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Crystal structure, energy transfer and tunable luminescence of $Ca_8(Mg,Zn)Ce(PO_4)_7:Eu^{2+}$ solid solution phosphor

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ABSTRACT

Here we investigated the tunable luminescence properties of $Ca_8(Mg_{1-x}Zn_x)Ce(PO_4)_7:Eu^{2+}$ as a function of Zn^{2+} concentration. All the synthesized phosphors shared the same whitlockite-type structure and crystallized in the rhombohedral unit cell with the space group $R3c$ (no.161). Energy can be efficiently transferred from Ce^{3+} to Eu^{2+} in $Ca_8(Mg_{1-x}Zn_x)Ce(PO_4)_7:Eu^{2+}$ phosphors. Furthermore, the color of these phosphors can turn from blue to green with increasing the Zn content (x). Such tunable luminescence cannot be attributed to the effect of crystal field splitting or energy transfer between Ce^{3+} and Eu^{2+} ions. It is found that the modification of host composition via Zn substitution causes different Eu^{2+} sensitization efficiencies and induces the luminescence tuning. This mechanism may be general in iso-structural solid-solution phosphors and will be useful in tuning optical and other properties whose sensitization efficiency is sensitive to the host composition.

1. Introduction

Recently, inorganic phosphors have attracted more and more attention due to their broad applications in lighting and display fields [1,2]. Rare earth (RE) ions usually act as important activators due to their abundant emission colors based on the $4f-4f$ or $5d-4f$ transitions [3,4]. To meet the needs for various lighting sources, many efforts have been made in searching phosphors with good luminescent properties and high thermal stability. In this case, the design of a single-phase and color-tunable phosphor is obvious interest and importance [5]. In order to realize color-tunable emission in a single phase phosphor, the commonly used way is to utilize the principle of energy transfer between the co-doped activators [6,7], such as Ce^{3+}/Eu^{2+}, Ce^{3+}/Tb^{3+}, Ce^{3+}/Mn^{2+}, Eu^{2+}/Tb^{3+}, and Eu^{2+}/Mn^{2+}. On the other hand, Eu^{2+} or Ce^{3+}-doped phosphors possess a broadband emission due to the parity-allowed 5d–4f transition [8]. The variations of host compositions can change the local environment surrounding Eu^{2+} or Ce^{3+} ions, leading to different luminescent properties. As a result, the emitting color of Ce^{3+} or Eu^{2+} singly doped phosphors can be tuned via modifying the composition of host lattice through a solid solution with similar crystal structure [9–11] or changing the dopant concentration through energy transfer between different sites of Ce^{3+} or Eu^{2+} ions [12–14]. Furthermore, the combination of the above two methods may be more efficient to realize a single phase phosphor with ideal optical properties [15,16].

Phosphates have been widely used as the hosts for luminescence materials. Among numerous phosphates, whitlockite-type orthophosphates with chemical formula $Ca_8MgRE(PO_4)_7$ have attracted much interest, which can accommodate other cations with similar radii and charges without significant changes to the structural frame. Some $Ca_8MgRE(PO_4)_7$-type phosphors, such as $Ca_8MgGd(PO_4)_7:Eu^{2+}$ [17], $Ca_8MgR(PO_4)_7:Eu^{3+}$ (R = La, Gd, Y) [18], $Ca_8MgY(PO_4)_7:Eu^{2+},Mn^{2+}$ [19], $Ca_8MgLu(PO_4)_7:Tb^{3+}/Eu^{3+}$ [20], and $Ca_8MgLu(PO_4)_7:Ce^{3+},Tb^{3+},Mn^{2+}$ [21] have been reported. Being isostructural with β-$Ca_9In(PO_4)_7$ [22], the $Ca_8MgCe(PO_4)_7$ compound crystallizes in a rhombohedral cell (space group $R3c$ (No. 161)) with lattice constants of $a = 10.3842$ Å, $c = 37.223$ Å, $V = 3476.07$ Å^3, and $Z = 6$. Ce^{3+} acts as one of the matrix cations, and the concentration of Ce^{3+} is up to 100%, which can transfer a large amount of energy to the co-doping activator. To our knowledge, the related research about the $Ca_8MgCe(PO_4)_7$ compound is rarely reported. In this work, Eu^{2+} doped $Ca_8MgCe(PO_4)_7$ phosphor was prepared and the energy transfer between Ce^{3+} and Eu^{2+} ions was discussed. What is more, the similar ionic radii between Mg^{2+} and Zn^{2+} may make it possible to form a solid solution between $Ca_8MgCe(PO_4)_7$ and $Ca_8ZnCe(PO_4)_7$. The progressive substitution of Mg by Zn in $Ca_8MgCe(PO_4)_7$ host leads to different luminescence properties. Thus, a series of Eu^{2+}-doped $Ca_8(Mg_{1-x}Zn_x)Ce(PO_4)_7$ solid-solution phosphors were also synthesized. The structural evolution and the tunable luminescence properties with varied Zn/Mg ratio were discussed.

