

# Energy transfer and thermal studies of Pr<sup>3+</sup> doped cerium oxalate crystals

R PRAGASH, GIJO JOSE, N V UNNIKRISHNAN and C SUDARSANAKUMAR\*

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, India

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**Abstract.** Energy transfer process at room temperature for cerium (sensitizer) oxalate single crystals doped with different concentrations (10, 13, 15, 17 and 20%) of praseodymium ions (activator) grown by hydro silica gel method has been evaluated. The analysis of energy level diagrams of cerium and praseodymium ions indicates that the energy gap between the sensitizer and the activator ions varies in a small range suggesting a possible energy transfer from the Ce<sup>3+</sup> to Pr<sup>3+</sup>. The emission and absorption spectra of these crystals were recorded. The overlapping of the absorption spectra of Pr<sup>3+</sup> and emission spectra of Ce<sup>3+</sup> at wavelengths 484 and 478 nm, respectively, strongly supports the possible energy transfer process in this system. From the absorption spectra, oscillator strength, electric dipole moment, branching ratio and Judd–Ofelt parameters of this system were evaluated by least square programming. The quantum efficiency, energy transfer probabilities and thermal properties have been studied.

**Keywords.** Optical materials; crystal growth; optical spectroscopy; thermal analysis.

## 1. Introduction

High quality, defect free crystals doped with trivalent lanthanides always attract attention of researchers because of their smart optical and spectroscopic properties. The 4f<sup>n</sup> energy level configuration of these dopant materials have been studied extensively (Dieke 1968; Weber 1973; Lee *et al* 1984). Among the different lanthanides, cerium always plays a vital role as best host as well as dopant due to its 4f<sup>1</sup> configuration. Studies on the spectroscopic properties of Ce<sup>3+</sup> and Pr<sup>3+</sup> ions in various phosphors, crystals, and glasses (Loh 1967; Quimby *et al* 1998; Ajithkumar and Unnikrishnan 2000; Cheng *et al* 2001) reveal that the energy gap between these two ions are very small to transfer energy from Ce<sup>3+</sup> to Pr<sup>3+</sup> ions. Energy transfer (ET) studies of systems in which different divalent and trivalent ions codoped with Ce<sup>3+</sup> ions where Ce<sup>3+</sup> ions in the 4f<sup>1</sup> configuration have large oscillator strengths and hence show efficient luminescence owing to the 4f–5d transitions (Cross White and Moos 1968). Mixed rare earth oxalate crystals were grown and reported by many authors (Cyriac Joseph *et al* 1997; Raju *et al* 1998; John and Ittyachen 2001) but energy transfer studies of rare earth oxalate crystals are scanty. In this report we use Pr<sup>3+</sup> ions doped cerium oxalate [Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O] crystals for energy transfer and thermal studies. The energy transfer process depends on the

overlapping of the emission and the absorption spectra of the donor and the acceptor ions, respectively. It depends also the relative orientation of the interacting dipoles and the donor and acceptor distance. Another important phenomenon related with the energy transfer process is the sensitized luminescence in solids. This phenomenon is potentially of great importance in increasing the laser efficiency of a material. It is possible to reduce the threshold energy of oscillation in laser materials. Hence this phenomenon has a significant application in the research and development of new laser materials. The analysis of optical absorption spectra of the dopant Pr<sup>3+</sup>, using Judd–Ofelt (J–O) (Judd 1962 and Ofelt 1962) theory of crystal field induced electric dipole transitions yields some valuable spectroscopic parameters such as radiative lifetime, radiative transfer probabilities, branching ratios and optical quantum efficiencies. The Ce–O bond formations were confirmed by recording the FTIR spectra of the samples. Pr<sup>3+</sup> ions doped cerium oxalate crystals were subjected to thermal analysis to find out the number of water molecules present. Analyses of TGA/DTA spectra show that there were 8 water molecules in this system.

