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Research Article

Synthesis of $KZnF_3$ Phosphors by Co-Precipitation Method

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Abstract. Synthesis of $KZnF_3$ is rather tedious. Typical problems of fluoride synthesis are faced with more acuteness. Even in wet chemical preparations, use of hygroscopic starting materials like zinc chloride or nitrate presents considerable difficulties. A simple precipitation synthesis of $KZnF_3$ with aqueous solutions of zinc sulfate and potassium fluoride is described. Precipitation at the room temperature produces the compound profoundly contaminated with hydroxide phase. Phase pure compound is obtained when boiling solutions are mixed. Activators Cerium and europium could be incorporated by adding the corresponding sulfates to zinc sulfate solution during the precipitation. As prepared phosphor exhibited typical Ce^{3+} luminescence. For obtaining Eu^{2+} luminescence, the phosphor had to be given reducing treatment.

Keywords. Photoluminescence, Fluorides, Fluoroperovskite, Coprecipitation synthesis, $KZnF_3$

PACS. 33.50.-j (Luminescence of molecules), 85.60.-q (Optoelectronic devices), 42.79.Vb (Optical storage devices)

1. Introduction

The complex fluorides of metal have received lot of interest due to their remarkable magnetic [8], piezoelectric [13] and photoluminescence properties [17], insulator behaviour [18]. Among the perovskite fluorides, $KZnF_3$ based materials have received attention due to their luminescence properties. These have been considered to be promising candidates for various applications like lasers and scintillation detection [30]. $KZnF_3$ incorporating 3d transition activators possess several properties like luminescence conducive for lasing and magnetism.

Photoluminescence and/or magnetic properties of $3d^n$ ions like Mn^{2+} [3, 27, 40], Mn^{4+} [19], Ni^{2+} [28, 48], Co^{2+} [5, 45], Cr^{3+} [49], Cr^{2+} [14, 31], Cu^{2+} [12], 4fⁿ lanthanides like Yb^{3+} [4, 25, 39], Tm^{3+} [41], Dy^{3+} [15], Ce^{3+} , Eu^{2+} [20], Eu^{3+} [34], Tb^{3+} [9] and ns² ion Tl^+ [2] have been studied quite extensively. $KZnF_3:Tl^+$ is of interest as a promising material for tunable lasers in the UV region [1] and scintillator [2] while $KZnF_3:Co^{2+}$ serves similar purpose in mid infrared region [7, 23, 33]. Upconversion involving various ion pairs such as $Yb^{3+}-Mn^{2+}$ [43], $Yb^{3+}-Er^{3+}$ [22, 44], $Yb^{3+}-Tm^{3+}$ [41], $Yb^{3+}-Ho^{3+}$ [6], $KZnF_3$ shows intrinsic luminescence [42] though it does not show any cross-luminescence [10]. $KZnF_3$ is of importance in geophysical studies also, being an analogue of $MgSiO_3$ in the lower mantle of earth [24, 32].

Conventional solid state synthesis of $KZnF_3$ is difficult. It involves heating of constituent fluorides in H_2 [31] or HF [7] atmosphere at 800 C. To overcome the problems involved in such procedure, various novel techniques have been tried. These include solid-state metathesis, solvothermal [21, 29, 44, 47] microwave method [34], glass ceramics [28], coprecipitation [19, 26, 46], fluorolytic Sol-Gel Synthesis [35], etc.

In this paper we describe a very simple wet Chemical route for the synthesis of $KZnF_3$.

2. Experimental

All the reagents used were of the Analytical Reagent grade. KF solution was freshly prepared by dissolving K_2CO_3 in HF. Aqueous solution of $ZnSO_4 \cdot 7H_2O$ was slowly added to the solution of KF at above 85°C. The KF should be taken 10 times in excess of stoichiometric proportion. Precipitate of $KZnF_3$ thus formed was filtered, washed repeatedly by double distilled water, and dried under the blower.

The chemical reaction proceeds in the following way:



K_2SO_4 is water soluble and can be removed completely during filtration followed by washing with distilled water. For doping appropriate sulfate salts were added to $ZnSO_4$ solution.

“X-ray diffraction patterns were recorded on a Philips PANalytical X’pert Pro diffractometer. Photoluminescence (PL) spectra at room temperature in the spectral range 220-700 nm were recorded on Hitachi F-4000 spectro-fluorimeter with spectral slit widths of 1.5 nm”.

