SYNTHESIS, CHARACTERIZATION AND LUMINESCENCE STUDIES OF Li\(^+\) AND Ca\(^{2+}\) BASED BORATE NANOPHOSPORS DOPED WITH METALS AND LANTHANIDES

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Abstract

Synthesis of the Li\(^+\) and Ca\(^{2+}\) based borate nanoparticles and studies of their luminescence properties are presented in this work. The borate materials are chosen for this study as borate based phosphors have a distinct advantage of responding to mixed neutron and gamma field with suitable doping of neutron sensitive isotopes of boron. In addition to this advantage, these materials are easy to prepare, have simple dosimetric peak at reasonably high temperatures, exhibit linear dose response on an average, over doses ranging two to three orders of magnitude, have excellent storage stability and have simple annealing procedure for reuse. Among the borates Lithium tetraborate (LTB) and calcium tetraborate (CTB) are chosen for this work due to their tissue equivalent effective atomic numbers, which is one of the most preferable properties of ideal dosimeters. The Lithium tetraborate phosphors with proper dopants have an effective atomic number of \(\approx 7.4\) which nearly equivalent to biological tissue whereas calcium tetraborate has an effective atomic number of \(\approx 12.5\) which is very near to effective atomic number of bone tissue.

In chapter 1, a general introduction on luminescence is given and discussed in details. The types of luminescence with its characteristics are also presented in this chapter. The photoluminescence (PL), thermoluminescence (TL) and optically stimulated luminescence (OSL) phenomenon are discussed in details with their mechanism and applications with proper literatures. The chapter also discussed the introduction of lithium tetraborate (LTB) and calcium tetraborate (CTB) in TL and OSL dosimetry applications.

In chapter 2, the instruments used in the course of this work are described with respective block diagrams. The main instruments used such as X-ray diffraction (XRD) instrument, Transmission electron microscope (TEM) instrument, Fourier transform infrared spectroscopy (FTIR), Fluorescence spectrophotometer (PL) instrument and TL/OSL readers with working are explained in this chapter. The methods of analysis of the recorded TL and OSL with their proper equations are also given in this chapter.
In chapter 3, the synthesis methods and characterization of the LTB and CTB nanoparticles are presented. The LTB nanoparticles doped with Cu, Ag and co-doped Cu-Ag are synthesized using solid state sintering technique and CTB nanoparticles doped with different concentrations of lanthanide ions such as Dy, Tm and Tb using solution combustion method. These two methods of synthesis are chosen for the present work, because of the fact that these methods are economical and can easily synthesized bulk amount of nanophosphors in very short period of time. The formation and structure of the synthesised LTB and CTB nanoparticles are confirmed using X-Ray diffraction patterns, TEM images and FTIR spectra. The LTB nanoparticles doped with metal ions such as Cu, Ag and Cu-Ag are successfully synthesized using solid state sintering method. The LTB nanoparticles doped with different concentrations of these dopants are synthesized using this method. The X-ray diffraction pattern of the synthesized LTB nanoparticles matches with the diffraction pattern of the JCPDS card no. 00-040-0505 with no additional peak within the resolution limit of the diffractometer. The particle size of the synthesized nanoparticles are calculated from the XRD using Scherrer’s formula and found to be 32 nm, 35 nm and 36 nm for LTB:Cu, LTB:Ag and LTB:CuAg nanoparticles respectively. The prepared LTB samples exhibits tetragonal structure with calculated unit cell volume 912.9057 Å$^3$, 918.4926 Å$^3$ and 924.7299 Å$^3$ for LTB:Cu, LTB:Ag and LTB:AgCu respectively. The unit cell volume of the LTB:Ag is larger than that of the LTB:Cu as ionic radius of Ag is larger than Cu ion. The TEM images of the LTB nanoparticles shows the particles are evidently clustered/aggregated spherical in shape with average particle size of 45 nm. The SAED pattern also confirms the crystalline nature of the LTB nanoparticles. The FTIR spectra of the LTB nanoparticles have four major absorption peaks at 1600-1200 cm$^{-1}$, 1500-700 cm$^{-1}$, 950-870 cm$^{-1}$ and 870-415 cm$^{-1}$ which 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. This also confirms the formation and bond structures of the LTB nanoparticles synthesized using sintering method.
The CTB nanoparticles doped with different concentrations of lanthanide ions such as Dy, Tm and Tb are successfully synthesized using solution combustion method using citric acid as the fuel. 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%) are synthesized. The XRD pattern of all the CTB nanoparticles doped Dy\(^{3+}\), Tm\(^{3+}\) and Tb\(^{3+}\) shows similar diffraction lines which matches with the JCPDS card no. 01-083-2025. The calculated average particle sizes are found to be around 20 nm for CTB:Dy and CTB:Tm while 25 nm for CTB:Tb having monoclinic crystal structure with space group P\(_{21}/n\) and space group no. 14. The unit cell volume of the CTB nanoparticles increases with the increased in doping concentration, which can be attributed due to incorporation of Dy\(^{3+}\), Tm\(^{3+}\) and Tb\(^{3+}\) ions respectively toward the lattice site of CTB. The TEM images of the CTB nanoparticles shows that the particles are evidently clustered/aggregated spherical in shape with average particle size of 25 nm for Dy and Tm doping while 35 nm for CTB doped with Tb. The selected area electron diffraction (SAED) pattern suggested the crystalline nature of the synthesized CTB nanoparticles which is also in agreement with the XRD pattern. The IR spectra of the CTB nanoparticle mainly have four active region of vibration modes of borate network such as 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.

