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Full Length Article

# A double perovskite $Ca_2MgWO_6:Bi^{3+}$ yellow-emitting phosphor: Synthesis and luminescence properties

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ABSTRACT

Novel double perovskite $Ca_2MgWO_6:Bi^{3+}$ (CMW:$Bi^{3+}$) yellow-emitting phosphor is synthesized by solid-state reaction method in air. Host $Ca_2MgWO_6$ with excitation 297 nm emits blue light and the chromaticity coordinate is (0.169, 0.160). The spectroscopic properties of CMW:$Bi^{3+}$ phosphor are explained on the basis of the $Bi^{3+}$ ($6s^2$)–$W^{6+}$ ($5d^0$) metal-to-metal charge transfer (MMCT) transition. CMW:$Bi^{3+}$ phosphor with excitation 338 nm shows yellow light and the chromaticity coordinate is (0.383, 0.477). Broad emission band peaking at ~550 nm of CMW:$Bi^{3+}$ phosphor is observed in the range of 400–780 nm due to the D → $^1S_0$ radiative decay and the $^3P_{1,0} \rightarrow {}^1S_0$ transitions of $Bi^{3+}$ ion. Monitored at 550 nm, excitation spectrum of CMW:$Bi^{3+}$ phosphor including a strong excitation peak at ~338 nm covers the region from 200 to 400 nm owing to the $Bi^{3+} \rightarrow W^{6+}$ MMCT transition and the $^1S_0 \rightarrow {}^3P_1$ transition of $Bi^{3+}$ ion. The optimal $Bi^{3+}$ ion actual content is ~0.38 mol%. Emission spectra of CMW:$Bi^{3+}$ phosphor with excitation 338 nm shows blue-shift with increasing temperature from 50 to 300 K owing to the influence of temperature to electron transfer. The possible luminous mechanism of CMW:$Bi^{3+}$ phosphor is analyzed by energy level diagram of $Bi^{3+}$ ion in solid including $d^0$ cation.

## 1. Introduction

Bismuth (Bi) with $[Xe]4f^{14}5d^{10}6s^26p^3$ electronic configuration is known as a green main-group element owing to its non-carcinogenic and nontoxic properties [1]. Bi ion may show a variety of optoelectronic properties because of the strong interaction with the surrounding lattice and many valence states (e.g., +1, +2, and +3 etc.) [2–4]. Compared with $Bi^+$ and $Bi^{2+}$ ions, $Bi^{3+}$ ion is more common and more stable ionic in the number of materials. The ground state $^1S_0$ of $Bi^{3+}$ ion is from the $6s^2$ electronic configuration. Its excited states are the triplet levels ($^3P_0$, $^3P_1$, and $^3P_2$) and the $^1P_1$ singlet state, which is from the 6s6p electronic configuration [5]. The emission properties of $Bi^{3+}$ ion have been investigated widely in many host lattices. $Bi^{3+}$ doped materials usually show broad absorption band in the ultraviolet (UV) region and exhibit variable broadband emission extending from the UV to the red spectral range due to the $^3P_{1,0} \rightarrow {}^1S_0$ transitions [6]. The emission of $Bi^{3+}$ ion, which originates from the $6s^2$ electrons, is susceptible to the surrounding chemical environment (e.g., site symmetry, coordination number, covalency, and host stiffness) [7]. In addition to the above $6s^2 \rightarrow 6s^16p^1$ transitions of $Bi^{3+}$ ion, the D-level state is considered as a trapped excited state. D-level absorption is reported due to the transitions from the ground state of $Bi^{3+}$ ion to the conduction band states of host [8]. An emission arising from charge transfer (CT) transition between the activator $Bi^{3+}$ and the host metal cations with $d^0$ or $d^{10}$ configuration (e.g., $Ti^{4+}$, $Sn^{4+}$, $V^{5+}$, $Nb^{5+}$, $W^{6+}$, and $Mo^{6+}$ etc.), which is described as a metal-to-metal charge-transfer (MMCT), has also been reported [9,10]. Therefore, the host is also one of important factors to research the luminescence properties of $Bi^{3+}$ ion.

