

Synthesis of down-converting red emission $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$ phosphors for use in solar cells

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$\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$ ($x = 1, 3, 5$ mol%, CZAMO) phosphor materials were synthesized using the liquid phase precursor (LPP) method. Nanostructured cellulose was impregnated with metal-hydrate solution and then calcined to vaporize the cellulose. The impregnated cellulose was fired at 800 to 1200 °C to give the CZAMO phosphors. The particle size and crystal structure of the phosphors were analyzed by FE-SEM and XRD. Nano-sized particles with a dominant $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ structure (100 nm) were obtained by firing at 800 °C for 1 h. The red emission wavelength of the phosphors ranged from 650 to 750 nm, peaking at 713 nm.

Key words: $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$, Phosphor, Solar cell, Down-converting, LPP method.

Introduction

Crystalline silicon solar cells have been developed as a green energy source because of their excellent light-to-electricity conversion efficiency [1, 2]. However, crystalline silicon has an efficiency limit with respect to the solar spectrum where the wavelength range of 450–700 nm takes up a considerable part of the spectrum. On the other hand, the absorption of crystalline silicon is excellent in the wavelength range of 700–1000 nm. To improve this problem, the development of materials with down-conversion properties is required. Down-conversion involves transforming a high energy photon (UV to Visible) to a low energy photon (deep red to NIR) using a medium like phosphor [3–6].

$\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$ (CZAMO) is a phosphor material with a long range emission wavelength [7] and is based on $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ developed by Barbanyagre *et al.*, [8]. $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ is not a phosphor material with emission properties, but doping with Mn to make CZAMO lends the required emission properties.

In this study, CZAMO phosphor was synthesized using the liquid phase precursor (LPP) method [9, 10]. LPP is an environment-friendly method to obtain nanoparticles using metal hydrate solutions. To control the CZAMO phosphors, we used nanostructured cellulose and varied the firing temperatures.

Experimental Details

$\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$ (CZAMO, $x = 1, 3, 5$ mol%) phosphors were synthesized using the LPP method. The starting materials used were $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-aldrich, $\geq 99.0\%$), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-aldrich, $\geq 99.0\%$), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka, $\geq 98.0\%$) and $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Aldrich, $\geq 98\%$). The materials were dissolved in water with a concentration of ≈ 20 wt%. Nanostructured cellulose (Asahi chemical co., ltd, Japan, TG-101) was impregnated with nitrate solutions at a 1 : 1 weight ratio.

The firing process involved two steps. First, calcination was carried out to remove the cellulose by firing at 500 °C for 1 h at a heating rate of 5 °C/min in air. The second step was the firing of the calcined samples at 800, 900, and 1200 °C for 1 h at a heating rate of 50 °C/min in air.

The synthesized particles were analyzed by X-ray diffraction (XRD, $\text{CuK}\alpha$, 12 kW, Rigaku, Japan) with a scanning range of 10 ° to 90 ° and a speed of 6 °/min. The particle size and morphology of the obtained phosphor were observed by field emission scanning electron microscopy (FE-SEM, Jeol-JSM7000F). The emission properties of the particles were measured by photoluminescence spectrometry (PL, Scinco, FS-2).

Results and Discussion

Figure 1 shows the XRD patterns of the synthesized particles fired at 800, 900, and 1200 °C for 1 h as a function of Mn concentration (1, 3, and 5 mol%). The diffraction peaks agreed with the patterns of $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ (JCPDS 50-0426) and few CaO peaks

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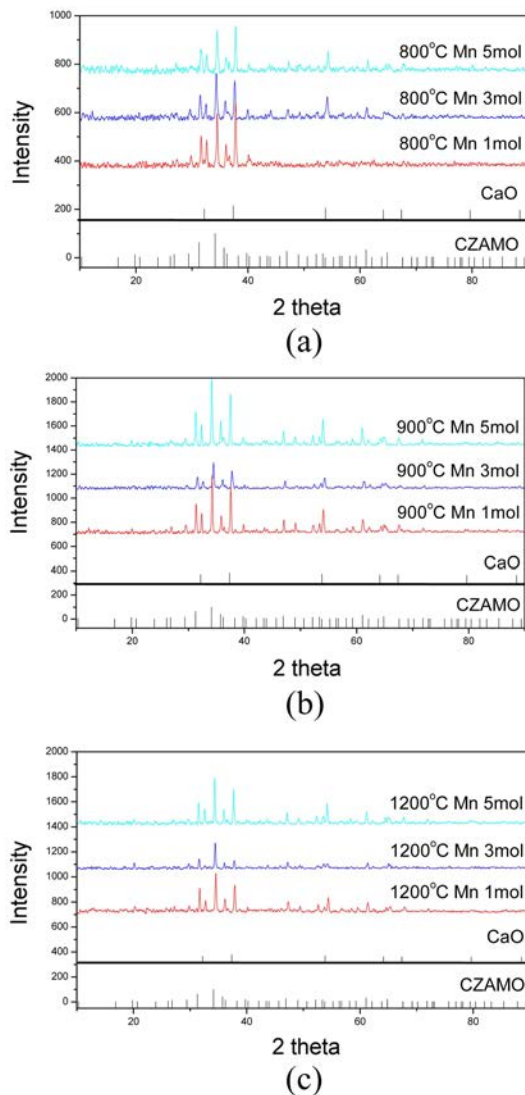


