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Synthesis, characterization and spectroscopy of the europium doped lanthanum trimetaphosphate

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Abstract

Orthorhombic modification of europium doped lanthanum trimetaphosphate has been prepared. The compound was obtained by precipitation of rare earth chloride solution with trimetaphosphoric acid. The characterizations were made using X-ray diffractometry, chemical analysis and infrared spectroscopy. Excitation and emission spectra were recorded at liquid nitrogen and room temperatures. Assignments of the $^5D_0 \rightarrow ^7F_J$ ($J=0, 1, 2, 3, 4, 5$) transitions were made and an unusual high $^5D_0 \rightarrow ^7F_4$ transition intensity with six split lines has been observed. Structural distortion of the crystal lattice may be caused by the Eu^{3+} ion inclusion. The simple overlap model was applied for the calculation of the total splitting of the $^5D_0 \rightarrow ^7F_1$ transition, the $^5D_0 \rightarrow ^7F_0 / ^5D_0 \rightarrow ^7F_2$ transition intensity ratio and the Ω_λ ($\lambda=2.4$) intensity parameters. Theoretical predictions showed to be in good accordance with the experimental data. © 1988 Elsevier Science S.A.

Keywords: Lanthanide trimetaphosphate; Orthorhombic structure; f–f intensities

1. Introduction

Over past twelve years there has been considerable interest in the luminescence properties in one-dimensional systems due to the migration of electronic excitation [1]. Among a number of compounds studied, the rare-earth metaphosphates allowed to follow the influence of dimensionality on the energy migration properties of concentrated Eu^{3+} systems [2,3]. Lanthanide metaphosphates crystallize in two different structural types. For the large rare earth ions (La^{3+}–Eu^{3+}) the orthorhombic structure is adapted, while for the small ones (Tb^{3+}–Lu^{3+}) the monoclinic structure is observed. Gadolinium compound is dimorphic [4]. The structure of crystalline LaP_3O_9 may be described as built of helical chains of corner-sharing PO_4 tetrahedra that proceed downward in the c direction as imposed by screw-axis symmetry [5]. Those oxygen atoms that do not link phosphate groups are involved in the lanthanum coordination polyhedron. Due to this peculiar structural characteristics this host was chosen to lodge the europium (III) ion in order to perform spectroscopic studies of this class of compounds.

The present work reports on the alternative route of introducing europium into the lanthanum sublattice. For this purpose the luminescence spectroscopy of the $La_{0.9}Eu_{0.05}P_3O_9$ system was carried out. The simple overlap model (SOM) [6] was applied for the calculation of the $^5D0_F - ^7F_1$ transition splitting (ΔE_{0-1}), the $^5D_0 - ^7F_0 / ^5D - ^7F_2$ intensity ratio (I_{0-0}/I_{0-2}) and the intensity parameters Ω_λ ($\lambda=2$ and 4).

2. Experimental

Doped metaphosphate was precipitated by addition of a freshly obtained trimetaphosphoric acid to the solution of lanthanum and europium chlorides (0.01 M) taken in proportion 0.95 $LaCl_3$: 0.05 $EuCl_3$, in accordance with a known technique [7]. Trimetaphosphoric acid was obtained in situ by passing a solution of $Na_3P_3O_9$ through the burette filled with DOWEX 50W X12 ion-exchange resin previously activated with 1 M hydrochloric acid. The reaction was carried out under constant stirring at the temperature 55°C which was maintained by employing a water bath. The precipitate was decanted, washed with deionized water, dried at room temperature in vacuo over P_4O_{10} and calcinated at 700°C for 24 h.

After alkaline fusion, lixiviation with water and masking rare earth by addition of EDTA solution taken in excess, phosphorus was determined by a gravimetric technique in the form of $Mg_2P_2O_7$. Rare earths were determined by titration with EDTA after destroying the primary complex

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with $KClO_3$ and re-precipitating both hydroxides. Analyses (two parallel determinations) gave following results: Σ(La+Eu) 35.36 wt% (calc. 7.06 wt%); P 24.76 wt% (calc. 24.69 wt%). X-ray pattern was recorded using a Siemens Kristallotlex diffractometer (Ni-filtered CuKα radiation) provided with a graphite monochromator. According to the X-ray pattern, $La_{0.95}Eu_{0.05}P_3O_9$ obtained belongs to orthorhombic system being a member of the first structural type of lanthanide polyphosphates [5].

