Luminescence and defect studies of Ce$^{3+}$ doped CaS phosphor synthesized via solid state diffusion method

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Abstract

Cerium doped CaS phosphor has been successfully prepared by solid state diffusion method. The phosphor is characterized by X-ray powder diffraction, transmission electron microscopy, selected area electron diffraction, thermogravimetric analysis and photoluminescence. Thermoluminescence and electron spin resonance studies also have been carried out on CaS:Ce phosphor. Irradiated CaS:Ce exhibits electron spin resonance (ESR) lines due to defect centres. The thermal annealing behaviour of one of the defect centres appears to correlate with the thermoluminescence (TL) peak at 135°C. The centre is characterized by an isotropic g-value of 2.0036 and is assigned to a F+ centre.

Keywords: Luminescence; Doping; Phosphors; Field-condensed matter and material physics

1. Introduction

During the last few decades many luminescence studies have been reported on sulfide compounds doped with rare earth ions [1–4]. A Ce ion was found to become efficient emission centres in these compounds, having relatively high transition probabilities originating from the 4f–5d electron configuration. It is shown that the Ce ion exhibits a blue emission with high color purity and stability suitable for full-color thin-film electroluminescence device applications [5–7]. Recently, rare earth and non-rare earth doped sulfide phosphors have attracted more attention because of the potential uses in many fields, for example, cathode ray tubes, infrared sensors, thermoluminescence and electroluminescence panels. Calcium sulfide has several technological applications when doped with Ce$^{3+}$. It forms a highly efficient blue-green phosphor for display applications. Nanometer-size semiconductor particles are currently investigated in many laboratories. Due to the spatial confinement of electrons and holes, the chemical and physical properties of these particles strongly differ from those of the bulk solids (size quantization effect) [8–12]. They become a totally new class of materials with potentially valuable applications. Nanocrystals doped with optically active luminescence centers create new opportunities for luminescence study and application of nanomaterials [13,14]. SrS, CaS, BaS and ZnS are wide-gap semiconductor materials and are commercially used as phosphors and also in thin-film electroluminescent devices [15–19]. The transition metallic ions co-activated sulfide nanoparticles (e.g. SrS, CaS, BaS and ZnS) which substantially change their properties, form a new class of luminescent materials. Several sulfide impurity activated phosphor have interesting properties useful for practical application, e.g. cathode ray tubes, TV screen, fluorescence lamps, TL-Dosimetry, X-ray imaging screens, high pressure mercury lamps, lasers, superconductive conductors, etc. ZnS was studied extensively. However, synthesis of rare earth doped CaS nanoparticles have received little attention. It was therefore decided to synthesis CaS:Ce nanoparticle using the solid state diffusion method.

The sulfides have a large amount of defects such as S vacancies and Ca vacancies. These defects are considered to cause luminescence quenching. On the basis of electron spin resonance (ESR) measurement, we shall try to understand the role of intrinsic defects governing the physical properties, which make them useful for device applications. Apart from defect centers, luminescence centers also play a vital role in thermoluminescence...
nitrates. The final powder was dried in an oven at about 60 °C. Warm distilled water and finally confirmed by the ring test for nitric acid of analytical reagent (AR) grade. The powder was used as the host system. The calcium powder was treated with talc lattice in presence of suitable fluxes. Calcium sulphate was by a reducing agent and (2) incorporation of activator in the crystal of firing: (1) reduction of alkaline earth sulphate to its sulfide diffusion. According to this method, in principle, two reactions are assumed to take place simultaneously at the higher temperature. According to this method, in principle, two reactions are assumed to take place simultaneously at the higher temperature. These reactions were carried out at 1000 °C and firing time was 2 h. After firing, the charge was transferred to a mortar and was rapidly pulverized while red-hot. The phosphor powder was then collected in clean and dry sample tubes.

