Journal of Luminescence 194 (2018) 542–546

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Rare-earth free broadband $Ca_3Mg_3P_4O_{16}:Mn^{2+}$ red phosphor: Synthesis and luminescence properties

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ARTICLE INFO

Keywords:
Phosphor
Phosphate
Mn^{2+} ion
Red-emitting

ABSTRACT

Rare-earth-free red-emitting $Ca_3Mg_3P_4O_{16}:Mn^{2+}$ (CMPO:Mn^{2+}) phosphor is synthesized by high temperature solid-state reaction method in air. The crystal structures and luminescence properties are investigated. Broad emission band peaking at ~ 625 nm of CMPO:Mn^{2+} phosphor with excitation 410 nm is observed in the range of 510 − 790 nm due to the $^4T_1(G) \rightarrow {}^6A_1$ transition of the Mn^{2+} ion. The full width at half-maximum is ~ 120 nm. Excitation bands are assigned to the [$^6A_1 \rightarrow {}^4E(^4D)$, $^4T_2(D)$, [$^4A_1(G)$, $^4E(^4G)$, and $^4T_1(G)$] transitions, respectively. The optimal Mn^{2+} ion concentration in CMPO:Mn^{2+} phosphor is ~ 5 mol%. The lifetime of CMPO:0.05Mn^{2+} phosphor is ~ 5.75 ms. The luminous mechanism of Mn^{2+} ion in CMPO:Mn^{2+} phosphor is explained by Tanabe-Sugano diagram and the simple energy level diagram of Mn^{2+} ion. The paper content is helpful for the research of novel Mn^{2+}-doped materials.

1. Introduction

In recent years, white-light emitting diodes (w-LEDs) have become an important lighting source and are used to replace conventional incandescent and fluorescent lamps because of their high luminous efficiency, long useful lifetime, environmentally friendly, and low energy cost [1–3]. The w-LED is usually fabricated by using a LED chip in combination with phosphors. So, the study of phosphor is very important task. It is well known that rare earth ions are used as an important activator in many phosphors. However, high price of rare earth has some influences to the phosphors practical application. So, Rare-earth-free ions as activator are considered as a new research object.

The rare-earth-free Mn^{2+} ion as a well activator in luminescence material has attracted more and more interest by many researchers [4]. The $Zn_2SiO_4:Mn^{2+}$ phosphor has been commercially used as a green-emitting phosphor [5,6]. Other phosphors with Mn^{2+} doping have been developed and their potential applications have also been widely investigated, e.g. $NaCaPO_4:Mn^{2+}$ [7], $Zn_3BPO_7:Mn^{2+}$ [8], $M_2(Mg, Zn)Si_2O_7:Mn^{2+}$ (M = Ca, Sr, and Ba) [9], $ZnGeN_2:Mn^{2+}$ [10], $M_2Si_5N_8:Mn^{2+}$ (M = Ca, Sr, and Ba) [11], $NaAl_{11}O_{17}:Mn^{2+}$ [12], and $Ba_2ZnS_3:Mn^{2+}$ [13]. Mn^{2+} ions often show a broad band emission due to the $^4T_1 \rightarrow {}^6A_1$ transition, which are strongly affected by crystal field strength. So, the emission band peaks of Mn^{2+} ions vary from green to deep-red region because of the influence of the host material crystal field [14]. In general, Mn^{2+} ions in the tetrahedral coordination may show green-light emission, whereas the octahedrally coordinated Mn^{2+} ions can give orange to red emission [7]. Phosphates as excellent host matrix for phosphors have been researched due to the moderate phonon energies and high chemical/thermal stability. $Ca_3Mg_3P_4O_{16}$ (CMPO) is one of the phosphates and has been studied with different dopants, such as CMPO:Eu^{3+} [15], CMPO:Sm^{3+} [16], CMPO:Eu^{2+}, Mn^{2+} [17]. At present, CMPO:Mn^{2+} phosphor has rarely been reported in detail.

In the work, CMPO: Mn^{2+} phosphor is synthesized by high temperature solid-state reaction method in air. The crystal structures, luminescence properties, and fluorescence lifetime are investigated by X-ray powder diffraction (XRD) and steady-state FLS980 spectrofluorimeter. The relation between Mn^{2+} ion concentration and luminescence properties is discussed. The luminous mechanism of CMPO:Mn^{2+} phosphor can be explained by Tanabe-Sugano diagram and the simple energy level diagram of Mn^{2+} ion.