The luminescence spectra of the polycrystalline powder were recorded on a Spex Fluorlog 212 L at room and liquid nitrogen temperatures.

3. Theoretical background

The ΔE_{0-1} and the $I_{0.0}/I_{0-2}$ intensity ratio are treated through the SOM as described in the literature [8–11]. The theoretical expression of the intensity parameters $\Omega_\lambda(\lambda=2$, 4 and 6) is

$$\Omega_\lambda = (2\lambda+1)\sum_{t,p}\frac{|B_{\lambda tp}|^2}{(2t+1)} \qquad (1)$$

where

$$\begin{aligned} B_{\lambda tp} = {} & \frac{2}{\Delta E}\left\langle r^{t+1}\right\rangle \theta(t,\lambda)\gamma_p^t \\ & - \rho(2\beta)^{\lambda+1}\left[\frac{(\lambda+1)(2\lambda+1)}{2\lambda+1}\right]^{1/2}\left\langle r^\lambda\right\rangle \\ & \times \left\langle f\|C^\lambda|\times|f\right\rangle \Gamma_p^t(\delta_{t,\lambda+1})^2 \end{aligned}$$

with $\lambda=2$, 4 and 6, $t=1$, 3, 5 and 7, $-t\leq p\leq t$, depending on symmetry restrictions. The radial integrals $\langle r_\lambda\rangle$ ($\lambda=2$, 4 and 6) are taken from the work of Freeman and Desclaux (FD) [12] and $\langle r^8\rangle$ is extrapolated via $\langle k\rangle=0.884\ e^{0.02425k^{2.5454}}$, because this function reproduces the FD values within an average relative deviation less then 6%.

The forced electric dipole mechanism and the dynamic coupling (DC) contribution are in the first term and in the second term of Eq. (1), respectively. Both mechanisms are well described in refs. [8,10,11]. The SOM factor, $\rho(2\beta)^{\lambda+1}$, has been successfully introduced in previous works in the DC mechanism [13,14], replacing both the Steinheimer shielding correction [15] and Karayianis–Mon-ison radial expansion factor [16]. Here it is applied to a classic chained structure.

4. Results and discussion

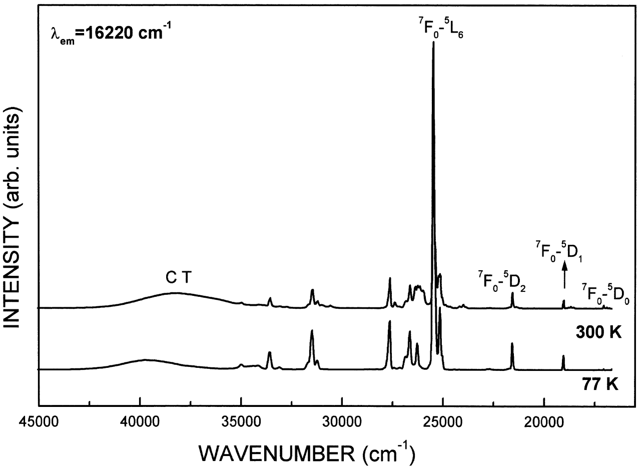

Fig. 1. Excitation spectra at (a) liquid nitrogen and (b) room temperature.

Fig. 1 shows the excitation spectra at liquid nitrogen and room temperatures, monitored at 16 220 cm^{-1} ($^5D_0\rightarrow{}^7F_2$ manifold). A broad band near 37 500 cm^{-1} assigned to a charge transfer (CT) band can be observed at both temperature conditions. In these spectra two features deserve comments. When the temperature decreases, the CT band maximum suffers a blue-shift and the CT/ $^7F_0\rightarrow{}^5L_6$ intensity ratio decreases. This can be explained by a slight shortening of the europium-oxygen bond length.

