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Effect of Bi ion on $Eu^{2+} \leftrightarrow Eu^{3+}$ conversion in CaF_2:Eu phosphors for RPL dosimetry

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Abstract UV photo-excited Eu^{2+} and Eu^{3+} luminescence from CaF_2:Eu and CaF_2:Eu, Bi phosphors were investigated. The effect of gamma exposure followed by temperature effect shows conversion mechanism between $Eu^{2+} \leftrightarrow Eu^{3+}$ ion in CaF_2:Eu and CaF_2:Eu, Bi phosphors which were studied for RPL dosimetry. The photoluminescence and X-ray diffraction characterization are reported in this article.

Introduction

Fluorides are well known as efficient host lattices of phosphors involved in numerous applications, instance as a media for laser action [1, 2], optical frequency upconverters [3], neutron scintillation detectors [4], and lamp phosphors [5, 6]. Fluorides have several specific features in the field of luminescent materials such as: good transparency in the vacuum ultraviolet (VUV) and visible range, weak crystal field, small refractive index, low phonon frequencies, and long lifetime of the excited states. These lead to a weak probability of non-radiative transitions and therefore it is very good material for luminescent and laser properties [7]. Moreover, fluorides are suitable host matrices for studying the luminescent properties of rare earth ions [8]. In the past few years, there has been an increased interest in the study of the VUV spectroscopy of rare earth ions which is the part of the effort to design new phosphors for displays, lamps, and scintillator materials [9, 10]. Among the fluoride compounds, CaF_2 is an attractive material because of its stability and non-hygroscopic behavior. Besides, recently CaF_2 gained a renewed interest as a laser material when doped with RE ions. In the case of CaF_2:Yb single crystal for instance, due to its broad emission bands, very good performances as tunable laser and ultra-short pulse laser generator have been demonstrated [11, 12]. Since Boutonnet et al. [13] reported the synthesis of monodispersed metallic particles, microemulsions have been successfully used for the synthesis of several undoped and RE-doped compounds.

The luminescence of europium, has been intensively studied during the last decades and several applications have been reported [14]. As a specific fact europium is able to occur both as divalent and trivalent ion and both of them are of practical interest: BaFBr:Eu^{2+} is an important X-ray storage phosphor in image plate detection systems and Y_2O_3:Eu^{3+} is used in the display technology. Blue light emitting $BaMgAl_{10}O_{17}$:Eu^{2+} is a very efficient lamp phosphor. Most of the luminescence studies of europium in solids were carried out on compounds where europium is coordinated by fluorine, chlorine, bromine, and/or oxygen. Recently, luminescence of materials containing europium coordinated by nitrogen has been reported [15]. In some cases, it is quite difficult to stabilize Eu^{2+} because of its lower stability compared with Eu^{3+} [16]. Rare earth ions

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are known to exist in various valence states although the trivalent state is the most prevalent. In particular, Sm and Eu ions are known to be stable in trivalent as well as divalent states. It is also known that exposure to ionizing radiation often results in $RE^{3+} \rightarrow RE^{2+}$ conversion [17]. In fact in the two well-known phosphors used in dosimetry of ionizing radiations using thermoluminescence technique, namely CaF_2:Dy and $CaSO_4$:Dy, such conversion has been proposed to play a major role in the thermoluminescence processes [18]. Several RE-doped phosphors such as $CaSO_4$:Dy, $LiYF_4$:Tm^{3+}, Tb^{3+}, Eu^{3+}, MgB_4O_7:Dy^{3+} find important applications in various fields. Only few studies have been made on the radiation effect of fluoride based materials.

In this article, we have reported CaF_2:Eu and co-doped Bi phosphors that possess the properties which are useful for radio photoluminescence dosimetry for ionizing radiations. Rare earth doped calcium fluoride based phosphor shows the $Eu^{2+} \leftrightarrow Eu^{3+}$ valencies transfer mechanism due to irradiation effect followed by temperature treatment.

Experimental

In the preparation of CaF_2:Eu and CaF_2:Eu, Bi phosphors, we used calcium chloride dehydrate ($CaCl_2{\cdot}2H_2O$, Merk-99.9%), europium oxide (Eu_2O_3, Himedia, 99.9%), nitric acid (conc. HNO_3, Merk-99.99%), ammonium fluoride (NH_4F, Merk-99.50%), bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, Merk-99.50%), and ethanol as raw materials. The CaF_2:Eu was prepared in the following method

Dehydrated calcium chloride and europium nitrate were mixed into alcohol to form transparent solution, and then ammonium fluoride was added in excess in the calcium chloride solution. Whitish solution was obtained, which was then stirred for 10–12 h. After that calcium chloride was mixed completely with ammonium fluoride solution. Then ethanol was added into the solution and kept on high speed centrifuge at 3000 rpm for 3 h at 22–25 °C, finally paste was formed in white color. This paste was dried at 60 °C for 12 h to get white luminescent powder. For the preparation of CaF_2:Eu, Bi, bismuth nitrate was added as impurity in the mixture of dehydrated calcium chloride, ammonium fluoride, and europium nitrate and the same procedure was repeated.

The prepared powder samples were characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.01°, continue time 20 s, in the 2θ range from 10° to 120°. Formation of the compound confirmed by XRD pattern matched with the standard data available in JCPDS file. PL characteristics were studied for 2 mg of sample each time using a RF-5301PC Shimadzu spectrofluorophotometer, at room temperature, using 1.5 nm spectral slit width in the range of 200–700 nm. To study the effect of gamma irradiation on their photoluminescent properties of the prepared phosphors, the samples were exposed to gamma rays from a ^{60}Co source at room temperature at the rate of 0.995 kGy/h.

