Original Article

Investigations of the crystalline phase and photoluminescence properties of white-light Ca$_x$ZnMoO$_{4+x}$ phosphors

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ABSTRACT

In this study, the solid-state reaction method was used to synthesize the undoped Ca$_x$ZnMoO$_{4+x}$ (without the addition of activators) compositions ($x=0$, 0.5, 1.0, and 1.5) at different temperatures and investigate them as the new luminescent phosphors. XRD patterns revealed that no raw materials were residual and no secondary phase was observed in the synthesized ZnMoO$_4$ powder. The applicable synthesis temperature of ZnMoO$_4$ powder was 800°C–900°C because it was melted as temperature was higher than 900°C. As 800°C and 900°C were used as the synthesis temperatures of Ca$_{0.5}$ZnMoO$_{4.5}$ composition, the CaMnO$_3$ was observed as the predominant crystalline phase and ZnMoO$_4$ was observed as the secondary phase. As the $x$ value of Ca$_x$ZnMoO$_{4+x}$ powders increased from 0 to 1.0, the applicable synthesis temperatures were raised from 900°C to 1200°C. The important novelties for all Ca$_x$ZnMoO$_{4+x}$ compositions are that they have special emission properties, and we call them Ca$_x$ZnMoO$_{4+x}$ phosphors. The PL spectra of all Ca$_x$ZnMoO$_{4+x}$ phosphors show that they had only one broad peak with centered optical wavelengths occurred at around 490 nm. The bandwidths and central wavelengths of all PL spectra were unchanged as the CaO content and synthesis temperature were changed. The approximate emission bandwidths of all Ca$_x$ZnMoO$_{4+x}$ phosphors were in optical wavelengths of 350 nm–550 nm and their maximum emission intensities increased with CaO content. Even the crystalline phases of Ca$_x$ZnMoO$_{4+x}$ phosphors were different from their original compositions, all of them would emit the white light.

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1. Introduction

Compared to conventional white-light illuminating lamps, the white-light emitting diodes (WLEDs)-based light sources have the merits of long lifetime, low energy consumption, and high efficiency and reliability, which also have the significant advantages of reductions in pollution from fossil fuel power plants. In the past, many methods had been developed to investigate WLEDs, the compositions of LED chips and phosphors were the most used method [1]. S. Nakamura and G. Fasol were the first to feature a blue LED with a yellow (YAG)3(AlG)3O12:Ce3+ (YAG:Ce) phosphor and achieve the commercially WLEDs in 1996 [2]. Also, other yellow phosphors, for example Li2Sr1-xBa2SiO4:Eu2+ [3] and γ-Ca2SiO4:Ce3+Li+ phosphors [4], were also used to investigate the WLEDs. White-light emission can also be realized by adopting differently two-complementary systems such as yellow-red phosphors, cyan-red phosphors, or green/yellow-red phosphors under blue or ultraviolet (UV) excitations [5,6].

Guo et al. investigated Ca3Lu(BO3)3-based phosphors with the co-dopants of Eu2+ and Mn2+ ions. The Eu2+ ions dominate a broad blue-green emission light centered at 480 nm, due to the transition from the lowest energy level of the 5d state to the 4f ground state [7]. Mn2+ ions dominate the emission light centered at 645 nm, which is attributed to the 4T1g–5A2g forbidden transition [7]. Zhong et al. synthesized Eu3+-activated La2Ti2O7 composition as the red phosphors, which consist of a series of emission peaks in the region of 580–710 nm due to 5D0–7Fj (j = 0–4) transitions of Eu3+ ions [8]. Both the synthesized La2Ti2O7:Eu3+ and commercial YAG:Ce3+ phosphors could be incorporated into a low-melting glass to form phosphor-in-glass composite, and the composite could emit a white light [8].

Also, white-light emission can also be realized in combining three-primary emitting such as blue-green-red phosphors under excitation of UV light [3,4]. Zhang et al. investigated a single phase Eu2+, Ce3+, and Mn2+ doped Ba3Lu2Si2O8 phosphors by solid-state reactions, in which Eu2+, Ce3+, and Mn2+ generated the blue, green, and red emission, respectively [9]. However, if a composition with white-light emission can be investigated and the phosphor can be excited by light in the UV region or in blue and other wavelengths, then we can construct a featured WLED. In the past, we had investigated the crystalline and optical properties of the Eu3+-doped double perovskite Ba2ZnMoO5 phosphors [10]. We found that after being excited the undoped Ba2ZnMoO5 powder could not emit light as a phosphor and Eu3+-doped Ba2ZnMoO5 powders would emit red light. Many researchers have investigated on the luminescent properties of different lanthanide ions doped CaMoO4. For example, Sinha et al. used polyol method to prepare Er3+/Yb3+ doped CaMoO4 powder as the infrared to green upconversion phosphor [11]. Ansari and Alam used polyol and Stober surface coating process to synthesize CaMoO4:Sm and their silica-coated CaMoO4:Sm nanoparticles acted as a red phosphor [12].

