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Thermoluminescence and photoluminescence properties of $K_2Ca_2(SO_4)_3$:Cu nanophosphor for gamma radiation dosimetry

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Nanocrytstalline $K_2Ca_2(SO_4)_3$:Cu was synthesized by chemical co-precipitation method and annealed at 400°C. These nanocrytstalline samples were irradiated with gamma radiation for the dose varying from 500 Gy to 2000 Gy. The pre and post irradiated samples were characterized by the techniques such as XRD, SEM, UV, FTIR, photoluminescence (PL) and thermoluminescence (TL). XRD spectra show the orthorhombic structure and the crystallite size ~ 25 nm. The same is also confirmed in SEM, where the size of nanoparticles was varied from 20 to 40 nm and also shows monodispersed. Formation of the compound was also checked by FTIR, where the S-O stretching and bending mode have been observed. Whereas, in case of UV visible spectra, the band gap observed to be marginally decreased with gamma dose. In PL spectra, the emission bands are observed at 403 and 419 nm, respectively and their respective intensity increases linearly with the increase in gamma dose. In TL spectra, two dosimetric peaks have been observed at 144°C and 287°C, respectively and their intensity tends to be increased with gamma radiation dose. This particular aspect shows the wide range linear TL response to the high gamma dose. Moreover, a significant shift in the peak towards lower temperature has been observed. This indicates the disorganization of the initial energy bands in the nanophosphor. In conclusion, the $K_2Ca_2(SO_4)_3$:Cu nanophosphor is useful for high dose gamma ray dosimetry.

Keywords: Nanophosphor, Thermoluminescence, Photoluminescence

1 Introduction

Thermoluminescence (TL) is a well known technique that is widely used in the dose measurement of ionizing radiations such as UV, X-rays, gamma rays and ion beam. Recently, nanocrystalline materials have attracted many researchers due to their potential applications in many diverged fields such as drug delivery, labeling of DNA, gas sensing, etc. Nanophase materials can form new and metastable crystal structures and have potential as efficient phosphors in display applications such as new flat-panel displays with low energy excitation sources, solar-energy converters and optical amplifiers. Nanophosphors have found their place for the measurements of high doses of ionizing radiations,where most of the microcrystalline TLD phosphors saturate[1,2]. Recently published reports describes about some of the phosphors such as nanocrytstalline $CaSO_4$:Dy, $K_2Ca_2(SO_4)_3$:Eu, LiF:Mg, Cu, P, $Ba_{0.97}Ca_{0.03}SO_4$:Eu and found that they are quite suitable for estimating very high doses(~100kGy) for high-energy radiations like gamma rays, protons and heavy ions[1-3]. In the present study, $K_2Ca_2(SO_4)_3$:Cu nanocrytstalline phosphor has been synthesized using chemical co-precipitation route and its photo-luminescence (PL) and thermoluminescence (TL) characteristics have been correlated with gamma radiation dose.

2 Experimental Details

Nanoparticles of the $K_2Ca_2(SO_4)_3$:Cu was prepared by taking into consideration of the following reaction:

$$2CaCl_2+2KCl+3(NH_4)_2SO_4+CuCl_2\,(0.2\%) \rightarrow K_2Ca_2(SO_4)_3:\,Cu+6NH_4Cl$$

