

## Spectroscopic properties of Pr<sup>3+</sup>-doped erbium oxalate crystals

R PRAGASH\*, N V UNNIKRISHNAN and C SUDARSANAKUMAR

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, 686 560, India

\*Corresponding author. E-mail: pragashramnivas@yahoo.co.in

MS received 6 September 2010; revised 22 February 2011; accepted 19 May 2011

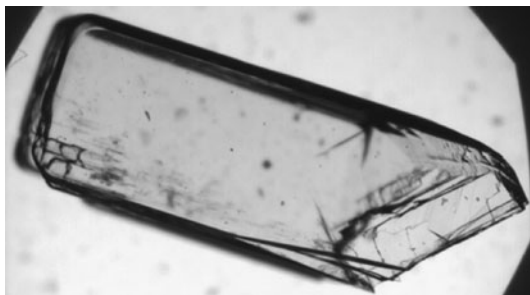
**Abstract.** Spectroscopic properties of praseodymium ions-doped erbium oxalate ( $\text{Er}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ ) crystals have been investigated. The crystals were grown by hydro silica gel method under suitable pH conditions and by single diffusion method. The well-grown crystals are bright and transparent. The dark green colour of these crystals changes with the variation of the concentrations of the dopant ions. The absorption spectra have been measured in the region 200–800 nm at room temperature. Judd–Ofelt intensity parameters for f–f transitions of the Pr<sup>3+</sup> ions have been determined as  $\Omega_2 = 166.7$ ,  $\Omega_4 = 1.103$  and  $\Omega_6 = 2.898$ . Analyses of the absorption spectra also show a possible energy transfer from the host material to the dopant.

**Keywords.** Crystal growth; gel method; erbium oxalate; absorption spectra.

**PACS Nos** 33.15.Hp; 32.30.–r; 42.70

### 1. Introduction

Spectroscopic properties of rare earth (RE) ions-doped phosphate, silicate and borate glasses and crystals were studied extensively [1–5]. Besides optical and spectroscopic property studies, the energy transfer (ET) mechanism provides strong evidence for the lasing action of these materials. Mixed rare earth oxalate crystals were grown and reported by many authors [6,7] but energy transfer studies of doped rare earth oxalate crystals are rare in literature. In this paper we report the analysis of optical properties and ET mechanism of praseodymium-doped erbium oxalate single crystals. The erbium oxalate crystals doped with a wide range of concentrations of praseodymium (9%, 12%, 15%, 18% and 21%) were grown by hydro silica gel method [8]. The absorption spectra of these samples show that the intensities of the characteristic peaks of praseodymium steadily increase upto 15% and then start to decrease at 18% of Pr<sup>3+</sup> while that of erbium ions decrease upto 15% and then starts to increase at 18%. This is due to the ET mechanism of this system. By analysing the optical absorption spectra of the dopant Pr<sup>3+</sup> for all the five concentrations



**Figure 1.** Micrograph of the sample.

using Judd–Ofelt (J–O) [9,10] theory we calculated the radiative lifetime, radiative transfer probabilities, branching ratios and the J–O intensity parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ .

