results compared to water/solution assisted synthesis for all concentrations of main activator copper. Hence, high temperature solid state synthesis is adopted as the production method for lithium tetraborate synthesis. In pursuit of high temperature solid state synthesis and solution assisted doping, and acceptance of solid state synthesis as the matrix formation technique, the doping procedure is diverted to high temperature solid state doping. Figure 4.20 displays the TL output for such samples. As it may easily be noticed from the illustration below when the material produced is doped by high temperature solid state doping a very complex glow curve distribution is observed. All of the samples displayed several

peaks at some random temperatures. Moreover a correlation between the dopant concentration and the TL signal could not be detected. This is because no sound trend could be observed for these samples. This may mainly be attributed to the fact that doping is a tedious job concerning the total homogenization of two powder forms in hand.

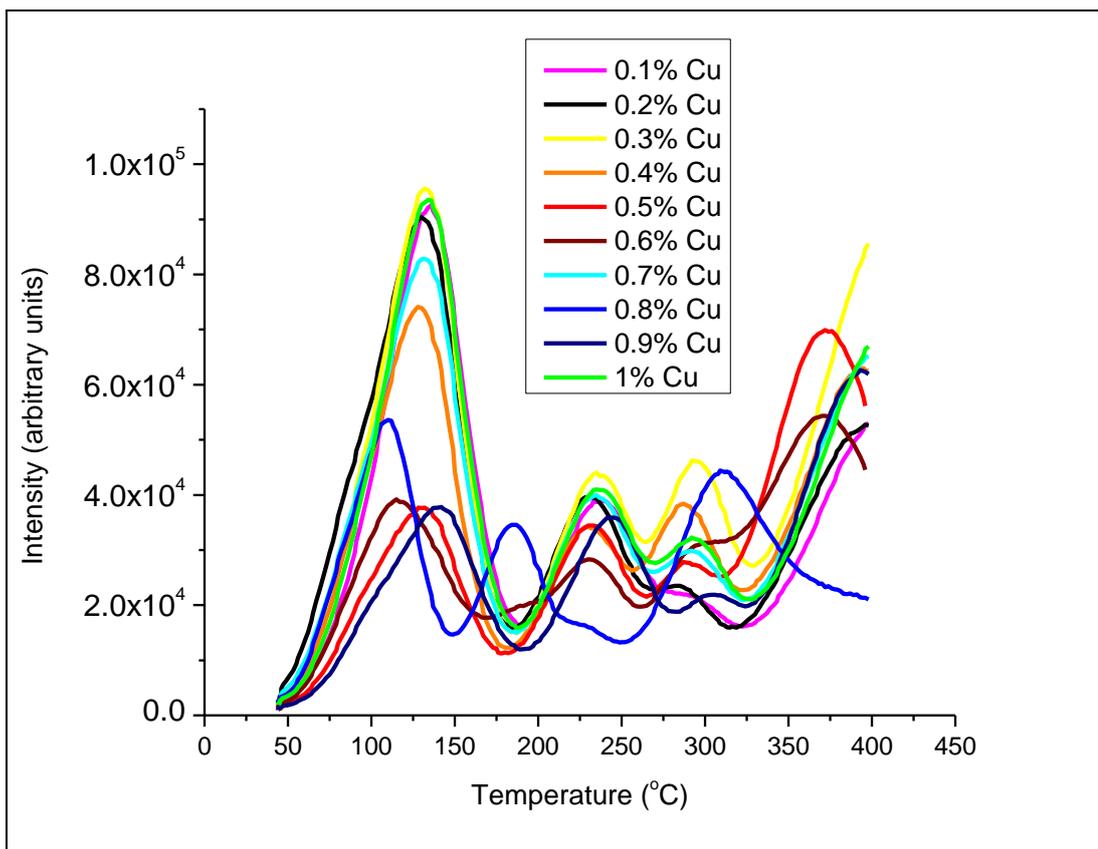


Figure 4.20 Glow curves of  $\text{Li}_2\text{B}_4\text{O}_7$  synthesized and Cu doped by high temperature solid state method

By comparison of the TL results of solid state synthesized and solution assisted doped lithium tetraborate and that both synthesized and doped by solid state method, the resultant preference became in the favor of solid state synthesis with solution assisted doping. Upon making the decision on the method, addition of different concentrations of the co-dopants Ag and In with different concentrations of copper is commenced. Figure 4.21, 4.22 and 4.23 display the TL responses which allow the

comparison of effect of co-dopant. Moreover, in these figures copper concentrations were changed in order to take the interaction of the dopant and co-dopant into account. Furthermore, the interpretation of whether addition of silver changes the inverse proportion between copper addition and TL intensity in single dopant copper case can be made by this figure. In Figure 4.21, the glow curves were similar to those without Ag considering the temperatures that the TL peaks exist at. However, it can be seen that addition of Ag together with copper increases TL intensity up to a certain concentration which is 0.04% Ag and starts to decrease when the co-dopant concentration is further increased. The two best results were observed for this case and for 0.05% co-dopant concentration. Additionally, it is beneficial to recall that the maximum intensity reached in absence of Ag was  $2 \times 10^5$  which is about 5 times greater when 0.04 % Ag is added together with copper. (Figure 4.19)

