



# Photoluminescence in Various Phases of Cerrous Sulphate

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## ABSTRACT

$Ce_2(SO_4)_3$  exists in several phases. The most common phase is  $Ce_2(SO_4)_3 \cdot 8H_2O$  and reported  $Ce^{3+}$  emission corresponding to this phase, however significant changes are observed in  $Ce^{3+}$  emission when it crystallizes into different phases. The lot of micro changes was observed with both the samples which indicate the phase change at various temperatures. This can be correlated with the Photoluminescence (PL) spectra. The method of preparation, photoluminescence spectra, phase change,  $Ce^{3+}$  to  $Tb^{3+}$  energy transfer process and the effect of temperature on the morphology of cerrous sulphate are described in this paper.

**Key Words:** Photoluminescence, Cerrous Sulphate, Hexagonal, Orthorhombic and anhydrous phase

## INTRODUCTION

Cerrous sulphate exists in hydrated form and has different phases, due to this it is an interesting host to study decomposition and phase transfer. The most common hydrated form of  $Ce_2(SO_4)_3$  is  $0.8H_2O$ , which crystallizes in the orthorhombic phase [1]. The uncommon phases are  $0.9H_2O$ ,  $0.5H_2O$  etc., and can be synthesized by varying synthesis conditions [1-2]. The stoichiometric cerium compounds have attracted attention for the several good properties they possess. Cerium phosphate has shown to possess high temperature phase stability, high melting point, low thermal conductivity, optical fluorescence and catalytic properties [3].  $Ce^{3+}$  to  $Tb^{3+}$  energy transfer process in several hosts have extensively studied [4-6]. The luminescence study of Cerrous Sulphate reveals that there is no concentration quenching and hence negligible energy transfer is observed. This may be ideally suited for the miniature laser emitting in the near infrared region. The preparation process for controlling the particle size and phases,  $Ce^{3+}$  to  $Tb^{3+}$  energy transfer and the effect of temperature on the morphology of cerrous sulphate are presented in this paper.

## EXPERIMENTAL

Cerrous sulphate was prepared using the method described in the paper [7]. 0.1 molar Cerrous sulphate was prepared

using  $CeCl_3$  solution with  $(NH_4)_2SO_4$  in stoichiometric ratio.  $CeCl_3$  was dissolved in alcohol and the alcoholic solution of  $(NH_4)_2SO_4$  was added drop wise with constant stirring. The drop rate was adjusted to 30 drops per minute. Slowly the solution became turbid indicating the formation of  $Ce_2(SO_4)_3$ . The precipitate was centrifuged then washed with absolute alcohol 5-6 times to remove residue. Washed precipitate was allowed to dry under heating lamp for several hours. The dried powder is  $Ce_2(SO_4)_3$ . This powder was heated at various temperatures for further investigation. This sample is labeled as  $S_2$ .  $Ce_2(SO_4)_3$  was also prepared by fast precipitation method for comparison and termed as  $S_1$ .

XRD measurements were carried out on 'Philips' machine. PL spectra of various samples were studied on a Hitachi F-4000 fluorescence spectrophotometer. The slit width for recording emission and excitation spectra is 1.5mm. DTA measurements were carried out on Shimadzu Spectrophotometer UV-1700.

## RESULTS AND DISCUSSION

Fig.1 shows the PL spectra of  $S_1$  and  $S_2$ . The intense emission is observed for the sample  $S_1$  (bulk). The excitation to this band is broad and peaks at 265nm with shoulder at 295nm (fig 1(a)). Emission spectra of the sample  $S_1$  shows double humped band at 324nm and 337nm (fig 1(d)). This band could be assigned to the transition of  $^5D - ^2F_{5/2}$  to  $^5D$

