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Optical and thermal behaviors of high efficient $K_2TiF_6:Mn^{4+}$ red phosphor prepared by modified two-step co-precipitation method

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ABSTRACT

High efficient red phosphor $K_2TiF_6:Mn^{4+}$ was successfully prepared though a modified two-step co-precipitation method under room temperature. Pure phase of the K_2TiF_6 powder, with various doping concentration of Mn^{4+} range from 4 at.% to 9 at.%, was determined by the X-ray diffraction (XRD) analysis. The Mn^{4+} ions were clearly detected by the X-ray photoelectron spectroscopy (XPS) measurement and the electron paramagnetic resonance (EPR). The average particle size, i.e. D50, is around ~30 μm scanned by laser particle size analyzer. The highest emission peak centered at about 633 nm was observed from the photoluminescence spectra. The 6 at.% concentration of Mn^{4+} shows the best internal emission efficiency of around 99%, which also gives the excellent thermal quench performance. We demonstrated that the maximum color rendering index (CRI) was 85.1 with luminous efficiency as high as 143.82 lm/W, indicating that $K_2TiF_6:Mn^{4+}$ phosphors had a promising potential for white light-emitting diodes (WLEDs).

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1. Introduction

The solid-state lighting devices has attracted increasing attention in recent years for its low energy cost, long lifetime, and free of mercury comparing to the traditional lighting source [1,2]. Nowadays, the widely used white light-emitting diodes (WLEDs) are usually fabricated by blue InGaN chips combined with yellow YAG:Ce phosphors. However, because of the lack of red component in the system, this fabrication technique has been proved with two obvious drawbacks, i.e. low color rendering index (CRI) and high correlated color temperature, both of which seriously limit its application in the indoor lighting [3,4].

To overcome the defects mentioned above, a lot of related research activities have been dedicated to required red phosphors. Currently, the commercialized rare-earth doped (oxy) nitride red phosphors can be massively fabricated. Unfortunately, this phosphor possesses two serious defects, which limit its application in LED field. The first one is the high cost due to the use of the rare-earth raw materials and the rigorous fabrication conditions. Next is the re-absorption phenomenon which gives rise to color change and lower luminous efficacy of WLEDs [5,6]. Hence, the new type of red phosphors with low cost and high luminescence properties become a research hot recently.

Manganese (Mn) is well known to have several valence states, and among them the Mn^{4+} ion with electronic configuration of $3d^3$ is no doubt of much significance [7–10]. For example, we could achieve the most intense broad-band excitation and very sharp emission peak by doping Mn^{4+} ions into fluoride hosts in octahedral coordination [7,10,11–23]. Actually, the family of Mn^{4+} doped fluoride compounds performs excellent properties as red phosphors, which could be better applied to warm white LEDs by combination with blue chip and YAG:Ce yellow phosphor. At present, great efforts have been made for the investigation on this phosphor. There already are some kinds of red phosphors reported in recent years, e.g. $K_2SiF_6:Mn^{4+}$ [7,11–18], $Na_2SiF_6:Mn^{4+}$ [19,20], $K_2TiF_6:Mn^{4+}$ [21–23], $BaTiF_6:Mn^{4+}$ [24], $K_2GeF_6:Mn^{4+}$ [25], $BaGeF_6:Mn^{4+}$ [26], and most of them are synthesized by wet chemical etching method, which means expensive pure silicon or metal (germanium or titanium) and solutions composed of rich HF and $KMnO_4$ are required, in order to synthesize these alkaline metal fluoride red phosphors. The high cost and unkindly to the environment inspired a new method called co-precipitation to synthesize the red phosphors, and $Na_2SiF_6:Mn^{4+}$ and $BaGeF_6:Mn^{4+}$ has been successfully synthesized by using this method [22].

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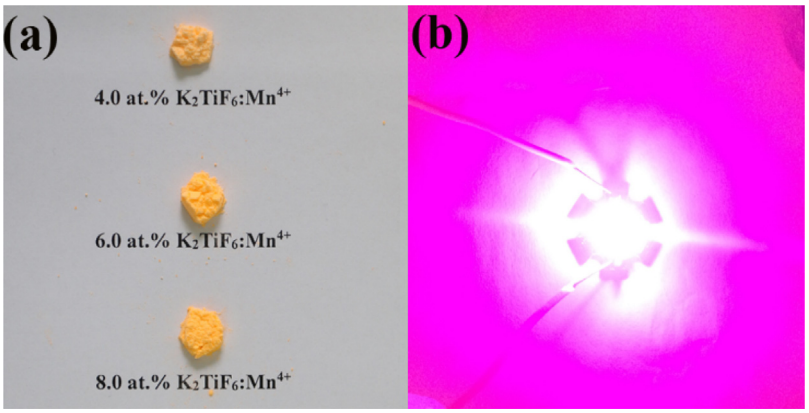

Fig. 1. (a) Photo of the obtained red-phosphors with various Mn^{4+} ions doping concentrations. (b) Red-emission image by using a blue-chip to excite the KTFM with a 3 V voltage.

