

## Electronic spectral studies on rare earth doped pseudogarnets

RASHMI SINGHAI, SUDHIR N LIMAYE and M C SAXENA\*

Department of Chemistry, Dr H S Gour University, Sagar 470 003, India

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**Abstract.** Spectral parameters viz. oscillator strengths ( $P$ ), Judd–Ofelt parameters ( $\tau_\lambda$ ), inter-electronic repulsion (Racah)  $\partial E^k$  parameters (IERP) and nephelauxetic ratio ( $\partial E^3/\partial E^1$ ) have been determined using aqueous solutions of representative lanthanide (rare earth) (III) ions, Pr(III), Nd(III), Sm(III), Eu(III), and Er(III) and rare earth-doped concentrated ( $\sim 1.0$  M) solutions of pseudogarnets sodium *m*-silicate, sodium molybdate and sodium *m*-vanadate. These parameters have been studied as a function of (i) symmetry around the Ln(III) ions, and (ii) matrix environment due to different pseudogarnets.

The electronic transitions for various Ln(III) ions and changes in their positions due to corresponding changes in matrix environment are observed to show red shift. The oscillator strength values increase significantly in the sequence aqua  $< \text{MoO}_4^{2-} < \text{VO}_3^- < \text{SiO}_3^{2-}$ . The  $\tau_\lambda$  values are found to lie in the order  $\tau_6 > \tau_4 > \tau_2$ . The  $\partial E^k$  and  $\partial E^3/\partial E^1$  values are observed to lie in the theoretically calculated ranges. The nature of dopant-matrix interaction appears to change from ionic to ionocovalent on going across the Ln(III) series.

**Keywords.** Rare earth dopants; pseudogarnet matrices; spectral parameters; dopant-matrix interaction.

### 1. Introduction

Some of the chief characteristics of lanthanide (III) [Ln(III)] or rare earth ions, are the “hard acid” or class “A” of the ions character, similar electronic  $4f^q$  ( $q = \text{no. of } 4f\text{-electrons in the Ln(III) ion configurations (Moeller } et al 1965)$ , decrease in cationic size on going across the Ln(III) series (Kasimov 1982) and predominantly ionic nature of the metal–ligand bond in complexation. Although the nature of the  $4f$  shell is believed to be preserved (Jorgensen 1983) in metal–ligand interactions, a certain degree of variation from ionic to ionocovalent or covalo-electrostatic (Faucher *et al* 1992) cannot be ruled out in the case of higher Ln(III) ions. Since the oxoanions silicate, molybdate and vanadate (termed “pseudogarnets” due to their similarity to tetrahedral silicate (garnet)) exhibit strong complexing tendencies (Richardson *et al* 1990, 1992) preferring the electrostatic mode of interaction (Wilkinson 1989), rare earth-doped pseudogarnet solutions may be well-suited for studying the nature of dopant-matrix interaction.

The  $f$ – $f$  transitions in Ln(III) ions lead to sharp absorption bands permitting the determination of spectral parameters with much precision. Ln(III) doped matrices are expected to give sharp and intense bands and hence spectral parameters are well suited

\*For correspondence

for the study of dopant–matrix interactions. Such systems may help in spectral probing also.

Keeping in view the above, and in continuation of our earlier investigations (Limaye 1994), the present work was undertaken to study the absorption spectra of some representative aqueous Ln(III) ions viz. Pr(III) ( $4f^2$ ), Nd(III) ( $4f^3$ ), Sm(III) ( $4f^5$ ), Eu(III) ( $4f^6$ ) and Er(III) ( $4f^{11}$ ) in aqueous medium and also in pseudogarnet environments using sodium *m*-silicate ( $\text{SiO}_3^{2-}$ ), sodium molybdate ( $\text{MoO}_4^{2-}$ ) and sodium *m*-vanadate ( $\text{VO}_3^-$ ). These spectral measurements have led to the determination of spectral parameters – oscillator strengths ( $P$ ), Judd–Ofelt parameters ( $\tau_\lambda$ ), inter electronic repulsion (Racah)  $\delta E^k$  parameters (IERP) and nephelauxetic ratio ( $\delta E^3/\delta E^1$ ) and their analysis vis-a-vis dopant-matrix interaction and variation in  $4f^q$ -configuration of Ln(III) ions.

