

LUMINESCENCE SPECTRA AND CRYSTAL FIELD CALCULATION OF Pr³⁺ ION IN CRYSTAL LiYF₄

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Abstract

Luminescence of LiYF₄: Pr³⁺ in the visible and near ultraviolet region is investigated. In the visible region, the emissions observed were attributed to intra-4f²-configuration transitions. It has been shown that these transitions take place predominantly from ³P₀ level and nonradiative relaxation rate between ³P₀ and ¹D₂ is weak even at room temperature. The emission and excitation bands observed in the ultraviolet region were assigned to 4f²-4f5d interconfigurational transitions. The energy levels of Pr³⁺ 4f² configuration are fitted by using the crystal field method. The set of free-ion and crystal field parameters corresponding to the best fits allow to reproduce satisfactorily the experimental spectra.

1. Introduction

The last few years, the Pr³⁺ doped compounds acquired a particular importance because of the possibilities of application in new scintillator materials [1] or tunable UV lasers [2]. The LiYF₄ crystal is one of the most promising candidates for this last application [3]. The aim of this work is the investigation of LiYF₄: Pr³⁺ luminescence in the visible and near ultraviolet (UV) regions and the calculation of energy levels of Pr³⁺ 4f² configuration in this host matrix by using the crystal field method.

2. Experimental details

The method of preparing the LiYF₄: 0.24 at. % Pr³⁺ crystal has been described in [4]. X-ray diffraction analysis revealed that LiYF₄ is isostructural with the scheelite (CaWO₄) which exhibits a tetragonal structure [5]. The space group of symmetry is C_{4h}⁶ (I4_{1/a}) with four LiYF₄ molecules by elementary cell. The Li atom is placed in the center of a tetrahedron formed by 4 atoms of fluorine; 8 such tetrahedrons surround each Y³⁺ ion. When the Pr³⁺ ions are embedded in the LiYF₄ matrix they substitute certain Y³⁺ ions, no compensator of charge being then necessary. Only one site of symmetry characterizes the ions Pr³⁺, it is of S₄ type.

We carried out luminescence measurements using a Perkin-Elmer LS 55 luminescence spectrometer at room and liquid nitrogen temperatures. A powder holder was placed at a suitable angle to the excitation and emission beams to achieve maximum emission and minimum scattering. The emission spectra were corrected for wavelength dependent detection efficiency using the correction curve delivered by the spectrometer supplier.

3. Experimental results and discussion

In the visible region, the emissions observed are attributed to the $4f^2 - 4f^2$ intraconfigurational transitions with low intensities, as they are parity forbidden. Furthermore, as Pr^{3+} site in LiYF_4 does not exhibit inversion symmetry, one may expect forced electric dipole transitions to play a prominent role.

Figure 1 displays emission spectra of $\text{LiYF}_4: \text{Pr}^{3+}$ measured under $^3\text{P}_2$ excitation (440 nm) at room temperature and at 77 K. The most intense peaks correspond to transitions from $^3\text{P}_0$ to $^3\text{H}_6$, $^3\text{F}_2$ and $^3\text{H}_4$ levels. However peaks of lower intensity involving $^3\text{P}_1$ and $^1\text{D}_2$ levels are also observed. It is important to note that transitions which take place starting from $^1\text{D}_2$ level located at about 3500 cm^{-1} below $^3\text{P}_0$ are of much lower intensity compared to those resulting from $^3\text{P}_0$. This indicates that the probability of nonradiative relaxation from $^3\text{P}_0$ to $^1\text{D}_2$ is weak in this compound even at room temperature.