3. Results and Discussion

Figure 1(A) shows the comparison of XRD patterns of the as prepared $KZnF_3$ powder precipitated at room temperature with the ICDD data file 89-4110. A large number of extra

lines are seen. This could be identified as unwanted hydroxide phase $ZnOHF$ (ICDD 32-1469). It is thus seen that hydrolysis of ZnF_2 is rather acute, when wet chemical method of synthesis is used and the reaction is carried out at room temperature. This is consistent with observation of previous workers that wet chemical synthesis does not lead to phase pure $KZnF_3$. Zinc Hydroxide is not stable above $60^\circ C$ and it was thought that precipitation at temperatures well above $60^\circ C$ may help in avoiding hydroxide formation. Precipitation synthesis was thus repeated with the change that $ZnSO_4$ solution was added to KF solution maintained at $85^\circ C$. Even in this sample $ZnOHF$ phase was found in considerable fraction. Finally, phase pure $KZnF_3$ was obtained when boiling solutions of KF and $ZnSO_4$ were mixed. Figure 1(B) shows XRD pattern of the compound so formed. It is seen that all lines in the pattern match with those for $KZnF_3$ (ICDD 89-4110). No other phase is observable.

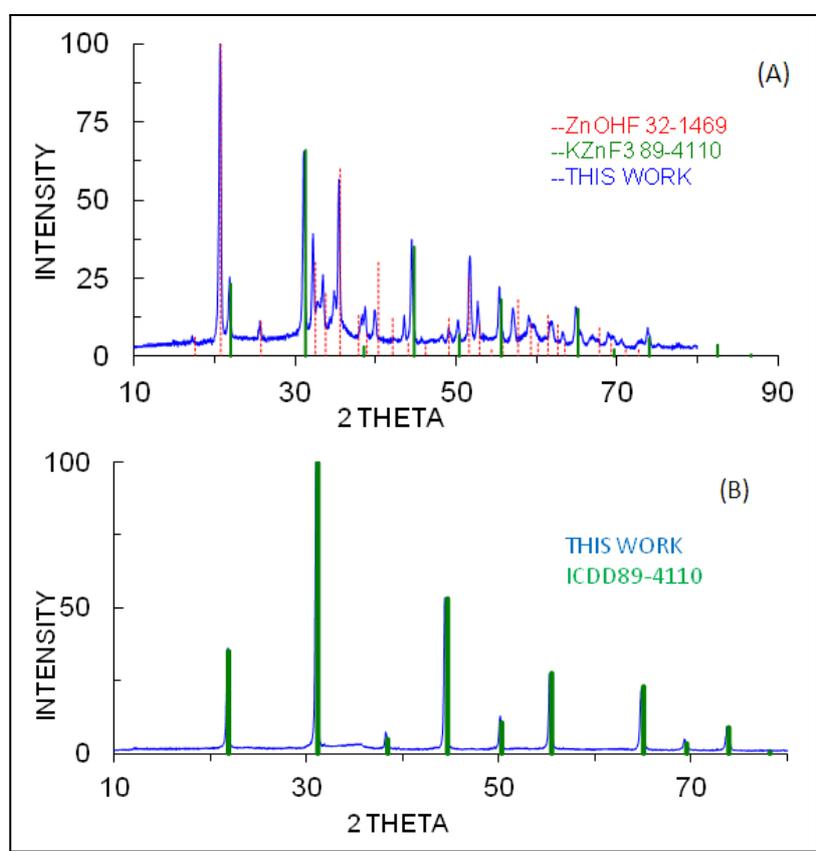


Figure 1. (A) XRD pattern of the compound prepared by precipitation at room temperature, (B) XRD pattern of $KZnF_3$ prepared by mixing boiling solutions of $ZnSO_4 \cdot 7H_2O$ and KF

$KZnF_3$ crystallizes in the cubic perovskite ABF_3 -type system with space group $Pm-3m$ (Figure 2), where the B cations are coordinated by six F anions, while the A cations present a coordination number of 12 (also coordinated by F anions). The F anions are coordinated by two B cations, since the A–F distance is about 40% larger than the B–F bond distance.

