Accepted Manuscript

Host composition dependent tuneable morphology and luminescent property of the $Ca_XSr_YBa_{1-X-Y}WO_4:RE^{3+}$ (RE=Pr, Ho, and Er) phosphors

Linlin Li, Hong-Yue Wu

PII: S0925-8388(17)30289-X

DOI: 10.1016/j.jallcom.2017.01.255

Reference: JALCOM 40622

To appear in: Journal of Alloys and Compounds

Received Date: 13 November 2016

Revised Date: 17 January 2017

Accepted Date: 22 January 2017

Please cite this article as: L. Li, H.-Y. Wu, Host composition dependent tuneable morphology and luminescent property of the $Ca_XSr_YBa_{1-X-Y}WO_4$:RE³⁺ (RE=Pr, Ho, and Er) phosphors, *Journal of Alloys and Compounds* (2017), doi: 10.1016/j.jallcom.2017.01.255.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





Host composition dependent tuneable morphology and luminescent property of the $Ca_{X}Sr_{Y}Ba_{1-X-Y}WO_{4}$:RE³⁺ (RE=Pr, Ho, and Er) phosphors

Linlin Li^{a*}, Hong-Yue Wu^b

^aDepartment of Chemistry, Tonghua Normal University, Tonghua 134002, PR China

^bCollege of Chemistry, Jilin University, Changchun 130026, PR China

*Corresponding author. Tel.: +86 0435 3208077.

E-mail address: mumuandchacha@163.com

Abstract

Novel Pr^{3+} , Ho^{3+} , and Er^{3+} single-doped $Ca_XSr_YBa_{1-X-Y}WO_4$ phosphors were successfully prepared via a facile hydrothermal method. The hydrothermal process was conducted in aqueous condition without the use of any organic solvent, surfactant, or catalyst. The effects of doping-host composition and RE³⁺ doping concentration on the emission intensity were investigated to optimize the luminescent properties of Ca_XSr_YBa_{1-X-Y}WO₄:RE³⁺ phosphors. Experimental results demonstrate that the morphologies of the products vary gradually and regularly with the change of the host composition, in which the anisotropic growth played a key role. Moreover, the down-conversion emissions of Pr^{3+} , Ho^{3+} , and Er^{3+} in $Ca_X Sr_Y Ba_{1-X-Y} WO_4$ host were successfully $Ca_{0.4}Sr_{0.6}WO_4:0.01Pr^{3+}$, realized. properties, After optimizing the luminescent $Ca_{0.8}Sr_{0.2}WO_4:0.01Ho^{3+}$, and $Ca_{0.6}Sr_{0.4}WO_4:0.005Er^{3+}$ exhibited optimal luminescent property, with orange, yellowish-green, and green emissions, respectively.

Keywords: Hydrothermal method; Doping-host combination; Tungstate; Phosphor

1. Introduction

Rare-earth (RE) ions have received enormous attention based on their unique electronic and optical characteristics developed from the different arrangement of their 4f electrons [1]. Therefore, most rare-earth elements are often doped into many hosts and used as light-emitting materials and laser materials. Luminescence of rare-earth ions can be categorized as down-conversion and up-conversion emission processes, based on the mechanism of luminescence [2]. Among them, the down-conversion process is the conversion of higher energy photons into lower energy photons, which obeys Stokes' law [3]. The up-conversion process can emit a higher energy photon. In this process, the sequential absorption of two or more photons leads to the

emission of light, which is well known as an anti-Stokes emission process under near-infrared (NIR) or infrared light (IR) (low energy) excitation [4,5]. Accordingly, phosphors can be divided into down-conversion phosphors and up-conversion phosphors, which are usually distinguished by the doped rare-earth ions. The commonly used down-conversion activators include Eu^{3+} , Tb^{3+} , Sm^{3+} , and Dy^{3+} , which have abundant emission peaks in the whole visible region under UV light excitation [6-8]. Pr^{3+} , Er^{3+} , Tm^{3+} , and Ho^{3+} ions are the most common activators that generate up-conversion luminescence because of the ladder-like arrangement of their energy levels [9,10]. Among them, Er³⁺ shows the highest up-conversion efficiency, which could be due to the similar energy gaps from ${}^{4}I_{15/2}$ to ${}^{4}I_{11/2}$ and ${}^{4}I_{11/2}$ to ${}^{4}F_{7/2}$ [11]. However, in up-conversion process, some additional sensitizers must be added to donate their absorbed energy to the above activators, and Yb^{3+} ion is a particularly suitable sensitizer for these activator ions [12,13]. Pr^{3+} , Ho^{3+} , and Er^{3+} ions also can be excited by UV, near-UV, and blue light and then emit their nature light in the visible region. However, reports on this subject are still limited. As far as we know Tamrakar et al. [14] and Upadhyay et al. [15] prepared a $Gd_2O_3:Er^{3+}$ phosphor via the combustion synthesis method. Xin et al. [16] used solid-state method to synthesize a versatile phosphor $Sr_{10}[(PO_4)_{5,5}(BO_4)_{0,5}](BO_2):Pr^{3+}$. Zou et al. [17] developed a novel red emitting long persistent luminescent phosphor $Ca_2Ga_2GeO_7$: Pr^{3+} by mean of solid state reaction. All the above works have studied the down conversion properties of Er^{3+} and Pr^{3+} .

Metal tungstates have emerged as an important family of luminescent materials owing to their excellent spectroscopic properties, chemical stabilities [18], and potential applications as a catalyst [19], as a scintillator [20], for production of laser and phosphors and optical fibers [21-23]. MWO₄ (M=Ca, Sr, and Ba) possess the tetragonal scheelite structure with the space group $I4_1/a$. In these

compounds, W^{6+} is coordinated by four O^{2-} at a tetrahedral site, which makes WO_4^{2-} relatively stable. M^{2+} ions are coordinated by eight O^{2-} from near four WO_4^{2-} with S_4 symmetry [24]. As well known, WO_4^{2-} group has strong absorption in the UV region, so the energy transfer process from WO_4^{2-} group to rare-earth ions can easily occur, which can greatly enhance the external quantum efficiency of rare-earth ions doped materials [25]. Therefore, the MWO₄ could be a suitable host for Pr³⁺-, Ho³⁺-, and Er³⁺-activated phosphors. For instance, the emission spectrum of pure CaWO₄ shows an intense broadband ranging from 300 to 600 nm with a maximum at approximately 420 nm, and the blue emission band of CaWO₄ is due to its intrinsic emission. A number of studies concerning alkaline earth metal ions replace with each other (entirely or partly) in the same host, and some results show that the optical property of RE ions can been changed [24]. A variety of methods, such as sol-gel process, co-precipitation, hydrothermal and sonochemical methods, have been developed to prepare tungstates. Particularly, the hydrothermal method has been proven to be an efficient and convenient technique for the large-scale production of inorganic materials with diverse morphologies and regular particle sizes under practicable environments [26]. As a typical solution-based approach, this route is based on solution-phase colloidal chemistry, in which the reactants can be homogeneously mixed at molecular or ion level in solutions, thereby allowing the products to be precisely tuned in terms of composition, shape, and size [3]. Alkaline earth metal ions can replace each other in the same host due to the similar chemical properties and small ionic radius difference. Thus, Ca_XSr_YBa_{1-X-Y}WO₄ materials can be prepared by hydrothermal method.

The emission intensity of RE³⁺-doped phosphors could be manipulated by some conventional factors, such as doping-host composition, particle size, shape, phase, electric-field, doping

concentration, and so on. According to the reports, the rare-earth ions are embedded into the host lattice in low concentration (on the whole $\leq 5 \mod \%$) to reduce the concentration quenching of luminescence, and not changing the crystal structure of the host material [27,28]. Generally, an optimal doping concentration exists, at which the emission intensity has the maximum value. Many studies also showed that the emission intensities of RE^{3+} -doped phosphors are dependent on their size. Larger phosphors will show stronger total luminescence emission and a sharp increase in quantum yield. Less activator ions are found on the surface that suffer from the ligand induced or surface defect induced quenching of luminescence, as larger phosphors have smaller surface area, eventually resulting in less non-radiative relaxations of the surface activator ions [3,29,30]. As for the host composition, which can form solid solutions by adjusting the cations or anions of the host compound [31], the sub-lattice structures around the luminescent center ions (RE^{3+}) will be expected to be somewhat diverse. Therefore, the luminescent intensity of rare-earth ions should be enhanced. Unfortunately, reports about the effect of doping-host composition on the luminescent property are scarce and unsystematic. Because the host composition also can affect other factors, such as particle size, shape, phase, and electric-field, and these effects are complicated and hard to control.

