Chalcogenide Letters Vol. 6, No. 9, September 2009, p. 445 – 453

THERMOLUMINESCENCE CHARACTERISTICS OF CaS: Ce NANOPHOSPHORS

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The thermoluminescence characteristics of cerium doped calcium sulphide nanoparticles under UV radiations have been studied. The average grain size of the nanoparticles is found to be 53nm which is confirmed by TEM micrograph. The TL glow curve shows a single peak at 376K. TL intensity increases linearly unto 2hr UV exposure. Further increase in the dose results into a decrease of TL intensity. Variation in TL intensity as a function of cerium concentration is studied and 0.4mol% is found to be the optimum concentration for TL. The trap parameters namely, activation energy *(E)*, order of kinetics *(b)* and frequency factor *(s)* of CaS: Ce (0.4 mole %) sample have been determined using Chen's method. The order of Kinetics is found to be 2 indicating retrapping of charge carriers in CaS: Ce nanoparticles. The effect of different heating rates has also been studied. The PL emission spectrum shows two peaks at 506nm and 565nm when excited at 450nm.

(Received August 31, 2009; accepted September 29, 2009)

Keywords: CaS:Ce, Thermoluminescence, Nanophosphors, TEM, UV

1. Introduction

Thermoluminescence is the emission of light from a solid either inorganic, semiconductor or an insulator when it is heated after its exposure to some radiation [1] Thermoluminescence is one of the long investigated fields. Various aspects of TL have been theoretically as well as experimentally studied till date [2-5]. $CaSO_4$: Dy and LiF-TLD 100 are a couple of good thermo luminescent phosphors. Tissue equivalence, reusability, stability, high sensitivity, a simple glow curve structure and dose linearity are some of the characteristics of an ideal TL material. Since no phosphor can behave in an ideal way hence there have always been attempts to prepare new phosphors with improved TL characteristics or improve upon the already existing phosphors. The most widespread applications of TL phenomenon is the radiation dosimetery in health physics, biological sciences and radiation protection. Besides this TL is a tool to study the defects and traps structure inside the host lattice.

Calcium Sulphide, a member of II-VI family has been long investigated for its dosimeteric properties [6-7] for various radiations such as U.V. and gamma rays. Earlier Vinay et al [8-9] has explored the potential of CaS:Bi nanophosphors as UV and gamma dosimeter. Recently the thermoluminescent behavior of SrS:Ce nanophosphors have been studied[10]. In this paper we report the TL characteristics of CaS:Ce nanophosphors exposed to UV radiation. The effect of different dopant concentrations and different heating rates on the glow curves has been studied. Kitis et al [11] second order kinetic equation is applied to experimentally obtained glow curve and it describes quite satisfactorily the single glow curve.

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2. Experimental

2.1 Method of preparation

The nanoparticles for the study are prepared by solid state diffusion method [12]. Calcium sulphate, cerium nitrate, sodium thoisulphate, carbon powder and ethanol were the starting materials. All the starting materials were of analytical reagent (AR) grade. Carbon acts as a reducing agent for the reduction of sulphate to sulphide at high temperature and cerium acts as an activator. Sodium thoisulphate (15%) acts as a flux for the reaction. The calculated quantity of calcium sulphate, carbon powder, cerium nitrate (0.4mol %) and the flux were taken and mixed thoroughly with the help of an agate pestle and mortar. To cause uniform distribution of dopant in the charge, it was dissolved in few ml of ethanol and then this solution was mixed with the entire charge. The charge was placed in clean graphite crucible (which was already baked at the firing temperature) and a thin layer of carbon powder was spread over it. This crucible was covered with another similar crucible. The thin layer of the carbon over the charge created a reducing environment over the charge at high temperature. This whole arrangement was placed in a muffle furnace and charge was fired at 950^0C for 2hrs. Due to the use of two crucibles, this method is also known as double crucible method. The firing at high temperature causes the incorporation of cerium in the host lattice. After 2hrs the charge was taken out and rapidly crushed while red hot with the help of pestle and mortar. The powder so formed was CaS: Ce and collected in dry sample tubes for further studies.