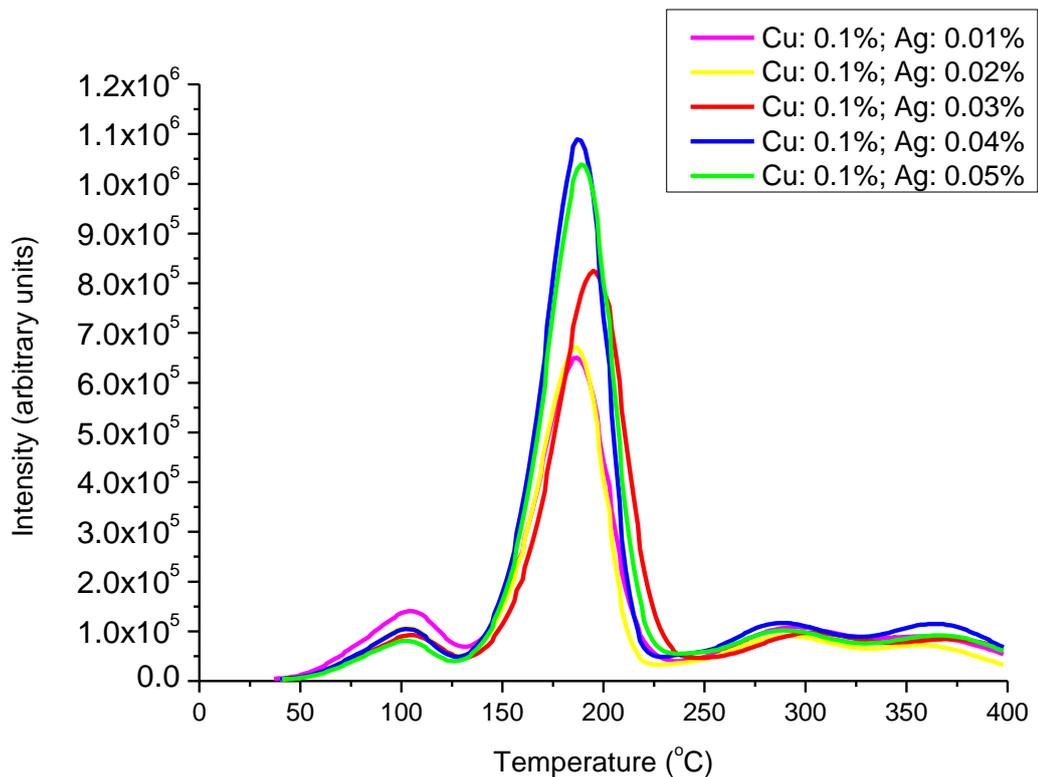


Figure 4.21 Glow curves of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.1% Cu and 0.01-0.05 % Ag

Figure 4.22 includes the glow curves for the same concentrations of Ag with increased Cu (0.3%). The decrease in TL intensities can directly be detected compared to the intensities for 0.1% Cu with 0.01-0.05% Ag. Nevertheless, an important point to focus on is that there is a noticeable difference between the TL intensities between those containing 0.04 and 0.05% Ag with those possessing less Ag concentration. Moreover, it can be inferred from the figure that the TL intensities decrease down to the values observed in case of solely copper doping when the matrix is doped with 0.3% copper together with 0.01-0.05% Ag. Besides in Figure 4.22 Lithium tetraborate with 0.04% Ag which yielded the best result for 0.1% Cu is caught up by 0.05% Ag when the major activator concentration is 0.3.