In the past, Sharma et al. found that the CaMoO4 phosphor could emit a strong blue color with a wide band, which was located from 400 to 550 nm and had the maxima at 470 and 494 nm. They said that the emission spectrum is attributed to an intrinsic emission of MoO42- ions [13]. In an unexpected research, we had found that the undoped Ca2ZnMoO4+x compositions would also act as phosphors and they would emit one broad band with the property of white light. For that, we had well investigated the Ca2ZnMoO4+x phosphors by solid-state reaction method and we would show three important novelities in the synthesized Ca2ZnMoO4+x compositions. The first important novelty is that we had synthesized Ca2ZnMoO4+x compositions as the host materials of phosphors without the addition of activators (transition elements) and we had well investigated their crystalline and luminescent properties. The second novelty is that the Ca2ZnMoO4+x phosphors had only one emission peak, which was ranged from 380 nm to 640 nm and centered at around 490 nm. The final novelty is that the CaO content had large influences on the synthesis temperatures and optical properties of synthesized Ca2ZnMoO4+x phosphors. We had also well investigated the effects of CaO content and synthesis temperature on the variations of the crystalline and photoluminescence (PL) properties of Ca2ZnMoO4+x phosphors.

2. Experimental procedure

In our experience, the main compositions of the used materials have a large effect on the PL properties of synthesized phosphors. In the present study we used CaCO3 (Isuzu Inc., purity 98%, particle sizes small than 5 μm), MoO3 (US Research Nanomaterials Inc., purity 99.8%, particle sizes small than 6 μm), and ZnO (US Research Nanomaterials Inc., purity 99.5%, particle sizes small than 1 μm) particles in these proportions: x CaCO3 + MoO3 + ZnO. The resulting compositions were denoted as Ca2+xZnMoO4+x, where x = 0, 0.5, 1.0, and 1.5, respectively. After the powders were mixed with acetone using ball milling method, dried, and ground, then the Ca2+xZnMoO4+x compositions were synthesized at temperatures of 800°C for 2 h in air. Where the highest synthesis temperature was dependent on the CaO content, and it increased from the 900 °C to 1200 °C as the CaO content increased from 0 to 1.0 and then saturated at 1200 °C. When the Ca2+xZnMoO4+x compositions were synthesized above the highest temperature, they would be melted. X-ray diffraction (XRD) patterns were used to analyze the crystalline phases for determining the effect of synthesis temperature on the crystalline properties of synthesized Ca2+xZnMoO4+x powders. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were measured from room temperature to 1400 °C with a heating rate of 10 °C/min to observe the temperatures starting weight loss and the melting temperatures of Ca2+xZnMoO4+x powders. Scanning electron microscopy (FESEM, JEOL JSM 6700) was used to observe the morphologies of all Ca2+xZnMoO4+x powders with an accelerating voltage of 10 kV. The elemental maps obtained by FESEM equipped with Energy Dispersive Spectrometer (EDS) for elemental Zn, Mo, and Ca were also used to find their distributions on the synthesized Ca2+xZnMoO4+x powders. The PL properties of the synthesized phosphors were recorded in the wavelength range of 200–700 nm on a Hitachi F-4500 fluorescence spectrophotometer and 3D scanning was used to find the optimum PL excitation wavelength (PLE). We had found that the optimum excitation wavelengths of the
Ca$_2$ZnMoO$_{4+x}$ phosphors were located at ultraviolet ray (UV) of 270nm to 290 nm, which were dependent on the CaO content and synthesis temperature. After finding the optimum PLE wavelengths of all synthesized Ca$_2$ZnMoO$_{4+x}$ phosphors, the PL properties were also recorded at room temperature in the wavelength range of 300–700 nm on the fluorescence spectrophotometer. Finally, the Commission Internationale de l’Eclairage (CIE) chromaticity diagram was applied to verify the extent of color distortion.

3. Results and discussion

XRD patterns of synthesized Ca$_2$ZnMoO$_{4+x}$ powders were investigated as a function of CaO content and synthesis temperature. XRD patterns shown in Fig. 1 were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) files of No. 800347 for MoO$_3$, No. 890510 for ZnO, No. 350765 for ZnMoO$_3$, and No. 851267 for CaMoO$_4$, respectively. Fig. 1 shows that as different CaO contents were added and different synthesis temperatures were used, the synthesized Ca$_2$ZnMoO$_{4+x}$ powders revealed different crystallization results. When the ZnMoO$_3$ composition was synthesized at 800 °C, as shown in Fig. 1(a), the only predominant crystalline phase was ZnMo$_4$, and the unidentified phases were really observed. They comprised precursor materials or secondary phases and some of their diffraction peaks overlapped with those of ZnMoO$_3$ phase, and they were difficult to be differentiated from each other. When the synthesis temperature was increased to 900 °C, the diffraction intensity of the ZnMoO$_3$ phase was apparently increased and the mainly crystalline peak changed from (220) plane to (120) plane. Fig. 1(a) also shows that as the synthesis temperature increased from 800 to 900 °C, the 2θ value of the (220) peak underwent no apparent change and the full width at half maximum (FWHM) value of the (220) peak underwent apparent change, from 0.21° to 0.16°. As 1000 °C was used as synthesis temperature, the ZnMoO$_3$ material would melt. These results suggest that 900 °C is the applicable synthesis temperature for the precursors to form ZnMoO$_3$ phase.