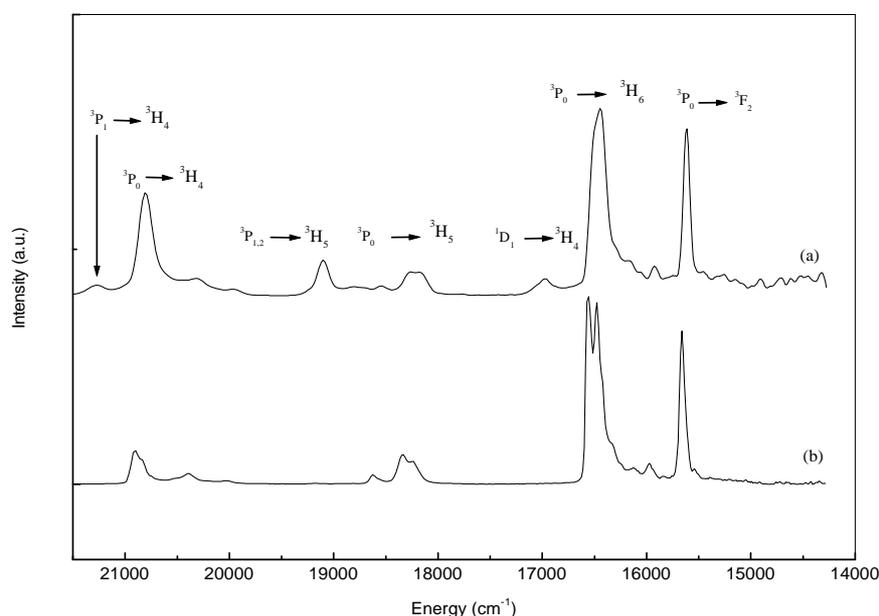


Figure 1 : Emission spectra of $\text{LiYF}_4: \text{Pr}^{3+}$ under $^3\text{P}_2$ excitation (440 nm), (a) at room temperature and (b) at 77 K.

This property is common to the fluorides which have rather weak frequencies of lattice vibration (460 cm^{-1} for LiYF_4). At 77 K, the transitions starting from $^1\text{D}_2$ vanish, as the nonradiative relaxation rate decreases with the lowering of temperature [6]. The transitions $^3\text{P}_1 - ^3\text{H}_4$ and $^3\text{P}_1 - ^3\text{H}_5$ are observed at room temperature but vanish at 77 K, which suggests we are in presence of thermal population of $^3\text{P}_1$ from $^3\text{P}_0$. The same phenomenon has been reported previously in $\text{PrP}_5\text{O}_{14}$ [7] and in $\text{BaSO}_4: \text{Pr}^{3+}$ [8]. Our suggestion is supported by the fact that under $^3\text{P}_0$ excitation $^3\text{P}_1 \rightarrow ^3\text{H}_5$ emission transition is observed at room temperature, but vanishes at 77 K.

Excitation spectra of $\text{LiYF}_4: \text{Pr}^{3+}$ measured for $^3\text{P}_0 \rightarrow ^3\text{H}_6$ emission wavelength at room and liquid nitrogen temperatures show excitation transitions from the fundamental level $^3\text{H}_4$ to $^3\text{P}_0$, $^3\text{P}_1 + ^1\text{I}_6$ and $^3\text{P}_2$ excited levels.

Figure 2 shows excitation spectra of $\text{LiYF}_4: \text{Pr}^{3+}$ at room temperature between 20000 and 50000 cm^{-1} measured for different emission transitions. All these spectra exhibit a similar

shape and are characterized by two regions of efficient excitation: (i) the low energy region situated between 20000 and 23000 cm^{-1} in the visible part of the spectrum corresponds to intra- $4f^2$ -configuration excitation transitions, (ii) the high energy region in the near UV (45000-50000 cm^{-1}) is assigned to $4f^2(^3H_4)$ - $4f5d$ interconfigurational transitions. In addition to these two regions, a broad excitation band with weak intensity is observed around 27000 cm^{-1} . It could be related to an unknown intrinsic defect level.

Figure 3 shows that excitation in the lowest level of $4f5d$ configuration yields in the ultraviolet and blue regions broad emission bands which can be attributed, in order of decreasing energy, to the emission from this level to the following groups of $4f^2$ ground configuration levels: 3H_4 , 3H_5 , (3H_6 , 3F_2), (3F_3 , 3F_4), 1D_2 and ($^3P_1 + ^1I_6$).

