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Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Optical behaviour of samarium doped potassium yttrium double phosphates

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ARTICLE INFO

Article history:

Received 9 November 2014

Received in revised form

16 December 2014

Accepted 18 December 2014

Keywords:

Sm³⁺

Phosphates

Absorption and emission spectra

Judd–Ofelt parameters

Cross-relaxation

ABSTRACT

Among a wide variety of solid state materials, alkali lanthanide double phosphates are the subject of extensive spectroscopic investigations for their application as laser active materials. The edge of absorption in this compound is at rather high energies, which makes them suitable as efficient host for luminescent materials.

Spectroscopic properties of Sm³⁺-doped K₃Y(PO₄)₂ are reported basing on the high resolution absorption and emission spectra for various temperatures mainly at 4, 10, and 293 K from UV to IR range. The effects of concentration and temperature on intensities and shape of the observed bands were studied. Radiative transition probabilities were calculated from absorption spectra and Judd–Ofelt parameters evaluated. The excited state dynamics will be discussed based on the decay time measurement.

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1. Introduction

The alkali lanthanide inorganic materials, especially double phosphates [1–8] are the objects of wide investigations due to their useful luminescent. The absorption edge of alkali Y(III), La(III), Lu(III) double phosphates is at rather high energies thus they are the efficient host for luminescent materials. It is known from reported data that the rare earth phosphates display a variety of structures, they appear in hexagonal, tetragonal, orthorhombic and monoclinic modifications and other structures [9,10].

The existence of a particular modification depends both on the alkali metal and the ionic radius of the lanthanide as well as the temperature applied during the synthesis. It has been reported that sodium compounds crystallize as orthorhombic in the space group Pbc2₁ (No. 29, Z=24) [11–13], potassium ones as monoclinic with P2₁/m (No. 11, Z=2) space group [14] and rubidium crystals as hexagonal from Dy to Lu and Y (space group P3̄m, No. 164, Z=1) [15,16], or monoclinic from La up to Tb (space group P2₁/m No. 11, Z=2) [17].

Since the double phosphates may be used in laser devices not only in the single crystal form but also as powder laser but also in other optical applications thus there has been an increased interest in investigation of the various spectral properties of these phosphates even in the nanocrystal dimensions.

Recently we have reported results of the spectroscopic studies for the series of double La(III), Lu(III), Y(III) phosphates of Rb, Na, K, salts doped by Pr(III), Nd(III), Eu(III), Yb(III) as well as Pr(III)/Yb(III) co-doped double phosphates. On the other hand selected data are reported for nanostructural phosphates using Pechini method of the synthesis, however their structural characteristic is not quite clearly documented.

In this paper, we report on spectroscopic features of Sm³⁺ ions-doped K₃Y(PO₄)₂ crystals with special attention directed towards relaxation dynamics of the ⁴G(4)_{5/2} luminescent level. Experimental decay times were compared with those obtained with Judd–Ofelt theory and discussed.

2. Experimental

The samples of Sm³⁺-doped K₃Y(PO₄)₂ were synthesized using a high temperature solid-state reaction technique according to the procedure published in the previous work [18]. The following analytical grade materials were used as starting materials: Y₂O₃ (99.999%), H₃PO₄ (85%), K₃PO₄ × 3H₂O (99.99%), Sm₂O₃ (99.99%). YPO₄ was obtained from 0.4 mass% of Y₂O₃, 15 mass% of P₂O₅ (as H₃PO₄) and 84.6 mass% of distilled water. Anhydrous K₃PO₄ was prepared from K₃PO₄ × 3H₂O by heating at 900 °C for 1 h. All samples were synthesized by means of solid phase reaction by sintering a stoichiometric mixture of the initial tetraoxophosphates(V) of YPO₄, K₃PO₄ and Sm₂O₃ at 1200 °C for 4 h. The obtained Sm³⁺: K₃Y(VO₄)₂ powders were melted in closed

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platinum–rhodium tube in the argon atmosphere at 1440 °C. The doping concentrations of Sm^{3+} were 0.1, 1.0 and 5 at% with respect to Y^{3+} ions.

The samarium content were determined by the inductively coupled plasma method (ICP) using an ARL spectrometer Model 3410 ICP (Fisons Instruments). The refractive index (n) of the undoped $\text{K}_3\text{Y}(\text{PO}_4)_2$ was assumed to be 1.9. The electronic unpolarized absorption spectra recorded at room temperature on Cary 5000 SCAN NIR-VIS-UV spectrophotometer (Agilent Technologies). Samples in form of compressed and polished pellets were fixed in spectrophotometer on a copper holder and they were used in order to obtain high-quality absorption spectra. The fluorescence spectra were recorded at 11 and 293 K on a high resolution OceanOptics HR-4000 spectrometer equipped with a 15 μm slit assuring resolution of about 0.13 nm. For low-temperature measurements a closed cycle helium cryostat equipped with a refrigerator APD Cryogenics (ARS-2HW) and temperature controller was used. The fluorescence decay curves were measured at 293 K with a fluorescence scanning spectrophotometer CaryEclipse (Agilent Technologies) upon excitation from an Xe source.

