



Synthesis and lyoluminescence characterization of rare earth activated $K_2Ca_2(SO_4)_3$ phosphors

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Abstract

Synthesis and lyoluminescence (LL) characterization of rare earth (RE) doped $K_2Ca_2(SO_4)_3$ phosphors prepared by solid state reaction technique are reported in this paper. XRD pattern of the samples matched well with the standard data of JCPDS (File no. 00-040-0545). It was found the undoped phosphor does not show any remarkable LL. Doping of rare earth enhances the LL yield of $K_2Ca_2(SO_4)_3$ phosphors; but the LL yield depends on the nature of dopant and on its concentration. Ce was found to be the most suitable dopant to enhance the LL yield of $K_2Ca_2(SO_4)_3$ system. All the samples showed simple glow curve having single peak. It is found that LL yield increases with increasing gamma-ray dose given to the sample upto 1.395 kGy. Various aspects of LL dosimetry have been studied and the results showed that rare earth doped $K_2Ca_2(SO_4)_3$ phosphors have potential for dosimetric applications.

Keywords: Lyoluminescence, Synthesis, $K_2Ca_2(SO_4)_3$, phosphors

1.1 Introduction

Effects of ionizing radiation in qualitative and quantitative terms have become very important in the present day context due to the influence of nuclear technology in various areas that include radiation medicine, radiotherapy, food processing, radiation based polymerization and nondestructive testing techniques using radiography. Dependable radiation dosimetric procedures need to be developed over wide range of dose levels. Lyoluminescence is the phenomenon of light emission when certain substances irradiated with ionizing radiation, are dissolved in a suitable solvent. It was first reported in 1895, by Widdmann and Schmidt [1]. Apparently there was no investigation of LL during the next five decades. Lyoluminescence was rediscovered in 1959, by Ahnstrom and Ehrenstein [2]. The quantum of light yield produced is generally proportional to absorbed dose in the solid. The lyoluminescence phenomenon, owes its origin to the transfer of energy from the radiation-induced free radicals to the solvent molecules, a part of which gets transposed to visible light. The integrated light yield has been implied upon to provide a measure of the absorbed dose. The absorbed dose range covered by lyoluminescence dosimetry with different phosphors begins from 0.1 Gy onwards and extends to 20 kGy. In the past few years thermoluminescence (TL) investigations on mixed sulphate based phosphors such as $K_2Ca_2(SO_4)_3:Eu$, $LiNaSO_4:Eu$, $Na_{21}Mg(SO_4)_{10}Cl_3:Dy$, $Ba_{0.97}Ca_{0.03}SO_4:Eu$, $Na_6Mg(SO_4)_4:Ce$ and $Na_6Mg(SO_4)_4:Tb$, have been carried out by various authors [3–11]. They found that some of the prepared phosphors are useful for radiation dosimetry due to their high TL sensitivity and other TL characteristics. Since most of the TL phosphors also show LL, we have chosen Ce, Dy, Eu and Tb doped $K_2Ca_2(SO_4)_3$ phosphors for their LL studies.