Based on the above investigations and motivated by the attempt to develop novel efficient phosphors, series of Pr^{3+} , Ho^{3+} , and Er^{3+} single-doped $Ca_XSr_YBa_{1-X-Y}WO_4$ phosphors were prepared via a facile hydrothermal method. The morphologies of the products vary gradually and regularly with the change of the host composition. The down-conversion emissions of Pr^{3+} , Ho^{3+} , and Er^{3+} in $Ca_XSr_YBa_{1-X-Y}WO_4$ host were successfully realized in our work. Additionally, after optimizing their luminescent properties, $Ca_{0.4}Sr_{0.6}WO_4$:0.01 Pr^{3+} , $Ca_{0.8}Sr_{0.2}WO_4$:0.01 Ho^{3+} , and Ca_{0.6}Sr_{0.4}WO₄:0.005Er³⁺ exhibited the optimal luminescent property.

2. Experimental

2.1. Sample preparation

Ca_xSr_yBa_{1-X-y}WO₄:RE³⁺ (RE=Pr, Ho, and Er) phosphors were synthesized via a facile hydrothermal method. Na₂WO₄·2H₂O (A.R.), Ca(NO₃)₂·4H₂O (A.R.), Sr(NO₃)₂ (A.R.), Ba(NO₃)₂ (A.R.), Pr₆O₁₁ (99.99 %), Ho₂O₃ (99.99 %), and Er₂O₃ (99.99 %) were used as starting materials. Rare-earth nitrate aqueous solutions were produced by dissolving the corresponding rare-earth oxides in nitric acid solution under stirring. The resulting solutions were evaporated with heating, and then the residues were again dissolved in distilled water, transferred to a volumetric flask, and diluted. All the doping ratios of Pr^{3+} , Ho^{3+} , and Er^{3+} were molar in our experiments. In a typical synthesis process, the stoichiometric weights of M(NO₃)₂·nH₂O (M=Ca, Sr, and Ba) were dissolved into 20 mL deionized water, and then the required volume of RE(NO₃)₃ solution was added into the above solution, resulting in the formation of the mixed colorless solution of RE(NO₃)₃ and M(NO₃)₂ (labeled as M(NO₃)₂:RE³⁺). Meanwhile, 3.0 mmol of Na₂WO₄·2H₂O was dissolved into 15 mL deionized water. Then, under vigorous stirring, the above M(NO₃)₂:RE³⁺ mixed solution was slowly dropped into Na₂WO₄ solution. White precipitate was immediately observed in the glass beaker. The vigorous stirring was maintained for 30 min. Finally, the precursor solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was subsequently sealed and maintained at 120 °C for 12 h. After that, the autoclave was allowed to cool down to room temperature naturally. The resulted precursor was separated by centrifugation, washed by deionized water and absolute ethanol for several times, and then dried in vacuum at 70 °C. At last, the final sample was obtained.

Series of phosphors with different proportion of Ca, Sr, and Ba were synthesized to optimize the luminescent properties of $Ca_XSr_YBa_{1-X-Y}WO_4$:RE³⁺. These phosphors are marked as No. 1-21, and showed in table 1. Total ionic radius of alkaline earth ions is X $r(Ca^{2+}) + Y r(Sr^{2+}) + (1-X-Y)$ $r(Ba^{2+})$ for $Ca_XSr_YBa_{1-X-Y}WO_4$ host, and all the total ionic radii were listed in table 1.

2.2. Characterization

The samples were examined by X-ray diffraction (XRD) measurements performed on a Rigaku D/max-II B X-ray diffractometer with monochromatic Cu K_{α} radiation. Morphology and size of the as-synthesized products were characterised by field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi), and employed the accelerating voltage of 5 kV. Constituent elements of the as-prepared phosphors were detected by energy dispersive spectroscopy (EDS) using an X-ray detector attached to the FE-SEM instrument. Detailed morphological and structural analyses were observed by using a Hitachi 8100 transmission electron microscope (TEM, Hitachi, Tokyo, Japan). Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W Xe lamp as the excitation source. Photoluminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tuneable laser as the excitation. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Phase structure and composition

Measurements on the powder X-ray diffraction for all the samples were performed to verify the phase purity, and all the diffraction peaks can be well indexed to the standard data of pure single-phase scheelite structure CaWO₄, SrWO₄, or BaWO₄. The XRD patterns of all samples are

almost the same as each other, hence only the typical XRD patterns of Er³⁺-doped samples No. 7-11 are shown in Fig. 1a, as well as the standard data of SrWO₄ (JCPDS No. 08-0490). It can be seen that the diffraction patterns of $Ca_X Sr_Y Ba_{1-X-Y} WO_4: 0.005 Er^{3+}$ (X=0.2; Y=0.8, 0.6, 0.4, 0.2, 0) can be indexed with the pure tetragonal phase (space group: $I4_1/a$), and they are mostly consistent with the standard data of scheelite structured SrWO₄, except that there is a discernible shift in the position of the diffraction peaks, which can be explained by the difference in the total ionic radii of alkaline earth ions. The ionic sizes (CN=8) of these alkaline earth ions follow the trend: $r(Ca^{2+})$ $(1.12 \text{ Å}) < r(\text{Sr}^{2+}) (1.26 \text{ Å}) < r(\text{Ba}^{2+}) (1.42 \text{ Å}) [32]$. With increasing Ba^{2+} ions concentration, the total ionic radii increased as shown in table 1, and the diffraction peaks of $Ca_{X}Sr_{Y}Ba_{1-X-Y}WO_{4}:0.005Er^{3+}$ shift to a lower degree, in accordance with the Bragg equation: $\lambda = 2d\sin\theta$. From the schematic illustration of the tetragonal phase structure Ca/Sr/BaWO₄ (Fig. 1b), it can be seen that the central W^{6+} is coordinated by four equivalent O^{2-} at a tetrahedral site, while M^{2+} (M=Ca, Sr, or Ba) ions share corners with eight adjacent O²⁻ from near four WO₄²⁻ without an inversion centre. Considering the smaller ionic radius difference between M^{2+} and Er^{3+} , the doped Er³⁺ ions are expected to randomly occupy the Ca/Sr/Ba sites in the host lattice, thus no peaks corresponding to any other phases or impurities can be detected, which confirmed by the XRD results. Moreover, the above results also confirm that these products are pure substance, rather than a mixture of CaWO₄, SrWO₄, and BaWO₄.

EDS analysis of some scientifically selected products was performed to verify the presence of RE^{3+} and determine the chemical composition of the as-prepared phosphors. However, this analysis cannot be performed on the samples which contain both Sr and W, because the L_{α} signal of Sr overlaps with the M_{α} signal of W in the energy scale of about 1.9 keV. So only the EDS

spectra of $Ca_{0.8}Ba_{0.2}WO_4:0.01Ho^{3+}$, $Ca_{0.6}Ba_{0.4}WO_4:0.01Pr^{3+}$, $Ca_{0.4}Ba_{0.6}WO_4:0.005Er^{3+}$, and $Ca_{0.2}Ba_{0.8}WO_4:0.005Er^{3+}$ phosphors are presented in Fig. 2. These EDS data confirm the presence of calcium (Ca), barium (Ba), tungsten (W), oxygen (O), and the corresponding rare-earth element (Ho, Pr, and Er). With increasing Ba²⁺ concentration, it also can be seen clearly that the intensity of Ca peak decreased while that of Ba peak increased. The approximate molar ratios of Ca and Ba extracted from the EDS data are about 3.8, 1.5, 0.66, and 0.24 respectively, which is considerably closer to the theoretical value of 4.0, 1.5, 0.67, and 0.25. The results reveal that the obtained phosphors are consistent with the originally designed composition, and the phosphors with different proportion of Ca, Sr, and Ba can be successfully prepared by the hydrothermal method.