## 2. Experimental

Cerium oxalate crystals doped with a wide range of impurity (Pr<sup>3+</sup>) concentrations were grown in hydro silica gel prepared from sodium metasilicate (SMS). Cerium nitrate, praseodymium nitrate, oxalic acid and nitric acid

\*Author for correspondence (csudarsan1@sify.com)

all AR grade samples with 99.99% purity were used for the sample preparation.

The SMS solution of density  $1.04 \text{ g/cm}^3$  was mixed with 1 M oxalic acid to obtain a mixed solution of pH 6. This solution was transferred to a test tube of dimension 2.5 cm in diameter and 20 cm in length to fill half of its volume and then kept undisturbed for 24 h for proper gellation. A mix of 0.25 M cerium nitrate solution and 0.25 M praseodymium nitrate solution along with equal volume of concentrated nitric acid was transferred carefully and gently through the wall of the test tube on to the set gel column and closed tightly with a cork. The test tube with hydro silica gel along with the top solution was kept undisturbed for nucleation process and then again for 20 days for proper crystal growth. This procedure was followed for different volume composition of the top solution. The volume of the cerium nitrate solution was kept constant and that of praseodymium nitrate solution was varied to 10, 13, 15, 17 and 20% of the total volume of the top solution. Well-grown crystals after 21 days were taken out carefully from the gel column and thoroughly washed with distilled water.

The emission spectra of the above samples were recorded in a Shimadzu Spectrofluorophotometer (RFPC 5301) and absorption spectra recorded in a Shimadzu Spectrophotometer (UV 2400 PC). By using KBr pellet method the FTIR spectra for cerium oxalate crystals with 20%  $\text{Pr}^{3+}$  concentration, pure cerium oxalate and pure praseodymium oxalate crystals were recorded on a Shimadzu IR-84000 spectrometer. All measurements were done at room temperature. Thermal analyses of the sample were done using TGA (Mettler TA 3000 system) and DTA techniques.

### 3. Results and discussion

#### 3.1 EDAX studies

The EDAX patterns of 20% Pr doped cerium oxalate crystal is shown in figure 1. The two prominent peaks at 4.839 and 5.372 KeV correspond to  $L_a$  and  $L_b$  energies of cerium and the peaks at 5.033 and 5.502 KeV correspond to  $L_a$  and  $L_b$  energies of praseodymium. The EDAX data gives the atomic weight percentage of Ce ( $L_a$  and  $L_b$ ) and Pr ( $L_a$  and  $L_b$ ) for 20% Pr doped cerium oxalate crystal.

#### 3.2 Absorption spectra

The absorption spectra of the  $\text{Pr}^{3+}$  doped cerium oxalate crystals are shown in figure 2a. It shows that the intensities of absorption peaks of the samples increase up to 17% of  $\text{Pr}^{3+}$  ions concentration and then starts to decrease at 20 % due to the concentration quenching.

As shown in figure 2 the prominent peaks at 254 nm obtained for all samples are due to the presence of

oxalate group. The absorption spectrum of cerium oxalate alone consists of a peak at 254 nm and a shoulder at 294 nm; the later is due to the absorption transition from  $4f-5d$  of  $\text{Ce}^{3+}$  ions. The ground state of  $\text{Ce}^{3+}$  is a doublet  $^2F_{5/2}$  and  $^2F_{7/2}$  separated by  $2000 \text{ cm}^{-1}$  and the excited state is most probably  $^2D_{3/2}$  and  $^2D_{5/2}$ . Energy transfer from  $\text{Ce}^{3+}$  to  $\text{Pr}^{3+}$  takes place efficiently for the 294 nm-excitation wavelength. The absorption spectra show that  $\text{Pr}^{3+}$  has no appreciable absorption around 294 nm indicating that energy transfer is nonradiative. The absorption peaks at 445, 470, 484 and 591 nm are due to the transitions from  $^3H_4$  to  $^3P_2$ ,  $^3P_1$ ,  $^3P_0$  and  $^1D_2$ , respectively (Alexander A Kaminski 1989). Intensity of absorbance is different for different energy transitions. For 470, 484 and 591 nm the intensities increase with concentration of  $\text{Pr}^{3+}$  and starts to decrease at 20%. Contrary to this at 445 nm the peak intensity for 15% is greater than that of 17% as shown in figure 2b. The magnified peak at 591 nm (figure 2c) indicates that the peak intensities of 10% and 13% are considerably differentiated when compared with other three peaks corresponding to 445, 470 and 484 nm.