## 2. Experimental procedure

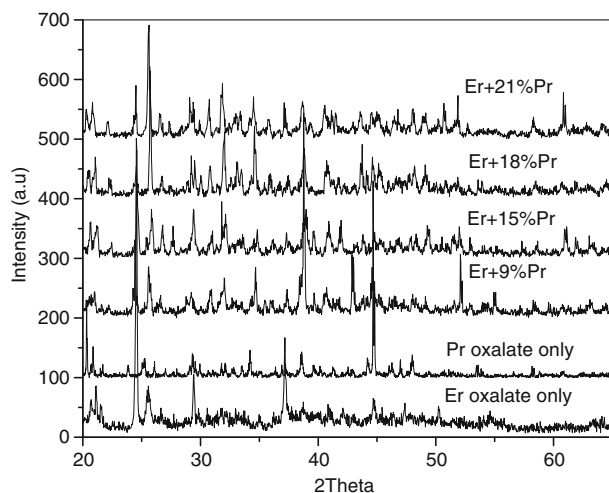
The test tube diffusion method was employed for the growth of erbium oxalate crystals doped with a wide range of impurity ( $\text{Pr}^{3+}$ ) concentrations. Sodium metasilicate (SMS) solution with specific gravity  $1.04 \text{ g/cm}^3$  was mixed homogeneously with 0.5 M oxalic acid to get a solution of pH 6. The prepared solution was transferred carefully to a crystallizer having 1.5 cm diameter and 20 cm length to fill half of its volume. A homogeneous mixture of 0.5 M erbium nitrate and 0.5 M praseodymium nitrate solutions along with 2% of concentrated nitric acid were transferred carefully and gently through the wall of the test tube on to the set gel column and closed tightly with cork. The test tube with hydro silica gel along with the top solution was kept undisturbed for nucleation process for 25 days for proper crystal growth. This procedure was followed for different volume compositions of the top solution. The volume of the erbium nitrate solution was kept constant and that of praseodymium nitrate solution was varied as 9%, 12%, 15%, 18% and 21% of the total volume of the top solution. The growth conditions were kept constant except the composition of the mixed solution. Defect-free crystals were observed to grow inside the gel column. After 26 days, well-grown crystals were taken out carefully from the gel column. The obtained crystals show high optical quality and 3 mm size. The micrograph of the sample is shown in figure 1.

## 3. Results and discussion

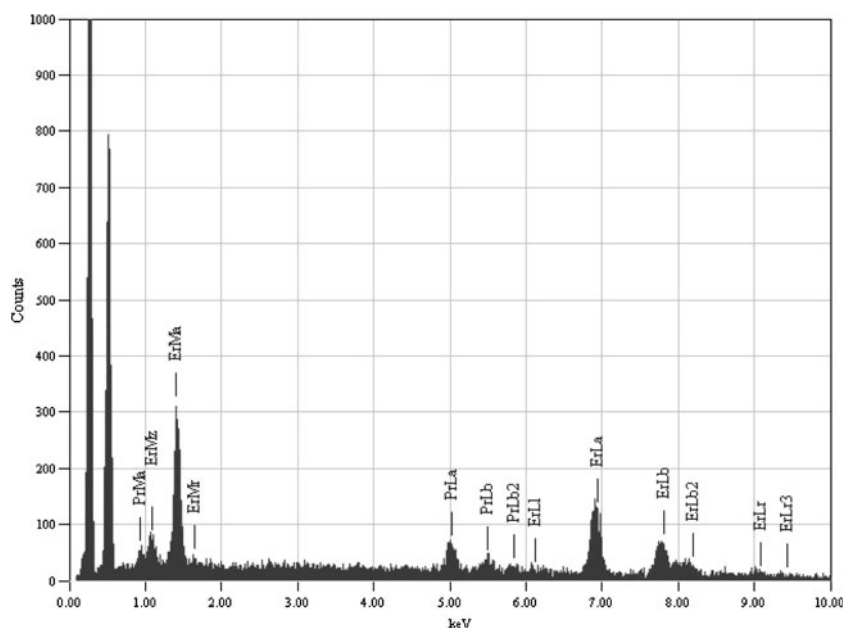
### 3.1 X-ray powder diffraction

Figure 2 shows the X-ray patterns of  $\text{Pr}^{3+}$ -doped erbium oxalate crystals for different concentrations. Well-defined Bragg peaks at specific  $2\theta$  angles in the powder diffraction pattern suggest that the samples are crystalline in nature. The intensity of peaks appearing at diffraction angle  $2\theta = 26^\circ$  and  $33^\circ$  increases with the dopant concentration.