3.2. Morphological analysis

The morphology and size of a series of $0.5\% \text{ Er}^{3+}$ -doped Ca_xSr_yBa_{1-x-y}WO₄ were investigated by FE-SEM. The SEM images of Er³⁺-doped single-component CaWO₄, SrWO₄, and BaWO₄ are presented in Fig. S1 (in the Supporting Information). In order to write concisely, only the chemical formulas of the host are employed in this section. From Fig. S1a, it can be seen clearly that the as-prepared CaWO₄ shows the microsphere-like shape with an average diameter of about 5 µm. SEM image of SrWO₄ shown in Fig. S1b reveals that the product is composed of abundant hamburger-like microstructures, and the diameter of these micro-hamburgers is about 6 µm. Moreover, each micro-hamburger has a joint boundary dividing the particle into two hemispheres or four quarter spheres like SrWO₄. This phenomenon can be assigned to crystal twinning and splitting [33]. Fig. S1c displays the morphology of the BaWO₄. It can be seen clearly that the product is composed of uniform micro-cylinders, and there are some sawtooth at both ends of the cylinder. These cylinders are about 2 µm in length and 1 µm in diameter.

SEM images of SrWO₄:0.0025Er³⁺, SrWO₄:0.005Er³⁺, SrWO₄:0.01Er³⁺, and SrWO₄:0.015Er³⁺ were displayed in Fig. S2. It can be observed from Fig. S2 that with the increase of Er^{3+} ions doping concentration the shape and size of these samples are almost the same. It is because that the Er^{3+} ions have been embedded into the SrWO₄ lattices and the doping concentrations of Er^{3+} ions were so few that can't change the crystal structure and morphology of the sample.

SEM images of Er^{3+} -doped double-component $Ca_XSr_{1-X}WO_4$ (X=0.8, 0.6, 0.4, and 0.2) and CaWO₄, SrWO₄ for comparison are shown in Fig. 3. The images show that the morphologies of these samples change from microsphere-like to hamburger-like shape gradually with increasing Sr^{2+} ions concentration. As shown in Fig. 3b and c, both the $Ca_{0.8}Sr_{0.2}WO_4$ and $Ca_{0.6}Sr_{0.4}WO_4$ present a microsphere-like shape similar to that of CaWO₄, the average diameters of them are about 3 µm and 6 µm, respectively. With further increase of Sr^{2+} ions concentration, the joint boundary begins to appear and the joint boundary becomes more and more obvious as shown in Fig. 3d and e.

Fig. 4 shows the SEM images of Er^{3+} -doped double-component $Ca_XBa_{1-X}WO_4$ (X=0.8, 0.6, 0.4, and 0.2), as well as CaWO₄, BaWO₄ for comparison. It can be observed in Fig. 4 that the morphologies of these particles change from microsphere-like to microcylinder-like shape regularly with increasing Ba²⁺ ions concentration. $Ca_{0.8}Ba_{0.2}WO_4$ reveals a near microsphere-like shape with inhomogenous size ranging from 2 µm to 3 µm, as shown in Fig. 4b. SEM image of $Ca_{0.6}Ba_{0.4}WO_4$ in Fig. 4c shows that the middle parts of these microspheres begin to crack. With further increasing Ba²⁺ ions concentration, the micro-cylinders with about 3 µm in length and 2 µm in diameter appeared, as shown in Fig. 4d. It can be clearly observed that the $Ca_{0.2}Ba_{0.8}WO_4$ sample is also composed of micro-cylinders (Fig. 4e) and closer to the shape of BaWO₄. The average length of these micro-cylinders is about 3 μ m, and the average diameter is about 2 μ m. Moreover, it can be obviously seen that the sawtooth at the ends of the micro-cylinder becomes more and more obvious with increasing Ba²⁺ ions concentration.

Fig. 5 depicts the SEM images of Er^{3+} -doped double-component $Sr_XBa_{1-X}WO_4$ (X=0.8, 0.6, 0.4, and 0.2) and $SrWO_4$, $BaWO_4$ for comparison. By comparing the morphologies, it can be seen that the shapes of these particles change from hamburger-like to cylinder-like gradually with increasing Ba^{2+} ions concentration. Similar to the shape of $SrWO_4$, $Sr_{0.8}Ba_{0.2}WO_4$ shows a hamburger-like shape with an average diameter of about 3 µm (Fig. 5b). As shown in Fig. 5c, the morphology of $Sr_{0.6}Ba_{0.4}WO_4$ has a great change, and shows a dumbbell-like microstructure. The length of such $Sr_{0.6}Ba_{0.4}WO_4$ dumbbell is about 4 µm, and the width of the two terminals is about 3 µm, while the middle parts come near to 2 µm. It can be seen clearly from Fig. 5d that the as-prepared $Sr_{0.4}Ba_{0.6}WO_4$ shows the micro-cylinder shape with some sawtooth at both ends of the cylinder, and the average length of these cylinders is about 4 µm. With increasing Ba^{2+} ions concentration, the morphologies are more and more close to the micro-cylinder. The SEM image in Fig. 5e illustrates that the $Sr_{0.2}Ba_{0.8}WO_4$ sample is composed of a uniform cylinder-like structure with a length of about 3 µm.

Fig. 6 displays the SEM images of Er^{3+} -doped three-component $Ca_{0.6}Sr_{0.2}Ba_{0.2}WO_4$, $Ca_{0.4}Sr_{0.4}Ba_{0.2}WO_4$, $Ca_{0.4}Sr_{0.2}Ba_{0.4}WO_4$, $Ca_{0.2}Sr_{0.6}Ba_{0.2}WO_4$, $Ca_{0.2}Sr_{0.4}Ba_{0.4}WO_4$, and $Ca_{0.2}Sr_{0.2}Ba_{0.6}WO_4$ samples, respectively. These images clearly indicate that the final products tend to form the similar morphology to the single component CaWO₄, SrWO₄, or BaWO₄, depending on their main component. Fig. 6a gives the SEM image of Ca_{0.6}Sr_{0.2}Ba_{0.2}WO₄, it can be seen that the as-prepared product consists of microspheres with an average diameter of about 2.5

μm. In the case of Ca_{0.4}Sr_{0.4}Ba_{0.2}WO₄ sample (Fig. 6b), the morphology is also the microspheres-like shape with about 3 μm in diameter. From Fig. 6c, it can be seen that with increasing the Ba²⁺ ions concentration, the intermediate position of the Ca_{0.4}Sr_{0.2}Ba_{0.4}WO₄ microspheres has an obvious crack. Similar to the morphology of SrWO₄, the microstructure of Ca_{0.2}Sr_{0.6}Ba_{0.2}WO₄ is near the hamburger-like shape, and each micro-hamburger has a joint boundary dividing the particles into two hemispheres, as shown in Fig. 6d. The morphology of Ca_{0.2}Sr_{0.4}Ba_{0.4}WO₄ is converted to uniform dumbbell-like microstructure. The length of such Ca_{0.2}Sr_{0.4}Ba_{0.4}WO₄ dumbbell is about 3.5 μm, and the width of the two terminals is about 3 μm, while the middle parts come near to 2 μm. From Fig. 6f, it can be seen that the Ca_{0.2}Sr_{0.2}Ba_{0.6}WO₄ product exhibits cylinders-like shape with some sawtooth at both ends of the cylinder. The low magnification SEM images of typical three-component phosphors are also indicated in Fig. S3. It can be seen that these samples are consists of almost mono-dispersed and homogeneous particles with narrow size distribution.

TEM and selected area electron diffraction (SAED) analysis of the representative Er³⁺-doped three-component products was performed to obtain the detailed morphology and crystal structure of the above deferent shapes. The TEM images in Fig. 7 clearly illustrate that both the morphologies and sizes of these six samples are consistent with that observed from the SEM images which shown in Fig. 6. All the shapes of SAED patterns (inserted in TEM images) are fully concentric rings, implying that the products are polycrystalline. The interplanar spaces were calculated from the diameters of the rings, and compared with those in the JCPDS standard. Moreover, all SAED patterns show the same (1 1 2), (2 0 4), (1 1 6), and (3 1 6) planes which in good accordance with the XRD results.