Results and discussion

X-ray diffraction properties of CaF_2 host

Figure 1 shows the X-ray diffraction pattern of CaF_2 host lattice. XRD analysis with monochromatic Cu-Kα radiation (K = 0.1505 nm), respectively, 2θ range of the X-ray diffraction is from 0° to 120° and the peak was detected in the order of 0.01°. The X-ray diffraction pattern did not indicate presence of the constituent's calcium chloride or ammonium fluoride and other likely phases like europium nitrate, which is an indirect evidence for the formation of the desired compound. The detected peak preferred orientation indicating that the crystal is cubic structure and all angles α, β, and γ are of 90°. The degree of crystallization of the phosphor is defined as ratio of $I_{(2\ 0\ 0)}$. The $I_{(2\ 0\ 0)}$ are the intensity of the X-ray peak at (2 0 0) direction. The well crystallized CaF_2 crystal has preferred orientation of (2 0 0) directions indicating the cubic structure, the other observed X-ray peak at (2 2 0), (2 2 2), (4 0 0), (4 2 0), (4 2 2), (4 4 0), and (6 0 0) all are indicating cubic nature of the crystal and the higher intensity ratio of (2 0 0) means the better crystallization to (2 0 0) direction. The crystal structure according to the detected X-ray peaks is coincident with that of CaF_2 shows that the crystal is of cubic structure. Formation of the compound was confirmed by taking the X-ray diffraction pattern of prepared CaF_2 host which matched with the standard data available in JCPDs file

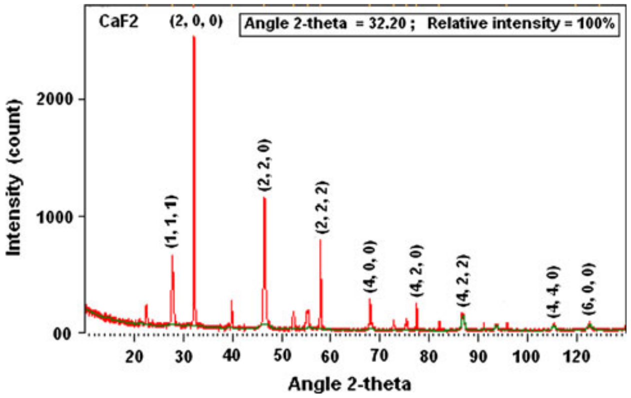

Fig. 1 X-ray diffraction pattern of CaF_2 host

number 035-0816. These results indicate that the final product was formed in homogeneous form.

Photoluminescent properties of CaF_2:Eu phosphor

Photoluminescence spectrum of prepared CaF_2:Eu phosphor is shown in Fig. 2. The two different broad band excitation peaks were observed at around 342 nm due to $f \rightarrow f$ transition corresponding to Eu^{2+} PL emission (428 nm) and Eu^{3+} PL emission (613 nm). The PL emission spectra of Eu^{2+} as well as Eu^{3+} ions in CaF_2:Eu phosphor originates at same excitation wavelength. The different molar concentrations of europium ion shows same emission wavelength with varying intensity under the same excitation of 342 nm wavelengths of UV light. A broad band emission spectrum of Eu^{2+} ions was observed at 428 nm, which are assigned to $4f \rightarrow 5d$ transition of Eu^{2+} ion. PL emission of Eu^{3+} ions gives $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_3$ all possible transitions of Eu^{3+} ions. $^5D_0 \rightarrow {}^7F_2$ transition gives sharp emission peaks which were observed at 613 nm under 342 nm excitation wavelength. It shows that there is PL emission of both Eu^{2+} and Eu^{3+} ions, when CaF_2:Eu phosphor is excited at same excitation wavelength. With increasing concentration of dopant ions relative PL emission intensity of both 428 and 613 nm peak increases as shown in Fig. 2. Increase in PL intensity of Eu^{2+} and Eu^{3+} was observed with variation in the concentration of Eu ion from 0.2 to 2 m% in CaF_2 as shown in Fig. 3. In this host, it is also found that for 1 m% concentration of europium ion PL intensity is maximum and PL intensity get quenched for higher concentrations. Hence this material is suitable for higher concentration of europium ion at 1 m%. Hence CaF_2:Eu phosphors with 1 m% of Eu are suitable for studying the effect of gamma irradiation and temperature quenching on the PL behavior.

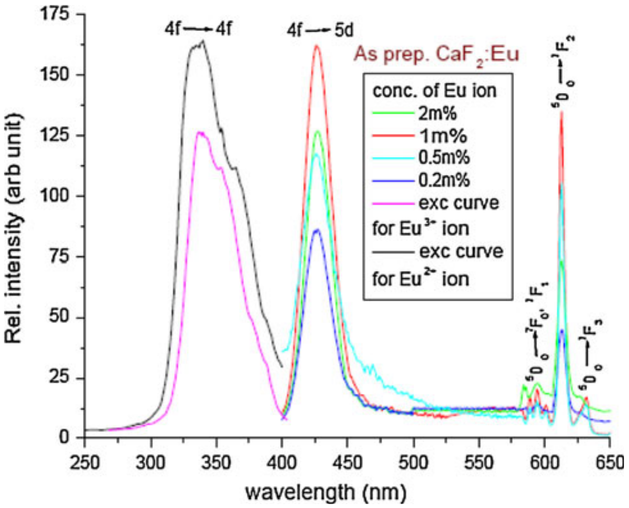

Fig. 2 PL spectrum of CaF_2:Eu, where 342 nm excitation was monitored at 428 and 613 nm emission

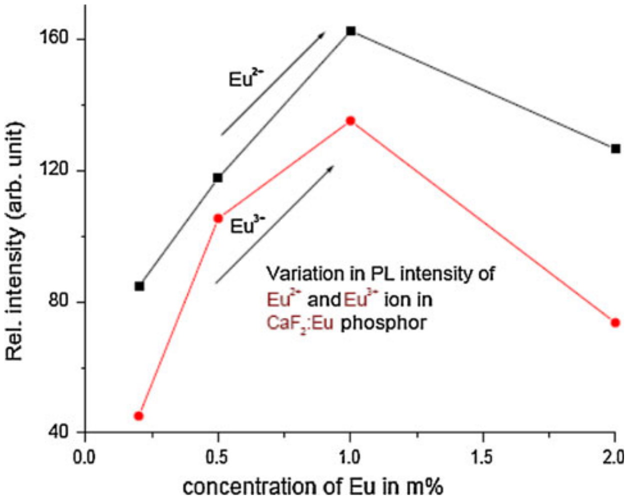

Fig. 3 Variation in PL intensity of Eu^{2+} and Eu^{3+} ion in CaF_2:Eu phosphor with concentration of Eu ion