2. Experimental procedures

2.1. Synthesis

A series of CMPO:xMn^{2+} (x = 0, 1, 2, 3, 4, 5, and 6 mol%) phosphors are synthesized by high temperature solid-state reaction in air, starting from a mixture containing $CaCO_3$ (A.R. 99.9%), $(NH4)_2HPO_4$ (A.R. 99.9%), MgO (A.R. 99.99%), and $MnCO_3$ (A.R. 99.9%) in the given stoichiometric ratio. The raw materials without further purification are mixed and ground thoroughly in an agate mortar. The mixture was firstly heated at 650 °C for 5 h in the furnace. Then, in order to

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http://dx.doi.org/10.1016/j.jlumin.2017.10.079
Received 30 December 2016; Received in revised form 27 October 2017; Accepted 29 October 2017
Available online 31 October 2017
0022-2313/ <outputStr5>

improve the homogeneity and obtain the final product, the above precursor is reground, and heated up to 1100 °C for 6 h in air. All samples can be obtained after natural cooling to room temperature.

2.2. Measurements

XRD (Philips Model PW1830 and Cu-Ka l = 1.5406 Å) is used for structural phase identification. The applied voltage and current were set to be 40 kV and 40 mA, respectively. The XRD pattern data are collected in the 2θ range of 10 − 90° at room temperature. Room temperature luminescence properties, quantum efficiency (QE) and fluorescence lifetime of samples are measured by a steady-state FLS980 spectrofluorimeter (Edinburgh Instruments, UK, Edinburgh) with a high spectral resolution (signal to noise ratio > 12000:1) and a photomultiplier tube operating at 400 V and a 450 W ozone free xenon lamp used as the excitation lamp. A microsecond pulsed xenon flash lamp μF900 with an average power of 60 W is available to record the emission decay curves for lifetimes. All the measurements in the same series have been conducted under strictly the same experimental conditions. QE is measured by the steady-state FLS980 spectrofluorimeter with integrating sphere.

3. Results and discussion

3.1. XRD analysis and crystal structure

Fig. 1 shows the typical powder XRD patterns of Joint Committee on Powder Diffraction Standards (JCPDS) card no. 73–1182 (CMPO), blank CMPO, and CMPO:xMn^{2+} (x = 2, 4, and 6 mol%) phosphors. From the diagram, all the XRD patterns are found to match well with the JCPDS card no. 73–1182 and other impurity peaks are not found, indicating that the obtained samples are a single phase and the doping Mn^{2+} ions does not generate any impurity or cause any significant changes in the host structure.

Fig. 2 shows the unit cell of CMPO drawn on the basis of Inorganic Crystal Structure Database (ICSD) #23642. It has been known that CMPO is described as a monoclinic structure with a space group of *C*12/*c*1(15) and lattice constants of a = 22.841(3) Å, b = 9.994(1) Å, c = 17.088(5) Å, V = 3845.76(134) $Å^3$, and Z = 12 [18]. In the lattice of CMPO, there are five different Ca sites. Each Ca site has different structural information such as coordination number (n): Ca(1), Ca(3) and Ca(4) are defined as 8-coordinated, Ca(2) is defined as 7-coordinated and Ca(5) is defined as 6-coordinated [15,17]. Here, the effective ionic radius of Ca is ~ 1.00 Å (CN = 6), 1.06 Å (CN = 7), and 1.12 Å (CN = 8) [17,19,20]. Mg tends to substitute for the same Ca sites. P is defined as 4-coordinated with the effective ionic radii ~ 0.15 Å. In host CMPO lattice, Mn^{2+} ion will substitute the Mg^{2+} ion site due to their same charge and similar effective ionic radii (CN = 6) (Mg^{2+}: ~ 0.72 Å and Mn^{2+}: ~ 0.67 Å) [19].

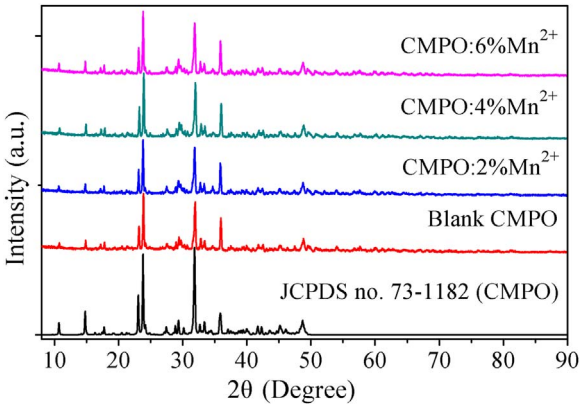

Fig. 1. XRD patterns of JCPDS card no. 73–1182 (CMPO), blank CMPO, and CMPO:xMn^{2+} (x = 2, 4, and 6 mol%) phosphors.

