

# Wet Chemical Synthesis of $\text{KCaI}_3:\text{Eu}^{2+}$ Phosphor

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**Abstract.**  $\text{KCaI}_3:\text{Eu}^{2+}$  is recently discovered scintillator with high light yield and energy resolution. Conventionally, the phosphor is prepared by melting the constituent iodides. An alternative, simpler, wet chemical synthesis of  $\text{KCaI}_3:\text{Eu}$  phosphor is described. From photoluminescence characterization it is inferred that the phosphor is successfully synthesized.

## INTRODUCTION

In the recent years, a series of  $\text{Eu}^{2+}$ -doped halide scintillators based on perovskite-structure and chemical formula  $\text{ABX}_3$  (A=alkali, B=alkaline earth and X=halogen) have been developed because of their attractive scintillation properties. Among these,  $\text{KCaI}_3:\text{Eu}^{2+}$  has the best performance with respect to light yield (70,000 ph/MeV) and energy resolution of 3% at  $^{137}\text{Cs}$  decay energy of 662 KeV [1-9]. Conventional method for the crystal growth involves melting the constituent iodides together. In this method one has to use commercially available iodides which could be contaminated during storage, or synthesize two iodides ( $\text{KI}$  and  $\text{CaI}_2$ ). Due to hygroscopic nature, the synthesis and crystal growth has to be carried out with special apparatus. In our earlier work, we have described a wet chemical procedure for synthesizing highly efficient,  $\text{Eu}^{2+}$  activated phosphors based on alkali alkaline earth double halides with strong excitation in nUV region [10-14]. We successfully prepared  $\text{KCaI}_3:\text{Eu}^{2+}$  powders by this method. Synthesis and photoluminescence characterization of these phosphors are described in this paper.

## EXPERIMENTAL

Samples were prepared by dissolving desired quantities of metal carbonates and  $\text{Eu}_2\text{O}_3$  in HI. Excess acid was then boiled off and the solutions were evaporated to dryness. The resulting mass was dried at 475 K for 2 hours in air, crushed to fine powders (<72 microns) and then annealed for 1 hour at temperatures ranging between 750 K in a reducing atmosphere provided by burning charcoal so as to reduce the activator to divalent state. The annealed powders were quickly sandwiched between quartz plates and transferred to photoluminescence (PL) cell. Photoluminescence spectra and decay curves were recorded in the range 220-700 nm on Hitachi F-7000 spectrofluorimeter with spectral slit widths of 1 nm. Lifetime measurements were carried out on Horiba Fluorolog TCSPC spectrofluorimeter.

## RESULTS AND DISCUSSION

We could not record XRD pattern for  $\text{KCaI}_3$  due to its hygroscopic nature. However, the formation of the phosphor could be confirmed by studying the luminescence properties and drawing comparison with the literature. Luminescence of  $\text{KCaI}_3:\text{Eu}^{2+}$  had been described by several authors.  $\text{Eu}^{2+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  $^8\text{S}_{7/2}$  state of  $4f^7$  configuration. The excitation arises from the transition from  $^8\text{S}_{7/2}$  state of  $4f^7$  configuration to the states belonging to  $4f^65d^1$  configuration. The ground state electronic configuration of  $\text{Eu}^{2+}$  is  $4f^7$ .

This results in a  $^8S_{7/2}$  level for the ground state. The next  $f^7$  manifold ( $^6P_7$ ) lies approximately  $28000\text{ cm}^{-1}$  higher. The most commonly observed emission is the dipole and spin allowed d-f-emission starting from the relaxed  $4f^6(^7F_0) 5d^1$  level. Due to allowed nature of the transition, d-f emission is intense. As the d shell electron is not shielded unlike that in f shell, both the excitation and emission spectra are in form of broad bands.