## 2. Experimental

Ln(III) nitrates of 99.99% purity were supplied by the Indian Rare Earths Ltd. Other chemicals were also of standard purity (BDH-AnalaR, Fluka, Sigma). All the solutions were prepared in double-distilled water. Hot solutions of pseudogarnets ( $\text{MoO}_4^{2-}$ ,  $\text{VO}_3^-$ ,  $\text{SiO}_3^{2-}$ ) were prepared so as to obtain their standard ( $\sim 1$  molar) solutions. Known amounts of Ln(III) ions were doped in the matrix solutions. The turbidity formed was dissolved by adding measured quantities of 1.0 M  $\text{HNO}_3$  so as to maintain the final pH of the solution at  $\sim 3.5 - 3.8$ . The final concentrations of Ln(III) ions were kept at  $\sim 0.037$  M by adding requisite amounts of water. The electronic spectra were recorded on a Perkin–Elmer Lambda-3B self-recording spectrophotometer using a 1.0 cm cuvette. The chart speed was kept at 80 nm/min.

Representative electronic spectra for Nd(III) ion in aqueous solution and the three pseudogarnet media are reproduced in figure 1. The prominent  $f-f$  transitions,  $\nu(\text{cm}^{-1})$  are recorded for this representative case in table 1. The average values  $\nu_{\text{ave}} = [\sum(\nu_1 + \nu_2 + \dots + \nu_n/n)]$  (where  $n$  = total number of bands) of  $\nu$  and the shifts  $\Delta\nu = \nu_{\text{ave}}(\text{aqua}) - \nu_{\text{ave}}(\text{matrix medium})$  have been calculated (Brucher *et al* 1981; Brucher and Zekany 1981) and recorded in table 2 for all the dopant-matrix systems. Other spectral parameters have been evaluated by using appropriate expressions as under.

(i) Oscillator strengths ( $P$ ) may be obtained using the general expression

$$P = \frac{8\pi^2 mc}{3h} \times \frac{\sigma}{(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda(\psi_\lambda J \| U^\lambda \| \psi'_\lambda J'), \quad (1)$$

where  $\|U^\lambda\|$  stands for tensor operators, the values for which have been obtained from literature (Reisfield and Jorgensen 1977) for the evaluation of theoretical values of oscillator strengths ( $P$ ). Other terms have their usual meanings. The experimental values of  $P$  may be calculated using (2) below which is obtained from (1) after substitution of values of standard constants

$$P = 4.318 \times 10^{-9} \times \frac{m^0 M_x \times M_y}{m' \times l \times C}, \quad (2)$$

where  $m^0$  and  $m'$  are the ratios of weighted averages of the peak areas and the unit area ( $\text{cm}^2$ ) of the surfaces, respectively.  $M_x$  stands for the rate of change of  $E(\text{cm}^{-1})$  of the electronic spectra during its recording of the spectra and  $M_y$  represents the sensitivity,  $l$  = thickness of cuvette (in cm) and  $C$  = molar concentration of dopant.