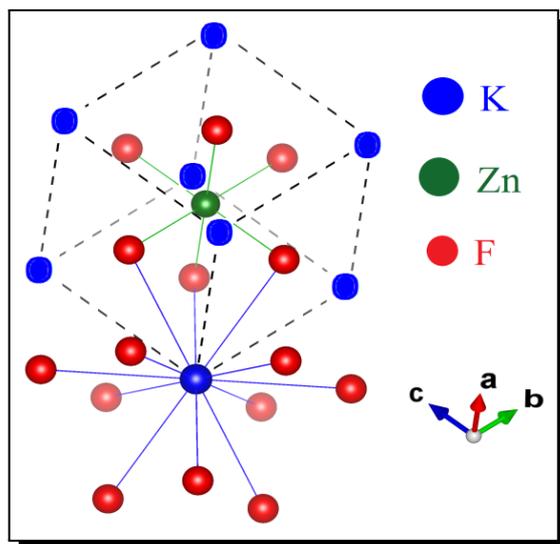


Figure 2. Cation coordination in $KZnF_3$

3.1 $KZnF_3:Ce^{3+}$

In $KZnF_3$, there are two cation sites. 12-coordinated K^+ and 6 coordinated Zn^{2+} . Ionic radii of K^+ (12 coordination) and Zn^{2+} (6 coordination) are 1.65 Å and 0.72 Å, respectively. Ce^{3+} in 12 coordination has ionic radius of 1.34 Å [37]. It is thus expected that Ce^{3+} will enter K^+ sites. Charge compensation can be achieved by incorporation of fluorine interstitials or creation of cation vacancies. As prepared Ce doped sample shows PL emission. Therefore, no thermal treatment was given to the sample before taking measurements. Figure 3(A) shows the PL spectra of $KZnF_3:Ce$ for different concentrations. The intensity increases with increase in dopant concentration. The maximum PL emission is observed for Ce(1%). Figure 3(A) (curve (e,f)) represents the PL spectra of $KZnF_3:Ce$ with K:Ce ratio 99:1. The excitation spectra consist of two peaks around 255 and 299 nm, last one being more prominent. The excitation arises from transitions from the ground state $^2F_{5/2}$ of $4f^0$ configuration to the excited states of $4f^05d^1$ configuration (Figure 3(B)). Excitation by 299 nm yields emission peak at 339 nm with a shoulder at 353 nm. This arises from split ground state ($^2F_{5/2}, ^2F_{7/2}$). These positions are different than that reported by Hua *et al.* [20]. They observed emission at 383 nm for 253 nm excitation. $KMgF_3$ has similar structure. Ce^{3+} occupies K^+ site in this lattice [16]. In our earlier work [38] we reported emission at 330 nm for $KMgF_3:Ce$. Emission at longer wavelength in $KZnF_3:Ce$ indicates somewhat stronger crystal field.

3.2 $KZnF_3:Eu^{2+}$

Using Dorenbos formula [11], it is possible to predict Eu^{2+} emission position from that of Ce^{3+} .

$$E(Eu^{2+}) = (0.64 \pm 0.02)E(Ce^{3+}) + (0.53 \pm 0.06) \text{ eV.}$$

From data on Ce^{3+} presented above, it is predicted that Eu^{2+} emission in $KZnF_3:Eu^{2+}$ should be at 412-452 nm.

