Chapter-3

Synthesis and characterization
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Synthesis and characterization

This chapter presents a description of the synthesis of Li$^+$ and Ca$^{2+}$ based borate nanoparticles doped with metal ions and lanthanide ions by simple solid state sintering and combustion method. The raw materials used in the synthesis of the nanoparticles and the steps followed during solid state sintering and combustion are described in details. The characterizations of the synthesized nanoparticles are performed by XRD, FTIR and TEM and are described in details.

3.1 Synthesis of borates

Development of tissue equivalent TL/OSL materials suitable for clinical and personnel dosimetry applications and phosphors with combined neutron and gamma sensitivities has attracted considerable interest. TL phosphors based on borates play an important role because of their near tissue equivalent absorption coefficient in this regard and its neutron sensitivity due to high thermal neutron absorption cross-section of $^{10}$B [1,2]. TL characteristics of the mixed borate LiCaBO$_3$ (LCB) doped with rare earth elements and lithium magnesium borates have also been studied due to their neutron sensitivity and relatively lesser effective atomic number [3,4] and their feasibility in radiation dosimetry applications have been demonstrated. There are various methods of synthesis of different borate compounds reported by different authors [5–49]. Borate compounds may form crystalline as well as glassy phase based on the preparation technique. The efficiency of the TL/OSL materials is also dependent on the crystalline forms of the materials. There are also reports of the TL/OSL properties of the phosphor depend on the starting materials used for the synthesis of phosphors [50]. Some of the popular methods of synthesis of borate based phosphors are the melting method [51], combustion method [52], growing of single crystals [53], Sol-gel method [54], hydrothermal synthesis [55] etc. All the phosphors used in the present study were synthesized by solid state sintering technique and combustion method as these methods of synthesis are simple and can synthesized bulk amount in less time which lowers the preparation cost.
3.2 Lithium tetraborate (Li$_2$B$_4$O$_7$) nanoparticles doped with metals

3.2.1 Synthesis

LTB doped with Cu, Ag and co-doped Cu-Ag nanoparticles were synthesized by solid state sintering technique. Lithium Carbonate (Li$_2$CO$_3$, Alpha Aesar) and Boric Acid (H$_3$BO$_3$, Alpha Aesar) were used as starting materials. Copper chloride (CuCl$_2$, Sigma Aldrich) and silver nitrate (AgNO$_3$, Alpha Aesar) were used as the dopant sources of Cu$^{2+}$ ions and Ag$^{+}$ ion. The stoichiometric ratios of the starting materials were mixed thoroughly in a quartz crucible. The calculated amounts in gm of the starting materials for Cu and Ag doping are given in table 3.1 and 3.2 respectively. Appropriate amounts of dopants were calculated in terms of atomic weight per cent and added in the mixture. The synthesis was completed in two stages. In the first stage the mixture was heated at 350° C in a muffle furnace for 3 hours and grind to get a homogenous mixture. In the second stage, the mixture was heated linearly at 700° C for 4 hours such that intermittent mixing and grinding were done after the first 2 hours. The process of synthesis is given schematically in figure 3.1.

The reaction mechanism is given below:

\[
\text{Li}_2\text{CO}_3 + 4\text{H}_3\text{BO}_3 \rightarrow \text{Li}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O} + \text{CO}_2
\]

In this process nanoparticles of LTB:Cu (0.025, 0.05, 0.1, 0.3, 0.5, 1, 3, 5 at.wt.%), LTB:Ag (0.025, 0.05, 0.1,0.3, 0.5, 1,3,5 at.wt.%) and LTB:CuAg \{(0.5,0.5), (1,1), (1,3), (3,1) at.wt.%\} were synthesized. The synthesized nanoparticles were then used to study their TL and OSL properties.

![Figure 3.1: Schematic representation of the process of synthesis of Li$_2$B$_4$O$_7$ nanoparticles.](image-url)
Table 3.1: The calculated stoichiometric weights for the synthesis of LTB nanoparticles doped with Cu.

| Li$_2$CO$_3$ (gm) | H$_3$BO$_3$ (gm) | CuCl$_2$ (gm) | Dopant (at.wt.%)
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Table 3.2: The calculated stoichiometric weights for the synthesis of LTB nanoparticles doped with Ag.

| Li$_2$CO$_3$ (gm) | H$_3$BO$_3$ (gm) | AgNO$_3$ (gm) | Dopant (at.wt.%)
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3.2.2 Characterization

