



Preparation and luminescence properties of phosphors of rare earth complexes based on polyoxotungstates



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ABSTRACT

Three new phosphors of rare earth complexes based on polyoxotungstates, $K_3Cs_8[Eu(PW_{11}O_{39})_2] \cdot 11H_2O$ (**1**), $K_3Cs_8[Sm(PW_{11}O_{39})_2] \cdot 10H_2O$ (**2**), and $K_5Cs_6[Dy(PW_{11}O_{39})_2] \cdot 15H_2O$ (**3**) have been prepared and characterized. The crystallographic analyses reveal that these compounds consist of two monovacant keggin anions $[PW_{11}O_{39}]^{7-}$ connected by a rare earth ion in a sandwich structure. The investigations of photoluminescence properties show that phosphor **1** emits strong red light at 614 and 702 nm, **2** emits strong orange-red light at 598.7 nm, and **3** exists two strong emissions at 479 nm (blue) and 574 nm (orange). The luminescence properties suggest that the **1** can be applied as the potential red-emitting crystal phosphor, and the **3** may be regarded as a potential white light material for LEDs.

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1. Introduction

In the past years the studies on the rare earth luminescence materials mainly have focused on the oxides [1–5] and rare earth-doped compounds, such as borates [6], aluminates [7], molybdates [8,9], phosphates [10], and tungstates [11] etc. The most of these luminescence materials are powder, and there are few reports about the crystal phosphors [12]. The crystal phosphors have the advantage for enhancing the light extraction efficiency owing to its lower scattering compared with powder phosphors used for light-emitting diodes (LEDs). The flux growth is usually adopted as the preparation method of crystal phosphors, which needs high temperature and a long growth period [12]. Therefore, the preparation of the crystal phosphors with high efficiency of emission and great color purity is currently a challenging target for material scientists. Polyoxometalates have been extensively studied because of their important applications in various areas ranging from catalysis, electrochemistry, photochromism, medicine, to magnetism [13,14]. Recently, the luminescence materials of rare earth complexes based on polyoxometalates have attracted extensive interests because of the potential important application [15,16]. Polyoxometalates not only are a kind of anionic materials of

metal–oxygen clusters, but also important versatile inorganic building blocks for the polyoxometalate complexes with interesting structures, magnetism and luminescence properties [17–22]. Recently, considerable attention has been focused on the lanthanide ions substituted polyoxometalates [23–26] because (1) lanthanide ions have special electronic shell structures for the requirements of optical, electrical and magnetic materials and strong bonding force to the oxygen atoms at the defect sites in lacunary polyoxoanions; (2) lanthanide ions can readily link different lacunary polyoxoanions together leading to some novel oligomers or aggregates with unexpected structures, magnetism and photoluminescence properties; (3) the incorporation of lanthanides into polyoxometalates may extend their range of physical and chemical properties and allow access to an array of new potential applications of the resulting compounds.

The monovacant Keggin Polyoxometalate species, $[XW_{11}O_{39}]^{n-}$ ($X=Si^{IV}, P^V; n=7$ or 8) are the most common and widely used lacunary polyoxoanions [27]. Peacock and Weakley first put forward that the combination of $[XW_{11}O_{39}]^{n-}$ with lanthanide ions can form both 1:1-type and 1:2-type derivatives in solution [28]. Blasse et al. predicted that the structure of 1:2-type $[Ln(SiW_{11}O_{39})_2]^{13-}$ is an eight-coordinate environment which the lanthanide ion is sandwiched by two monovacant Keggin polyoxoanions [29]. Kortz et al. prepared a family of monolanthanide substituted Keggin silicotungstates, $[Ln(SiW_{11}O_{39})_2]^{13-}$ ($Ln=La^{III}, Ce^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Yb^{III}, Lu^{III}$) by the reaction of Ln^{3+} ions with the precursors $[SiW_{11}O_{39}]^{8-}$ in a 1:2 molar ratio in

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Table 1

The elemental analyses of compounds **1**, **2** and **3** (mass%, calculated values in parentheses).

Compound	1	2	3
Ln	2.205 (2.207)	2.198 (2.190)	2.387 (2.396)
W	58.675 (58.744)	58.785 (58.912)	59.615 (59.628)
K	1.702 (1.704)	1.705 (1.709)	2.924 (2.926)
Cs	15.438 (15.443)	15.478 (15.487)	11.763 (11.756)

aqueous solution [30]. Mialane, et al. investigated the luminescence properties of $K_{13}[Eu(SiW_{11}O_{39})_2] \cdot nH_2O$ compound, which may be potential candidates for efficient luminescence materials in the visible region [31]. Fedotov et al. investigated the lanthanide complexes with $[PW_{11}O_{39}]^{7-}$ in solution by NMR methods [32], and Zhang et al. studied the preparation and crystal structure of complex $[Eu(PW_{11}O_{39})_2]^{11-}$ [33]. However, there are rare reports on the preparation and luminescent properties of crystalline lanthanide complexes based on $[PW_{11}O_{39}]^{7-}$, especially the crystal phosphors. In this paper, we report the preparation and characterization of the crystal phosphors of lanthanide complexes based on the monovacant Keggin polyoxotungstates, $K_{11-x}Cs_x[Ln(PW_{11}O_{39})_2] \cdot nH_2O$ (Ln = Eu^{III}, Sm^{III}, Dy^{III}). Their crystal structures and photoluminescence properties were studied in detail.

