CHAPTER 4: Phosphates

4.1. Introduction: Phosphates of Ga\(^{3+}\), Sb\(^{3+}\) and Bi\(^{3+}\) are of interest because of their potential technological applications [212-220]. For example, GaPO\(_4\) is a good piezo-electric material whereas SbPO\(_4\) and BiPO\(_4\) are used as catalysts as well as in optical/photonic devices [221-225]. Doping lanthanide ions in such phosphates is an attractive option for making materials with multi-functional applications. Under ambient conditions, GaPO\(_4\) exists in hexagonal form whereas SbPO\(_4\) and BiPO\(_4\) adopt a monoclinic structure. BiPO\(_4\) is also known to exist in hexagonal form [226, 227]. Unlike this, LnPO\(_4\) (Ln = lanthanide) exist mainly in two crystalline modifications, viz. monazite and xenotime [228]. Monazite structure is adopted by lanthanide phosphates with relatively larger lanthanide ions (i.e., La\(^{3+}\)-Gd\(^{3+}\)) while xenotime structure is formed by smaller lanthanide ions (i.e., Tb\(^{3+}\)-Lu\(^{3+}\)). Essential difference in both the structures is that in the xenotime structure, Ln\(^{3+}\) ions exist as regular LnO\(_8\) polyhedra whereas in the monazite structure, lanthanide ions (Ln\(^{3+}\)) exist as LnO\(_9\) polyhedra [228]. For making lanthanide ions based luminescent materials using phosphate hosts like GaPO\(_4\), SbPO\(_4\) and BiPO\(_4\), it will be ideal if solid solution formation between these phosphates and lanthanide phosphates exist. The major problem with the solid solution formation in this system is the large difference in the ionic radii of the cations and difference in their coordination numbers, particularly for Ga\(^{3+}\) and Sb\(^{3+}\) ions in GaPO\(_4\) and SbPO\(_4\) respectively. Further, the solubility product values are significantly different for GaPO\(_4\) (10\(^{-21}\)), BiPO\(_4\) (10\(^{-23}\)) and LnPO\(_4\) (~10\(^{-26}\) to 10\(^{-25}\)) [229-231] which prevent the formation of solid solution between these compounds through co-precipitation techniques. However, if the metal phosphate nanoparticles are prepared under alkaline conditions in aqueous or alcoholic solutions, the surface hydroxyl groups on nanoparticles may undergo ion exchange with lanthanide ions. Such an ion exchange process will lead to the formation of nanoparticles.
having surface lanthanide ions. This is particularly valid for GaPO$_4$, as the Ga$^{3+}$ ionic radius is much smaller as compared to lanthanide ions, besides significant difference in the coordination numbers around the cations. Situation is slightly different for SbPO$_4$ nanomaterials as the ionic radius of Sb$^{3+}$ (0.76Å) [177] is expected to be comparable with that of lanthanide ions with coordination number four, although lanthanide ions with such low coordination are not commonly observed. In contrast to this, Bi$^{3+}$ ions in BiPO$_4$ have comparable ionic size to that of lanthanide ions and crystal structure of BiPO$_4$ is similar to that of lanthanide phosphates, there by facilitating the improved solubility of lanthanide ions in BiPO$_4$.

In the present study Eu$^{3+}$, Ce$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Sm$^{3+}$ ions were chosen for doping in the above mentioned hosts. The luminescence characteristics of Eu$^{3+}$ with respect to different environments are well understood and hence can be used as a probe to monitor the structural changes taking place with a host lattice. The ions Ce$^{3+}$ and Tb$^{3+}$ are known to have strong absorption in the UV region with Tb$^{3+}$ ions emitting strongly in the visible region. In addition Ce$^{3+}$ is an efficient sensitizer to Tb$^{3+}$ (due to energy transfer from Ce$^{3+}$ to Tb$^{3+}$ ions) and therefore materials doped with Ce$^{3+}$ and Tb$^{3+}$ have been developed to generate efficient green light for display applications. This energy transfer between Ce$^{3+}$ and Tb$^{3+}$ ions is very sensitive to the crystal structure of the host, surface modification, etc. [112, 113, 232]. For example in CePO$_4$:Tb$^{3+}$ and CePO$_4$:Dy$^{3+}$ nanomaterials strong energy transfer has been observed from Ce$^{3+}$ to Tb$^{3+}$ or Dy$^{3+}$ ions. However, in Ce$^{3+}$ co-doped YAG:Tb$^{3+}$ nanoparticles, energy transfer occurs from Tb$^{3+}$ to Ce$^{3+}$ [94]. Furthermore, in Ce$^{3+}$ co-doped Y$_2$Sn$_2$O$_7$:Tb$^{3+}$ nanoparticles, strong energy transfer from Ce$^{3+}$ to Tb$^{3+}$ occurs only after covering the nanoparticles with SiO$_2$ [233]. This has been attributed to the diffusion of lanthanide ions towards the interface region between Y$_2$Sn$_2$O$_7$ nanoparticles and silica.
This chapter is divided into three sections. The first section deals with structural and luminescence properties of GaPO₄ nanoparticles having different concentration of Eu³⁺ ions. The results obtained from this study is used to understand the luminescence properties of other lanthanide ions (Tb³⁺, Dy³⁺, Er³⁺, etc.) doped nanoparticles. The second section describes synthesis and optical properties of lanthanide doped SbPO₄ nanomaterials. Incorporation of lanthanide ions in such low symmetry environments (coordination number 4) and their luminescence properties are discussed. Vibrational spectroscopy has been used to confirm incorporation of lanthanides ions in the SbPO₄ host. Changes in the experimental conditions like synthesis temperature, doping concentration and varying the relative volume of solvent, etc., on the vibrational and luminescence properties from such nanomaterials are investigated. Luminescence properties of these nanomaterials are compared with the lanthanide ions doped bulk materials obtained by solid-state reaction. Energy transfer between Ce³⁺ and Tb³⁺ ions and its effect on the decay profiles of the excited state of Tb³⁺ ions in SbPO₄ host is also discussed in this section. In the third section synthesis and characterization of lanthanide doped BiPO₄ nanomaterials is discussed in detail. Lanthanide ions doped BiPO₄ nanomaterials with different crystal structures have been prepared at a relatively low temperatures and the effect of crystal structure on luminescence properties of the lanthanide ions is also investigated.

4.2. Studies on GaPO₄ and lanthanide ions containing GaPO₄ nanomaterials: GaPO₄ nanoparticles were prepared at 140°C in glycerol by precipitating Ga³⁺ with ammonium dihydrogen phosphate. For europium containing samples, appropriate concentration of Eu³⁺ ions is also used along with Ga³⁺ ions.

4.2.1. XRD, FT-IR and TEM study: XRD patterns of GaPO₄ nanoparticles containing 0, 2.5 and 5 at % Eu³⁺ ions are shown Fig.54. For the purpose of comparison XRD pattern of a standard hexagonal GaPO₄ (JCPDS file no. 080497) is also included in this figure. The
diffraction patterns from the GaPO$_4$ nanoparticles match well with the pattern reported in JCPDS data. The lattice parameters were calculated and are found to be $a = 4.900(2)$ Å and $c = 11.041(3)$ Å with a unit cell volume $229.5(2)$ Å$^3$ for un-doped GaPO$_4$ nanoparticles. The lattice parameters are unchanged with increase in Eu$^{3+}$ content in the sample suggesting that GaPO$_4$ lattice is unaffected by increase in Eu$^{3+}$ concentration in the sample.

![Figure 54](image)

**Fig.54.** XRD patterns of (a) hexagonal GaPO$_4$ standard corresponding to JCPDS file no. 080497 (b) GaPO$_4$ nanoparticles, (c and d) GaPO$_4$ nanoparticles with 2.5 and 5 at % Eu$^{3+}$, respectively.

The average crystal size of GaPO$_4$ nanoparticles was calculated from the line width of highest intense XRD peak by using Debye–Scherrer formula and is found to be $\sim 30$ nm. The particle size is also unaffected by increasing the Eu$^{3+}$ contents in GaPO$_4$ samples. From the XRD results, it can be inferred that Eu$^{3+}$ ions are not replacing Ga$^{3+}$ ions in GaPO$_4$ lattice. Had it been the case, the lattice parameters of GaPO$_4$ nanoparticles would have increased significantly due to the higher ionic radii of Eu$^{3+}$ (0.947Å) compared to Ga$^{3+}$ (0.62Å) [172]. In order to characterize the nanocrystalline nature of the above samples detailed TEM studies have been carried out.
Figure 55 shows the representative TEM image and selected area electron diffraction (SAED) pattern from as prepared GaPO$_4$ nanoparticles. The particle sizes are in the range of 25-35 nm. There are also some particle aggregates having size in the range of 40 - 65 nm. The SAED patterns consist of dots, which are characteristic of randomly oriented single crystalline nanoparticles. The TEM images of 2.5 at % Eu$^{3+}$ containing GaPO$_4$ sample is comparable with that of the undoped GaPO$_4$ nanoparticles (not shown). Based on the TEM studies it is inferred that as prepared Eu$^{3+}$ containing sample consists of crystalline GaPO$_4$ nanoparticles of average size of 30 nm. This suggests that Eu$^{3+}$ doping has no effect on the particle size of GaPO$_4$ nanoparticles. Even though the particle size and crystallinity of the GaPO$_4$ nanoparticles containing different amounts of Eu$^{3+}$ ions are same, it is quite possible that the photoluminescence properties of Eu$^{3+}$ ions can change significantly depending on the interaction of Eu$^{3+}$ ions with the GaPO$_4$ nanoparticles. To understand such interactions, detailed luminescence studies have been carried out on these samples.

