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Abstract

In this work we prepared KCaF₃ Co-doped with Gd^{3+} , Eu^{3+} phosphor synthesis via reactive atmosphere process. Powder X-ray diffraction analysis shows structural purity of as-synthesized phosphor. The emission and excitation spectra of KCaF₃: Gd^{3+} , Eu^{3+} were investigated using the VUV beam line of the Beijing Synchrotron Radiation Facility (BSRF). Hear we investigate the mechanism of Energy transfer in Gd^{3+} ions to Eu^{3+} through cross relaxation process. In this phosphor we got negative results. The excitation peak of 273 nm was very much greater than that of the excitation peak of 147 nm at emission wavelength 593 nm. Hence there was no energy transfer in between the ions Gd^{3+} and Eu^{3+} . The results was no quantum cutting in the given phosphor material.

Keywords: Reactive Atmosphere Process (RAP), Quantum cutting (QC), Vacuum Ultraviolet (VUV)

Introduction

For the development of mercury free florescent lamps and plasma display panels (PDPs), we require phosphor having quantum efficiency is greater than unity under VUV excitation. The phosphors having quantum efficiency is greater than unity are called quantum cutting phosphors. Quantum cutting provides a means to obtain two or more low energy photons for each high energy absorbed photon. Therefore it serves as a down converting (DC) mechanism with quantum efficiency greater than unity and it offers the prospect of providing enhanced energy effectiveness in lighting devices [1]. Calcium fluoride with rare earth doped phosphor has conventional attention for numerous research works [2]. B. Herden *et al.* reported photon cascade emission in Pr^{3+} doped fluorides with CaF_2 structure [3]. W. Binder *et al.* reported CaF_2 :Sm³⁺ Phosphor was used for the application of solid state laser materials [4]. R. Wegh *et al.* explain detail about visible quantum cutting through down-conversion in rare-earth compounds [5]. B. Liu *et al.* also explain visible quantum cutting in BaF₂: Gd; Eu via down-conversion in which one VUV photon absorbed by Gd³⁺ can be split into two visible photons emitting by Eu³⁺ through cross relaxation between Gd³⁺ and Eu³⁺[6].

Experimental

KCaF₃: Gd³⁺, Eu³⁺ phosphor was synthesis via reactive atmospheric process. In this method we used metal nitrate like Ca (NO₃)₂ (99.99% A.R.) and potassium nitrate KNO₃ as a precursor. The above both inorganic precursors were taken in Teflon beaker. A little amount of double distilled water was added in beaker and stired it, then hydrofluoric acid (HF) added in it to get slurry. The slurry was dried by blowing air or heating on hot plate (80°C). A freshly prepared KCaF₃ host was obtained. Gd₂O₃ (AR 99.9%) and Eu₂O₃ (AR 99.9%) were boiled in HNO₃ and evaporated to dryness, so as to convert them into relevant nitrates. The aqueous solution of these nitrates where use as a dopants. The 1 mol% of gadolinium nitrate and 1mol% of europium nitrate where assorted in the host material and dehydrated completely.

The dried powder was transferred to a glass tube and about 1.0 wt. % RAP agent was added. In this process we used ammonium fluoride as a RAP agent. The tube was closed with a tight stopper and slowly heated to 500°C for 3 h. The stopper was removed and the powders were transferred to a graphite crucible preheated to a suitable temperature. After heating in the graphite crucible for 1 h the resulting phosphor was rapidly quenched to room temperature. Belsare *et al.* well discussed about RAP in their literature [7]. The complete process involved in the reaction was represented as a flow chart in Fig. 1.

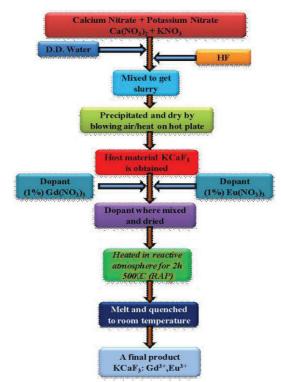
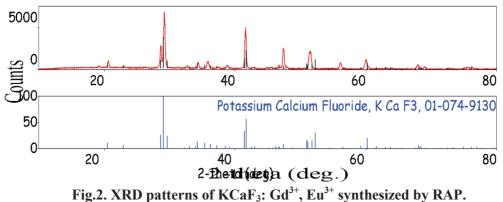


Fig.1. Flow chart of KCaF₃: Gd³⁺, Eu³⁺ prepared via RAP.

Results And Discussion

XRD Analysis

The formation of the KCaF₃: Gd^{3+} , Eu^{3+} sample in the crystalline phase synthesized by RAP was confirmed by XRD pattern as shown in Fig.2. The XRD pattern for KCaF₃: Gd^{3+} , Eu^{3+} agreed well with the standard data from ICDD file (01-074-9130). Also the XRD pattern show that KCaF₃ lattice possesses Orthorhombic structure with a space group Pnma(62) with lattice parameters a= 6.2288 b= 8.7003 c= 6.1121and interfacial angles Alpha= 90.000 Beta= 90.000 Gamma= 90.000 . XRD pattern of CaF₂: Gd^{3+} , Eu^{3+} phosphor as shown in fig.2.