It is interesting to note that as CaO was added to form the Ca$_{0.5}$ZnMoO$_{4.5}$ composition and 800 °C and 900 °C were used as the synthesis temperatures, the CaMo$_4$ was observed as the predominant crystalline phase and ZnMoO$_3$ was observed as the secondary phase because of its lower diffraction intensity. The residual precursors ZnO and MoO$_3$ phases and some unidentified phases were also observed in the synthesized Ca$_{0.5}$ZnMoO$_{4.5}$ powders. When the synthesis temperature was increased from 800 °C to 900 °C, the diffraction intensity of the CaMnO$_4$ phase appeared to increase and the FWHM value of the (112) plane decreased; When the synthesis temperature was increased from 900 °C to 1000 °C, the diffraction intensity of the CaMnO$_4$ phase appeared to decrease and the FWHM value of the (112) plane increased. As the synthesis temperature increased from 800 °C, 900 °C, to 1000 °C, the FWHM values of the (112) plane were 0.19°, 0.18°, and 0.26° and the 2θ values of the (112) plane were unchanged and located at 28.76°. The results in Fig. 1(b) show that 900 °C was the applicable synthesis temperature and 1000 °C was too high for Ca$_{0.5}$ZnMoO$_{4.5}$ composition because the diffraction intensity of (112) peak decreased.

With CaZnMoO$_5$ and Ca$_{1.5}$ZnMoO$_{5.5}$ as the compositions and 800 °C as the synthesis temperature, the only predominant crystalline phase was CaMoO$_4$ (we will prove that the predominant crystalline phase is CaMoO$_4$ phase rather than (Ca$_{0.5}$ZnMoO$_{4.5}$) and the precursor ZnO phase was residual. Thus, the ZnMoO$_3$ phase, the MoO$_3$, or the unidentified or secondary phases were not observed. As Fig. 1(c) and (d) shows the mainly crystalline phase and peak of CaZnMoO$_5$ and Ca$_{1.5}$ZnMoO$_{5.5}$ compositions were CaMoO$_4$ phase and (112) plane (located at 28.76°). The 2θ values of the (112) plane were unchanged as the composition and synthesis temperature were changed. The FWHM values of synthesized CaZnMoO$_5$ and Ca$_{1.5}$ZnMoO$_{5.5}$ powders first increased as the synthesis temperature increased from 800 °C, reached a maximum at 1000 °C, and then decreased as the 1200 °C was used. For synthesized CaZnMoO$_5$ (Ca$_{1.5}$ZnMoO$_{5.5}$) powders, the FWHM values of the (112) peak were 0.19° (0.20°), 0.19° (0.19°), 0.15° (0.18°), 0.19° (0.20°), and 0.22° (0.21°) as the synthesis temperatures were 800 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C, respectively.

The results in Fig. 1 suggest that the different CaO contents have a large effect on the crystalline phases of Ca$_{2+x}$ZnMoO$_{4+x}$ powders. These results prove that as CaZnMoO$_5$ and Ca$_{1.5}$ZnMoO$_{5.5}$ are used as the compositions, as shown in Fig. 1(c) and (d), all the diffraction peaks of the two synthesized powders are in accordance with the tetragonal structure (CaMoO$_4$) and they are not in accordance with other MoO$_3$-based compositions, such as the Ca$_2$ZnMoO$_6$ with orthorhombic structure (JCPDS file of No. 480797) and the Sr$_2$ZnMoO$_4$ with double perovskite (faceted-centered) structure (JCPDS file of No. 742474) or with tetragonal (body-centered) structure (JCPDS file of No. 150599). However, compared the 2θ values of the (112) diffraction peak of CaMoO$_4$ phase in Fig. 1(b)–(d) they were almost unchanged as the CaO content was increased. In fact, the crystalline phase changes as observed on these XRD patterns can be correlated to the structural modifications induced by the CaO addition to form the CaMnO$_4$ phase.

The zoom-in XRD patterns of the synthesized ZnMoO$_4$, Ca$_{0.5}$ZnMoO$_{4.5}$, and CaZnMoO$_4$ powders are shown in Fig. 2(a–c) as a function of synthesis temperature to demonstrate the variations of the crystalline phases. Also, as CaO is added into ZnMnO$_4$ to form the Ca$_2$ZnMoO$_{4+x}$ compositions, the degree of interaction between the O–Mo–O bonds and bond length and angle will be changed, which will cause the structural variations of order–disorder in the lattice. For that, as CaO is added into ZnMnO$_4$ to form the Ca$_2$ZnMoO$_{4+x}$ compositions, the crystalline phase of changes from ZnMnO$_4$ to CaMnO$_4$. In order to confirm the CaO will react with MnO$_2$ to form the CaMnO$_4$ compound, the CaCO$_3$ precursor is heated at 900 °C for 2 h. We believe that the CaCO$_3$ will decompose into CaO and CO$_2$ (this will be proven in Fig. 8 for the TGA and DTA spectra of Ca$_{2+x}$ZnMoO$_{4+x}$ powders). The CaO powder was prepared by heating the CaCO$_3$ powder to 1200 °C, and we believed that the CaCO$_3$ had decomposed into CaO and CO$_2$. Then the XRD analysis was recorded, and the pattern of the prepared CaO powder is shown in Fig. 2(d). Apparently, the main crys-
Fig. 1 – XRD patterns of (a) ZnMoO$_4$, (b) Ca$_{0.5}$ZnMoO$_{4.5}$, (c) CaZnMoO$_5$, and (d) Ca$_{1.5}$ZnMoO$_{5.5}$ powders as a function of synthesis temperature.