In this method, copper chloride, calcium chloride, potassium chloride, ammonium sulphate and ethanol were taken of analytical reagent grade (AR grade) and used without further purification.5.88 g of calcium chloride was dissolved in 200 ml double distilled water (Cu^{2+} solution) and then added 0.2 mol% of copper chloride in the solution. Moreover, 2.98 g of potassium chloride was dissolved in 200 ml double distilled water (K^+ solution). Further, chloride salts of calcium and potassium were mixed together. In addition, 300 ml of ethanol was added to the Ca^{2+} and K^+ solution. The same solution was then stoichiometrically mixed with ammonium sulphate solution (7.93 g ammonium sulphate in 300 ml double distilled water) added with drop wise till the precipitation completes. The co-precipitants were filtered out and washed several times with distilled water. Nanocrytstalline $K_2Ca_2(SO_4)_3$:Cu was finally prepared by heating the co-precipitants for about 10 h at 160°C. The powder was annealed in a quartz boat at 400°C for 2 h in air and quenched by taking the boat out of the furnace and placing it on a metal block. To confirm the formation of the compound and nanoparticles, X-ray diffraction pattern was studied at room temperature by using Cu-target (Cu-K_α= 1.54Å) on Bruker AXS D8 Advance X ray Diffractometer and matching with the standard data available (JCPDS card No 20-0867). Further, different samples were exposed to Co^{60} gamma radiation with doses varied from 500 Gy to 2000 Gy. Post gamma irradiated nanophosphors were characterized by other techniques such as UV(JASCO V-670), Photoluminescence(Perkin Elmer LS55) and Thermoluminescence(TL 1009I supplied by Nucleonix Systems Private Limited Hyderabad, India).The TL glow curves were recorded for 5mg of sample each time by heating the samples at a uniform rate of 5°C/s with the help of a temperature controller.

3 Results and Discussion

3.1 XRD, SEM and EDS analysis

The XRD spectrum shown in Fig. 1 reveals the different peaks at (211), (302), (411), (233) etc. which exhibit orthorhombic structure. The average particle size of the nanoparticles is estimated from the line broadening of the XRD peaks assuming the particles are stress free and therefore, the size can be estimated from a single diffraction peak using Scherrer's formula. The average grain size of the concerned phosphor is estimated to be ~25 nm which confirms its nanocrystalline form. The shape size and distribution of these particles are also confirmed using SEM as shown in Fig. 2. It shows that the spherical size of the particles varied in the range 25-40 nm and has uniform distribution. Moreover, incorporation of impurity and different components such as K, Ca, S, O in the nanocrystallites also confirmed using EDS technique.

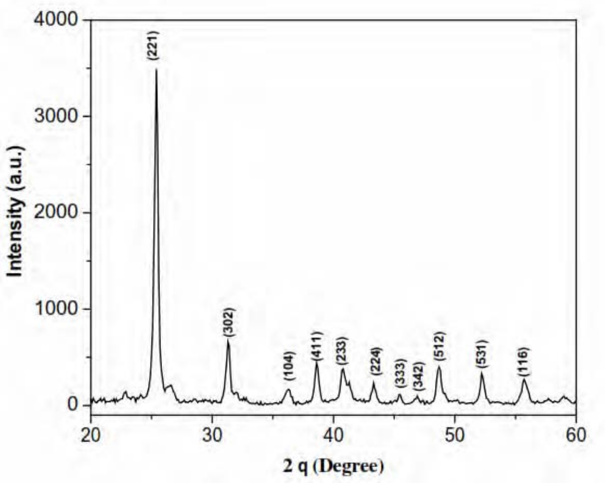

Fig. 1 — XRD spectrum of $K_2Ca_2(SO_4)_3$:Cu nanophosphor annealed at 400°C

3.2 FTIR analysis

The FTIR spectrum shown in Fig. 3 exhibits the presence of bands corresponding to sulphate anions around 1115.62 and 620.96 cm^{-1}. The 1115.62 cm^{-1} peak is due to the S–O stretching mode and the