The luminescence properties such as photoluminescence (PL), thermoluminescence (TL) and optically stimulated luminescence (OSL) of LTB nanoparticles doped with Cu, Ag and co-doped Cu, Ag are presented in chapter 4. The PL spectrum LTB:Ag nanoparticles have a broad emission peak at around 270 nm and excitation peak at around 205 nm which corresponds to the 4d\(^{10}\) \(\rightarrow\) 4d\(^9\)5s\(^1\)
transition of the Ag$^+$ ion. The LTB:Cu and LTB:CuAg nanoparticles did not show any particular PL excitation and emission peaks.

The effect dopant concentrations of Cu, Ag and co-doped Cu-Ag on the TL glow curves of the β-irradiated LTB nanoparticles are studied. The LTB:(0.05%)Cu has the maximum TL intensity among the different concentrations of Cu doping. The LTB:(1%)Ag gives the maximum TL intensity among different concentrations of Ag and LTB:(3%)Cu(1%)Ag has the maximum TL intensity among the Cu-Ag co-doped LTB nanoparticles. Concentration quenching phenomena is observed after 0.05 at wt.% of Cu for LTB:Cu nanoparticles and 1 at wt.% of Ag for LTB:Ag for LTB:Ag nanoparticles. The TL glow curve of the 400 mGy β irradiated LTB:(0.05%)Cu recorded at the heating rate of 1 K/s have three TL peaks at around 395 K, 465 K and 525 K in which the peak at 465 K is the most prominent and main dosimetric peak. For the LTB:(1%)Ag, the main dosimetric peak is at around 455 K with two shoulder peaks at around 365 K and 565 K respectively. But for the LTB:(3%)Cu(1%)Ag nanoparticles, the TL glow curve show two TL peaks at around 450 K and 525 K in which TL peak at 450 K is the main prominent dosimetric peak for this nanoparticle. The lower temperature peaks of the LTB:(0.05%)Cu and LTB:(1%)Ag are unstable and completely faded away after 16 hours. The kinetic parameters of the TL glow peaks of these nanoparticles are calculated using “tgcd” deconvolution technique, initial rise method and Chen’s peak shape method in which the evaluated kinetic parameters with these three different methods are found to be in agreement with each other. The lifetime of the main dosimetric peaks of the LTB nanoparticles are calculated and found to be 2.24, 11.35 and 0.71 years for the LTB:(0.05%)Cu, LTB:(1%)Ag and LTB:(3%)Cu(1%)Ag respectively which is quite stable. The β dose responses of the LTB nanoparticles are studied in the range of 20 mGy to 50 Gy. The LTB:(1%)Ag nanoparticle is found to have linear dose response in this range of study and will be useful in dosimetry applications. The LTB:(0.05%)Cu and LTB:(3%)Cu(1%)Ag are found to show superlinear and sublinear dose response respectively, in these range of study in which the two samples might be usable in dosimetry applications after proper calibration of the nanophosphors.
The CW-OSL decay curves of LTB:(0.05%)Cu, LTB:(1%)Ag and LTB:(3%)Cu(1%)Ag, measured at blue light stimulation time of 60 s, after irradiation with 400 mGy of β-dose follows non-first order kinetics. The CW-OSL decay curves of the LTB nanoparticles are fitted with the sum of three first order exponential decay curves having three different photo-ionization cross sections. The LM-OSL glow curves of the LTB:(1%)Ag and LTB:(3%)Cu(1%)Ag have calculated shape factor $\mu_g$ to be $\approx 0.77$ and $\approx 0.72$ which indicates the fact that the OSL glow curves of the two LTB nanoparticles follow non-first order kinetics. This observation is in agreement with the CW-OSL decay curve fitted as the sum of three first orders exponential decay curves. The TL glow curves of the LTB:(1%)Ag and LTB:(3%)Cu(1%)Ag nanoparticles are affected by optical bleaching showing the active participation of the TL glow peaks in the OSL process. The CW-OSL decay curves of the LTB:(1%)Ag and LTB:(3%)Cu(1%)Ag nanoparticles are also affected by optical bleaching in which the CW-OSL intensity decreases with the increases in bleaching time. The dose response of the synthesized LTB:(1%)Ag is found to be linear and super linear ($b=1.4$) for