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Wet chemical synthesis of $LiBaF_3$ phosphor

Vartika S. Singh [a,*], C.P. Joshi [a], S.V. Moharil [b]

[a] Physics Department, Shri Ramdeobaba K.N. Engineering College, Katol Road, Nagpur 440 013, India
[b] Department of Physics, R.T.M. Nagpur University, Nagpur 440 010, India

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ABSTRACT

$LiBaF_3$ has great potential applications as X-ray storage phosphor, slow neutron imaging, scintillator, vacuum ultraviolet (VUV) optical lithography, etc. Conventionally, $LiBaF_3$ is prepared by solid state reaction between the constituent fluorides. However, the preparation of phase pure material and especially single crystals is rather tricky due to incongruent melting. For the first time, a wet chemical preparation of rare earth activated $LiBaF_3$ is described here. As precipitated powders containing Ce^{3+} or Tb^{3+} exhibited characteristic luminescence. For observing Eu^{2+} emission, it was necessary to heat the powders in a reductive atmosphere. It is suggested that phosphors prepared by this method may prove useful in applications like OSL, X-ray imaging, etc. which do not require large single crystals.

1. Introduction

$LiBaF_3$ was discovered by Ludekens and Welch way back in 1952 [1]. BaLiF3 prepared with solid state reaction and LiF-BaF_2 as a raw material has been reported since the 1970s [2]. It was found to be incongruently melting and crystals could be grown from melt of non-stoichiometric compositions [3]. Luminescence of Eu^{2+} was studied quite early and found to be interesting as f–f line emission was noticed [4–6]. Luminescence of other lanthenides like Ce^{3+} [6,7], Yb^{2+} [8], Er^{3+}[2], Sm^{2+} [9,10] has also been studied subsequently. Interesting luminescence properties were also obtained with 3d activators like Ni^{2+} [11–13], Cr^{3+} [14], Cu^{+} [15], Co^{2+}, [3] Mn^{2+} [16,17]. Due to matching sizes, 3 d ions can be substituted at Li^{+} site. The initial investigations were carried out with the idea that it is a wide band-gap dielectric [18] and it might be a good host lattice for incorporating the ions with a lasing effect in the UV as well as NIR region. During crystal growth of fluorides, PbF_2 is used as scavenger, and emission of Pb^{+} as well as Pb^{2+} was studied in $LiBaF_3$ in which Pb was doped intentionally or otherwise [19,20].

Though initial studies were related to optical properties relevant for obtaining solid state lasers, other applications were also discovered soon. Pure $LiBaF_3$ [21,22], as well as Ce-doped and Rb-doped crystals, are scintillators, enabling one to discriminate the thermal neutron and gamma radiations [23]. Fast (ns), cross luminescence at shorter wavelengths is seen with gamma rays but not neutrons, while STE emission can be seen in scintillations with gamma rays as well as neutrons [24]. It is well-established [25] that $LiBaF_3$ has great potential applications in X-ray storage phosphors [26], slow neutron imaging [27], vacuum ultraviolet(VUV) optical lithography [18], and other luminescent devices [28].

Growth of $LiBaF_3$ single crystals is not straightforward as this compound is incongruently melting and crystals have to be grown from melt of non-stoichiometric compositions. On the other hand in several applications like X-ray imaging screens, TL/OSL dosimetry there is no need to grow single crystals and microcrystalline powders suffice. $LiBaF_3$ powders are usually prepared by solid state reaction between LiF and BaF_2, though in relatively recent works novel methods like pyrolysis of metal trifluoroacetates [29] solvothermal [30,25] sol–gel [31] have been attempted. When phosphors are prepared by the conventional solid state route involving heating in air, usually unwanted impurities like OH^{-}, O_2^{-}, etc. get incorporated. Such impurities can be quite harmful to the luminescence processes. Especially, fluorides are highly susceptible to hydrolysis [32]. Moreover, they are highly reactive and can attack the crucible material during high temperature processing. Use of freshly synthesized powders and inert atmosphere becomes necessary to prevent the hydrolysis and the reaction with the crucible. Scavengers like PbF_2 have also been used to get rid of OH^{-}. In recent years, some wet chemical syntheses for preparation of OH^{-} free fluorides have been described [33–35]. The fact that the presence of chlorine ions prevents hydrolysis is exploited in these methods. We have attempted synthesis of $LiBaF_3$ using similar methods. The results are reported in this paper.