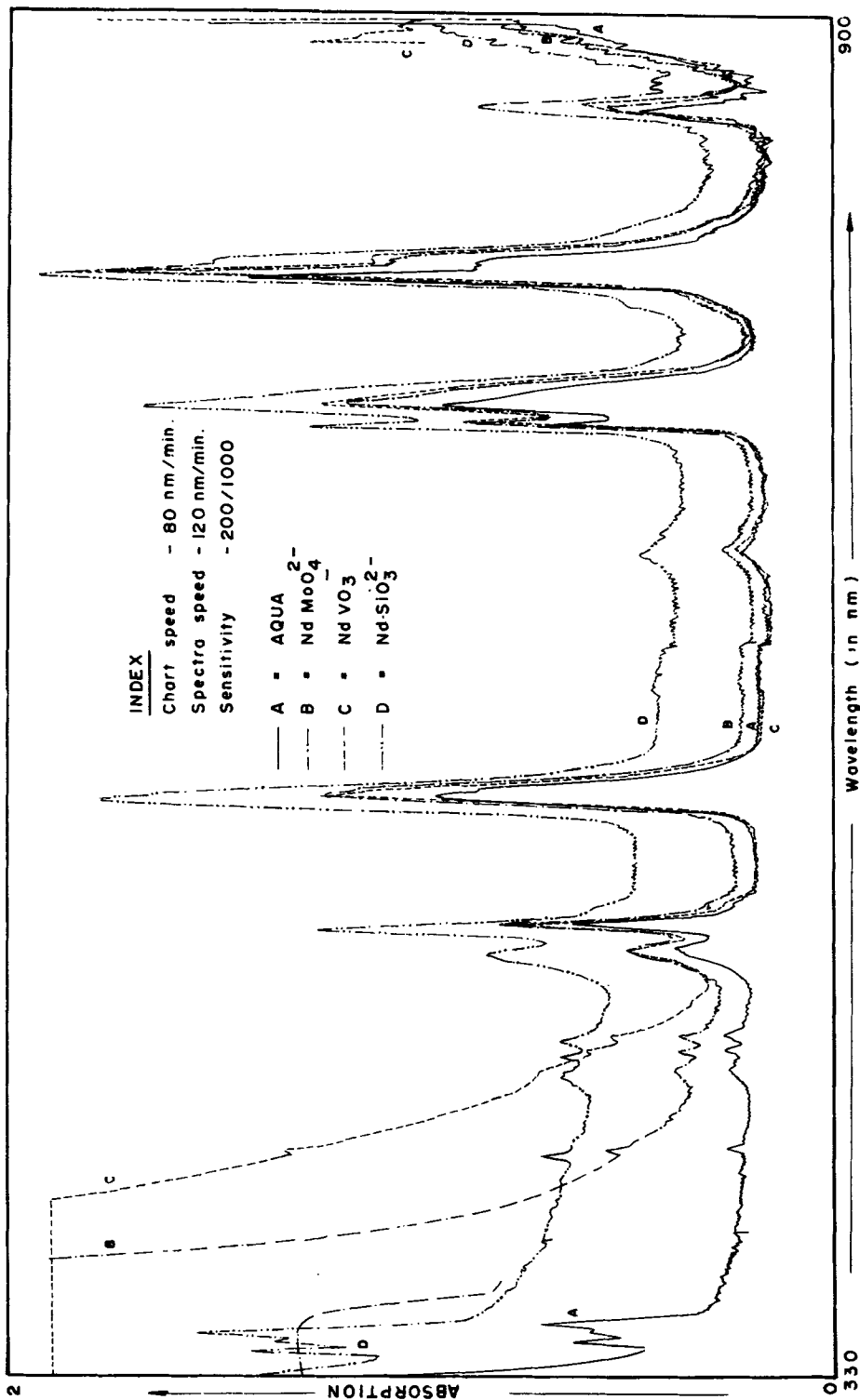


Figure 1. Representative electronic spectra of Nd<sup>3+</sup> in aqua and various pseudogarnet media.

**Table 1.** Values of  $\nu$  (in  $\text{cm}^{-1}$ ) for the standard Nd(III) ion aqueous in various pseudogarnet media.

Assignment	$E_{\text{std}}$	aqua	$\text{MoO}_4^{2-}$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
4F <sub>3/2</sub>	11450	11603	11544	11569	11569
4F <sub>5/2</sub>	12500	12546	12564	12503	12585
2H <sub>9/2</sub>	12600	12646	12664	12603	12680
4F <sub>7/2</sub>	13400	13563	13469	13511	13552
4S <sub>3/2</sub>	13500	13727	13672	13660	13687
4G <sub>7/2</sub>	17300	17346	17279	17339	17357
4G <sub>7/2</sub>	17400	17346	17379	17449	17455
2K <sub>13/2</sub>	19000	19148	19131	19028	19144
2G <sub>7/2</sub>	19100	19268	19241	19228	19294
4G <sub>9/2</sub>	19500	19668	19628	19642	19652
2P <sub>1/2</sub>	23250	23516	23679	23608	23556
4D <sub>3/2</sub>	28300	28250	—	—	28294
4D <sub>5/2</sub>	28500	28529	—	—	28424
2I <sub>11/2</sub>	28600	28770	—	—	—
2L <sub>15/2</sub>	29200	29138	—	—	29085