Fig.55. TEM images of (a) GaPO$_4$ nanoparticles. The selected area electron diffraction pattern from nanoparticles is shown in Fig.55 (b)

**4.2.2. Luminescence studies:** Figure 56 shows the emission spectra from GaPO$_4$ nanoparticles containing 2.5 and 5 at % Eu$^{3+}$ along with that from pure EuPO$_4$ nanoparticles obtained after excitation at 260 nm. All the patterns are characterised by transitions from $^5D_0$
level to $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ levels of Eu$^{3+}$ ions. The transitions $^5D_0\rightarrow^7F_1$ and $^5D_0\rightarrow^7F_2$ are purely magnetic and electric dipole allowed respectively. The relative intensity ratio of $^5D_0\rightarrow^7F_2$ to $^5D_0\rightarrow^7F_1$ transition, known as the asymmetric ratio of luminescence, is a very sensitive parameter which depends on the environment around Eu$^{3+}$ ions [234, 235]. The value is found to be 2.2 for 2.5 at % Eu$^{3+}$ containing sample. With increasing Eu$^{3+}$ content (i.e. for 5 at % Eu$^{3+}$ containing sample) the asymmetric ratio decreases to 1.0 (Fig.56 (b)). Significant change in the asymmetric ratio of luminescence indicates a drastic change in the environment around Eu$^{3+}$ ions, which could be due to the formation of separate Eu$^{3+}$ containing phase. It can be either the pure EuPO$_4$ or a complex of Eu$^{3+}$ formed with ligands (glycerol) present in the reaction medium.

![Emission spectrum from GaPO$_4$ nanoparticles containing (a) 2.5 at % and (b) 5 at % Eu$^{3+}$ ions. The corresponding pattern from EuPO$_4$ nanoparticles is shown in Fig.56 (c). All samples were excited at 260 nm.](image)

To check this aspect, emission spectrum from pure EuPO$_4$ sample prepared in an identical method as that used for GaPO$_4$ nanoparticles is shown in Fig.56 (c). The pattern is same as that of 5 at % Eu$^{3+}$ containing GaPO$_4$ nanoparticles. The asymmetric ratio of luminescence is
found to be 0.97. A comparison of the emission spectrum shown in Fig.56 (b and c) suggests that Eu$^{3+}$ ions exist as a separate EuPO$_4$ phase in 5 at % Eu$^{3+}$ containing sample. However, for 2.5 at % Eu$^{3+}$ containing sample, the asymmetric ratio of luminescence is quite different from EuPO$_4$ phase, suggesting that Eu$^{3+}$ ions are in a different environment in GaPO$_4$ nanoparticles containing 2.5 at % Eu$^{3+}$. Presence of Eu$^{3+}$ ions during precipitation reaction to form GaPO$_4$ can either lead to the formation of europium hydroxide phase or result in replacing protons of the surface hydroxyl groups attached to surface gallium or phosphorus species present on the nanoparticles.

In order to check the first possibility, Eu$^{3+}$ ions were subjected to hydrolysis in glycerol medium using urea as the reagent for hydroxide formation (urea and not ammonium dihydrogen phosphate was used for precipitation to prevent the formation of EuPO$_4$ phase). Emission spectrum from the sample obtained after 260 nm excitation is shown in Fig.57. The asymmetric ratio of luminescence is found to be 4.2 which is significantly higher than the value 2.2 observed from GaPO$_4$ nanoparticles containing 2.5 at % Eu$^{3+}$ ions. These data suggest that Eu$^{3+}$ ions do not exist as europium hydroxide phase along with the GaPO$_4$ nanoparticles.

![Fig.57 Emission spectrum of europium hydroxide sample prepared in glycerol medium by the identical method as that employed for GaPO$_4$ and EuPO$_4$ nanoparticles, except that urea rather than ammonium dihydrogen phosphate was used to create the alkaline environment and to prevent the formation of EuPO$_4$ phase.](image-url)
The second possibility is the exchange of protons of OH groups attached to phosphorus or gallium ion at the surface of GaPO\textsubscript{4} nanoparticles. Such ion exchange process is expected to affect the electronic environment around P and this will be reflected in the $^{31}$P Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectrum of the samples. Hence the $^{31}$P MAS NMR patterns of the samples were recorded and are described below.

4.2.3 $^{31}$P MAS NMR studies: Figure 58 shows the $^{31}$P MAS NMR patterns of GaPO\textsubscript{4} nanoparticles containing different amounts of Eu$^{3+}$ ions. As prepared GaPO\textsubscript{4} sample showed a sharp peak around $\delta$ -10 ppm with weak shoulder around -6 ppm in the $^{31}$P MAS NMR spectrum (Fig.58 (a)). Based on the previous $^{31}$P MAS NMR studies on GaPO\textsubscript{4} and Al$_{x}$Ga$_{1-x}$PO\textsubscript{4} samples [236, 237] the peak at -10 ppm has been attributed to the P structural units having four Ga$^{3+}$ ions as its next nearest neighbors (first neighbor being the oxygen atom). The weak shoulder has been attributed to P structural units existing at the surface of the nanoparticles which have got linkages with the OH groups. Shoulder peak is more broadened compared to the main peak, due to the strong dipolar interaction between $^{31}$P and $^1$H nuclei.

With incorporation of 2.5 at % Eu$^{3+}$, the peak maximum of the main and shoulder peaks remained same, however their line widths are higher compared to GaPO\textsubscript{4} nanoparticles (Fig.58 (b)). With increase in Eu$^{3+}$ concentration, the line width of the peak increases and the shoulder is merged with the main peak around -10 ppm (Fig.58 (c and d)) due to increased line broadening. The peak maximum is found to be same for all the samples confirming that neither there is any solid solution formation between GaPO\textsubscript{4} and EuPO\textsubscript{4} nor there is any formation of P-O-Eu$^{3+}$ linkages. Broadening of the peaks can be attributed to the existence of paramagnetic europium species along with the GaPO\textsubscript{4} nanoparticles. EuPO\textsubscript{4} phase formation, as revealed by luminescence studies for samples containing higher Eu$^{3+}$ contents (5% or more), could not be confirmed by $^{31}$P MAS NMR as it showed no resonance signal due to the higher extent of paramagnetic broadening brought about by the presence of four europium...
ions as next nearest neighbors around P in orthophosphate structural units. Significantly different values of solubility product for Ga(OH)$_3$ (7.3 x 10$^{-36}$) and Eu(OH)$_3$ (9.4 x 10$^{-27}$) further suggests that the ion exchange process is quite favorable in these system [177].

Fig.58. $^{31}$P MAS NMR patterns of GaPO$_4$ nanoparticles containing (a) 0 at %, (b) 2.5 at %, (c) 5 at % and (d) 10 at % Eu$^{3+}$ ions. Samples were spun at 10000Hz.

To get insight regarding the electronic environment around P in these samples, principal values of the $^{31}$P chemical shift anisotropy tensor ($\delta_{11}$, $\delta_{22}$ and $\delta_{33}$) for GaPO$_4$ nanoparticles containing different amounts of Eu$^{3+}$ ions have been calculated from the intensity of spinning sidebands observed in the $^{31}$P MAS NMR patterns (recorded at a spinning speed of 5000 Hz) (Table 6). The anisotropy parameter has been calculated from the difference of $\delta_{11}$ and $\delta_{33}$ values and found to be around 20 ppm for GaPO$_4$ and 27 ppm for 2.5 at % Eu$^{3+}$ containing GaPO$_4$ nanoparticles. For 5 and 10 at % Eu$^{3+}$ containing sample, the
chemical shift anisotropy is much higher and the value significantly increases with increase in Eu$^{3+}$ content in the sample (viz. Table 6). Comparable values of chemical shift anisotropy for both GaPO$_4$ and 2.5 at % Eu$^{3+}$ incorporated GaPO$_4$ nanoparticles, further confirm the absence of P-O-Eu$^{3+}$ linkages in the sample. In other words Eu$^{3+}$ ions are not in the near vicinity of P and must be in the vicinity of Ga$^{3+}$ ions, as Ga-O-Eu linkages formed by undergoing surface ion exchange with protons of the Ga-OH linkages. For GaPO$_4$ nanoparticles with higher Eu$^{3+}$ concentrations (5 at % and more), there is an increase in fluctuating magnetic field created around P by paramagnetic EuPO$_4$ nanoparticles. Similar increase in the side band intensities and anisotropy values are also observed in $^{29}$Si and $^{27}$Al MAS NMR patterns of alumino silicates containing paramagnetic iron compounds [238, 239]. A schematic diagram showing the ion exchange process leading to the formation of Ga-O-Eu linkages is shown in Fig.59. No separate peaks corresponding to EuPO$_4$ phase is seen in the XRD patterns for sample corresponding to more than 2.5 atom % Eu$^{3+}$. This is because of its relatively smaller concentration and poor crystallinity associated with its nanophase nature.

Table 6. The anisotropy parameter ($\Delta\delta$) obtained form the components of the chemical shift tensor ($\delta_{11}$, $\delta_{22}$ and $\delta_{33}$) which are calculated from the side band intensities observed form the $^{31}$P MAS NMR patterns of GaPO$_4$ sample containing different amounts of Eu$^{3+}$ ions. The line width of the peak ($\Gamma$) is also given in the table. Error in the chemical shift values is ±1 ppm.

| Structural Configuration of $^{31}$P | Value of $\delta_{iso}$ (ppm) | Value of $\Gamma$ (Hz) | Value of $\delta_{11}$ (ppm) | Value of $\delta_{22}$ (ppm) | Value of $\delta_{33}$ (ppm) | Value of $\Delta\delta$ (ppm) | $|\delta_{33}-\delta_{11}|$ |
|-----------------------------------|-----------------------------|---------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| GaPO$_4$                          | -10                         | 344                 | 2                          | -14                         | -18                         | 20                          | 20                          |
| GaPO$_4$ with 2.5 at % Eu$^{3+}$  | -10.3                       | 472                 | 7                          | -17                         | -20                         | 27                          | 27                          |
| GaPO$_4$ with 5 at % Eu$^{3+}$    | -10.3                       | 516                 | 21                         | -23                         | -29                         | 50                          | 50                          |
| GaPO$_4$ with 10 at % Eu$^{3+}$   | -10.3                       | 626                 | 29                         | -24                         | -36                         | 65                          | 65                          |
Fig. 59. Schematic diagram of Eu$^{3+}$ species present on the surface of the GaPO$_4$ nanoparticles.