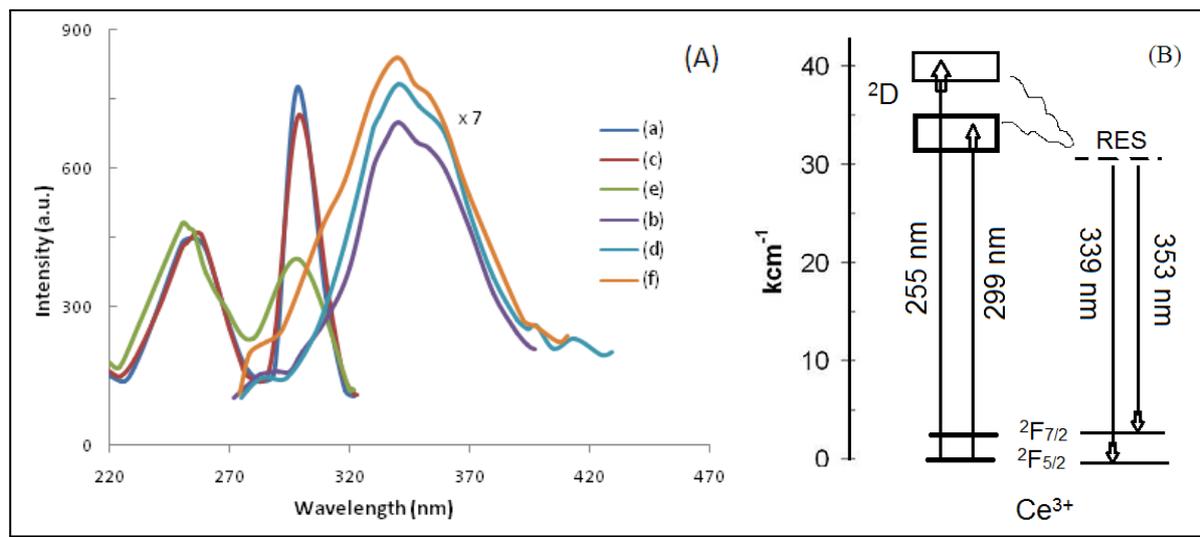


Figure 3. (A) PL emission and excitation spectra for $KZnF_3:Ce^{3+}$, excitation for $\lambda_{em}=339$ nm for (a) Ce(0.1%), (c) Ce(0.2%) and (e) Ce(1%) and emission for $\lambda_{ex}=299$ nm (b) Ce(0.1%), (d) Ce(0.2%) and (f) Ce(1%), (B) Ce^{3+} energy levels in $KZnF_3$

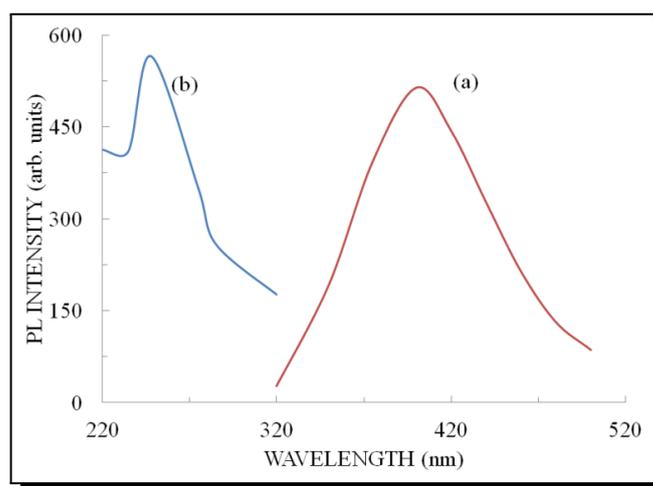


Figure 4. PL emission and excitation spectra for $KZnF_3:Eu^{2+}$ ((a) Emission for $\lambda_{ex}=400$ nm, and (b) excitation for $\lambda_{em}=254$ nm)

This was experimentally verified by preparing $KZnF_3:Eu^{2+}$ sample. As prepared Eu-doped samples do not show PL emission attributable to Eu^{2+} . In order to reduce europium to Eu^{2+} , sample was melted at $870^\circ C$ in graphite crucible and then quenched to room temperature. PL emission was observed. Figure 4 shows the PL spectra for $KZnF_3:Eu^{2+}$ (0.5%). The positions of excitation and emission maxima obtained in our sample are again different from the one reported by Ruinian Hua and co-workers [20]. We observed emission at 400 nm for 254 nm excitation. This is in reasonably good agreement with the predicted value. This shows that Ce^{3+} and Eu^{2+} are at the similar sites (12 coordinated K^+). This is consistent with the fact that in high coordination these two ions have similar ionic radii. Again, when we compare $KZnF_3:Eu^{2+}$ with $KMgF_3:Eu^{2+}$ it is seen that f-f emission is observed in the latter [36], while d-f emission in

the former. This indicates that Eu^{2+} experiences much stronger crystal field in $KZnF_3:Eu^{2+}$ than in $KMgF_3:Eu^{2+}$.

4. Conclusions

Phase pure $KZnF_3$ can thus be prepared using wet chemical method if precipitation is carried out at sufficiently high temperature. Activators also can be conveniently incorporated. Use of non-hygroscopic $ZnSO_4$, instead of $ZnCl_2$ or nitrate further simplifies the synthesis.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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