

EFFECT OF Ce^{3+} ION ON THE X-RAY INDUCED FLUORESCENCE EMISSION FROM CaS

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The effect of Ce^{3+} on the fluorescence emission from $CaS:Ce^{3+}$ phosphor is studied using X-ray excitation. Apart from the emission in the visible region, the phosphor also shows fluorescence emission in the ultraviolet region. Variation in wavelengths and intensities of these emissions due to change in dopant concentration is also analysed.

1. Introduction

Effect of rare earth ions (RE^{3+}) on the luminescence properties of alkaline earth sulphide phosphor has been studied by various workers.¹⁻⁵ Modifications of luminescence emission from such phosphors due to various dopants are important in the context of both basic science and technology. Most of the studies in this direction have been concentrated on the excitation of phosphors using ultraviolet radiation. It has been observed that the presence of RE^{3+} modifies the self-activation centres of host lattice apart from exhibiting the characteristic emission lines of RE^{3+} in the luminescence spectrum.^{4,5} It has been found that ion lattice interactions split the energy levels of RE^{3+} in the host lattice environments.⁴⁻⁶ In order to extend the studies in the UV region, one has to use high-energy excitation sources like X-rays, γ -rays etc. Literature survey shows that luminescence studies of rare earth doped sulphide phosphors using X-ray excitation are very few, so that there are only limited information in the UV region of luminescence emission. Studies in the UV region are important in cases like Ce^{3+} , since the characteristic $4f^1-5d^1$ spectrum of Ce^{3+} ion lies in the UV region.

2. Sample Preparation

The starting materials used for the preparation of the phosphor were ultra pure calcium sulphate and spectroscopically pure activated carbon powder. For the proper crystallization of the phosphor, sodium thio sulphate was used as flux. The dopant was added along with the flux to the starting material. This slurry was dried at 50°C and the dried mass was crushed using a mortar and pestle. The mixture so obtained was fired in the central zone of a high temperature furnace at 1000°C for one hour. After firing, it was suddenly quenched to room temperature. The phosphor so obtained was finely powdered and was used for the study. X-ray diffraction study showed the absence of oxygen content in the sample indicating the complete reduction of CaSO_4 to CaS .

3. Experimental

A few milligrams of the powdered sample were uniformly spread over approximately 1 cm² area and glued with suitable gum to the surface of a special planchet which was kept at 3 cm from the window of the X-ray tube for irradiation purpose and the X-ray excited fluorescence spectra were recorded. The schematic of the experimental set-up is given in Fig. 1. In this set-up, X-rays from the tungsten target of an X-ray generator operating at 40 kV and 20 mA were directed towards the sample. The resulting X-ray excited fluorescence spectra were recorded using a 0.25 m Jarrel Ash monochromator, photo multiplier, DC amplifier and a two-pen Omniscrite strip chart recorder.

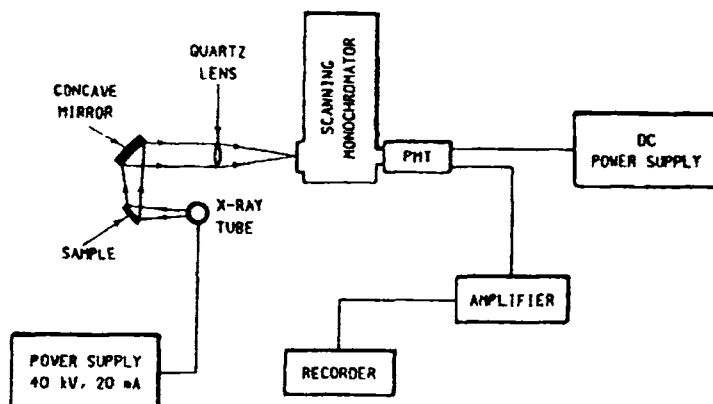


Fig. 1. Schematic diagram of experimental set-up for X-ray excited optical luminescence studies.

4. Results and Discussion

Figure 2 shows the fluorescence emission spectra at various dopant (Ce^{3+}) concentrations in CaS phosphor. Results obtained from the present studies are summarized

in Table 1. The undoped sample exhibits a single broad peak in the visible region of the spectrum at 485 nm. There is no spectral emission in the UV region. The emission in the visible region is due to self-activation centres arising from lattice defects, like vacancies. On increasing the dopant concentration, the emission peak in the visible region shifts towards the longer wavelength side and a well defined shoulder is developed on the longer wavelength side of the main peak. These results show that the presence of dopant modifies the distribution of self-activation centres in the host lattice. Figure 3 shows the fluorescence emission intensity variation as a function of dopant concentration indicating the usual concentration quenching for all peaks.