Spectroscopic parameters such as radiative lifetime, radiative transfer probabilities and branching ratios were calculated using J-O theory. Experimental ( $F_{\text{exp}}$ ) and calculated ( $F_{\text{cal}}$ ) oscillator strengths of various absorption transitions are well agreed except for  $^3H_4 \rightarrow ^1D_2$  transition (table 1). Oscillator strength for  $^3H_4 \rightarrow ^3P_2$  transition has larger value compared with other transitions. A least squares fitting of measured line strength ( $S_m$ ) to calculated line strength ( $S_{\text{cal}}$ ) provide the three J-O parameters for the praseodymium ions in cerium oxalate crystals. Table 2 gives the calculated J-O parameters for the five concentrations of the dopant material. Analysis of these J-O parameters reveals that  $\Omega_2$  has much higher values than the other two parameters ( $\Omega_4$  and  $\Omega_6$ ). The Q factor values vary in tune with the variation of the emis-

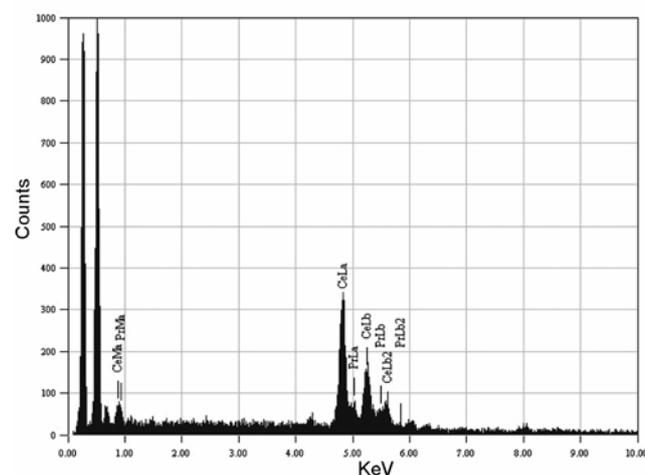
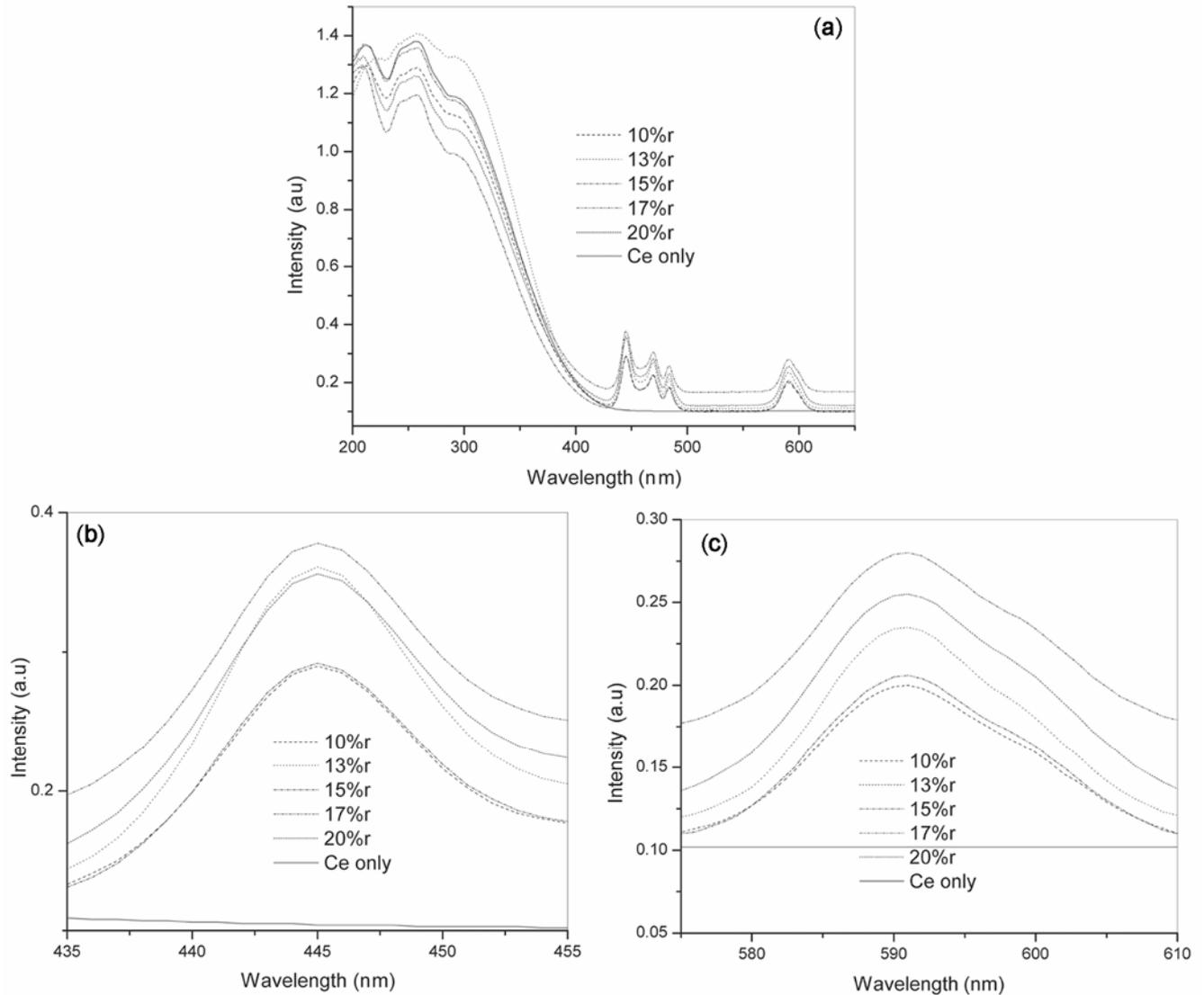


