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Structural and optical studies of $KErP_2O_7$ diphosphate

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ABSTRACT

$KErP_2O_7$ diphosphate has been synthesized by solid state reaction. It is characterized by X-ray diffraction, Raman and infrared spectroscopies. This compound crystallizes in the monoclinic system with space group $P2_1/c$ and cell parameters: a = 7.568(2) Å, b = 10.899(2) Å, c = 8.579(2) Å, β = 106.796° (2), Z = 4. The structure of $KErP_2O_7$ consists of a three-dimensional framework of ErO_6 octahedra, linked by P_2O_7 diphosphate units, forming tunnels running parallel to [001] which are occupied by K^+ atoms. For the first time absorption, excitation and emission spectra of $KErP_2O_7$have been investigated; they show characteristic energy levels of the Er^{3+} ion. The decay time curve for $^4F_{7/2}$ level of Er^{3+} ion has also been studied.

1. Introduction

Until now rare earth diphosphates have attracted much attention in recent years, due to their interesting structural and electrical properties to specify some mechanisms of transport [1–6] also their optical properties [7–11] partially due to the fact that Ln–Ln distances are relatively large in these compounds, leading to a very weak concentration fluorescence quenching [12]. Which indicates the nature of the applications as X-ray and gamma-radiation scintillators [13–14], lighting, display phosphors. [15], solid-state lasers [16], catalysts and ion conductors [17].

According to Anisimova [18] $ALnP_2O_7$ where A = K, Rb, Cs, and Ln = Y and rare earths have fourth types of structures, they crystallize in the flowing system: monoclinic system (type I), orthorhombic system (type III) and hexagonal system (type IV). The type II contains the binary phosphates $NaM^{III}P_2O_7$ and $AgM^{III}P_2O_7$ (M^{III} = trivalent elements and some rare earth elements have been presented in Ref. [19]). It has been found that the formation of $AM^{III}P_2O_7$ diphosphates and their crystal structures depend on the ionic radii ratio r_A/r^{III}_M [20].

In this context potassium rare earth diphosphates, are also defined by three different structure types. The diphosphate $KTbP_2O_7$ [24] was described in the hexagonal system (type IV), $KLnP_2O_7$ (Ln = Yb [21], Tm, Lu, Ho [18], La [22] and Y [23]) in the monoclinic system (type I) with space group ($P2_1/c$) and $KLnP_2O_7$ (Ln = Er, Ho, Dy [18] and Y [24]) in the orthorhombic system (type III).

Among the lanthanide (III) ions, trivalent erbium $Er^{3+}$is the most popular as well as one of most efficient ions [25–26]. It is characterized by visible spectral emission around 650 nm through the $^4I_{15/2} \rightarrow {}^4F_{9/2}$ transition and by infrared spectral emission around 1530 nm through the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition [27]. Many studies have been carried out on Er^{3+}introduced into different host matrix such as oxides [28], borates [29], fluorides [30], tellurite glasses [31] and phosphates [32,33].

To our knowledge, the investigation of erbium optical properties in the $KErP_2O_7$ diphosphate has not reported yet. In this work, we will discuss the crystal structure resolution obtained by Rietveld refinement of powder x-ray diffraction (XRD) profiles and the optical proprieties of $KErP_2O_7$ (type I).

2. Experimental

2.1. Synthesis

The $KErP_2O_7$ compound was prepared by solid state chemistry. Stoichiometric quantities of potassium carbonate K_2CO_3 (ALDRICH, 99%), the ammonium hydrogenophosphate $(NH_4)_2HPO_4$ (MERK, 99%) and erbium oxide Er_2O_3 (Fluke, 99.99%) as starting materials were well ground and mixed. The mixture was then placed in a

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Table 1
Crystal data and details of data collection and structural refinement for $KErP_2O_7$.

Formula unit	$KErP_2O_7$
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	7.5687(2)
b(Å)	10.8998(2)
c(Å)	8.5796(2)
β(Å)	106.7976(2)
V(Å^3)	677.5895(1)
Z	4
Angular range	($10° \leq 2\theta \leq 120°$)
Step scan increment	0.017°
Zero point (2θ)	−0.0006
No. of refined parameters	57
Pref. orientation parameter	1.0628(2)
R_P	16.3
R_{wp}	14.2
R_{exp}	7.75
χ^2	3.37
R_B	8.93
R_F	11.5

Table 2
Atomic positions and thermal parameters B_{iso} (Å^2) for $KErP_2O_7$.