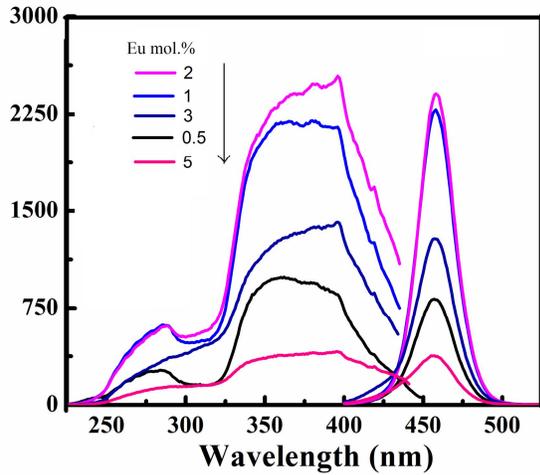


FIGURE 1. PL emission and excitation spectra

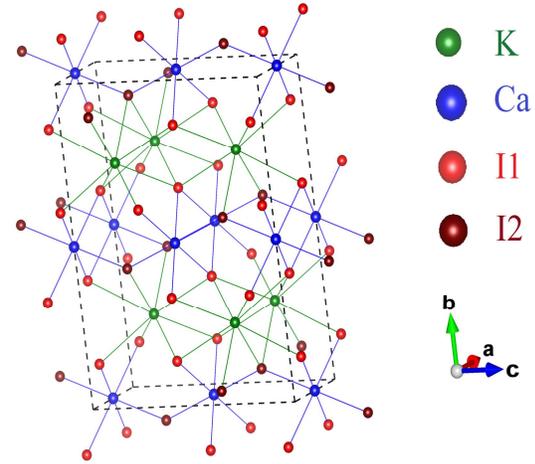


FIGURE 2. Unit cell of  $\text{KCaI}_3$

Fig.1 shows PL emission and excitation spectra for  $\text{KCaI}_3:\text{Eu}^{2+}$  phosphors. An intense emission in form of a band peaking around 457 nm can be seen. The excitation spectrum consists of two bands around 285 and 375 nm with considerable structure. These results are in good agreement with the previous reports [5]. Intensity is maximum for 2 mol.%  $\text{Eu}^{2+}$ . From these data critical distance for  $\text{Eu}^{2+} - \text{Eu}^{2+}$  transfer can be calculated using the formula [15].

$$R_c = 2 (3V/4\pi x_c N)^{1/3} \quad (1)$$

where  $x_c$  is the critical concentration (0.02),  $N$  is the number of Ca sites in the unit cell (4) and  $V$  is the volume of the unit cell ( $798.5344 \text{ \AA}^3$ ).  $R_c$  comes out to be  $26.72 \text{ \AA}$ .  $\text{Eu}^{2+}$  is expected to substitute for  $\text{Ca}^{2+}$  in  $\text{KCaI}_3$  host.  $\text{KCaI}_3$  has an orthorhombic structure with space group  $\text{Cmcm}$ . Potassium ions are in 8 coordination while Ca 6 (Fig.2).

Results of lifetime measurements are presented in Fig.3. The decay curve can be fitted to a single exponential with  $\tau = 560 \text{ ns}$  which is again in good agreement with the literature results [5].

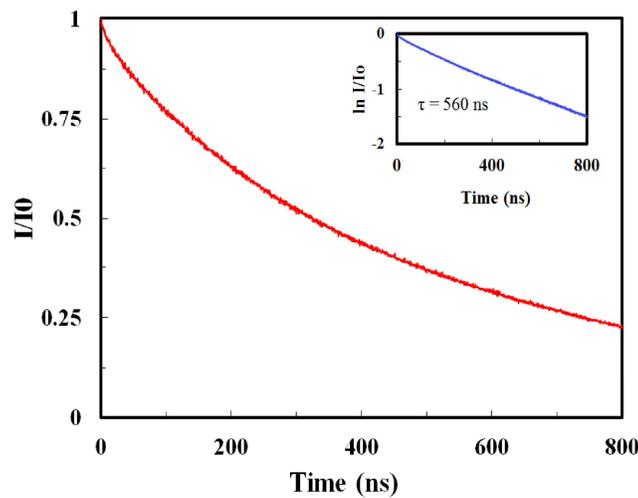


FIGURE 3. Luminescence decay for  $\text{KCaI}_3:\text{Eu}^{2+}$

Lifetime measurements were carried out on Horiba Fluorolog TCSPC spectrofluorimeter. Horiba N-370 Nano LED was used as a source of excitation.