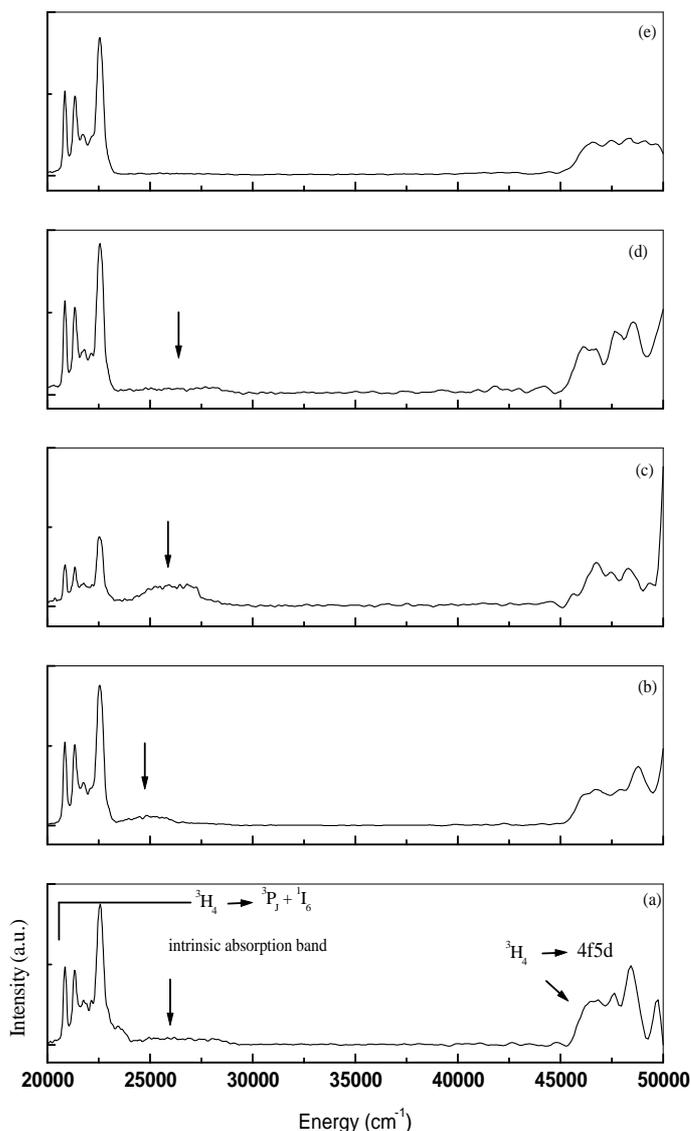


Figure 2: Room temperature excitation spectra of $\text{LiYF}_4: \text{Pr}^{3+}$ measured for the emission transitions: (a) $^3P_0 \rightarrow ^3F_2$ (640 nm); (b) $^3P_0 \rightarrow ^3H_6$ (607 nm); (c) $^1D_2 \rightarrow ^3H_4$ (590 nm); (d) $^3P_0 \rightarrow ^3H_5$ (548 nm) (e) $^3P_1 \rightarrow ^3H_5$ (523 nm)

Thus, following $4f5d$ excitation, the higher levels of $4f^2$ configuration are populated, in particular 3P_J triplet. The emission starting from these levels yields spectra identical to those measured by exciting directly towards 3P_J triplet. It appears that intensity of emission originating from 3P_0 is stronger than that of $4f5d \rightarrow ^3P_J + ^1I_6$. The same phenomenon has been reported by Oskam *et al* [9] in $\text{CaF}_2: \text{Pr}^{3+}$ at 6 K and explained by a direct nonradiative relaxation from $4f5d$ excited state to the 3P_J , 1I_6 levels in addition to population of these levels by radiative decay from $4f5d$. This may also explain why in Fig.2, the intensity of the $4f^2(^3H_4)$ - $4f5d$ electric dipole transitions is comparable and even weaker than that of the parity forbidden intra- $4f^2$ -configuration

transitions.

