

Photoluminescence and structural properties of $Zn_{1-x}Ga_2S_4:xMn$ red-emitting phosphors

Ha-Chul Song and Young-Duk Huh*

Department of Chemistry, Institute of Nanosensor and Biotechnology, Dankook University, Seoul 140-714, Korea

ABSTRACT

A series of $Zn_{1-x}Ga_2S_4:xMn$ have been synthesized by solid-state reaction at 900°C. The photoluminescence and structural properties of $Zn_{1-x}Ga_2S_4:xMn$ phosphors have been investigated. $ZnGa_2S_4:Mn$ shows a red emission band at about 635 nm due to the $Mn^{2+} \ ^4T_1 \rightarrow \ ^6A_1$ transition. The luminescence band shifts to longer wavelength with increasing Mn^{2+} content. $ZnGa_2S_4:Mn$ has a strong absorption at 380 nm, which is an emission wavelength of near-UV LED. $ZnGa_2S_4:Mn$ can be used as a red-emitting phosphor pumped by the near-UV LED.

Key words : $Zn_{1-x}Ga_2S_4:xMn$ phosphors, near-UV LED

Introduction

The advent of blue InGaN technology has made it possible to produce a conventional white LED in which white light is obtained by yellow emitting $(Y_{1-x}Gd_x)(Al_{1-y}Ga_y)_3O_{12}:Ce$ phosphor onto a blue LED chip (1, 2). However, the spectral composition of the light produced by the conventional white LED differs from that of natural white light, particularly in the red region. This color property can be improved by generating three-band white LED where green and red emitting phosphors are coated onto a blue LED (3, 4). Another approach is to produce a three-band white using near-UV LED with blue, green, and red emitting phosphors (5). The $M^{II}Ga_2S_4$ type thiogallates are suitable host materials for absorption of near-UV and visible light because they have band gaps below 4.0 eV (6). $SrGa_2S_4:Eu$ is suitable green emitting phosphor excited by blue and near-UV LED (3, 7). $SrGa_2S_4:Ce$ is used for blue emitting phosphor excited by a near-UV LED (8). $ZnGa_2S_4:Mn$ emits a red emission due to Mn^{2+} transition from

$\ ^4T_1$ state to $\ ^6A_1$ state by excited near-UV (9). $ZnGa_2S_4:Mn$ can be used as red emitting phosphor excited by near-UV LED.

However, there is limited information on the optical properties of $Zn_{1-x}Ga_2S_4:xMn$ phosphors. In this study, we synthesized a series of $Zn_{1-x}Ga_2S_4:xMn$ phosphors. The photoluminescence and structural properties of $Zn_{1-x}Ga_2S_4:xMn$ phosphors were investigated.

Experimental

ZnS (Aldrich) and Ga_2S_3 (Alfa) were used as starting materials for the host, and MnS (Aldrich) was used as the activator. An appropriate amount of KBr was added as a flux to decrease the calcination temperature. Starting materials were weighed out stoichiometrically, mixed and ground with a mortar and pestle, and placed an alumina crucible that was heated in box-type furnace at 900°C for 1.5 h. A double crucible configuration was used. One crucible was nestled in the other with an activated carbon in between, thus preventing the phosphors from oxidation. The resulting sintered phosphor cake was removed from the furnace and mortared prior to evaluation. X-ray diffraction (XRD) patterns of $Zn_{1-x}Ga_2S_4:xMn$

* Corresponding author :
Young-Duk Huh
Tel : +82-2-709-2409
Fax : +82-2-792-9269
E-mail : ydhuh@dankook.ac.kr

phosphors ($x = 0.02, 0.04, 0.06, 0.08$) were obtained using a X-ray diffractometer (Simens D5000) with $Cu K\alpha_1$ radiation. Diffraction patterns were taken over the range $10^\circ < 2\theta < 90^\circ$ with a scan rate of 1/min. The particle shapes of the resulting phosphor powders were measured using scanning electron microscopy (SEM; Phillips XL30 ESEM-FEG).

Photoluminescence excitation and emission were measured using a spectrum analyzer (DARSA II, PSI) with a 0.275 m monochromator, a photomultiplier tube, and a 500-W Xe lamp as the excitation source. The incident beam was perpendicular to the surface of the sample, and the observation angle was 45° relative to the excitation source. A commercial near-UV LED ($\lambda_{max} = 380$ nm) was used. $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor suspension was coated onto the surface of the near-UV LED. The suspension was made by dispersing the phosphor in poly-vinyl-alcohol (polymerization degree: 200).