The emission spectra at liquid nitrogen and room temperatures obtained through excitation at 25 510 cm^{-1} ($^7F_0\rightarrow{}^5L_6$) (Fig. 2) show the $^5D_0\rightarrow{}^7F_J$ ($J=0$, 1, 2, 3, 4, 5) transitions. Two facts deserve to be noted. First, the I_{0-2}/I_{0-1} intensity ratio decreases, when the temperature decreases, probably due to a slight symmetry increase. Second, an unusual high $^5D_0\rightarrow{}^7F_4$ transition intensity is observed. By accurately analysing the LnP_3O_9 structures [4,5] and using group theory to assign the number of split lines, one can assert that the point symmetry of the Eu^{3+} ion site is very close to C_{2v}. This feature has been observed in other systems [17], but not for the Eu:LaP_3O_9 compound. Since C_{2v} point symmetry has no inversion centre, one possible explanation is that, in this chained

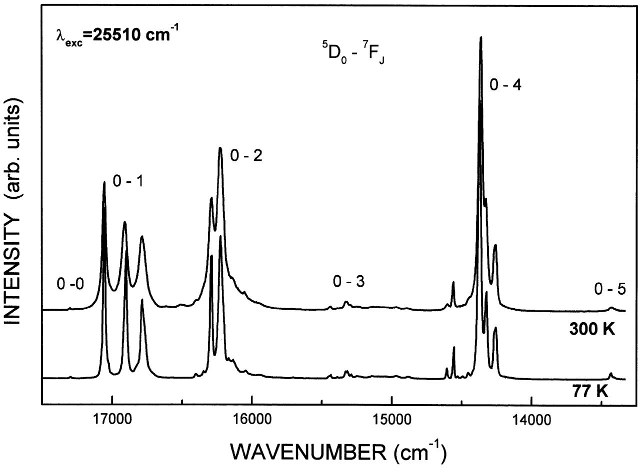

Fig. 2. Emission spectra at (a) liquid nitrogen and (b) room temperature.

Table 1
Experimental results and theoretical predictions of ΔE_{0-1} (cm^{-1}), I_{0-0}/I_{0-2} and Ω_λ ($\times 10^{-20}$ cm^2)

Parameters	Exper.	SOM
ΔE_{0-1}	278	259
I_{0-0}/I_{0-2}	0.015	0.013
Ω_2	1.7	1.5
Ω_4	3.1	3.1

structure, a J-mixing leads the $^5D_0$ level to couple with the $^7F_4$ level quite well, but not with the $^7F_2$ level.

The effective charge of the oxygen used in the calculation was $g = 2/3$. The reason to choose this value could be understood if one supposes both electrons of the O^{2-} ion shared between the Eu–O bond and the phosphate group. The values of their polarizabilities as function of the metal–ligand distance [R_j(Å)/α_j(Å^3)] are as follow: 2.334/2.3, 2.355/2.2, 2.375/0.6, 2.670/0.1 [4,5]. So, it was not possible to use an isotropic polarizability as usually adopted [10,13,14] in order to reconcile theoretical predictions and experimental results (Table 1). This may be an effect of introducing the SOM factor, $\rho(2\beta)^{\lambda+1}$, in the DC contribution. This could be an indication that now one has to be aware of the ligand ion surroundings, since the SOM factor implies the correction in the position of the metal–ligand interacting charge.

5. Conclusions

The europium doped lanthanum trimetaphosphate was prepared, chemically characterised and analysed through luminescence techniques. The unusual high $^5D_0$–$^7F_4$ transition intensity is interpreted through a J-mixing effect. The simple overlap model was applied to calculate the $^5D_0$–$^7F_1$ transition splitting, the $^5D_0$–$^7F_0$/$^5D_0$–$^7F_2$ intensity ratio and the intensity parameters Ω_λ ($\lambda = 2$ and 4) making usage of reasonable values for the effective charge and anisotropic polarizabilities. The theoretical predictions are in good agreements with experimental results, showing that the simple overlap model is adequate for the interpretation of 4f–4f transition characteristics.

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