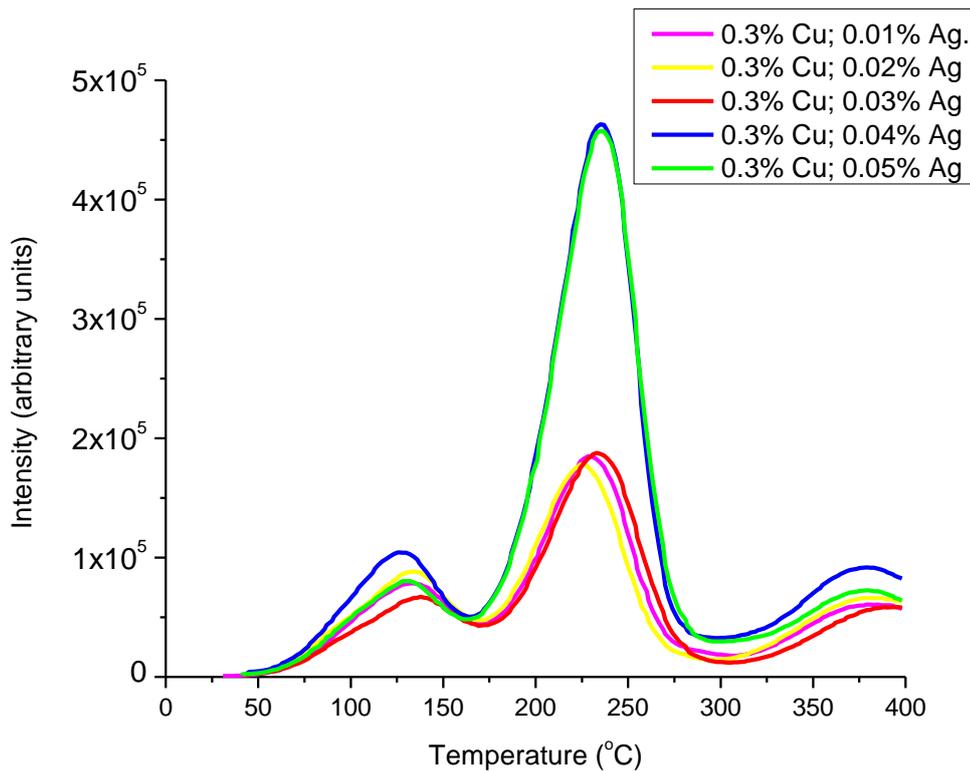


Figure 4.22 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.3% Cu and 0.01-0.05% Ag

Before triple doping, i.e. copper (as main activator), silver and indium (as co-activators) the experiments made for Ag as single co-dopant were performed for indium as well. Figure 4.23 displays the glow curves for lithium tetraborate doped with 0.1% Cu and co-doped with 0.01-0.05% In. In this case again we observe that the sample having the highest TL intensity is the one containing 0.04% co-dopant together with 0.1% copper. However it is also obvious that none of these samples could reach the performance of the sample including 0.1% copper and 0.04% Ag. Moreover, the succession of the curves for the indium doped case is rather complicated compared to silver case.

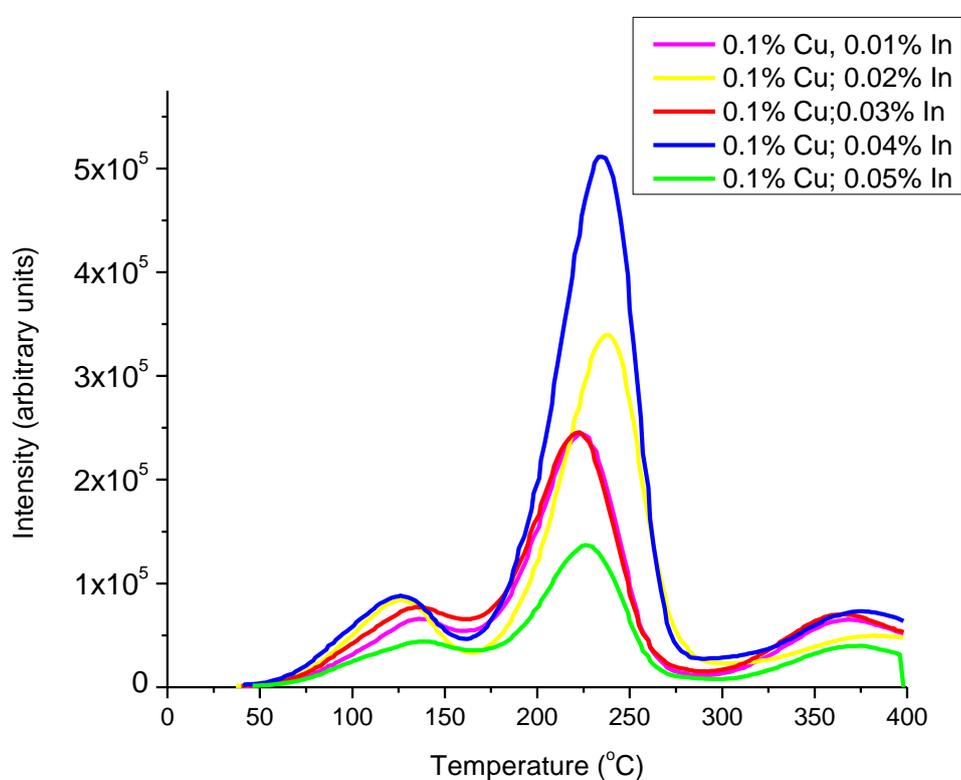


Figure 4.23 Glow curves of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.1% Cu and 0.01-0.05% In

When the copper concentration is increased with the same concentration interval of co-dopant indium, the figure encountered got yet more interesting (Figure 4.24), although the samples, apart from the one comprising 0.02% In, gave peaks with intensities around  $2 \times 10^5$ , while that with 0.02% In increased in intensity from values around  $3 \times 10^5$  to  $7 \times 10^5$ .

