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Photoluminescence Studies of Eu^{3+} Doped $CaBaAlF_7$ Prepared by Solid State Metathesis Method.

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Abstract
In this paper recently synthesized fluoride Eu doped $CaBaAlF_7$ reported first time. Synthesis of Fluorides like $KMgF_3$:Eu, CaF_2:Eu, $CaSrF_2$:Eu and CaF_2:Ce phosphors is possible by solid state metathesis. Fluorides have wide applications in optics as windows, lenses, scintillation crystals, and they are also used as host crystals for rare earth ions (Ho, Er, Eu, Nd, Ce) exhibiting interesting properties in optoelectronics such as lasing, light amplification, etc. These fluorides could be prepared in several minutes using domestic microwave oven. Though $CaBaAlF_7$ is formed by metathesis, luminescence centers were not formed in one step; as-prepared samples did not show any luminescence. Samples reduced at 1000 C for 1 hour exhibited very intense, characteristic emission. Activator concentration, and in turn, the intensity of luminescence depends on the partition coefficient of the activator in the host and the washable reaction products (KCl in the present case).
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1. Introduction

The ternary systems MF_2-MF_2-$A1F_3$ where M= Ca, Sr, or Ba, were examined for compatibility triangles and compounds [1]. The compounds $SrCaA1F_7$ and $BaCaA1F_7$ were found, each with three polymorphs. The β- and γ-forms in the $SrCaA1F_7$ compound could be quenched. The two low-temperature (α) forms show strong line emission at 358 to 360 nm with Eu^{2+} activation, resulting from absorption into the 5d states and emission from the $^6P_{7/2}$ levels to the $^8S_{7/2}$ ground state. The β- and γ-forms of $SrCaA1F_7$ contain a band emission and a much weaker line. In the pseudo ternary system $MF_2/M'F_2/AlF_3$ with M, M' = Ca, Sr, Ba three alkaline earth aluminium fluorides, $CaSrAlF_7$, $BaCaAlF_7$[1] and $Ba_{0.43}Sr_{0.57}AlF_5$ [2], have so far been described. Eu^{2+} ($CaSrAlF_7$ and $CaBaAlF_7$) and Sm^{2+} ($Ba_{0.43}Sr_{0.57}AlF_5$) activation within these crystal structures has also been investigated. For $CaSrAlF_7$ and $CaBaAlF_7$ polytypism has been revealed by thermal analysis showing the existence of three modifications, α, β, and γ [1]. For all three modifications of $CaSrAlF_7$ there are powder data entries in the Powder Diffraction File (PDF numbers α: 28-0787, β: 28-0808, γ : 28-0238), whereas for $CaBaAlF_7$ only one form, α- $CaBaAlF_7$, has been isolated and X-ray powder data deposited (PDF number 27-0090).

Complex fluorides are proper host materials for optical hole burning or for doping with luminescent ions, e.g., Eu^{2+} or Sm^{2+} [3,4].Some complex aluminum

fluorides are also tried by microwave assisted solid state metathesis method. Aluminum fluorides involving two alkaline earth metal ions in the formula are $CaBaAlF_7$ and $CaSrAlF_7$. In contrast to the earlier phosphors; none of these phosphors is formed immediately after SSM method.

However when the precipitated powders are melted their XRD matched very well with the ICDD files. It is quite remarkable that such complex fluorides were formed by simple method of preparation.

2. Experimental

All the reagents used were of the analytical reagent grade. $CaCl_2$:Eu powders were first prepared by dissolving $CaCO_3$ and Eu_2O_3 in concentrated HCl. Also $BaCl_2$ powders were first prepared by dissolving $BaCO_3$ in concentrated HCl. The excess acid was distilled off in a closed assembly. $CaCl_2$:Eu and $BaCl_2$ powder so obtained was thoroughly mixed with anhydrous potassium fluoride in the proportion compatible with the reaction:

$$CaCl_2{:}Eu + BaCl_2 + AlCl_3 + 7KF = CaBaAlF_7{:}Eu + 7KCl.$$

A china dish containing the resulting mixture was placed in a domestic microwave oven operating at 2.45 GHz with a 900 W microwave power. After 05 min, the china dish was removed from the oven. The products obtained were washed with distilled water several times to remove the unreacted KF and/or $CaCl_2$, $BaCl_2$,$AlCl_3$ and the KCl formed in the metathesis, and then dried on a hot plate at 90°C overnight. The insoluble matter was used for further experiments. For reducing europium to divalent form, the $CaBaAlF_7$:Eu powder formed in the metathesis reaction was heated at 750°C for 1 hr in a reducing atmosphere provided by the burning charcoal. $CaBaAlF_7$:Eu powders with Eu concentrations of 1mol % were prepared.