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2. Experimental section

$Ca_{8-y}(Mg_{1-x}Zn_x)Ce(PO_4)_7$:$y$$Eu^{2+}$ phosphors were synthesized by a combustion assisted synthesis method [23]. Stoichiometric amount of starting materials $NH_4H_2PO_4$ (analytical reagent, AR), $Ca(NO_3)_2·4H_2O$ (AR), $Mg(NO_3)_2·6H_2O$ (AR), and $Zn(NO_3)_2·6H_2O$ (AR) were thoroughly mixed, and an appropriate amount of $CO(NH_2)_2$ (AR) was added as fuel. $Ce(NO_3)_3·9H_2O$ (99.99%) 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 5% H_2/95%N_2 mixture gas to form crystalline phosphates. The samples prepared were cooled to room temperature in the furnace, and then ground to powders for subsequent measurements.

The X-ray powder diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer (Bruker Co., Karlsruhe, Germany) in the 2θ range from 10° to 80°, with graphite monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm) operating at 40 kV and 40 mA. Structure refinements were carried out using the General Structure Analysis System (GSAS) program [24]. The excitation (PLE) and emission (PL) spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer (Hitachi Co., Japan) with spectral resolution of 1.0 nm. The spectrophotometer was equipped with a 150 W xenon lamp as the excitation light source. For comparison, all measurements were performed at room temperature with the identical instrumental parameters.

3. Results and discussion

3.1. Phase identification and crystal structure

Fig. 1 shows the XRD profiles of the synthesized $Ca_{7.9}(Mg_{1-x}Zn_x)Ce(PO_4)_7$:0.1$Eu^{2+}$ ($0 \le x \le 1$) samples with various Zn^{2+} contents (x). The standard pattern of $Ca_8MgCe(PO_4)_7$ phase (JCPDS file no. 46–0419) is also given as a comparison. The diffraction peaks can be well indexed to the standard data except for a little shift, manifesting that these samples are isostructural with $Ca_8MgCe(PO_4)_7$ and doping of Eu^{2+}/Zn^{2+} ions has little influence on the structure. Fig. 1b shows the enlarged XRD patterns from 30 to 35°. With increasing the Zn^{2+} content (x), the diffraction peaks monotonically shift towards smaller angles, which is related to the substitution of smaller Mg^{2+} ($r = 0.72$ Å, CN = 6) by the larger Zn^{2+} ($r = 0.74$ Å, CN = 6) [25].

XRD Rietveld refinement was performed to check the chemical purity and phase homogeneity of the $Ca_{7.9}(Mg_{1-x}Zn_x)Ce(PO_4)_7$:0.1$Eu^{2+}$ samples. $Ca_8MgCe(PO_4)_7$ has a rhombohedral unit cell with the space group $R3c$ (no.161) [21]. No record of $Ca_8ZnCe(PO_4)_7$ is available in Joint Committee on Powder Diffraction Standards (JCPDS) or Inorganic Crystal Structure Database (ICSD). Since the $Ca_8ZnCe(PO_4)_7$ compound may be isostructural with $Ca_8MgCe(PO_4)_7$, the structural parameters reported on $Ca_8MgCe(PO_4)_7$ were used as initial parameters in Rietveld refinement. The experimental, calculated and difference results from the Rietveld refinement of the two end members $Ca_{7.9}MgCe(PO_4)_7$:0.1Eu^{2+} and $Ca_{7.9}ZnCe(PO_4)_7$:0.1Eu^{2+} are shown in Fig. 2. The refinement was convergent well with low residual factors, which demonstrated the single-phase nature of the phosphors.