LTB: (3%)Cu(1%)Ag in the range of 20 mGy to 50 Gy of β dose. The wide range of dose linearity for low β- doses makes the LTB:(1%)Ag nanoparticle, a suitable candidate for OSL dosimeter. The fading characteristics of the CW-OSL decay curves of the LTB:(1%)Ag and LTB:(3%)Cu(1%)Ag nanoparticles are studied for 8 days. After 1 day the CW-OSL intensity of the LTB:(1%)Ag nanoparticles decreases about 30% from the CW-OSL intensity recorded just after the irradiation. It agrees with the observation that the lower temperature peak of the TL glow curve of the LTB:(1%)Ag faded completely after 16 hours. At the end of the 8 days the CW-OSL decreases about 10% from the CW-OSL intensity recorded after 1 day. In case of the LTB:(3%)Cu(1%)Ag sample, fading occurs more rapidly than that of the LTB:(1%)Ag sample. The CW-OSL decreases about 37% after the first day and about 28% after 8 days from the CW-OSL intensity recorded after 1 day. This shows that CW-OSL signal of the LTB:(1%)Ag nanoparticles is quite stable. The minimum detectable dose of the LTB nanoparticles are also calculated and found to be around 15 µGy. This shows that synthesized LTB nanoparticles will be useful in the lower dose dosimetry.
The luminescence properties such as photoluminescence (PL), thermoluminescence (TL) and optically stimulated luminescence (OSL) of CTB nanoparticles doped with Dy, Tm and Tb are presented in chapter 5. The photoluminescence excitation spectrum of CTB:Dy monitored at the wavelength of 572 nm show peaks at around 262 nm which may be associated with absorptions due to charge transfer state (CTS) because of Dy$^{3+}$– O$^{2-}$ interactions and four other peaks centered on 320 nm, 345 nm, 360 nm and 390 nm, which correspond to the transitions ($^6$H$_{15/2}$ → $^6$P$_{3/2}$), ($^6$H$_{15/2}$ → $^4$P$_{7/2}$), ($^6$H$_{15/2}$ → $^4$P$_{5/2}$) and ($^6$H$_{15/2}$ → $^4$F$_{7/2}$) respectively, typical of the Dy$^{3+}$ ions. The photoluminescence emission spectra of CTB:Dy for different doping concentrations of Dy$^{3+}$ excited with 262 nm and 345 nm respectively show bands centered at 480 nm and 574 nm owing to electronic transitions of $^4$F$_{9/2}$ → $^6$H$_{15/2}$ and $^4$F$_{9/2}$ → $^6$H$_{13/2}$, which is characteristic of Dy$^{3+}$ ions. The luminescence emission intensity of the samples excited with 262 nm (Dy-O) charge transfer shows more intense emission peaks compared with the emission excited with 374 nm. The photoluminescence excitation spectra of the CTB:Tm nanoparticles monitored at 451 nm has a broad band centered at around 355 nm which is associated with the $^3$H$_6$→$^1$D$_2$ transition of Tm$^{3+}$ . The emission spectrum of CTB:Tm excited with 355 nm different concentrations of Tm$^3$ shows emission band centered at around 451 nm which belongs to $^1$D$_2$→$^3$F$_4$ transitions of Tm$^{3+}$. The photoluminescence excitation spectra of the CTB:Tb nanoparticles monitored at 545 nm has a peak around 262 nm which represents the $4f^8$→$4f^75d^1$ broad band absorbability known as the Tb-O charge transfer peak and the three other peaks which are centered at 315 nm, 350 nm and 374 nm which is associated with the transitions from the $^7$F$_6$ ground state to the excited states $^5$D$_{1,0}$, $^5$G$_5$, and $^5$L$_{10}$ levels of Tb$^{3+}$. The photoluminescence emission spectra of CTB:Tb nanoparticles doped with different concentration of Tb$^{3+}$ excited with 262 nm and 374 nm shows most intense green emission band at around 545 nm which corresponds to $^5$D$_4$→$^7$F$_{5}$ transition and four other bands at around 420 nm, 485 nm (blue bands), 590 nm and 625 nm (yellow bands) belongs to the $^5$D$_j$→$^7$F$_j$ ($J = 0$ to 6), $^5$D$_4$→$^7$F$_6$, $^5$D$_3$→$^7$F$_4$ and $^5$D$_3$→$^7$F$_3$
transitions of Tb\(^{3+}\) respectively. The luminescence emission intensity of the samples excited with 262 nm (Tb-O) charge transfer shows eight fold intense compared with excitation \(f_{\text{f}}(374 \text{ nm})\).