The alkaline earth tungstates with excitation UV light may emit blue or green light and can be used as efficient luminescence host. Luminescence properties of $CaWO_4:Bi^{3+}$ single crystal have been reported [11]. A double perovskite has the formula $A_2BB'X_6$ (A = Ca, Sr, and Ba; B = Mg, Ni, Fe, Co, and Zn; B′ = W and Mo), and the related crystal structure is essentially governed by the ionic radii and charges of the A, B, and B′ cations [12]. The mixed alkaline earth tungstates have similar luminescence properties with the alkaline earth tungstates and attract the attentions owing to their structural diversity as well as physical properties, such as chemical flexibility, ferroelectric, and dielectric properties [13,14]. $Ca_2MgWO_6$ (CMW) is one of the mixed alkaline earth tungstates. At present, luminescence properties $Ca_2MgWO_6:Bi^{3+}$ (CMW:$Bi^{3+}$) phosphor has rarely been reported.

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In the work, CMW:$x$Bi$^{3+}$ ($0 \le x \le 4$ mol%) phosphors are synthesized by high temperature solid-state reaction method in air. The crystal structures, fluorescence lifetimes, and luminescence properties are investigated and analyzed. The influence of Bi$^{3+}$ doping concentration and temperature to emission intensity and lifetime of CMW:Bi$^{3+}$ phosphor is discussed. The possible luminous mechanism of CMW:Bi$^{3+}$ phosphor is analyzed and explained by energy level diagram of Bi$^{3+}$ ion in solid including d$^0$ cation.

## 2. Materials and experimental

All the chemicals are purchased from the Aladdin Chemical Reagent Company in Shanghai China, such as $CaCO_3$ (A.R. 99.5%), MgO (A.R. 99.9%), $WO_3$ (A.R. 99.9%), and $Bi_2O_3$ (99.99%). A series of CMW:$x$Bi$^{3+}$ ($x$ = 0, 0.5, 1, 2, 3, and 4 mol%) phosphors are synthesized by high temperature solid-state reaction method in air. The stoichiometric amount of raw materials is well grounded in an agate mortar without further purification, then sintered at 600 °C for 6 h, subsequently grounded again and sintered at 1200 °C for 5 h in air. All products are obtained after natural cooling to room temperature. Repeated grindings are performed between two sintering processes to improve the homogeneity.

The crystal structures of phosphors are checked by X-Ray Powder Difffraction (XRD) (Philips Model PW1830) with Cu-Kα radiation at 40 kV and 40 mA at room temperature. The data are collected in the $2\theta$ range of 10–90°. The element content is tested by S4800-Hitachi Energy Disperse Spectroscopy (EDS) and Inductively Coupled Plasma (ICP) spectrometer. Luminescence properties and fluorescence lifetimes of phosphors are investigated by using a steady-state FLS980 spectrofluorimeter (Edinburgh Instruments, UK, Edinburgh) with a high spectral resolution (signal to noise ratio $>$ 12,000:1) at room temperature. A 450 W ozone free xenon lamp is used for steady-state measurements. A microsecond pulsed xenon flash lamp μF900 with an average power of 60 W is available to record the emission decay curves for lifetimes.

## 3. Results and discussion

The unit cell of CMW drawn on the basis of the Inorganic Crystal Structure Database (ICSD) #155217 is shown in Fig. 1. CMW is described as the monoclinic crystal system with space-group P21/n (14) and the lattice parameters $a = 5.4255(0)$ Å, $b = 5.551(1)$ Å, $c = 7.7224(1)$ Å, $v = 232.57(0)$ Å$^3$, and $z = 4$ [15]. The CMW crystal structure contains [$CaO_8$] polyhedron and [$WO_6$] octahedra. W atom with six oxygen atoms forms [$WO_6$] octahedra. The eight coordinated [$CaO_8$] polyhedron is formed with the Ca–O bond lengths within the range 2.35–.74 Å. The Ca atom is also considered as 12-coordinated if the additional four longer bonds (3.14–3.4 Å) are considered [12]. In the host CMW lattice, Bi$^{3+}$ ions will replace Ca$^{2+}$ ions sites owing to their similar ionic radii (Ca$^{2+}$: ~0.99 Å and Bi$^{3+}$: ~1.08 Å) [16]. In host CMW lattice, Bi$^{3+}$ ion cannot be fully introduced into the Ca$^{2+}$ ion site due to the different charge between Bi$^{3+}$ and Ca$^{2+}$ ions, and have to form pairs by trapping an interstitial O$^{2-}$ ion in order to keep the charge balance in host lattice [7].