The formation of the LTB nanoparticles and phase analysis was done by using Philips PANanalytical X'Pert XRD. The particle morphology of the prepared LTB samples were also studied using TEM images. Surface characterization was done by Fourier transform infrared (FTIR) spectroscopy. The infrared (IR) vibrational modes in LTB samples were studied using Bruker Eco-ATR FTIR Infrared spectrometer. The synthesized nanoparticles are used for further studies of the luminescence properties of the LTB nanoparticles such as PL, TL and OSL after characterization of the formation of the nanoparticles

3.2.2.a XRD study

Figure 3.2 shows the XRD pattern of (a) LTB:Cu(0.05%), (b) LTB:Ag(1%) and (c) LTB:Cu(3%)Ag(1%), it is observed that all the diffraction peaks corresponds to the JCPDS card no. 00-040-0505 and no additional peak could be determined within the resolution limit of the diffractometer.

The average particle sizes were calculated using Scherrer’s equation [56]:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

(3.1)

Where \(D\) is the average particle size, \(\lambda\) is the incident wavelength, \(\beta\) is the full width half maximum in radians and \(\theta\) is the Bragg’s angle.

The particle sizes calculated from the XRD pattern of LTB:Cu(0.05%), LTB:Ag(1%) and LTB:Cu(3%)Ag(1%) are 32, 35 and 36 nm respectively. The prepared LTB samples exhibits tetragonal structure having lattice parameters (a) \(a = b = 9.4740\, \text{Å}, c = 10.1708\, \text{Å}\) and \(V = 912.9057\, \text{Å}^3\) for LTB:Cu(0.05%), (b) \(a = b = 9.4639\, \text{Å}, c = 10.2551\, \text{Å}\) and \(V = 918.4926\, \text{Å}^3\) for LTB:Ag(1%) and (c) \(a = b = 9.5139\, \text{Å}, c = 10.2165\, \text{Å}\) and \(V = 924.7299\, \text{Å}^3\) for LTB:Cu(3%)Ag(1%) respectively. It is found that the unit cell volume (\(V\)) increases as LTB:Cu < LTB:Ag < LTB:CuAg. This increase in unit cell volume may be because of the insertion of doping ions in the Li sites of LTB. The ionic radius of \(\text{Cu}^{2+}\) ion is 0.73 Å and \(\text{Ag}^+\) ion is 1.15 Å. That is why the unit cell volume of LTB:Ag bigger than the LTB:Cu samples. As both \(\text{Cu}^{2+}\) and \(\text{Ag}^+\) ions enter the LTB site LTB:CuAg sample have the biggest unit cell volume.
Figure 3.2: XRD patterns of 700°C annealed (a) LTB:Cu(0.05%), (b) LTB:Ag(1%) and (c) LTB:Cu(3%)Ag(1%). The inset figure shows the changes of unit cell volume of LTB with different dopants.
3.2.2.b TEM study

Figure 3.3 shows the TEM image of LTB nanoparticles. It is observed that the particles are evidently clustered/aggregated spherical in shape with particle size 45 nm. All the samples are having nearly uniform particle size distribution. The inset picture shows the SAED pattern of the particles. It is found that the diffraction pattern showed both dots as well as concentric circles, suggesting the aggregated but crystallite nature. Average crystallite size observed from XRD pattern is found to be smaller compared to that observed from TEM images. This is understandable as line width of XRD peak is a measure of the coherent regions present in a particle whereas TEM images gives actual size of the particle.

3.2.2.c FTIR study

The Fourier transform infrared (FT-IR) spectra were investigated in the range of 500 cm$^{-1}$ to 4000 cm$^{-1}$ wavenumbers. The phosphor is finely ground and mixed with KBr with which the sample is usually ground with an agate mortar and pestle to make a clear transparent disc. FTIR measurements were carried out in the transmission mode in which the infrared radiation from the source is allowed to pass through the sample and the portion of the beam that is transmitted, i.e. not absorbed by the sample is recorded. Figure 3.4 shows the FTIR spectra of the (a) LTB:Cu(0.05%), (b) LTB:Ag(1%) and (c) LTB:Cu(3%)Ag(1%). From the spectra it is found that there are four major absorption peaks at around 1600-1200 cm$^{-1}$, 1500-700 cm$^{-1}$, 950-870 cm$^{-1}$ and 870-415 cm$^{-1}$. These major peaks are assigned as 1600–1200 cm$^{-1}$ to be the asymmetric stretching vibrations of B–O in BO$_3$, 1500–700 cm$^{-1}$ to be the B–O–H in plane bending of BO$_4$ tetrahedral, 950–870 cm$^{-1}$ to be the stretching of Tetrahedral BO$_4$, 870–415 cm$^{-1}$ to be the O–B–O deformation mode of BO$_4$ tetrahedral [57,58].

