

Red light emission of Mn doped beta-tricalcium phosphate $\beta\text{-Ca}_3(\text{PO}_4)_2$

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Abstract

This paper is the first report on the red light emission of manganese (Mn) doped beta-tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$, TCP) synthesis by co-precipitation method followed by thermal annealing. The annealed Mn doped TCP phosphor showed dominant spheres with a diameter of about 500 nm. The influences of the Mn concentration, annealing temperature, and atmospheres on the photoluminescence intensities of the phosphors were investigated and the results indicate that the annealing temperatures and Mn concentrations are the main factors. The phosphor showed visible emission peaks appeared at about 660 nm and 580 nm results in from the ${}^4\text{T}_1\text{-}{}^6\text{A}_1$ transitions within Mn^{2+} ion. The Mn-TCP phosphor may serve as a candidate for light-emitting diode application in agriculture lighting.

Keywords. Hydroxyapatite; manganese; luminescence; tricalcium phosphate.

1. INTRODUCTION

Along with hydroxyapatite (HA), beta-tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$, (TCP) has received considerable attention as a host material in designing the light emission materials because of its biosafety, nontoxicity and easily incorporated a wide variety of substitutions for Ca^{2+} and PO_4^{3-} based on flexibility of its structure [1, 2]. In order to enhance light emission of the device performance and its agriculture products, it is necessary to combine the advantages of environmental friendly properties with light emission [3, 4]. In particular, synthetic light source with deeply red light beyond at 660 nm is beneficial to plants growth and development since some flowers and fruit products can accelerate development, flowering and yielding under red light illumination [5-8]. Therefore, considerable effort has been made to functionalize phosphors that can be emitted the light in the desire spectra for maximum the photosynthetic efficiency of plant growth and developments [9, 10].

Manganese (Mn) is a suitable activator for doping into host materials due to their exhibiting important advantages compared with available activators such as lower toxicities, photostabilities, high thermal and chemical stabilities, and economics [11, 12]. Thus far, several papers have reported on using Mn as an activator in the rare earth

free matrix such as $\text{Zn}_2\text{SiO}_4\text{:Mn}$ [13], $\text{Zn}_2\text{SiO}_4\text{:Mn@SiO}_2$ [14], ZnS:Mn [15] and ZnO:Mn [18, 19]. In particular, to our knowledge, there are no previous reports on the effect of manganese concentration and annealing condition on controlling the intensity of wide-band red luminescence of Mn doped beta-tricalcium phosphate (TCP) for the environmentally friendly phosphor. Therefore, this study proposes a novel way of controlling the broad red light emission of the Mn doped TCP, which can be achieved by applying a thermal annealing in the protected atmosphere. The microstructure and chemical composition of the Mn doped TCP were characterized by field emission scanning electron microscopy (FE-SEM). The crystal structure of the specimen was characterized by X-ray diffraction. The light emission of phosphor was determined by photoluminescence spectrometer.

2. MATERIALS AND METHOD

Manganese doped tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$, (TCP) was synthesized through a co-precipitation method, as follows: an aqueous solution with stoichiometric amount of $(\text{NH}_4)_2\text{HPO}_4$ (0.2M, 99.9 % purity, Aldrich) solution was added over an aqueous solution containing $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.2 M, 99.9 % purity, Aldrich), and various amount of $\text{Mn}(\text{NO}_3)_3$ (99.9 % purity, Aldrich) with vigorous

stirring. The reaction mixture was stirred for 0.5 h followed by precipitation method at 80 °C and the pH was adjusted to 11 by using aqueous ammonia. The resulting precipitates were washed three times, and then annealed at 1000 °C and 1100 °C for 1 h in Ar and Ar+5 %H₂. The crystalline structures of the Mn doped TCP were characterized by X-ray diffraction (XRD, D8 Avance, Bruker, Germany). The Mn doped TCP was placed on a silicon (Si) wafer, and the microstructure as well as chemical composition of the Mn doped TCP was determined by field emission scanning electron microscopy (JEOL, JSM-6700F, JEOL Techniques, Tokyo, Japan). Photoluminescence (PL) tests were performed to evaluate the optical properties of the Mn doped TCP. NANO LOG spectrofluorometer (Horiba, USA) equipped with 450 W Xe arc lamp and double excitation monochromators was used. The PL spectra were recorded automatically during the measurements.

3. RESULTS AND DISCUSSION

Figure 1 show XRD diagram of the 6Mn-TCP annealed at 1000 °C, 1100 °C in Ar and Ar+5%H₂. The specimen showed peaks which match the standard patterns of Ca₃(PO₄)₂, beta-tricalcium phosphate (TCP) (PDF 09-0169) and a trace of hydroxyapatite (HA), Ca₁₀(PO₄)₆(OH)₂ (PDF 01-084-1998) [3]. Beta-tricalcium phosphate (TCP) plays an important role in biomedical research because TCP has a level of accelerating the mineralization and crystallization of calcium phosphate in the bone forming process comparable to that of HA [17, 18]. Moreover, the dominant phase of TCP found on the 6Mn-TCP may suggest a better performance in the optoelectronic field because of the strong light emission of doped activator into the TCP host [19, 20].