2.2 Characterization

For the conformation of the compound so formed, XRD pattern was recorded at room temperature for CaS: Ce nanoparticles by using Cu target (CuKα_1 line, λ=1.5Å) on Bruker Advance D8 XRD machine and matched with standard data available (JCPDS Card No 77-2011). TEM micrograph has been obtained on Transmission Electron Microscope, H-7500 (Hitachi Ltd. Japan) operated at 80 kV, by depositing the suspension in ethanol on carbon coated gold grids.

For recording TL, samples were exposed to UV radiations from UVGL-58 handheld UV lamp operating at 230V-50Hz (emitting 253nm). TL glow curves were recorded on a Harshaw TLD reader (Model 3500) fitted with 931B photomultiplier tube (PMT) by taking 5mg of sample each time. The photoluminescence measurements were recorded on a Fluoro Max-3 (Jobin-Yvon, Edision, NJ, USA) equipped with a photomultiplier tube and a xenon lamp of power 150W.

3. Result and discussion

Particle shape and size

Fig.1 shows the XRD pattern of CaS: Ce nanoparticles. The XRD pattern matched perfectly with standard data available in JCPDS (77-2011). The pattern clearly indicates cubic CaS phase with lattice constant, a=5.686Å. The average crystallite size of the nanoparticles is calculated from FWHM of the most intense XRD peak using Debye Scherrer formula [13].

$$D = 0.89\, \lambda / \beta \, \mathrm{Cos}\theta \qquad (1)$$

Where D is the average grain size of the crystallite, λ is the wavelength of CuKα (0.154nm) radiation, β is the diffracted full-width at half-maximum (in radian) caused by the crystallites and θ is the Bragg angle. The average grain size was found to be approximately 53nm. The particle shape and size of the prepared nanocrystalline powdered material was determined by TEM. The TEM micrographs are shown in Fig 2 which indicates an average size of ~50nm and an irregular shape of the nanoparticles. TEM micrograph confirms the XRD result.

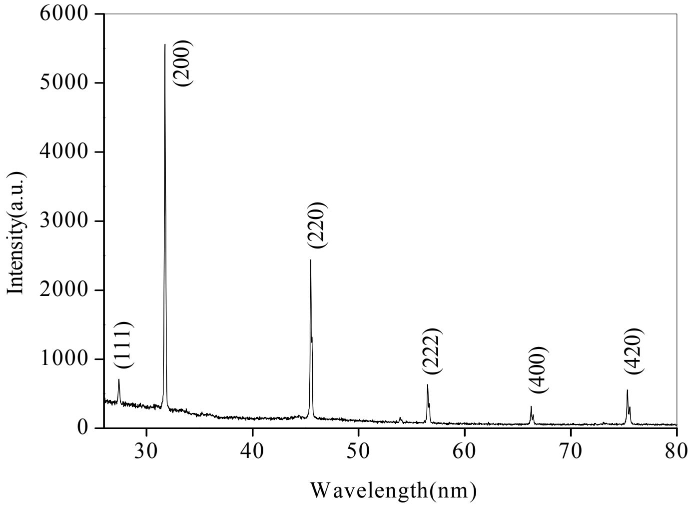

Fig.1 XRD pattern of CaS: Ce

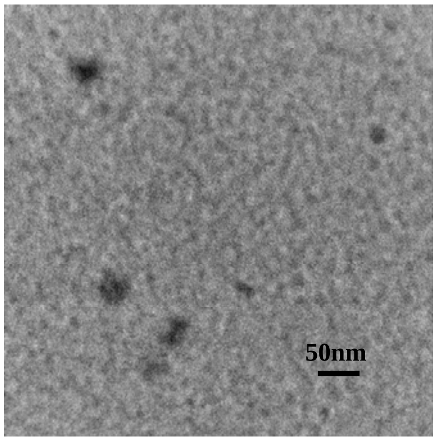

Fig 2. TEM image from CaS:Ce

TL Characteristics

Fig. 3 shows the TL glow curves for different concentrations of cerium in mol% for a UV exposure of 2hrs. Luminescence of a phosphor is affected largely by the impurity concentration in it. If the concentration of impurities increases from a particular amount, they may act as self quenchers by non-radiative transitions resulting in fall in the intensity of the luminescence. In the present case the TL intensity increases with cerium concentration up to 0.4mol% and afterwards it decreases [Figure 3 (inset)]. The fall in the TL intensity may be attributed to the well known concentration quenching effect of dopant. Hence the optimum impurity concentration of Ce in CaS for 2hr UV exposure is 0.4mol% since at higher concentrations the TL intensity falls.