*Spectroscopic properties of Pr<sup>3+</sup>-doped erbium oxalate crystals*



**Figure 2.** XRD curve of Pr<sup>3+</sup>-doped erbium oxalate crystals for different concentrations.



**Figure 3.** EDAX curve of 21% Pr<sup>3+</sup>-doped erbium oxalate crystals.

### 3.2 EDAX spectrum

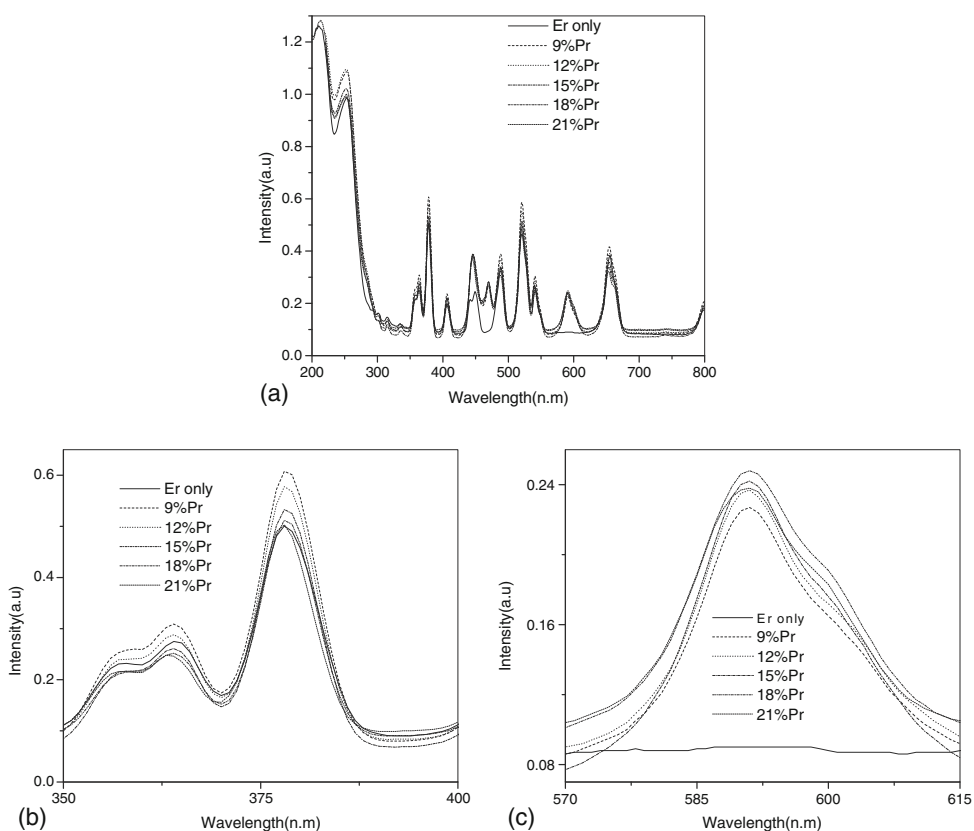
Chemical composition of the grown crystal (21% Pr<sup>3+</sup>-doped erbium oxalate crystals) was confirmed with the EDAX spectrum which is shown in figure 3. The presence of the constituent elements of the Pr<sup>3+</sup>-doped erbium oxalate crystals was confirmed by the occurrence

of their respective peaks. The stoichiometric proportions of the crystal as well as the EDAX results are in good agreement.

### 3.3 Absorption spectra

The Shimadzu Spectrophotometer (UV 2400 PC) was used to record the absorption spectra. Spectroscopic parameters can be evaluated from both absorption and emission spectra. The absorption spectra of all the five concentrations are found to be almost identical in nature except in their peak intensities. The absorption spectra of the  $\text{Pr}^{3+}$ -doped erbium oxalate crystals are shown in figure 4. The absorption spectra show four prominent peaks of  $\text{Pr}^{3+}$  at 446, 470, 488 and 591 nm due to the transitions from  $^3\text{H}_4$  to  $^3\text{P}_2$ ,  $^3\text{P}_1$ ,  $^3\text{P}_0$  and  $^1\text{D}_2$ , respectively [11]. The prominent absorption peaks of erbium oxalate crystals are 378, 406, 520, 541 and 653 nm.

