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Structure–property correlations in Eu-doped tetra calcium phosphate phosphor: A key to solid-state lighting application

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ABSTRACT

The unique emission characteristics and the crystal structure of Ca₄(PO₄)₂O:Eu²⁺ were studied. Considerably broad emission from 500 nm to 800 nm was measured at 77 K when the material was excited at 365 nm. Its crystal structure was refined using neutron diffraction, allowing precise and accurate oxygen positions to be determined. This enabled a relationship between the optical properties and the crystal structure crucial for achieving a large redshift of the 5d level of Eu²⁺ to be established, which is important to match the excitation energy band with near-ultraviolet or blue light-emitting-diodes used for solid-state lighting. The importance of the anion polarizability and the distortion of the coordination polyhedron were also discussed.

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1. Introduction

Solid-state lighting (SSL) is a new generation lighting technology with many advantages including superior efficiency, longer lifetime and reliability. This enables more energy-saving and environmental-friendly light sources compared with traditional fluorescent and incandescent lamps. As the demand for SSL grows, white light-emitting-diodes (LEDs) have been intensively improved. The development of phosphors has been contributing to this since the fabrication of white LEDs currently relies on the use of phosphors to convert high energy blue or near-ultraviolet (UV) LED light into lower energy visible light [1,2]. Currently, the most common approach for white LEDs is to combine a blue LED with a color-converting phosphor, first achieved using a YAG:Ce³⁺ phosphor for blue-to-yellow down conversion. Most oxide phosphors for LED use have been adapted from those used in cathode ray tubes (CRTs) or lamps, and there are few examples of new oxide-based phosphors that exhibit good excitation and emission performance when combined with blue LEDs. The phosphors suitable for use in practical application for SSL comprise a crystalline oxide, nitride, oxy-nitride,

or oxy-fluoride host doped with small amounts of Ce³⁺ or Eu²⁺. They need a large redshift in the 5d energy level such that it absorbs in the near-UV or blue region. Discovering the key factors required to achieve a large redshift is crucial for developing suitably improved phosphors for creating better white LEDs.

The optimum absorption of Eu-doped phosphate phosphors rarely matches the emission of blue LEDs. For example, a series of ABPO₄:Eu²⁺ type phosphors was reported, where in A is alkali metal and B is alkali earth metal [3]. While most of these are excited at UV and some at near-UV, none of them can be excited by blue light. Another series of alkali earth metal based on orthophosphate and pyrophosphate such as (Ca,Ba)₂P₂O₇:Eu²⁺, Ca₂Ba(PO₄)₂:Eu²⁺ and (Ca,Ba)₃(PO₄)₂:Eu²⁺ were reported [4], but again they were only excited in the UV. We have previously reported Ca₆BaP₄O₁₇:Eu²⁺ [5], which is a rare bright yellow phosphor that can be excited using blue light. The related Ca₄(PO₄)₂O:Eu²⁺ (hereafter referred to as TTCP:Eu²⁺) is a red phosphor reported to have the longest excitation wavelength [6]. It is important to understand the key factor which allows Eu²⁺ to have a large redshift in this material. Our further investigation of TTCP:Eu²⁺ revealed it contains different emission colors in one host. We therefore conducted neutron diffraction on this compound to determine the exact oxygen positions in its structure so that the crystal structure can be related to emission characteristics. We report herein the importance of the anion polarizability and the distortion of the coordination polyhedra around Eu to tune the redshift of its 5d energy level.

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2. Experimental

A phase pure sample of TTCP:Eu²⁺ was synthesized by conventional solid-state reaction of CaCO₃ (Hakushin Chemicals), CaHPO₄ (Alfa Aesar) and Eu₂O₃ (Alfa Aesar). The ground mixtures of the raw materials were placed in alumina crucibles and heated in a reducing atmosphere of 5% H₂+95% N₂ in the temperature range of 1250–1300 °C for 10 h. After the synthesis, the samples were ground into fine powders for characterization. Laboratory powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer (Bragg–Brentano geometry) using Cu-K α radiation and a position-sensitive detector (LynxEye). Time of flight powder neutron diffraction data were recorded on the diffractometer HRPD, ISIS, Rutherford Appleton Laboratory. Structure refinement was performed by the Rietveld method using program GSAS [7,8]. The crystal structure of TTCP:Eu²⁺ was depicted in VESTA, in which the effective coordination numbers (EConNs) were also calculated [9]. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature and 77 K were measured using a Horiba FluoroLog-3 spectrometer. The UV–vis reflectance spectra were measured using a PerkinElmer Lambda 750 spectrophotometer. To evaluate the band gap of TTCP, density functional theory (DFT) calculations with hybrid nonlocal exchange–correlation functional (HSE) were performed by applying the Vienna Ab initio Simulation Package (VASP) code. The electron–ion interaction was described by the projector augmented wave (PAW) method. The basis set cutoff was 400 eV [10–12].