2. Experimental

2.1. Materials

All the chemicals of $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%), $Sm(NO_3)_3 \cdot 6H_2O$ (99.99%), $Dy(NO_3)_3 \cdot 6H_2O$ (99.99%), CsCl (analytical reagent) and CH_3COOK (analytical reagent) were commercially available and used without further purification.

2.2. Preparation of the complexes

$H_3[PW_{12}O_{40}]$ was prepared according to the literature methods [34]. $H_3[PW_{12}O_{40}]$ (0.2 mmol) was dissolved in water and heated to 90 °C, then the solution of rare earth nitrate (0.30 mmol) was added into the above solution of $H_3[PW_{12}O_{40}]$ drop-wise under stirring, and the pH of the mixture was readjusted to 4–5 with KAc–HAc buffer solution (pH 4.3). After filtering and cooling, the filtrate was kept at 5 °C, the microcrystal of $K_{11}[Ln(PW_{11}O_{39})_2]$ (Ln = Eu^{III}, Sm^{III}, Dy^{III}) was obtained after several days. The $K_{11}[Ln(PW_{11}O_{39})_2]$ (1.00 mmol) was dissolved in water and heated to 70 °C, then the same molar amount of CsCl solid was added into the solution under stirring. After filtering, the filtrate was kept at room temperature for slow evaporation, the water white block crystals of $K_{11-x}Cs_x[Ln(PW_{11}O_{39})_2] \cdot nH_2O$ (Ln = Eu^{III}, Sm^{III}, Dy^{III}) were obtained after a few days.

Table 2

Summary of crystallographic data for compounds **1**, **2**, and **3**.

	1	2	3
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	12.309	12.233	12.958
<i>b</i> (Å)	19.811	19.726	19.811
<i>c</i> (Å)	21.905	21.800	21.829
α /deg	114.376	114.326	65.228
β /deg	94.937	95.0730	89.051
γ /deg	98.129	98.0210	74.869
Reflections collected/unique	40,140/16240 [<i>R</i> (int)=0.0523]	27,670/15177 [<i>R</i> (int)=0.0562]	33,614/17021 [<i>R</i> (int)=0.1001]
Goodness of fit	1.273	1.041	1.247
Final <i>R</i> ₁ , <i>wR</i> ₂	0.1119, 0.3026	0.0640, 0.1705	0.1688, 0.4062

2.3. Methods

The elemental analyses for Ln, W, K, Cs were performed on a Prodigy-XP ICP Emission Spectrometer. The elemental analyses results of these compounds are shown in Table 1. The crystal structures of these complexes were characterized by single-crystal X-ray diffraction. Single crystal X-ray diffraction data was collected on a Smart Bruker Apex II CCD diffractometer equipped with a graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å) at room temperature. Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using the SADABS routine. The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on *F*² (SHELXTL Version 5.1). All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms were assigned to calculated positions. The *R*₁ values are defined as $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. The details of the crystal parameters, data collection, and refinement are summarized in Table 2. The excitation and emission spectra and the luminescence decay were recorded on an Edinburgh instruments FLS920 spectrofluorimeter.

3. Results and discussion

3.1. Crystal structures

The crystal structure refinements show that compounds **1–3** crystallized in the triclinic space group *P*-1, and have similar structures to $[Ln(SiW_{11}O_{39})_2]^{13-}$ [29]. These compounds consist of complex anion $[Ln(PW_{11}O_{39})_2]^{13-}$, K⁺, Cs⁺ and crystalliferous H₂O. The different compound contains slightly unequal amounts of K⁺, Cs⁺ and crystalliferous H₂O. For complex $[Ln(PW_{11}O_{39})_2]^{11-}$ anion, the two monovacant Keggin $[PW_{11}O_{39}]^{7-}$ anions were connected by a Ln³⁺ ion with eight Ln–O(W) bonds to form the sandwich structure (see Fig. 1). The lanthanide ion is eight-coordinated with slightly different bond lengths of Ln–O, and the eight coordinated oxygen atoms are from the lacunary site of two monovacant Keggin, which construct the polyhedron structure (Fig. 2, left). The four coordinated terminal oxygen atoms from the lacunary site of monovacant Keggin unit form an approximate square, and the two slightly unequal squares are alternate to each other (see Fig. 2, right). We can quantify the above observation by using the twist angle θ which refers to the offset of the two unequal approximate squares built up from the respective four oxygen atoms at the lacunary site of each of the two Keggin units (see Fig. 2). The twist angle θ is close to 45°, and the bond lengths of Ln–O in $[Ln(PW_{11}O_{39})_2]^{11-}$ are in the range of 2.260–2.455 Å. The above results show that the Ln³⁺ ion locates in an eight-coordinated asymmetrical coordination environment with C₁ point group.

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