Figure 1. EDAX spectra.



**Figure 2.** (a) Absorption spectra of Pr<sup>3+</sup> doped cerium oxalate crystals, (b) magnified peak at 445 nm of figure 2a and (c) magnified peak at 591 nm of figure 2a.

**Table 1.** Experimental and calculated oscillator strength of various absorption transitions.

Energy level	10%		13%		15%		17%		20%	
	$F_{\text{exp}} \times 10^{-5}$	$F_{\text{cal}}$								
<sup>3</sup> P <sub>2</sub>	0.515	0.514	0.581	0.579	0.776	0.774	0.681	0.679	0.501	0.499
<sup>3</sup> P <sub>1</sub>	0.112	0.133	0.261	0.203	0.347	0.264	0.164	0.169	0.268	0.237
<sup>3</sup> P <sub>0</sub>	0.139	0.121	0.134	0.185	0.167	0.239	0.160	0.154	0.189	0.216
<sup>1</sup> D <sub>2</sub>	0.579	0.193	0.741	0.246	0.848	0.282	0.572	0.190	0.937	0.312

**Table 2.** Calculated J–O parameters for the five concentrations of the dopant material.

J–O parameters	10%	13%	15%	17%	20%
$\Omega_2 \times 10^{-20} \text{ cm}^2$	68.9762	99.7054	91.7673	59.9401	12.6901
$\Omega_4 \times 10^{-20} \text{ cm}^2$	0.2586	0.5139	0.3958	0.3313	0.4632
$\Omega_6 \times 10^{-20} \text{ cm}^2$	1.1296	1.6673	1.2456	1.4950	1.0418
Q factor	0.2289	0.3082	0.3178	0.2216	0.4446