According to the above results, it can be seen that each sample have only one shape, also proving that the products are pure substance, rather than a mixture of CaWO₄, SrWO₄, and BaWO₄. Moreover, in our experiments, the morphologies of the products vary gradually and regularly with the change of the host composition when other conditions are kept constant, which suggests that the composition plays a crucial role in the formation of Ca_xSr_yBa_{1-x-y}WO₄ with different morphologies. It is believed that the morphologies of the final products mainly relate to the intrinsic structure of the sample, the growth kinetics during the reaction, and the surface charge distribution of the crystal nucleus in the growth process [34-36]. Based on the experimental phenomena and the above results, we can carefully conclude that the formation of the above morphologies can be explained through three consecutive stages. Firstly, fast nucleation: at the initial stage, direct mixing of two solutions which containing Ca/Sr/Ba(NO₃)₂ and Na₂WO₄, white precipitate was immediately observed, due to the simple precipitation reaction. The formed tiny nuclei of Ca/Sr/BaWO4 can serve as precursors of the crystal. Secondly, dissolution and re-crystallization: when the precipitate was transferred into the autoclave, under the hydrothermal condition, the original nuclei dissolved and released Ca^{2+} , Sr^{2+} , Ba^{2+} , and WO_4^{2-} gradually. This step made the next reaction of Ca^{2+} , Sr^{2+} , Ba^{2+} and WO_4^{2-} slow down, and results in the formation of different shape Ca/Sr/BaWO₄ particles. Because the crystal faces of the samples with different proportion of Ca, Sr, and Ba have different growth rate. Even in on sample, the growth rates of different faces are different, which is called anisotropic growth. Eventually, further growth: each particle aggregated during the reaction process, which driven by the electrostatic interaction and the minimization of the total energy of the system, and finally result in the formation of the above different morphologies. Anisotropic growth is believed to be an important process to form diverse

morphologies [37], and the different proportion of Ca, Sr and Ba is a sensitive factor in deciding the anisotropic growth, so the morphologies change with the host composition.

3.3. Luminescence properties of Pr³⁺, Ho³⁺ and Er³⁺ single-doped SrWO₄ phosphors

Fig. 8a illustrates the excitation (EX) and emission (EM) spectra of SrWO₄:0.01Pr³⁺ phosphor. Monitored at 644 nm, the excitation spectrum consists of an intense broadband and three sharp excitation peaks. The wide band ranging from 250 to 320 nm is responsible for the charge transfer band (CTB) of $O^{2-}\rightarrow W^{6+}$ within the tungstate group. The strong CTB is favourable for the effective energy transfer and luminescence of Pr³⁺. The sharp excitation peaks which located at 448, 472, and 485 nm are corresponded to ${}^{3}H_{4}\rightarrow {}^{3}P_{2}$, ${}^{3}H_{4}\rightarrow {}^{3}P_{1}$, and ${}^{3}H_{4}\rightarrow {}^{3}P_{0}$ transitions of Pr³⁺, respectively [38]. It can be seen that the SrWO₄:Pr³⁺ phosphor can be effectively excited by blue light. Under the excitation of 448 nm light, the corresponding emission spectrum exhibits a series of emission peaks belonging to the characteristic transitions of Pr³⁺. Seven major emission peaks at about 528, 553, 600, 616, 644, 682, and 736 nm are assigned to the ${}^{3}P_{1}\rightarrow {}^{3}H_{5}$, ${}^{3}P_{0}\rightarrow {}^{3}H_{5}$, ${}^{1}D_{2}\rightarrow {}^{2}H_{4}$, ${}^{3}P_{0}\rightarrow {}^{3}H_{2}$, ${}^{3}P_{0}\rightarrow {}^{3}F_{3}$, and ${}^{3}P_{0}\rightarrow {}^{3}F_{4}$ transitions, respectively [39]. The strong sharp red emission peak at 644 nm should be of value in improving the colour rendering index.

The measured excitation and emission spectra of $SrWO_4:0.01Ho^{3+}$ phosphor are presented in Fig. 8b. The excitation spectrum was obtained by monitoring 657 nm emission which corresponding to the ${}^5F_5 \rightarrow {}^5I_8$ transition of Ho^{3+} . Its excitation spectrum also consists of two parts, one is an intense broadband ranging from 250 to 320 nm attributed to the CTB, the other one is composed of some sharp lines from 350 to 500 nm, which is ascribed to the intra f-f transitions of Ho^{3+} ions. These obvious excitation peaks at 360, 400, 417, 450, and 482 nm are attributed to the electronic transitions from the 5I_8 ground state to the 5G_2 , 5G_4 , 5G_5 , 5F_1 , and 5F_2 excited states of

Ho³⁺ ions, respectively. The remarkable excitation bands locate in the blue region indicate that the SrWO₄:0.01Ho³⁺ can act as a potential blue light exciting phosphor. From the corresponding emission spectrum excited at 450 nm, we can see that the emission spectrum consists of three prominent peaks centered at 541, 614, and 657 nm. These peaks are assigned to the ${}^{5}F_{4}/{}^{5}S_{2}\rightarrow {}^{5}I_{8}$, ${}^{5}F_{2}\rightarrow {}^{5}I_{7}$, and ${}^{5}F_{5}\rightarrow {}^{5}I_{8}$ transitions of Ho³⁺ ions, respectively [40]. Moreover, the strongest emission at 657 nm is observed as two sub-peaks, due to the Stark energy splitting, which is the (2*J*+1) Stark components of *J*-degeneracy splitting. It is influenced by the crystal field around Ho³⁺ ions in the host lattice.

Fig. 8c presents the excitation and emission spectra of the SrWO₄:0.005Er³⁺ phosphor. Monitored with the characteristic ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ emission of Er³⁺ at 550 nm, the excitation spectrum contains the absorption of the host and the general f-f transitions of Er³⁺ ions. The strongest excitation peak centered at 378 nm is due to the transition of Er³⁺ ions from the ground state ${}^{4}I_{15/2}$ to the excited state ${}^{4}G_{11/2}$. Upon the excitation of 378 nm light, the emission spectrum of SrWO₄:0.005Er³⁺ phosphor should be divided into three parts: the sharp peaks in the 513-536 nm and 536-569 nm green region are assigned to the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transitions respectively, while the weak peaks in the 644-678 nm red region are assigned to ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition [41]. Moreover, each emission is found to be two sub-peaks just like that of Ho³⁺ ions. In order to clearly show the transition process of these rare-earth ions, the energy level schemes of Pr³⁺, Ho³⁺, and Er³⁺ are shown in Fig. 8d. According to the above results, it can be seen that the down-conversion emission of Pr³⁺, Ho³⁺, and Er³⁺ in SrWO₄ host have been successfully realized in our work.

The photoluminescence decay curves of SrWO₄:0.01Pr³⁺, SrWO₄:0.01Ho³⁺, and

SrWO₄:0.005Er³⁺ phosphors were monitored at their strongest emission peaks and shown in Fig. 9. It indicates that all the decay curves can be well fitted into a single exponential function as $I=I_0$ exp (- t/τ), in which *I* is the emission intensity at time t, τ is the decay lifetime. The fitting results were 0.38499, 1.5078, and 0.52749 ms for SrWO₄:0.01Pr³⁺, SrWO₄:0.01Ho³⁺, and SrWO₄:0.005Er³⁺ phosphors, respectively.

3.4. Influence of the doping concentrations on the luminescent properties of Pr^{3+} , Ho^{3+} , and Er^{3+} doped SrWO₄ phosphors

The emission intensity of RE^{3+} -doped phosphors could be manipulated by doping-host combination, particle size, shape, phase, electric-field, doping concentration, and so on, as mentioned above. Therefore the influences of doping concentrations and host compositions on the luminescent properties of Pr^{3+} , Ho^{3+} , and Er^{3+} single-doped $Ca_XSr_YBa_{1-X-Y}WO_4$ phosphors are systematically studied in this section.

The emission spectra of SrWO₄ phosphors with different RE³⁺ concentrations excited at their strongest excitation wavelength were presented in Fig. 10a-c, and the variation trend of relative emission intensity with different RE³⁺ concentrations was shown in Fig. 10d. It can be observed from the emission spectra of SrWO₄:xPr³⁺ (Fig. 10a) that the peak positions and their regular pattern of every curve are very similar except for the intensity. With increase of Pr³⁺ ions concentration, the emission intensities increase firstly and reach a maximum at x=0.01, then decrease with the further increase of Pr³⁺ ions concentration, excessive doping leads to concentration quenching of the Pr³⁺ emission. The emission spectra of SrWO₄:yHo³⁺ reveal the similar variation trend as SrWO₄:xPr³⁺, as shown in Fig. 10b. When Ho³⁺ ions are doped into SrWO₄ host, an initial increasing of emission intensity is observed with increase of Ho³⁺ ions

doping concentration, which can be summarized as the increase of luminescence centres. Then the emission intensity reaches the maximum value at y=0.01 and finally decreases beyond 0.01 due to concentration quenching, which results from energy transfer between adjacent luminescence centers. It can be seen clearly from Fig. 10c that the intensities of emission transitions of SrWO₄:zEr³⁺ phosphors enhance with the increase of Er³⁺ ions concentration and reach a maximum at z=0.005. Then they reduce inversely because of concentration quenching. In summary, the above results suggest that the optimum doped concentrations of Pr³⁺, Ho³⁺, and Er³⁺ in SrWO₄ host are 0.01, 0.01, and 0.005, respectively.