2. Experimental

All the reagents used were of the Analytical Reagent grade. First we tried to synthesize $LiBaF_3$ using the wet-chemical method developed successfully for other fluorides [33–35]. The method exploits the fact that chlorine ions prevent hydrolysis. Accordingly, aqueous solutions of LiCl and $BaCl_2$ were mixed in equimolar

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* Corresponding author. Tel.: +91 712 2283708; fax: +91 712 2249875.
E-mail address: svmoharil@yahoo.com (V.S. Singh).

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proportions. Solutions were heated to 85 °C. In a typical experiment, 0.352 g of LiCl was dissolved in minimum amount of triply distilled, deionized water. Solution of 2 g of $BaCl_2$ was similarly prepared. Two solutions were mixed, stirred and heated to 85 C and HF (48%) was added drop wise till precipitation completed. Resulting precipitate was filtered, washed repeatedly with distilled water, dried and used in further experiments. However, though other double fluorides had been successfully synthesized by this method, the method did not yield $LiBaF_3$, BaFCl was formed instead. It was thought that by eliminating use of chlorides, BaFCl formation can be avoided and $LiBaF_3$ may be obtained. Accordingly, nitrates were used in place of chlorides. Though barium nitrate has limited solubility (10.3 g/100 ml), sufficient quantity could be dissolved in hot distilled water. However, no precipitation resulted from nitrate solutions.

In the second method, metal acetates were freshly prepared by dissolving corresponding carbonates in acetic acid. In a typical experiment, 0.66 g of lithium acetate and 2.73 g of barium acetate were dissolved separately in minimum amount of triply distilled, deionized water. Both acetates are readily soluble (Barium acetate 79.2 g/100 ml, lithium acetate (45 g/100 ml). Rest of the procedure was same as in method 1. This method met with partial success. $LiBaF_3$ was formed, but BaF_2 was the major phase.

In the third method, the precipitant was changed and reverse strike was used. Hot metal chloride solutions were added to the precipitant solution. KF was used as the precipitant. KF was freshly synthesized by neutralizing HF with K_2CO_3. In a typical experiment, 0.352 g of LiCl was dissolved in minimum amount of triply distilled, deionized water. Solution of 2 g of $BaCl_2$ was similarly prepared. Two solutions were mixed, stirred and heated to 85 C. Solutions of dopant chlorides were also added in the desired concentrations. Amount of dopant refers to this value and actual concentration incorporated was not measured. This was then added to hot aqueous solution containing 12 g KF in 50 ml distilled water. This amount is nearly seven times more than required by stoichiometry. However, this was the optimum amount for obtaining phase pure $LiBaF_3$. Use of smaller quanitity leads to contamination of $LiBaF_3$ phase by BaF_2. Use of excess KF may have also helped in prevention of BaFCl formation. Rest of the procedure was same as in method 1.

As prepared Eu-doped sample did not show PL emission. Dopant is not well dispersed or it is not incorporated in divalent form. For reducing it to Eu^{2+} the powder was heated at 750 C for 1 h in a reducing atmosphere provided by burning charcoal.

X-ray diffraction patterns were recorded on a Philips PANalytical X'pert Pro diffractometer. Photoluminescence spectra were recorded on a Hitachi F-4000 spectro-fluorimeter with spectral slit width of 1.5 nm in the spectral range 220–700 nm.

3. Results and discussions

Fig. 1 shows the XRD pattern of the compound prepared with chlorides as starting materials and HF as precipitating agent. XRD pattern did not match with that for $LiBaF_3$, but resembles that for BaFCl (ICDD 76-1374). Relative intensities are somewhat different. It appears that the major phase is BaFCl and small amount of $LiBaF_3$ might have been formed.