The effect dopant concentrations of Dy, Tm and Tb on the TL glow curves of the X-ray irradiated CTB nanoparticles are studied. The CTB:(0.05\%)Dy has the maximum TL intensity among the different concentrations of Dy doping. The CTB:(0.05\%)Tm gives the maximum TL intensity among different concentrations of Tm and CTB:(1\%)Tb has the maximum TL intensity among the Tb doped CTB nanoparticles. Concentration quenching phenomenon is observed for the TL glow curves of CTB nanoparticles in which 0.05 at.wt\% of Dy and Tm are found to be the optimum dopant concentration of CTB doped with Dy and Tm while 1 at.wt.\% Tb is found to be the optimum concentration of Tb doping which gives the maximum TL intensity. The TL glow curve of the CTB:(0.05\%)Dy is deconvoluted into five individual glow peaks with maximum peak temperatures at around 410 K, 470 K, 525 K, 563 K and 593 K. The kinetic parameters calculated from the “tgcd” and Chen’s peak shape method is in agreement. The preannealing studies show presence of five peaks which is similar with “tgcd”, thus confirms that CTB:(0.05\%)Dy nanoparticles have five TL trap centers. The TL glow curve of the CTB:(0.05\%)Tm is also deconvoluted into four individual glow peaks with maximum peak temperatures at around 382 K, 418 K, 470 K and 550 K. For the CTB:(0.05\%)Tm also the kinetic parameters calculated from the “tgcd” and peak shape method are in agreement. The preannealing studies show presence of four peaks which is similar with “tgcd”, thus confirms that CTB:(0.05\%)Tm nanoparticles have four TL trap centers. The TL glow curve of CTB:(1\%)Tb nanoparticles is deconvoluted in five individual TL glow peaks with peak temperatures at 418 K, 548 K, 585 K, 625 K and 670 K. The kinetic parameters calculated from the CGCD and peak shape method are in agreement for the TL glow curves of CTB:(1\%)Tb nanoparticles. The preannealing studies show presence of five peaks which is similar with “tgcd” which confirms that the CTB:(1\%)Tb nanoparticles have five trap centers. The TL glow curves of the \(\gamma\)-irradiated CTB nanoparticles shows similar characteristics as that of the TL glow curves of X-ray irradiated CTB nanoparticles recorded at 5 K/s. \(\gamma\)-Dose response of the CTB nanoparticles are studied by irradiating the samples with Co-60.
\(\gamma\) source in the range of 1 Gy to 20 Gy. The dose responses for the dosimetric peaks of all the CTB nanoparticles (CTB:(0.05%)Dy, CTB:(0.05%)Tm and CTB:(1%)Tb) are found to be linear in this range of study. The fading characteristics of the TL signals are studied by irradiating several samples of equal weights of CTB:(0.05%)Dy, CTB:(0.05%)Tm and CTB:(1%)Tb with 6 Gy of X-ray dose and stored in dark at room temperature. The fading characteristics shows that TL signal of CTB:(1%)Tb is very stable and will be useful for applications in dosimetry.