**Table 3.** Theoretically computed radiative transition parameters.

Transition from $^1D_2$	$\text{cm}^2$			$\text{cm}^2$			$\text{cm}^2$			$\text{cm}^2$		
	$S_{\text{ed}} \times 10^{-20}$	$A(s-1)$	$\tau(\mu\text{s})$	$\beta(\%)$	$S_{\text{ed}} \times 10^{-20}$	$A(s-1)$	$\tau(\mu\text{s})$	$\beta(\%)$	$S_{\text{ed}} \times 10^{-20}$	$A(s-1)$	$\tau(\mu\text{s})$	$\beta(\%)$
$^1G_4$	26.767	1993	2883	18	35.593	2651	63	18	32.293	1734	104	18
$^3F_4$	35.491	7571	1095	68	47.214	1007	68	68	30.849	6581	68	68
$^3F_3$	2.074	646	935	5.8	2.759	860	68	5.8	1.837	562	104	5.8
$^3F_2$	0.925	589	860	5.3	1.234	707	68	5.3	8.121	518	50	5.3
$^3H_6$	0.023	6.73	12.4	0.06	0.033	9.49	0.06	0.06	0.030	8.71	10.4	0.06
$^3H_5$	0.001	0.46	0.82	0.01	0.001	0.62	0.01	0.01	0.011	0.599	0.01	0.01
$^3H_4$	0.198	209	307	1.8	0.251	266	1.8	1.8	0.199	210	331	1.6

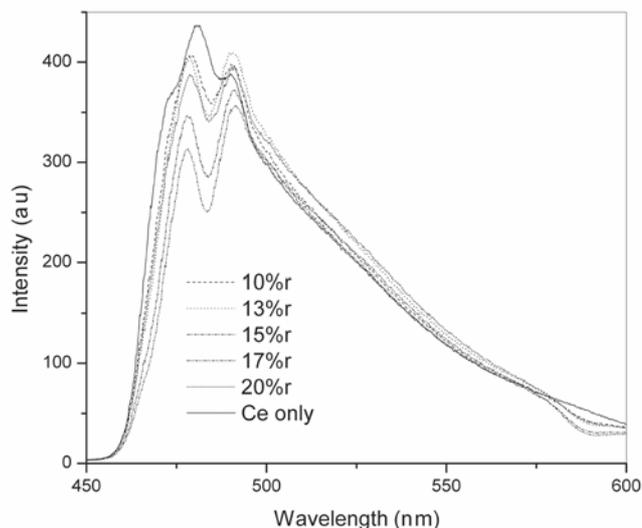
sion peak intensities. The theoretically computed radiative transition parameters are given in table 3. The radiative lifetime for an excited state (J) was calculated by

$$\tau(r) = \frac{1}{\sum A(J \rightarrow J')}, \tag{1}$$

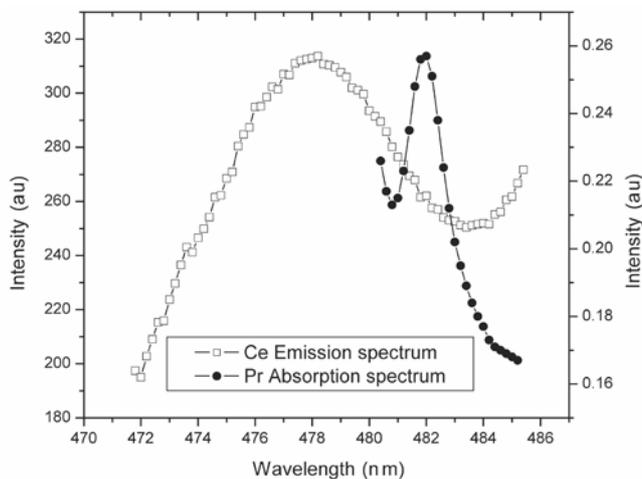
where the sum runs over all final lower lying states  $J'$ . The fluorescence branching ratios,  $\beta(J \rightarrow J')$  can be determined from the following equation

$$\beta(J \rightarrow J') = \frac{A(J \rightarrow J')}{\sum A(J \rightarrow J')} = A(J \rightarrow J')\tau(r). \tag{2}$$

Calculations show that the branching ratio for the transition  $^1D_2 \rightarrow ^3F_4$  has the highest value of 68.6 which strongly predicts a prominent  $\text{Pr}^{3+}$  emission peak at 1032 nm in the IR region (Blasse and Brill 1967).