Fig. 2 – XRD patterns of (a) ZnMoO$_4$, (b) Ca$_{0.5}$ZnMoO$_{4.5}$, and (c) CaZnMoO$_5$ powders as a function of synthesis temperature. (d) XRD pattern of CaO powder.
talline peak of CaO was (200) plane, which could not be found in all synthesized Ca$_2$ZnMoO$_4$x powders. This result proves that the CaO will form a chemical compound with the MoO$_3$ and/or ZnO precursors to form the CaMoO$_4$ or (Ca, Zn)MoO$_4$ phase. Thus, we will prove that the CaO will form a chemical compound with the MoO$_3$ to form the CaMoO$_4$ phase rather than with MoO$_3$ and ZnO to form the (Ca, Zn)MoO$_4$ phase.

The SEM images in Figs. 3–6 show the morphologies of ZnMoO$_4$, Ca$_{0.5}$ZnMoO$_4$, CaZnMoO$_4$, and Ca$_{1.5}$ZnMoO$_{4.5}$ powders synthesized at different temperatures. Even with the ZnMoO$_4$ crystallization phase, the ZnMoO$_4$ particles synthesized at 800 °C had an irregular shape and with particle size larger than 40 μm, as Fig. 3(a) shows. When the synthesis temperature was increased to 900 °C, as Fig. 3(b) shows, the ZnMoO$_4$ particles were enlarged and larger than 60 μm. These results indicate that the ZnMoO$_4$ particles are not suitable for using as phosphors because of their large particle sizes. When synthesis temperature was higher than 900 °C, the ZnMoO$_4$ powder would melt and its particle sizes could not be observed.

The surface morphologies of Ca$_{0.5}$ZnMoO$_4$,$x$ particles synthesized at different temperatures are shown in Fig. 4. As the synthesis temperature increased from 800 °C to 1000 °C, the particle size and morphology of Ca$_{0.5}$ZnMoO$_4$,$x$ powder appeared to be changed. Even the ZnMoO$_4$ and CaMoO$_4$ crystallization phases were coexisted in the 800 °C-synthesized Ca$_{0.5}$ZnMoO$_{4.5}$ powder, the particles had a long-string shape, aggregated characteristics, and small sizes, and their average width and length were in the ranges of 1.4–3.3 μm and 2.8–10.2 μm, as Fig. 4(a) shows. Synthesized at 900 °C, as Fig. 4(b) shows, the long-string grains were also observed and their diameter and length apparently increased as compared with the results in Fig. 4(a). As the synthesis temperature was increased to 1000 °C, the Ca$_{0.5}$ZnMoO$_{4.5}$ particles had a nearly cubic shape, the grain sizes critically increased and they had a diameter of larger than 15 μm, as Fig. 4(c) shows. Hence, we will show that 900 °C is the applicable temperature to synthesize the Ca$_{0.5}$ZnMoO$_{4.5}$ phosphor because the 900 °C-synthesized phosphor has the optimum optical properties.

In contrast, Fig. 4(d–f) shows the corresponding SEM images of 1000 °C-synthesized Ca$_{0.5}$ZnMoO$_{4.5}$ particles (Fig. 4c) the elemental maps obtained by FESEM equipped with EDS for elemental Zn, Mo, and Ca. For the Zn (Fig. 4d), Mo (Fig. 4e), and Ca (Fig. 4d) elements were observed on all of the area of all particles. These results suggest even the Ca$_{3}$MoO$_{4}$ and ZnMoO$_{3}$ phases are really observed in the XRD patterns, the two phases are uniformly distributed in the Ca$_{0.5}$ZnMoO$_{4.5}$ particles. For the 1000 °C-synthesized Ca$_{0.5}$ZnMoO$_{4.5}$ particles (Fig. 4c), some adsorbing materials (small particles) were observed on the surfaces of the large particles. Because the composition of small particles in Fig. 4(c) is same with that of big ones, we believe the adsorbing materials are the residual material after the re-crystallization of small particles in Fig. 4(b) to larger ones.

Comparison of the results in Figs. 5 and 6 shows that as Ca$_{3}$ZnMoO$_{4}$ and Ca$_{1.5}$ZnMoO$_{4.5}$ compositions were synthesized at the same temperature, their particle sizes and morphologies had no apparent change. Synthesized at 800 °C and 1000 °C, large and irregular shape particles were distributed in the small-size matrix, and all the particle sizes increased with synthesis temperature, as these results in Figs. 5(a,b) and 6(a,b) are compared. When the synthesis temperature was increased to 1100 °C, as shown in Figs. 5(c) and 6(c), the crystallized Ca$_{3}$ZnMoO$_{4}$ and Ca$_{1.5}$ZnMoO$_{4.5}$ particles with irregular shape were revealed and their sizes were in the ranges of 0.5–1.5 μm and 0.6–1.8 μm. These results suggest that the reaction and crystallization of Ca$_{3}$ZnMoO$_{4}$ and Ca$_{1.5}$ZnMoO$_{4.5}$ compositions are significantly increased as the synthesis temperature is higher than 1000 °C. However, as 1200 °C was used as synthesis temperature, as shown in Figs. 5(d) and 6(d), the particles showed a uniform and round shape, and the sizes of Ca$_{3}$ZnMoO$_{4}$ and Ca$_{1.5}$ZnMoO$_{4.5}$ powders had increased to the ranges of 1.3–4.5 μm and 1.4–4.2 μm, respectively. These results prove that when the solid-state reaction method is used to synthesize Ca$_{3}$ZnMoO$_{4+x}$, phosphors, CaO content and heating temperature are two important factors to affect their crystalline properties. In this study, even though the Ca$_{3}$ZnMoO$_{4+x}$ phosphors have different morphologies, we will show that they have similar and never appearance PL properties.

