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Investigations of vibrational, structural and optical properties of erbium polyphosphate micro-powders

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ABSTRACT

Polycrystallines powders of $KEr(PO_3)_4$ are grown by solid state reaction. The obtained powders are identified by X-ray diffraction. This compound crystallizes in the monoclinic system, with space group $P2_1/c$. Infrared and Raman spectroscopies are used to identify the titled compound. They show that the present structure based upon polyphosphate long chain. The optical properties of the Er^{3+} ions in this compound have been investigated in detail based on the crystal structure, particle-size distribution, the diffuse reflectance, the excitation and the emission spectra. The optical band gap energy ($Eg \approx 4.61$ eV) has been calculated from the diffuse reflectance by using the Kubelka–Munk function and Tauc's relation. The emission and excitation spectra show the characteristic emission bands of Er^{3+} in studied compound. The CIE chromaticity coordinates reveal that this phosphor can be a promising green luminophore for application in LED.

1. Introduction

In the last two decades, several researches have been carried for rare earths doped phosphates due to the rapid increase of information capacity and also their prospective applications as phosphors for white light emitting diodes (WLEDs) [1], lighting of mini-lasers, quantum electronics and fiber optics [2,3], laser technology [4–6], Dermatology and dentistry (Er: YAG laser) [7].

In this context, rare earth polyphosphates with general formula $M^{I}M^{III}(PO_3)_4$ (M^{I} = monovalent cation, M^{III} = rare earths) have a particular interest, essentially due, to their potential technological and commercial applications [8–12]. Indeed, alkali lanthanide phosphates are well studied, in one hand, that they are relatively stable under normal conditions of temperature and humidity. Moreover, their crystallinity can be kept in a perfect state for many years. They are not soluble in water and produce glasses when heated to their decomposition points [13]. In other hand, they are well used due to the fact that Ln–Ln distances are relatively large [14].

It is well known, crystal structure and chemical composition of the host matrix have, undoubtedly, great influence in the optical properties. $KNd(PO_3)_4$ crystal, for example, is not only potentially useful as laser material for miniature laser devices [15], but also has attractive performances to non-linear optical process [16]. $KLn(PO_3)_4$ (Ln = Nd, Gd) crystals have been used as second harmonic generation due to their asymmetric properties [17,18].

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Among the lanthanide (III) ions, trivalent erbium (Er^{3+}) attract considerable interest because of its potential applications in laser materials which covering the UV–vis and IR region. In fact, many studies have been carried out on Er^{3+} introduced into different host matrix such as oxide [19], borates [20], fluorides [21], tellurites glasses [22] and phosphates [23]. They show that Er^{3+} substitution remarkably affects the crystallinity, morphology and enhances the photoluminescence intensity. Essentially, Er^{3+} is the most popular as well as one of most efficient ions [24,25]. It is characterized by infrared spectral emission around 1530 nm through the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, which exhibit extensive applications such as Er^{3+} doped fiber amplifier (EDFA), Yb^{3+}–Er^{3+} -co-doped $LiLa(PO_3)_4$ glass appears as a potential eye-safe laser material [26].

$KEr(PO_3)_4$ (type: IV) is a member of the $M^IM^{III}(PO_3)_4$ family. We note that, $KEr(PO_3)_4$ polyphosphate has been previously synthesized as powder by Dago et al. [27] and Férid et al. [28]. In order to enrich this family of compounds, our research initially attempt to present Vibrational spectroscopy and distribution size of the present polyphosphate. Then, we have presented optical properties including optical band gap energy, excitation and emission measurements of the titled polyphosphate.

2. Experimental

2.1. Powder synthesis

All reagents were purchased commercially and used without further purification. A polycrystalline sample of $KEr(PO_3)_4$ was synthesized by a conventional solid state reaction starting from a stoichiometric mixture amount mainly leads to the formation of only one phase of the expected condensed polyphosphate. In fact, the corresponding reactive K_2CO_3 (ALDRICH, 99%), $(NH_4)_2$ HPO_4 (MERK, 99%) and Er_2O_3 (Fluka, 99.99%) are finely grinded in an agate mortar to ensure the best homogeneity and reactivity. The mixture was then placed in a platinum crucible and heated progressively from room temperature to 400 °C (0.25 °C/min) for 24 h to obtain the expected phase. The main reaction was presented by the following equation (Férid and Kbir-Ariguib [28]):

$$8(NH_4)_2HPO_4 + K_2CO_3 + Er_2O_3 \rightarrow 2KEr(PO_3)_4 + 16\overset{\uparrow}{NH_3} + 12\overset{\uparrow}{H_2O} + \overset{\uparrow}{CO_2}.$$

Those supplementary calcinations of this compounds of $KEr(PO_3)_4$, were summers made for different temperatures successively: 200–550 °C, in order to eliminate residual water, CO_2, NH_3.

2.2. Characterization techniques

The purity of the resulting powder has been checked from the examination of its X-ray powder diagram collected on a PANalytical diffractometer using CuKα radiation (λ = 1.5418 Å). The crystalline phase has been determined by comparison of the registered patterns with the International Center for Diffraction Data (ICDD)-Powder Diffraction Files (PDF). IR spectrum has been recorded by a Perkin Elmer (FTIR 2000) spectrometer in the range of 4000–400 cm^{-1} using KBr pellets. The Raman and PL spectra were recorded using HORIBA Scientific (labRAM HR) spectrometer equipped with Laser source (633 nm and 325 nm) and CCD detector. The diffuse reflectance measurement was recorded by using an UV–visible spectrophotometer (lambda 950). The excitation spectrum has been done by a Perkin-Elmer spectrophotometer (LS 55) with Xenon lamp (200–700 nm). The Visible and IR photoluminescence measurement was performed under 488 nm line of an argon ion Ar^+ laser source. For laser granulometry measurement, we have used a Microtrac S3500 Series Particle Size Analyzer with Tri-laser Technology in a range from 0.02 to 2800 lm and solid laser of 780 nm. Particle-size distributions were expressed in volume units. All these analysis have been carried out at room temperature.

3. Results and discussion

3.1. Powders characterization

The registered XRD pattern of the polycrystalline $KEr(PO_3)_4$ was shown in Fig. 1. All picks were indexed to a monoclinic phase with space group $P2_1/c$ (no.14), with lattice parameters: a = 10.798(1) Å; b = 8.833(4) Å; c = 12.651(7) Å; β = 128.208(8)° and Z = 4. Based on ICDD-PDF, these peaks are related to single phase of condensed polyphosphate with linear chain (PDF no. 84-0030).

3.2. Spectroscopic analysis

3.2.1. Infrared spectroscopy

After literature survey, and according Dago et al. [27], in $KEr(PO_3)_4$ (with space group $P2_1/c$), Er^{3+} atom occupies 4e crystallographic position (general positions), coordinated by eight O atoms forming a distorted ErO_8 polyhedra with Er–O bond lengths in the order of 3.21 Å. In addition, ErO_8 polyhedra are isolated from each other by $(PO_3)_n$ zig-zag chains formed by corner sharing of PO_4 tetrahedra (Fig. 2).

In order to get a better insight into the chemical bonds in our sample, FTIR and Raman measurements were used. Fig. 3 shown the characteristic spectrum of condensed polyphosphate, being by the appearance of wide band around 1250 cm^{-1},