2. Experimental

2.1. Sample preparation

The method of preparation adopted for this work is solid state diffusion. According to this method, in principle, two reactions are assumed to take place simultaneously at the higher temperature of firing: (1) reduction of alkaline earth sulphate to its sulfide by a reducing agent and (2) incorporation of activator in the crystal lattice in presence of suitable fluxes. Calcium sulphate was used as the host system. The calcium powder was treated with nitric acid of analytical reagent (AR) grade. The powder was soaked in excess of dilute nitric acid (30%) and kept over night. It was then heated for about half an hour to ensure the conversion of all metallic impurities into their respective nitrates. These soluble nitrates were eliminated by repeated washing in warm distilled water and finally confirmed by the ring test for nitrates. The final powder was dried in an oven at about 60 °C and collected in bottles.

Carbon powder of analytical reagent grade was used as the reducing agent. The carbon powder was boiled in excess of distilled water for half an hour and filtered. The residue in filter paper was repeatedly washed with warm distilled water, dried in an oven and finally collected in bottle. In the present investigation, sodium thiosulphate (AR grade) was used as flux. Cerium (0.1 mol%) was used as activator. Solutions of this compound were preferred for uniform distribution. The ingredients, calcium sulphate, carbon and flux, were taken according to the proportion. They were mixed initially with the help of a good pestle and mortar. The required amounts of activators and few drops of rectified spirit were added and the whole charge was thoroughly mixed with pestle and mortar. The rectified spirit served to disperse the activator in the entire charge. Graphite crucibles were used for firing the charge. First they were baked at the operating temperature and then cleaned by removing all dust. The prepared charge was packed in a crucible and a thin layer of carbon powder was spread over it. It was covered with another similar crucible. The two crucibles at the high temperature of firing formed an airtight chamber. Thus the top layer of carbon powder was made to keep a reducing atmosphere over the charge. The firing was carried out in a muffle furnace provided with an automatic temperature control. The final firing temperature was 1000 °C and firing time was 2 h. After firing, the charge was transferred to a mortar and was rapidly pulverized while red-hot. The phosphor powder was then collected in clean and dry sample tubes.

2.2. Instruments

Powder XRD pattern was performed on a Philips X'pert X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.15418 nm) and nickel filter at a scanning step of 0.03°, continue time 10 s, in the 2θ range from 10° to 80°. TEM images and SAED images were recorded on a JEOL-JEM 200CX transmission electron microscope. The sample used for TEM observations were prepared by dispersing products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. Thermoluminescence analysis was carried out on a Lahys-TG-DSC16 system. The experiment was conducted in nitrogen atmosphere at a heating rate of 20 °C/min. PL experiments were carried out on a LAB2 Luminescence Spectrometer at room temperature. Thermoluminescence glow curves were recorded with the usual setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (951B), dc amplifier and a millivolt recorder. ESR measurements were carried out on a Varian E-112 E-Line Century series X-band ESR spectrometer. TCNE (g = 2.00277) was used as a standard for g-factor measurements. Step heat treatments were performed to follow the decay and evolution of the defect centres. These were carried out in situ in the ESR cavity using the Varian variable temperature accessory.

3. Results and discussion

3.1. XRD, TEM, TGA and PL studies

In order to study the nature and morphology of the sample, various techniques such as X-ray diffraction, transmission electron microscopy and selected area electron diffraction (SAED) were employed. The formation of the compound was confirmed by XRD. Fig. 1 shows the XRD patterns of the products. All the reflections can be indexed to the cubic CaS phase. The XRD pattern matched perfectly with the ICPSD (77-2011). TEM images of prepared CaS:Ce are shown in Fig. 2. It can be seen that the CaS:Ce display an irregular aggregate morphology with an average diameter of 20–30 nm. The inserted SAED (Fig. 2) recorded on a CaS:Ce shows the presence of clear diffraction rings, which correspond to the cubic phase of CaS with polycrystalline nature. Sulfide could be obtained by varying different parameters such as firing temperature, duration of firing, reducing agent and ambient atmosphere. Thermal analyses like DTA, TGA, DTG, etc., are used to determine the optimum values of the above parameter. The thermogravimetric analysis of CaS:Ce prepared by reducing CaSO₄ with pure carbon is shown in Fig. 3. From
The reduction process started from 420 °C and attained a maximum at 600 °C and ended at around 850 °C.