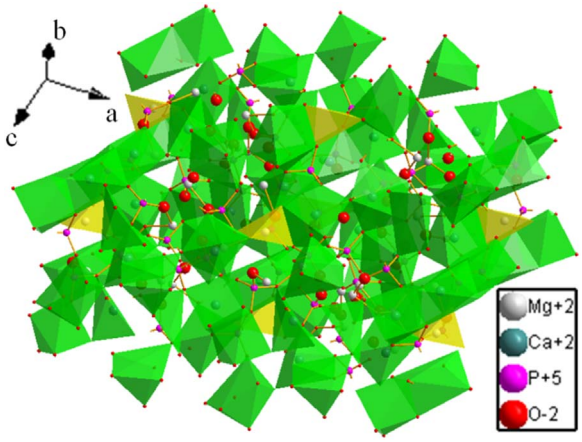

Fig. 2. The unit cell of CMPO drawn on the basis of ICSD #23642.

3.2. Luminescence properties

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of CMPO:Mn^{2+} phosphor (λ_{em} = 625 nm; λ_{ex} = 410 nm) and the corresponding Commission Internationale Ed I'eclairage (CIE) chromaticity diagram at room temperature are shown in Fig. 3. The PLE spectrum of CMPO:Mn^{2+} phosphor monitored at 625 nm contains many PLE band peaks from 210 nm to 580 nm, which is assigned to the host lattice absorption (~ 255 nm), $^6A_1 \rightarrow {}^4E(^4D)$ (~ 347 nm), $^6A_1 \rightarrow {}^4T_2(D)$ (~ 361 nm), $^6A_1 \rightarrow [{}^4A_1(G), {}^4E(4\,G)$ (~ 410 nm), and $^6A_1 \rightarrow {}^4T_1(G)$ (~ 513 nm) transitions of Mn^{2+} ion, respectively [21,22]. The strongest PLE band is attributed to $^6A_1 \rightarrow [{}^4A_1(G), {}^4E(^4G)$ (~ 410 nm) transition of Mn^{2+} ion, which is important for LED. CMPO:Mn^{2+} phosphor exhibits red emission and the same PL spectral shape and peak position upon 347, 361, 410, and 513 nm excitation. The emission spectra of CMPO:Mn^{2+} phosphor excited by different wavelength lights consist of a single broad PL band peaking at ~ 625 nm in the range of 510 − 790 nm, which is assigned to the $^4T_1(G) \rightarrow {}^6A_1$ transition of the Mn^{2+} ion [23,24], indicating that Mn^{2+} ion occupys the same coordination site, which is in a good line with the structure analysis. The full width at half-maximum (FWHM) of the PL band is ~ 120 nm. The corresponding CIE chromaticity coordinates are ~ (0.5847, 0.4135) (λ_{ex} = 347 nm), (0.6064, 0.3923) (λ_{ex} = 361 nm), (0.5970, 0.4016) (λ_{ex} = 410 nm), and (0.6087, 0.3904) (λ_{ex} = 513 nm), respectively. The small difference of chromaticity coordinate is caused by PL intensity. The QE is measured directly by the steady-state FLS980 spectrofluorimeter with integrating sphere. The QE of CMPO:5%Mn^{2+} phosphor is ~ 25.7% at the excitation of 410 nm, which should be further improved in order to the real application. Table 1 shows red-emitting Mn^{2+}-doped other phosphates. It can be found that their PL peak position are different, indicating that luminescence properties of Mn^{2+} ion are affected by the different crystal field environment of Mn^{2+}.

PL spectra of CMPO:xMn^{2+} phosphors(1 mol% ≤ x ≤ 6 mol%) with excitation 410 nm at room temperature are shown in Fig. 4. The nature of PL spectra remains the same for all the Mn^{2+} ion concentrations. However, the intensity of PL band varies with changing Mn^{2+} ion concentration. There is an increase in the intensity of PL band when the concentration increases from 1 − 5 mol%. > 5 mol% of Mn^{2+} ion concentration, the PL band intensity decreases because there is concentration quenching. So, 5 mol% is recorded to be the critical Mn^{2+} ion concentration. From diagram, it can be found that PL peak position has slight red shift with increasing Mn^{2+} concentration. There is as follows explanation. As known, the emission properties of Mn^{2+} in different host lattices depend on the different crystal field environment.