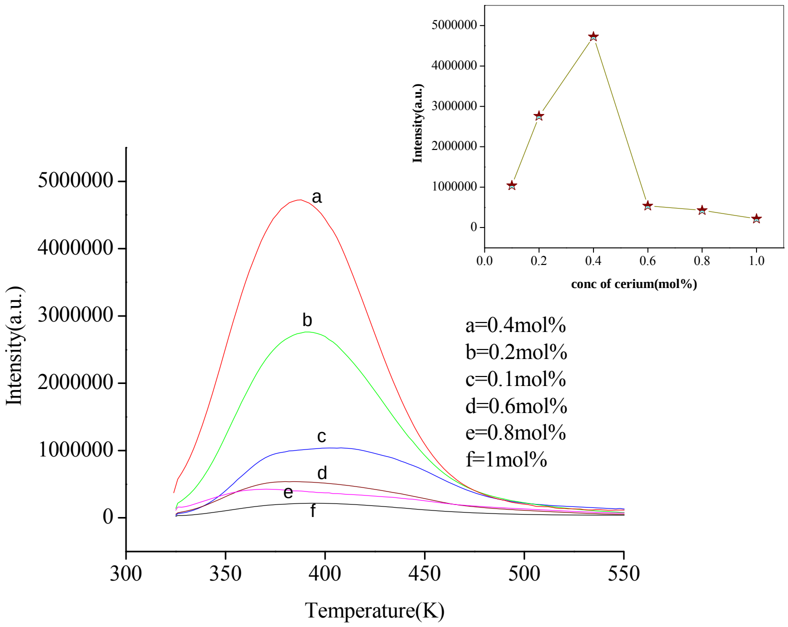

Fig. 3 TL glow curves for CaS: Ce with different concentrations of Ce in CaS and inset shows the variation in TL intensity as a function of cerium concentration

Fig.4 shows the TL response curve for CaS: Ce (0.4mol %) nanoparticles for different UV exposure time. For a phosphor to be used as thermoluminescent dosimeter the dose response should be linear. From Fig.4 it is clear that CaS: Ce (0.4mol %) shows almost linear dose dependence up to a 2hr exposure time.

The variation in the TL intensity for CaS: Ce (0.4mol %) as a function of UV exposure time is shown in fig.5. The TL intensity increases up to 2hrs of UV exposure and afterwards it decreases. In case of UV irradiated phosphors the TL response mainly generates from the surface traps, since these radiations cannot penetrate deeper and hence will not induce lattice defects. The density of surface defects increases with increase in the UV exposure leading to increase in peak intensity. The fall in the TL intensity at higher doses has been reported earlier by several authors [14, 15] and usually a consequence of competition between radiative and nonradiative centre or between different kinds of trapping centers [16].

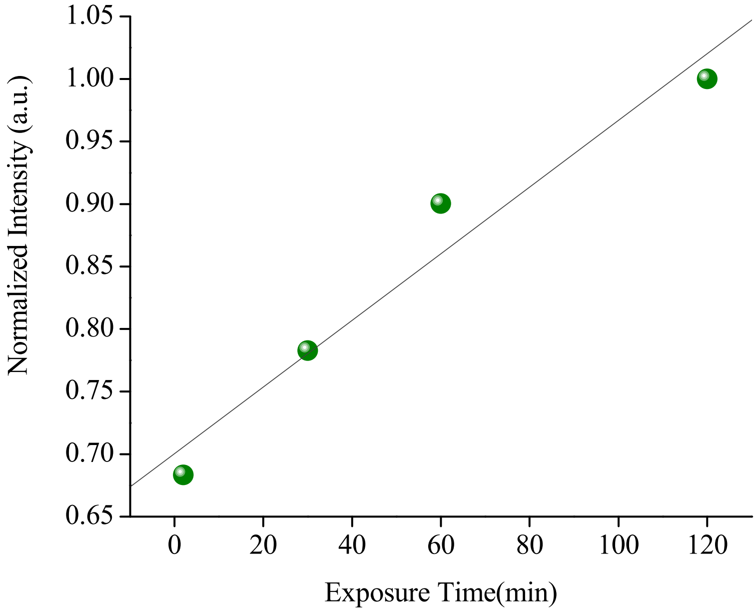

Fig.4 TL response curve for CaS: Ce (0.4 mol %) nanoparticles for different UV exposure time.