For understanding the nature of interaction of ligands (glycerol molecule) with the surface Ga$^{3+}$/Eu$^{3+}$ species present in GaPO$_4$ nanoparticles, FT-IR spectra were recorded for both GaPO$_4$ nanoparticles and GaPO$_4$ nanoparticles containing 2.5 at % Eu$^{3+}$ ions and are shown in Fig. 60. Both the patterns are identical with peak positions around 3403, 2948, 2117, 2356 and 1654 cm$^{-1}$ as can be seen from Fig. 60. In fact, the spectra for the 5 and 10 atom % Eu$^{3+}$ containing samples are also same as that of undoped GaPO$_4$ nanoparticles. The peaks centered around 3403 and 1654 cm$^{-1}$ correspond to stretching and bending vibrations respectively of O-H groups present on the surface of the nanoparticles as well as from glycerol molecule [240]. The less intense peak ~ 2948 cm$^{-1}$ is assigned to asymmetric and symmetric stretching vibrations of C-H linkages of the stabilizing glycerol molecules. The weak peaks around 2117 and 2356 cm$^{-1}$ can be considered as the overtones of the $\delta$(OH) bending vibrations [241]. There is no change in the line shape and peak positions of the peaks corresponding to the different vibrational modes of the ligand molecules present with both undoped and 2.5 at % Eu$^{3+}$ containing GaPO$_4$ nanoparticles. This suggests that Eu$^{3+}$ ions do
not have strong interaction with the ligand molecules. Hence from the luminescence, FT-IR and $^{31}$P MAS NMR spectrum, it is confirmed that up to 2.5 at % Eu$^{3+}$ containing GaPO$_4$ nanoparticles, Eu$^{3+}$ replaces protons of the Ga-OH linkages, forming Ga-O-Eu type of linkages and beyond which separate EuPO$_4$ phase is formed.

![FT-IR Spectrum](image)

Fig.60. FT-IR spectrum of GaPO$_4$ nanoparticles containing 0 % and 2.5 at % Eu$^{3+}$

4.3. Studies on Antimony phosphate nanomaterials: Antimony phosphate nanomaterials were prepared at 130°C by precipitating Sb$^{3+}$ using ammonium dihydrogen phosphate in ethylene glycol, glycerol and mixture of them.

4.3.1. Effect of ethylene glycol to glycerol ratio on size and shape of SbPO$_4$:Ln nanomaterials: Figure 61 shows XRD patterns of as prepared SbPO$_4$ sample, obtained by using pure glycerol, mixtures of glycerol and ethylene glycol and pure ethylene glycol. For samples prepared in glycerol as well as mixture of glycerol and ethylene glycol, crystalline SbPO$_4$ with monoclinic structure has been observed. It should be noted here that for samples prepared in pure ethylene glycol, no sharp peak characteristic of crystalline material is observed revealing that reaction in pure ethylene glycol leads to the formation of an amorphous product. Average crystallite sizes as calculated from the line width of the XRD
peaks are found to decrease with increase in ethylene glycol content in the reaction medium. Table 7 shows the variation in average crystallite size as a function of relative amounts of ethylene glycol and glycerol in the reaction medium. From these results, it is inferred that the average crystallite size can be tuned by varying the relative amounts of ethylene glycol and glycerol in the reaction medium. The observed variation in the crystallite size with change in the relative concentration of the solvent has been explained based on the increase in viscosity of the medium with increase in the relative concentration of glycerol and associated increase in growth rate. XRD patterns are least square fitted to determine the lattice parameters. The values for un-doped SbPO$_4$ samples are $a = 5.099(1)$ Å, $b = 6.767(2)$ Å, $c = 4.749(1)$ Å with $\beta = 94.73$. Corresponding values for the 5% Tb$^{3+}$ doped nanoparticles are $a = 5.093(1)$ Å, $b = 6.769(2)$ Å, $c = 4.733(1)$ Å with $\beta = 94.69$. There is no significant change in the values of lattice parameters for both doped and un-doped samples. This can be attributed to the comparable ionic radii of Sb$^{3+}$ and Tb$^{3+}$ under a coordination number of four. In order to check the nature of amorphous product obtained when pure ethylene glycol is used as the solvent, IR patterns were recorded for the amorphous product and it is compared with the patterns obtained from crystalline SbPO$_4$ sample. Figure 62 shows IR spectra of as prepared SbPO$_4$ sample obtained by using pure ethylene glycol, pure glycerol and a mixture of glycerol and ethylene glycol (10 ml each).

Table 7. Effect of variation volume of solvents on the average crystallite size of SbPO$_4$ nanomaterials.

<table>
<thead>
<tr>
<th>Volume of glycerol (ml)</th>
<th>Volume of ethylene glycol (ml)</th>
<th>Average crystallite size (nm)</th>
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<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>46</td>
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<tr>
<td>10</td>
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<td>8</td>
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<td>0</td>
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Fig. 61. XRD Patterns of SbPO$_4$:Tb$^{3+}$ nanomaterials synthesized from (a) 20 ml glycerol, (b) 10 ml ethylene glycol and 10 ml glycerol, (c) 12 ml ethylene glycol and 8 ml glycerol and (d) 20 ml ethylene glycol.

Fig. 62. FT-IR Spectra of SbPO$_4$:Tb$^{3+}$ samples obtained in (a) ethylene glycol medium, (b) glycerol medium and (c) mixture of ethylene glycol and glycerol medium (10 ml each).
All the patterns were characterized by three intense peaks centered around 958, 1040 and 1135 cm$^{-1}$. Based on previous investigations [242-244] these peaks have been assigned to three non-degenerate P-O stretching vibrations of P-O-Sb$^{3+}$ linkages. The peaks around 640 and 590 cm$^{-1}$ have been attributed to the stretching vibration of Sb-O linkages present in P-O-Sb$^{3+}$ linkages [244]. Peaks are slightly broadened in the case of amorphous product, indicating the higher extent of disorder present in the sample. The FT-IR pattern indicates that the product obtained from pure ethylene glycol is amorphous SbPO$_4$:Tb$^{3+}$.

Figure 63 shows the TEM images of SbPO$_4$: Tb$^{3+}$ samples prepared by using ethylene glycol-glycerol mixture. The images indicate the presence of both nanoribbons and nanoparticles of SbPO$_4$: Tb$^{3+}$. The ribbons have length and width in the ranges of 500-700 and 100-200 nm, respectively (Fig.63 (a)). The images also have very fine nanoparticles of the size varying between 2 and 5 nm Fig.63 (b). Selected area electron diffraction patterns of both nanoribbons and particles showed crystalline nature of the samples (Fig.63 (c)). Further symmetry in the SAED patterns indicate the preferential orientation/alignment of the nanoribbons existing in the sample. This is also in agreement with the powder XRD results (Fig.61). High-resolution image from a nanoparticle is shown in Fig.63 (d). The line spacing of $3.39 \pm 0.05$ Å between the lattice fringes matches well with the distance between the (020) planes of SbPO$_4$ lattice. Depending on the relative percentages of ethylene glycol and glycerol, the tunability in the morphology of SbPO$_4$ can be achieved. For example, carrying out the reaction in pure ethylene glycol leads to the formation of very small particles of SbPO$_4$ whereas carrying out the reaction in pure glycerol yields primarily nanoribbons. Anisotropic growth mechanism generally leads to the formation of nanorods or nanoribbons whereas the isotropic growth mechanism gives nanoparticles. This change in morphology has been again attributed to the wide difference in the viscosity of ethylene glycol and glycerol. Lower viscosity of ethylene glycol favors a faster diffusion of the precursor ions to the
growth centre compared to higher viscosity glycerol. This leads to the isotropic growth of the material in ethylene glycol compared to glycerol.

Fig. 63. TEM images of (a) SbPO₄: Tb³⁺ nanoribbons and (b) SbPO₄: Tb³⁺ nanoparticles. The selected area electron diffraction pattern from the sample and the high resolution TEM image of a nanoribbon is shown in Fig. 63 (c and d) respectively.

4.3.2 Luminescence studies on SbPO₄: Ln nanoparticles/ nanoribbons: Luminescence property of these nanomaterials needs to be understood before incorporating them into different matrices like glassy materials or thin films for various optical applications. Figure 64(a and b) shows the emission spectra of SbPO₄: Eu³⁺ (5%) and SbPO₄: Tb³⁺ (5%) nanoparticles/ nanoribbons. For Eu³⁺ doped samples, the spectrum consists of mainly two peaks around 590 and 616 nm. The peak around 590 nm is characteristic of magnetic dipole (⁵D₀→⁷F₁) transition and that around 616 nm is characteristic of electric dipole (⁵D₀→⁷F₂) transition. Asymmetric ratio of luminescence (defined as the ratio of the relative intensity of
$^{5}D_0 \rightarrow ^{7}F_2$ to $^{5}D_0 \rightarrow ^{7}F_1$ transition) is calculated from the emission spectrum and found to be 1.14. The excitation spectrum corresponding to 616 nm emission is shown as an inset in Fig.64 (a). In addition to the sharp peaks characteristic of intra 4f transitions of Eu$^{3+}$ ions, a broad asymmetric peak centered on 250 nm with a shoulder around 220 nm is observed in the excitation spectrum. Based on detailed luminescence studies on Eu$^{3+}$ doped and un-doped SbPO$_4$ nanoparticles/ nanoribbons, the broad peak centered on 250 nm has been attributed to the Eu-O charge transfer process and the weak shoulder around 220 nm to the host absorption. Eu$^{3+}$ emission has been observed from these samples after excitation at 250 and 220 nm indicating that there is energy transfer from the host to Eu$^{3+}$ ions.

![Emission spectrum of (a) SbPO$_4$:Eu$^{3+}$, (b) SbPO$_4$:Tb$^{3+}$ nanoparticles/ nanoribbons obtained after 220 nm excitation. Insets show corresponding excitation spectrum monitored at 616 and 545 nm emission.](image)

For Tb$^{3+}$ doped SbPO$_4$ nanoparticles/ nanoribbons (Fig.64 (b)), strong Tb$^{3+}$ emission characteristic of $^5D_4 \rightarrow ^7F_3$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_5$ and $^5D_4 \rightarrow ^7F_6$ transitions have been
observed after excitation at 250 and 220 nm. Excitation spectrum corresponding to 545 nm emission from these nanoparticles/nanoribbons is shown as an inset in Fig.64 (b). Along with less intense sharp peaks characteristic of intra 4f transitions of Tb$^{3+}$ ions, broad peak around 250 nm, which is characteristic of 4f→5d transition of Tb$^{3+}$ ions is also observed. The host absorption around 220 nm characteristic of SbPO$_4$ is not clearly observed as it is masked under the intense 4f→5d transition peak. The intensity of 250 nm peak increases with increasing Tb$^{3+}$ concentration in SbPO$_4$ nanoparticles/nanoribbons.