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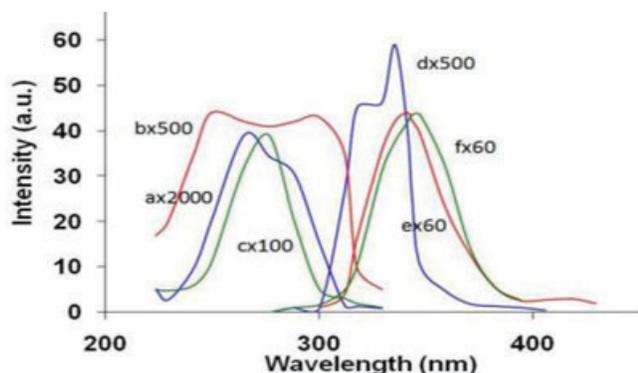
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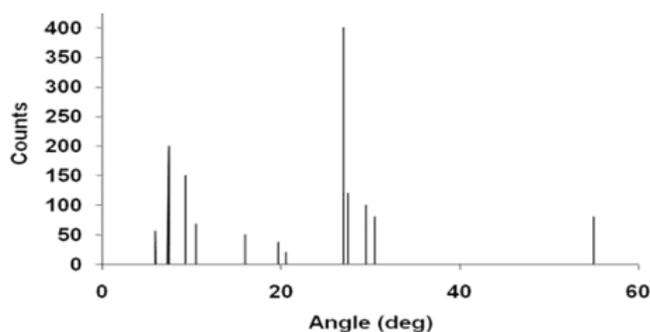
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$-^2F_{7/2}$ . However the emission of sample  $S_2$  is different than that of  $S_1$ .

The emission spectra of the sample  $S_2$  is slightly red shifted and the emission is observed at 344nm with the shoulder at 366nm (fig.1(f)) with the excitation maxima at 263nm shown in fig.1(c). It is tempting to check whether the change of spectra is due to particle size. However it is observed that the structure of  $S_1$  and  $S_2$  are different. Sample  $S_1$  belongs to the well known hydrated phase  $Ce_2(SO_4)_3 \cdot 8H_2O$  which is Orthorhombic(not shown). Majority of the peaks of sample  $S_2$  matches well with the  $Ce_2(SO_4)_3 \cdot 9H_2O$  hydrated form which crystallizes in hexagonal phase (fig. 2(JCPDF No. 18-0321)). It was observed from fig.1(e) that the sample  $S_1$  at 600° gives different emission spectra than that of  $S_1$ .



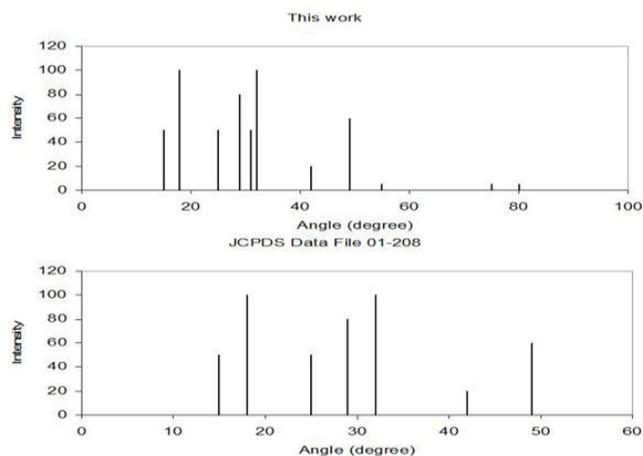
**Figure 1:** (d) emission spectra of  $S_1$  at 324nm, 337nm for the excitation 295nm shoulder at 265nm(a) , (f) the emission spectra of  $S_2$  at 344nm, shoulder at 366nm for the excitation 263nm ( c). (e) emission of  $S_1$  at 600°C is 337nm for the excitation at 263nm.