1.2 Materials and Methods

For preparation of $K_2Ca_2(SO_4)_3:RE$ phosphors, (Ce_2O_3 , Dy_2O_3 , Eu_2O_3 and Tb_4O_7) were incorporated first in K_2SO_4 . To incorporate rare earth in K_2SO_4 , aqueous solution of K_2SO_4 and solution of requisite amount of oxide of rare earths are mixed. $CaSO_4$ is separately dissolved in dilute HCl. These two solutions were then mixed in a beaker. This mixture was dried by heating at 80 °C for 8 hours and then crushed in motor and pestle for an hour and sieved to yield particle size 100-125 μm . The powder was then placed in furnace and fired at 800 °C for 24 hours in the open air, and then slowly cooled to room temperature. Samples were then annealed at 750 °C for 1 hour and quenched to room temperature. Phosphors prepared for the present investigation were characterized by Philips Panalytical X'pert Pro X-ray diffractometer. Gamma irradiation is carried out using ^{60}Co source. The LL read out system fabricated for lyoluminescence measurements consists of a lyoluminescence cell, a light detector, signal processor and signal recorder. The lyoluminescence cell and the photomultiplier tube (PMT) are kept in the light-tight box. A circular hole was cut on the top surface of the box into which a glass tube (8 mm diameter and 4 cm) was fitted. This glass tube is acted as the dissolution vessel. It rests just in front of the window of the PMT. The solvent is injected into the vessel with the help of a conventional hypodermic syringe. The light emitted during the dissolution was detected by RCA-931 photomultiplier tube. To bias the various dynodes of the PMT, a high voltage power supply was used. The output from PMT was amplified by a DC amplifier. The amplified output was fed to X-Y recorder. All the experiments were conducted in a dark room at room temperature. The mass of the samples used for recording LL data was kept nearly the same (~2 mg) in each case and as the solvent; dilute HCl (pH ~ 5.0) has been used to dissolve the sample. The volume of the solvent was 1.0 ml

in each case. For reading LL spectra, filters were placed between LL cell and the PMT. For each point at least three observations were recorded in identical experimental conditions to ensure the reproducibility.

1.3 Results

Fig 1 shows the XRD pattern of the $K_2Ca_2(SO_4)_3$ phosphors. The XRD data of prepared material matched well with the standard data of JCPDS (File no. 00-040-0545).

Fig. 2 shows the time dependence of LL intensity of rare earth doped $K_2Ca_2(SO_4)_3$ phosphors exposed to gamma dose 1.395 kGy. It is observed that Ce doped $K_2Ca_2(SO_4)_3$ phosphors shows maximum LL intensity. It is also observed that t_m (i.e. time corresponding to LL peak) is slightly less for undoped and Eu doped $K_2Ca_2(SO_4)_3$ phosphors

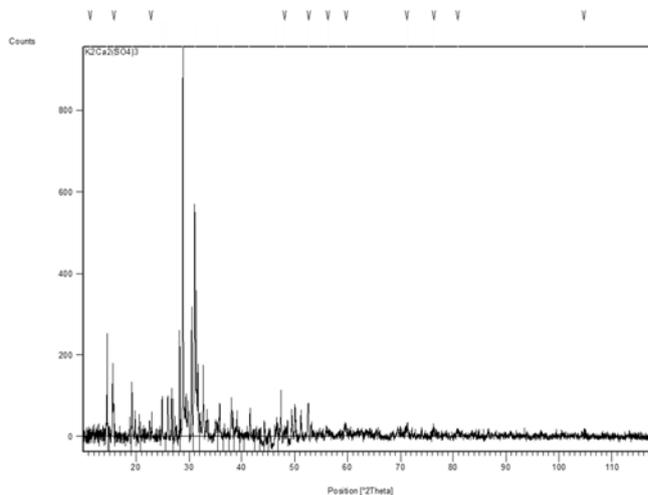


Fig. 1 XRD pattern of $K_2Ca_2(SO_4)_3$ phosphors

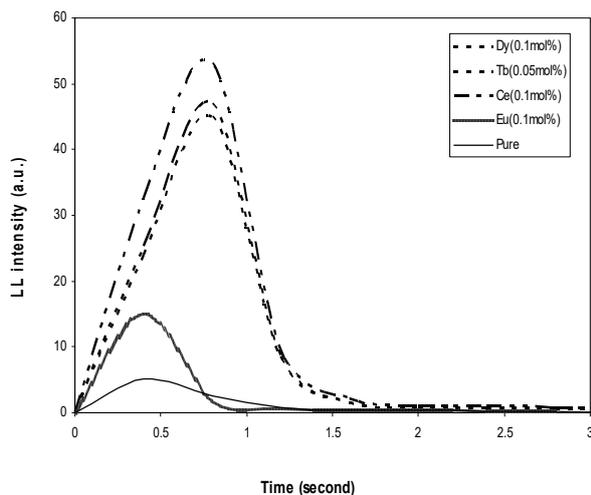


Fig 2 LL glow curves of $K_2Ca_2(SO_4)_3$:RE phosphors exposed to gamma dose 1.395 kGy