Figs. 7 and 8(b–e) show the corresponding SEM images of 1200 °C-synthesized Ca$_{3}$ZnMoO$_{4.5}$ particles shown in Fig. 7(a), the elemental maps obtained by FESEM equipped with EDS for elemental Zn, Mo, and Ca. For the 1200 °C-synthesized Ca$_{1.5}$ZnMoO$_{4.5}$ powders (Fig. 7a), the Mo (Fig. 7c) and Ca (Fig. 7d) elements were observed on all the area of all particles but Zn (Fig. 7b) element was observed on the small area of all particles. These results match the results of XRD patterns shown in Fig. 1(a), the mainly crystalline phase is the CaMoO$_{4}$ and raw material ZnO is residual. Because the Zn element cannot be detected on the surfaces of 1200 °C-synthesized Ca$_{1.5}$ZnMoO$_{4.5}$ powder, these results prove that the predominant crystalline phase is CaMoO$_{4}$ phase rather than (Ca,Zn)MoO$_{4}$ phase.

DTA and TGA curves of all Ca$_{x}$ZnMoO$_{4}$,$x$ powders are shown in Fig. 8 as a function of heating temperature. These DTA curves of Ca$_{0.5}$ZnMoO$_{4.5}$ (Fig. 8b), Ca$_{1.0}$ZnMoO$_{4.5}$ (Fig. 8c), and Ca$_{1.5}$ZnMoO$_{4.5}$ (Fig. 8d) powders show an unapparent endothermic peak at about 610–640 °C. The decomposition of CaCO$_{3}$ into CaO and CO$_{2}$ is the reason to cause this result because this peak cannot be observed in the curves of ZnMoO$_{4}$ powder (Fig. 8a). DTA curves also show that as the CaO (CaCO$_{3}$) content increased, the endothermic peak at temperature higher than 1000 °C was shifted to higher temperature, which suggest the melting temperatures of Ca$_{x}$ZnMoO$_{4}$,$x$ powders increased with CaO content. Fig. 8 proves that the starting temperatures for endothermic peaks (melting temperatures) of ZnMoO$_{4}$, Ca$_{0.5}$ZnMoO$_{4.5}$, Ca$_{1.0}$ZnMoO$_{5.0}$, and Ca$_{1.5}$ZnMoO$_{5.5}$ powders are about 998 °C, 1053 °C, 1241 °C, and 1255 °C. The melting temperatures of ZnO, CaO, MoO$_{3}$, ZnMoO$_{4}$, and CaMoO$_{4}$ are 1975 °C, 2572 °C, 795 °C, 950 °C, and 962 °C, respectively. For that we believe the low melting temperatures of Ca$_{x}$ZnMoO$_{4}$,$x$ powders are caused that they are the MoO$_{3}$-based compositions.

For Ca$_{0.5}$ZnMoO$_{4.5}$, Ca$_{1.0}$ZnMoO$_{5.0}$, and Ca$_{1.5}$ZnMoO$_{5.5}$ powders, as Fig. 8(b,c) shows, the weight loss started at about 600 °C and the ratio of weight loss increased with CaCO$_{3}$ content. The weight losses of ZnMoO$_{4}$, Ca$_{0.5}$ZnMoO$_{4.5}$, CaZnMoO$_{4}$, and Ca$_{1.5}$ZnMoO$_{5.5}$ compositions measured from Fig. 8 were 0%, 7.5%, 13.1%, and 16.8%. As the CaCO$_{3}$ decomposes into CaO
Fig. 3 – SEM images showing the morphologies of ZnMoO$_4$ powders at different synthesis temperatures: (a) 800 °C and (b) 900 °C.

Fig. 4 – SEM images showing the morphologies of Ca$_{0.5}$ZnMoO$_{4.5}$ powders at different synthesis temperatures: (a) 800 °C, (b) 900 °C, and (c) 1000 °C. Elemental maps for (d) Zn, (e) Mo, and (f) Ca for the corresponding SEM image of (c).

Fig. 5 – SEM images showing the morphologies of CaZnMoO$_5$ powders at different synthesis temperatures: (a) 800 °C, (b) 1000 °C, (c) 1100 °C, and (c) 1200 °C.

and CO$_2$, the calculated weight loss of ZnMoO$_4$, Ca$_{0.5}$ZnMoO$_{4.5}$, CaZnMoO$_5$, and Ca$_{1.5}$ZnMoO$_{5.5}$ compositions are 0%, 8.0%, 13.5%, and 17.6%, these values match the measured variations of TGA curves in Fig. 8. These results prove that the decomposition of CaCO$_3$ into CaO and CO$_2$ is the reason to cause the weight loss at about 600 °C. These TGA curves show that the temperatures started to lose weight of ZnMoO$_4$, Ca$_{0.5}$ZnMoO$_{4.5}$, Ca$_{1.0}$ZnMoO$_{5.0}$, and Ca$_{1.5}$ZnMoO$_{5.5}$ powders were about 1013 °C, 1068 °C, 1254 °C, and 1269 °C. From the EDS analyses for elemental Zn, Mo, and Ca we can find that the
Fig. 6 – SEM images showing the morphologies of Ca$_{1.5}$ZnMoO$_{5.5}$ powders at different synthesis temperatures: (a) 800 °C, (b) 1000 °C, (c) 1100 °C, and (c) 1200 °C.