**Figure 3.** Emission spectra of cerium ions at 478 nm.



**Figure 4.** Overlapping spectra.

### 3.3 Emission spectra

The emission spectra of pure and Pr<sup>3+</sup> doped cerium oxalate crystals are shown in figure 3. The samples were excited with 294 nm excitation wavelength to obtain these emission spectra, which correspond to transitions from the 5d states of Ce<sup>3+</sup> and terminate on the 4f states. The Ce<sup>3+</sup> emission intensities decrease with Pr<sup>3+</sup> concentration, reaching a minimum after which it starts to increase. The linear variation of the transfer probabilities corresponding to the variation of concentration of dopant ions reveals the electric dipole-dipole interactions between donor and acceptor ions of this system. The overall decrease in the intensities of Ce<sup>3+</sup> peaks implies that the energy transfer has been occurring from the Ce<sup>3+</sup> to the Pr<sup>3+</sup> ions and the overlapping of the absorption and emission spectra at wavelengths 484 nm and 478 nm, respectively, of Pr<sup>3+</sup> and Ce<sup>3+</sup> strongly support the possible energy transfer process (figure 4). The broad peak at 478 nm is due to the crystal field splitting of 5d

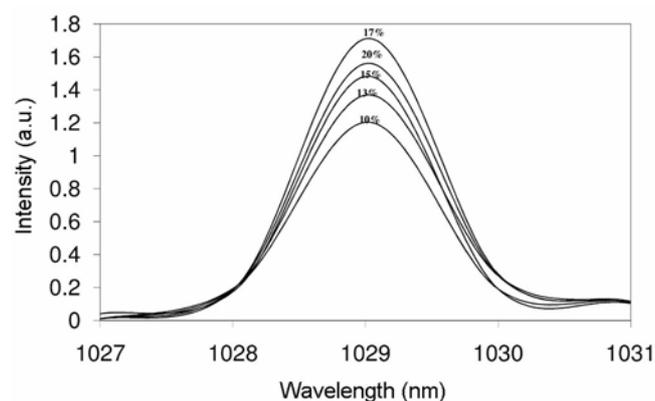


Figure 5. Emission spectra of praseodymium ions at 1029 nm.

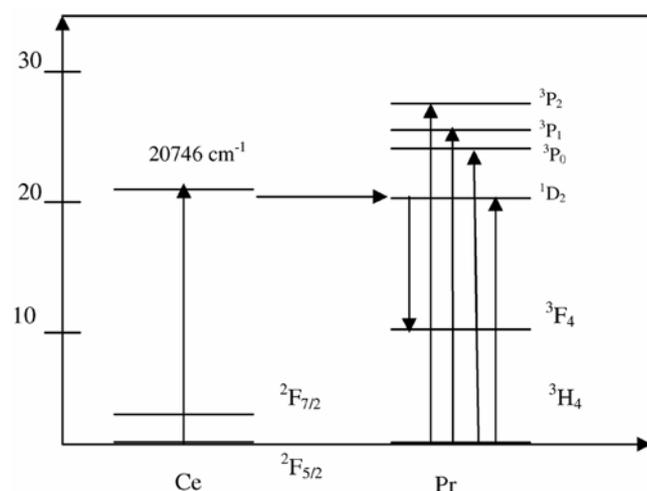


Figure 6. Simplified energy level diagram.

(<sup>2</sup>D) state of Ce<sup>3+</sup> (McKeever *et al* 1986). The emission spectra for the five concentrations of the praseodymium corresponding to the transition <sup>1</sup>D<sub>2</sub> → <sup>3</sup>F<sub>4</sub> are shown in figure 5.

A simplified energy level diagram of this system is shown in figure 6. This diagram was constructed from the absorption and emission spectra of the sample to label the different transitions involved.