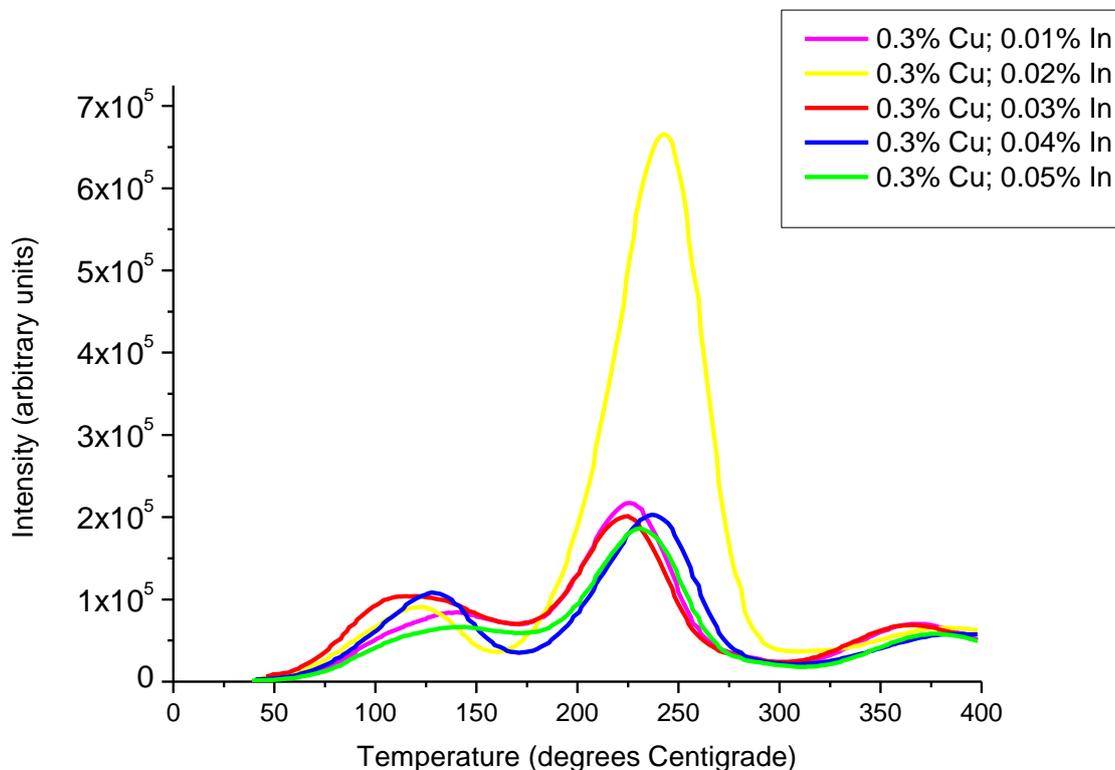


Figure 4.24 Glow curves of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.3% Cu and 0.01-0.05 % In

On the other hand, the regular trend in silver doped samples could not be reached in indium doped samples.

For the samples to investigate TL intensity in presence of 2 co-activators, the samples that gave the best TL intensities with single dopant were used with alternating concentration of the major dopant and the other co-activator, namely, indium. In these experiments the aim is to see whether addition of indium increases the intensity reached by addition of 0.1% copper with 0.04 or 0.05% Ag. Figure 4.25, 4.26, 4.27, 4.28 are devoted to representation of the influence of second activator on the TL intensity of the samples with best two results.

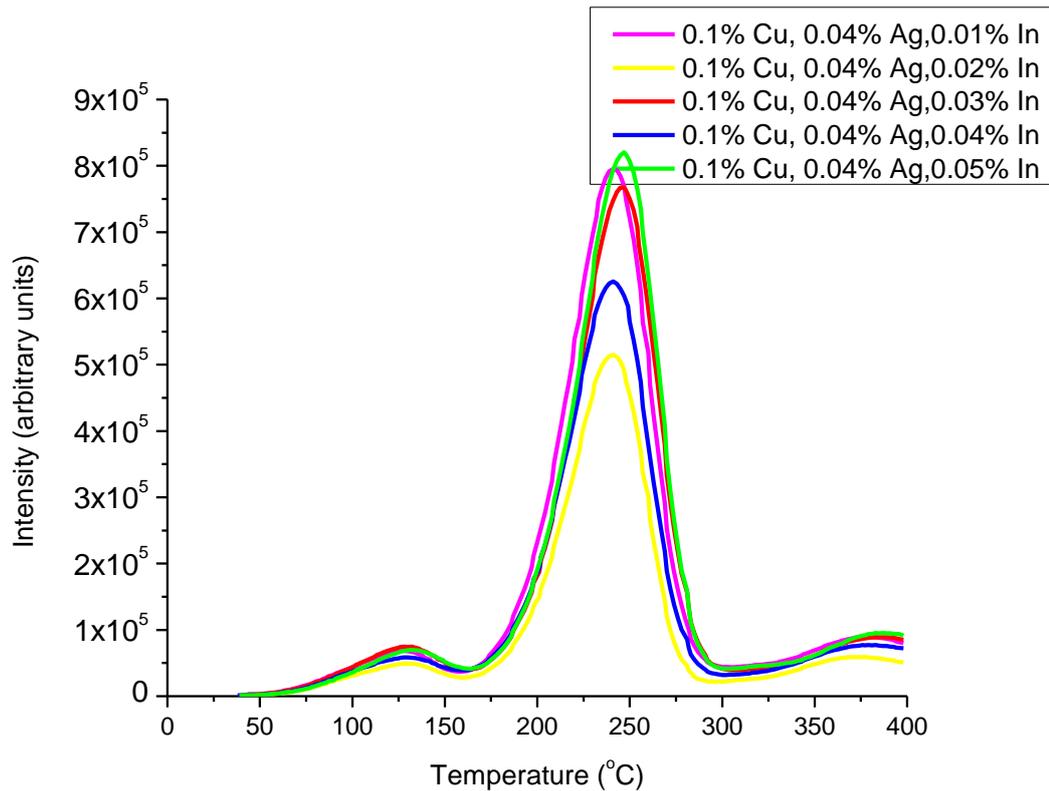


Figure 4.25 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.1% Cu, 0.04% Ag and 0.01-0.05% In