To confirm incorporation of lanthanide ions in the SbPO$_4$ host, pure EuPO$_4$ and TbPO$_4$ samples were prepared in a manner identical to the synthesis of SbPO$_4$:Eu$^{3+}$ and SbPO$_4$:Tb$^{3+}$. No emission could be seen from TbPO$_4$ sample under all excitation wavelengths, whereas weak emission with asymmetric ratio of luminescence 0.78 has been observed from EuPO$_4$ sample (Fig.65).

![Emission spectrum of EuPO$_4$ sample obtained after 250 nm excitation.](image)

Fig.65. Emission spectrum of EuPO$_4$ sample obtained after 250 nm excitation.

Poor emission from these samples has been attributed to the significant quenching due to decreased Eu$^{3+}$-Eu$^{3+}$ distance brought about by high lanthanide ion concentration. The asymmetric ratio of luminescence, which is very sensitive to the Eu$^{3+}$ local environment, is quite different for EuPO$_4$ (0.78) as compared to SbPO$_4$:Eu$^{3+}$ (1.14). Observation of strong Eu$^{3+}$ and Tb$^{3+}$ emission from SbPO$_4$:Eu$^{3+}$ and SbPO$_4$:Tb$^{3+}$ along with quite different values of
asymmetric ratios of luminescence for SbPO$_4$:Eu$^{3+}$ and EuPO$_4$ samples confirm that no separate EuPO$_4$/ TbPO$_4$ phase is formed, instead lanthanide ions like Tb$^{3+}$ and Eu$^{3+}$ are incorporated in SbPO$_4$ host. Had these ions formed separate phase, strong Tb$^{3+}$ and Eu$^{3+}$ emission would not have been observed from the lanthanide ions doped SbPO$_4$ samples. Final confirmation for the lanthanide ion incorporation in the SbPO$_4$ host comes from the lifetime values of $^5$D$_{0}$ level of Eu$^{3+}$ in SbPO$_4$:Eu$^{3+}$ and EuPO$_4$. The $^5$D$_{0}$ lifetime of Eu$^{3+}$ is 2.0 ms (97%) and 0.004 ms (3%) for SbPO$_4$:Eu$^{3+}$ and the corresponding values are 0.8 ms (73%) and 0.42 ms (27%) for EuPO$_4$. Significantly higher $^5$D$_{0}$ lifetime value corresponding to Eu$^{3+}$ ion in SbPO$_4$:Eu$^{3+}$ compared to that of EuPO$_4$ further substantiate the fact that Eu$^{3+}$ ions are incorporated in the SbPO$_4$ host and not existing as separate EuPO$_4$.

With a view to compare the photoluminescence intensities of SbPO$_4$:Ln$^{3+}$ nanoparticles/ nanoribbons with that of bulk materials, SbPO$_4$:Eu$^{3+}$ and SbPO$_4$:Tb$^{3+}$, bulk materials were prepared by solid-state reaction between Sb$_2$O$_3$ and ammonium dihydrogen phosphate at 500°C. XRD patterns of the reaction product confirmed formation of crystalline SbPO$_4$. Figure 66 shows the emission and excitation spectra from these samples. For the same amount of sample, photoluminescence intensities of bulk materials are comparable with that of nanomaterials. (Host absorption around 220 nm is more clearly seen in the inset of Fig.66 (a)). Based on these results it is inferred that the luminescent SbPO$_4$ nanomaterials prepared at low temperature are equally good as bulk materials and has an added advantage of dispersability in methanol and water.

Luminescence measurements were also carried out for SbPO$_4$ nanoparticles/ nanoribbons as a function of Tb$^{3+}$ doping concentration. Figure 67 shows the emission spectrum from SbPO$_4$ nanoparticles/ nanoribbons containing different amounts of Tb$^{3+}$ ions and excited at 250 nm. The emission intensity is maximum for 2 atom % Tb$^{3+}$ doped samples and it systematically decreased with further increasing Tb$^{3+}$ concentration due to
concentration quenching. Tb\(^{3+}\) luminescence improves by co-doping of Ce\(^{3+}\) in SbPO\(_4\):Tb\(^{3+}\) nanomaterials. This has been attributed to the energy transfer from Ce\(^{3+}\) to Tb\(^{3+}\) ions in the lattice. In the following section, structure, morphological and luminescence characteristic of Ce\(^{3+}\) co-doped SbPO\(_4\):Tb\(^{3+}\) nanomaterials are discussed.

Fig.66. Emission spectrum of (a) SbPO\(_4\): Eu\(^{3+}\) and (b) SbPO\(_4\): Tb\(^{3+}\) bulk materials prepared by solid state reaction (excitation wavelength was 220 nm). Insets show corresponding excitation spectrum monitored at 616 and 545 nm emission.

Fig.67. Emission spectra of SbPO\(_4\) nanoparticles/ nanoribbons doped with 1, 2, 2.5, and 5 at % Tb\(^{3+}\) ions. Samples were excited at 250 nm.
4.3.3 Studies on Ce$^{3+}$ co-doped SbPO$_4$:Tb$^{3+}$ nanomaterials and their dispersion in silica:

Figure 68 shows TEM images of SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) samples dispersed in SiO$_2$. The ribbons are shown in Fig.68 (a). Their length and width are in the range of 700-800 and 20-50 nm, respectively. In addition to these nanorods, nanoparticles of size 2-5 nm are also present as revealed by the TEM image (Fig.68 (b)). Nanoribbons are aggregated and are surrounded by silica, as can be seen from the contrast difference observed in the TEM image arising due to the high refractive index of SbPO$_4$ compared to silica. Selected area diffraction from the sample is shown in the Fig.68 (c).

![TEM images of SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) nanoribbons in silica and nanoparticles in silica.](image)

Fig.68. TEM images of (a) SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) nanoribbons in silica and (b) SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) nanoparticles in silica. A representative selected area electron diffraction pattern and a high resolution TEM image from these nanoribbon are shown in Fig.68 (c and d), respectively.
Compared to the selected area electron diffraction pattern shown in Fig.63 (c), the
dots corresponding to the diffraction patterns observed in Fig.68 (c) are not symmetrically
placed, indicating that there exists lesser extent of preferential orientation in the sample after
dispersion in silica. High-resolution image of a nanoparticle is shown in Fig.68 (d). Lattice
fringes can be clearly seen in the image. The distance between the lattice planes, 3.32 ± 0.05
Å, match well with the (020) plane of SbPO$_4$ phase. XRD and TEM studies do not give any
indication regarding the incorporation of the lanthanide ions in SbPO$_4$ lattice. In order to
confirm this aspect, detailed structural studies have been carried out using infrared and
Raman spectroscopic techniques.

4.3.4 Proof for the incorporation of lanthanide ions into SbPO$_4$ lattice: Figure 69 shows
the Raman spectrum of un-doped SbPO$_4$, SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%),
SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%)-SiO$_2$ samples. The patterns appear identical for all the samples.
All the patterns are characterised by sharp peaks at ~ 210, 350, 471, 578, 618, 971 and 1048
cm$^{-1}$. In addition to this, broad peaks at ~ 437, 664, 770 and 931 cm$^{-1}$ are observed. The
position of these peaks is in close agreement with those reported by Nalin, et al. [245]. The
SbPO$_4$ crystallize in C$_{2h}$ space group and comprises of PO$_4$ tetrahedral units bound to the
Sb(III) polyhedral units (trigonal bipyramidal configurations) through asymmetrical bridging
oxygen atoms [246]. The isolated PO$_4$ groups with T$_d$ symmetry, when placed at C$_{2h}$ sites,
(corresponding to the monoclinic SbPO$_4$ unit cell) results in the decomposition of the
vibrational species into the following modes.

\[
\text{A}: \quad \text{A} + \text{B} , \quad 2\text{F}: \quad 4\text{A} + 4\text{B} + 2\text{A} + 2\text{B} , \quad \text{E}: \quad \text{A} + \text{B} + \text{A} + \text{B} ,
\]

Among these, the six A$_g$ and three B$_g$ modes are Raman active while the 3A$_u$ and 6B$_u$ modes
are IR active. The peaks at ~ 355, 623, 976 and 1053 cm$^{-1}$ are of the A$_g$ type, while peaks at ~
476 and 583 cm$^{-1}$ are of the B$_g$ type. Replacement of Sb$^{5+}$ by lanthanide ions (Ce$^{3+}$ or Tb$^{3+}$) is
expected to have significant effect on the P-O stretching modes of PO$_4$ units in SbPO$_4$. We
have noticed that the peak maximum at \( \sim 1053 \text{ cm}^{-1} \) characteristic of the asymmetric stretching vibration of \( \text{PO}_4 \) structural units, decreases with doping lanthanide ions in the SbPO\(_4\) lattice, as can be seen from Fig.69 (b). Shifting of the peak maximum corresponding to the asymmetric P-O stretching mode of \( \text{PO}_4 \) units to lower wave numbers has been attributed to the combined effect of heavier mass of \( \text{Ce}^{3+} \) and \( \text{Tb}^{3+} \) ions compared to Sb\(^{3+}\) ion and decrease in the covalency of P-O linkages brought about by replacement of Sb\(^{3+}\) by Ce\(^{3+}\) and Tb\(^{3+}\) ions in SbPO\(_4\) lattice.