Forster (1948) worked out a direct energy-transfer theory for singlet-singlet (allowed transition (dipole-dipole)) transfer and Dexter (1953) developed the triplet-triplet (forbidden transitions (dipole-quadrupole)) resonance transfer theory which were later extended by Inokutty and Hirayama (1965). The transfer probability for a dipole-dipole energy transfer process is given by

$$P_{AS} = 1/\tau_s (I_{so}/I_s - 1), \quad (3)$$

where  $I_{so}$  is the intensity of the sensitizer in the absence of the activator and  $I_s$  the intensity of the sensitizer in the presence of the activator.

The energy transfer efficiency from the fluorescence yield can be calculated from the expression

$$\eta_T = 1 - I_s/I_{so} \quad (4)$$

and in terms of life times this can be written as

$$\eta_T = 1 - \tau_s/\tau_{so} \quad (5)$$

where  $\tau_s$  and  $\tau_{so}$  are the decay times of donor in the presence and absence of the acceptor. Donor decay time in the absence of acceptor ions was observed as 30 ns. The value of  $\tau_s$  can be calculated by knowing the values of  $I_s$ ,  $I_{so}$  and  $\tau_{so}$  as

$$\tau_s = \tau_{so} (I_s/I_{so}). \quad (6)$$

The energy transfer efficiency or quantum efficiency of energy transfer can be calculated using

$$\eta_T = P_{SA} \tau_s / (1 + P_{SA} \tau_s). \quad (7)$$

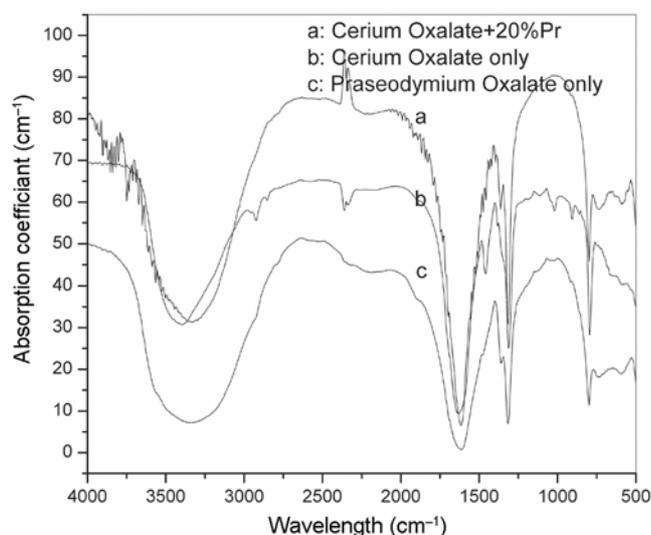
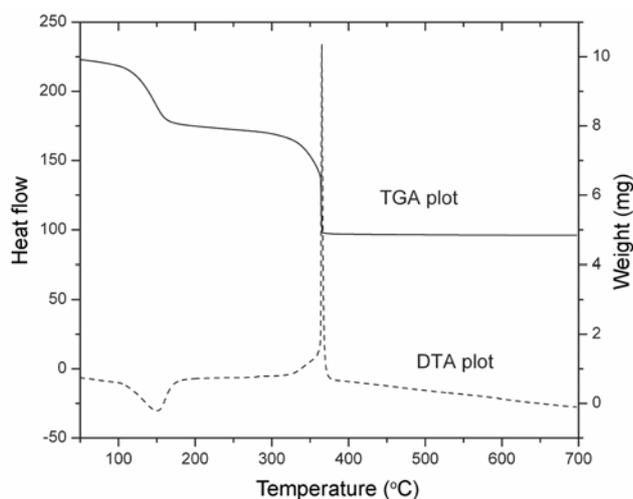
The energy transfer efficiency shows a steady increase with Pr<sup>3+</sup> ions concentration from 10–17% and then decreases at 20%. The calculated values of quantum efficiencies and transfer probabilities are given in table 4.