**Table 2.**  $\nu_{\text{ave}}$  and  $\Delta\nu$  values for Ln(III) dopants in various pseudogarnet media.

Ln(III)	Property	HOH	$\text{MoO}_4^2$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
Pr(III)	$\nu_{\text{ave}}$	20252	20517	20514	20512
	$\Delta\nu$	—	8	11	23
Nd(III)	$\nu_{\text{ave}}$	15395	15356	15378	15395
	$\Delta\nu$	—	39	17	0
Sm(III)	$\nu_{\text{ave}}$	24410	—	—	24454
	$\Delta\nu$	—	—	—	(44)
Eu(III)	$\nu_{\text{ave}}$	26826	—	—	26952
	$\Delta\nu$	—	—	—	(130)
Er(III)	$\nu_{\text{ave}}$	20546	20531	20480	20439
	$\Delta\nu$	—	15	66	107

- (ii) The values of Judd–Ofelt parameters (Judd 1962; Ofelt 1962) have been calculated using a multiexpressional three-parameter equation (Reisfeld and Jorgensen 1977; Joshi 1983) subjected to a self-devised PASCAL compiled software (Limaye et al 1990, 1991a; Limaye 1994) using the following expression:

$$T_{\lambda} = (2J + 1)\Omega_{\lambda}, \quad (3)$$

where  $J$  = multiplicity value ( $L \pm S$ ).

- (iii) The values of inter electronic repulsion Racah parameters (IERP)  $\delta E^k$  have been evaluated employing Wong's approach (Racah 1947; Wong 1961) using the expression

$$\Delta E = E_J^0 + (\partial E_J + \partial E^k) \partial E^k + (\partial E_J / \partial \zeta) \partial \zeta_{4f}, \quad (4)$$

where  $\partial E^k$  = changes in IERP; and  $k = 0, 1, 2, 3$ ;  $\zeta$  = spin-orbit coupling constant and  $\Delta E$  = numerical difference in the  $E(M_{\text{aqua}}) - (M_{\text{med}})$ . The  $\Delta E$  values thus obtained were subjected to a four-parameter expression using PASCAL software

**Table 3.** Oscillator strength values for prominent electronic transitions for Pr(III) in various pseudogarnet matrices.

$E(\text{cm}^{-1})$	Assignment	HOH	$\text{MoO}_4^{2-}$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
16850	$^1D_2$	1.304	1.598	1.986	1.58
20800	$^3P_0;$	0.956	1.117	—	0.92
21400– 21700	$^3P_1$ $^1I_6$	2.02	2.32	—	2.41
22600	$^3P_2$	5.63	6.25	—	7.10

**Table 4.** Oscillator strength values for prominent electronic transitions for Nd(III) in various pseudogarnet matrices.

$E(\text{cm}^{-1})$	Assignment	HOH	$\text{MoO}_4^{2-}$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
11000	$^4F_{3/2}$	0.45	0.51	0.82	1.26
12000– 13000	$^4F_{5/2};$ $^3H_{9/2}$	3.56	3.92	7.83	5.67
13000– 14000	$^4F_{7/2}$ $^4S_{3/2}$	4.03	3.99	4.81	5.56
17000– 18000	$^2G_{7/2}$ $^4G_{5/2}$	4.09	5.81	8.22	7.30
19000– 20000	$^2K_{13/2};$ $^4G_{9/2}$	2.89	3.55	4.83	4.42
28000– 29000	$^2D_{11/2};$ $^2L_{11/2}, ^4L_{5/2}$	3.26	—	—	5.94

**Table 5.** Oscillator strength values for prominent electronic transitions for Sm(III) in various pseudogarnet matrices.

$E(\text{cm}^{-1})$	Assignment	HOH	$\text{MoO}_4^{2-}$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
21100	$^4I_{11/2}$	1.65	—	—	1.41
21600	$^4I_{13/2}$	0.72	—	—	0.96
24000– 24550	$^6P_{5/2}$ $^2L_{13/2}$	0.59	—	—	0.58
24950	$^6P_{3/2}$	0.43	—	—	0.96
26750	$^6P_{7/2}$	7.24	—	—	6.01
27700	$^4D_{3/2}$	1.85	—	—	1.07
29100	$^4D_{7/2}$	3.45	—	—	—

to yield  $\partial E^k$  values, which have been in turn used to evaluate the nephelauxetic ratio (Jorgensen 1979) as under

$$\text{Nephelauxetic ratio} = (\partial E^3 / \partial E^1). \quad (5)$$

The calculated values of various spectral parameters as above are presented in tables 3–8. Changes in IERP and the corresponding values of nephelauxetic ratio are given in table 9.