Fig. 1. XRD patterns of $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$ ($x = 1, 3, 5$ mol%) phosphors fired at (a) 800 °C, (b) 900 °C, and (c) 1200 °C.

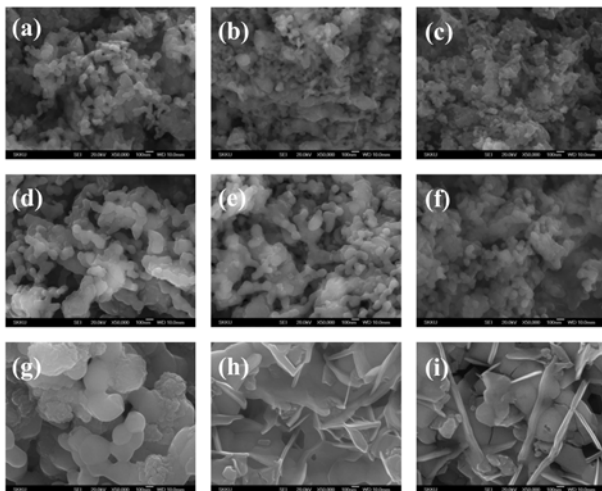


Fig. 2. FE-SEM image of synthesized phosphors fired at (a) 800 °C, Mn 1 mol%; (b) 800 °C, Mn 3 mol%; (c) 800 °C, Mn 5 mol%; (d) 900 °C, Mn 1 mol%; (e) 900 °C, Mn 3 mol%; (f) 900 °C, Mn 5 mol%; (g) 1200 °C, Mn 1 mol%; (h) 1200 °C, Mn 3 mol%; (i) 1200 °C, Mn 5 mol%.

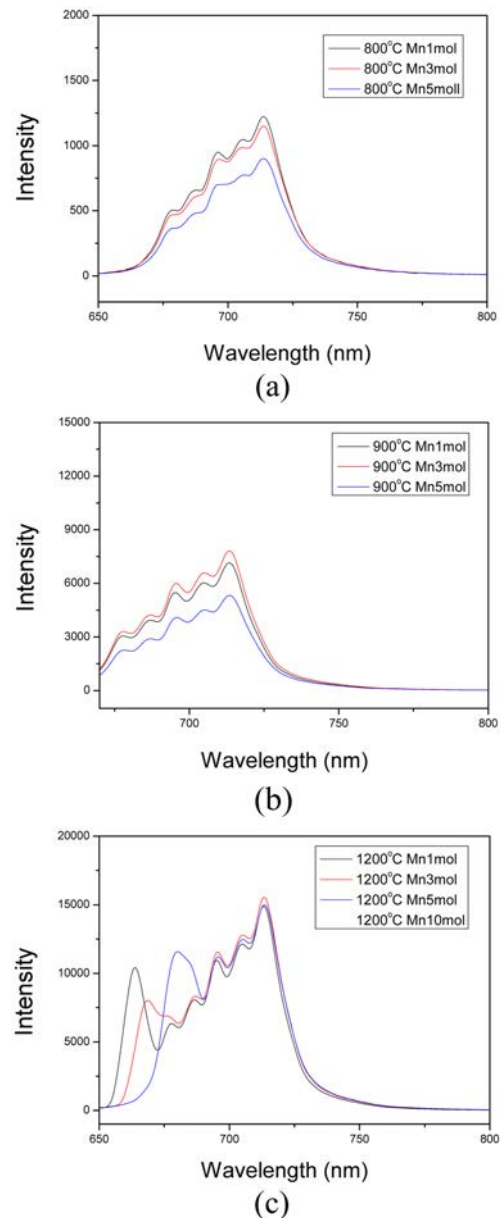


Fig. 3. Emission spectra (observed at 342 nm) of synthesized phosphor fired at (a) 800 °C, (b) 900 °C, and (c) 1200 °C.

were found (JCPDS 37-1479). The change in diffraction peaks as a function of temperature and Mn concentration was not observed.