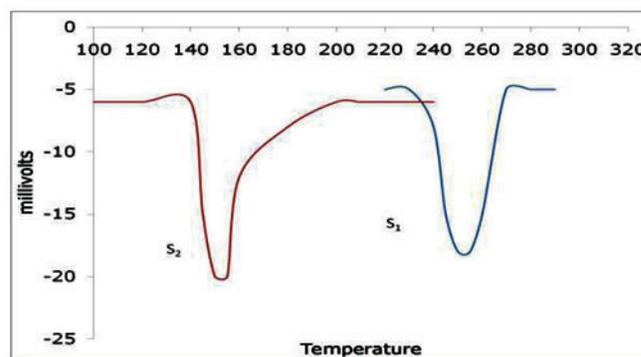
**Figure 2:** X.R.D. of cerrous sulphate crystallizes in  $Ce_2(SO_4)_3 \cdot 9H_2O$  hexagonal phase (JCPDF No. 18-0321).

This can be related to the anhydrous phase of  $Ce_2(SO_4)_3$  ((fig. 3 JCPDF No. 01-208))[3]. Hence the change in  $Ce^{3+}$  emission is due to change of phase. This is also observed for the other systems of cerrous sulphate [8]. To investigate further both the samples  $S_1$  and  $S_2$  were subjected to heat treatment and thermal analysis. The D.T.A. curve of sample  $S_1$  shows that at 220°C the sudden decrease in weight is observed up to 260°C. In this temperature range a large endotherm peak is observed indicating a phase change in the sample. For  $S_2$

the exotherm peak is observed at 60°C up to 140°C. For  $S_2$  the loss of weight also observed in this vicinity as shown in figure 4. Such phase change is reported for  $CaSO_4 \cdot Ce$  [9]. The variation of PL spectra with the temperatures for both  $S_1$  and  $S_2$  are described in the table-1. PL spectra of sample  $S_1$  heated at various temperatures shows a broad emission peak around 337nm with a shoulder at 324nm at 100°C. The excitation is also broad in the range of 260-300nm. The PL spectra of the sample  $S_1$  heated at 200 °C shows a single peak around 337nm with drastic reduction in intensity of 324nm peak. This indicates the substantial loss of water molecules [3]. The drastic change is observed in the emission spectra of the sample heated at 250°C. The emission is blue shifted and observed at 317nm. The intensity of emission is almost half of the sample heated at 100°C. At 600 °C the intensity of the emission recovers and is nearly equal to the unheated sample (fig. 1(e)). PL spectra of sample  $S_2$  shows that the emission shifted to 337nm from 344nm at 100°C. The intensity of emission reduces to almost half to that of unheated sample  $S_2$  (fig.(1f)). The spectra show the double humped nature with peak appearing at 337nm and 324nm.



**Figure 3:** X.R.D. of cerrous sulphate crystallizes in anhydrous orthorhombic phase (JCPDF No. 01-208).



**Figure 4:** DTA curve of sample  $S_1$  and  $S_2$ .



Figure 5: S.E.M. of  $S_2$



Figure 6: S.E.M. of  $S_2$  at.

Similar results are observed for the samples heated at 150°C and 200°C except that the shoulder gets more pronounced with temperature. The sample heated at 250°C shows a shift in emission similar to sample  $S_1$  at 317nm. But the intensity of emission is significantly reduced as compared to sample  $S_1$ . Sample  $S_2$  heated at 600°C doesn't show any emission. This can be explained on the basis of the difference in the particle size which shows recovery of emission when heated at 600°C for  $S_1$ . The particle size of  $S_2$  is small (<5micron), DTA curve shows that the particles are less stable. On heating they quickly react with oxygen and therefore the exotherm peak appears at a lower temperature. When  $S_2$  is heated at 600°C it reacts with oxygen more vigorously and gets converted into the form in which the valency of Ce is 4+. Such conversion is due to Auger loss, well explained by Blasse for  $CeF_3$  compound [10]. S.E.M. micrograph of sample  $S_2$  shows that the particles are well separated and have uniform spherical porous morphology as shown in Fig.5. However, the morphology changes when heated at 250°C. It shows hexagonal rod-like morphology with the aspect ratio of 5 as shown in Fig.6. The S.E.M. photographs also confirm the less stability of  $S_2$  particles.