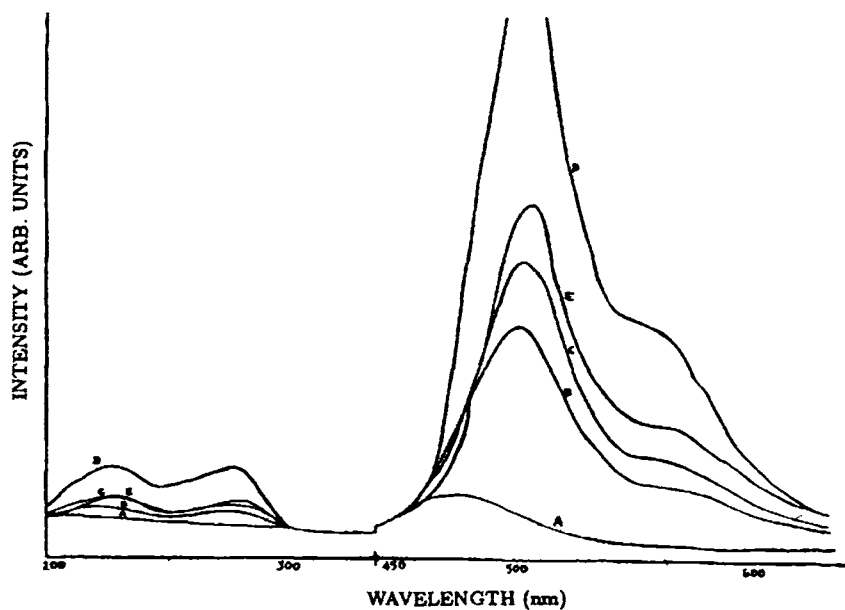


Fig. 2. Fluorescence emission spectra of $CaS:Ce^{3+}$ phosphor for different Ce concentrations (in mole %): (A) undoped (B) 0.0175 (C) 0.035 (D) 0.175 and (E) 0.350.

Table 1. Dopant concentration, wavelength of emission and intensity of prominent peaks in the fluorescence spectra of $CaS:Ce^{3+}$.

Concentration of dopant (mole %)	Wavelength of peaks (nm)			Intensity of peaks (arbitrary units)		
	(a)	(b)	(c)	(a)	(b)	(c)
0	-	-	485	-	-	2.3
0.0175	222	275	500	0.5	0.7	10.8
0.035	224	277	503	1.0	1.1	14.1
0.175	225	278	505	2.6	3.0	31.0
0.350	228	282	508	1.1	1.2	16.9

Apart from the emission in the visible region, the spectrum of CaS:Ce phosphor shows broad twin peaks in the UV region at wavelengths 225 nm and 278 nm. The UV emission intensity is very small as compared to that of visible region.

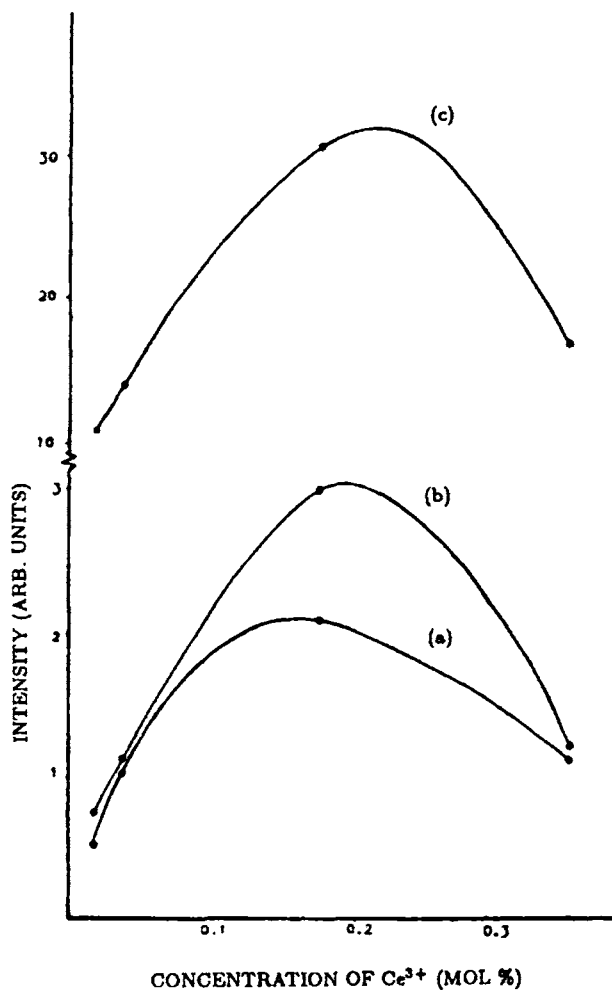


Fig. 3. Variation of fluorescence emission intensity with dopant concentration in CaS:Ce for the three prominent peaks at (a) 225 nm (b) 278 nm and (c) 500 nm in its emission spectra.

Relevant transition in Ce³⁺ ions corresponding to UV emission are given in Fig. 4. The free ion term ²D arising from 5d¹ configuration of Ce³⁺ splits into ²E and ²T states in CaS lattice with doublet separation 8470 cm⁻¹.

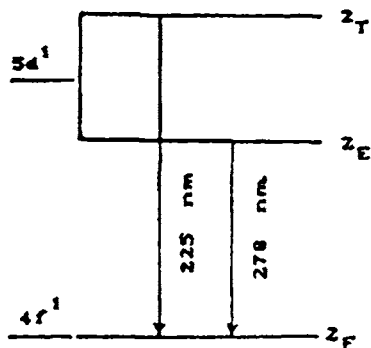


Fig. 4. Relevant transitions in Ce^{3+} ion corresponding to UV emission.

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