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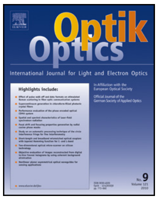

Original research article

Self-activated luminescent material $K_3Dy(PO_4)_2$: Crystal growth, structural analysis and characterizations

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ABSTRACT

A potassium dysprosium orthophosphate $K_3Dy(PO_4)_2$ has been prepared using high temperature flux method and structurally characterized by single crystal X-ray diffraction (SC-XRD) analysis. Its structure features a two-dimensional (2D) layer structure that is composed of $[Dy(PO_4)_2]_\infty$ anionic layers and K_∞ cationic layers alternatively stacking along the *a*-axis. The diverse excitation and emission photoluminescence spectra, fluorescence lifetime and color CIE coordinates for $K_3Dy(PO_4)_2$ were discussed. Although with high Dy^{3+} concentration, the emission spectrum excited at 350 nm shows strong green-yellow emission bands corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions, respectively. The results show that $K_3Dy(PO_4)_2$ can be potentially used as a green-yellow phosphor for fields of near UV-excited white-light-emitting diode and opto-electronic devices.

1. Introduction

Rare-earth photoluminescence (PL) materials for converting UV or near UV-blue radiation into visible light have a broad range of applications such as light emitting diodes (LEDs), cathode ray tubes, and field-emission displays [1–5]. Rare-earth ions can be excited resonantly through $f \rightarrow f$ transitions or $f \rightarrow d$ transitions or non-directly in charge transfer process or dipole–dipole energy transfer. Among rare-earth ions, the Dy^{3+} ion with $4f^9$ configuration is one of the excellent activators in PL materials. Dy^{3+} usually shows strong fluorescent transitions in the bluish (485 nm) region corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and yellowish (575 nm) region corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, which is necessary for the development of white light emitting diodes (LEDs) as well as optical display systems.

Among the PL materials, inorganic phosphates have their host absorption edge at rather short wavelengths which make them suitable as the host for active rare-earth ions. Moreover, phosphates have significant advantages for using as PL materials including low sintering temperature, low cost, broad band gap, high luminous efficiency and high chemical stability. Recently, study on phosphate based luminescent materials have produced a large amount of literatures, such as $KLn(PO_3)_4$ (Ln = Ce, Eu) [6], $Na_2SrMg(PO_4)_2$: Eu^{3+} [7], $KSrBP_2O_8$: Dy^{3+} [8], $KBaBP_2O_8$:Tb^{3+} [9]. The study of phosphates with the general formula $A_3Ln(PO_4)_2$ (Ln = alkali metals; Ln = rare-earth elements) was conspicuous and some inspiring results have been recently achieved. Jiang et al. has reported new PL material $K_3Gd(PO_4)_2$: (Tb^{3+}, Eu^{3+}), whose color emission can be easily tuned from yellowish-green to reddish-orange by adjusting the Eu^{3+} concentration [10]. The other $A_3Ln(PO_4)_2$ based phosphor include $Na_3Ln(PO_4)_2$: Yb^{3+} [11], $Na_3Gd(PO_4)_2$: (Dy^{3+}, Tm^{3+}) [12], $K_3Gd(PO_4)_2$: Sm^{3+} [13], $K_3Gd(PO_4)_2$: (Ce^{3+}, Tb^{3+}) [14]. In

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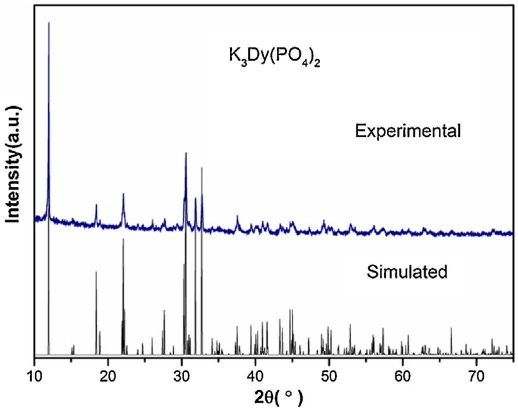

