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Crystal structure, energy transfer and tunable luminescence properties of $Ca_8ZnCe(PO_4)_7$:Eu^{2+},Mn^{2+} phosphor

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ABSTRACT

Single-phased $Ca_8ZnCe(PO_4)_7$:Eu^{2+},Mn^{2+} phosphors with whitlockite-type structure have been prepared via the combustion-assisted synthesis technique. The XRD pattern show that the as-obtained phosphors crystallize in a trigonal phase with space group of *R*-3*c* (161). $Ca_8ZnCe(PO_4)_7$ host is full of sensitizers (Ce^{3+}) and the Ce^{3+} emission at different lattice sites has been discussed. The efficient energy transfers from Ce^{3+} ions to Eu^{2+}/Mn^{2+} ions and from Eu^{2+} to Mn^{2+} have been validated. Under UV excitation, the emitting color of $Ca_8ZnCe(PO_4)_7$:Eu^{2+}/Mn^{2+} samples can be modulated from violet blue to green and from violet blue to red-orange by the energy transfers of $Ce^{3+} \rightarrow Eu^{2+}$ and $Ce^{3+} \rightarrow Mn^{2+}$, respectively. Additionally, white emission has been obtained through adjusting the relative concentrations of Eu^{2+} and Mn^{2+} ions in the $Ca_8ZnCe(PO_4)_7$ host under UV excitation. These results indicate that as-prepared $Ca_8ZnCe(PO_4)_7$:Eu^{2+},Mn^{2+} may be a potential candidate as color-tunable white light-emitting phosphors.

1. Introduction

In recent years, rare-earth ions and transition-metal-ion-doped phosphors have attracted much interest due to their wide applications in lightings and displays. Rare-earth ions, such as Eu^{2+}, Ce^{3+}, Tb^{3+}, and transition-metal ion Mn^{2+}, usually act as luminescence centers in various phosphors [1]. Typically, by co-doping rare earth ions and/or Mn^{2+} ions into a proper host, the tunable emitting color could be realized through energy transfer between sensitizer and activator ions [2]. Various single-phase phosphors involving Eu^{2+}-Tb^{3+}/Mn^{2+} [3], Ce^{3+}-Tb^{3+}/Mn^{2+} [4], Ce^{3+}-Eu^{2+}-Mn^{2+} [5] and Ce^{3+}-Tb^{3+}-Eu^{3+} [6] have been developed and exhibit tunable white light emission by mixing the respective emission spectra, which can meet the requirements for different luminous environment.

Phosphate hosts for the luminescent materials have the merits of low synthetic cost, outstanding thermal stability and stabilization of ionic charge in the lattice. Being isostructural with β-$Ca_9In(PO_4)_7$ (space group *R*3*c*), phosphate compound with the chemical formula $Ca_9R(PO_4)_7$ (R = Y, La, Gd, Lu) [7–10] and $Ca_8MgR(PO_4)_7$ [11–14] have been widely studied as hosts for rare-earth ions and/or Mn^{2+}. Various Eu^{2+} and Mn^{2+} co-doped $Ca_9R(PO_4)_7$ phosphors with color-tunable white-light emission have been developed for use in UV-excited white LEDs. Ce is a cheap rare earth element and the Ce^{3+} ion has been acted as an activator in numerous phosphors due to its special optical properties of broad band emission. Very recently, Ce^{3+} has been used as one of the matrix cations in some orthophosphate phosphors, such as $Sr_3Ce(PO_4)_3$:Eu^{2+} [15], $Ca_9Ce(PO_4)_7$:Eu^{2+}, Mn^{2+} [16], $Ba_3Ce(PO_4)_3$:Eu^{2+} [17], $Ba_3Ce(PO_4)_3$: Tb^{3+}, Mn^{2+} and $Ba_3Ce(PO_4)_3$:Tb^{3+},Sm^{3+} [18]. $Ca_8ZnLa(PO_4)_7$:Eu^{2+},Mn^{2+} phosphor has also been reported to be with whitlockite-type structure and exhibit green emission [19]. However, as far as we know, the crystal structures and optical properties of $Ca_8ZnCe(PO_4)_7$ compound have not been reported as yet.

In this study, we report on the synthesis and Rietveld structural refinement of whitlockite-type phosphate $Ca_8ZnCe(PO_4)_7$. Eu^{2+} and Mn^{2+} ions are introduced into the $Ca_8ZnCe(PO_4)_7$ host and energy transfer from Ce^{3+} to Eu^{2+}/Mn^{2+} and coexcitation of Eu^{2+} and Mn^{2+} to generate white light are investigated. A wide range color-tunable tri-chromatic emission is realized by adjusting the Eu^{2+} and Mn^{2+} contents.