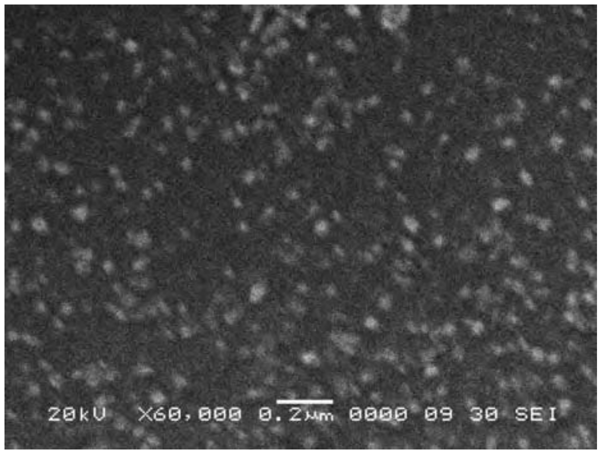

Fig. 2 — SEM image of $K_2Ca_2(SO_4)_3$:Cu nanophosphor annealed at 400°C

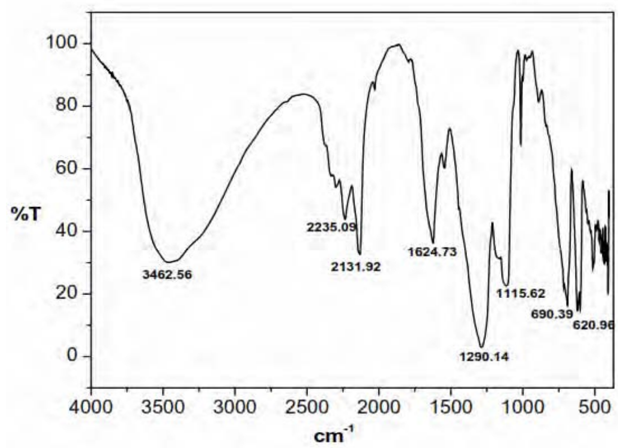

Fig. 3 — FTIR spectrum of $K_2Ca_2(SO_4)_3$:Cu nanoparticles

620.96 cm^{-1} peak is due to the S–O bending mode[4]. These prominent peaks confirm the formation of sulphate bonding in the sample. Characteristic bands around 3462 and 1625 cm^{-1} are ascribed to atmospheric water vapour since KBr readily absorbs moisture in the air. This indicates that the prepared sample consists of a certain amount of moisture.

3.3 UV-visible analysis

The UV absorption spectra of the $K_2Ca_2(SO_4)_3$:Cu nanophosphor for different gamma doses is shown in Fig. 4. It is observed from Fig. 4 that the band gap marginally decreased from 3.84 eV to 3.65 eV with increase in the gamma dose. This mainly attributes to the disorganization of the energy levels due to trapping centers.

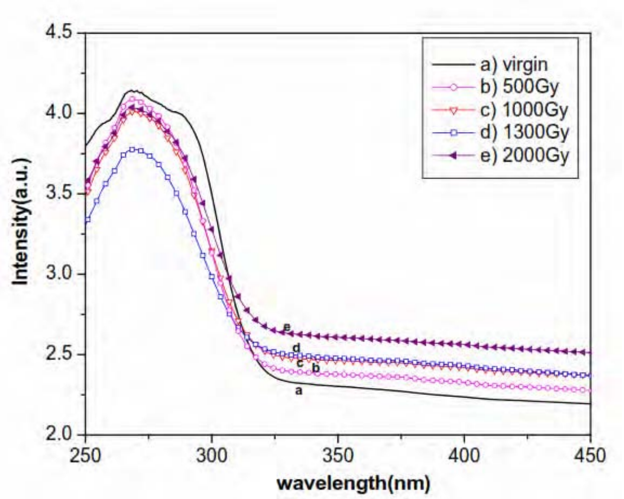

Fig. 4 — UV absorption spectra for the $K_2Ca_2(SO_4)_3$:Cu nanophosphor irradiated at different doses of gamma irradiation