Fig. 3 shows the dependence of LL intensity of $K_2Ca_2(SO_4)_3$:RE phosphors on concentration of dopant. It is observed that undoped phosphor shows very weak LL intensity. LL intensity initially increases with increasing dopant concentration attains maximum value for a particular concentration, and then decreases with further increase in concentration. It is also observed that t_m i.e. time corresponding to LL peak does not change significantly with change in concentration of dopant.

Fig.4 shows show the dependence of total LL intensity on gamma dose given to $K_2Ca_2(SO_4)_3$:RE phosphors respectively. It is seen that non-irradiated phosphors do not show LL. However, LL intensity in all case increases with increase in gamma dose.

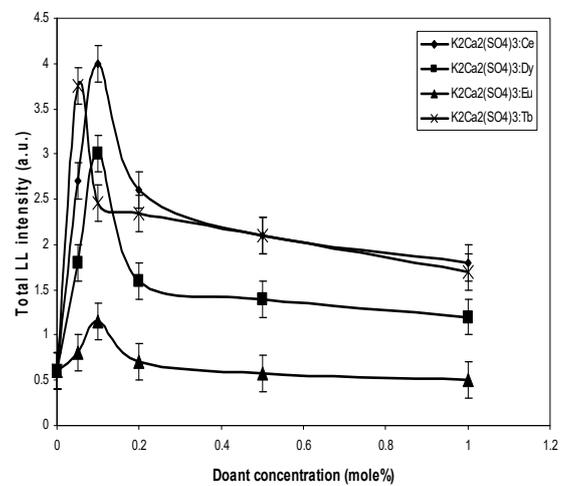
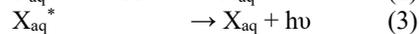
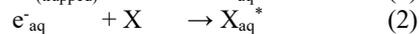
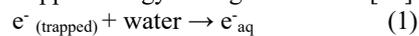


Fig 3 Variation in total LL intensity with concentration of dopant of $K_2Ca_2(SO_4)_3$:RE samples exposed to gamma dose 1.395 kGy.

1.4 Discussion

Sulphates under γ -rays irradiation are known to produce various defect centers such as SO_4^- , SO_3^- , O_3^- , O_2^- etc., only with trapped electron centers. On dissolving such sulphates in suitable solvent the LL is observed due to release of trapped energy during dissolution [12].



Where $X = SO_4^-, SO_3^-, O_3^-, O_2^-$ etc.

It is possible that steps (2) and (3) occur together without the intermediate state X_{aq}^* .

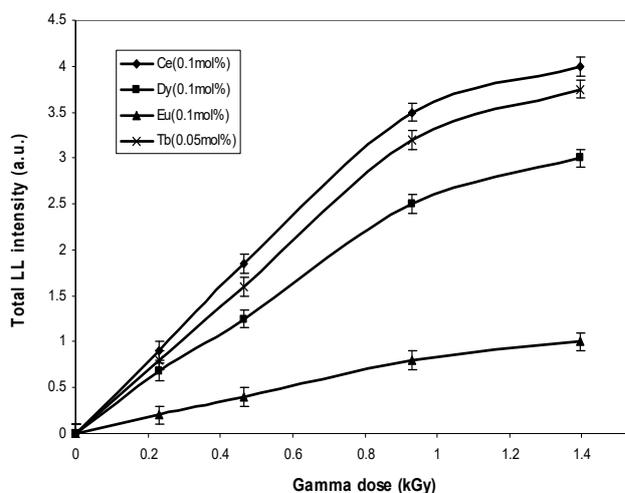


Fig. 4. Variation in total LL intensity with gamma dose given to $K_2Ca_2(SO_4)_3:RE$ samples

Spectroscopic studies of the LL emission indicate that rare earth impurity doped in the sulphate based phosphors act as luminescence centers. It can be assumed that energy released shown in equation (3) is non-radiatively transferred to the rare earth ions present in host lattice, which excites that rare earth ions; the de-excitation of the rare earth ions give rise to the luminescence.