Atom	x (σ)	y (σ)	z (σ)	Biso (σ)
K	0.18658(9)	0.32387(5)	0.06872(7)	5.2801(2)
P1	0.44877(2)	0.63767(2)	0.18540(2)	2.3742(2)
P2	0.13047(2)	0.89924(2)	0.80297(2)	1.8210(2)
Er	0.23137(3)	0.594310(2)	0.74655(4)	1.8312(2)
O1	0.3430(2)	0.56769(2)	0.3006(2)	3.8481(1)
O2	0.0677(2)	0.72201(2)	0.2405(2)	1.0899(2)
O3	0.6370(2)	0.6064(2)	0.2523(2)	2.9434(2)
O4	0.1552(3)	0.60174(2)	0.4664(2)	3.8942(1)
O5	0.3480(3)	0.61159(2)	0.01230	1.6696(2)
O6	0.00000	0.50676(2)	0.2026(2)	2.0554(2)
O7	0.4658(3)	0.77119(2)	0.2318(2)	3.3238(1)

platinum crucible and heated progressively from room temperature to 650 °C (0.25 °C/min) for 48 h to obtain the expected phase.

2.2. Characterization techniques

The obtained powders are checked by X-ray diffraction (XRD) using an X'PERT Pro PANAnalytical diffractometer with CuKa radiation of wavelength 1.5418 Å. The IR measurement was recorded by a Perkin Elmer (FTIR2000) spectrometer in the wave number range 400–4000 cm^{-1}. The Raman scattering was recorded using a HORIBA Scientific (lab RAM HR) spectrometer equipped with Laser source (632 nm) and CCD detector. The diffuse reflectance spectrum was registered by using a Perkin Elmer UV–Vis-NIR spectrophotometer (lambda 950). The excitation, emission spectra and luminescence lifetime have been performed by a Perkin-Elmer spectrophotometer (LS 55) with Xenon lamp (200–700 nm). The IR photoluminescence measurement was excited using the 488 nm line of an argon ion laser. All these analysis have been made at room temperature.

2.3. Structural refinement

The full pattern refinement was carried out by means of the Rietveld method [34] using the Fullprof program [35]. The atomic positions of $KFeP_2O_7$ (S. G: $P2_1/c$ (No. 14) with Z = 4) [36] were used as the starting model for $KErP_2O_7$.

Crystal data and refinement conditions are summarized in Table 1. Final atomic coordinates and thermal displacement parameters are given in Table 2. Observed, calculated and difference profiles are plotted in Fig. 1. A small amount of second phase of $ErPO_4$ was found in the $KErP_2O_7$ sample.

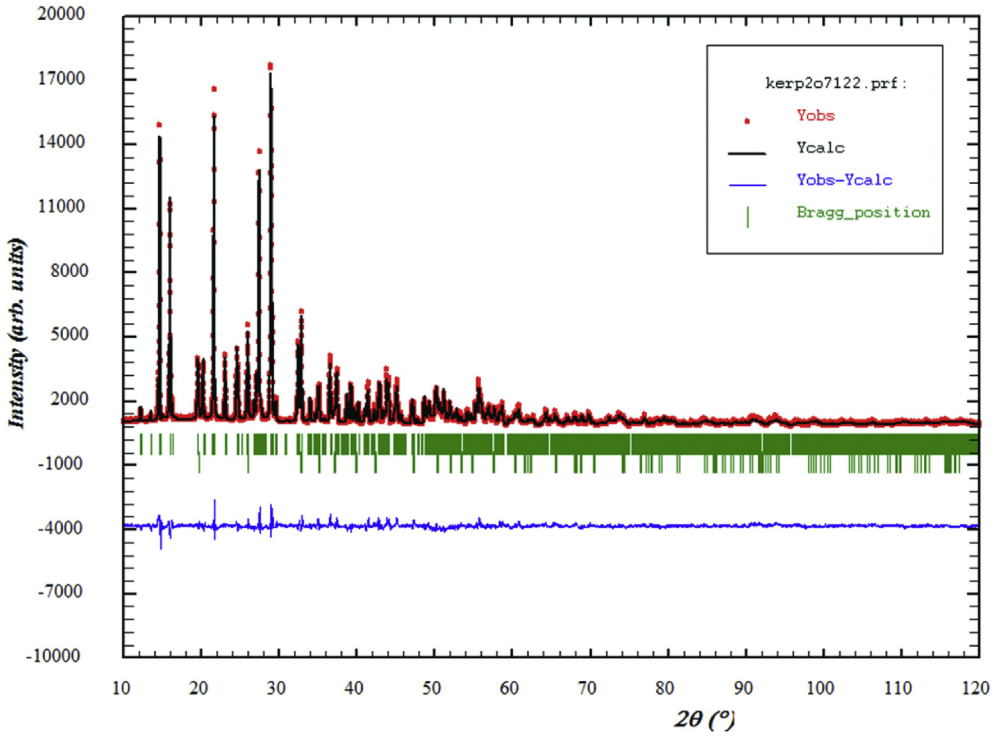

Fig. 1. Observed (dots), calculated (solid line) and difference XRD patterns of $KErP_2O_7$. The second row of Brag positions belongs to the second phase $ErPO_4$with content of 2 wt%.