![Fig.69. Raman spectrum over the entire region (a) corresponding to un-doped SbPO\(_4\), SbPO\(_4\):Ce\(^{3+}\)(2.5%),Tb\(^{3+}\)(5%) and SbPO\(_4\):Ce\(^{3+}\)(2.5%),Tb\(^{3+}\)(5%)-SiO\(_2\) samples dispersed in silica. The peak corresponding to the asymmetric stretching vibrations of \( \text{PO}_4 \) tetrahedra in these samples observed over the region of 1000-1080 cm\(^{-1}\) is shown in Fig.69 (b).](image)

Similar trend is also observed for the asymmetric stretching vibration of the \( \text{PO}_4 \) units in the IR spectrum (Fig.70 (a)). In addition to the vibrations of \( \text{PO}_4 \) stretching, the vibrations characteristic of Sb-O linkages (peak observed \( \sim 640 \text{ cm}^{-1} \)) is also affected (Fig.70 (b)). The peak at 640 cm\(^{-1}\) shows a systematic lowering with increase in lanthanide ion concentration in SbPO\(_4\). This is not very clear in the Raman spectrum due to weak intensity for peak corresponding to Raman mode of Sb-O linkages. Hence based on the IR and Raman studies it is established that lanthanide ions such as Ce\(^{3+}\) and Tb\(^{3+}\) replace Sb\(^{3+}\) ions in the SbPO\(_4\).
lattice. Lanthanide ions occupying such a low symmetry environments (coordination number 4) in inorganic hosts is observed for the first time.

![FT-IR patterns](image)

**(a)**

Fig.70. FT-IR patterns corresponding to SbPO₄ nanoribbons/ nanoparticles containing different concentrations of Tb³⁺ ions. The peak corresponding to the Sb-O stretching vibration in these samples observed over the region of 600-700 cm⁻¹ is shown in Fig.70 (b).

The effect of SiO₂ coating is very clearly seen in the symmetric PO₄ stretching mode at ~ 930 cm⁻¹ (Fig.71). The peak at ~930 cm⁻¹ for undoped SbPO₄ and SbPO₄:Ce³⁺(2.5%),Tb³⁺(5%) sample remains unchanged. The increased width in silica coated SbPO₄:Ce³⁺(2.5%),Tb³⁺(5%) sample is due to random distribution of phosphate structural units in the SiO₂ matrix. The presence of Si attached with the PO₄ tetrahedra (P-O-Si linkages) results in weakening of the νₛₚₐ₄ vibrational group frequencies at ~930 cm⁻¹. In fact, a careful analysis of the 930 cm⁻¹ peak (Fig.71 (c)) indicates that there are two overlapping peaks, one at ~930 cm⁻¹ similar to what is observed for the undoped and SbPO₄:Ce³⁺(2.5%),Tb³⁺(5%) sample and another at ~ 921 cm⁻¹ which represent the changed bonding configuration of the PO₄ units in the silica matrix. Thus, the phosphate groups are present in two different environments. One such possible change in the bonding environment is the terminal O atoms of surface PO₄ tetrahedron of SbPO₄ nanoribbons/ nanoparticles.
being bonded with the Si atoms (i.e. P-O-Si type of linkages). Phosphorus being more electronegative than Si, this will result in a reduction in the force constants, and hence lowering of Raman frequency. This effect is more prominent for the symmetric PO$_4$ vibration and hence we observe two peaks in the present case.

![Figure 71](image)

Fig. 71 Raman spectrum corresponding to symmetric PO$_4$ stretching mode of (a) un-doped SbPO$_4$ (b) SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) and (c) SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) samples dispersed in silica.

4.3.5 Luminescence studies on SbPO$_4$:Ce, Tb and effect of incorporation of nanomaterials in silica: Figure 72 shows the emission spectra of SbPO$_4$:Tb$^{3+}$(5%), SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) and SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%)-SiO$_2$ obtained after 250 nm excitation. The peaks observed ~ 489, 543, 585, and 621 nm correspond to transitions from $^5$D$_4$ level to $^7$F$_6$, $^7$F$_5$, $^7$F$_4$ and $^7$F$_3$ levels, respectively of Tb$^{3+}$ ion. It is worth noting that, unlike Tb$^{3+}$ or Ce$^{3+}$-Tb$^{3+}$ doped SbPO$_4$ samples, pure TbPO$_4$ prepared by the identical method as that of SbPO$_4$:Tb$^{3+}$ samples did not show any emission (inset of Fig.72). This aspect substantiate the fact that Tb$^{3+}$ ions are getting incorporated in SbPO$_4$ lattice and do not exist as separate TbPO$_4$ phase, a fact which is also confirmed from the vibrational studies described above. It is also observed that Ce$^{3+}$ ion shows very weak emission in the UV region. A representative Ce$^{3+}$ emission spectrum from SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) sample
obtained after 275 nm excitation is shown as an inset in Fig.72. Weak emission has been attributed to the enhanced non-radiative decay of Ce$^{3+}$ ions in the present host.

Since the samples are powder in nature, it is not very accurate to compare the peak intensities of the emission spectra, while comparing their luminescence properties. Instead, the lifetime of the $^5\text{D}_4$ level of Tb$^{3+}$ in these samples can be compared for judging their luminescent efficiencies. The decay curve corresponding to the $^5\text{D}_4$ level of Tb$^{3+}$ obtained after exciting the samples at $\sim$ 250 nm ($4f\rightarrow5d$ transition of Tb$^{3+}$) and monitoring the emission at $\sim$ 544 nm ($^7\text{D}_4\rightarrow^7\text{F}_5$ transition of Tb$^{3+}$) for these samples are shown in Fig.73. The decay curves are found to be bi-exponential in nature for both SbPO$_4$:Tb$^{3+}$(5 at %) and SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) nanoribbons/ nanoparticles, and single exponential in nature for SbPO$_4$:Ce$^{3+}$(2.5%),Tb$^{3+}$(5%) nanoribbons/ nanoparticles incorporated in silica. The measured
lifetime values along with their relative contribution to the overall decay profile are shown in Table 8. The lifetime values of the \( ^{5}D_{4} \) level of Tb\(^{3+} \) in the SbPO\(_{4}\):Tb\(^{3+}\) (2.5 at %) sample are 0.4 ms (\( \tau_1 \)) and 2.1 ms (\( \tau_2 \)) and the values corresponding to Ce\(^{3+} \) co-doped SbPO\(_{4}\):Tb\(^{3+}\) (5 at%) sample are 0.4 ms (\( \tau_1 \)) and 2.4 ms (\( \tau_2 \)) with their relative contribution in the ratio \( \sim 22 : 78 \) for both the samples. In the case of SbPO\(_{4}\):Ce\(^{3+}\) (2.5 at %), Tb\(^{3+}\) (5 at %)-SiO\(_{2}\) samples, the faster component is absent.

![Decay curves](image)

**Fig.73.** Decay curves corresponding to the \( ^{5}D_{4} \) level of Tb\(^{3+} \) ions from nanoribbons / nanoparticles of (a) SbPO\(_{4}\):Tb\(^{3+}\) (5 at %), (b) SbPO\(_{4}\):Ce\(^{3+}\) (2.5 at %),Tb\(^{3+}\) (5 at %) and (c) SbPO\(_{4}\): Ce\(^{3+}\) (2.5 at %), Tb\(^{3+}\) (5 at %) dispersed in silica. The samples were excited at 250 nm and emission was monitored at 544 nm.

Table 8. The lifetime values corresponding to the \( ^{5}D_{4} \) level of Tb\(^{3+} \) ions in SbPO\(_{4}\):Ce\(^{3+}\), Tb\(^{3+}\) nanoribbons/ nanoparticles along with the \( \chi^2 \) values obtained from fitting. The numbers in brackets give the relative concentration of each lifetime components. Error in the lifetime values are within 5% as revealed by the duplicate measurements

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Lifetime values</th>
<th>Effective lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_1 ) (ms)</td>
<td>( \tau_2 ) (ms)</td>
</tr>
<tr>
<td>SbPO(_{4}):Tb(^{3+}) (5%)</td>
<td>0.4 (23%)</td>
<td>2.1 (77%)</td>
</tr>
<tr>
<td>SbPO(_{4}):Ce(^{3+}) (2.5%),Tb(^{3+}) (5%)</td>
<td>0.4 (22%)</td>
<td>2.4 (78%)</td>
</tr>
<tr>
<td>SbPO(<em>{4}):Ce(^{3+}) (2.5%),Tb(^{3+}) (5%) - SiO(</em>{2})</td>
<td>-</td>
<td>2.2 (100%)</td>
</tr>
</tbody>
</table>
The luminescence dynamics associated with multiple lifetime components can be better pictured through effective lifetime ($\tau_{\text{eff}}$). The effective lifetime ($\tau_{\text{eff}}$), which is measure of the average environment around the $\text{Tb}^{3+}$ ions in the sample, is calculated based on the equation (20).

$$
\tau_{\text{eff}} = \frac{\int_{0}^{\infty} t \cdot I(t) \, dt}{\int_{0}^{\infty} I(t) \, dt}
$$

where $I(t)$ is the intensity at any time $t$

From Table 8 it is evident that, $\text{Ce}^{3+}$ co-doping in $\text{SbPO}_4: \text{Tb}^{3+}$, leads to slight increase in the $\tau_2$ component of the decay corresponding to the $^5\text{D}_4$ level of $\text{Tb}^{3+}$ ions. This increase in the $\tau_2$ component is responsible for the increased $\tau_{\text{eff}}$ values. The bi-exponential nature of the decay curves of $\text{SbPO}_4: \text{Tb}^{3+}(5\%)$ and $\text{SbPO}_4: \text{Ce}^{3+}(2.5\%), \text{Tb}^{3+}(5\%)$ nanoribbons/ nanoparticles can be attributed to the presence of $\text{Tb}^{3+}$ ions in at least in two different environments, namely the one at the bulk and the other at the surface of the nanoribbons/ nanoparticles. The luminescence originating from the surface of the nanoribbons/ nanoparticles is responsible for the $\tau_1$ component whereas that originating from the bulk is responsible for $\tau_2$ component. The lanthanide ions at the surface will undergo faster quenching compared to the ones at the bulk due to the presence of stabilising ligands at the surface. The vibrations associated with the C-H, O-H and C-O linkages of the stabilising ligands are responsible for the non-radiative decay of the lanthanide ions excited states. The presence of stabilising ligand with the $\text{SbPO}_4$ nanoribbons/ nanoparticles has been confirmed from IR pattern of the sample. Thus an increased component of the non-radiative transition in case of samples which are not incorporated in silica, results in a shorter lifetime component. However, when the nanoribbons/ nanoparticles are dispersed in silica, the ligands are removed from the surface, thereby leading to the appearance of a single exponential decay curve. The similar $\tau_1$ values
that are observed for both the SbPO₄:Tb³⁺(5%) and SbPO₄:Ce³⁺(2.5%),Tb³⁺(5%) samples further support that the faster component (τ₁) is originating from the lanthanide ions present at the surface of the nanoribbons/ nanoparticles. Replacement of the ligands from the surface of the nanoparticles by silica matrix is schematically shown in Fig.74.