Figure 4 shows the effect of gamma irradiation on the photoluminescent properties of the prepared CaF_2:Eu phosphor. The samples were exposed to gamma rays from a ^{60}Co source at room temperature at the rate of 0.995 kGy/h with different exposures as 0.4975, 0.995, 1.99, 3.98, and 5.97 kGy. Photoluminescence spectrum CaF_2:Eu phosphor was undergone irradiation and change in valencies of doped europium ion was observed. The irradiation source and rate of irradiation was constant, i.e., 0.995 kGy/h through out the experiment. It was observed that at lower irradiation time, i.e., 0.4975 kGy, there is no transfer of valencies from $Eu^{2+} \rightarrow Eu^{3+}$ ion were observed. As the irradiation exposure increases, it shows the effect of gamma irradiation on their valencies. Intensity of Eu^{3+} ion increases slightly from 0.995 to 1.99 kGy and decrease in PL intensity of Eu^{2+} ions were observed shown in Fig. 5. The complete transfer of $Eu^{2+} \rightarrow Eu^{3+}$ ions was observed for higher exposure, i.e., for 3.98 and 5.97 kGy. It is concluded that no any vacancies were formed at lower exposure dose but when exposure rate is increased slowly traps, vacancies were formed. Those formed traps and vacancies are responsible for increase in Eu^{3+} ions emission as shown in Fig. 5. When exposure increases there is complete transfer of $Eu^{2+} \rightarrow Eu^{3+}$ ion were observed. It proves that no vacancies or traps are remained for the Eu^{2+} ion emission in CaF_2 host. Hence prepared phosphor purely gives Eu^{3+} ion emission for higher exposure, as shown in Fig. 6. Figures 4 and 6 show the conversion of ionic valency by gamma irradiation. Figure 4 shows the Eu^{2+} and Eu^{3+} emissions in the CaF_2 host lattice, while, by gamma irradiation all Eu^{2+} ions are converted in the Eu^{3+} ions. This property of prepared phosphor is very applicable for RPL dosimetry.

The phenomenon of transfer mechanism of valencies is explained on the basis of Fig. 7. It indicates a change of the surrounding of the Eu^{2+} ions at higher exposure in the CaF_2:Eu lattice. The induced luminescence of Eu^{3+} via the radiative energy transfer consists of six processes, as shown in Fig. 7. The population at the $^5D_3$ level of Eu^{3+} increases via the radiative energy transfer from $Eu^{2+} \rightarrow Eu^{3+}$. Finally, the population arrives at the emitting $^5D_0$ level via non-radiative transitions from the upper levels. The trivalent europium ion is very useful for studying the nature of metal coordination in various systems, owing to its non-degenerate emitting $^5D_0$ state.

Figure 8, shows the effect of quenching temperature on CaF_2:Eu phosphor after gamma rays exposure from a ^{60}Co source of 0.995 kGy/h on their photoluminescent properties. CaF_2:Eu phosphor were undergone quenching at different rates as 100, 200, 400, 600, and 700 °C for 5 h. Photoluminescence spectrum of quenched phosphors shows major changes in their valencies of doped europium ion. It is observed that at lower temperature range at 100 °C, there is no change in transfer of valencies from $Eu^{3+} \rightarrow Eu^{2+}$ ions or no any other effect was observed. As the quenching temperature was increased, it shows effect of heat treatment on their valencies. Intensity of Eu^{2+} ion increases slightly at 200 and 400 °C and decrease in PL intensity of Eu^{2+} ions were observed as shown in Fig. 9. The complete transfer of $Eu^{3+} \rightarrow Eu^{2+}$ ions were observed for higher quenching temperature, i.e., for 600 and 700 °C. It is concluded that no any vacancies were formed at lower quenching temperature, but when quenching temperature increased slowly, traps and vacancies were formed. Those formed traps and vacancies are responsible for increase of Eu^{2+} ions emission. When quenching temperature increases the complete transfer of $Eu^{3+} \rightarrow Eu^{2+}$ ions were observed and it proves that no vacancies or traps is remained for the Eu^{3+} ion emission in CaF_2 host. Hence prepared phosphor purely gives Eu^{2+} ion emission for higher quenching temperature, as shown in Fig. 10.

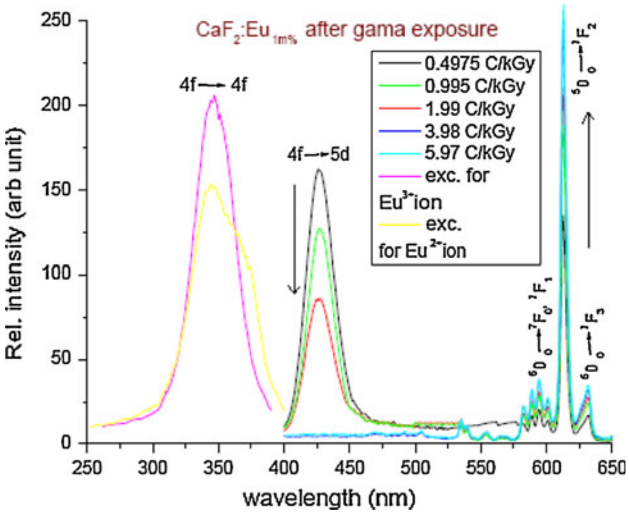

Fig. 4 Effect of gamma exposure on PL spectrum of CaF_2:$Eu_{1m\%}$ at different exposure