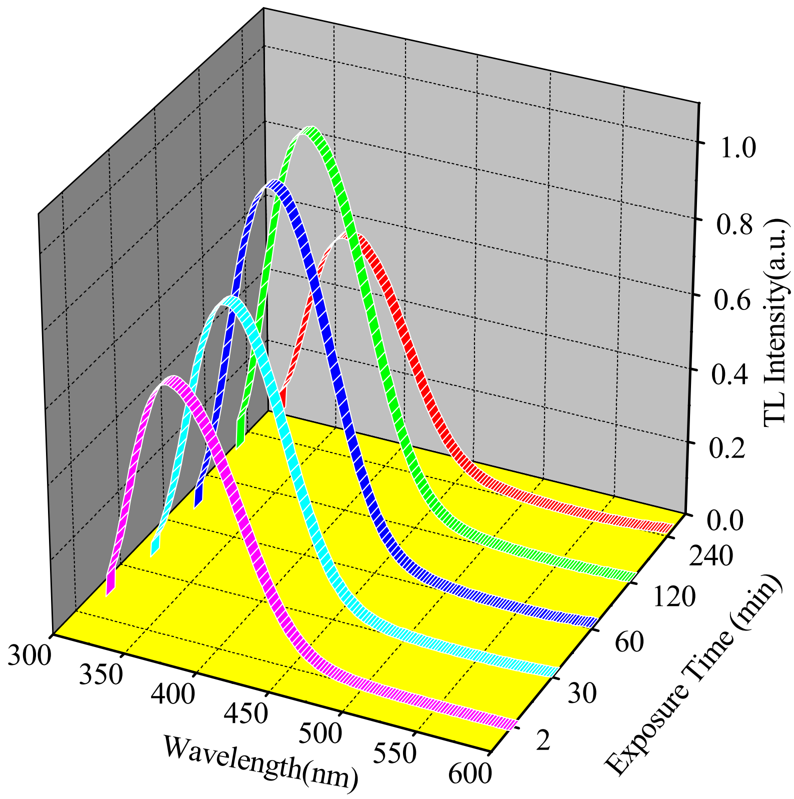

Fig. 5: Variation in the TL intensity for CaS: Ce (0.4mol %) as a function of UV exposure time

Fig. 6 shows the effect of heating rate on the TL glow curves of CaS: Ce (0.4mol %) nanoparticles for a UV exposure of 2hrs. With increasing heating rate the peak position and intensity of peak changes. The peak temperature shifts to higher side and the peak intensity falls which may be attributed to thermal quenching of TL due to an increase in heating rate.

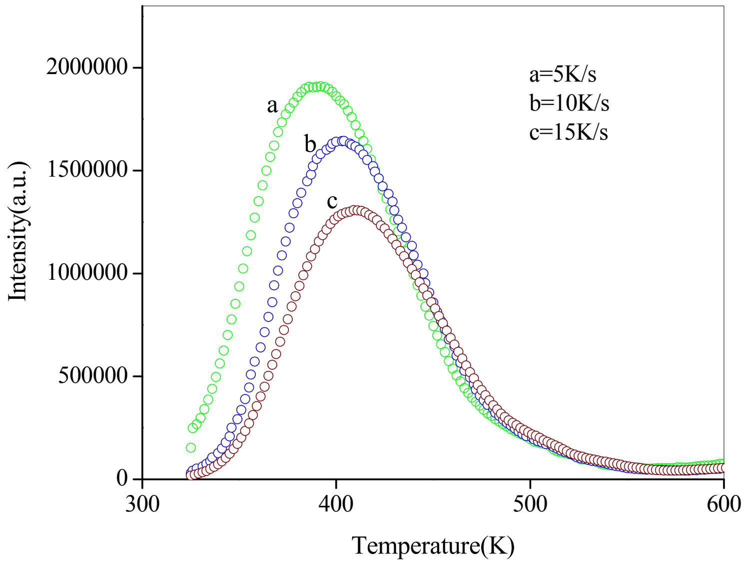

Fig.6 Effect of heating rate on the TL glow curves of CaS: Ce (0.4mol %) nanoparticles.