With the increase of RE³⁺ ions concentration, the average distance between RE³⁺ ions will reduce. The excitation energy may transfer between the close RE³⁺ ions [42]. For this reason, it is necessary to obtain the critical distance (R_c), which is the critical separation between donors (activators) and acceptors (quenching site). The critical distance R_c of the energy transfer between the same activators Pr³⁺, Ho³⁺, or Er³⁺ in the SrWO₄ host can be estimated according to the following equation:

$$R_c = 2 \left(\frac{3V}{4\pi x_c N} \right)^{\frac{1}{3}} \tag{1}$$

Where χ_c is the critical concentration, *N* is formula units in the SrWO₄ unit cell and *V* is the volume of the unit cell. By taking the experimental and analytic values of χ_c , *N*, and *V* (0.01, 4, 349.80 Å³ for Pr³⁺; 0.01, 4, 348.48 Å³ for Ho³⁺; 0.005, 4, 350.66 Å³ for Er³⁺, respectively) the critical transfer distances of Pr³⁺, Ho³⁺, and Er³⁺ in the SrWO₄ host are found to be about 25.57, 25.53, and 32.24 Å, respectively.

In addition, concentration quenching usually is the result of non-radiative energy transfer among luminescent centers. Non-radiative energy transfer from one RE^{3+} to another RE^{3+} may

take place via exchange interaction, radiation reabsorption, or electric multipolar interaction [43]. The exchange interaction needs a large direct or indirect overlap between donor and acceptor, which is responsible for the energy transfer for forbidden transitions and shorter critical distances of less than 5 Å [44]. In single-doped SrWO₄ phosphors the R_C are much larger than 5 Å, hence, the mechanism of exchange intercalation is ineffective. The mechanism of radiation reabsorption comes into force only when the emission and the excitation spectra have broad overlap. Thus, the small spectra overlap for the SrWO₄:Pr³⁺/Ho³⁺/Er³⁺ phosphors indicates that the radiation of reabsorption can be ignored in this case. As a result, the energy transfer process of RE³⁺ ions in SrWO₄ would be due to electric multipolar intercalation. There are three electric multipolar interactions: dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole, respectively.

According to the theory of Dexter, The emission intensity *I* is expressed by the formula given in the following [45]:

$$I / x = k[1 + \beta(x)^{\theta/3}]^{-1}$$
⁽²⁾

Where *x* is the activator concentration, *k* and β are constants under the same excitation condition for a certain system, θ represents the interaction mechanism between rare-earth ions, and $\theta = 6, 8$, or 10 for electric dipole-dipole, dipole-quadrupole, or quadrupole-quadrupole interactions, respectively. Fig. 11 shows that the relationship of log(I/x) versus logx is linear and the slopes are -3.60, -2.11, and -2.54 for Pr³⁺, Ho³⁺, and Er³⁺ respectively. By using the above formula (2), the values of θ are found to be 10.80, 6.33, and 7.62, which are approximately equal to 10, 6, and 8. Therefore, the dominant concentration quenching mechanisms for Pr³⁺, Ho³⁺, and Er³⁺ in SrWO₄ host are electric quadrupole-quadrupole, dipole-dipole, and dipole-quadrupole interaction, respectively.

3.5. Influence of the host compositions on the luminescent properties of Pr³⁺, Ho³⁺, and Er³⁺ doped Ca_XSr_YBa_{1-X-Y}WO₄ phosphors

Series of phosphors with different proportion of Ca, Sr, and Ba were synthesized to further optimize the luminescent properties of $Ca_XSr_YBa_{1-X-Y}WO_4:RE^{3+}$. The excitation and emission spectra of all these phosphors were examined. There are so many spectra, so only that of the typical Pr^{3+} -doped three-component samples were presented in Fig. 12. It can be clearly observed that the peak positions and their regular pattern of both excitation and emission spectra are very similar with each other except for the intensity. All the strongest excitation peaks are located at 448 nm, and the strongest emission peaks are located in a very narrow range (644-648 nm, show in the insert of Fig. 12b). These transitions are assigned to the 4f-4f intra-configurational transitions, which are shielded by neighbouring $5s^25p^6$ shells, so these transitions have low susceptibility to crystal-field and environment.

Fig. 13 a, b, and c show the intensity variation trend of $Ca_xSr_yBa_{1-X-Y}WO_4:0.01Pr^{3+}$ at 644 nm, $Ca_xSr_yBa_{1-X-Y}WO_4:0.01Ho^{3+}$ at 657 nm, and $Ca_xSr_yBa_{1-X-Y}WO_4:0.005Er^{3+}$ at 550 nm, respectively. In order to ensure the repeatability and accuracy of these data, three repeated tests have been conducted under the same reaction conditions.

It can be seen from Fig. 13a that the luminescent intensity of the phosphors prepared three times may change slightly, but they have the same variation trend in the three tests (in addition to the second point in the test 3). The optimum doping-host composition is $Ca_{0.4}Sr_{0.6}WO_4$ for Pr^{3+} ions. The emission at 644 nm is ascribed to the ${}^{3}P_0 \rightarrow {}^{3}F_2$ hypersensitive transition of Pr^{3+} ($\Delta S=0$, $\Delta J=2$, $\Delta L=2$) [46], which is corresponding to the forced electric dipole transition, and strongly varies with the chemical environment surrounding of Pr^{3+} . The f-f hypersensitivity transition of

rare-earth ions is related to numerous factors. Moreover, the factors that affect the transitions are very complicated [47]. The ionic radius, morphology, and crystallinity of the prepared phosphors in our experiment all varied with the host composition, which leads to the emission intensities reveal a non-monotonic decreasing (or increasing) variation trend. On one hand, it is possible that increasing the total ionic radius of alkaline earth metal ions can distort the hosts' structures. In other words, it can lead to the larger degree of disorder and lower local symmetry of Pr^{3+} ions. Eventually, it can improve the ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$ transition of Pr^{3+} . On the other hand, with the increasing of the total ionic radius, the bond covalency of Ca_xSr_yBa_{1-X-Y}-O will decrease and the length of the Pr-O bond becomes longer. Depending on the theory of B. R. Judd, the higher covalency has the greater transition intensity [46], and the long $Pr^{3+}O^{2-}$ distance decreases the exchange interaction probability for Pr³⁺ ions to transfer energy. So the lower covalency and longer distance of Pr-O bond may result in the decrease of ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$ transition intensity. And the results of the emission intensity led by the above two aspects are contradictory. Furthermore, the morphology and size of the synthetic phosphors also have great influence on the emission intensity of RE^{3+} -doped phosphors. The phosphors with nearly spherical shape and big size will have stronger emission intensity. Because larger crystals imply a smaller surface area and less RE³⁺ ions near to the surface to suffer from the ligand-induced and surface-defect quenching of luminescence, resulting in less nonradiative decay losses of the surface luminescence ions [3]. The improved emission intensity in the spherical phosphors can be basically attributed to the high packing densities and low scattering of light [48]. Eventually, as a comprehensive result of the above factors, the emission intensities reveal a non-monotonic decreasing (or increasing) variation trend, as shown in Fig. 13a.

The emission intensity variation trend of $Ca_XSr_YBa_{1-X-Y}WO_4:0.01Ho^{3+}$ at 657 nm shows that the emission intensities of the phosphors prepared three times have the same variation trend (Fig. 13b). The optimum host composition is $Ca_{0.8}Sr_{0.2}WO_4$ for Ho^{3+} ions. The intensity variation trend of $Ca_XSr_YBa_{1-X-Y}WO_4:0.005Er^{3+}$ at 550 nm is also the same (except the fifth point in the test 1), as shown in Fig. 13c. The optimum host composition is $Ca_{0.6}Sr_{0.4}WO_4$ for Er^{3+} ions. Like $Ca_XSr_YBa_{1-X-Y}WO_4:0.01Pr^{3+}$, the emission intensities of $Ca_XSr_YBa_{1-X-Y}WO_4:0.01Ho^{3+}$ and $Ca_XSr_YBa_{1-X-Y}WO_4:0.005Er^{3+}$ phosphors also reveal a non-monotonic decreasing (or increasing) variation trend due to the multiple factors. Unfortunately, the present work did not obtain a precise rule, because these effects are complicated and hard to control, needing further investigation. As can be seen from the present results, the optimum host compositions only contain Ca and Sr. So in our later work, we will research the influence of different proportion of Ca and Sr on the luminescent properties of $Ca_XSr_{1-X}WO_4:RE^{3+}$ phosphors.