Fig. 7 – (a) SEM images showing the morphologies of 1200 °C-synthesized Ca$_{1.5}$ZnMoO$_{5.5}$ powder. Elemental maps for (b) Zn, (c) Mo, and (d) Ca for the corresponding SEM image of (a).

CaMoO$_4$ phase is stabilized and observed as the synthesis temperature is 1200 °C, even its melting point is only 962 °C. These TGA and DTA analyses of Ca$_x$ZnMoO$_{4+x}$ phosphors shown in Fig. 8 prove that as the temperatures are higher than their melting points, the vaporization of MoO$_3$ is the reason to cause the weight loss.

The room-temperature PLE spectra of Ca$_{x}$ZnMoO$_{4+x}$ phosphors were recorded in the wavelength range of 200–300 (or 320) nm ($\lambda_{ex}$) and the results are shown in Fig. 9, while the PLE spectra were measured at an emission wavelength of 490 nm. Fig. 9(a) shows the PLE spectra of ZnMoO$_4$ phosphor, when the synthesis temperature was increased from 800 °C to 900 °C, only one broad excitation band was observed and the centered wavelength of the main PLE spectra was 277 nm. However, even the maximum excitation intensity (PLE$_{max}$) increased with synthesis temperature, the PLE spectra in Fig. 9(a) only had very weak value. For Ca$_{0.5}$ZnMoO$_{4.5}$ phosphor, as Fig. 9(b) shows, also only one broad excitation band was observed and the centered wavelength of the main PLE spectra increased from 281 nm to 290 nm as synthesis temperature increased from 800 °C to 1000 °C, and the 900 °C-synthesized phosphor had the highest PLE$_{max}$ value.
Fig. 8 – Differential thermal analysis and thermal gravimetric analysis of (a) ZnMoO$_4$, (b) Ca$_{0.5}$ZnMoO$_{4.5}$, (b) Ca$_{1.0}$ZnMoO$_{5.0}$, and (d) Ca$_{1.5}$ZnMoO$_{5.5}$ powders as a function of heating temperature.

Fig. 9 – PLE spectra of (a) ZnMoO$_4$, (b) Ca$_{0.5}$ZnMoO$_{4.5}$, (c) CaZnMoO$_5$, and (d) Ca$_{1.5}$ZnMoO$_{5.5}$ phosphors, as a function of synthesis temperature.

Fig. 4(c) shows that the particle sizes of 1000 °C-synthesized Ca$_{0.5}$ZnMoO$_{4.5}$ phosphor critically increased. As the particle sizes of phosphors are in larger sizes (for example, 10 μm), the light is difficult to emit from the powders and the PLE$_{\text{max}}$ value decreases.

For both CaZnMoO$_5$ and Ca$_{1.5}$ZnMoO$_{5.5}$ phosphors, as shown in Fig. 9(c) and (d), the centered wavelength of the main PLE spectra was shifted from 270 nm to 277 nm as synthesis temperature increased from 800 °C to 1200 °C. As the same synthesis temperature was used, the PLE$_{\text{max}}$ value of the
Ca$_{1.5}$ZnMoO$_{4+x}$ phosphor was higher than that of CaZnMoO$_4$ phosphor. These results suggest that as CaO is added into ZnMoO$_4$ to form the Ca$_x$ZnMoO$_{4+x}$ compositions, the optical properties will be enhanced. We will show in Fig. 9 that the PL spectra of Ca$_x$ZnMoO$_{4+x}$ phosphors have the similar tendencies.

In the past, we had found that the room-temperature PLE spectra of undoped ZnO films and grown ZnO nanowires existed in the range of 200–320 nm and centered at around 242 nm, while monitoring at 400 nm emission [14]. For that, we believe that the intensity enhancements of PLE (Fig. 9) and PL (Fig. 10) spectra are not caused by the ZnO phase observed in Fig. 1. However, the reasons to cause the Ca$_2$ZnMoO$_{4+x}$ with the properties of phosphors are not really known, and we would try to find the reasons for the Ca$_x$ZnMoO$_{4+x}$ phosphors with white lights. The PLE values for the Ca$_2$ZnMoO$_{4+x}$ phosphors to obtain the optimum PL properties were really dependent on the CaO content and synthesis temperature, which were in the range of 270290 nm. The PL spectra of Ca$_x$ZnMoO$_{4+x}$ phosphors are achieved in Fig. 10(a–d) under 270290 nm excitation within UV and visible ranges from 300 to 700 nm as a function of CaO content, synthesis temperature, and PLE value. From the PL spectra in Fig. 10(a–d) we found that all Ca$_x$ZnMoO$_{4+x}$ phosphors had only one broad emission band, which was ranged from 385 to 630 nm. The spectra of Ca$_x$ZnMoO$_{4+x}$ phosphors excited by other wavelengths also had one broad emission band but weaker PL intensities. As the same CaO content was used, except the Ca$_{0.5}$ZnMoO$_{4.5}$ phosphor, the maximum intensity of emission peak increased with synthesis temperature. Also, as the same synthesis temperature was used, the maximum intensity of emission peak increased with CaO content. These results prove again that the CaO content and synthesis temperature are two most important factors to influence the optical properties of Ca$_x$ZnMoO$_{4+x}$ phosphors.