The CW-OSL decay curves of the 6 Gy X-ray irradiated CTB nanoparticles are recorded using two types of stimulation light, one was blue LED light of wavelength 465 nm and the other was green LED light of wavelength 525 nm for same stimulation time of 150 seconds. The CW-OSL decay curves for both the blue and green light stimulation can be fitted with the sum of three first order exponential decay curves for the CTB nanoparticles doped with Dy, Tm and Tb. The CW-OSL intensity of the CTB nanoparticles with green light stimulation is very less in comparison to the CW-OSL intensity of the CTB nanoparticles with the blue light stimulation. The LM-OSL glow curves of the CTB:(0.05%)Dy and CTB:(0.05%)Tm are very less sensitive and did not show proper LM-OSL glow curve in this condition of study. For the case of CTB:(1%)Tb nanoparticles, the geometrical shape factor \(\mu_g\) of the recorded LM-OSL glow curve is evaluated and found to be ~0.79 which follows non-first order kinetics. The LM-OSL curve of the CTB:(1%Tb) could be approximated with the linear combination of three first-order components which is in agreement with the CW-OSL decay curves. The residual TL of the 6 Gy irradiated CTB nanoparticles are recorded after the CW-OSL measurement with blue light stimulation for 150 seconds acquiring time. The study shows that all the TL peaks are participated in the CW-OSL phenomenon for CTB:(0.05%)Dy and CTB:(0.05%)Tm nanoparticles with total loss of TL counts after CW-OSL are 16.51\% and 11.87\%. But for the case of CTB:(1%)Tb nanoparticles out of the five TL glow peaks, the first three lower temperature peaks; peak 1, peak 2 and peak 3 are affected by the CW-OSL measurements but it had no effect on the higher temperature TL peaks; peak 4 and peak 5. The CW-OSL decay curves of the CTB:(0.05%)Dy, CTB:(0.05%)Tm and CTB:(1%)Tb nanoparticles are faded up to about 55.68\%, 59.27\% and 37.91\% in 4 days which is little unstable but remains
almost constant after 22 days till the time it is studied that is 40 days. The CW-OSL decay curves of CTB:(1%)Tb nanoparticles are more stable than other samples.

Chapter 6, is the brief conclusion and summary of the important findings of the synthesis, characterization and luminescence studies of the LTB nanoparticles doped with Cu, Ag and co-doped Cu, Ag and CTB nanoparticles doped with Dy, Tm and Tb. Some of the future directions such as application of the synthesized nanoparticles in neutron dosimetry and proper studies of energy response of these nanophosphors are given in this chapter. The requirement of proper field test of the synthesized nanophosphors is also mention in this chapter.