Figure 2 shows the SEM image of the obtained phosphor; the change with the increase in Mn concentration is not shown. The size of the phosphor synthesized at 800 and 900 °C was around 100 nm (Fig. 2(a)-(c)) and 100-150 nm (Fig. 2(d)-(f)), respectively. The phosphor fired at 1200 °C was several microns and aggregated (Fig. 2(g)-(i)), and its morphology changed to round and needle-shaped mixtures.

Figure 3 shows the PL property of phosphors as a function of Mn concentration., CZAMO phosphor emitted a deep red range (650-750 nm) photon when excited at 342 nm. The highest emission peak was at

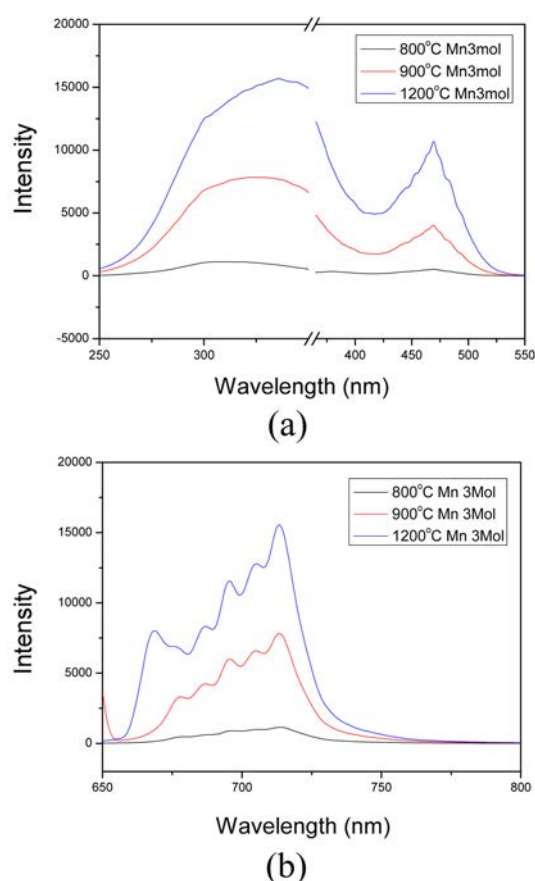


Fig. 4. PL spectra of (a) excitation (observed at 713 nm) and (b) emission (observed at 342 nm) spectra of synthesized phosphor (Mn 3 mol%) as a function of temperature.

713 nm irrespective of the Mn concentration. Due to concentration quenching, the highest emission intensity of phosphor fired at 800 and 900 °C was decreased when the Mn concentration was 5 mol%. However, the phosphor fired at 1200 °C did not show concentration quenching [11].

Figure 4 shows the PL property of the phosphor (Mn = 3 mol%) as a function of firing temperature. The synthesized phosphor had a broad excitation range from UV to visible (Fig. 4(a)). A strong excitation was observed at 340 and 470 nm. The break range (350–365 nm) was the lamp peak from the equipment.

Figure 4(b) shows the emission property of synthesized phosphor (Mn = 3 mol%). The highest peak is at 713 nm and the PL intensity greatly increases as a function of temperature.

CZAMO phosphor is shown to be an excellent down-converting material. In particular, the excitation from the UV to visible range and the emission from a deep red range were excellent. The improvement of crystalline silicon solar cell efficiency is expected by using CZAMO phosphor.

Conclusions

$\text{Ca}_{14}\text{Zn}_6\text{Al}_{10-x}\text{Mn}_x\text{O}_{35}$ ($x = 1, 3, 5$ mol%) phosphors were synthesized by the LPP method. The diffraction peaks of the phosphor analysed by XRD mainly agreed with the pattern of $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$. The particle size of phosphor obtained at 800 °C was 100 nm and increased with the increase in firing temperature. The red emission wavelength of phosphors ranged from 650 to 750 nm and peaked at 713 nm irrespective of the Mn concentration.

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