2. Experimental details

2.1. Sample preparation

$Ca_{8-x}Zn_{1-y}Ce(PO_4)_7$:$x$$Eu^{2+}$,$y$$Mn^{2+}$ (abbreviated as CZCP:$x$$Eu^{2+}$, $y$$Mn^{2+}$) samples were synthesized by a combustion-assisted

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synthesis method [20]. The stoichiometric amount of raw materials $NH_4H_2PO_4$ (analytical reagent, AR), $Ca(NO_3)_2 \cdot 4H_2O$ (AR), and $Zn(NO_3)_2 \cdot 6H_2O$ (AR) were thoroughly mixed, and an appropriate amount of $CO(NH_2)_2$ (AR) was added as fuel. $Ce(NO_3)_3 \cdot 9H_2O$ (99.99%), $MnCO_3$ (AR) and Eu_2O_3 (99.99%) were dissolved in HNO_3. These reagents were dissolved in water with continuous stirring for over 30 min and introduced into a muffle furnace maintained at 600 °C for 5 min. The obtained precursors were sintered at 1200 °C for 4 h under a H_2 atmosphere to form crystalline phosphates.

2.2. Characterizations

The crystal structure of CZCP:Eu^{2+},Mn^{2+} phosphors was checked using a D8 ADVANCE powder diffractometer (Bruker Corporation, Karlsruhe, Germany) with CuKα radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA. The structure refinement was carried out using the general structure analysis system (GSAS) program [21]. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with a Hitachi F-7000 fluorescence spectrometer equipped with 150 W xenon lamps used as the excitation source. The CIE chromaticity coordinates were calculated using the emission spectrum data. All the above-mentioned measurements were carried out at room temperature.

3. Results and discussion

3.1. Structure analysis

Fig. 1 illustrates the representative XRD patterns of the CZCP host and Eu^{2+}/Mn^{2+} doped CZCP samples, along with the reference diffraction lines based on the JCPDS card with no. 46-0409. All the reflection peaks of CZCP host can be indexed to the standard data of $Ca_8MgCe(PO_4)_7$ (JCPDS card no. 46-0409). This fact indicate that the CZCP host retains the single-phase structure of $Ca_8MgCe(PO_4)_7$. We can see that doping activators (Eu^{2+} or Mn^{2+}) are incorporated in the CZCP host and no impurity peaks or structural changes are observed, indicating that the as-prepared CZCP:Eu^{2+},Mn^{2+} samples are single phase, and the incorporations of Eu^{2+} and Mn^{2+} ions don't cause any obvious change in the host structure.

To further investigate the structure of the obtained samples, Rietveld refinement of undoped CZCP and CZCP:0.02Eu^{2+},0.16Mn^{2+} samples is performed with the experimental powder diffraction data. In the refinement, the starting mode comes from $Ca_8MgCe(PO_4)_7$ because CZCP host is isostructural with $Ca_8MgCe(PO_4)_7$, in which Mg site in $Ca_8MgCe(PO_4)_7$ phase is occupied by Zn. The initial structure model that approximates the actual structure of undoped CZCP and CZCP:0.02Eu^{2+},0.16Mn^{2+} is constructed with crystallographic data taken from the structure of $Ca_8MgCe(PO_4)_7$ [22]. The experimental and calculated diffraction XRD profiles as well as their difference for the Rietveld refinement of undoped CZCP and CZCP:0.02Eu^{2+},0.16Mn^{2+} samples are shown in Fig. 2. The refinement of undoped CZCP sample (Fig. 2a) finally converges to low R-factors, $R_{wp} = 9.63\%$, $R_p = 6.76\%$, $\chi^2 = 2.665$, indicating the obtained CZCP is of single phase. The result of the Rietveld refinement shows that the CZCP matrix belongs to the hexagonal unit cell with $R3c$ (No. 161) as the space group and cell parameters $a = b = 10.480$ Å, $c = 37.563$ Å, $V = 3572.8$ Å^3. The simulation of crystal structure of CZCP and the coordinated condition of CaCe1(18b), CaCe2(18b), CaCe3(18b) and Zn(6a), which are 8, 8, 9, and 6-coordinated, respectively, are displayed in Fig. 3. The refinement of CZCP:0.02Eu^{2+},0.16Mn^{2+} sample eventually converges to $R_{wp} = 9.32\%$, $R_p = 6.74\%$, and $\chi^2 = 2.626$, indicating that neither doped Eu^{2+} ions nor doped Mn^{2+} ions caused any impurity in CZCP host structure, as shown in Fig. 2b. The lattice parameters of CZCP:0.02Eu^{2+},0.16Mn^{2+} sample are $a = b = 10.490$ Å, $c = 37.553$ Å, $V = 3578.4$ Å^3. The ionic radii for 8 and 9-coordinated Ca^{2+} are 1.12 and 1.18 Å, 6-coordinated Zn^{2+} is 0.74 Å, respectively [24]. However, the ionic radii for 6-, 8- and 9-coordinated Eu^{2+} are 1.17, 1.25, and 1.3 Å. On the basis of ionic radii, the Eu^{2+} ions tend to randomly occupy the Ca^{2+} sites in the CZCP host. Mn^{2+} ions are expected to mainly occupy the Zn^{2+} sites due to the similar radii of Mn^{2+}