When glow curve plot in Figure 4.25 for indium added with 0.1% Cu and 0.04% Ag is examined, we observe that no serious change occurs with increasing indium concentration. If the curves in this graph are compared to that without indium it can be seen that the intensity reached in absence of indium is at higher values. The same situation is valid for the doping concentrations 0.3% Cu, 0.04% Ag, 0.01-0.05% In; 0.1% Cu, 0.05% Ag, 0.01-0.05% In and 0.3% Cu, 0.05% Ag, 0.01-0.05%. The overall inspection of Figures 4.25, 4.26, 4.27, 4.28 show that, in each case the most intense peak includes different amount of indium and an attention taking result is not countered. Besides, none of the intensities obtained from two co-dopant case exceeds the TL results obtained from 0.1% Cu with 0.04% Ag.

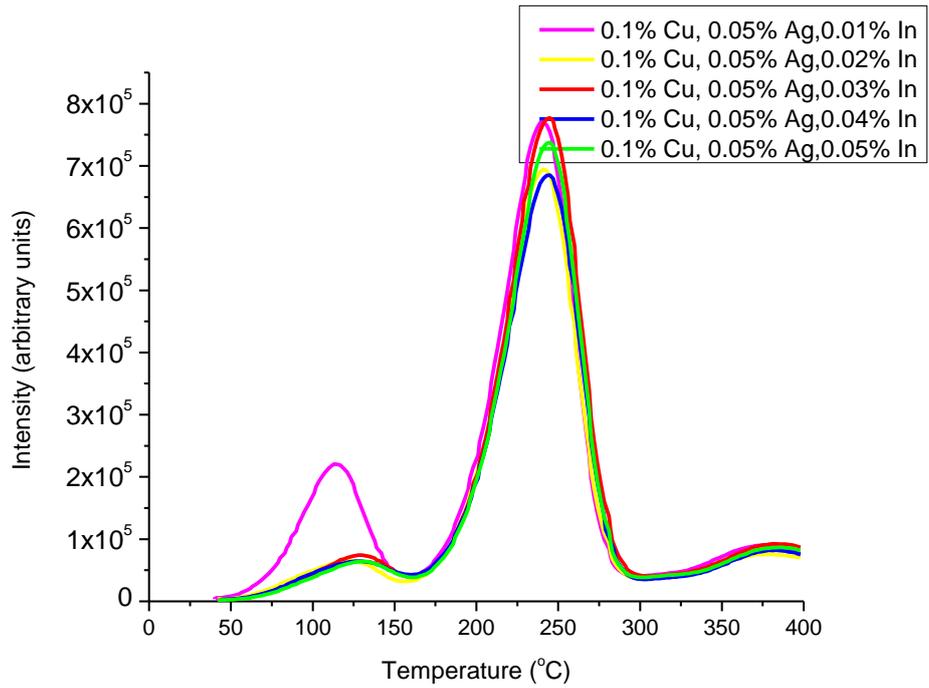


Figure 4.26 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.1% Cu; 0.05 % Ag and 0.01-0.05% In

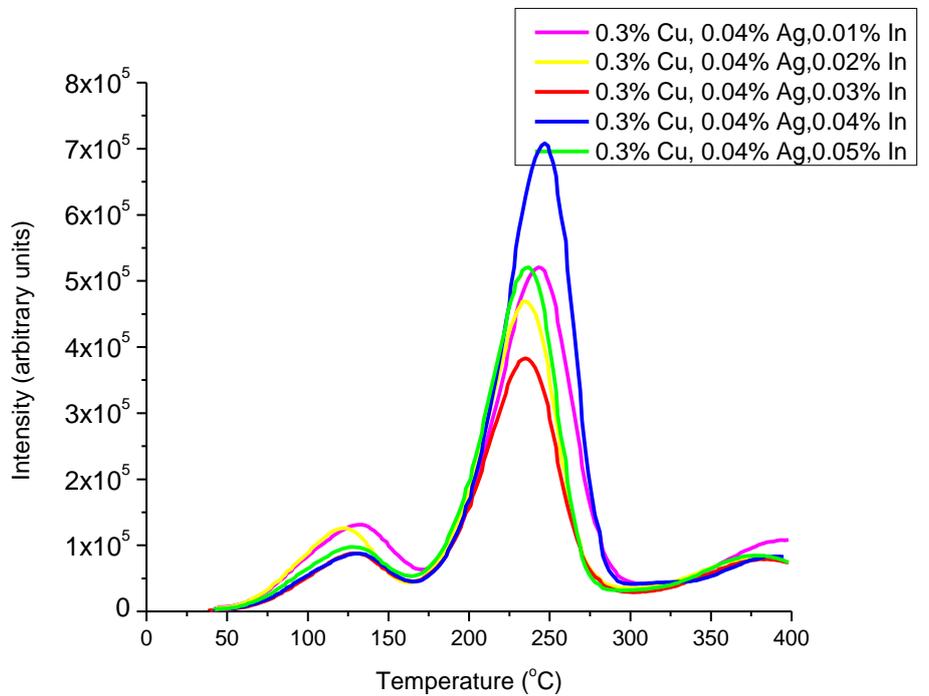


Figure 4.27 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.3% Cu; 0.04 % Ag and 0.01-0.05% In