While, very few reports about using co-precipitation method to synthesize the K_2TiF_6:Mn^{4+} red phosphors have been published.

In this work, we fabricated Mn^{4+} doped potassium hexafluorotitanate (K_2TiF_6:Mn^{4+}, KTFM) prepared by co-precipitation with a modified two steps route. The phase identification and microstructure were investigated. The optical properties of the fluoride complexes were determined by photoluminescence, photoluminescence excitation, thermal luminescence, and luminescence decay time. The obtained results exhibited the strong dependence of emission properties on doping concentration. Using K_2TiF_6: 6 at. % Mn^{4+} red phosphors, we prepared a warm white LED with high CRI (R_a = 85.1) and high luminous efficiency of 143.82 lm/W under a drive current of 60 mA.

2. Experiment

2.1. Synthesis of red phosphor

Commercially available powders of K_2TiF_6 (≥99.95%, Aladdin, China), $KMnO_4$ (≥99.0%), KHF_2 (≥99.0%), H_2O_2 (30 wt.%) and reagents of HF (49 wt.%, ≥99.99998% metals basis, Aladdin, China) were used as raw materials. To obtain K_2TiF_6:Mn^{4+} (KTFM) red phosphor, the first step is synthesizing K_2MnF_6. The reaction for producing K_2MnF_6 is:

$$2KMnO_4 + 2KHF_2 + 8HF + 3H_2O_2 \rightarrow 2K2MnF_6 + 8H_2O + 3O_2 \quad (1)$$

In above equation, the presence of H_2O_2 is used to reduce Mn^{7+} to Mn^{4+} at room temperature. Then the red phosphor was synthesized by following processes. Firstly, K_2MnF_6 powder was mixed with HF solution for 2 h to form a golden solution. Later, K_2TiF_6 powder was added to the above solution with further strongly stirring for 2 h to obtain tiny-yellow mixture. After filtering, the mixture was dried at 80 °C for 6 h before obtaining red phosphors.

2.2. Characterization

The XRD measurements of the as-prepared samples were carried out on a D8 Advance (Bruker, Germany) X-ray powder diffraction system using graphite monochromatized Cu Kα radiation (λ = 0.15406 nm). Phase identification was made using standard JCPDS files. Morphology of the particle was characterized through the image analysis of photographs obtained by a field scanning electron microscopy (SEM, FEI, NOVA, NANOSEM, 450). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific, USA) measurements were performed to examine the chemical compositions of the obtained phosphors. Electron paramagnetic resonance (EPR) spectra was measured by using an ELEXSYS A300 (Bruker). The average particle size is gained by laser particle size analyzer (Winner 2000).

Diffuse reflectance spectrum was measured by using a spectrometer (Lamda 950) at 300 K. Room-temperature photoluminescence (PL) and excitation (PLE) spectra were measured by using a fluorescence spectrometer (F-7000, Hitachi, Japan). These spectra were measured by excitation at λ_{ex} = 450 nm (PL) or by monitoring at λ_{em} = 633 nm (PLE). For photoluminescence quantum yield (QY) measurement, the red phosphors were put inside an optical integrating sphere coupled to a F-7000 spectrometer. Temperature-dependent PL measurements were carried out by a florescence spectrophotometer (F-4600, Hitachi, Japan) equipped with a photomultiplier tube operating at 400 V, and a 150 W Xenon lamp as the excitation source. Luminescence lifetime measurements were performed using a FLSP9200 fluorescence spectrophotometer (Edinburgh Instruments Ltd., U.K.), and a nF900 flash lamp was used as the excitation resource.

3. Results and discussion

3.1. Structural properties

Fig. 1(a) exhibits the photos of red phosphors with various Mn^{4+} ions doping concentrations. All samples show yellow color under the sunlight, and the color becomes gradually bright with the increase of Mn^{4+} concentrations. Under the excitation of a blue-chip with 3 V voltage, strongly red emission was generated, as shown in Fig. 1(b).

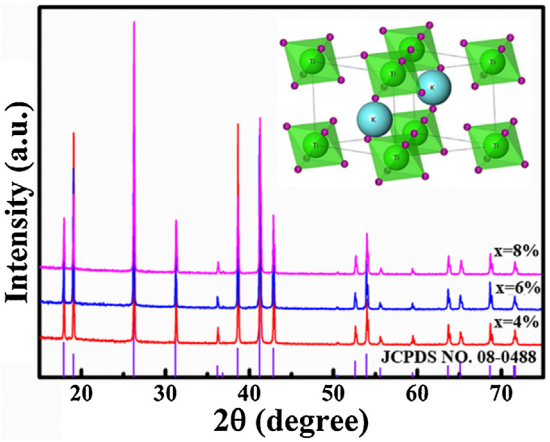

Fig. 2. XRD patterns of $K_2Ti_{(1-x)}Mn_xF_6$ phosphors with different Mn^{4+} ions doping concentrations. The inset shows the crystal structure of K_2TiF_6.

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