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Synthesis and luminescence characteristics of Dy^{3+} doped $KLa(PO_3)_4$

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ABSTRACT

Polycrystalline powders of $KLa_{(1-x)}Dy_x(PO_3)_4$ (x=0.5%, 1%, 5% and 10%) with linear chain have been grown by solid state reaction. The obtained powders are characterized by X-ray powder diffraction, FTIR and Raman spectroscopies. Emission, excitation spectra and decay curves analysis have been used to study the spectroscopic properties of Dy^{3+} in $KLa(PO_3)_4$. The photoluminescence spectra show two characteristic blue and yellow bands of Dy^{3+}. The yellow-to-blue emission intensity ratios and CIE chromaticity coordinates have been determined from emission spectra to evaluate the emitted light as function of Dy^{3+} concentration. The measured decay rates for $^4F_{9/2} \rightarrow {}^6H_{15/2}$ deviated from exponential to non-exponential shape with increase of Dy^{3+} concentration. The observed non-exponential behavior of the decay curve has been fitted to Inokuti–Hirayama model, which indicates that the energy transfer between the donor and the acceptor is of dipole–dipole nature. The energy transfer, between the donor (excited Dy^{3+}) and the acceptor (unexcited Dy^{3+}), increases with Dy^{3+} ions concentration.

1. Introduction

In last decades, several materials are activated by rare earths ions such as borates [1], phosphates [2–4], aluminates [5,6], silicates [7], vanadates [8], etc. Among them, alkali lanthanide phosphates crystals are the subject of many studies in the past years due to their excellent role for the development of optical devices including optical fibers and amplifiers, visible luminophores, laser materials and display devices [3,4,9,10]. Particularly, rare earth doped condensed polyphosphates with general formula $M^{I}Ln^{III}(PO_3)_4$ (where M^{I} are alkali metal ions and Ln^{III} lanthanide ions) have been assumed mainly due to their relatively easy synthesis, reasonable stability in lamp application and good chemical durability [11–14]. The polyphosphate have relatively low multiphonon relaxation and high internal quantum efficiency [3,4]. Because of its abundant emission colors according to their 4f–4f transitions, Dy^{3+} ($4f^9$) is one of the most efficient rare earth ions for mid-IR lasers and telecommunication for the development of optical amplifier systems [15,16]. The analysis of luminescence from $^4F_{9/2}$ level of dysprosium ion is very appealing as it covers the visible and near-infrared regions. It is well known from the literature data that the active Dy^{3+} ion possesses two strong luminescence bands in the visible range including blue (B) ($^4F_{9/2} \rightarrow {}^6H_{15/2}$, 486 nm) and yellow (Y) ($^4F_{9/2} \rightarrow {}^6H_{13/2}$, 576 nm) which are easily affected by the external crystal field. The combination of these two primary colors provides a mechanism producing white light which has been intensively applied in the solid-state lighting technology in the past few years [17]. The change of Y/B ratio with increasing Dy^{3+} concentration can be explained by structural changes in the environment around Dy^{3+} ions which is not observed in $NaGd(PO_3)_4$ polyphosphate crystallizing in the same monoclinic system [13].

In this paper, we present the synthesis and characterization of Dy^{3+} doped $KLa(PO_3)_4$ powder. The excitation, emission spectra and decay rates were measured for different concentrations of Dy^{3+} ions. The effects of Dy^{3+} concentration on the fluorescent intensity, lifetime and chromatic coordinates were also discussed. The calculated Y/B ratios and chromatic coordinates indicate that the title compound can be used as a potential two-primary-color phosphors.

2. Experimental techniques

2.1. Synthesis

The polycrystalline powders of Dy^{3+}-doped $KLa(PO_3)_4$ (x=0.5%, 1%, 5% and 10%) have been prepared by solid state reaction [2]. Stoichiometric ratio of $(NH_4)_2HPO_4$ (MERK, 99%), K_2CO_3 and Dy_2O_3 for 0.4 g of La_2O_3 (Fluka, 99.98%) were used as starting reagents according to the following reaction:

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$8(NH_4)_2HPO_4 + xDy_2O_3 + (1-x)La_2O_3 + K_2CO_3 \rightarrow 2KLa_{1-x}Dy_x(PO_3)_4 + 16NH_3\uparrow + 12H_2O\uparrow + CO_2\uparrow$.

The mixture was finely ground in an agate mortar to ensure the best homogeneity and reactivity. Then, it was poured into platinum crucible and heated progressively from room temperature to 400 °C (0.5 °C/min) and kept for 2 days at this temperature. In the last step the obtained product was calcined at 600 °C (10 h) to eliminate residual water, CO_2 and NH_3.

2.2. Measurements

The obtained polycrystalline powders are checked by X-ray diffraction (XRD) at room temperature using an X'PERT Pro PANAnalytical diffractometer with CuKα radiation of wavelength 1.5418 Å. The crystalline phases have been determined by comparison of the registered patterns with the International Center for Diffraction Data (ICDD)-Powder Diffraction Files (PDF). Infrared spectra have been recorded by a Perkin-Elmer (FTIR2000) spectrometer using KBr pellets in the region of 4000–400 cm^{-1}. Raman scattering spectra have been recorded using HORIBA Scientific (lab RAM HR) spectrometer equipped with laser source (632 nm) and CCD detector. The excitation, emission spectra and luminescence decay time curves have been done by a Perkin-Elmer spectrophotometer (LS 55) with Xenon lamp (200–700 nm). All these analysis have been made at room temperature.