The literature method [35] for wet-chemical preparation of fluorides thus fails for $LiBaF_3$. To avoid formation of BaFCl, we tried nitrates as the starting materials and HF as precipitating agent, however no precipitate was obtained. Precipitation occurred when acetates were used as starting materials. Fig. 2 shows the XRD pattern of the compound prepared with acetates as starting materials and HF as precipitating agent (method 2). Stick patterns of $LiBaF_3$ (ICDD 18-0176) and BaF_2 (ICDD 88-2466) are also shown for the comparison. Several lines (marked by $\surd$) match with $LiBaF_3$. However, stronger lines (marked by crosses) match with BaF_2 pattern. Best results were obtained for the third method in which reverse strike was used. Hot metal chloride solutions were added to the precipitant solution. KF was used as the precipitant. XRD pattern of the compound so prepared matches excellently with that for $LiBaF_3$ (ICDD 18-0176). Line at 12.672 characteristic of BaFCl is totally absent. Use of excess KF may have helped in prevention of BaFCl formation. When minutely observed, very weak lines of BaF_2 can be seen (Fig. 3). All subsequent samples were thus prepared by method 3.

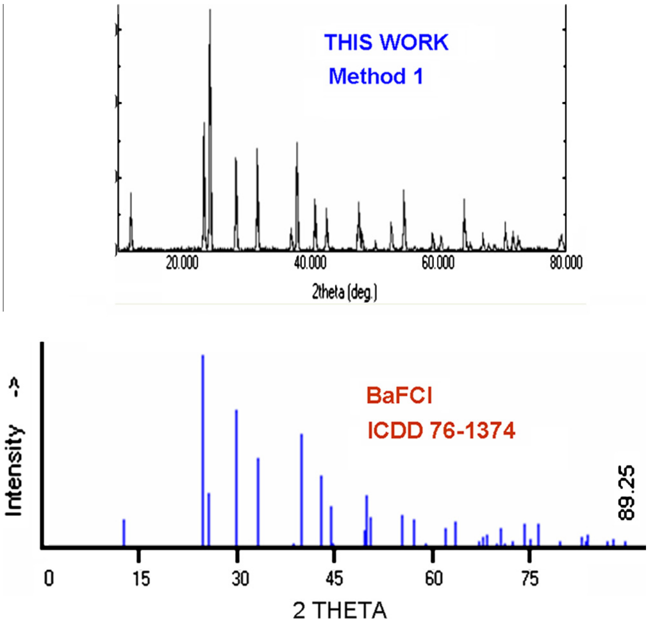

Fig. 1. XRD pattern of attempted $LiBaF_3$ using method 1 (precipitation from aqueous chloride solution using HF) When precipitation synthesis of $LiBaF_3$ was attempted from aqueous solutions of LiCl and $BaCl_2$, using HF as precipitating agent, BaFCl is formed as shown by excellent matching with ICDD data file 76-1374.

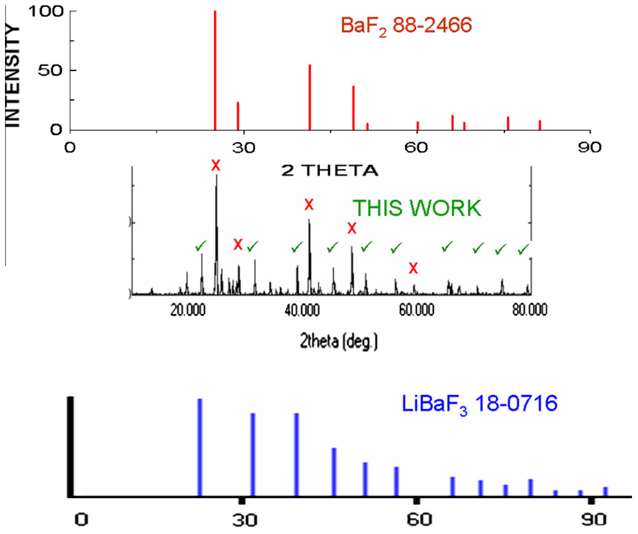

Fig. 2. XRD pattern of attempted $LiBaF_3$ using method 2 (precipitation from aqueous acetate solution using HF). When precipitation synthesis of $LiBaF_3$ was attempted from aqueous solutions of lithium and Barium acetates, using HF as precipitating agent, mixed phase compound was formed. The phases cane be identified as BaF_2 (marked by crosses, ICDD data file 88-2466), and $LiBaF_3$ (marked by tick marks, ICDD data file 18-0716).