Initially the number of luminescence centers and defect centers increases with increasing concentration of dopant, which causes increase in LL intensity with increasing dopant concentration. For the higher values of dopant concentration, concentration quenching of luminescence centers may take place and therefore, the LL intensity decreases with further increasing in concentration of the dopant. As a matter of the fact, the LL intensity is optimum for a particular concentration of the dopant.

When sulphate based phosphors are exposed to high radiations like γ -rays, X-rays etc. excitation of electrons from valence band to conduction band takes place. Some of the electrons return immediately from the conduction band to the valence band; however, some of the electrons get trapped in the negative ion vacancies. Similarly, holes can also trap in the positive ions vacancies. The density of the trapped electrons or holes increase with increasing radiation dose and hence luminescence intensity increases with increasing radiation dose; but when the sample is exposed to the sample for long duration to the gamma rays recombination between electron and holes take place. Consequently, the density of trapped electron or holes can attain saturation value, when higher dose is given to the sample.

1.5 Conclusions

It is found that the Ce, Dy, Eu and Tb doped $K_2Ca_2(SO_4)_3$ phosphors are LL sensitive. A single peak is observed in the glow curve of Ce, Dy, Eu and Tb doped $K_2Ca_2(SO_4)_3$

phosphors. LL intensity in these phosphors depends on the concentration of doped rare earth impurity and gamma dose given to the samples. LL intensity initially increases with increasing concentration of dopant, attains maximum value for a particular doping concentration; then decreases with further increase in concentration of dopant. LL increases with increasing gamma doses given to the samples. The simple glow curve and near linear dose response makes rare earth doped $K_2Ca_2(SO_4)_3$ phosphors suitable candidates for LL dosimetry.

References:

1. E. Widdmann, G.C. Schmidt, *Annal. Phys. Chem.* 604 (1895) 54.
2. G. Ahnstrom, G.V. Ehrenstein, *Acta. Chem. Scand.* 13 (1959) 109.
3. A Pandey, R G Sonkawade and P D Sahare *J. Phys. D: Appl. Phys.* 35 (2002) 2744
4. N Salah, P D Sahare, S Nawaz and S P Lochab, *Radiat. Eff. Defects Solids* 159(2004) 32
5. A Pandey, P D Sahare, J S Bakare, S P Lochab, F Singh and D Kanjilal *J. Phys. D: Appl. Phys.* 36(2003) 2400
6. P D Sahare and S V Moharil *Radiat. Eff. Defects Solids* 114(1090) 167
7. B P Kore, N S Dhoble, K Park K and S J Dhoble *J. Lumin.* 143(2013) 337
8. B P Kore, N S Dhoble and S J Dhoble *J. Lumin.* 145(2014) 888
9. S P Lochab, D Kanjilal, N Salah, S Habib, S P Lochab, R Ranjan, V E Aleynikov, A A Rupasov and A Pandey *J. Appl. Phys.* 104 (2008) 033520
10. B P Kore, N S Dhoble and S J Dhoble *Radiat. Meas.* 67(2014) 35
11. S P Lochab, Anant Pandey, V E Aleyonikov, A G Molokanov and Pratik Kumar, *Radiation Physics and Chemistry*, 81(11) (2012) 1683-1687.
12. H J Arnikar, P S Damle and B D Chaur, *J. Chem. Phys.*, 228 (1971) 357.