**Table 6.** Oscillator strength values for prominent electronic transitions for Eu(III) in various pseudogarnet matrices.

$E(\text{cm}^{-1})$	Assignment	HOH	$\text{MoO}_4^{2-}$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
25050	$^5L_6$	3.28	—	—	1.34
26000– 26350	$^5L_7$ $^5G_5$	1.27	—	—	0.45
30700– 31200	$^5H_7$ $^5H_5$	0.99	—	—	0.18

**Table 7.** Oscillator strength values for prominent electronic transitions for Er(III) in various pseudogarnet matrices.

$E(\text{cm}^{-1})$	Assignment	HOH	$\text{MoO}_4^{2-}$	$\text{VO}_3^-$	$\text{SiO}_3^{2-}$
15300	$^4F_{9/2}$	18.62	2.68	0.477	3.923
18400	$^4S_{3/2}$	12.12	—	5.91	8.97
19200	$^2H_{11/2}$	2.46	—	1.84	1.84
20500	$^4F_{7/2}$	12.81	11.04	—	6.43
22200	$^4F_{5/2}$	16.65	8.98	—	5.90
22600	$^4F_{3/2}$				
24600	$^2G_{9/2}$	0.89	3.43	—	11.03
26400	$^4G_{11/2}$	5.90	21.40	—	6.96
27400	$^4G_{9/2}$	27.12	—	—	16.81
27600– 28000	$^2K_{15/2}, ^2G_{7/2}$				

### 3. Results and discussion

The spectral data in table 2 show, in general, positive values of  $\Delta\nu$  (i.e. a red shift in  $\nu_{\text{ave}}$ ) in the presence of pseudogarnets, which is indicative of a significant dopant-matrix interaction.

The  $^2P_{1/2}$  assignment for Nd(III) (cf. table 1) is susceptible to the nature of donor atom, shift in its position as indicated by variations in the corresponding values of oscillator strengths (table 3) is evidently a consequence of change in the dopant environment from aqua to various pseudogarnet matrix anions.

The values of oscillator strength (tables 3–7) exhibit a general sequence  $\text{aqua} < \text{MoO}_4^{2-} < \text{VO}_3^- < \text{SiO}_3^{2-}$  with respect to the pseudogarnet environment, which indicates a gradual increase in the degree of intensity of specific electronic transitions with change in environment. The break up of oscillator strength values in terms of  $\tau_\lambda$  parameters, i.e.  $\tau_2$ ,  $\tau_4$  and  $\tau_6$  (where  $\tau_2$  is a covalency indicative parameter and  $\tau_4$  and  $\tau_6$  are symmetry indicative parameters) shows an interesting sequence  $\tau_6 > \tau_4 > \tau_2$  (table 8) which is the order of sensitivity of these parameters with respect to dopant-matrix interaction. It appears from this sequence that the changes in  $\tau_\lambda$  values are derived more from the changes in symmetry around the Ln(III) cations than from the covalency. The values of individual parameters when seen with respect to various Ln(III) ions under study lead to interesting conclusions. The  $\tau_2$  parameter appears to