Having successfully prepared $LiBaF_3$ by co-precipitation, next step is to attempt preparation of $LiBaF_3$ based phosphors. We attempted incorporation of Ce^{3+}. Eu^{2+}, Tb^{3+} activators. Fig. 4 (curve a) shows PL emission of Ce^{3+} activated $LiBaF_3$. It is remarkable that characteristic emission is observed in as-precipitated powders without any further thermal treatment except that used for drying purpose. The broad emission band peaks at 358 nm. The corresponding excitation spectrum (Fig. 4, curve b) contains prominent bands at 290 and 261 nm with shoulders around 308, 250 and 238 nm. These values, and in general the shapes of the PL curves are in excellent agreement with those reported by Tan and Shi [36]. However, it may be mentioned that different workers have reported various values for emission and excitation bands of Ce^{3+} in $LiBaF_3$ (Table 1). Reason for such diversity of reported results can be understood by considering the crystal structure of $LiBaF_3$. $LiBaF_3$ has an inverted perovskite cubic structure with space group Oh (Pm3m), where the monovalent Li^+ ion is at the center of a F6 octahedron and the Ba^{2+} divalent ion locates at the corners of a cube

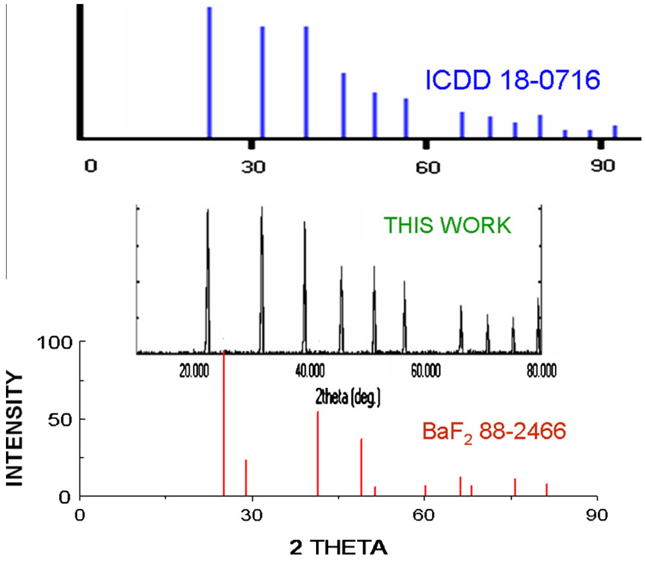

Fig. 3. XRD pattern of $LiBaF_3$ using method 3. An excellent match with ICDD data file 18-0716 is seen.

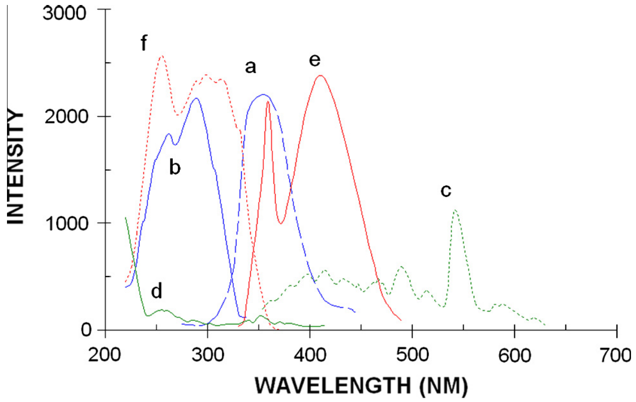

Fig. 4. a > Ce^{3+} Emission for 290 nm excitation. b > Excitation for 358 nm emission of $LiBaF_3:Ce^{3+}$ c > Tb^{3+} Emission for 220 nm excitation. d > Excitation for 543 nm emission of $LiBaF_3:Tb^{3+}$ e > Eu^{2+} Emission for 320 nm excitation. f > Excitation for 410 nm emission of $LiBaF_3:Eu^{2+}$.

Table 1
Summary of Reported data on Ce^{3+} PL in $LiBaF_3$.