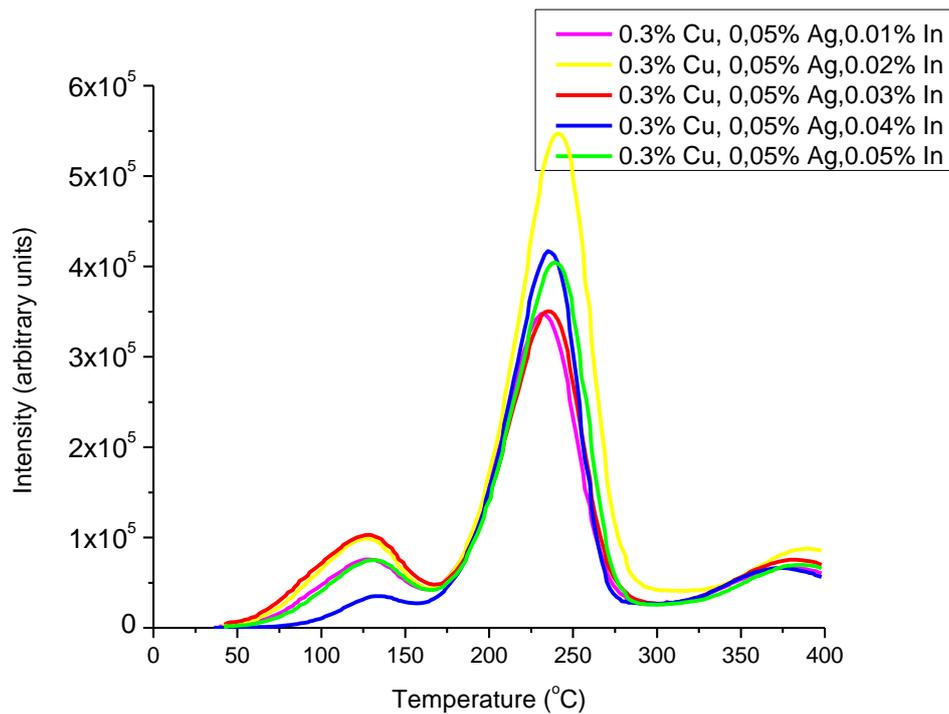


Figure 4.28 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.3% Cu; 0.05 % Ag and 0.01-0.05

In

Along with the decision that the sample doped with 0.1% Cu with 0.04% Ag yield the highest TL signal, the retention time and reaction temperature experiments were performed in order to search whether higher intensities can be reached with changing these conditions or not. As it is quite noticeable from Figure 4.29 which shows the effect of retention time on TL intensity, the results of higher retention times fall behind those obtained from lower retention times. In this situation again, the retention time adopted at the initial experiment (2 hours). Another significant subject to pay attention is that the high intensity peak expected to be around  $200^\circ\text{C}$  has shifted to temperatures more than  $230^\circ\text{C}$  up to  $250^\circ\text{C}$  which are values near to those recorded by Cuong [9].