Chromaticity coordinates is one of the important factors in evaluating the performance of the chromaticity coordinates of $Ca_{0.4}Sr_{0.6}WO_4:0.01Pr^{3+}$, prepared phosphors. the So Ca_{0.8}Sr_{0.2}WO₄:0.01Ho³⁺, and Ca_{0.6}Sr_{0.4}WO₄:0.005Er³⁺ phosphors have been calculated based on the corresponding emission spectrum and using the CIE 1931 colour matching functions. The chromaticity coordinates are (0.572, 0.420), (0.393, 0.591), and (0.290, 0.686) respectively, and they have been represented in Fig. 13d. The corresponding correlated colour temperatures are 1865, 4617, and 6224 K respectively. It can be seen that the $Ca_{0.4}Sr_{0.6}WO_4:0.01Pr^{3+}$ phosphor will orange light, $Ca_{0.8}Sr_{0.2}W0_4:0.01Ho^{3+}$ emit will emit yellowish green light, and $Ca_{0.6}Sr_{0.4}WO_4:0.005Er^{3+}$ will emit green light.

4. Conclusions

In summary, $Ca_XSr_YBa_{1-X-Y}WO_4:RE^{3+}$ (RE=Pr, Ho, and Er) phosphors have been successfully prepared via a facile hydrothermal method. The morphologies of the products vary gradually and regularly with the change of the host composition, in which the anisotropic growth has played a key role. Down-conversion emissions of Pr^{3+} , Ho^{3+} , and Er^{3+} in $Ca_XSr_YBa_{1-X-Y}WO_4$ host have been successfully realized. The emission intensities of $Ca_XSr_YBa_{1-X-Y}WO_4:RE^{3+}$ phosphors reveal a non-monotonic decreasing (or increasing) variation trend due to the multiple factors. Additionally, among these phosphors, $Ca_{0.4}Sr_{0.6}WO_4:0.01Pr^{3+}$, $Ca_{0.8}Sr_{0.2}WO_4:0.01Ho^{3+}$, and $Ca_{0.6}Sr_{0.4}WO_4:0.005Er^{3+}$ have the optimal luminescent property, and these phosphors will emit orange, yellowish green, and green light, respectively.

Acknowledgment

This present work was financially supported by Department of Chemistry, Tonghua Normal University and College of Chemistry, Jilin University.

References

[1] D. Singh, V. Tanwar, A.P. Simantilke, B. Mari, P.S. Kadyan, I. Singh, Rapid synthesis and photoluminescent characterization of $MAl_2O_4:Eu^{2+},Dy^{3+}$ (M=Ca/Ca⁺ Ba/Ca⁺ Mg) blue nanophosphors for white lighting display applications, Adv. Mater. Lett. 7 (2016) 47-53.

[2] Y. Zhang, X. Li, D. Geng, M. Shang, H. Lian, Z. Cheng, J. Lin, YOF nano/micro-crystals: morphology controlled hydrothermal synthesis and luminescence properties, CrystEngComm 16 (2014) 2196-2204.

[3] S. Gai, C. Li, P. Yang, J. Lin, Recent progress in rare earth micro/nanocrystals: soft chemical synthesis, luminescent properties, and biomedical applications, Chem. Rev. 114 (2014) 2343-2389.

[4] G. Li, C. Li, Z. Xu, Z. Cheng, J. Lin, Facile synthesis, growth mechanism and luminescence properties of uniform $La(OH)_3$:Ho³⁺/Yb³⁺ and La_2O_3 :Ho³⁺/Yb³⁺ nanorods, CrystEngComm 12 (2010) 4208-4216.

[5] R.K. Tamrakar, D.P. Bisen, K. Upadhyay, I.P. Sahu, Upconversion and colour tunability of Gd_2O_3 : Er^{3+} phosphor prepared by combustion synthesis method, J. Alloys Compd. 655 (2016) 423-432.

[6] D. Yue, W. Lu, C. Li, X. Zhang, C. Liu, Z. Wang, Controllable synthesis of Ln³⁺ (Ln=Tb, Eu) doped zinc phosphate nano-/micro-structured materials: phase, morphology and luminescence properties, Nanoscale 6 (2014) 2137-2145.

[7] H. Xu, Q. Sun, Z. An, Y. Wei, X. Liu, Electroluminescence from europium (III) complexes, Coordin. Chem. Rev. 293-294 (2015) 228-249.

[8] S. Ye, F. Xiao, Y.X. Pan, Y.Y. Ma, Q.Y. Zhang, Phosphors in phosphor-converted white light-emitting diodes: recent advances in materials, techniques and properties, Mater. Sci. Eng. R 71 (2010) 1-34.

[9] J. Zhang, J. Jia, Morphologies and up-conversion luminescence of $Gd_4O_3F_6$:RE³⁺ (RE=Yb, Er, Ho and Tm) phosphors by hydrothermal synthesis, J. Lumin. 174 (2016) 1-5.

[10] J. Tang, J. Gou, G. Li, H. He, Y. Li, C. Li, Tunable upconversion luminescence from the phosphors of Yb^{3+} , Tm^{3+} and Ho^{3+} tri-doped Re_2TeO_6 (Re=La, Gd, and Lu), J. Alloys Compd. 672 (2016) 1-6.

[11] H. Dong, L. Sun, C. Yan, Energy transfer in lanthanide upconversion studies for extended optical applications, Chem. Soc. Rev. 44 (2015) 1608-1634.

[12] X. Wang, Q. Liu, Y. Bu, C. Liu, T. Liu, X. Yan, Optical temperature sensing of rare-earth ion

doped phosphors, RSC Adv. 5 (2015) 86219-86236.

[13] A. Kumar, S.P. Tiwari, K. Kumar, V.K. Rai, Structural and optical properties of thermal decomposition assisted Gd_2O_3 :Ho³⁺/Yb³⁺ upconversion phosphor annealed at different temperatures, Spectrochim. Acta A 167 (2016) 134-141.

[14] R.K. Tamrakar, D.P. Bisen, K. Upadhyay, I.P. Sahu, M. Sahu, The down conversion properties of a Gd_2O_3 : Er^{3+} phosphor prepared via a combustion synthesis method, RSC Adv. 6 (2016) 92360-92370.

[15] K. Upadhyay, R.K. Tamrakar, D.P. Bisen, I.P. Sahu, M. Sahu, Enhancement of photoluminescence behavior of Gd_2O_3 :Er³⁺ phosphor by alkali metal, Optik 127 (2016) 3693-3697.

[16] S. Xin, G. Zhu, The synthesis and photoluminescence properties investigation of a versatile phosphor Sr₁₀[(PO₄)_{5.5}(BO₄)_{0.5}](BO₂):Sb³⁺/Eu³⁺/Pr³⁺/Dy³⁺, J. Lumin. 181 (2017) 443-447.

[17] Z. Zou, C. Cao, T. Zhang, L. Feng, J. Zhang, Z. Ci, Z. Zhang, Y. Wang, Structure, long persistent luminescent properties and mechanism of a novel efficient red emitting Ca₂Ga₂GeO₇:Pr³⁺ phosphor, J. Alloys Compd. 680 (2016) 397-405.

[18] Y. Zhang, W. Gong, J. Yu, Z. Cheng, G. Ning, Multi-color luminescence properties and energy transfer behaviour in host-sensitized CaWO₄:Tb³⁺,Eu³⁺ phosphors, RSC Adv. 6 (2016) 30886-30894.

[19] J. Lin, J. Yang, J. Gao, Q. Wang, Template synthesis, structure, optical and catalytic properties derived from novel cadmium tungstates, Polyhedron 113 (2016) 102-108.

[20] S.B. Arab, A. Belkahia, Low background detector with enriched ¹¹⁶CdWO₄ crystal scintillators to search for double β decay of ¹¹⁶Cd, J. Instrum. 6 (2011): 29-33.