Extn. (nm)	Emn. (nm)	Refs.
254	287,295	Ref. [25]
243, 257, 297	361	Ref. [36]
204, 218, 240 and 250	312, 328	Ref. [40]
254 and 297	340	Ref. [30]
235, 256	287, 300	Ref. [42]
265, 299	367	Ref. [41]
240	280, 320	Ref. [6]
261, 290	358	This Work

with the 12-fold environment site (Fig. 5), resulting in a different field interaction from the classic perovskite structure. Ce^{3+} is trivalent, and size wise may be expected to be at Ba substitutional site. This requires charge compensation which can be achieved in a variety of ways. Most obvious being incorporation of Li^+ vacancy, Ba^{2+} vacancies, O^{2-} substitution at fluorine site or interstitial fluorine. Tan and Shi [36] found that oxygen containing $LiBaF_3$:Ce gives emission at longer wavelengths (370–379 nm). Considering sizes and valencies, the occurence of Ba vacancies in A site of perovskite is more probable. Again, the charge compensating defect may be located close to Ce^{3+} or a few lattice spacings away. Whichever case of charge compensation exists, the symmetry of the Ce^{3+} site is lowered from cubic to C_{3v}, C_{4v} or even lower. Existence of as many as five bands/shoulders in the excitation spectrum also indicates lower symmetry. Various local environments are thus possible for Ce^{3+} in $LiBaF_3$ host. This may be responsible for observed variations in literature results on PL of Ce^{3+}. Ce^{3+} excitation results from transition from ground state $^2F_{5/2}$ of $4f^1$ configuration to excited states of $5d^1$ configuration. In crystal, the excited states may broaden and split into up to 5 bands. Number and positions of the bands depend on the site symmetry and coordination [37]. Emission comes from lowest of the excited states of $5d^1$ configuration to $^2F_{5/2}$, $^2F_{7/2}$ states of $4f^1$ configuration. The Stokes shift also strongly depends on the local environment of Ce^{3+}. Thus, we presume that the diversity of the published results on PL spectra of $LiBaF_3$:Ce is due to such effects.

From ESR measurements Yamaga et al. [38,39] suggested two types of defect centers associated with Ce^{3+} in $LiBaF_3$ which were designated as T_1 and T_2. They assigned centers T_1 and T_2 to Ce^{3+} at the 12-fold coordinated Ba^{2+} sites associated with, respectively, a substitutional Li+ and Ba^{2+} vacancy (V_{Ba}) at the nearest Ba^{2+} sites along [001] axis because of charge compensation. Recently, Wen-Chen et al. [40] questioned this assignment and suggested that centers T_1 and T_2 are the substitution of Ce^{3+} for Ba^{2+} with, respectively, a nearest interstitial F^- and a nearest Ba^{2+} vacancy along C_4 axis because of charge compensation.

It is thus seen that defect centers associated with Ce^{3+} in $LiBaF_3$ can be of several types and their detailed structures debatable. However, it is not the objective of the present paper to review the debate over these structures. The main objective is to show that $LiBaF_3$ based phosphors can be prepared by simple wet chemical procedure.

Tb^{3+} can enter $LiBaF_3$: lattice much the same way as Ce^{3+}. In contrast to $LiBaF_3:Ce^{3+}$, PL emission of Tb^{3+} is very weak (Fig. 4, curve c). The reason is that f–d excitation bands of Tb^{3+} are located at very high energies lying outside the range of our instrument. Recently, Zhu et al. [41] reported f–d excitation of $LiBaF_3:Tb^{3+}$ at 217 nm. All the same, upon 220 nm excitation, shortest wavelength possible with our instrument, narrow emission bands around 543 and 487 nm corresponding to transitions $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_6$ can be seen just above the background noise. Excitation spectrum (Fig. 4, curve c) shows some f–f structure and tail of the f–d band. Significant fact is that the as-prepared phosphor shows characteristic Tb^{3+} emission, although feeble, without any thermal treatment.

In contrast to $LiBaF_3:Ce^{3+}$, and $LiBaF_3:Tb^{3+}$, as-prepared powders of $LiBaF_3$:Eu did not show Eu^{2+} emission. Heating in reductive atmosphere provided by burning charcoal yielded a strongly emitting $LiBaF_3:Eu^{2+}$ phosphor. PL spectra are included in Fig. 4. Eu^{2+} emission is in form of a narrow line at 358 nm and a broad band around 411 nm (Fig. 4, curve e). The corresponding excitation spectrum (Fig. 4, curve f) shows two prominent bands around 250 and 310 nm with some structure, particularly a staircase structure for the latter. These results are in excellent agreement with the literature. It may be suspected that presence of small amount of BaF_2 can affect the PL results. However, Eu^{2+} does not show any PL in BaF_2 due to photoionization. The ground state of the Eu^{2+} ion is the spherically symmetrical $^8S_{7/2}$. $LiBaF_3$, Eu^{2+} is at 12-coordinated, Ba^{2+} substitutional site (Fig. 5). The crystal field splits the Eu^{2+} $4f^65d^1$ electronic configuration into the lower t_{2g} and the upper e_g levels, respectively. Depending on the strength of the crystal field, the absorption or the excitation spectrum of octahedrally coordinated Eu^{2+} ion is characterized by two broad and well-isolated bands. The low and high-energy bands are associated with the $4f^7$ $[^8S_{7/2}]$–$4f^65d^1[t_{2g}]$ and the $4f^7$ $[^8S_{7/2}]$–$4f^65d^1[e_g]$ optical transitions, respectively. The latter is responsible for excitation band around 250 nm in $LiBaF_3:Eu^{2+}$. The low energy excitation