Fig.74. Schematic representation showing the effect of incorporation of nanoparticles in silica matrix.

In order to confirm whether energy transfer is taking place between Ce³⁺ and Tb³⁺ ions in the SbPO₄:Ce³⁺, Tb³⁺ nanoribbons/ nanoparticles, excitation spectra were recorded by monitoring the 5D₄→7F₅ transition of Tb³⁺ ions at 545 nm (Fig.75). The excitation spectrum of SbPO₄:Tb³⁺(5%) (Fig.75 (a)) has a broad and intense band at ~250 nm and sharp and weak features at 284, 303, and 318 nm. The former broad band at ~250 nm corresponds to allowed 4f to 5d transition of Tb³⁺ and latter sharp peaks belong to intra 4f transitions of Tb³⁺ ion. The lower intensity of latter peaks is because of forbidden nature of f-f transitions. The shielding of 4f electrons by 5s and 5p electrons from surroundings results in the relatively sharper peaks. Co-doping SbPO₄:Tb³⁺(5%) nanoribbons/ nanoparticles with Ce³⁺ results in an additional peak centered around 278 nm with two shoulders. As 4f→5d transition of Tb³⁺ and Ce³⁺ ions have very high value of oscillator strength and assuming comparable transition probabilities for the 4f→5d transition of Tb³⁺ and Ce³⁺ ions, the excitation spectrum has been de-convoluted based on a Gaussian fit. De-convolution of the excitation spectrum revealed
that the broad peak can be resolved into three peaks, with an intense peak centered at 278 nm and two less intense peaks around 300 and 257 nm.

![Fig. 75. Excitation spectrum corresponding to the $^5\!D_4 \rightarrow ^7\!F_5$ transition of Tb$^{3+}$ ions (544 nm) from nanoribbons/ nanoparticles of (a) SbPO$_4$:Tb$^{3+}$(5%), (b) SbPO$_4$: Ce$^{3+}$(2.5%), Tb$^{3+}$(5%) and (c) SbPO$_4$: Ce$^{3+}$(2.5%), Tb$^{3+}$(5%) dispersed in silica.](image)

Based on the comparison of the spectra shown in Fig. 75, it is inferred that the peak around 257 nm is due to the 4f→5d transition of Tb$^{3+}$ and the remaining two peaks are due to the 4f→5d transition of Ce$^{3+}$. This is further confirmed from the excitation spectrum of SbPO$_4$:Ce$^{3+}$(5%) which gave an excitation peak centered around 278 nm with an asymmetry around 300 nm (not shown). Slight red shift (~ 7 nm) in the excitation peak maximum of 4f→5d transition of Tb$^{3+}$ can be attributed to the changes in the SbPO$_4$ lattice brought about by both Tb$^{3+}$ and Ce$^{3+}$ ions doping. Observation of 4f→5d excitation peaks for both Tb$^{3+}$ and Ce$^{3+}$ ions in the excitation spectrum obtained by monitoring Tb$^{3+}$ emission around 544 nm confirms the existence of energy transfer from Ce$^{3+}$ to Tb$^{3+}$ ions in Ce$^{3+}$ co-doped SbPO$_4$:Tb$^{3+}$ nanoribbons/ nanoparticles. The relative intensity of 4f→5d transition of Tb$^{3+}$ to
Ce$^{3+}$ ions is in the ratio of around 40:60 for both SbPO$_4$:Ce$^{3+}$(2.5%), Tb$^{3+}$ (5%) nanoribbons/nanoparticles as well as the nanoribbons/nanoparticles dispersed in silica, suggesting that the extent of energy transfer is approximately 60%. The values are comparable with the energy transfer efficiency estimated from the Ce$^{3+}$ emission in SbPO$_4$ host using the equation $\eta = 1 - I/I_0$, where $I$ and $I_0$ are the intensities of Ce$^{3+}$ emission in the presence and absence, respectively of Tb$^{3+}$ ions. The comparable efficiency of energy transfer for the as prepared nanomaterials and nanomaterials incorporated in silica matrix are understandable as the phonon energies are comparable for both SbPO$_4$ and SiO$_2$ lattices. Hence, identical extent of quenching is expected for lanthanide ion excited states from these matrices. However, the silica covering on the nanoribbons/nanoparticles have additional advantage of removing the asymmetric environment created at the surface by the stabilising ligands. Energy transfer must also reflect in the Ce$^{3+}$ excited state lifetimes. However, the decay curves obtained corresponding to the excited state of Ce$^{3+}$ were close to the instrument response (less than 1 ns) and hence the values could not be accurately calculated from the decay curves.

It will be interesting to understand the mechanism of the energy transfer between the Ce$^{3+}$ and Tb$^{3+}$ ions. The energy transfer between Ce$^{3+}$ and Tb$^{3+}$ depends on extent of overlap between donor (D) emission peak (Ce$^{3+}$ emission peak in the present case) and acceptor (A) absorption peak (Tb$^{3+}$ excitation peak in the present case) and expressed by the equation [21]

$$P_{DA} = \frac{4\pi}{h} \sum_D |D, A| H_{DA} |D^*, A| g_D(E) g_A(E) dE$$

where, $P_{DA}$ is the rate of energy transfer from donor to acceptor. The first term in the above expression represents the transition dipole moment between the $|D^*, A>$ and $|D, A*>$ states via the interaction Hamiltonian $H_{DA}$. $D^*$ and $A^*$ represent the excited state of the donor and acceptor, $H_{DA}$ is the interaction Hamiltonian. The parameters $g_D(E)$ and $g_A(E)$ are normalized population density function representing the optical line shapes of donor and acceptor.
respectively. Value of this integral depends on the extent of overlap between the donor emission and acceptor absorption profiles. $P_{DA}$ depends strongly on the critical distance between donors, as well as on their excited state lifetimes. The critical distance is the minimum distance between donor and acceptor above which no energy transfer between them is possible. In the SbPO$_4$ lattice, each SbO$_4$ polyhedron is separated by PO$_4$ tetrahedron and the minimum average distance between Sb$^{3+}$ ions is around 5.01Å [226]. As only 2.5 at % of Ce$^{3+}$ and 5 atom % of Tb$^{3+}$ are randomly distributed at the Sb$^{3+}$ site in the lattice the average distance between Ce$^{3+}$ and Tb$^{3+}$ ions will be significantly higher than 5.01Å thereby resulting in an increased distance between the donor and acceptor. Hence, the possibility of energy transfer either by the exchange mechanism or by the multi-polar interactions is ruled out. Based on these results, it is inferred that a long-range energy migration from different Ce$^{3+}$ to Tb$^{3+}$ ions is taking place in SbPO$_4$:Ce$^{3+}$, Tb$^{3+}$ nanomaterials.

The steady state and time resolved luminescence studies described above establish that covering the nanoribbons/ nanoparticles with silica matrix is very effective in reducing the surface contribution to luminescence from nanomaterials. Further, these studies also confirmed that the energy transfer takes place from Ce$^{3+}$ to Tb$^{3+}$ ions, which are occupying Sb$^{3+}$ site in SbPO$_4$ lattice, a low symmetric environment with a coordination number of four.

4.4 **Bismuth phosphate nanomaterials**: Different forms of BiPO$_4$ nanomaterials were prepared by adding ammonium dihydrogen phosphate solution to ethylene glycol containing bismuth nitrate followed by refluxing at various temperature for two hours.

4.4.1 **Effect of reaction temperature on the particle size, shape and crystal structure**: Figure 76 shows the XRD patterns Eu$^{3+}$ doped BiPO$_4$ nanomaterials prepared at different temperatures namely room temperature, 100, 125 and 185°C. For samples prepared at room temperature, XRD pattern is characteristic of hydrated hexagonal form of BiPO$_4$. With increase in the reaction temperature, it slowly converted to anhydrous hexagonal BiPO$_4$ at
100°C. On further increasing the reaction temperature (at 125°C) the hexagonal form gets partially converted to monoclinic phase and at 185°C it transforms completely into monoclinic BiPO₄. The average crystallite sizes are calculated by using Debye-Scherrer formula and are found to be 25, 47 and 51 nm for hydrated hexagonal BiPO₄, hexagonal BiPO₄ and monoclinic BiPO₄, respectively. The increase in crystal size may be explained based on the Ostwald ripening phenomenon where in, with increase temperature, bigger particles starts growing at the expanse of smaller particles.

![XRD patterns of 2.5 at % Eu³⁺ doped BiPO₄ samples prepared at room temperature, 100, 125 and 185°C.](image)

Fig. 76. XRD patterns of 2.5 at % Eu³⁺ doped BiPO₄ samples prepared at room temperature, 100, 125 and 185°C.

In order to evaluate the conversion of hydrated hexagonal BiPO₄ to hexagonal and then to monoclinic from combined thermo-gravimetric and differential thermal analysis (TG-DTA) patterns of hydrated BiPO₄ sample were recorded (Fig.77). In TG, the weight losses are obtained mainly in the ranges of 50-180°C and 200-750°C. The former corresponds to the loss of water molecules adsorbed on the surface and the latter to the decomposition of
ethylene glycol moiety (stabilizing ligand). In DTA pattern mainly a sharp exothermic peak centered at 600°C was observed which is attributed to the phase transformation from hexagonal BiPO$_4$ to monoclinic BiPO$_4$.