## CONCLUSIONS

Luminescence results of the sample prepared in this work are in good agreement with those reported for  $\text{KCaI}_3:\text{Eu}^{2+}$ . It can thus be concluded that this phosphor can be prepared by wet chemical method. This can be much better than the conventional method which involves melting of the constituent iodides which can cause loss of stoichiometry due to differences in the melting points ( 681 C for KI and 779 C for  $\text{CaI}_2$ ) and vapour pressures of KI and  $\text{CaI}_2$ .

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## REFERENCES

1. A. C. Lindsey, M. Zhuravleva, L. Stand, Y. T. Wu, and C. L. Melcher, *Opt. Mater.* **48**, 1-6 (2015).
2. Y. T. Wu, Q. Li, B. C. Chakoumakos, M. Zhuravleva, A. C. Lindsey, J. A. Johnson II, L. Stand, M. Koschan, and C. L. Melcher, *Adv. Opt. Mater.* **4**, 1518-1532 (2016).
3. Y. T. Wu, A. C. Lindsey, M. Zhuravleva, M. Koschan and C. L. Melcher, *Cryst. Growth Des.* **16**, 4129-4135 (2016).
4. Y. T. Wu, A. C. Lindsey, M. Zhuravleva, M. Koschan, and C. L. Melcher, *CrystEngComm* **18**, 7435-7440 (2016).
5. A.C. Lindsey, M. Zhuravleva, Y. Wu, L. Stand, M. Loyd, S. Gokhale, M. Koschan and C.L. Melcher, *J. Cryst. Growth* **449**, 96-103 (2016).
6. Adam C. Lindsey , Yuntao Wu, Mariya Zhuravleva, Matthew Loyd, Merry Koschan and Charles L. Melcher, *J.Crystal Growth* **470**,20-26 (2017).
7. Yuntao Wu, Qi Li, Steven Jones, Chaochao Dun, Sheng Hu, Mariya Zhuravleva, Adam C. Lindsey, Luis Stand, Matthew Loyd, Merry Koschan, John Auxier II, Howard L. Hall, and Charles L. Melcher, *Phys. Rev. Applied* **8**, art. no.034011 (2017).
8. Adam C. Lindsey , Matthew Loyd, Maulik K. Patel, Ryan Rawl, Haidong Zhou, Merry Koschan, Charles L. Melcher and Mariya Zhuravleva, *Mater. Chem. Phys.* **212**, 161-166 (2018).
9. Yuntao Wu, Qi Li, Daniel J. Rutstrom, Mariya Zhuravleva, Matthew Loyd, Luis Stand, Merry Koschan and Charles L. Melcher, *Phys. Status Solidi RRL* **12**, art. no. 1700403 (2018).
10. P.K. Tawalare, V.B. Bhatkar, S.K. Omanwar and S.V. Moharil *Opt. Mater.* **79**, 470–474 (2018).
11. Priya Tumram, P.D.Sahare and S.V.Moharil *J.Lumin* **199**, 78-81 (2018).
12. D.H.Gahane, N.S.Kokode, P.L.Muthal, S.M.Dhopte and S.V.Moharil, *J.Lumin.* **130**, 254-257 (2010).
13. J.R.Raipurkar, R.G.Atram, P.L.Muthal, S.M.Dhopte and S.V.Moharil *J.Lumin.* **136**, 365-368 (2013).
14. J.R.Raipurkar, R.G.Atram, P.L.Muthal, S.M.Dhopte and S.V.Moharil, *Opt.Mater.* **35**, 1243-46 (2013).
15. G. Blasse, *Philips Res. Rep.* **24**, 131-144 (1969).