3. Results and discussion

3.1. Powder characterization

The crystalline phase of each obtained samples was checked by X-ray powder diffraction (XRD) (Fig. 1). All peaks are related to single phase of condensed polyphosphate $KLa(PO_3)_4$ identified by (ICDD) PDF file no. 75-2478 [18]. These samples crystallized in the monoclinic system with space group $P2_1$ (no. 4). Only one peak observed for 5% Dy^{3+} at $2\theta = 20.1°$ was assigned to secondary phase of polyphosphate $K_2La(PO_3)_5$ with a triclinic structure and space group P1 (PDF no. 038-0005) [19]. The smaller ionic radii of Dy^{3+} (1.027 Å) compared to that of substituted La^{3+} (1.16 Å) in the eight-fold coordination environment facilitates the substitution and the incorporation of the dopant ions in the $KLa(PO_3)_4$ matrix [20].

The infrared and Raman spectra of Dy^{3+} doped $KLa(PO_3)_4$ ($x = 0.5\%$, 1%, 5% and 10%) have been investigated and shown in Figs. 2 and 3, respectively. Based on data from infrared and Raman spectroscopy provided for other isotopic condensed polyphosphates, the bands positions, shapes and intensities of samples are characteristic of a monoclinic structure ($P2_1$) type formed by infinite chain of PO_4 tetrahedra bound by bridging oxygen [21]. The similarity between all FTIR spectra indicates that IR results are in good agreement with RXD results. In IR spectra, the characteristic frequencies of obtained polyphosphate chains such as the (ν_{as}) of OPO^- are detected between 1200 and 1330 cm^{-1}. While,

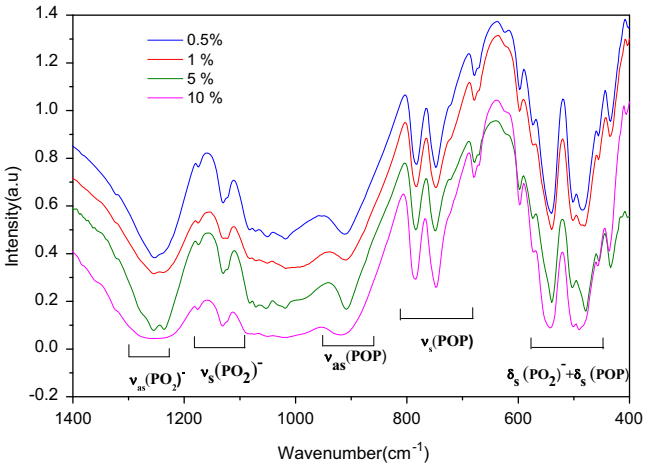

Fig. 2. FTIR spectra of $KLa_{1-x}Dy_x(PO_3)_4$ powders ($x = 0.5\%$, 1%, 5% and 10%).

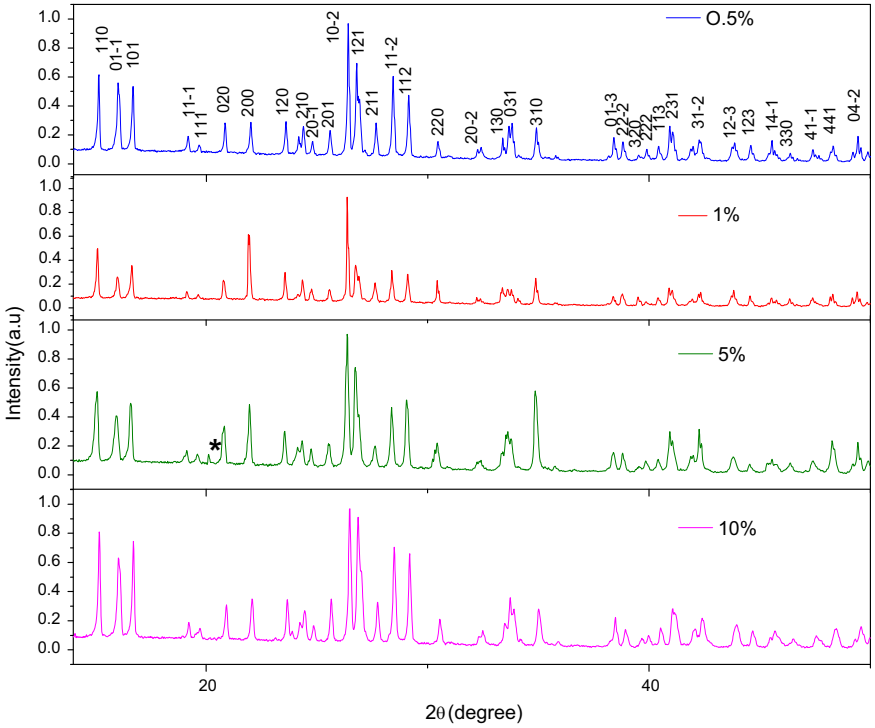

Fig. 1. XRD patterns of $KLa_{1-x}Dy_x(PO_3)_4$ powders ($x = 0.5\%$, 1%, 5% and 10%).