3. Results and discussion

3.1. Absorption spectrum of $\text{Sm}^{3+} : \text{K}_3\text{Y}(\text{PO}_4)_2$

Room-temperature absorption spectrum of samarium-doped yttrium double phosphate is shown in Fig. 1. For the Sm(III) ion-doped phosphate crystals the ${}^6\text{H}_{5/2}$ ground state is separated from the higher ${}^6\text{H}_{7/2}$ term by $\sim 1100 \text{ cm}^{-1}$ [19]. In the Sm(III) aqua ion spectrum [20,21] and phosphate glasses [22] this separation was evaluated as 1030 cm^{-1} and 1065 cm^{-1} , respectively, and seems to be comparable to that in our system. The comparison of the crystal-field splitting of separated levels for the title double phosphates and the aqua ion spectrum is possible because the theoretical and experimental studies of many of the 206 possible multiplet levels in the $4f^6$ configuration have been made by Magno and Dieke [23]. Their experimental results agree with those obtained by Gobrecht [24].

Comparison of our double phosphate crystal spectra with data [25] at ca 7000 cm^{-1} reported earlier shows a structure of the

lines for the ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{5/2}$ transition (as assigned in the most of the absorption spectra of Sm(III) ions) that is too complex if we consider the one site of the Sm(III) ion in the structure. In the region of $7150\text{--}6850 \text{ cm}^{-1}$ very complex bands are observed as mentioned above in which the number of components corresponds to that expected for the ${}^6\text{H}_{5/2} \rightarrow {}^6\text{H}_{15/2}$ transitions. However, from the low values of the matrix elements of the unit tensor operator $U(\lambda)$ reported by Carnall et al. for this transition [20] it is necessary to exclude this assignment. Thus the complex structure of this band can only be explained by strong vibronic coupling with some vibrations observed in the IR and Raman spectra of lanthanide double phosphates as it was reported by us earlier [1].

3.2. Spectral intensities of $\text{Sm}^{3+} : \text{K}_3\text{Y}(\text{PO}_4)_2$

In the analysis of spectral intensities we have followed the theory derived by Judd and Ofelt [26a,b] and applied by various authors for lanthanide and actinide spectra [27]. The observed $4f^5 \rightarrow 4f^5$ absorption bands were integrated and the experimental oscillator strengths (f_{exp}) were determined from the equation:

$$f_{\text{exp}} = 4.318 \times 10^{-9} \int \varepsilon(\nu) d\nu, \quad (1)$$

where ε is the molar extinction coefficient at the $\nu(\text{cm}^{-1})$ wavenumber. According to the Judd–Ofelt theory [26a,b] the intensity of the electric-dipole (ED) transitions can be described in terms of three phenomenological parameters Ω_2 , Ω_4 and Ω_6

$$f_{\text{calc}} = \frac{8\pi^2 m c \nu}{3h(2J+1)} \chi_{\text{ed}} \sum_{\lambda=2,4,6} \Omega_{\lambda} \left(\Psi J || U^{\lambda} || \Psi' J' \right)^2, \quad (2)$$

where Ω_{λ} are empirical least-squares fitted parameters and $||U^{\lambda}||$ are doubly reduced matrix elements of the unit tensor operator of rank $\lambda=2, 4, 6$, calculated for the intermediate coupling approximation. The factor $\chi_{\text{ed}} = \left(\frac{n^2+2}{9n} \right)^2$ represents the local field correction of the ion in a dielectric host medium, where n is the refractive index. The matrix elements do not depend on the host; therefore their values given in Ref. 20 were used for the calculation. For Sm^{3+} ions all transitions were assumed to be electric dipole nature, but the ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{3/2}$, ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{5/2}$ and ${}^6\text{H}_{5/2} \rightarrow {}^4\text{G}(4)_{5/2}$ transitions possess a magnetic dipole component. The

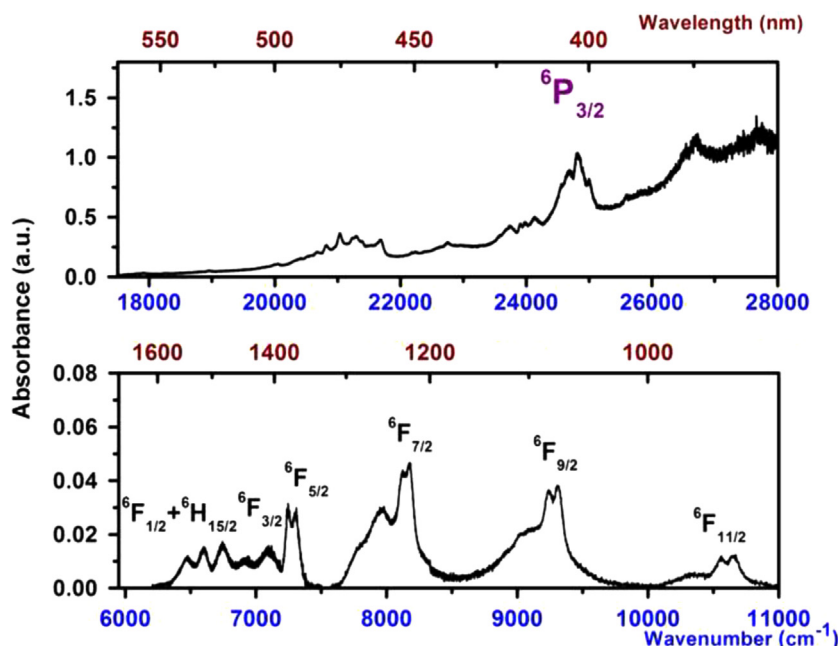


Fig. 1. Absorption spectrum of $\text{Sm}^{3+} : \text{K}_3\text{Y}(\text{PO}_4)_2$ recorded at $T=293 \text{ K}$.

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