3. Results and Discussion

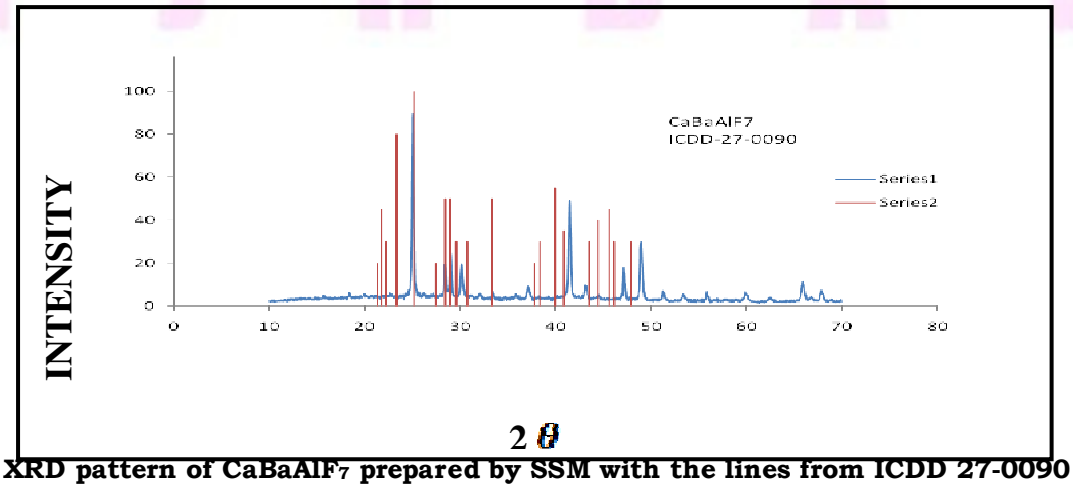

Fig.1: XRD pattern of $CaBaAlF_7$ prepared by SSM with the lines from ICDD 27-0090 files.

Fig. 1 shows XRD pattern of double alkaline earth fluorides along with the lines from ICDD files. An excellent match is not seen with the lines of ICDD files. Some extra line of CaF_2 or BaF_2 or any residual fluoride is observed .In $CaBaAlF_7$ several phases exist and Eu^{2+} luminescence in these hosts are different for various phases [5].

The system CaF_2-BaF_2-$A1F_3$ is the least complex, and contains one ternary compound at $BaCaA1F_7$, and a limited amount of solid solution in $Ba_9A1_2F_{24}$, based on a shift in observed d spacing[6].

Divalent Eu activation in alkaline earth aluminum fluorides has been found to give two types of emission, the band emission normally associated with Eu^{2+} 5d to $4f^7$ transitions, and line emission from transitions within the $4f^7$ configuration. A general description of both types has been reported [7].

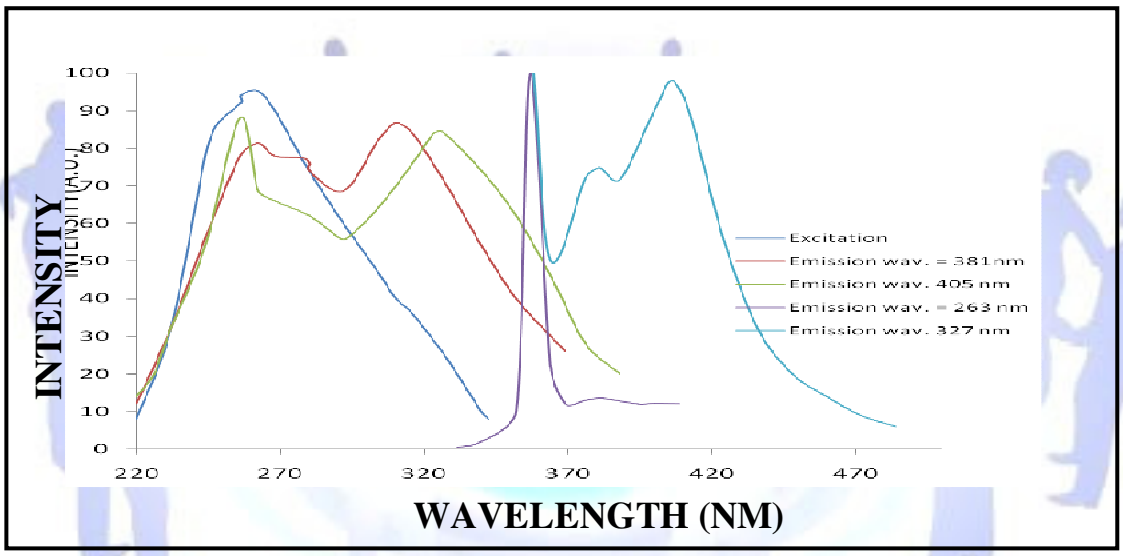

Fig.2: The Photoluminescence (PL) spectra of $CaBaAlF_7$:Eu^{2+}

Fig. 2 shows the PL emission spectra of $CaBaAlF_7$:Eu^{2+}. An intense emission at 357.8 nm is observed in $BaCaAlF_7$: Eu ,which is due to transition from $^6P_{7/2}$ to $^8S_{7/2}$ energy levels of Eu^{2+} ions. A small kink at 354 nm can ascribed to $^6P_{5/2} \rightarrow {}^8S_{7/2}$ transition of Eu^{2+}. A broad excitation spectrum of this sample has two small peaks at 241 nm and 259 nm. Excitation is due to the transition from ground state $^8S_{7/2}$ to the $4f^6$5d states.

Luminescence spectra of $BaCaAlF_7$:Eu is in good agreement with those reported by Hoffman. The various structures which can be obtained in the ternary compounds all show emission with Eu^{2+} with the two low-temperature polymorphs showing predominantly line emissions at 358-360 nm.

4. Conclusion

$CaBaAlF_7$:Eu is formed by solid state metathesis which is a fast method for synthesis. However, preparation of phosphors is not straight forward. Activator is not properly dispersed and high temperature annealing is necessary for activation.

5. References

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