**Table 8.** Variation in  $\tau_\lambda$  parameters for doped Ln(III) ions in different pseudogarnets.

Solvent (matrix)	$\tau_\lambda (\times 10^{-5})$ parameters		
	$\tau_2$	$\tau_4$	$\tau_6$
<b>Pr(III)</b>			
Water (HOH)	-15.47	2.86	17.38
MoO <sub>4</sub> <sup>2-</sup>	-12.507	3.221	19.28
VO <sub>3</sub> <sup>-</sup>	—	—	—
SiO <sub>3</sub> <sup>2-</sup>	-11.6	2.928	22.02
<b>Nd(III)</b>			
Water (HOH)	1.716	1.649	4.585
MoO <sub>4</sub> <sup>2-</sup>	1.825	3.866	4.271
VO <sub>3</sub> <sup>-</sup>	1.575	7.563	5.990
SiO <sub>3</sub> <sup>2-</sup>	2.968	3.269	6.538
<b>Sm(III)</b>			
Water (HOH)	0	1.513	33.923
MoO <sub>4</sub> <sup>2-</sup>	—	—	—
VO <sub>3</sub> <sup>-</sup>	—	—	—
SiO <sub>3</sub> <sup>2-</sup>	0	2.461	30.022
<b>Eu(III)</b>			
Water (HOH)	0	-25.25	-17.625
MoO <sub>4</sub> <sup>2-</sup>	—	—	—
VO <sub>3</sub> <sup>-</sup>	—	—	—
SiO <sub>3</sub> <sup>2-</sup>	0	33.96	13.57
<b>Er(III)</b>			
Water (HOH)	1.001	1.236	1.368
MoO <sub>4</sub> <sup>2-</sup>	0.797	-1.468	1.782
VO <sub>3</sub> <sup>-</sup>	0.636	-1.19	1.44
SiO <sub>3</sub> <sup>2-</sup>	-0.015	0.297	0.91

**Table 9.** Values of changes in inter-electronic repulsion Racah parameters IERP ( $\delta E^k$ ) and nephelauxetic ratio ( $\delta E^3/\delta E^1$ ).

Medium (matrix)	$\delta E^1$	$\delta E^3$	( $\delta E^3/\delta E^1$ )
<b>Pr(III)</b>			
Water (HOH)	-685	99	-0.145
MoO <sub>4</sub> <sup>2-</sup>	-768	111	-0.145
VO <sub>3</sub> <sup>-</sup>	—	—	—
SiO <sub>3</sub> <sup>2-</sup>	-186	27	-0.183
<b>Nd(III)</b>			
Water (HOH)	35	5.52	0.154
MoO <sub>4</sub> <sup>2-</sup>	124	1.84	0.014
VO <sub>3</sub> <sup>-</sup>	145	3.35	0.014
SiO <sub>3</sub> <sup>2-</sup>	-11.5	0.09	-0.008
<b>Er(III)</b>			
Water (HOH)	124	3.35	-0.027
MoO <sub>4</sub> <sup>2-</sup>	111	5.52	0.0497
VO <sub>3</sub> <sup>-</sup>	145	9.5	0.0655
SiO <sub>3</sub> <sup>2-</sup>	138	14.0	0.1014

be more susceptible for the larger cations Pr(III) and Nd(III) than for the smaller Er(III) which may be a consequence of greater deformation of the  $f$ -shell possible with Er(III) due to relatively closer dopant-matrix approach as compared to Pr(III) and Nd(III). A similar supporting sequence is seen in the values of the  $\tau_4$  and  $\tau_6$  parameters. The values of the three parameters collectively indicate a general change in the nature of dopant-matrix interaction from predominantly ionic to ionocovalent on going from the Ln(III) configurations  $4f^3$ ,  $4f^5$ , to  $4f^{11}$ . The extent of partial covalency has been observed to increase with decrease in the dopant size.

The calculated values of IERP,  $\delta E^k$  and the nephelauxetic ratio  $\partial E^3/\partial E^1$  (table 9) lie well within the range of theoretically calculated values, i.e.  $\partial E^k \sim 1\%$  of  $E^1$  or  $E^3$  and  $\partial E^3/\partial E^1$  lying in the range  $-0.091 < \partial E^3/\partial E^1 < 0.214$ , which proves the validity of calculated data. An analysis of the IERP data shows the sequence  $\delta E^k(\text{Er}) > \delta E^k(\text{Nd})$  which may be due to relatively greater deformability of the Er(III)  $4f$  shell. A similar trend in the values of nephelauxetic ratio lends further support to the above inference regarding change in the nature of dopant-matrix interaction from ionic at  $4f^3 - 4f^5$  towards ionocovalent at  $4f^{11}$  configuration.

The general sequence in the values of spectral parameters with respect to Ln(III) ions may be noted as Pr(III) < Nd(III) > Sm(III)  $\sim$  Eu(III)  $\ll$  Er(III) which is significantly in accordance with the tetradic pattern (Limaye *et al* 1991b; Limaye and Saxena 1992, 1994) in the  $4f$  metal ions and also that the  $4f$ -shell characteristics of these dopants is still retained.

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