These PL spectra in Fig. 10(a–d) also show that all the centered wavelengths (the wavelengths reveal the maximum intensity of emission peak) of the main PL spectra occurred around 490 nm and they were almost unchanged as the CaO content and synthesis temperature were changed. These results suggest that as the CaO content in Ca$_x$ZnMoO$_{4+x}$ compositions increases and even the crystalline phases are changed, the mechanism for causing the emission of Ca$_x$ZnMoO$_{4+x}$ phosphors is the same. Also, we had investigated the PL emission spectra of the undoped ZnO films and grown ZnO nanowires registered at the excitation wavelength of 242 nm and recorded in the range of 200–800 nm. The wavelength for revealing the maximum intensity of emission peak was 392 nm for the undoped ZnO films and 395 nm for ZnO nanowires. These results prove again that the PL emission spectra of Ca$_x$ZnMoO$_{4+x}$ phosphors are not caused by the ZnO phase observed in Fig. 1.

When different host and activator materials are used to synthesize the phosphors, different activator ions can cause different energy level transitions in different energy bands, which will cause the phosphors to relax lights with different emission peaks (or wavelengths). Klinbumrung et al. found that as the orthorhombic α-MoO$_3$ powder was excited using 380 nm wavelength at room temperature, the PL spectrum presented a broad peak over the 400–600 nm range and the emission light centered at 430–440 nm [15]. The band-to-band transitions in the MoO$_3$ powders are thought as the reason to cause this emission property [16]. Sharma et al. found that CaMoO$_4$ phosphors could emit a strong blue color, which had two maxima peaks at 470 and 494 nm and had a wide band located from 400 to 550 nm. For CaMoO$_4$ phosphor, green emission appears under UV-light excitation wavelength of 250–310 nm [17]. These results are believed to be attributed to an intrinsic emission of MoO$_4^{2–}$ ions [18].

In the compositions of Ca$_x$ZnMoO$_{4+x}$ phosphors, because no specific ions are used as activators, for that the special transitions in different energy bands of activators will not happen. As the CaO content and the synthesis temperature increase, the bandwidths of PL spectra and the wavelengths to reveal the PL max are almost unchanged even the wavelengths of PLE max have few variations. These results prove again that all Ca$_x$ZnMoO$_{4+x}$ phosphors have the same emission mechanism. Even the different CaO contents and synthesis temperatures will cause the Ca$_x$ZnMoO$_{4+x}$ phosphors having different crystalline phase (Fig. 1), the emission mechanism has not been changed. For that, we believe these emission spectra of Ca$_x$ZnMoO$_{4+x}$ phosphors are caused by the intrinsic emission peaks of MoO$_4^{2–}$ ions, which are ultimately overlapping with each other to form a broad emission band.

The color purity of the luminescence emissions are usually described by using Commission Internationale de l’Eclairage (CIE) chromaticity diagram. For that, the CIE chromaticity diagram of Ca$_x$ZnMoO$_{4+x}$ phosphors synthesized at different temperatures was measured, which can also prove that Ca$_x$ZnMoO$_{4+x}$ phosphors emit white light (not shown here). The color coordinates of Ca$_x$ZnMoO$_{4+x}$ Phosphors, which are located on (0.296, 0.392), (0.295, 0.391), (0.295, 0.392), and (0.297, 0.393), are corresponding to ZnMoO$_4$, Ca$_{0.5}$ZnMoO$_{4.5}$, CaZnMoO$_5$, and Ca$_{1.5}$ZnMoO$_{5.5}$ phosphors synthesized at 800 °C, 1000 °C, 1200 °C, and 1200 °C. Even the maximum emission peak is located at 490 nm, the CIE chromaticity diagram finds that the color rendering properties of all Ca$_x$ZnMoO$_{4+x}$ phosphors reveal the white light.

The decay time of the phosphor materials is the time defined for the intensity of a single emission peak (usually using the peak with the maximum emission intensity) to decrease to 1/e (approximately 37%) of its original intensity. For the Ca$_x$ZnMoO$_{4+x}$ phosphors investigated, the wavelengths of the exciting light were dependent on the composition and synthesis temperature. The wavelength of 490 nm was used to measure the decay time, because it had the maximum emission intensity in the Ca$_x$ZnMoO$_{4+x}$ phos-
Fig. 11 – Decay-time curves of (a) ZnMoO₄, (b) Ca₀.₅ZnMoO₄₋ₓ, (c) CaZnMoO₄, and (d) Ca₁.₅ZnMoO₄₋ₓ phosphors, as a function of synthesis temperature.

Table 1 – Decay times of the synthesized CaₓZnMoO₄₋ₓ phosphors as a function of CaO content and synthesis temperature (unit: ms).