VUV-UV PL Analysis

The process transfer of energy and quantum splitting can happen by the combination of Gd^{3+} and Eu^{3+} in which Gd^{3+} absorbing a VUV photon corresponding to ${}^{8}S_{7/2} \rightarrow {}^{6}G_{J}$. The incident high energy photon is cut into two visible photons emitted by Eu^{3+} ions. The whole process is called as quantum cutting [5]. But in the KCaF₃:Gd³⁺, Eu³⁺sample, the absorption peaks of a VUV photon corresponding to ${}^{8}S_{7/2} \rightarrow {}^{6}G_{J}$ and ${}^{8}S_{7/2} \rightarrow {}^{6}D_{J}$ does not observed under the excitation wavelength of 593nm and 612 nm in excitation spectrum as shown in fig. 3.

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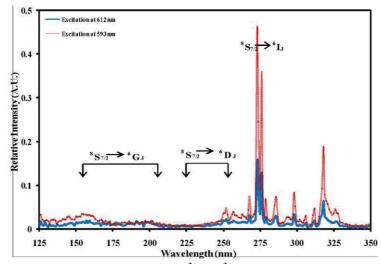


Fig.3. Excitation spectrum of KCaF₃:Gd³⁺, Eu³⁺ monitored at 593 nm and 612 nm.

Upon excitation in ${}^{6}I_{J}$ level with 273 nm, the quantum cutting never occurs because no cross-relaxation exists, so the ${}^{5}D_{J} \rightarrow {}^{7}F_{J}$ transitions emission of Eu³⁺ has a normal branching ratio between ${}^{5}D_{0}$ and ${}^{5}D_{1, 2, 3}$. Upon 147 nm and 172 nm excitation in ${}^{6}G_{J}$ level with, the quantum cutting can occur via two-step energy transfer, but there were no excitation peaks observed in between 140 nm to 200 nm wavelengths. It means that the synthesized phosphor material does not absorbed high energy VUV photons. The emission spectra under excitation of 273 nm, 172 nm and 147 nm are shown in Fig 4. The intensity peak under the excitation of wavelength 273 nm is much greater than that of excitation wavelength of 147 nm and 172 nm under the emission of wavelength 593 nm.

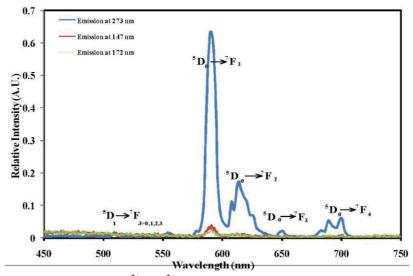


Fig.4. Emission spectra of KCaF₃:Gd³⁺, Eu³⁺ at excitation wavelength 147 nm, 172 nm and 273 nm.

Conclusions

The inorganic material KCaF₃: Gd^{3+} , Eu^{3+} was successfully prepared through reactive atmosphere process. The XRD pattern confirmed its orthorhombic structure. The excitation peak of 273 nm was very much greater than that of the excitation peaks of 147 nm and 172 nm at emission wavelengths 593 nm. Hence there were no energy transfer in between the ions Gd^{3+} and Eu^{3+} . The results were no quantum cutting in the synthesized phosphor material.

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References

- 1) C.R. Ronda, J. Alloys Compd. 225 (1993) 534.
- 2) S. Pote, C. Joshi, S. Moharil, P. Muthal, S. Dhopte. ISSN 1061-3862, International Journal of Self Propogating High-Temperature Synthesis. 22 (2013) 37-40
- 3) B. Herden, A. García-Fuente, H. Ramanantoanina, T. Jüstel, C. Daul, W. Urland, Chemical physics letter. 620 (2015) 29-34.
- 4) W. Binder, S. Dislerhoff, J. Cameron, Dosim etric Properties of CaF2: Dy, (a) Proc. II Int. Conf. on Lumin. Dosim., Gatlinberg, 1968, pp. 45–53; (b) Health Phys., 1969, vol. 17, no. 4, pp. 613–618.
- 5) R.T. Wegh, E.V.D. van Loef, A. Meijerink, J. Lumin., 90 (2000) 111.
- 6) B. Liua, Y. Chena, C. Shia, H. Tanga, Y. Tao, Journal of Luminescence 101 (2003) 155–159.
- 7) P. Belsare, C. Joshi, S. Moharil, V. Kondawar, P. Muthal, S. Dhopte, J. Alloys Compd. 450 (2008) 468-472.