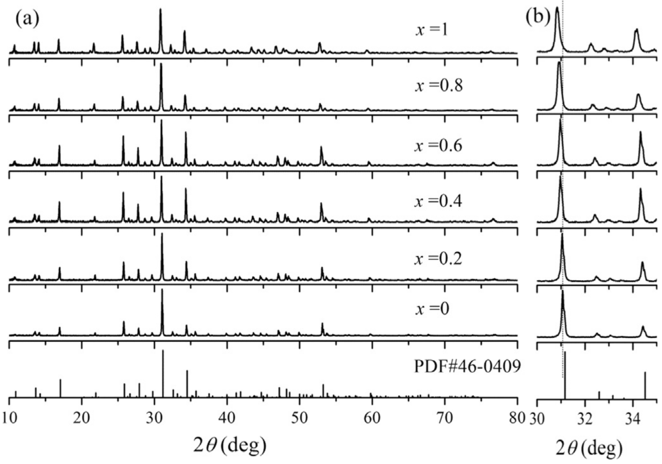

Fig. 1. XRD patterns of $Ca_{7.9}(Mg_{1-x}Zn_x)Ce(PO_4)_7$:0.1$Eu^{2+}$ samples and standard data for JCPDs no. 46–0409 (a); and the enlarged XRD patterns in the region from 30 to 35° (b).

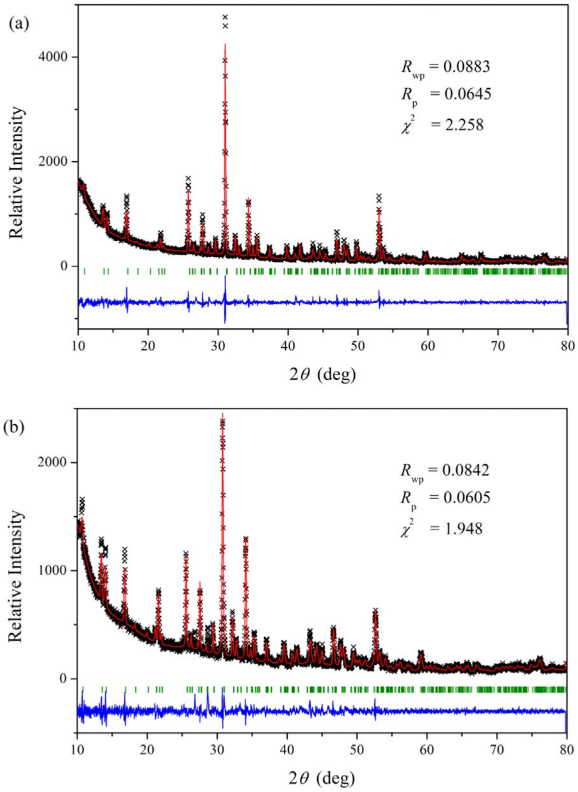

Fig. 2. Observed (crosses), calculated (solid line), and difference (bottom) powder XRD profiles for the Rietveld refinement of (a) $Ca_{7.9}MgCe(PO_4)_7$:0.1Eu^{2+} and (b) $Ca_{7.9}ZnCe(PO_4)_7$: 0.1Eu^{2+}. Bragg reflections are indicated by tick marks.

The crystal structure of $Ca_8(Mg_{1-x}Zn_x)Ce(PO_4)_7$ is depicted in Fig. 3. The whitlockite-type compound has six different metal sites (M1–M6) in the crystal lattice: the M4/M6 sites are vacant, and the M1, M2, M3 and M5 sites are 8, 8, 9 and 6 coordinated by oxygen atoms, respectively. Ca^{2+} and Ce^{3+} ions randomly occupy the M1, M2 and M3 sites, while Mg^2/Zn^{2+} ions occupy the M5 site. The Rietveld refinement results indicate that neither doping Eu^{2+} ions nor the substitution of Zn^{2+} for Mg^{2+} caused any impurity or secondary phases in Ca_8MgCe

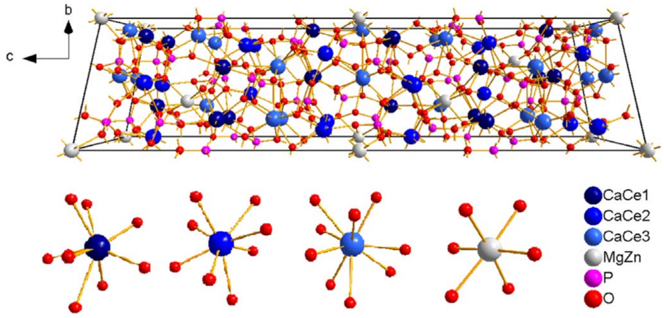

Fig. 3. Crystal structure of $Ca_8(Mg_{1-x}Zn_x)Ce(PO_4)_7$ along the a-axis direction and the coordination condition of Ca^{2+}, Ce^{3+}, Mg^{2+}, and Zn^{2+} ions.