3.3 Calcium tetraborate (CaB$_4$O$_7$) nanoparticles doped with lanthanides

3.3.1 Synthesis

The CaB$_4$O$_7$ (CTB) nanoparticles doped with different concentrations of Tb were synthesized using solution combustion method. High purity Ca(NO$_3$)$_2$ (Sigma-Aldrich, 99.997%) and H$_3$BO$_3$ (Sigma-Aldrich, 99.5%) were used as the starting materials.
Figure 3.3: TEM micrograph of (a) LTB::Cu(0.05%), (b) LTB::Ag(1%) and (c) LTB::Cu(3%):Ag(1%), the inset shows the SAED pattern respectively.
Figure 3.4: FTIR spectra of 700°C annealed LTB:Cu(0.05%), LTB:Ag(1%) and LTB:Cu(3%)Ag(1%) nanoparticles.

And Dy$_2$O$_3$ (Sigma-Aldrich, 99.99%), Tm$_2$O$_3$ (Sigma-Aldrich, 99.99%), and Tb$_2$O$_3$ (Sigma-Aldrich, 99.99%) are used as the dopant source. Citric Acid (Sigma-Aldrich, 99.5%) was used as fuel in the synthesis. The appropriate quantity of fuel was calculated to maintain the elemental stoichiometric coefficient $\varphi = 1$ required for the combustion [59]. The calculated values of starting materials in gm for all the dopants are given in table 3.3, 3.4 and 3.5 for CTB:Dy, CTB:Tm and CTB:Tb respectively. The synthesis was completed in four steps. In the first step, the starting materials and the dopants were dissolved separately in doubled distilled water on a hot plate at 120°C for 1 hour. The dissolved materials were also added to the mixture. In the second step, the mixture was heated on a hot plate at 350°C until the water was evaporated. Then in the third step, the temperature of the hot plate was increased to 500°C for the combustion to be proceeded. Finally in the
fourth step, the samples were annealed in a pre-heated muffle furnace at 850°C for a period of 2 hours. The whole process of synthesis is presented schematically in figure 3.5. In this method various samples with different concentrations of Dy$^{3+}$ (0.025, 0.05, 0.1, 0.5, 1 and 2 at.wt.%), Tm$^{3+}$ (0.025, 0.05, 0.1, 0.5, 1 and 2 at.wt.%) and Tb$^{3+}$ (0.025, 0.05, 0.1, 0.5, 1 and 2 at.wt.%) were synthesized.

![Figure 3.5: Schematic picture of process involved in combustion synthesis of Calcium tetraborate nanoparticles.](image)

Table 3.3: The calculated stoichiometric weights for the synthesis of CTB nanoparticles doped with Dy.

<table>
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<tr>
<th>Ca(NO$_3$)$_2$ (gm)</th>
<th>H$_3$BO$_3$ (gm)</th>
<th>C$_6$H$_8$O$_7$ (gm)</th>
<th>Dy$_2$O$_3$ (gm)</th>
<th>Dopant (at.wt.%)</th>
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Table 3.4: The calculated stoichiometric weights for the synthesis of CTB nanoparticles doped with Tm.

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<th>Tm$_2$O$_3$ (gm)</th>
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Table 3.5: The calculated stoichiometric weights for the synthesis of CTB nanoparticles doped with Tb.

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3.3.2 Characterization

The crystalline phase and particle size of the synthesized CaB$_4$O$_7$ (CTB) nanoparticles was investigated by X-Ray diffraction (XRD) using GNR Explorer of resolution 0.0001°. The particle shape and size of the CTB nanoparticles were also investigated using TEM images and SAED patterns by JEOL 2100. The bonding nature and structure of the synthesized nanoparticle were studied using Fourier Transform Infrared Spectroscopy using Bruker Eco-Alpha T FTIR.

3.3.2.a XRD study

The XRD pattern of all the CTB nanoparticles doped Dy$^{3+}$, Tm$^{3+}$ and Tb$^{3+}$ are shown figure 3.6; all the samples shows similar diffraction lines which matches with the JCPDS card no. 01-083-2025.