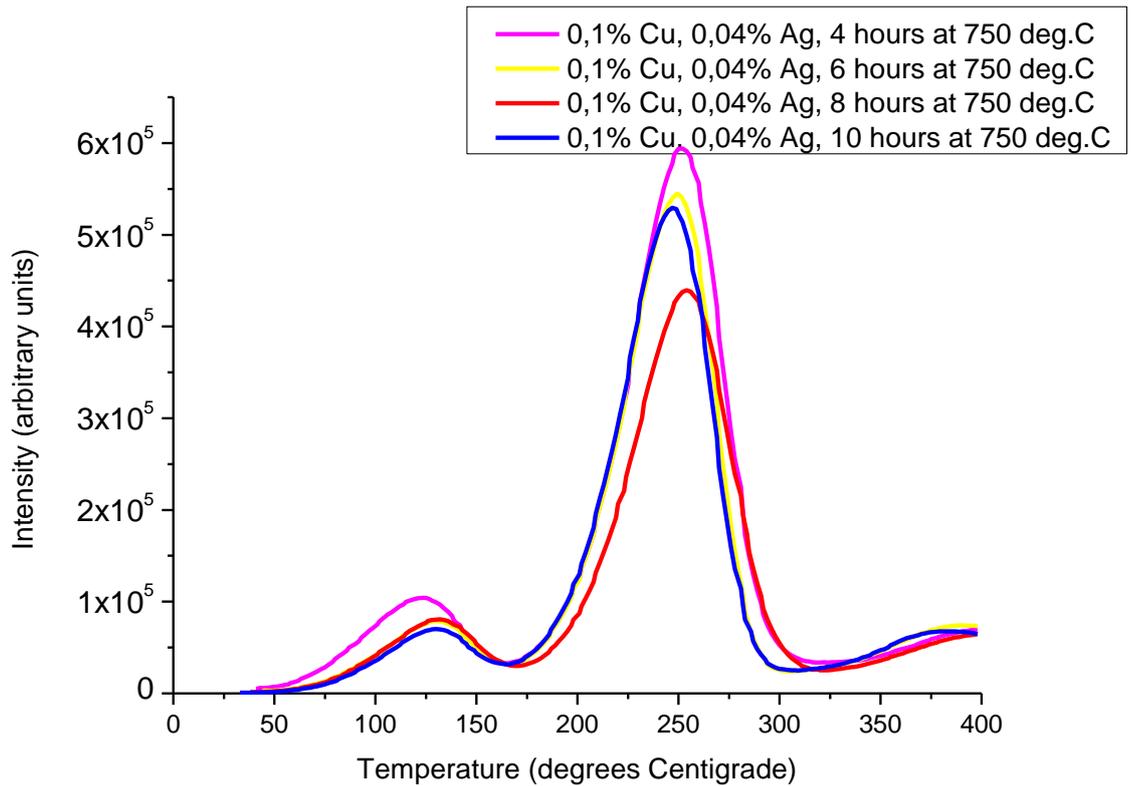


Figure 4.29 Glow curve of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with 0.1% Cu; 0.04 % Ag for retention times 4, 6,8,10 hours

Figures 4.30 4.31, 4.32 and 4.33 are illustrations of the effect of doping temperature on TL signal. Figure 4.30 and 4.32 are for the sample doped 0.1% Cu and 0.04% Ag while Figure 4.31 and 4.33 compare the TL signal at temperatures 750 and 800°C for 0.1% Cu and 0.05% Ag

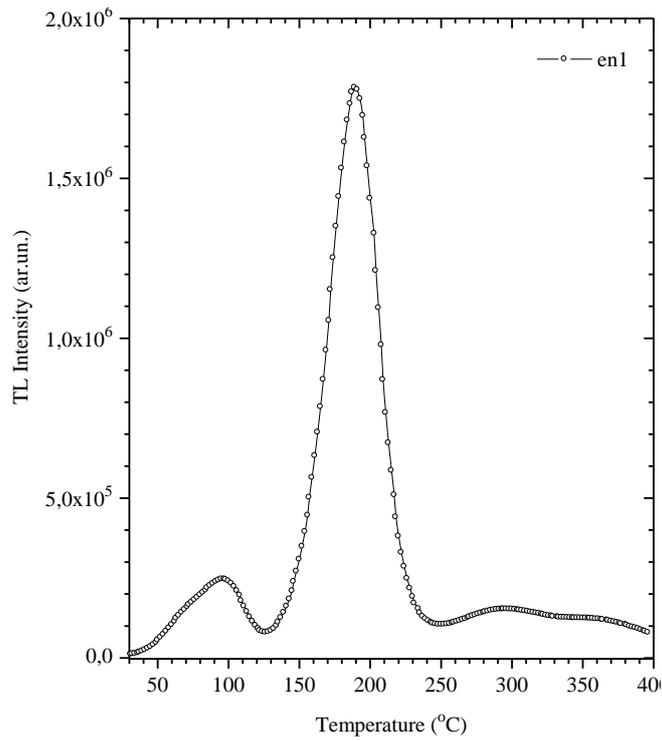


Figure 4.30 TL response of 0.1 % Cu, 0.04% Ag doped lithium tetraborate doped at 750°C

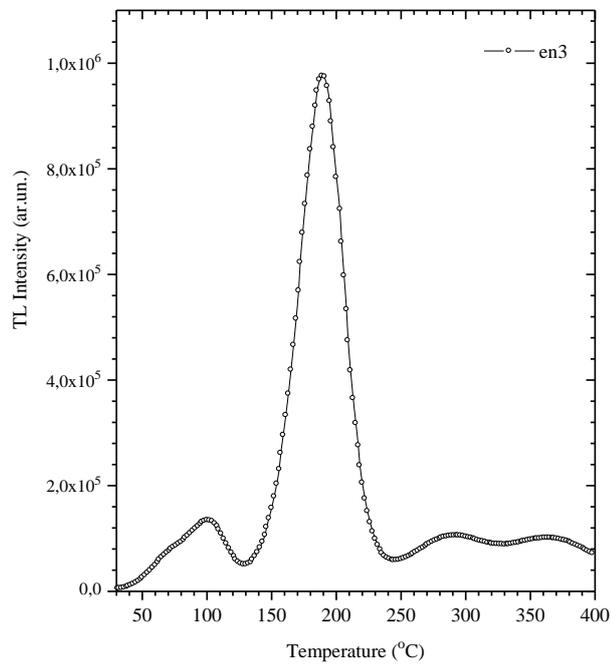


Figure 4.31 TL response of 0.1 % Cu, 0.04% Ag doped lithium tetraborate doped at 800°C