Results and Discussion

$Zn_{1-x}Ga_2S_4:xMn$ phosphors were prepared by solid state reactions. **Fig 1** shows that the XRD patterns and Miller indices of $Zn_{1-x}Ga_2S_4:xMn$ phosphors. The crystal structure of $ZnGa_2S_4$ is tetragonal, with $a = b = 5.297$, $c = 10.363$ Å for space group $I4_2m$ (10). $Mn_{0.75}Ga_{2.17}S_4$ is also tetragonal, with $a = b = 5.456$, $c = 10.220$ Å (11). $Zn_{1-x}Ga_2S_4:xMn$ was indexed

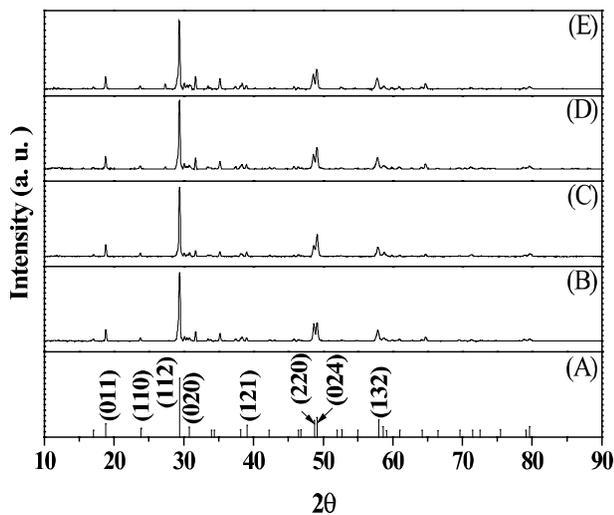


Fig 1. XRD patterns of and Miller indices of (A) $ZnGa_2S_4$, (B) $Zn_{0.98}Ga_2S_4:0.02Mn$, (C) $Zn_{0.96}Ga_2S_4:0.04Mn$, (D) $Zn_{0.94}Ga_2S_4:0.06Mn$, and (E) $Zn_{0.92}Ga_2S_4:0.08Mn$ phosphors.

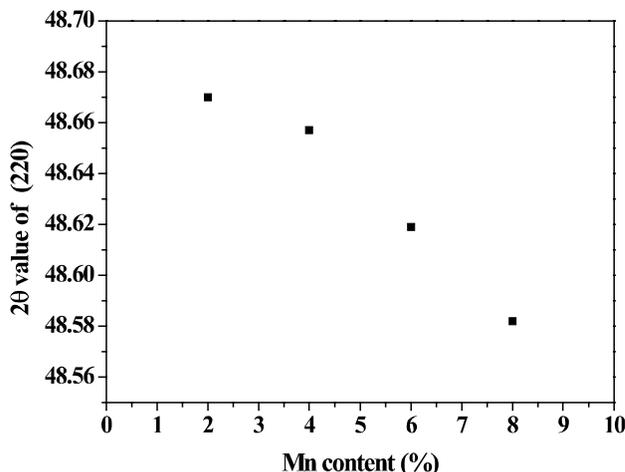


Fig 2. 2θ values of (220) peak of $Zn_{1-x}Ga_2S_4:xMn$ with different contents of Mn.



Fig 3. SEM micrograph of $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor.

based on the $ZnGa_2S_4$ structure because of the similarities of the crystal structures of $ZnGa_2S_4$ and $Mn_{0.75}Ga_{2.17}S_4$. XRD shows that $Zn_{1-x}Ga_2S_4:xMn$ phosphors were well synthesized as a single phase. The correlation between 2θ value of (220) peak and Mn content in $Zn_{1-x}Ga_2S_4:xMn$ phosphors is shown in **Fig 2**. The (220) peak is shifted to the lower angle with increasing amounts of substituted Mn in $Zn_{1-x}Ga_2S_4:xMn$ series. This is caused by the difference in lattice parameter between $ZnGa_2S_4$ and $Mn_{0.75}Ga_{2.17}S_4$. The lattice parameter of $ZnGa_2S_4$ ($a = b = 5.297$ Å) is smaller than that of $Mn_{0.75}Ga_{2.17}S_4$ ($a = b = 5.456$ Å). The linear relationship between (220) peak position and $Zn_{1-x}Ga_2S_4:xMn$ indicates that $Zn_{1-x}Ga_2S_4:xMn$ phosphors are synthesized in a single phase. **Fig 3** shows the