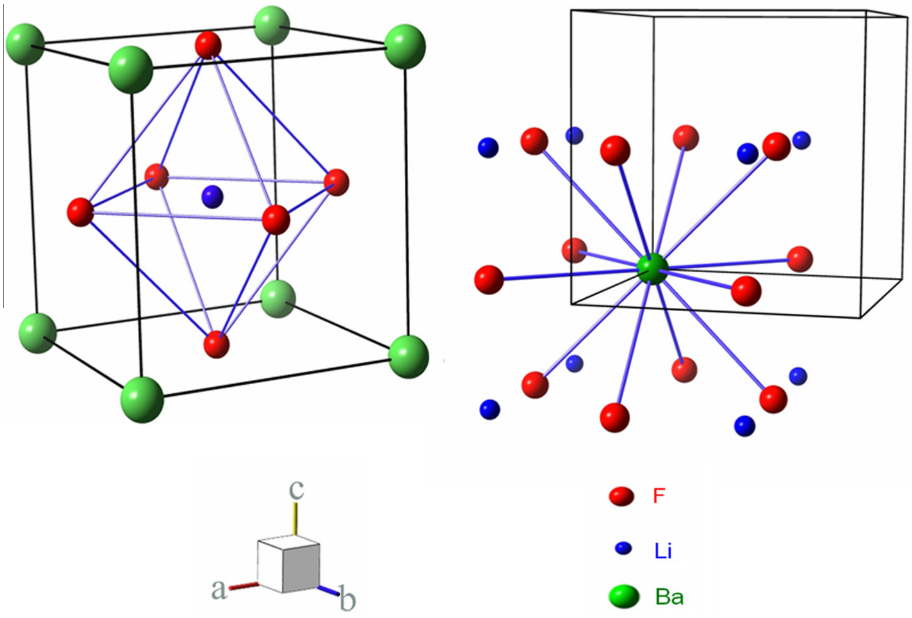

Fig. 5. Co-ordination sphere for cations in $LiBaF_3$ 8-coordination of Li^+ and 12-coordination of Ba^{2+} are depicted.

band due to $4f^7$ $[^8S_{7/2}]$–$4f^65d^1[t_{2g}]$ transition exhibits the characteristic "staircase" spectrum, which retain the character of the seven (Eu^{3+}) $4f^6$ levels ($^7F_{0–6}$) [42,43]. The staircase spectrum is due to the transition from the Eu^{2+} $^8S_{7/2}$ ground state to the seven ^7F_J (J = 0–6) multiplets of the excited $4f^6$ $[^7F_J(J = 0–6)]5d^1$ electronic configuration. Observed excitation bands around 288, 298, 312 nm and the shoulder around 332 nm in $LiBaF_3$:$Eu^{2+}$are due to such transitions. Band emission around 411 nm is due to transition from the lowest band of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ state of $4f^7$configuration. The line emission at 358 is due to $^6P_j \rightarrow {}^8S_{7/2}$ transitions between states of $4f^7$configuration.

4. Conclusions

A simple co-precipitation method using KF as precipitating agent is developed for the preparation of $LiBaF_3$. The method is much simpler compared to the conventional solid state reaction, especially in view of the fact that $LiBaF_3$ is incongruently melting. Activation by rare earth ions is also demonstrated. For Ce^{3+} and Tb^{3+}, characteristic emission was observed in as-precipitated powders, without taking recourse to any thermal treatment. For Eu^{2+} activation, heating in reductive atmosphere was necessary. Phosphors prepared by this method may prove useful in applications like OSL, X-ray imaging, etc. which do not require large single crystals.

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