The emission spectra were taken by exciting the sample at 465 nm. Trivalent cerium produced two emission bands in calcium sulfide—one prominent peak around 498 nm and the other broad peak in the range of 550–570 nm. Spectral energy distribution of these bands are shown in Fig. 4. Energy difference between these peaks is found to be almost the same order as reported [20,21] for the two lowest states ($^2F_{5/2}$ and $^2F_{7/2}$) of the single 4f electron of Ce$^{3+}$. It can, therefore, be reasonably assumed that the electronic transitions for the luminescence terminate in these two states. CaS has a NaCl-type structure with an O$_h$ site symmetry at the Ca site. The excitation band (Fig. 5) at 465 nm is assigned to the $5d$ crystal field splitting levels, corresponding to $T_{2g}$. No further splitting of the $T_{2g}$ peak was
observed. This indicates that the site symmetry of Ce$^{3+}$ in CaS remains close to $O_h$.

### 3.2. TL and ESR studies

The TL glow curve observed in CaS:Ce is shown in Fig. 6. The TL glow curve shows a dominant peak at 65°C followed by other peaks at 135°C, 332°C and 375°C. Unirradiated CaS:Ce showed weak lines from a species (centre I) which were characteristic of a centre exhibiting a rhombic $g$-tensor. After irradiation, these lines were found to increase in intensity and were found to dominate other ESR lines from new defect centres created by irradiation. These lines are shown in Fig. 7(a). However, the lines from centre I could be clearly seen without any interference after annealing at 300°C (Fig. 7(c)). The principal $g$-values were found to be $g_1 = 2.0022$, $g_2 = 2.0054$ and $g_3 = 2.0102$. This species is yet to be identified.

Apart from centre I, an additional line (centre II) has been observed after irradiation, close and to the left of the TCNE marker ($g = 2.0028$). This is shown in Fig. 7(b). The centre associated with this line has a principal $g$-value 2.0036 and a linewidth of 1.1 G. A likely trapping centre which can be formed in a system like CaS:Ce is the F$^+$ center (an electron trapped at an anion vacancy). This centre was first observed by Hutchison [22] in neutron irradiated LiF. In LiF, a single broad line (linewidth $\sim 100$ G) with a $g$-factor 2.008 was observed. A similar centre has been observed in other systems, notably in alkali halides after X-ray or gamma irradiation. The main characteristic features of such centres are: (1) a small $g$-shift, which may be positive or negative, (2) a large linewidth and (3) saturation properties characteristic of an inhomogenously broadened ESR line. The large linewidth arises from an unresolved hyperfine structure.

The F$^+$ centre consists of an electron occupying an anionic vacancy formed by the removal of a negative ion from the lattice. Hyperfine interactions with the nearest-neighbor cations account for most of the linewidth. Defect centre II formed in the present system is characterized by a small $g$-shift and the linewidth, however, is relatively small. The centre also does not exhibit any resolved hyperfine structure. On the basis of these observations and considerations of the characteristic features of the defect centres likely to be formed in a system such as CaS:Ce, centre II is tentatively assigned to a F$^+$ centre. It is to be mentioned that an intense signal at $g = 2.0032$ observed in X-ray irradiated undoped CaS at room temperature has been attributed to the F$^+$ centre (Ghosh and Shanker [23]).
The stability of centre II was measured using the step-annealing technique. The thermal annealing behaviour of centre II (Fig. 8) shows different temperature regions where there is a reduction in intensity of the corresponding ESR line. The first region from 110°C to around 170°C is likely to arise from recombination of charges, released from unknown traps, at F+ centre sites. This region appears to correlate with the observed TL peak at 135°C.

The thermal annealing behaviour of centre I is shown in Fig. 9. It is seen that the centre starts to decay from 250°C with its intensity approaching zero at higher temperatures. On the other hand, the thermal annealing behaviour of F+ centre is different particularly in the temperature region where the major TL glow peak is observed.

4. Conclusions

Based on the results presented above, the following conclusions may be highlighted:

1. CaS:Ce nanocrystallites have been successfully synthesized via a solid state diffusion route. PL spectra of CaS:Ce nanocrystallites has a blue-green shift in comparison with bulk material.
2. A defect centre formed in gamma irradiated CaS:Ce system is tentatively assigned to a F+ centre.
3. The 135°C TL peak appears to correlate with the F+ centre.

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References