Order of Kinetics

The curve with solid dots in Fig.7 is the experimental glow curve for CaS: Ce (0.4mol %) for a UV exposure of 2hrs at a heating rate of 5K/s. The order of kinetics and the activation energy of this glow curve was found using Chen's empirical formulae [17]. Theoretically the form factor μ_g is found using formula

$$\mu_g = (T_2-T_m)/(T_2-T_1) \tag{2}$$

where, T_m is the temperature corresponding to the maximum intensity, T_1 and T_2 are the temperatures corresponding to the half of the intensities on the either side of the maximum. Theoretically the form factor ranges between 0.37and 0.56, is close to 0.42 for first order kinetics and 0.52 for second order kinetics [18].

The trap depth or the thermal energy needed to free the trapped electrons can be calculated using the following equation

$$E_\alpha = c_\alpha (kT_m{}^2/\alpha) - b_\alpha (2kT_m) \tag{3}$$

$$\alpha=\tau,\ \delta,\ \omega, \qquad \tau = T_m-T_1,\ \delta = T_2-T_m,\ \omega = T_2-T_1$$

$$c_\tau = 1.51 + 3.0\ (\mu_g-0.42), \qquad c_\delta = 0.976 + 7.3\ (\mu_g-0.42)$$

$$c_\omega = 2.52 + 10.2\ (\mu_g - 0.42),$$

$$b_\tau = 1.58 + 4.2(\mu_g - 0.42), \qquad b_\delta = 0, \qquad b_\omega = 1$$

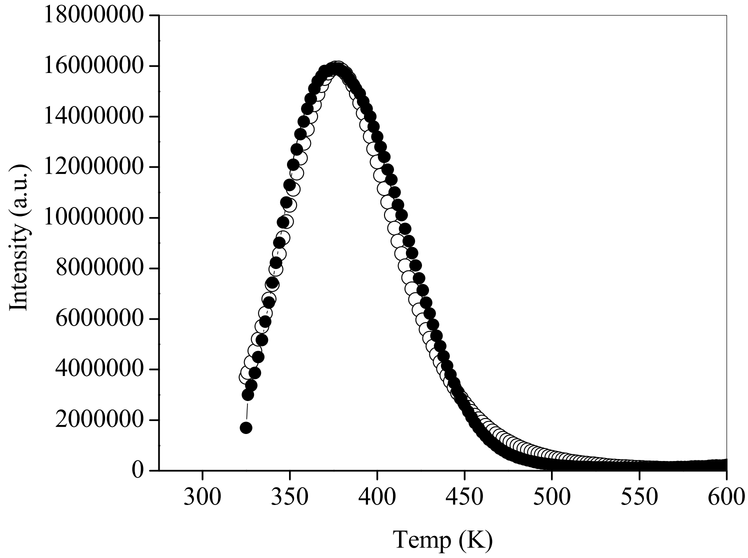

Fig. 7 Comparison between the experimentally obtained TL glow curve (••••••••••) and the theoretically fitted glow curve (○○○○○○○○○○) of CaS: Ce.

Using the value of T_m, T_1 and T_2 from the experimentally obtained TL glow curve in fig.7 the form factor for the CaS:Ce (0.4mol%) is found to be 0.56 indicating second order kinetics in it. The theoretical glow curve is generated by applying GCD function suggested by Kitis et al [11] for second order kinetics to the experimentally obtained glow curve of fig. 7 and the resultant curve is shown by circles in the same figure.

$$I(T) = 4I_m \exp\{(E/kT)(T-T_m)/T_m\}\,[(T^2/T_m^2)(1-\Delta) \times \exp\{E/kT\,(T-T_m)/T_m\}+1+\Delta_m]^{-2} \quad (4)$$

Where I(T) is the TL intensity at temperature T(K), I_m is the maximum peak intensity, E is the activation energy (eV) calculated using Chen's formula (equation 3), k is the Boltzmann constant (8.6×10^{-5} eV/K), Δ=2kT/E and $\Delta_m = 2kT_m/E$.

On comparing the two curves we find that there is very less difference between the experimental and the theoretical curve and GCD function for second order suggested by Kitis is quite successful in describing the single glow peak confirming second-order kinetics.

The frequency factor [19] was calculated from equation (5)

$$\beta E / kT_m^{\,2} = s \exp\{-E/kT_m\}[1+(b-1)\Delta_m] \quad (5)$$

The calculated trap parameters have been summarized in table 1.