![Fig.77. TG-DTA pattern of BiPO$_4$ sample prepared at room temperature.](image)

In order to understand structural changes occurring during the synthesis of BiPO$_4$ nanomaterials at different temperature, FT-IR spectra were recorded for these samples (Fig.78). The BiPO$_4$ nanomaterials prepared at room temperature and 100°C show similar spectra with sharp peaks at 539 and 600 cm$^{-1}$ together with broad bands centered around 1000 cm$^{-1}$ and 3500 cm$^{-1}$ (3500 cm$^{-1}$ band is not shown). The strong band centered at 1000 cm$^{-1}$ is due to $\nu_3$ stretching vibration of the PO$_4$ tetrahedra and the peaks at 600 and 539 cm$^{-1}$ correspond to $\delta$(0-P-O) and $\nu_d$(PO$_4$), respectively [227]. Samples prepared at 125 and 185°C show similar spectra except splitting of peaks corresponding PO$_4$ stretching vibrations. The fine structure of the bands corresponding to PO$_4$ vibrations has been assigned to the reduction of the crystal symmetry from pseudo T$_d$ to C$_1$. In order to check, whether the variation in reaction temperature and crystalline phase has any effect on the particle size and morphology of BiPO$_4$, detailed TEM studies were carried out. Figure 79 shows the TEM images of BiPO$_4$.
nanomaterials prepared at different temperatures and their insets show the corresponding SAED patterns.

Fig. 78. FT-IR spectra of BiPO₄ samples prepared at room temperature, 100, 125 and 185°C

Fig. 79. TEM images of BiPO₄ samples prepared at (a) room temperature, (b) 100, (c) 125 and (d) 185°C. Inset shows the SAED patterns of corresponding samples.
Room temperature and 100°C synthesized samples showed particles with size in the range of 50-80 nm and 70-100 nm, respectively. BiPO$_4$ samples prepared at 125 and 185°C shows rod shaped morphology with lengths in the range ~ 450-750 and 1000-1200 nm with corresponding widths ~ 50-120 and 100-170 nm, respectively. The SAED patterns show that these nanomaterials are single crystalline in nature and their crystallinity increases with increase in the reaction temperature. The possible reason for change in morphology with increase in temperature is the increasing concentration of nuclei and associated anisotropic growth brought about by the reaction temperature.

4.4.2 Effect of particle size and crystal structure on Eu$^{3+}$ emission from BiPO$_4$:Eu$^{3+}$ nanomaterials: Figure 80 (a) shows the emission spectra of Eu$^{3+}$ doped hydrated hexagonal BiPO$_4$, anhydrous hexagonal BiPO$_4$, and monoclinic BiPO$_4$ nanomaterials on 270 nm excitation. The intensity of Eu$^{3+}$ luminescence increases with increase in the reaction temperature. It has been attributed to the combined effect of improved crystallinity and removal of water molecules present in the lattice. Water molecules quench the excited state of Eu$^{3+}$, thereby reducing its luminescence intensity. Europium ions in the BiPO$_4$ lattice show four intense emission peaks at 590, 615, 650 and 700 nm and are due to $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ transitions of Eu$^{3+}$. Improved crystallinity of BiPO$_4$ samples with increase in temperature of synthesis is also clear from the fine structure of the emission spectrum (Fig 80 (a)), particularly for the 185°C heated samples. The corresponding excitation spectra monitored at 615 nm emission from the samples is shown in Fig.80 (b). It shows broad intense band centered at 270 nm with a shoulder at 255 nm along with many sharp peaks in the wavelength range of 310 - 420 nm. The broad band centered at 270 nm is due to the Eu-O charge transfer process and the shoulder at 255 nm is due to host absorption. Observation of host excitation peak while monitoring Eu$^{3+}$ emission from the sample confirm that the energy transfer takes place from host to Eu$^{3+}$ ions. The sharp peaks in the wavelength
range of 310 – 420 nm are assigned to the f-f transitions of Eu$^{3+}$ ions. It is necessary at this stage to find out whether the Eu$^{3+}$ ions goes to the lattice of BiPO$_4$ and replaces the Bi$^{3+}$ ions or exist at the interstitial or surface sites of BiPO$_4$ nanomaterials. Hence BiPO$_4$ nanomaterials were prepared with different concentrations of La$^{3+}$ ions (Eu$^{3+}$ ions are not used as the unpaired electrons in Eu$^{3+}$ can broaden the solid state NMR spectrum) and characterized by XRD, FT-IR and $^{31}$P MAS NMR techniques.

Fig. 80 (a) Emission spectra of BiPO$_4$ samples prepared at room temperature, 75 and 185°C after excitation at 270 nm and (b) corresponding excitation spectra monitored at 615 nm emission.

4.4.3 Solid solution formation between bismuth and lanthanide phosphates: XRD patterns corresponding to Bi$_{1-x}$La$_x$PO$_4$ (x = 0, 0.3, 0.5, 0.7, 1) are shown in the Fig. 81. All the samples are found to have monoclinic phase. The diffraction peaks have been shifted to lower 20 values with increasing the lanthanum concentration. This has been attributed to the higher ionic radius of La$^{3+}$ compared to the Bi$^{3+}$ and associated lattice expansion.

Figure 82 (a and b) shows the FT-IR spectra of Bi$_{1-x}$La$_x$PO$_4$ (x = 0, 0.3, 0.5, 0.7, 1) nanomaterials prepared at 185°C. The peaks present over the region 480-680 cm$^{-1}$ (Fig. 82 (a)) are mainly due to the PO$_4$ bending vibrations whereas absorption in the region 750-1330 cm$^{-1}$ (Fig. 82 (b)) is due to PO$_4$ stretching vibrations. Both the regions show systematic shift towards the higher frequency with increase in the La$^{3+}$ content in the lattice. Bismuth is
heavier metal ion as compared to La$^{3+}$ ion and hence it is expected that as La$^{3+}$ replaces Bi$^{3+}$ in BiPO$_4$ lattice there can be a blue shift in the peak maximum corresponding to PO$_4$ vibrations. These results also confirm the solid solution formation between the BiPO$_4$ and LaPO$_4$ lattices.

Fig. 81. XRD patterns of Bi$_{1-x}$La$_x$PO$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) nanomaterials prepared at 185°C.

Fig. 82. FT-IR patterns of Bi$_{1-x}$La$_x$PO$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) nanomaterials prepared at 185°C showing the regions (a) 480 – 680 cm$^{-1}$ and (b) 750 – 1300 cm$^{-1}$.
Figure 83 shows the $^{31}$P MAS-NMR spectra of Bi$_{1-x}$La$_x$PO$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) nanomaterials prepared at 185°C. With increase in La$^{3+}$ content in BiPO$_4$, there is a significant change in the line shape is observed. The line width of the peak increases significantly and peak maxima shift towards higher chemical shift ($\delta$) values with increase in La$^{3+}$ content in the lattice. This can be understood by considering the difference in the charge to radius ratio (2.46 and 2.56 for La$^{3+}$ and Bi$^{3+}$, respectively) between Bi$^{3+}$ and La$^{3+}$ ions. The lower charge to radius ratio of La$^{3+}$ compared to Bi$^{3+}$ leads to shifting of peak maxima towards higher $\delta$ values when Bi$^{3+}$ is replaced by La$^{3+}$ in BiPO$_4$ lattice. The sharpening of the peaks with increase in the La$^{3+}$ concentration can be explained based on the environment around ‘P’ in the solid solution. It is known that Bi$^{3+}$ is heavier ion compared to La$^{3+}$ and when heavier ions surround the probe nucleus ($^{31}$P), anisotropy in chemical environment around ‘P’ will be higher as compared to the situation in which ‘P’ is surrounded by lighter ions. Higher the anisotropy in chemical environment, greater will be the line width of the NMR absorption peak. These results further substantiate the solid solution formation between BiPO$_4$ and LaPO$_4$.

Fig.83. $^{31}$P MAS-NMR patterns of Bi$_{1-x}$La$_x$PO$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) nanomaterials prepared at 185°C.
Similar studies were also carried out for other lanthanide ions like Tb$^{3+}$ and the results are discussed below. Tb$^{3+}$ is chosen in the present study for doping because unlike BiPO$_4$ and LaPO$_4$ which have got monoclinic structure, TbPO$_4$ exists in the tetragonal form. Hence solid solution formation between BiPO$_4$ and TbPO$_4$ will be quite interesting both with respect to fundamental aspect as well as with respect to light emitting applications. Figure 84 shows the XRD patterns of BiPO$_4$ nanomaterials containing different amounts of Tb$^{3+}$. With increase in Tb$^{3+}$ to Bi$^{3+}$ ratio, the peaks maxima are shifted to higher 2$\theta$ values. This is explained based on the lattice contraction brought about by the replacement of the larger ionic radius Bi$^{3+}$ (1.11 Å) with the smaller ionic radius Tb$^{3+}$ (1.04 Å) ions. In pure TbPO$_4$ case, it is an entirely different crystalline phase with tetragonal structure (Fig.84). Hence, based on XRD, FT-IR and $^{31}$P MAS NMR studies of BiPO$_4$:Ln$^{3+}$ nanomaterials, it is confirmed that extensive solid solution formation occurs with BiPO$_4$ and LnPO$_4$. In the following section, luminescence properties of Ln$^{3+}$ doped BiPO$_4$ nanorods are discussed.

![XRD patterns of Bi$_{1-x}$Tb$_{x}$PO$_4$ (x = 0, 0.1, 0.25, 0.5, 1) nanomaterials prepared at 185°C](image)

Fig.84. XRD patterns of Bi$_{1-x}$Tb$_{x}$PO$_4$ (x = 0, 0.1, 0.25, 0.5, 1) nanomaterials prepared at 185°C
4.4.4 Luminescence studies on Eu$^{3+}$ doped BiPO$_4$ nanomaterials: Figure 85 (a) shows the emission spectra of 1, 2, 2.5 and 5 atom% Eu doped BiPO$_4$ nanorods excited at 275 nm. Strong orange and red emission is observed from the sample. The 590, 612, 650 and 700 nm peaks are due to $^5$D$_0$$\rightarrow$$^7$F$_1$, $^5$D$_0$$\rightarrow$$^7$F$_2$, $^5$D$_0$$\rightarrow$$^7$F$_3$ and $^5$D$_0$$\rightarrow$$^7$F$_4$ transitions of Eu$^{3+}$, respectively. The fine structure observed in the emission peaks shows the crystalline nature of host lattice.

As the concentration of Eu$^{3+}$ increases, the emission intensity initially increases up to 2.5 atom % and then decreases. Initially with increase in doping concentration, the number of luminescent centers increases and as a result, emission intensity increases. However, above certain doping concentration there is non-radiative decay due to energy transfer (migration) among different Eu$^{3+}$ ions until it reaches a quenching centre. As a result, emission intensity decreases. These results are further supported by the decay curve corresponding to the $^5$D$_0$ level of Eu$^{3+}$ in these samples.