[21] P.A. Loiko, K.V. Yumashev, N.V. Kuleshov, A.A. Pavlyuk, Thermo-optic coefficients of Nd-doped anisotropic KGd(WO₄)₂, YVO₄ and GdVO₄ laser crystals, Appl. Phys. B 102 (2016): 117-122.

[22] Y. Zheng, H. You, K. Liu, Y. Song, G. Jia, Y. Huang, M. Yang, L. Zhang, G. Ning, Facile selective synthesis and luminescence behavior of hierarchical NaY(WO₄)₂:Eu³⁺ and Y₆WO₁₂:Eu³⁺, CrystEngComm 13 (2011) 3001-3007.

[23] Y.Q. Chen, G.T. Yang, J.Y. Luo, Y.S. Yang, Q.G. Zeng, J.H. Jeong, Surfactant effect on formation of CaWO₄:Eu³⁺ crystals with distinguished morphologies in hydrothermal ambient, J. Nanosci. Nanotechnol. 16 (2016): 3930-3934.

[24] F.-w. Kang, Y.-h. Hu, L. Chen, X.-j. Wang, H.-y. Wu, Z.-f. Mu, Luminescent properties of Eu³⁺ in MWO₄ (M=Ca, Sr, Ba) matrix, J. Lumin. 135 (2013) 113-119.

[25] C.A. Kodaira, H.F. Brito, M.C.F.C. Felinto, Luminescence investigation of Eu^{3+} ion in the $RE_2(WO_4)_3$ matrix (RE=La and Gd) produced using the Pechini method, J. Solid State Chem. 171 (2003) 401-407.

[26] V. Mahalingam, J. Thirumalai, R. Krishnan, R. Chandramohan, Controlled synthesis and luminescence properties of $Ca_{0.5}Y_{1-x}(MoO_4)_2$:xRE³⁺ (RE=Eu, Pr, Sm, Tb, Dy, Yb/Er, Yb/Tm, and Yb/Ho) phosphors by hydrothermal method versus pulsed laser deposition, Electron. Mater. Lett. 12 (2016) 32-47.

[27] H. Wang, M. Yu, C. Lin, X. Liu, J. Lin, Synthesis and luminescence properties of monodisperse spherical Y₂O₃:Eu³⁺@SiO₂ particles with core-shell structure, J. Phys. Chem. C 111 (2007) 11223-11230.

[28] Z. Xu, X. Kang, C. Li, Z. Hou, C. Zhang, D. Yang, G. Li, J. Lin, Ln³⁺ (Ln=Eu, Dy, Sm, and

Er) ion-doped YVO₄ nano/microcrystals with multiform morphologies: hydrothermal synthesis, growing mechanism, and luminescent properties, Inorg. Chem. 49 (2010) 6706-6715.

[29] Z. Hou, Z. Cheng, G. Li, W. Wang, C. Peng, C. Li, P. Ma, D. Yang, X. Kang, J. Lin, Electrospinning-derived $Tb_2(WO_4)_3$:Eu³⁺ nanowires: energy transfer and tunable luminescence properties, Nanoscale 3 (2011) 1568-1574.

[30] T. Thongtema, S. Kungwankunakorn, B. Kuntalue, A. Phuruangrat, S. Thongtem, Luminescence and absorbance of highly crystalline CaMoO₄, SrMoO₄, CaWO₄ and SrWO₄ nanoparticles synthesized by co-precipitation method at room temperature, J. Alloys Compd. 506 (2010) 475-481.

[31] Z. Wang, H. Liang, L. Zhou, H. Wu, M. Gong, Q. Su, Luminescence of $(Li_{0.333}Na_{0.334}K_{0.333})Eu(MoO_4)_2$ and its application in near UV InGaN-based light-emitting diode, Chem. Phys. Lett. 412 (2005) 313-316.

[32] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomie distances in halides and chaleogenides, Acta Cryst. A32 (1976) 751-767.

[33] Y. Zheng, Y. Huang, M. Yang, N. Guo, H. Qiao, Y. Jia, H. You, Synthesis and tunable luminescence properties of monodispersed sphere-like CaWO₄ and CaWO₄:Mo/Eu,Tb, J. Lumin. 132 (2012) 362-367.

[34] X. Feng, D.C. Sayle, Z.L. Wang, M.S. Paras, B. Santora, A.C. Sutorik, T.X.T. Sayle, Y. Yang,Y. Ding, X. Wang, Y. Her, Converting ceria polyhedral nanoparticles into single-crystal nanospheres, Sci. 312 (2006) 1504-1508.

[35] X. Wang, Y. Bu, Y. Xiao, C. Kan, D. Lu, X. Yan, Size and shape modifications, phase transition, and enhanced luminescence of fluoride nanocrystals induced by doping, J. Mater. Chem.

C 1 (2013) 3158-3166.

[36] X. Huang, S. Han, W. Huang, X. Liu, Enhancing solar cell efficiency: the search for luminescent materials as spectral converters, Chem. Soc. Rev. 42 (2013) 173-201.

[37] Y. Mi, S. Zeng, L. Li, Q. Zhang, S. Wang, C. Liu, D. Sun, Solvent directed fabrication of Bi_2WO_6 nanostructures with different morphologies: synthesis and their shape-dependent photocatalytic properties, Mater. Res. Bull. 47 (2012) 2623-2630.

[38] D. Balaji, A. Durairajan, D. Thangaraju, K.K. Rasu, S.M. Babu, Investigation of structural and luminescent properties of Pr^{3+} activated CsGd(WO₄)₂ by sol-gel synthesis, Mater. Sci. Eng. B 178 (2013) 762-767.

[39] D. Zhang, S. Shi, M. Luo, J. Zhou, Solid state reaction preparation and enhanced red luminescence of S-doped La₂Mo₂O₉:Pr³⁺ phosphors, Ceram. Int. 39 (2013) 6299-6302.

[40] M. Shang, D. Geng, X. Kang, D. Yang, Y. Zhang, J. Lin, Hydrothermal derived LaOF:Ln³⁺
(Ln=Eu, Tb, Sm, Dy, Tm, and/or Ho) nanocrystals with multicolor-tunable emission properties, Inorg. Chem. 51 (2012) 11106-11116.

[41] P. Du, L. Luo, J.S. Yu, Upconversion emission, cathodoluminescence and temperature sensing behaviors of Yb^{3+} ions sensitized NaY(WO₄)₂:Er³⁺ phosphors, Ceram. Int. 42 (2016) 5635-5641.

[42] L. Yi, X. He, L. Zhou, F. Gong, R. Wang, J. Sun, A potential red phosphor $LiGd(MoO_4)_2$:Eu³⁺ for light-emitting diode application, J. Lumin. 130 (2010) 1113-1117.

[43] Z. Xia, R.-S. Liu, K.-W. Huang, V. Drozd, Ca₂Al₃O₆F:Eu²⁺: a green-emitting oxyfluoride phosphor for white light-emitting diodes, J. Mater. Chem. 22 (2012) 15183-15189.

[44] Y.-C. Wu, Y.-C. Chen, T.-M. Chen, C.-S. Lee, K.-J. Chen, H.-C. Kuo, Crystal structure

characterization, optical and photoluminescent properties of tunable yellow- to orange-emitting Y₂(Ca,Sr)F₄S₂:Ce³⁺ phosphors for solid-state lighting, J. Mater. Chem. 22 (2012) 8048-8056. [45] D. Deng, H. Yu, Y. Li, Y. Hua, G. Jia, S. Zhao, H. Wang, L. Huang, Y. Li, C. Li, S. Xu,

 $Ca_4(PO_4)_2O:Eu^{2+}$ red-emitting phosphor for solid-state lighting: structure, luminescent properties and white light emitting diode application, J. Mater. Chem. C 1 (2013) 3194-3199.

[46] C.K. Jørgensen, B.R. Judd, Hypersensitive pseudoquadrupole transitions in lanthanides, Mol.Phys. 8 (1964) 281-290.

[47] D-E. Henrie, Hypersensitivity in the electronic transitions of lanthanide and actinide complexes, Coord. Chem. Rev. 18 (1976) 199-224.

[48] J. Lin, M. Yu, C. Lin, X. Liu, Multiform oxide optical materials via the versatile pechini-type sol-gel process: synthesis and characteristics, J. Phys. Chem. C 111 (2007) 5835-5845.