![Figure 3.6: XRD patterns of 850°C annealed (a) CTB:Dy(0.05%), (b) CTB:Tm(0.05%) and (c) CTB:Tb(1%).](image-url)
The average particle sizes are calculated using Scherrer’s equation [56]. The calculated average particle size was found to be around 20 nm for CTB:Dy and CTB:Tm while 25 nm for CTB:Tb. All the prepared CTB nanoparticles show monoclinic crystal structure with space group P21/n and space group no. 14. It is found that the unit cell volume of the CTB nanoparticles increases with the increased doping concentration. This increase in unit cell volume with the increase in dopant concentration may be attributed due to incorporation of Dy\(^{3+}\), Tm\(^{3+}\) and Tb\(^{3+}\) ions respectively toward the lattice site of CTB. It may be worth to mention that the ionic radius of Dy\(^{3+}\), Tm\(^{3+}\) and Tb\(^{3+}\) are larger than that of the Ca\(^{2+}\) (0.99 Å), so with increase in the concentration of the dopants which replaces the Ca\(^{2+}\) site, the unit cell volume increases.

### 3.3.2.b TEM study

Figure 3.7 and 3.8 shows the TEM images of CTB:Dy(0.05%) and CTB:Tm(0.05%) nanoparticles annealed at 850°C. From the images (figure 3.7(a) and 3.8(a)), it is observed that the particle are evidently clustered/aggregated spherical in shape with particle size of about 25 nm. All the samples have nearly uniform particle size distribution. The respective SAED pattern show that the synthesized nanoparticles are of crystalline nature. Figure 3.9 shows the TEM micrograph images of CTB:(1%)Tb sample annealed at 850°C.

![Figure 3.7: (a) TEM micrograph of CTB:Dy(0.05%) and (b) the SAED pattern of CTB:Dy(0.05%) nanoparticles.](image)

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Figure 3.8: (a) TEM micrograph of CTB:Tm(0.05%) and (b) the SAED pattern of CTB:Tm(0.05%) nanoparticles.

Figure 3.9: (a) and (b) TEM micrograph of CTB:Tb(1%), (c) HRTEM of CTB:Tb(1%) and (d) the SAED pattern of CTB:Tb(1%) nanoparticles.
It is observed that the particles are also evidently clustered or aggregated with particle size 35 nm. This shows that the average particle size of the CTB nanoparticles calculated from the XRD are in agreement with the particle size observed from the TEM images. From the HRTEM image (figure 3.9(c)), it is observed that the lattice planes are parallel with regular spacing for each crystallite showing the crystalline nature of the CTB nanoparticles. The selected area electron diffraction (SAED) pattern (figure 3.9(d)) also suggested the crystalline nature of the synthesized CTB:Tb nanoparticles as shown in the figure. The SAED pattern was also in agreement with the XRD pattern.

3.3.2.c FTIR study

The same process of sample preparation and conditions as mention earlier for the case of LTB nanoparticles is followed. Figure 3.10 shows the FTIR spectra of 850°C annealed CTB nanoparticles. The IR spectra of the CTB nanoparticle mainly have four active region of vibration modes of borate network such as a band at around 1400 cm\(^{-1}\) which corresponds to the B-O stretching of trigonal BO\(_3\) units, 850-1200 cm\(^{-1}\) with absorption peaks at 862.36 cm\(^{-1}\), 908.62 cm\(^{-1}\), 947.62 cm\(^{-1}\), 968 cm\(^{-1}\), 1091 cm\(^{-1}\) and 1145.35 cm\(^{-1}\) which are associated with the B-O stretching of tetrahedral BO\(_4\) units, 600-850 cm\(^{-1}\) with absorption peaks at 633.96 cm\(^{-1}\), 741.72 cm\(^{-1}\) and 819.73 cm\(^{-1}\) are attributed to the bending vibrations of various borate segments and a band at around 703.17 cm\(^{-1}\) is associated with the bond bending of B-O-B bridges in the boron-oxygen network [60,61].
Figure 3.10: FTIR spectra of 850°C annealed (a) CTB:Dy(0.05%), (b) CTB:Tm(0.05%) and (c) CTB:Tb(1%) nanoparticles.
References


Y. Li, R.P.H. Chang, Synthesis and characterization of aluminum borate


Chapter-4

Luminescence properties of $\text{Li}_2\text{B}_4\text{O}_7$ nanoparticles