Fig. 1. Experimental and simulated X-Ray powder diffraction pattern of $K_3Dy(PO_4)_2$.

order to explore new PL materials, we started an explore within the K_2O–Dy_2O_3–P_2O_5 system and successfully prepared a ternary compound $K_3Dy(PO_4)_2$, which show good PL properties although with fully concentrated Dy^{3+}. Herein, we report the crystal growth, structural determination and self-activated PL properties of $K_3Dy(PO_4)_2$.

2. Experimental section

2.1. Preparation

Raw chemicals KF, K_2CO_3, Dy_2O_3 and $NH_4H_2PO_4$ were purchased from the Shanghai Reagent Factory. Single crystal of $K_3Dy(PO_4)_2$ was prepared by a molten salt method by using additional K_2O–KF–P_2O_5 as the flux. The mixture of initial reagents K_2CO_3(1.482 g, 10.72 mmol), Dy_2O_3 (1.000 g, 2.681 mmol), $NH_4H_2PO_4$(2.158 g, 18.77 mmol) and KF(0.779 g, 13.40 mmol) with the molar ratio of 4:1:7:5 was thoroughly ground in an agate mortar put into a platinum crucible. The mixture was heated in an oven at 900 °C for 24 h and then cooled slowly to 700 °C at a rate of 2 °C h^{-1} before the furnace was switched off. The flux attached to the crystal was readily dissolved in hot water.

After appropriate structural analysis, powder sample of $K_3Dy(PO_4)_2$ was obtained quantitatively by the solid state reaction of a mixture of $K_2CO_3/Dy_2O_3/NH_4H_2PO_4$ in the molar ratio of 3:1:4. The mixture was sintered in a platinum crucible for 24 h at 950 °C, with several intermediate grinding stages to ensure complete solid state reaction. XRD powder diffraction studies demonstrated that the powder sample was successfully obtained as the single phase (Fig. 1).

2.2. X-ray diffraction analysis

A suitable single crystal with dimensions of 0.20 × 0.05 × 0.05 mm was selected and mounted on a glass fibre for the single-crystal X-ray diffraction experiments. Data collection was performed using a Bruker Smart Apex2 CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation in the $\omega/2\theta$ scan mode at a temperature of 293 K. Lorentz and polarization corrections were applied to all data, and an empirical absorption correction was applied using SADABS program [15]. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by *Shelx*-2014 [16]. All of the atoms were refined with anisotropic thermal parameters. The final refined solution obtained was checked with the ADDSYM algorithm in the program PLATON [17], and no higher symmetry was found. Crystallographic data and structural refinement was summarized in Table 1.

3. Results and discussion

3.1. Crystal structure

Single crystal X-ray diffraction analysis revealed that compound $K_3Dy(PO_4)_2$ crystallizes in the monoclinic space group $P2_1/m$, and features a two-dimensional (2D) layer structure composed of $[Dy(PO_4)_2]_\infty$ anionic layers and K_∞ cationic layers alternatively stacking along the *a*-axis, as shown in Fig. 2a. In the asymmetric unit, there is one Dy atom, two P atom, three K atom, and six O atoms. P atoms are coordinated by three O atoms into PO_4 tetrahedra with the P—O bond distances ranging from 1.514(4) Å to 1.545(4) Å and O—P—O bond angles ranging from 105.5(2)° to 110.93(15)° (Table 2). These values are common values comparing with other reported rare-earth phosphates [18,19]. The PO_4 tetrahedra are isolated and are further interconnected by Dy atoms into a 2D infinite anionic layer of $[Dy(PO_4)_2]_\infty$, as shown in Fig. 2b. The Dy atom has a DyO_7 polyhedral geometry with the Dy—O bond distances ranging from 2.257(3) Å to 2.523(4) Å.