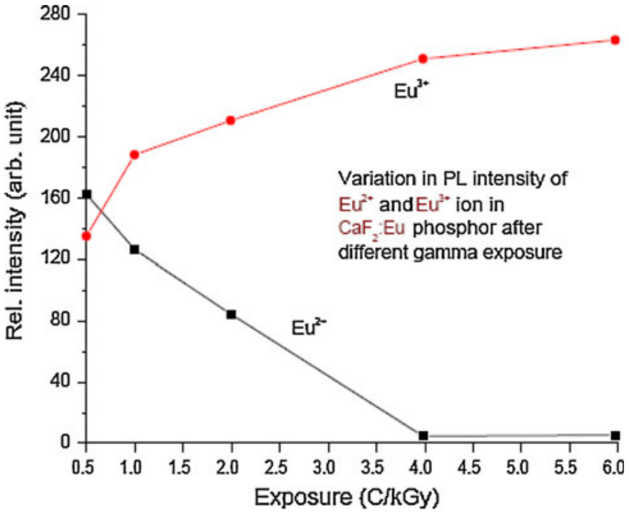

Fig. 5 Variation in PL intensity of Eu^{2+} and Eu^{3+} ion in CaF_2:Eu phosphor after different gamma exposures

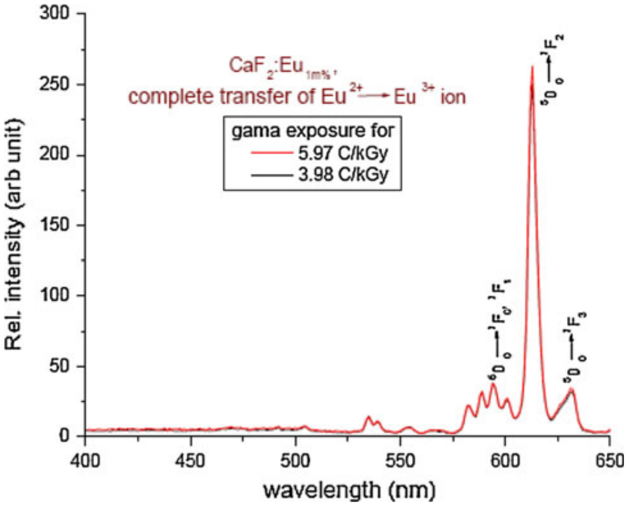

Fig. 6 Effect of gamma exposure on PL spectrum of CaF_2:$Eu_{1m\%}$ for higher exposure

The phenomenon of reverse transfer mechanism of valencies is explained on the basis of Fig. 11. This indicates a change of the surrounding of the Eu^{3+} ions at higher quenching temperature in the CaF_2:Eu lattice. The reverse transfer luminescence of Eu^{2+} ion via the quenching effect shows the population at the $4f^6 5d$ level of Eu^{2+} increases via heat energy transfer from $Eu^{3+} \rightarrow Eu^{2+}$. Finally, the population arrives via non-radiative transitions from the upper levels. The emission spectrum of the material has a peak in the range 400–500 nm, which may be attributed to the Eu^{2+} emissions. We may speculate that

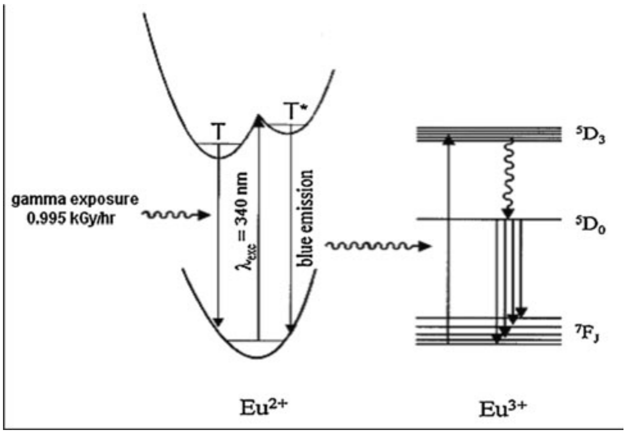

Fig. 7 A schematic diagram of the induced luminescence from CaF_2:Eu resulting from the radiative energy transfer from Eu^{2+} to Eu^{3+} ions

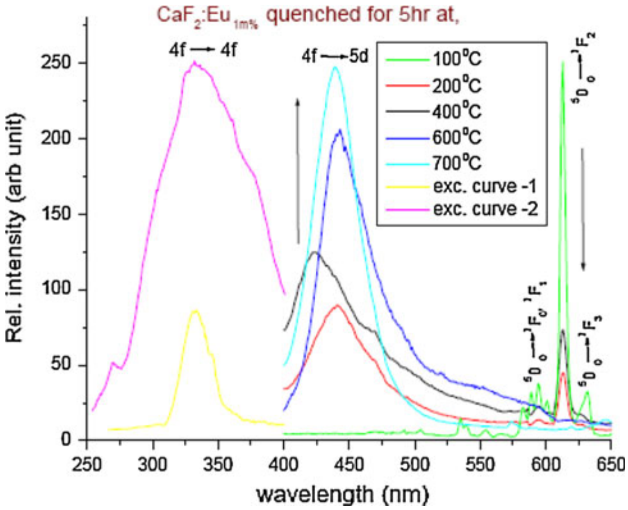

Fig. 8 Effect of temperature on PL spectrum of $CaF_2:Eu_{1m\%}$

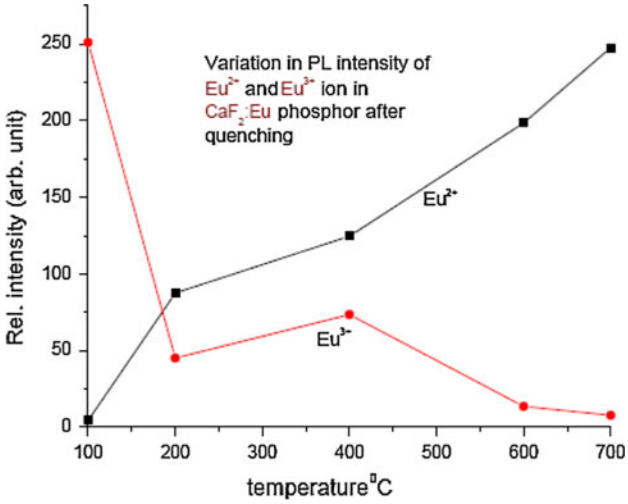

Fig. 9 Variation in PL intensity of Eu^{2+} and Eu^{3+} ion in CaF_2:Eu phosphor after different quenching temperature