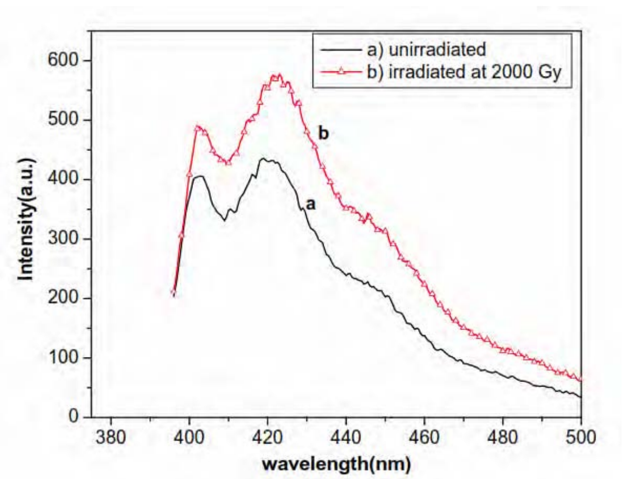

Fig. 5 — PL emission spectra of $K_2Ca_2(SO_4)_3$:Cu nanophosphor for excitation wavelength 370 nm (a)unirrdiated, (b) irradiated at 2000 Gy

3.4 Photoluminescence

Figure 5 shows the PL emission spectra of the $K_2Ca_2(SO_4)_3$:Cu nanophosphor. The emission spectra (excitation by 370 nm) consists of two bands, one at 403 nm and the other at 419 nm. The intensity of the respective peaks tends to be increased linearly with increase in gamma dose as shown in Fig. 6. The increase in PL intensity mainly attributes the activation of more number of copper ions in nanophosphor due to gamma irradiation[3].

3.5 Thermoluminescence glow curves

Figure 7 shows the TL glow curves of $K_2Ca_2(SO_4)_3$:Cu nanophosphor exposed to gamma radiation for different doses. TL spectra exhibit, two glow peaks at 144°C and 287°C, respectively. The

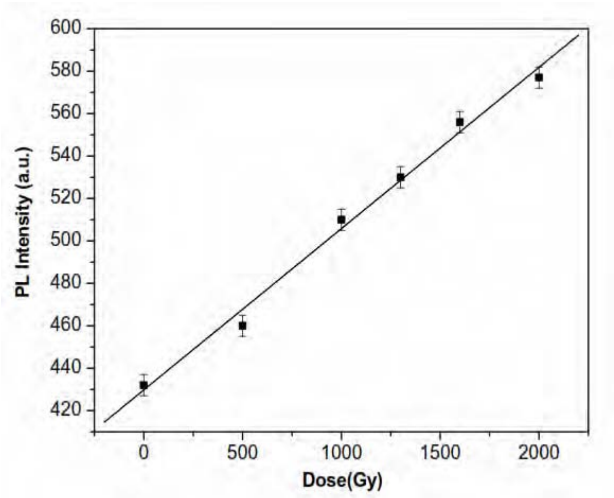

Fig .6 — Variation in peak intensity with gamma dose for $K_2Ca_2(SO_4)_3$:Cu nanophosphor

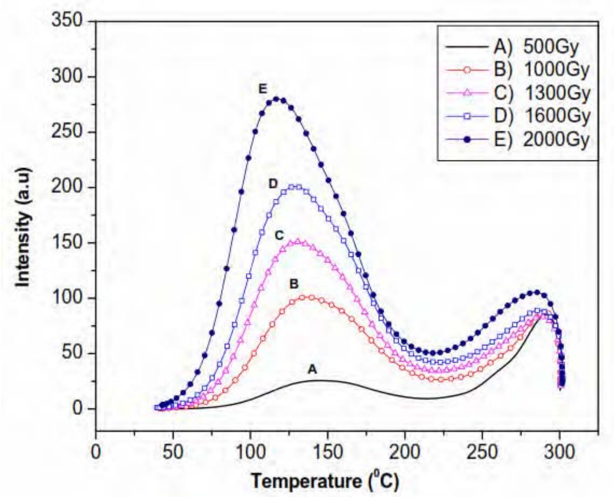

Fig. 7 — TL glow curves of $K_2Ca_2(SO_4)_3$:Cu nanophosphor exposed to different doses of gamma radiation