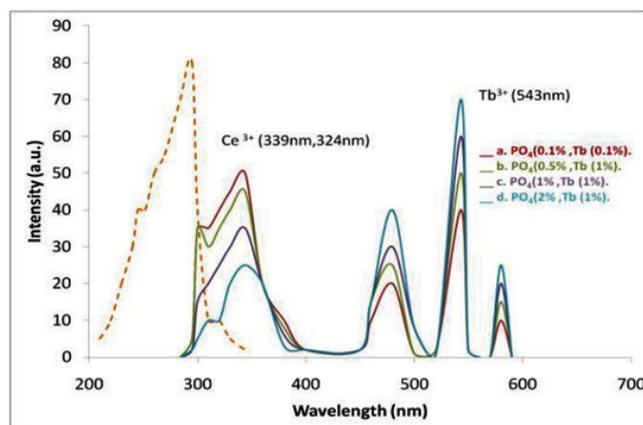


Figure 7: (a,b,c,d) are the emission spectra of  $Ce_{2(1-x)}Tb_x(SO_4)_3:PO_4$

For Ce to Tb energy transfer process the cerrous sulphate system has been prepared in sample  $S_1$  and  $S_2$ . The emission spectra of  $S_1$  is 324nm and 337nm with half intensity points at 312nm and 353nm and for the sample  $S_2$  the emission spectra is at 344nm with the shoulder at 366nm with the half intensity points at 320nm and 373nm overlap well with the excitation lines of  $Tb^{3+}$  present in between 300nm to 400nm. Hence it was expected that the energy transfer would be observed when the cerrous sulphate doped with terbium. However, no efficient energy transfer is observed in either case. When both  $S_1$  and  $S_2$  are doped with terbium as well as 0.1% of  $PO_4$  then there is a significant improvement in terbium emission. For  $Ce_2(SO_4)_3:Tb(1%):PO_4(2%)$  in  $S_2$  shows the incorporation of  $Tb^{3+}$  ions in the cerium lattice. The excitation of terbium is exactly the same as the emission of cerium. The  $Ce^{3+}$  emission is significantly quenched whereas terbium emission improves significantly. The ratio between  $Ce^{3+}$  to  $Tb^{3+}$  emission is 0.5 as described in figure 7.

Table:-1 Effect of temperature on PL spectra of

Cerrous Sulphate				
Sample	Temp (°C)	Phase	Emission (nm)	Excitation (nm)
$S_1$	unheated		324, 337	265-295
$S_1$	100	0.8H <sub>2</sub> O Orthorhombic	337	260-300
			shoulder	
			324	
$S_1$	150		337 shoulder 324	
$S_1$	200		337	
$S_1$	250		317	
$S_1$	600	anhydrous	324, 337	
		orthorhombic		
$S_2$	unheated	0.9H <sub>2</sub> O	344,366	263
$S_2$	100	Hexagonal	337	

S <sub>2</sub>	200	0.8H <sub>2</sub> O	337nm and 324nm
		Orthorhombic	
S <sub>2</sub>	250		317
S <sub>2</sub>	600	Ce <sup>4+</sup>	No emission

### CONCLUSION

Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> can be synthesized in various phases by controlling the concentration of precursor and precipitation rate. The change in PL spectra are observed in hexagonal, orthorhombic and anhydrous phase of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The emission intensity also gets recover in case of bulk sample at 600°C. While for hexagonal phase sample it converted to Ce<sup>4+</sup>. Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.9H<sub>2</sub>O particles possess uniform spherical morphology and changes to hexagonal rod shape when heated at 250°C. No Ce<sup>3+</sup> to Tb<sup>3+</sup> energy transfer is observed in pure Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> but the doping of PO<sub>4</sub> enhances the process and intense luminescence of terbium is observed. This opens up the possibility of developing cerrous sulphate as green phosphor.

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