Fig.85. (a) Emission spectra obtained after excitation at 275 nm, (b) decay curves corresponding to $^5$D$_0$ level of Eu$^{3+}$ from BiPO$_4$:Eu$^{3+}$ nanomaterials containing different amounts of Eu$^{3+}$.

The decay curves corresponding to $^5$D$_0$ level of Eu$^{3+}$ from these samples are shown in Fig.85 (b) and their corresponding lifetime values are given in Table 9. All these curves are bi-exponential in nature and based on the explanation given in the previous chapters, the
faster decay component is assigned to the surface Eu$^{3+}$ ions and slower component to Eu$^{3+}$ ions present in the bulk of the nanomaterials. Values of $^5D_0$ lifetimes increase with increase in Eu$^{3+}$ concentration up to 2.5 atom% and above this concentration the lifetime values started decreasing (Table 9 and Fig.85 (b)). Thus, the lifetime values support the inferences drawn from emission spectra.

Table 9. Lifetime values corresponding to $^5D_0$ level of Eu$^{3+}$ in BiPO$_4$ nanorods doped with different amounts of Eu$^{3+}$ ions.

<table>
<thead>
<tr>
<th>% of Eu$^{3+}$</th>
<th>$^5D_0$ lifetime values of Eu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$ (ms)</td>
</tr>
<tr>
<td>1 atom %</td>
<td>0.18 (35%)</td>
</tr>
<tr>
<td>2.5 atom %</td>
<td>0.31 (13%)</td>
</tr>
<tr>
<td>5 atom %</td>
<td>0.34 (30%)</td>
</tr>
</tbody>
</table>

4.4.5 Luminescence studies on Tb$^{3+}$ doped BiPO$_4$ nanorods: Figure 86 (a) shows the emission spectra of 1, 2.5, and 5 atom% Tb$^{3+}$ doped BiPO$_4$ nanorods. Emission peaks centered at ~ 487, 543, 585 and 621 nm correspond to transitions from $^5D_4$ level to $^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ levels respectively of Tb$^{3+}$ ions present in the BiPO$_4$ lattice.

Fig.86. (a) Emission spectra obtained after excitation at 255 nm, (b) decay curves corresponding to $^5D_4$ level of Tb$^{3+}$ ion from BiPO$_4$: Tb$^{3+}$ nanorods prepared at 185°C.
With increasing Tb$^{3+}$ ion concentration up to 2.5 atom%, the green emission (peak at 545 nm) intensity increases and above that concentration it started decreasing. The decrease in emission intensity beyond 2.5 at % is attributed to concentration quenching. Fig.86 (b) shows the decay curves corresponding to $^5D_4$ level of Tb$^{3+}$ from BiPO$_4$:Tb$^{3+}$ nanorods. All the samples showed bi-exponential decay and the lifetime values are given in the Table 10. Optimum lifetime values are obtained for 2.5 at % Tb$^{3+}$ doped BiPO$_4$ nanorods.

<table>
<thead>
<tr>
<th>% of Tb$^{3+}$</th>
<th>$^5D_4$ lifetime values of Tb$^{3+}$</th>
<th>$^5D_4$ lifetime values of Tb$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atom %</td>
<td>0.24 (13 %)</td>
<td>2.23 (87 %)</td>
</tr>
<tr>
<td>2.5 atom %</td>
<td>0.32 (11%)</td>
<td>2.62 (89%)</td>
</tr>
<tr>
<td>5 atom %</td>
<td>0.36 (15 %)</td>
<td>2.44 (85%)</td>
</tr>
</tbody>
</table>

4.4.6 Energy transfer from Tb$^{3+}$ to Eu$^{3+}$ ions in Tb$^{3+}$ co-doped BiPO$_4$:Eu$^{3+}$ nanorods: Figure 87 (a) shows the emission spectra of BiPO$_4$:Eu$^{3+}$ (5 at %) and 5 at % Tb$^{3+}$ co-doped BiPO$_4$:Eu$^{3+}$ (5 at %) nanorods obtained after excitation at 255 nm. It is observed that Tb$^{3+}$ emission intensity decreases after co-doping with Eu$^{3+}$. This indicates that energy transfer takes place from Tb$^{3+}$ to Eu$^{3+}$ ions in the co-doped samples. Fig.87 (b) shows the excitation spectra corresponding to Eu$^{3+}$ emission from both Eu$^{3+}$ single doped and Tb$^{3+}$ co-doped BiPO$_4$:Eu$^{3+}$ nanorods. Excitation spectrum corresponding to Eu$^{3+}$ emission from co-doped sample showed peaks characteristic of both Eu-O charge transfer and 4f-5d transitions of Tb$^{3+}$. Unlike this the excitation spectrum corresponding to Tb$^{3+}$ emission at 545 nm from the sample showed only 4f-5d transition of Tb$^{3+}$. These results confirm that energy transfer takes place from Tb$^{3+}$ to Eu$^{3+}$. This is also understandable by considering the energy values corresponding to 4f-5d transition of Tb$^{3+}$ and Eu-O charge transfer transition of Eu$^{3+}$. Figure 87 (c) shows the decay curve corresponding to $^5D_4$ level of Tb$^{3+}$ in the presence and absence of Eu$^{3+}$ ion. It is observed that lifetime of Tb$^{3+}$ ions decreases after doping with Eu$^{3+}$ ions. On
the other hand the Eu\(^{3+}\) lifetime has been found to increase after co-doping with Tb\(^{3+}\) ions. The lifetime values are given in the Table 11. The increase in lifetime corresponding to \(^5\)D\(_0\) level of Eu\(^{3+}\) and decrease in lifetime corresponding to \(^5\)D\(_4\) level of Tb\(^{3+}\) in co-doped samples compared to singly doped samples further confirms the energy transfer from Tb\(^{3+}\) ions to Eu\(^{3+}\) ions.

![Graph](image-url)

Fig. 87. (a) Emission spectra from BiPO\(_4\):Tb\(^{3+}\)(5 at\%) and BiPO\(_4\):Eu\(^{3+}\)(5 at\%), Tb\(^{3+}\)(5 at\%) nanomaterials after excitation at 255 nm. The corresponding excitation spectrum is shown in Fig. 87 (b). Decay curve corresponding to \(^5\)D\(_4\) level of Tb\(^{3+}\) from these samples are shown in Fig. 87 (c).

<table>
<thead>
<tr>
<th>sample</th>
<th>Lifetime of</th>
<th>(\tau_1) (ms)</th>
<th>(\tau_2) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiPO(_4):5% Eu(^{3+})</td>
<td>(^5)D(_0) level of Eu(^{3+})</td>
<td>0.34 (30%)</td>
<td>1.72 (70%)</td>
</tr>
<tr>
<td>BiPO(_4):5% Tb(^{3+})</td>
<td>(^5)D(_4) level of Tb(^{3+})</td>
<td>0.36 (15%)</td>
<td>2.44 (85%)</td>
</tr>
<tr>
<td>BiPO(_4):5% Eu(^{3+}), 5% Tb(^{3+})</td>
<td>(^5)D(_4) level of Tb(^{3+})</td>
<td>0.19 (27%)</td>
<td>1.77 (73%)</td>
</tr>
<tr>
<td></td>
<td>(^5)D(_0) level of Eu(^{3+})</td>
<td>0.66 (14%)</td>
<td>2.8 (86%)</td>
</tr>
</tbody>
</table>
4.4.7 Luminescence studies on Dy$^{3+}$ doped BiPO$_4$ nanorods: Figure 88 (a) shows the emission spectrum from BiPO$_4$ nanorods doped with 2.5 at % of Dy$^{3+}$ obtained after excitation at 350 nm. It consists of two peaks at 478, 573 nm corresponding to $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions, respectively of Dy$^{3+}$ ion in BiPO$_4$ nanorods. The corresponding excitation spectra monitored at 573 nm emission is shown in Fig.88 (b). It consists of a broad band centered at 255 nm along with sharp transitions above 300 nm. The broad band at 255 nm is due to host absorption. Observation of host absorption peak while monitoring Dy$^{3+}$ emission confirms the energy transfer from host to Dy$^{3+}$ ions. The less intense sharp peaks in the excitation spectrum are arising due to f-f transitions of Dy$^{3+}$ ion present in the lattice. The decay curve corresponding to $^4F_{9/2}$ level of Dy$^{3+}$ ion is shown in Fig.88 (c). It is a biexponential in nature with lifetime component 22 µs (15%) and 793 µs (85%).

Fig.88 (a) Emission spectrum obtained after excitation at 350 nm (b) excitation spectra monitored at 573 nm emission and (c) decay curve corresponding to $^4F_{9/2}$ level of Dy$^{3+}$ ion in BiPO$_4$:Dy$^{3+}$ nanorods.
4.4.8 Luminescence studies on Sm$^{3+}$ doped BiPO$_4$ nanorods: Figure 89 (a) shows the emission spectrum of Sm$^{3+}$ ions doped in BiPO$_4$ nanorods obtained after excitation at 402 nm. The spectrum consist of four peaks at 560, 597, 645 and 706 nm corresponding to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ transitions, respectively of Sm$^{3+}$ ion present in the BiPO$_4$ lattice.

(a)

(b)

(c)

Fig.89. (a) Emission spectrum obtained after 402 nm excitation, (b) excitation spectra monitored at 597 nm emission and (c) decay curve corresponds to $^4G_{5/2}$ level of Sm$^{3+}$ in BiPO$_4$:Sm$^{3+}$ nanorods.

The corresponding excitation spectrum monitored at 597 nm is shown in Fig.89 (b). The spectrum is similar to that of BiPO$_4$:Dy$^{3+}$ samples and consists of broad band centered at 255 nm along with sharp peaks above 320 nm. As explained in the case of BiPO$_4$:Dy$^{3+}$ samples, the broad band is arising due to energy transfer from host to Sm$^{3+}$ ion and the sharp peaks
corresponds to f-f transition of Sm$^{3+}$ ion. The decay curve corresponding to $^4G_{5/2}$ level of Sm$^{3+}$ has been shown in Fig.89 (c). Bi-exponential nature of the decay curve has been attributed to Sm$^{3+}$ ions present on the surface and in bulk of the nanorods.