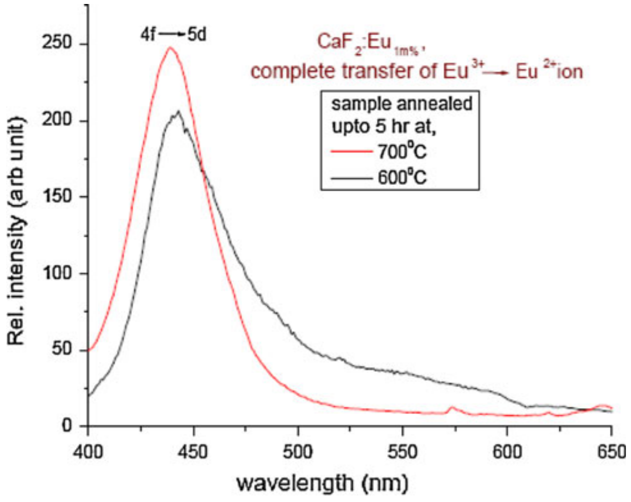

Fig. 10 Effect of temperature on PL spectrum of $CaF_2:Eu_{1m\%}$ at higher temperature

at around 428 nm wavelength corresponding to the Eu^{2+} ion emission rises due to transitions from $4f^7(^8S_{7/2}) \rightarrow 4f^65d$, but with the Eu^{2+} ions occupying only single lattice sites. The divalent europium ion is very useful in various field of science.

Photoluminescent properties of CaF_2:Eu, Bi phosphor:

From Fig. 12, CaF_2:Eu, Bi phosphor when excited at 340 nm wavelength shows similar emission properties like pure CaF_2:Eu phosphor. Prepared CaF_2:Bi phosphor does not show any luminescence behavior, when it is singly doped in CaF_2 host lattice. Bismuth impurity acts as sensitizer and enhances the PL intensity of europium ion shown in Fig. 13. The results show that the Eu emission intensity has been enhanced in $CaF_2:Eu_{1m\%}$, $Bi_{1m\%}$ very much and is about two times larger compared to $CaF_2:Eu_{1mol\%}$. It seems that the energy transfer from Bi to Eu ion. When CaF_2:Eu, Bi, phosphor is excited at same

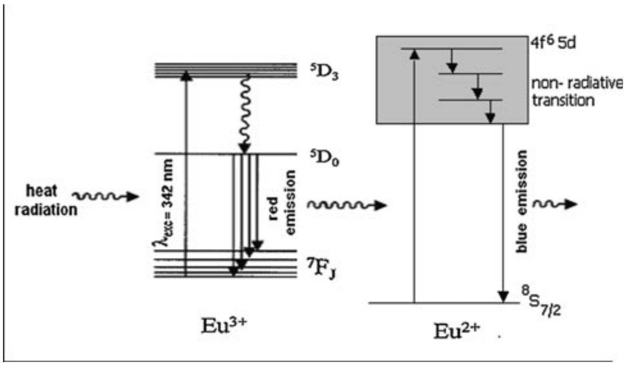

Fig. 11 A schematic diagram of the reversed luminescence from CaF_2:Eu resulting from the heat energy transfer from Eu^{3+} to Eu^{2+} ions

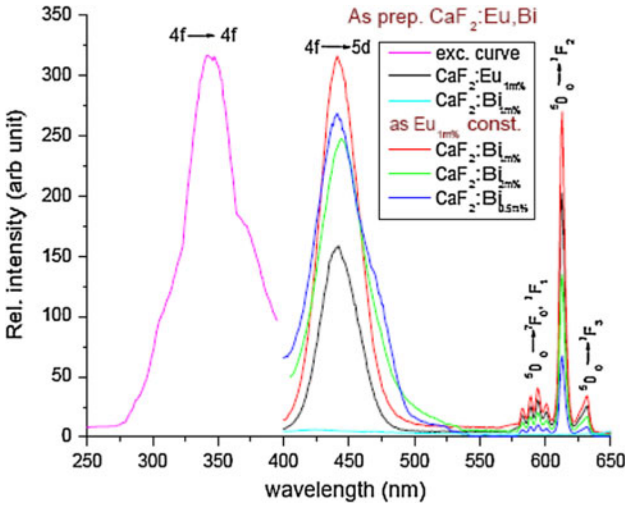

Fig. 12 PL spectrum of CaF_2:Eu, Bi, where 340 nm excitation was monitored at 440 and 613 nm emission

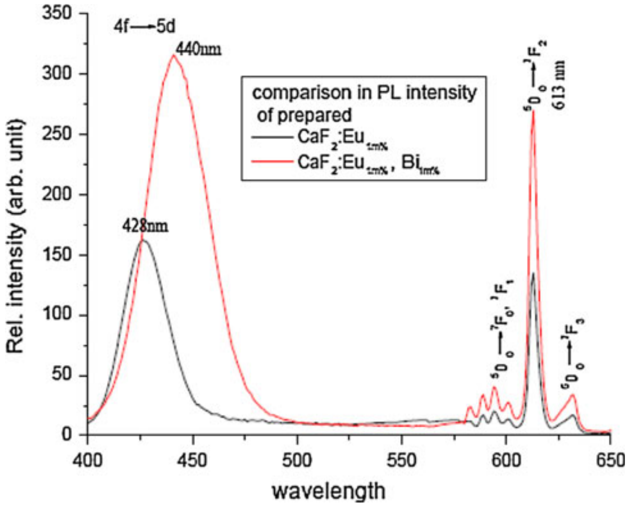

Fig. 13 Comparison in PL intensities of prepared $CaF_2:Eu_{1m\%}$ and $CaF_2:Eu_{1m\%}$, $Bi_{1m\%}$

