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Photoluminescence properties and crystal field analysis of a novel red-emitting phosphor $K_2BaGe_8O_{18}:Mn^{4+}$

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ABSTRACT

Novel red-emitting phosphors $K_2BaGe_8O_{18}:Mn^{4+}$ (KBGO:Mn^{4+}) were synthesized via the high-temperature solid-state reaction method. X-ray diffraction and Rietveld refinements illustrated that pure phase $K_2BaGe_8O_{18}$ was obtained from the as-prepared samples. The excitation spectrum of KBGO:0.002Mn^{4+} monitored at 666 nm showed a wide band with two obvious peaks at 319 and 468 nm. It can be deconvoluted into four bands with maxima at 313, 350, 391 and 462 nm which corresponded to Mn^{4+}-O^{2-} charge transfer, Mn^{4+} $^4A_2$-$^4T_1$, $^4A_2$-$^2A_2$ and $^4A_2$-$^4T_2$ transitions, respectively. Upon 468 nm excitation, the emission spectrum presented a narrow band from 600 to 700 nm (red region) with the maximum emission around 666 nm, which originated from Mn^{4+} ^2E_g-$^4A_2$ transition in GeO_6 octahedral environment. Therefore, $K_2BaGe_8O_{18}:Mn^{4+}$ phosphor can be considered as a red-emitting component candidate in UV and blue light excited white light-emitting diodes (w-LEDs).

1. Introduction

Energy saving has been one of the most important issues we are facing in 21th century since increasing energy consumption is continuous. As reported, energy for illumination, a kind of critical electric energy consumption, can occupy about 19% of electricity [1]. Phosphor conversion white light-emitting diodes (w-LEDs), the fourth-generation light source, has been considered to replace current fluorescent and incandescent lamps because it has superior merits such as high energy-utilization efficiency, environmental friendliness, compactness, long lifetime besides its low energy consumption [2–5]. Currently, there are two primary strategies to fabricate the w-LED. One is employing the blue LED with yellow-emitting phosphor $Y_3Al_5O_{12}$:Ce (YAG:Ce)+ nitride red phosphor [6,7], the other is combining UV LED chips with tri-color (blue, green, and red) phosphors, which also can produce white light with high quality [8,9]. Between these two methods, the red-emitting phosphor is the indispensable component to obtain the vivid and warm white light illumination. It is unfortunate that the currently available red phosphors are main Eu^{2+}-doped (oxy)nitrides which need severe conditions for preparation and the chemically unstable (for temperature and moisture) Eu^{2+}/Eu^{3+}-doped sulphides [10,11]. Therefore, Many investigations on developing novel red-emitting phosphors are conducted by researchers in recent years.

As a transitional metal element with 3 d^5 electron configuration, Mn has many valences including +7, +6, +4, +3, +2 and 0. Among these valences, the Mn with +4 and + 2 states can produce red emissions originated from spin- and parity-forbidden ^2E_g -$^4A_{2g}$ transition of Mn^{4+} at octahedra substituting Al^{3+}, Ti^{4+}, Zr^{4+}, Si^{4+} or Ge^{4+} in the hosts [12–16], and $^4T_1$-$^6A_1$ transition of Mn^{2+} at octahedra substituting Mg^{2+}, Zn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} etc. [17–21], respectively. However, the former emits a relative narrow red band in the region 620–750 nm upon UV/blue excitation Mn^{4+}-ligand hybridization, in which the Mn^{4+} activated fluorides with a weak hybridization effect locates at 620–640 nm [22], while changed to >650 nm in oxides with a strong hybridization effect [23], and the later produces a broad emission band upon UV/blue excitation depending on the crystal field around Mn^{2+} [24]. The broad emission bands from Mn^{2+} ion will restrict the maximum achievably luminous efficacies of high-quality warm w-LEDs since the spectrum extended into the red spectral region is insensitive to our naked eyes. Accordingly, Mn^{4+} doped inorganic phosphors with narrow emission bands for w-LEDs have attracted many attentions in luminescent materials investigations. Although some Mn^{4+} activated fluorides have been developed as good candidates for red

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emission supplement in w-LEDs [25–27], the unsatisfied sustainability of fluoride materials under a humid atmosphere and the requirement of toxic HF solution (which is injurious to the environment) in the prepared process limit their applications. Hence, Mn^{4+}-doped oxides with good chemical and thermal stabilities along with eco-friendly preparation procedure becomes a good choice as red emission component in w-LEDs.

Herein, we successfully synthesized novel Mn^{4+}-doped $K_2BaGe_8O_{18}$ phosphors with red emission under UV/blue excitation by solid-state reaction method in air. This kind of phosphor seems to be similar with $K_2Ge_4O_9:Mn^{4+}$ (trigonal in the $P3c1$ space group), $BaGe_4O_9:Mn^{4+}$ (Hexagonal in the $P321$ space group) and $Li_3RbGe_8O_{18}:Mn^{4+}$ (trigonal in the $P31m$ space group) phosphors, however, the structures are different from each other, which strongly rely on the size of elements and the Ge-O distance, resulting in different luminescent properties [28–30]. Moreover, the phase purity, the host crystal structure, the fundamental understanding on the relationships between the neighboring coordination environment around Mn^{4+}, fluorescence lifetimes, and the detailed luminescence properties and crystal field analysis for Mn^{4+} in $K_2BaGe_8O_{18}$ were investigated.