Figures 4b and 4c show the magnified peaks of figure 4a corresponding to  $\text{Er}^{3+}$  and  $\text{Pr}^{3+}$  ions respectively. It shows that the absorption peak intensities of  $\text{Er}^{3+}$  ions decrease



**Figure 4.** (a) Absorption spectra of  $\text{Pr}^{3+}$ -doped erbium oxalate crystals. (b) Magnified peak at 378 nm. (c) Magnified peak at 591 nm.

*Spectroscopic properties of Pr<sup>3+</sup>-doped erbium oxalate crystals*

initially and then start to increase at 18% of Pr<sup>3+</sup> ions concentration, due to the concentration quenching, whereas peak intensities of Pr<sup>3+</sup> ions increase upto 15% and then start to decrease due to energy transfer mechanism. It can be seen that the transitions from <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub>, <sup>1</sup>D<sub>2</sub> to <sup>3</sup>H<sub>4</sub> are involved for the cross-relaxation. A prominent peak at 254 nm obtained for all the samples are due to the presence of oxalate group. The peaks of Pr<sup>3+</sup> ions show that the full-width half-maxima (FWHM) do not change with increasing concentration of Pr<sup>3+</sup> ions. This means that the dopants are distributed homogeneously and no clustering is present in the crystal.

The spectroscopic parameters such as radiative lifetime, radiative transfer probabilities and branching ratios can be calculated from the analysis of absorption spectra of praseodymium ions in Pr<sup>3+</sup>-doped erbium oxalate crystals using J–O theory. Experimental ( $F_{\text{exp}}$ ) and calculated ( $F_{\text{cal}}$ ) oscillator strengths of various absorption transitions are tabulated in table 1. Experimental and calculated values for the oscillator strength agree well for <sup>3</sup>H<sub>4</sub> to <sup>3</sup>P<sub>2</sub> transition but not for the remaining transitions. Also, in general, the oscillator strength of the <sup>3</sup>H<sub>4</sub> to <sup>3</sup>P<sub>2</sub> transition is large compared to all other transitions. This can be explained as due to the hyperfine nature of the transition. The larger difference between the calculated and observed oscillator strengths arises because of the strong 4f-5d mixing [12] which is known to bring about contribution to intensities through the odd matrix elements which are usually neglected in the J–O model.

A least squares fitting of  $S_m$  to  $S_{\text{cal}}$  provides the three J–O parameters for the praseodymium in erbium 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  $\Omega_2$  have much higher values than the other two parameters ( $\Omega_{\lambda: \lambda=4,6}$ ). The theoretically computed radiative transition parameters are tabulated in table 3. Calculations show

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

Energy levels	9%		12%		15%		18%		21%	
	$F_{\text{exp}} \times 10^{-5}$	$F_{\text{cal}} \times 10^{-5}$	$F_{\text{exp}} \times 10^{-5}$	$F_{\text{cal}} \times 10^{-5}$	$F_{\text{exp}} \times 10^{-5}$	$F_{\text{cal}} \times 10^{-5}$	$F_{\text{exp}} \times 10^{-5}$	$F_{\text{cal}} \times 10^{-5}$	$F_{\text{exp}} \times 10^{-5}$	$F_{\text{cal}} \times 10^{-5}$
<sup>3</sup> P <sub>2</sub>	1.405	1.400	1.284	1.282	1.369	1.366	1.137	1.134	1.038	1.036
<sup>3</sup> P <sub>1</sub>	0.118	0.542	0.252	0.628	0.219	0.565	0.283	0.491	0.276	0.476
<sup>3</sup> P <sub>0</sub>	0.867	0.528	0.972	0.612	0.881	0.550	0.679	0.479	0.658	0.464
<sup>1</sup> D <sub>2</sub>	1.150	0.383	1.184	0.394	1.184	0.479	1.246	0.414	1.100	0.366