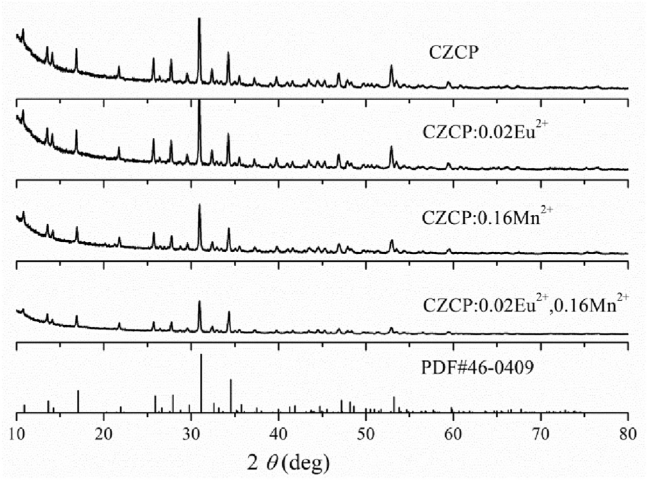

Fig. 1. Powder X-ray diffraction pattern of selected phosphors and JCPDS file no. 46-0409 ($Ca_8MgCe(PO_4)_7$) as a reference.

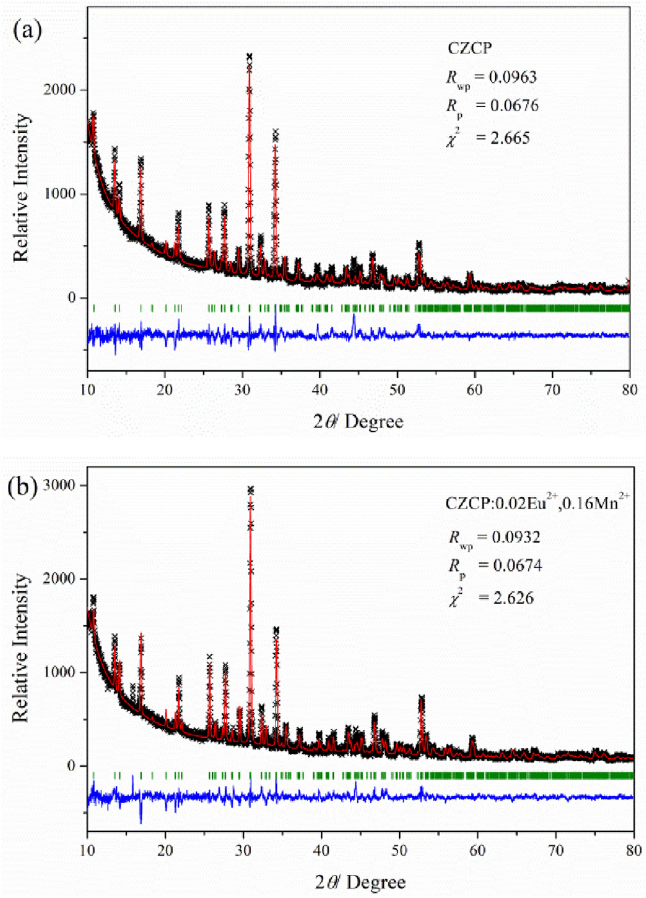

Fig. 2. Rietveld refinement results of the powder XRD pattern of (a) the CZCP matrix and (b) the CZCP:0.02Eu^{2+},0.16Mn^{2+} sample.