### 3.4 FTIR spectra

By using KBr pellet method the FTIR spectra for cerium oxalate, praseodymium oxalate and cerium oxalate doped with 20% of Pr<sup>3+</sup> ions concentration were recorded in a Shimadzu IR-480 spectrometer (figure 7). Many studies on metallic oxalates (Fujitha *et al* 1962; Gibson and Stump 1993) propose metal-oxygen bonds around 800 cm<sup>-1</sup> and 500 cm<sup>-1</sup>. All the three spectra show common features of A-O (A = Ce, Pr) bond formation. The intense broad band around 3174–3514 cm<sup>-1</sup> evidence the presence of water of crystallization. The sharp band

**Table 4.** Experimentally calculated values of quantum efficiencies and transfer probabilities.

Concentration of Pr <sup>3+</sup>	Donor fluorescence in the absence of acceptor $I_{s0}$	Donor fluorescence in the presence of acceptor $I_s$	Donor life time $\tau_s$ (ns)	Quantum efficiency $\eta_T$	Transfer probability $P_{SA} \times 10^6/s$
10	405	27.12	0.096	3.92	
13	380	25.45	0.152	7.03	
15	448	305	20.42	0.319	23.11
17	302	20.22	0.326	23.91	
20	380	25.45	0.152	7.03	

**Figure 7.** FTIR spectra.**Figure 8.** TGA/DTA plot.

observed at  $1623\text{ cm}^{-1}$  could be assigned to C = O stretch and the band at  $798\text{ cm}^{-1}$  corresponds to A–O (A = Ce, Pr) bond. The absorption coefficient for 20% Pr<sup>3+</sup> doped

cerium oxalate crystal is greater than that for pure cerium and praseodymium oxalate crystals.

### 3.5 Thermal analysis

Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) curves were recorded simultaneously on a thermal analyser over the temperature range 50–700°C. A sample of 9.988 g was used and the recordings were carried out in an oxygen atmosphere at a heating rate of 10°C/min. The TGA curve is shown in figure 8. It was observed that the onset of decomposition begins slightly at 104.41°C and continues up to 110°C, resulting in a weight loss of 20% of the total weight of the sample. In this stage all the 8 water molecules were eliminated and the sample reduced to anhydrous Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>. After this stage of decomposition of the sample remains stable for a temperature range of 110°C to 330°C. The second stage of decomposition starts at 335°C and continues up to 370°C. During this temperature range a total weight loss of 25% was observed. The DTA curve shows (figure 8) an endothermic peak at 133.87°C corresponding to the elimination of the eight water molecules. The exothermic peak at 387.03°C is due to the oxidation reaction taking place along with decomposition.

## 4. Conclusions

Spectroscopic analyses using the optical absorption and emission spectra of Pr<sup>3+</sup> ions in crystals sensitized with Ce<sup>3+</sup> ions yielded some of the important parameters of radiative and nonradiative processes. ET is mainly due to dipole–dipole interaction. The doping of Pr<sup>3+</sup> considerably influences the spectroscopic properties of the cerium oxalate single crystals. Fluorescence quenching was observed at 20% Pr<sup>3+</sup> concentration and it was confirmed by spectroscopic analysis. The emission intensity of Ce<sup>3+</sup> around 478 nm decreased considerably due to the presence of Pr<sup>3+</sup> strongly supporting the possible energy transfer from Ce<sup>3+</sup> to Pr<sup>3+</sup>. The emission spectrum is analysed in detail and it was seen that most of the efficient transitions are from the <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> manifolds. Fluorescence branching ratio and optical gain values are maximum for the

<sup>1</sup>D<sub>2</sub> → <sup>3</sup>F<sub>4</sub> transition. Different spectroscopic parameters such as spontaneous emission probabilities, branching ratio and radiative lifetime were calculated using J–O theory. The spectroscopic quality factor values for the five concentrations 10, 13, 15, 17 and 20% are 0.2289, 0.3082, 0.3178, 0.2216 and 0.4446, respectively. The minimum Q factor value among these five is for 17% and for that concentration the quantum yield is maximum and the calculated quantum yield of energy transfer is 32.6%. Analysis of TGA/DTA spectra shows that the material is thermally unstable.

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