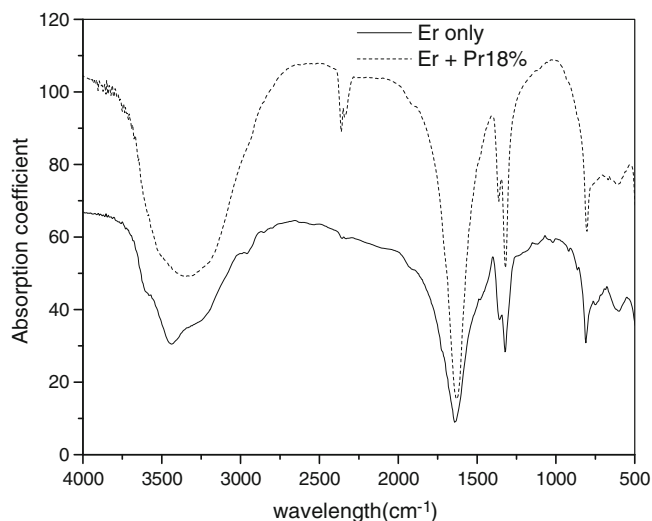
**Table 2.** Calculated J–O parameters for the five concentrations of the dopant material.

J–O parameters	10%	13%	15%	17%	20%
$\Omega_2 \times 10^{-20} \text{ cm}^2$	118.4	129.2	166.7	146.5	127.6
$\Omega_4 \times 10^{-20} \text{ cm}^2$	1.095	1.227	1.103	0.960	0.931
$\Omega_6 \times 10^{-20} \text{ cm}^2$	2.993	2.667	2.898	2.393	2.171
$Q$ factor	0.3659	0.4601	0.3806	0.4012	0.4288

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

Trans. from $^1D_2$	$S_{ed}$ $\times 10^{-20} \text{cm}^2$	$A(s-1)$	$\tau$ ( $\mu s$ )	$\beta$ (%)	$S_{ed}$ $\times 10^{-20} \text{cm}^2$	$A(s-1)$	$\tau$ ( $\mu s$ )	$\beta$ (%)	$S_{ed}$ $\times 10^{-20} \text{cm}^2$	$A(s-1)$	$\tau$ ( $\mu s$ )	$\beta$ (%)	$S_{ed}$ $\times 10^{-20} \text{cm}^2$	$A(s-1)$	$\tau$ ( $\mu s$ )	$\beta$ (%)	
$^1G_4$	46.07	3431	18	50.22	3740	18.03	64.750	4823	18.07	64.75	4823	18.07	64.75	4823	18.07	64.75	18.07
$^3F_4$	60.947	13001	68	66.48	14182	68.37	85.811	16081	68.57	85.81	18306	68.57	85.81	18306	68.57	85.81	68.6
$^3F_3$	3.57	1112	5.8	3.896	1214	5.844	5.022	1375	5.863	5.02	1565	5.863	5.02	1565	5.863	5.02	5.866
$^3F_2$	1.637	1044	5.4	1.637	1143	5.3	1.234	707	5.3	8.121	518	5.3	8.121	518	5.3	8.121	5.3
$^3H_6$	0.086	24.8	0.01	0.086	27.45	0.06	0.033	9.49	0.06	0.030	8.71	0.06	0.030	8.71	0.06	0.030	0.06
$^3H_5$	0.003	1.62	0.01	0.003	1.74	0.01	0.001	0.062	0.01	0.011	0.599	0.01	0.011	0.599	0.01	0.011	0.01
$^3H_4$	0.402	425	22	0.402	434	1.8	0.251	266	1.8	0.199	210	1.8	0.199	210	1.8	0.199	2.2

### *Spectroscopic properties of Pr<sup>3+</sup>-doped erbium oxalate crystals*



**Figure 5.** FTIR spectra for erbium oxalate and 18% Pr<sup>3+</sup>-doped erbium oxalate.

that the branching ratio for the transition  $^1D_2 \rightarrow ^3F_4$  has the highest value of 68.275 which strongly predicts a prominent Pr<sup>3+</sup> emission peak at 1029 nm in the IR region [11].