3. Results

3.1. The structure refinement of Ca₄(PO₄)₂O:Eu²⁺

The laboratory PXRD pattern agreed with JCPDS-ICDD-PDF no. 25-1137(space group: P2₁) for the tetra calcium phosphate. The unit cell parameters were similar to those obtained in the previous work on the TTCP:Eu²⁺ red phosphor confirming the same phase had formed [6]. The crystal structure of TTCP was previously studied using single crystal X-ray diffraction by Dickens [13]. In this work, neutron diffraction studies of TTCP:Eu²⁺ have enabled us to refine more precise oxygen positions. Fig. 1 shows the high quality of the Rietveld fits to the pattern obtained of TTCP:Eu²⁺ using the monoclinic P2₁ structure. Table 1 shows structural parameters for TTCP:Eu²⁺, including *R* indexes of *R*_{wp}=3.0% and *R*_p=4.2% by comparison with the values from previous work [13]. The crystal structure is illustrated in Fig. 2 and the atomic coordinates of TTCP are shown in Table 2.

The TTCP:Eu²⁺ phosphor has eight Ca sites, all Ca sites are coordinated by seven oxygen atoms with an average bond length from 2.44 Å to 2.52 Å. Bond valence sums were calculated to confirm the proper coordination number (Table 3) [14]. The four P sites are in PO₄ tetrahedra which are isolated from other PO₄ tetrahedra. The structure also contains two distinct oxide anions that are not part of a PO₄ tetrahedron (labeled O1 and O2).

3.2. Optical properties of Ca₄(PO₄)₂O:Eu²⁺

Fig. 3 shows the PL and PLE spectra of TTCP:Eu²⁺ at 1 mol% doping with respect to Ca, excited at 465 nm and monitored at 700 nm at room temperature, which are very similar to the previously reported PL and PLE spectra [6]. The sample used in this work is essentially identical to the reported red emitting phosphor of TTCP:Eu²⁺. However further investigation revealed it emitted yellow light when excited at 465 nm at 77 K as shown in Fig. 3. The obvious change in the emission spectrum shape was caused by a tremendous increase in the shoulder peak around 600 nm.

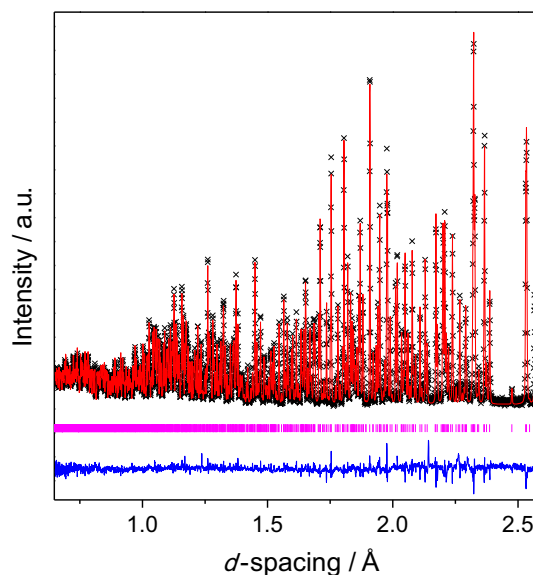


Fig. 1. Neutron diffraction patterns from the backscattered bank of the HRPD diffractometer. The crosses and upper and lower continuous lines are the experimental, calculated and difference profiles, respectively; the vertical lines are the allowed Bragg reflections markers.

Table 1
Crystallographic data and structure refinement.

| | This work | Previous work |
|----------------------|--|---|
| Unit cell dimensions | <i>a</i> =7.01444(5) Å <i>b</i> =11.9792(1) Å <i>c</i> =9.46490(7) Å β =90.8915(4) ^a | <i>a</i> =7.023(1) Å <i>b</i> =11.986(4) Å <i>c</i> =9.473(2) Å β =90.90(1) ^a |
| Cell volume | <i>V</i> =795.22(1) Å ³ | <i>V</i> =797.3 Å ³ |
| Space group | P2 ₁ | P2 ₁ |
| <i>R</i> indexes | <i>R</i> _{wp} =3.0% | <i>R</i> _p =4.2% |

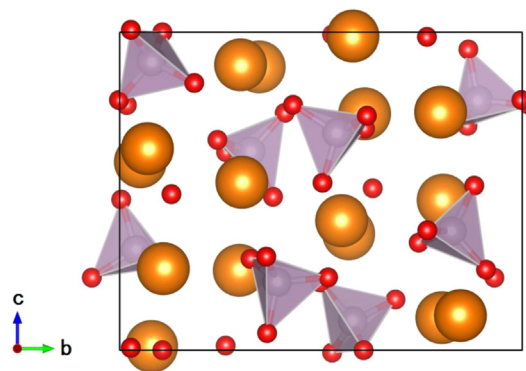


Fig. 2. Schematic crystal structure illustration of TTCP:Eu²⁺ projected onto the (100) plane. Ca, P and O atoms are shown as brown, mauve and red spheres respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Significant increased excitation at 350 nm is also observed, presumably due to different contributions from Eu²⁺ in the various coordination environments. Fig. 4 displays the photograph of the body color and emissions of TTCP:Eu²⁺. The photographs were taken under ambient light at room temperature, under 365 nm UV light at room temperature and 365 nm UV light at 77 K. The samples showed clear yellow emission colors at 77 K. The optimized PL and PLE spectra were measured for yellow emission at 550 nm and for red emission at 700 nm (Fig. 5) at 77 K.

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