The experimental $\text{Pr}^{3+} 4f^2$ energy levels of $\text{LiYF}_4: \text{Pr}^{3+}$ were obtained from [10,11]. The crystal field calculations were carried out using the SPECTRA program available on the Argonne National Laboratory website [12]. This program is based on the standard phenomenological model for a $4f^N$ ion embedded in a crystalline environment. As usual, the

parameters to be adjusted involve the F^2 , F^4 and F^6 Slater parameters describing the inter-electronic repulsion between the two electrons of the $4f^2$ configuration, the ζ_{4f} spin-orbit coupling constant ($\zeta_{4f} = \langle 4f | r | 4f \rangle$), the Trees parameters α , β , γ and the $(B_q^k)_{4f}$ crystal field parameters. Values of these parameters obtained for $\text{LaF}_3: \text{Pr}^{3+}$ were used as starting parameters [13]. In addition, the α , β , γ , M^0 and P^2 parameters were first set at the $\text{LaF}_3: \text{Pr}^{3+}$ values, $M^{2,4}$ and $P^{4,6}$ being set at zero. The set of free-ion and crystal field parameters corresponding to the best fit allow to reproduce satisfactorily the experimental spectra. The parameters leading to the best fit (standard deviation in the order of 29 cm^{-1}) are (in cm^{-1}): $F^2 = 69004$, $F^4 = 50610$, $F^6 = 33341$, $\zeta = 750$, $\alpha = 22.642$, $\beta = -653$, $\gamma = 1371$, $M^{0,2,4} = (2, 1.12, 0.76)$, $P^{2,4,6} = (202, 152, 101)$, $B_0^2 = 458$, $B_0^4 = -948$, $B_0^6 = -21$, $B_4^4 = 1248$, $B_4^6 = 1159$.

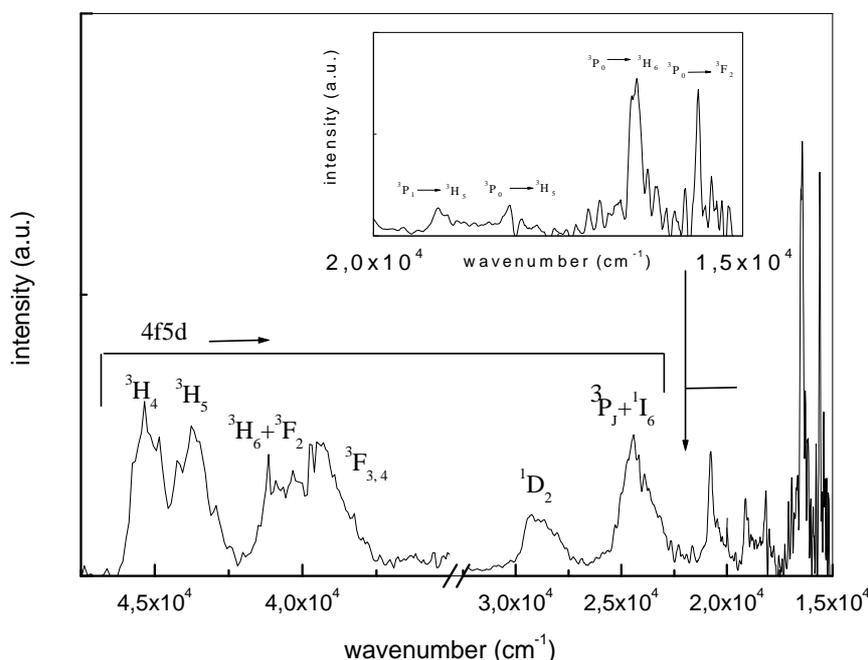


Figure 3: Emission spectrum of $\text{LiYF}_4: \text{Pr}^{3+}$ at room temperature upon $4f5d$ excitation (207 nm)

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