wavelength, i.e., 340 nm, with the introduction of Bi into CaF_2:Eu phosphor gives the Eu^{2+} emission peaks move to the higher wavelength side by a small amount [19] and no change in emission wavelength of Eu^{3+} ion. A broad band emission spectrum of Eu^{2+} ions were observed at 440 nm, which are assigned to $4f \rightarrow 5d$ transition of Eu^{2+} ion. The shift of emission bands to the higher wavelength side was explained to be due to an electron transfer from the 6*s* level of Bi^{3+} ion which is forbidden to the 5*d* level of Eu^{2+} ion [19, 20]. PL emission of Eu^{3+} ions gives $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_3$ all possible transitions of Eu^{3+} ions. $^5D_0 \rightarrow {}^7F_2$ transition gives sharp emission peaks observed at 613 nm under 340 nm excitation wavelength. These results are consistent with the earlier reported results [21–23]. Co-doped does not alter the PL behavior, it helped to enhance PL intensity of europium ion. To increase the luminescence output and to avoid concentration quenching, a small amount of a co-activator (called sensitizer, S) is desirable. The co-activator ion efficiently absorbs the excitation energy and transfers it to the activator ion. Previously, the energy transfer from Bi^{3+} to Eu^{3+} has been reported in oxide host materials [22, 24–26] and in tungstate host material [27]. The former transition corresponds to the longer wavelength. If the cubic symmetry in perfect, the other transitions are completely forbidden [28]. They may appear when there is any local asymmetry. For lower Bi concentrations, the emission intensity of the Eu ion enhances rapidly with Bi ions. Maximum Eu^{2+} as well as Eu^{3+} emission output was obtained for 1 mol% of Bi and decreases for higher Bi concentrations. The sensitization effect of the Bi ion on the emission of Eu varied with the Bi concentration. For higher concentration of Bi ions, Bi ion aggregates are formed $n > 1$. These aggregates act as trapping centers and dissipate the absorbed energy nonradiatively, instead of transferring it to activator ions. The energy transfer probability from Bi to Eu ion is strongly dependent on the Bi concentration in the calcium fluoride sample. In this investigation Bi ions are used for increasing the Eu^{2+} as well as Eu^{3+} PL emission intensity and higher PL intensity signals are use in RPL dosimetry.

It shows that the obtained PL emission of both Eu^{2+} and Eu^{3+} ions arises due to same excitation wavelength like pure CaF_2:Eu phosphor. PL intensity of both Eu^{2+} and Eu^{3+} ions increase due to increase in the concentration of Bi ion by keeping $Eu_{1m\%}$ at a constant ratio. Ratio between $Eu_{1m\%}$ and $Bi_{1m\%}$ gives maximum PL intensity as compared to other co-doped Bi ratio Fig. 14.

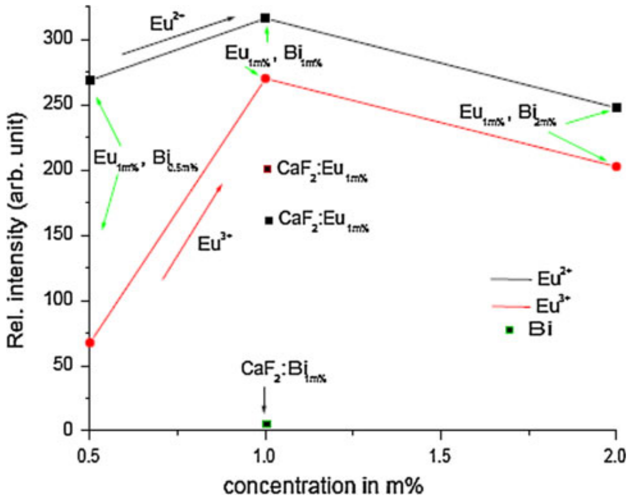

Fig. 14 Variation in PL intensity of Eu^{2+} and Eu^{3+} ion in CaF_2:Eu, Bi phosphor with concentration of Eu and Bi ion

Figure 15 shows the effect of gamma irradiation on the photoluminescent properties of the prepared CaF_2:Eu, Bi phosphor. Same exposure treatment was given to CaF_2:Eu, Bi like as pure CaF_2:Eu phosphor. Photoluminescence spectrum of CaF_2:Eu, Bi phosphor was undergone irradiation and shows prominent change in valencies of doped europium ion like CaF_2:Eu phosphor.

Similar results were obtained after irradiation by gamma source, variation in PL intensity as shown in Fig. 16 and complete transfer of $Eu^{2+} \rightarrow Eu^{3+}$ ions were observed for higher exposure as shown in Fig. 17. The phenomenon of transfer mechanism of valencies was explained previously on the basis of Fig. 7. Here, Bi^{3+} ions play important role for enhancement of luminescence intensity due to energy transfer mechanism. Therefore, it is possible to obtain both Eu^{2+} as well as Eu^{3+} ion emission in calcium fluoride based phosphors. There is the change of the surrounding of the Eu^{2+} ions at higher exposure in the CaF_2:Eu, Bi lattice. Figure 18 shows the effect of quenching temperature on CaF_2:Eu, Bi phosphor after gamma rays exposure from a ^{60}Co source of 0.995 kGy/h on their photoluminescent properties. The complete transfer of $Eu^{3+} \rightarrow Eu^{2+}$ ions were observed for higher quenching temperature, i.e., for 600 and 700 °C like CaF_2:Eu phosphor. Similar conclusions were drawn for CaF_2:Eu, Bi where no any vacancies were formed at lower quenching temperature, but when quenching temperature was increased slowly, traps and vacancies were formed. Those formed traps and vacancies are responsible for increase in Eu^{2+} ions emission. When