<table>
<thead>
<tr>
<th>x</th>
<th>800 °C</th>
<th>900 °C</th>
<th>1000 °C</th>
<th>1100 °C</th>
<th>1200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.368 ± 0.013</td>
<td>0.384 ± 0.011</td>
<td>xxx</td>
<td>xxx</td>
<td>xxx</td>
</tr>
<tr>
<td>0.5</td>
<td>0.275 ± 0.012</td>
<td>0.292 ± 0.009</td>
<td>0.279 ± 0.011</td>
<td>xxx</td>
<td>xxx</td>
</tr>
<tr>
<td>1.0</td>
<td>0.282 ± 0.012</td>
<td>0.315 ± 0.010</td>
<td>0.308 ± 0.008</td>
<td>0.328 ± 0.007</td>
<td>0.334 ± 0.007</td>
</tr>
<tr>
<td>1.5</td>
<td>0.286 ± 0.011</td>
<td>0.294 ± 0.009</td>
<td>0.293 ± 0.008</td>
<td>0.292 ± 0.007</td>
<td>0.299 ± 0.006</td>
</tr>
</tbody>
</table>

phors. Typically, the standard form of the single exponential decay function is:

\[ I(t) = I_0 \exp\left[-\left(t/t_\tau\right)\right] \]  

where \( \tau \) is the constant for the life (or called decay) time and refers to the time required for the intensity to drop to \( I_0/e \), \( t \) is time, \( I_0 \) is the initial intensity, and \( I(t) \) is the intensity at time \( t \). The decay times of all CaₓZnMoO₄₋ₓ phosphors can be directly measured from decay curves shown in Fig. 11 and the results are compared in Table 1. When different CaO contents in CaₓZnMoO₄₋ₓ phosphors were used, the average decay times of 0.368–0.384, 0.275–0.292, 0.282–0.334, and 0.286–0.299 ms were recorded with the PL spectra as the CaO content of the CaₓZnMoO₄₋ₓ phosphors was \( x = 0, 0.5, 1.0, \) and \( 1.5, \) respectively. The decay time has no apparent relationship with the variation of CaO content and as the results in Fig. 11 and Table 1 are compared, the decay time increases with \( \text{PL}_{\text{max}} \) value.

Guo et al. found that the decay times of Ca₉Gd(PO₄)₂:0.01Eu²⁺, yMn²⁺ phosphors decreased from 849 to 329 ns as the \( y \) value increased from 0.0 to 0.07 [19]. Huang et al. found that the average decay times of 410 nm emission (excited by 336 nm) of 0.2%-Bi³⁺ doped Ba₂Y-(BO₃)₂:Cl: Eu³⁺ phosphors were determined to be 228, 223, 216, 214, 207, 199, 196, and 201 ns in the 0.0%, 0.2%, 0.5%, 1%, 2%, 4%, 6%, and 8% Eu³⁺ doped phosphors [20]. They also found that the average decay times of 612 nm emission (excited by 336 nm) of 0.2%-Bi³⁺ doped Ba₂Y-(BO₃)₂:Cl: Eu³⁺ phosphors were determined to be 0.999, 1.036, 1.095, 1.113, 1.203, 1.152, and 1.042 ms in the 0.2%, 0.5%, 1%, 2%, 4%, 6%, and 8% Eu³⁺ doped phosphors, respectively. The revealed results in the two researchers suggest that the decay time of the white-light phosphor is dependent on the wavelength of emission peak and the concentration of using activators. There are no activators added into CaₓZnMoO₄₋ₓ phosphors. For that, we believe that the variation in the decay times of CaₓZnMoO₄₋ₓ phosphors is caused by the variations of the compositions and crystalline phase. As compared these results in Refs. [19] and [20], the observed decay curves and the measured decay times of CaₓZnMoO₄₋ₓ phosphors vary within narrow limits as the CaO content and synthesis temperature are changed.
4. Conclusions

In this study, Ca$_2$ZnMoO$_{4+x}$ phosphors with different CaO contents were synthesized using solid-state reaction method and the optimal synthesis temperatures for ZnMoO$_4$, Ca$_0.5$ZnMoO$_{4.5}$, Ca$_2$ZnMoO$_4$, and Ca$_1.5$ZnMoO$_{4.5}$ phosphors were 900, 900, 1200, and 1200 °C, respectively. The optimum PLE wavelengths of Ca$_2$ZnMoO$_{4+x}$ phosphors were dependent on the CaO content and synthesis temperature. The wavelengths of Ca$_2$ZnMoO$_{4+x}$ phosphors to reveal the maximum PL intensity were independent of the CaO content and synthesis temperature, and all of them were located at 490 nm. These results prove that the all Ca$_2$ZnMoO$_{4+x}$ phosphors have the same emission mechanism. As same CaO content was added, except Ca$_0.5$ZnMoO$_{4.5}$ phosphor, the emission intensities of PLE and PL spectra increased with synthesis temperature; As the same synthesis temperature was used, the emission intensities of PLE and PL spectra increased with CaO content. Decay times of 0.384–0.232, 0.275–0.292, 0.282–0.334, and 0.286–0.299 ms were recorded with the PL spectra as the CaO content of the Ca$_2$ZnMoO$_{4+x}$ phosphors was x = 0, 0.5, 1.0, and 1.5. All Ca$_2$ZnMoO$_{4+x}$ phosphors had only one broad PLE band, and their central wavelengths were dependent on the CaO content and synthesis temperature. Also, all Ca$_2$ZnMoO$_{4+x}$ phosphors had only one broad PL band, which was ranged from 385 to 630 nm, and their central wavelengths were 490 nm and independent of the CaO content and synthesis temperature.

Author contributions

S.F. Wei organized the paper and helped with writing it; C.Y. Lin and Y.K. Wang carried out the experiments, analyzed the data, and measurements; S.T. Tsai and C.F. Yang organized the data, wrote the paper, and helped with editing the English.

Conflicts of interest

The authors declare no conflicts of interest.

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