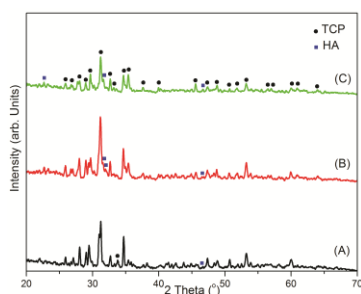


Figure 1: XRD patterns of the 6Mn-TCP (A) annealed at 1000 °C in Ar, (B) annealed at 1100 °C in Ar, (C) annealed at 1100 °C in Ar+5 %H₂

The representative microstructure and chemical composition of the 6Mn-TCP specimen annealed at

1100 °C was characterized by SEM and EDS, as shown in figure 2 (A) and (B). The specimen showed mostly spheres and rod-like morphology in lesser amount. The annealed particles present spheres, the diameter of about 500 nm whereas for the rod like particles, the morphology of 150 nm in wide and 300 nm length (figure 2 (A)). It is also noted that ionic radius of dopant Mn²⁺ (0.8 Å) is compared to Ca²⁺ (1 Å) size, the potential occupation of calcium sites can be obtained. So, a calculated (Ca+Mn)/P ratio of particle is of about 1.61. Such ratio of calcium phosphate particle has been documented previously, especially in case of calcium phosphate synthesized by wet chemical synthesis method [4]. Peaks corresponding to Mn elements was observed (figure 2 (B)), indicating the presence of the Mn into the TCP. In addition, a probed atomic concentration of the Mn incorporation into the specimens was as high as ~ 3.5 %, which would be suggested to the successful doping of Mn in the host TCP. The presence of Si peak in the EDS spectrum was relatively high signal because the Mn doped TCP powders were attached on conductive Si wafer for SEM imaging.

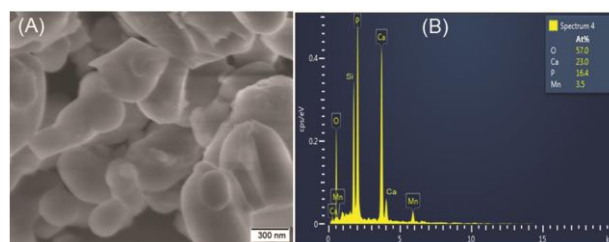


Figure 2: Microanalysis of 6Mn-TCP annealed at 1100 °C in Ar (A) SEM image, (B) EDS analysis of chemical composition

Figure 3 shows the emission spectra of Mn-TCP phosphor with variation of Mn concentrations annealed at 1100 °C in Ar excited at 350 nm. The Mn-TCP phosphor showed broad visible emission peaks appeared at about 580-660 nm and they can be attributed to the excited state ⁴T₁ to the fundamental ⁶A₁ transitions within Mn²⁺ dopants [13]. However, it should be noted that the PL intensity of the 6 % mol Mn of phosphor increased significantly. The higher PL intensity of the 6 % mol Mn of phosphor suggested that the 6 % mol Mn of phosphor could be the critical concentration point for optimizing the distance between neighboring Mn²⁺ ion in the host matrix resulting in enhancing PL. It is also noted that there were two emission bands at (580-660) nm indicating the involvement of two different emission centers in the radiative processes of the phosphor. An emission band observed at 580 nm of the phosphors may be attributed to the presence of HA

whereas 660 nm for the TCP host, suggesting that Mn^{2+} dopant is sensitive to its surrounding local environment. In particular, shorter Mn-O distances will result in stronger crystal field around Mn^{2+} ion leading to red shifted ${}^4T_1 - {}^6A_1$ as in the TCP in comparison to HA [12]. On the basis of these findings, the specimen with Mn concentration of 6 % mol was used for further characterizations.