2. Experimental section

2.1. Materials synthesis

A series of expected Mn^{4+}-doped $K_2BaGe_8O_{18}$ phosphors (abbreviated as KBGO:xMn^{4+}, $x = 0–0.08$) with different Mn^{4+} concentrations x were synthesized via the high-temperature solid-state reaction method. Typically, taking $x = 0.002$ as an example, raw materials of 0.001 mol K_2CO_3(AR), 0.001 mol $BaCO_3$(AR), 0.008 mol GeO_2(99.99%) and 2×10^{-6} mol MnO_2(99.9%) were first weighed, then thoroughly mixed and ground in an agate mortar for about 15 min with appropriate addition of ethanol (about 10 drops), after which they were dried and transferred to the crucible for calcination in a box furnace at 1050 °C for 6 h under air. Finally, the samples were cooled to room temperature and ground once again for subsequent characterizations.

2.2. Characterization

D8 Focus diffractometer equipped with graphite-monochromatized Cu Kα radiation ($l = 0.15405$ nm) was used to acquire the X-ray diffraction (XRD) profiles of as-prepared samples at a scanning rate of 10^0 min^{-1}. Rietveld refinements of the powder XRD profiles were conducted using GSAS system [31]. Infrared spectra were measured on a VERTEX 70 Fourier transform infrared (FT-IR) spectrometer (Bruker). The photoluminescence (PL) measurements were operated on the Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The fluorescent lifetimes were obtained from the Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation (Continuum Sunlite OPO) source. Absolute quantum yields (QYs) of phosphors were gained directly using an absolute PL quantum yield measurement system (C9920-02, Hamamatsu Photonics K. K., Japan), which can be calculated according to the equation below [32].

$$\eta = \frac{\int L_{emission}}{\int E_{blank} - \int E_{sample}} \qquad (1)$$

where $L_{emission}$ refers to the integrated value of the emission spectrum, E_{blank} and E_{sample} refer to the integrated value upon the "excitation" band of the blank and the integrated value upon the excitation band of the sample (since the sample absorbs part of the light, this value will be much smaller than E_{blank}), respectively.

3. Results and discussion

3.1. Phase and structure

The XRD patterns of representative samples KBGO:Mn^{4+} with different Mn^{4+} concentrations are shown in Fig. 1. The results indicate that all the diffraction peaks of KBGO host and Mn^{4+}-doped KBGO phosphors are well indexed into a pure $K_2BaGe_8O_{18}$ with corresponding standard JCPDS Card no. 83-1552. No other crystalline phase is formed after doping Mn^{4+} ions into the KBGO compound, illustrating the Mn^{4+} ions were successfully introduced into the KBGO host lattice and did not arouse any significant change of this crystal structure. In order to further understand the purity of the KBGO host and Mn^{4+}-doped KBGO, we performed the Rietveld refinements for representative KBGO host, KBGO:$0.002Mn^{4+}$, KBGO:$0.04Mn^{4+}$ and KBGO:$0.08Mn^{4+}$ with the aid of the GSAS program. The original structural model and crystallographic data for the refinements was referred to $K_2BaGe_8O_{18}$ compound (ICSD 100439). As displayed in Fig. 2a-d, the black crosses and olive solid line depict the experimental and calculated patterns, respectively. The differences between them are signed with cyan lines. Besides, the red bars at the bottom of the figure stand for the Bragg positions. All the atomic positions, fraction factors and thermal vibrational parameters were converged and refined. Table 1 presents the crystallographic data and detailed refined parameters of these four samples, in which the residual factors R_{wp}, R_p and χ^2 for KBGO, KBGO:$0.002Mn^{4+}$, KBGO:$0.04Mn^{4+}$ and KBGO:$0.08Mn^{4+}$ are acceptable, respectively, indicating their reliable refined results. We observed that the lattice parameters a, b, c and V increase monotonously with the increasing Mn^{4+} concentration in KBGO by comparing the refined results between them. This indicates that Mn^{4+} ions were successfully incorporated into the KBGO compound and the cell will be expanded, which is originated from the bigger ionic radius of Mn^{4+} [coordination number (CN) = 6, 0.54 Å,] replacing Ge^{4+}(CN = 6, 0.53 Å). The crystal structure of KBGO compound on the basis of Inorganic Crystal Structure Database in Fig. 3 belongs to hexagonal system with four kinds of six-

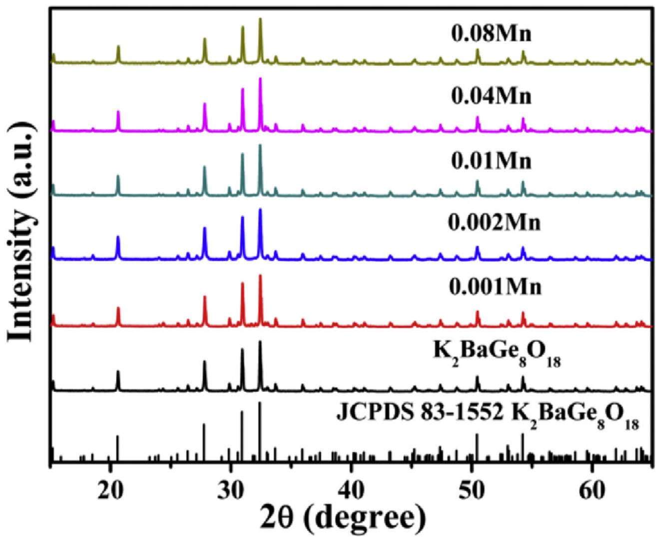

Fig. 1. XRD patterns of as-prepared $K_2BaGe_8O_{18}$ host and Mn^{4+} doped $K_2BaGe_8O_{18}$ phosphors with different concentrations.