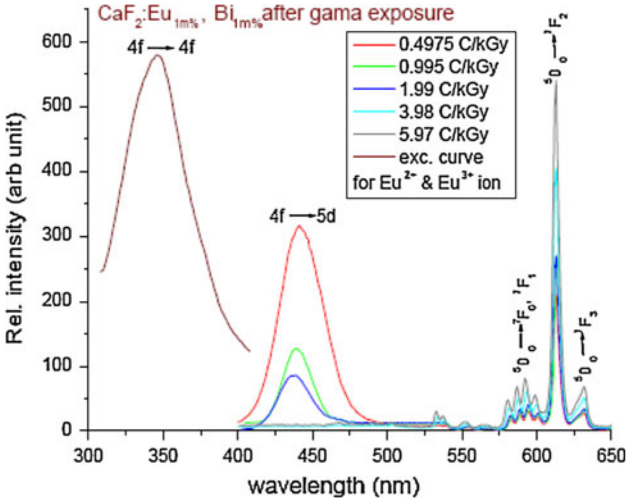

Fig. 15 Effect of gamma exposure on PL spectrum of $CaF_2:Eu_{1m\%}$, $Bi_{1m\%}$ at different exposure rates

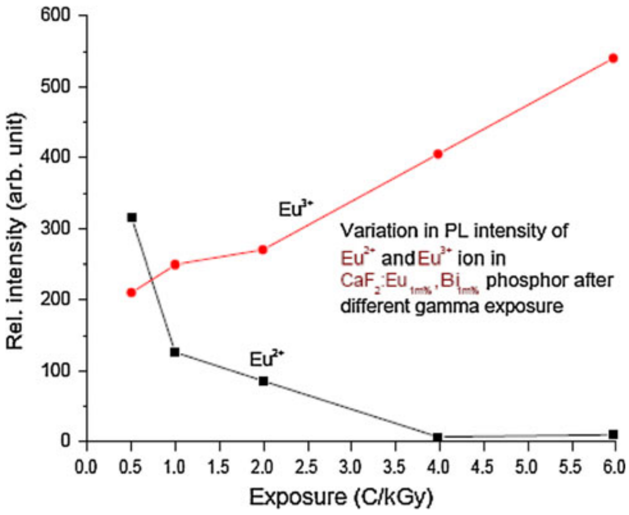

Fig. 16 Variation in PL intensity of Eu^{2+} and Eu^{3+} ion in $CaF_2:Eu_{1m\%}$, $Bi_{1m\%}$ phosphor after different gamma exposure rates

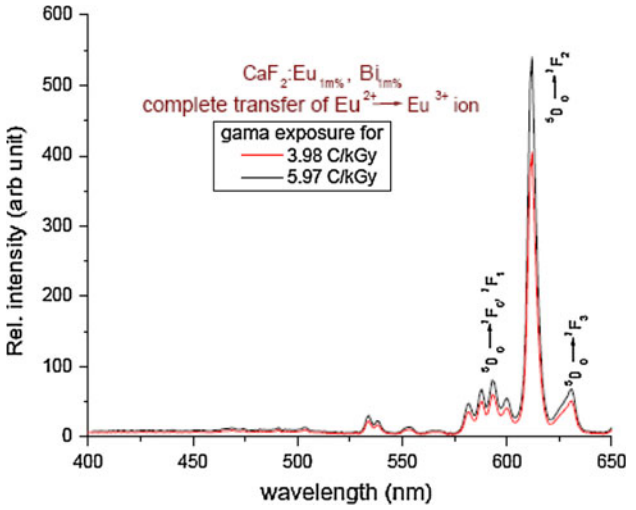

Fig. 17 Effect of gamma exposure on PL spectrum of $CaF_2:Eu_{1m\%}$, $Bi_{1m\%}$ for higher exposure rate

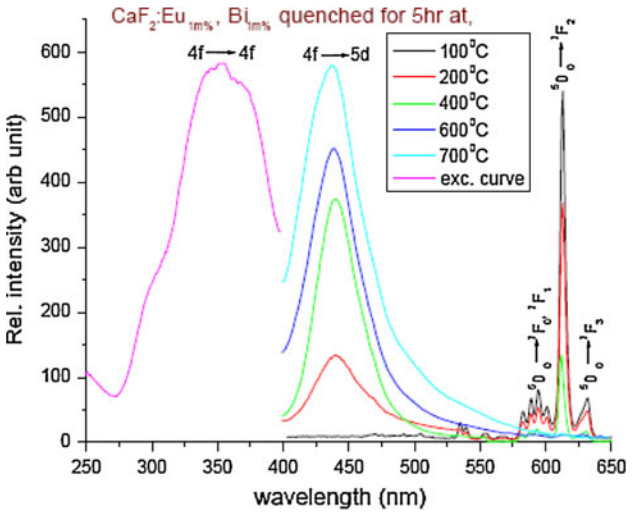

Fig. 18 Effect of quenching temperature on PL spectrum of $CaF_2:Eu_{1m\%}$,$Bi_{1m\%}$

quenching temperature increases variation in PL intensity of Eu^{2+} ion as shown in Fig. 19 and there is complete transfer of $Eu^{3+} \rightarrow Eu^{2+}$ ions were observed, which proves that no vacancies or traps remain present for the Eu^{3+} ion emission in CaF_2 host. Hence prepared phosphor purely gives Eu^{2+} ion emission for higher quenching temperature, as shown in Fig. 20. The phenomenon of reverse transfer mechanism of valencies was explained previously on the basis of Fig. 11. The 440 nm wavelength corresponding to the Eu^{2+} ion emission arised due to transitions from $4f^7(^8S_{7/2}) \rightarrow 4f^65d$, but with the Eu^{2+} ions occupying only single lattice sites.