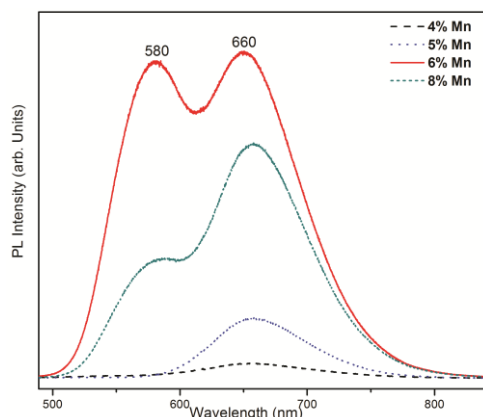


Figure 3: Photoluminescence spectra of Mn-TCP annealed at 1100 °C in Ar with Mn concentrations of 4 %, 5 %, 6 % and 8 % mol

The photoluminescence of the 6Mn-TCP phosphors annealing at different temperatures in Ar was characterized, as shown in Figure 4. As annealing temperature of 900 °C, the luminescence of the Mn-TCP was showed a dominated emission at 660 nm, but two emission centers at 580 nm and 660 nm when they were annealed at 1000-1100 °C. It also can be seen that the intensity of the PL increased with the increase of temperatures. It is well known the higher annealing temperature allows for the creation of well-crystalline structure via higher temperature [21]. The enhancing PL intensities of 6Mn-TCP phosphors should be mainly due to their well-crystalline phase of the phosphor prepared by higher annealing temperature.

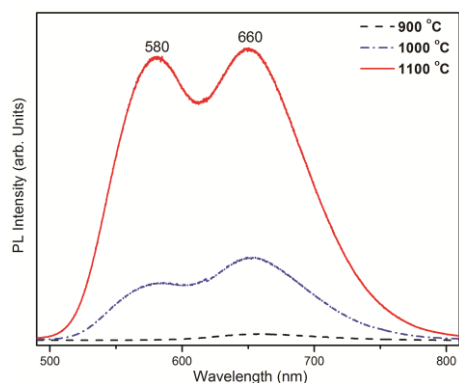


Figure 4: Photoluminescence spectra of 6Mn-TCP annealed at 900, 1000 and 1100 °C in Ar

The photoluminescence of the 6Mn-TCP annealed at 1100 °C with different annealing atmosphere was further characterized, as shown in figure 5. Two specimens showed the same typical PL feature with two emission centers at 580 nm and 660 nm when they were annealed in Ar and Ar+5% H_2 . However, it should be noted that the intensity of the PL increased for the phosphors annealed in Ar as compared to that of Ar+5% H_2 . These significant differences of band could be attributed to the presence of the well-crystalline structure of phosphors annealing in Ar compared to that in Ar+5% H_2 (figure 1).

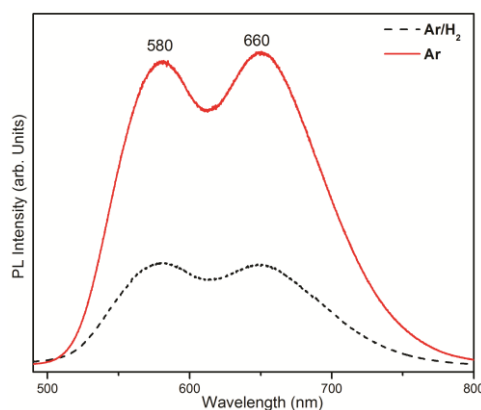


Figure 5: Photoluminescence spectra of 6Mn-TCP annealed at 1100 °C in Ar and Ar+5 H_2

Figure 6 shows the photoluminescence excitation (PLE) of the 6Mn-TCP prepared by coprecipitation annealed at 1100 °C in Ar. It could be noted that the PLE spectra of 6Mn-TCP showed broad excitation band ranging from (300-380) nm and (390-450) nm, suggesting its promising phosphor for agriculture lighting with UV LED chips or blue LED chips.

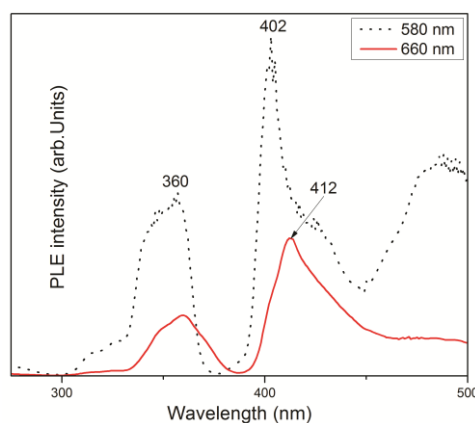


Figure 6: Photoluminescence excitation spectra of 6Mn-TCP annealed at 1100 °C in Ar

4. CONCLUSION

We herein demonstrated that the red light emission of Mn doped TCP phosphor could be obtained effectively by doping with manganese. In particular, photoluminescence intensity of the sample increases with the increasing of Mn concentrations. The photoluminescence of the Mn doped TCP with thermal annealing temperature of 1100 °C was displayed strongest band at (580-660) nm, which was much stronger than those of the 900 °C annealed Mn-TCP. This enhancement of the PL was mainly attributed to the well-crystalline material via high temperature annealing. These phosphors show potential applications in agriculture such as plant cultivation where require a combination of broad red light emission and environmentally friendly materials for photosynthesis in green agriculture crop.

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