#### 3.4 FTIR spectra

By using KBr pellet method the FTIR spectra for erbium oxalate and 18% Pr<sup>3+</sup>-doped erbium oxalates were recorded in a Shimadzu IR-480 spectrometer (figure 5). Many studies on metallic oxalates [13,14] propose metal–oxygen bonds around 800 and 500 cm<sup>-1</sup>. The two spectra show the common features of A–O (A = Er, Pr) bond formation. The intense broad band around 3174–3514 cm<sup>-1</sup> indicates the presence of water of crystallization. The sharp band observed at 1623 cm<sup>-1</sup> corresponds to C=O stretch and the band at 798 cm<sup>-1</sup> corresponds to A–O (A = Er, Pr) bond. The absorption coefficient for 18% Pr<sup>3+</sup>-doped erbium oxalate crystal is greater than that of pure erbium oxalate crystals.

#### 4. Conclusions

The optical properties of praseodymium-doped erbium oxalate single crystals are presented in this report. The Pr<sup>3+</sup> doping considerably influences the spectroscopic properties of the erbium oxalate single crystals. Because of the good optical properties of these doped crystals, these crystals can be used in technologically important laser devices. The calculated optical intensity parameters are  $\Omega_2 = 146.5$ ,  $\Omega_4 = 0.96$  and  $\Omega_6 = 2.393$  for 18% concentration of Pr<sup>3+</sup> and the  $Q$ -values for the five concentrations are 0.366, 0.460, 0.381, 0.401 and 0.429.

### **Acknowledgements**

The authors acknowledge the optical characterization facilities offered by Dr Beena Mathew, SCS, Mahatma Gandhi University, Kottayam. One of the authors, R Pragash, is grateful to UGC, New Delhi, Govt. of India for providing Teacher Fellowship.

### **References**

- [1] Se Ho Park, Dong Chin Lee, Jong Heo and Dong Wood Shin, *J. Appl. Phys.* **9**, 9072 (2002)
- [2] Se Ho Park, Dong Chin Lee, Jong Heo and Hyoun Soo Kim, *J. Am. Ceram. Soc.* **83**, 1284 (2000)
- [3] S Tanabe, T Ohyagi, N Soga and T Hanada, *Phys. Rev.* **B46**, 3305 (1992)
- [4] J A Capobianco, P P Proulx, M Bettinelli and F Negrisolo, *Phys. Rev.* **B42**, 5936 (1990)
- [5] D Haranath, A F Khan and Harish Chander, *J. Phys. D: Appl. Phys.* **39**, 4956 (2006)
- [6] Cyriac Joseph, M A Ittyachen and K S Raju, *Bull. Mater. Sci.* **20**, 37 (1997)
- [7] K S Raju, M V John and M A Ittyachen, *Bull. Mater. Sci.* **21**, 375 (1998)
- [8] Heninz K Henisch, *Crystals in gels and Liesegang rings* (Cambridge University Press, Cambridge, 1986)
- [9] B R Jude, *Phys. Rev.* **B127**, 750 (1962)
- [10] G S Ofelt, *J. Chem. Phys.* **37**, 511 (1962)
- [11] Alexander A Kaminskii, *Laser crystals: Their physics and properties*, 2nd edn (Springer-Verlag, New York, 1989)
- [12] M Eyal, E Greenberg, R Reisfeld and N Spector, *Chem. Phys. Lett.* **117**, 108 (1985)
- [13] J Fujitha, A E Martell and K Nakamoto, *J. Chem. Phys.* **36**, 324 (1962)
- [14] J K Gibson and N A Stump, *Thermochem. Acta* **226**, 301 (1993)