Table: 1 Trapping parameters of CaS: Ce (0.4 mole %) nanocrystalline samples for 2hr UV irradiation at room temperature.

CaS: Ce	T_m (K)	Order of Kinetics (μ_g)	Activation energy *E (eV)* E_δ	E_τ	E_ω	E_{av}	Frequency factor S(s^{-1})
(0.4 mol %) Heating Rate 5K/s	376 K	2 (0.56)	0.55	0.56	0.55	0.55	4.9×10^6

PL characteristics

Fig.8 shows the normalized excitation and emission spectra of CaS: Ce sample. The excitation spectrum shows a main peak around 460nm and a small peak at 350nm. The excitation band at 460nm can be attributed to the 5d crystal field splitted levels corresponding to T_{2g} where as the small peak at 350nm may be due to a charge transfer transition of Ce^{3+} from 4f to conduction band. The Ce doped CaS shows two peaks in emission spectrum at 506nm and 565nm when excited at 450nm. The spin orbit coupling causes the splitting of ground state, 4f of Ce^{3+} into two levels $^2F_{7/2}$ and $^2F_{5/2}$ having an energy difference of 2000cm^{-1} [20]. The excited state 5d of Ce^{3+} splits into a doublet E_g and a triplet T_{2g} levels due to crystal field splitting of CaS, with T_{2g} at lower energy. The two peaks at 506nm and 565nm are due to transition from T_{2g} sublevel of 5d excited state to $^2F_{5/2}$ and $^2F_{7/2}$ of 4f ground state of Ce^{3+} [21].

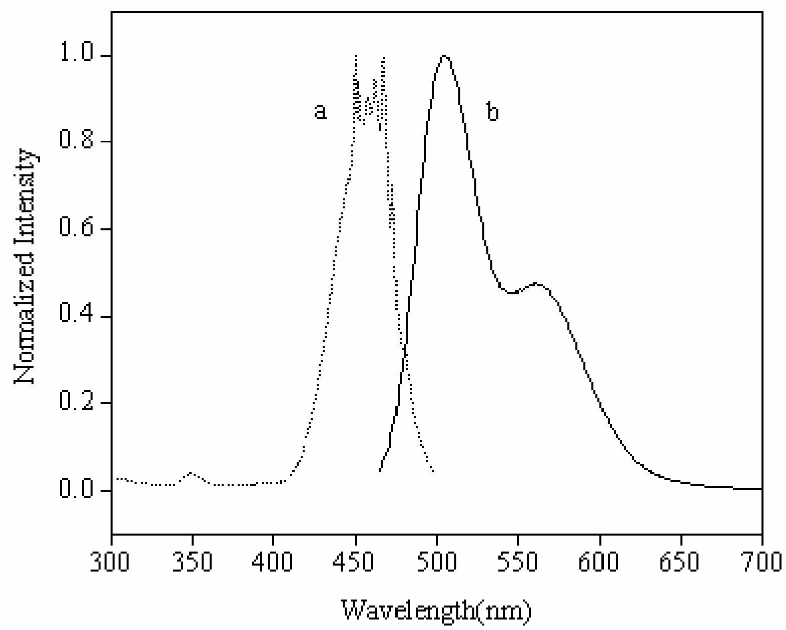

Fig. 8 (a) Excitation Spectrum (b) Emission Spectrum of CaS: Ce

4. Conclusions

The TL properties of CaS doped with cerium nanophosphors has been investigated for UV irradiation. The optimum concentration of Ce^{3+} is 0.4 mole%. The trapping parameters were calculated. The phosphor CaS: Ce is found to have second-order kinetics in TL emission suggesting retrapping of charges. It shows almost linear dose dependence up to a 2hr exposure time. The TL intensity increases up to 2hrs of UV exposure. Further increase in the dose results into decrease in TL intensity. The peak temperature shifts to higher temperature side and the peak intensity falls with increasing heating rate. PL emission spectrum shows two peaks at 506nm and 565nm when excited at 450nm due to the transition amoung the crystal field splitted levels of Ce in CaS.

Acknowledgement

One of the authors GS is thankful to I.U.A.C., New Delhi for financial help in the form of a fellowship under the project UFUP-44305.

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