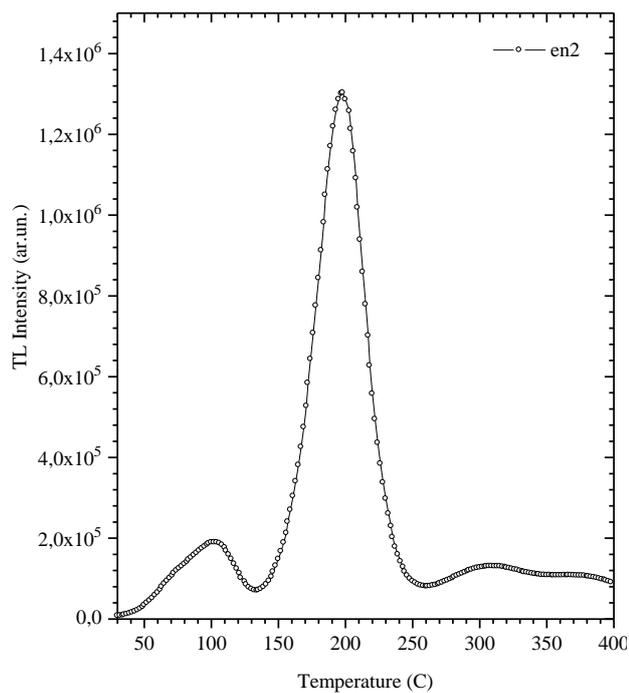


Figure 4.32 TL response of 0.1 % Cu, 0.05% Ag doped lithium tetraborate doped at 750°C

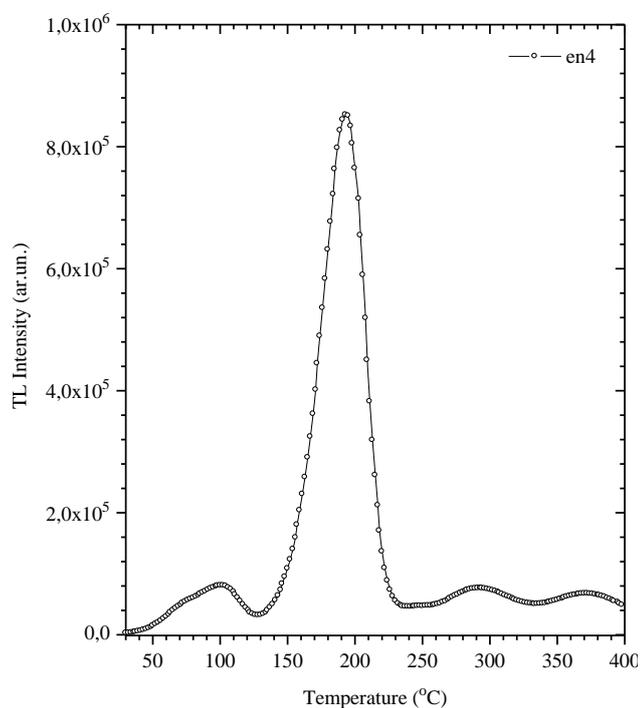


Figure 4.33 TL response of 0.1 % Cu, 0.05% Ag doped lithium tetraborate doped at 800°C

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

The study aimed at producing lithium tetraborate, comparing water/solution assisted and high temperature solid state synthesis methods and selecting an appropriate method and suitable amounts of activators for doping procedure in order to use it in TL dosimetry.

The conclusions derived from the investigations and experiments conducted are as follows:

1. Lithium tetraborate was synthesized by both high temperature solid state and water/ solution assisted synthesis by the exposing the reactants lithium carbonate and boric acid to final heating at 750°C for 3 hrs. Obtained matrix material was doped by different amounts and combinations of dopants: In, Ag, Cu. According to the XRD results it can be proposed that both water/solution assisted and solid state synthesis resulted in successful production of lithium tetraborate in powder form.
2. It can be inferred from the FT-IR records that addition of the activators Cu, Ag and In cause no noticeable change in vibrational modes of borates and the bond structure within the material.
3. DTA analysis were conducted on 5 samples: the lithium tetraborate produced by high temperature solid state synthesis, one synthesized by water/solution assisted technique, lithium tetraborate formed by high temperature solid state synthesis and doped with either of Cu,Cu-Ag, Cu-Ag-In by solution assisted doping. The melting point of the material produced ranged between 828°C and 865°C. The doped samples displayed double peaks which conveyed the conclusion that doping altered the thermal characteristics of lithium tetraborate produced. These results considerably differed from the DTA

4. Results in literature which stemmed from the fact that thermal analyses performed previously were conducted on single crystals.
5. The morphologies of the lithium tetraborates produced by high temperature solid state synthesis -doped by solution assisted doping and produced by water/solution assisted method-doped by solution assisted doping display different characteristics. The former one gave smoother surfaces with larger particles. This difference may be the root of difference in TL characteristics of the material obtained by these methods.
6. The TL results obtained showed that the material produced show TL response. Moreover it was realized that the lithium tetraborate produced by high temperature solid state synthesis yielded more meaningful results compared to those synthesized by water/solution assisted method. Besides, the glow curves of samples doped by solution assisted doping were more suitable for the potential use in TL dosimetry than the samples doped with high temperature solid state synthesis.
7. In the case where solely copper is added as dopant, sample with 0,1% Cu (lowest) dopant gave the best results among the concentration levels under investigation.
8. When the double doping is concerned, it is observed that co-dopant Ag increased the TL response in comparison to solely Cu doping experiments while In had no significant trend. Among the samples prepared with 0.1%Cu, 0.04% Ag coactivator gave the highest TL response.
9. In triple doping, addition of indium as the second co-dopant gave lower TL signals than copper, silver case.
10. Neither higher sintering temperatures nor longer retention times gave superior TL results. However, characterization and TL measurements could not be performed for temperatures more than 850°C due to glassification.
11. It is recommended that other lithium borates be searched for synthesis characterization and TL properties.

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