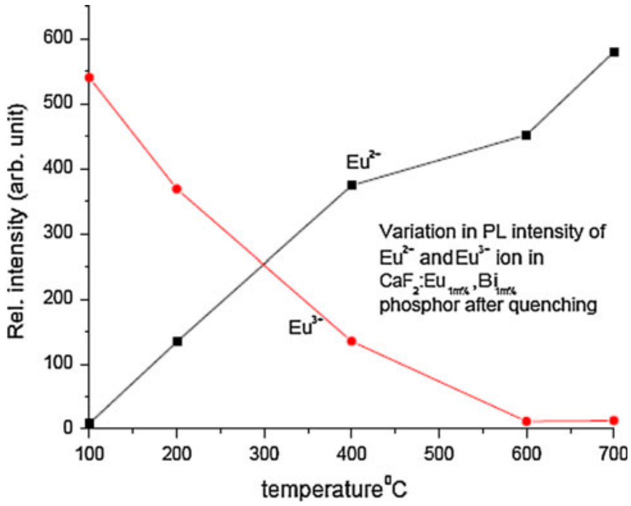

Fig. 19 Variation in PL intensity of Eu^{2+} and Eu^{3+} ion in CaF_2:Eu phosphor after different quenching temperature

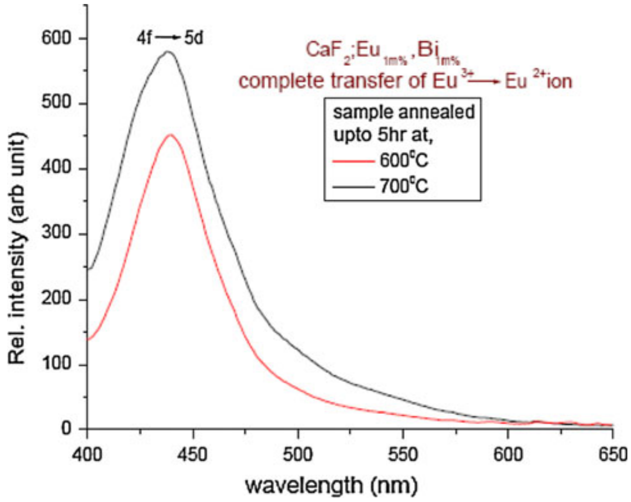

Fig. 20 Effect of temperature on PL spectrum of $CaF_2:Eu_{1m\%}$, $Bi_{1m\%}$ at higher temperature

Conclusion

The Eu^{2+} and Eu^{3+} activated CaF_2:Eu and co-doped Bi phosphors were prepared by precipitation followed by centrifuge technique. At the same range of excitation wavelength, CaF_2:Eu and CaF_2:Eu, Bi gives Eu^{2+} emission in the blue region and Eu^{3+} emission in the red region of the visible spectrum. Effect of gamma exposure on PL spectrum gives transfer of valencies from $Eu^{2+} \rightarrow Eu^{3+}$ ion and reverse effect were observed from $Eu^{3+} \rightarrow Eu^{2+}$ ion under temperature effect. Due to Bi^{3+} ions the PL intensity of Eu^{2+} and Eu^{3+} ions increases by two times and same ratio is observed during the conversion of $Eu^{3+} \rightarrow Eu^{2+}$ ions. Here, Bi^{3+} ions play important role for enhancement of luminescence intensity due to energy transfer mechanism. Hence, it is concluded that it is possible to obtain both Eu^{2+} as well as Eu^{3+} ion emission in calcium fluoride based phosphors. It proves that calcium fluoride based phosphors are more susceptible for gamma irradiation and followed by temperature treatment. Therefore, both CaF_2:Eu and CaF_2:Eu, Bi phosphors may be useful for radio photoluminescent dosimetry phosphor.

References

1. Harmer AL, Linz A, Gabbe D, Gillespie L, Janey GM, Sharp E (1967) Bull Am Phys Soc 12:1068
2. Sorokin PP, Stevenson M (1960) J Phys Rev Lett 5:557
3. Pollnau M, Lüthy W, Weber HP (1995) J Appl Phys 77:6128
4. Dujardin C, Pedrini C, Garnier N, Belsky AN, Lebbou K, Ko JM, Fukuda T (2001) Opt Mater 16:69
5. Shionoya S, Yen WM (1999) Phosphor handbook. CRC Press, Boca Raton
6. Kaminskii AA (1990) Lasers crystals. Springer-Verlag, New York
7. Kaminskii AA (1981) Handbook: laser crystals their physics and properties. Springer-Verlag, New York
8. Krupa JC, Mayolet A, Queffelec M (1998) Ann Chim Sci Mater 23:431
9. Wegh RT, Donker H, Meijerink A (1999) Science 283:663
10. Wang L, Wang YH (2004) J Rare Earths 22(6):863
11. Petit V, Doualan JL, Camy P, Menard V, Moncorge R (2004) Appl Phys B 78:681
12. Luccas A, Debourg G, Jacquemet M, Druon F, Balembois F, Georges P, Camy P, Doualn JL, Moncorge R (2004) Opt Lett 29(23):2767
13. Boutonnet M, Kizling J, Stenius P, Maire G (1982) Colloids Surf 5:209
14. Blasse G (1993) J Alloys Compd 192:17
15. Hintzen HT, Hanssen R, Jansen SR, Metselaar R (1999) J Solid State Chem 142:48
16. Blasse G (1996) Eur J Solid State Inorg Chem 33:175
17. Merz J, Pershan PS (1967) Phys Rev 162:217
18. Nambi KSV, Bapat VN, Ganguly AK (1974) J Phys C 7:4403
19. Blasse G, Bril A (1968) J Chem Phys 48:217
20. Fukuda A (1964) Sci Light 13:64
21. Daoudi A, Le Flem G (1982) J Solid State Chem 43:190

22. Tie S, Su Q, Yu Y (1995) Phys Status Solidi (a) 147:267
23. Meib D, Kemmler-Sack S (1993) Mater Chem Phys 35:114
24. Wang M, Fan X, Xiong G (1995) J Phys Chem Solids 56:859
25. Blasse G, Brill A (1966) J Chem Phys 45:2350
26. Blasse G (1966) J Chem Phys 45:2356
27. Pode RB, Dhoble SJ (1997) Phys Status Solidi (b) 203:571
28. Seitz F (1938) J Chem Phys 6:150