Figure Captions

Fig. 1. XRD patterns of $Ca_XSr_YBa_{1-X-Y}WO_4:0.005Er^{3+}$, and the standard data of SrWO₄ powder (JCPDS No. 08-0490) (a), structure diagram of tetragonal phase Ca/Sr/BaWO₄ (b).

Fig. 2. EDS spectra of $Ca_{0.8}Ba_{0.2}WO_4:0.01Ho^{3+}$ (a), $Ca_{0.6}Ba_{0.4}WO_4:0.01Pr^{3+}$ (b), $Ca_{0.4}Ba_{0.6}WO_4:0.005Er^{3+}$ (c), and $Ca_{0.2}Ba_{0.8}WO_4:0.005Er^{3+}$ (d).

Fig. 3. SEM images of Er^{3+} -doped double-component $Ca_{0.8}Sr_{0.2}WO_4$ (b), $Ca_{0.6}Sr_{0.4}WO_4$ (c), $Ca_{0.4}Sr_{0.6}WO_4$ (d), $Ca_{0.2}Sr_{0.8}WO_4$ (e) and $CaWO_4$ (a), $SrWO_4$ (f) for comparison,

Fig. 4. SEM images of Er³⁺-doped double-component Ca_{0.8}Ba_{0.2}WO₄ (b), Ca_{0.6}Ba_{0.4}WO₄ (c),

Ca_{0.4}Ba_{0.6}WO₄ (d), Ca_{0.2}Ba_{0.8}WO₄ (e) and CaWO₄ (a), BaWO₄ (f) for comparison.

Fig. 5. SEM images of Er^{3+} -doped double-component $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{WO}_4$ (b), $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{WO}_4$ (c), $\text{Sr}_{0.4}\text{Ba}_{0.6}\text{WO}_4$ (d), $\text{Sr}_{0.2}\text{Ba}_{0.8}\text{WO}_4$ (e) and SrWO_4 (a), BaWO_4 (f) for comparison.

Fig. 6. SEM images of Er^{3+} -doped three-component $Ca_{0.6}Sr_{0.2}Ba_{0.2}WO_4$ (a), $Ca_{0.4}Sr_{0.4}Ba_{0.2}WO_4$ (b), $Ca_{0.4}Sr_{0.2}Ba_{0.4}WO_4$ (c), $Ca_{0.2}Sr_{0.6}Ba_{0.2}WO_4$ (d), $Ca_{0.2}Sr_{0.4}Ba_{0.4}WO_4$ (e), and $Ca_{0.2}Sr_{0.2}Ba_{0.6}WO_4$ (f). Fig. 7. TEM images and SAED patterns of $Ca_{0.6}Sr_{0.2}Ba_{0.2}WO_4$ (a), $Ca_{0.4}Sr_{0.4}Ba_{0.2}WO_4$ (b), $Ca_{0.4}Sr_{0.2}Ba_{0.4}WO_4$ (c), $Ca_{0.2}Sr_{0.6}Ba_{0.2}WO_4$ (d), $Ca_{0.2}Sr_{0.4}Ba_{0.4}WO_4$ (e), and $Ca_{0.2}Sr_{0.2}Ba_{0.6}WO_4$ (f). Fig. 8. Excitation (EX) and emission (EM) spectra of $SrWO_4$:0.01Pr³⁺ phosphor (a), $SrWO_4$:0.01Ho³⁺ phosphor (b), $SrWO_4$:0.005Er³⁺ phosphor (c), and the energy level schemes of $Pr^{3+}/Ho^{3+}/Er^{3+}$ in $SrWO_4$ host (d).

Fig. 9. The decay curves of SrWO₄:0.01Pr³⁺ (a), SrWO₄:0.01Ho³⁺ (b), and SrWO₄:0.005Er³⁺ (c). **Fig. 10.** Emission spectra of SrWO₄:xPr³⁺ upon 448 nm excitation (a), SrWO₄:yHo³⁺ excited by 450 nm light (b), SrWO₄:zEr³⁺ upon 378 nm excitation (c), the dependence of the relative emission intensity on RE³⁺concentrations (d). **Fig. 11.** The relationship of log(I/x) versus logx for Pr^{3+} (a), Ho^{3+} (b), and Er^{3+} (c) in SrWO₄ host.

Fig. 12. Excitation (A) and emission (B) spectra of $Ca_{0.6}Sr_{0.2}Ba_{0.2}WO_4$ (a), $Ca_{0.4}Sr_{0.4}Ba_{0.2}WO_4$ (b),

 $Ca_{0.4}Sr_{0.2}Ba_{0.4}WO_{4}\ (c),\ Ca_{0.2}Sr_{0.6}Ba_{0.2}WO_{4}\ (d),\ Ca_{0.2}Sr_{0.4}Ba_{0.4}WO_{4}\ (e),\ and\ Ca_{0.2}Sr_{0.2}Ba_{0.6}WO_{4}\ (f).$

Fig. 13. The intensity variation trend of $Ca_XSr_YBa_{1-X-Y}WO_4:0.01Pr^{3+}$ at 644 nm (a), $Ca_XSr_YBa_{1-X-Y}WO_4:0.01Ho^{3+}$ at 657 nm (b), $Ca_XSr_YBa_{1-X-Y}WO_4:0.005Er^{3+}$ at 550 nm (c), and CIE chromaticity coordinates of $Ca_{0.4}Sr_{0.6}WO_4:0.01Pr^{3+}$, $Ca_{0.8}Sr_{0.2}WO_4:0.01Ho^{3+}$, $Ca_{0.6}Sr_{0.4}WO_4:0.005Er^{3+}$.

30

	Host compound	Total ionic radius of
	_	alkaline earth ions (Å)
1	$Ca_0Sr_1Ba_0WO_4$	1.260
2	$Ca_0Sr_{0.8}Ba_{0.2}WO_4$	1.292
3	$Ca_0Sr_{0.6}Ba_{0.4}WO_4$	1.324
4	$Ca_0Sr_{0.4}Ba_{0.6}WO_4$	1.356
5	$Ca_0Sr_{0.2}Ba_{0.8}WO_4$	1.388
6	$Ca_0Sr_0Ba_1WO_4$	1.420
7	$Ca_{0.2}Sr_{0.8}Ba_0WO_4$	1.232
8	$Ca_{0.2}Sr_{0.6}Ba_{0.2}WO_4$	1.264
9	$Ca_{0.2}Sr_{0.4}Ba_{0.4}WO_4$	1.296
10	$Ca_{0.2}Sr_{0.2}Ba_{0.6}WO_4$	1.328
11	$Ca_{0.2}Sr_0Ba_{0.8}WO_4$	1.360
12	$Ca_{0.4}Sr_{0.6}Ba_0WO_4$	1.204
13	$Ca_{0.4}Sr_{0.4}Ba_{0.2}WO_4$	1.236
14	$Ca_{0.4}Sr_{0.2}Ba_{0.4}WO_4$	1.268
15	$Ca_{0.4}Sr_0Ba_{0.6}WO_4$	1.300
16	Ca. Sr. Ba.WO.	1 176
10	$Ca_{0.6}SI_{0.4}Da_0 WO_4$	1.170
17	$Ca_{0.6}SI_{0.2}Da_{0.2}WO_4$	1.208
10	$Ca_{0.6}SI_0Da_{0.4}WO_4$	1.240
19	$Ca_{0.8}Sr_{0.2}Ba_0WO_4$	1.148
20	$Ca_{0.8}Sr_0Ba_{0.2}WO_4$	1.180
21	Ca1Sr0Ba0WO4	1.120

Table 1	
The sample numbers and total ionic radii of $Ca_{x}Sr_{y}Ba_{1,x,y}WO_{x}:RE^{3+}$ phospho	ors





Fig. 1



Fig. 2



Fig. 3



Fig. 4



Fig. 5



Fig. 6



Fig. 7



















Research highlights

- 1. Down-conversion emissions of Pr^{3+} , Ho^{3+} and Er^{3+} are successfully realized.
- 2. The morphologies of products vary regularly with the change of host combination.
- 3. These phosphors can be excited by both the near-UV and blue light.
- $4. \quad Ca_{0.4}Sr_{0.6}WO_4: 0.01Pr^{3+}, Ca_{0.8}Sr_{0.2}WO_4: 0.01Ho^{3+}, Ca_{0.6}Sr_{0.4}WO_4: 0.005Er^{3+} \ are \ best.$