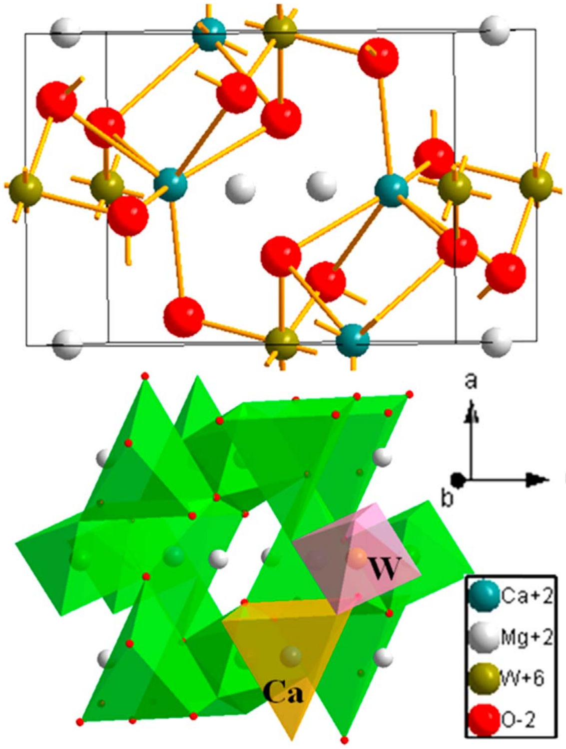

**Fig. 1.** The unit cell of CMW drawn on the basis of ICSD #155217.

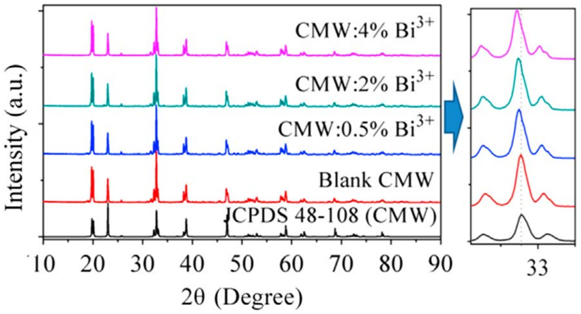

**Fig. 2.** XRD patterns of JCPDS card no. 48-108 (CMW), blank CMW, CMW:$x$Bi$^{3+}$ ($x$ = 0.5, 2, and 4 mol%) phosphors, and the enlarged figure in the $2\theta$ range of 32.1–33.5°.

XRD patterns of Joint Committee on Powder Diffraction Standards (JCPDS) card no. 48-108 (CMW), blank CMW, CMW:xBi$^{3+}$ ($x$ = 0.5, 2, and 4 mol%) phosphors are shown in Fig. 2. The XRD patterns of these samples match well with the standard data of JCPDS card (no. 48-108). The XRD patterns of other CMW:$x$Bi$^{3+}$ ($0 \le x \le 4$ mol%) phosphors are not displayed in Fig. 2, but those patterns are also in line with those of JCPDS card (no. 48-108). No other crystalline phase is formed after Bi$^{3+}$ ions are added. It is said that the doping Bi$^{3+}$ ions have no significantly effect to host lattice and the samples all have a pure phase CMW. However, after Bi$^{3+}$ ions are doped to replace Ca $^{2+}$ ions sites in the host CMW lattice, the XRD diffraction peaks of the doped samples are shifted towards lower angles due to their different ionic radii (Ca$^{2+}$: ~0.99 Å and Bi$^{3+}$: ~1.08 Å), which can be illustrated more clearly via the enlarged figure within the $2\theta$ range 32.1–33.5° in Fig. 2. The result indicates that there is an expansion of the lattice cell according to Bragg equation ($2d\sin\theta = \lambda$, where $\lambda$ and $\theta$ are the wavelength of the X-ray and diffraction angle, respectively [2].) owing to the substitution of Bi$^{3+}$ ions for Ca $^{2+}$ ions in host lattice.

The EDS spectrum of CMW:2%Bi$^{3+}$ phosphor and the corresponding element content in Fig. 3 further confirm that Bi$^{3+}$ ions can be doped into host CMW lattice by replacing Ca$^{2+}$ ions sites. According to the data in Fig. 3, the actual Bi$^{3+}$ ion doping concentration by calculating is about 0.38 mol%, which is much less than the nominal Bi$^{3+}$ doping concentration (2 mol%). The possible reason is that small part Bi$^{3+}$ ion is doped into the host CMW lattice and most Bi$^{3+}$ ion is closed because $Bi_2O_3$ has low boiling point and is sintered at the high temperature. In order to further