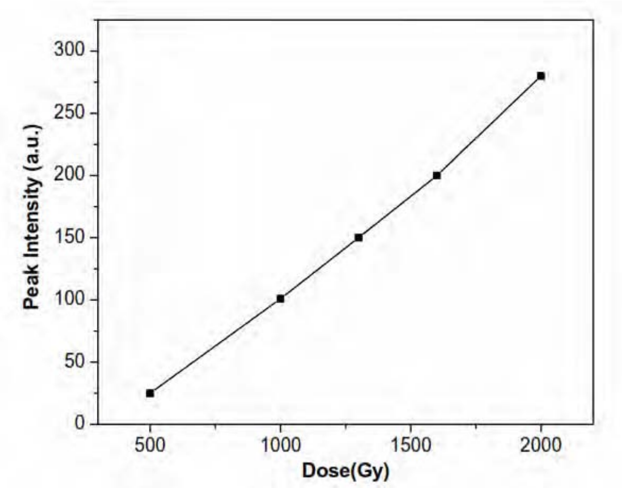

Fig. 8 — TL response of $K_2Ca_2(SO_4)_3$:Cu nanophosphor for different doses of gamma radiation

appearance of two peaks in the glow curve indicates that there is possibly two kinds of trapping sites due to gamma irradiation, one at lower temperature and other at higher temperature. There is also a shift in the peaks position towards lower temperature by around 26°C for the dose varied from 500 Gy to 2000 Gy. The shift in the peaks position is mainly due to the disorganization of trapping[5] centers(TCs)/luminescent centers (LCs). In addition, the shift also indicates that the peak is not of first order,it may be second or general order of kinetics[6]. For finding the order of kinetics and activation energy, deconvolution of glow curve is necessary. Moreover, TL glow curve structure does not change with gamma dose.

3.6 TL response curve

The TL response curve of $K_2Ca_2(SO_4)_3$:Cu nanophosphor exposed to different doses of gamma radiation is shown in Fig. 8. It is observed from Fig. 8 that the TL response in terms of intensity (peak intensity of TL glow curve) found to be increased linearly with increase in the gamma dose from 500 Gy to 2000 Gy.

The linearity of the TL response for the nanophosphors over a wide range of dose may attribute to high surface to volume ratio which results in a higher surface barrier energy for the nanoparticles. On increasing the gamma dose, the energy density crosses the threshold value of the surface barrier and thus large number of defects are produced in the nanophosphors. The number of defects created in the material keeps on increasing with gamma dose till saturation is obtained[2]. But, in the case of nanophosphor, a saturation did not occur because of the existence of some particles that would have been missed while being targeted by the high-energy radiation, due to their very tiny size. Thus, on increasing the gamma dose, these nanoparticles which had been left out from the interaction, now generate trapping centers (TCs)/luminescence centers (LCs). So nanophosphors do not show saturation at higher doses. Thus, nanophosphors gives good linearity over a wide range of the doses. Therefore, $K_2Ca_2(SO_4)_3$:Cu might be used as a dosimeter for the gamma dose from 500 Gy to 2000 Gy and onwards.

4 Conclusions

The $K_2Ca_2(SO_4)_3$:Cu nanophosphor exhibits orthorhombic structure and size of nanoparticles varied in the range 20-40 nm. The UV result showed decrease in energy band gap with gamma dose. The PL measurements have showed two emission bands at 403 nm and 419 nm after excitation at 370 nm and peak intensity linearly increases with increase in gamma dose. The TL glow curve structure does not show any change with dose. The nanophosphor exhibited a linear TL response for the entire range of gamma dose from 500 Gy to 2000 Gy. The easy method of preparation, simple glow curve structure and better TL response are some of the good features of the $K_2Ca_2(SO_4)_3$:Cu nanophosphor. Therefore, it can be used as a dosimeter for the estimation of gamma dose with wide range.

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