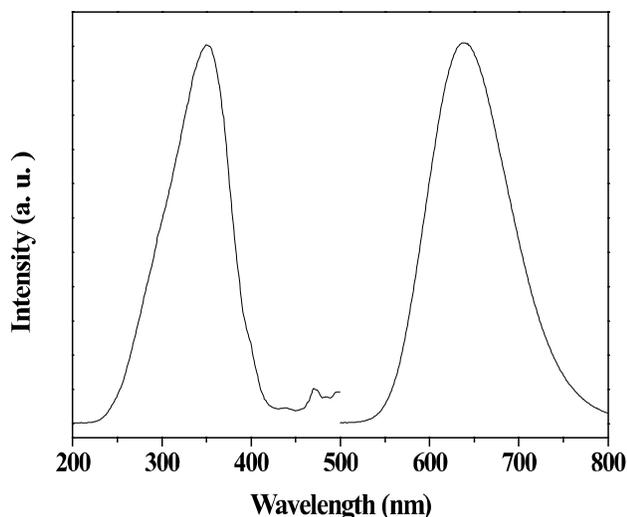


Fig 4. Photoluminescence excitation ($\lambda_{em} = 635$ nm) and emission ($\lambda_{ex} = 355$ nm) spectra of $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor.

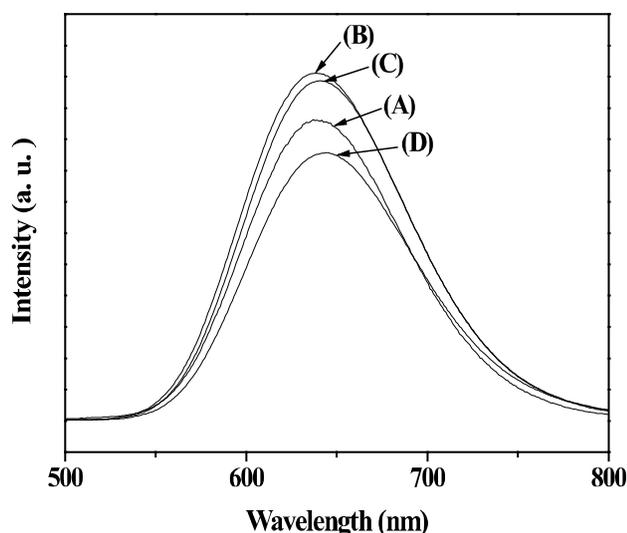


Fig 5. Photoluminescence spectra of $Zn_{1-x}Ga_2S_4:xMn$ phosphors at different values of (A) 0.02, (B) 0.04, (C) 0.06 and (D) 0.08.

SEM image of $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor. The column-shaped particles are about 200nm thick with lengths up to 1.5 μm .

Fig 4 shows photoluminescence excitation and emission spectra of $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor. The excitation spectra show that phosphor has a strong absorption at 355 nm, which is due to the band gap of $ZnGa_2S_4$. The emission spectrum of $Zn_{0.96}Ga_2S_4:0.04Mn$ contains a single symmetric band with maximum at 636 nm ($15,720$ cm^{-1}) and full width at half maximum (FWHM) of $2,440$ cm^{-1} . The broad band in the red region arises from a transition between the ${}^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} .

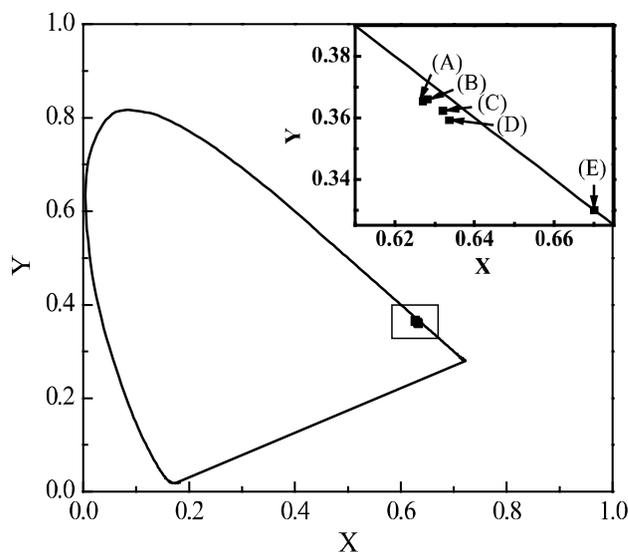


Fig 6. The CIE diagram and chromaticity coordinates of $Zn_{1-x}Ga_2S_4:xMn$ phosphors. The inset shows the enlarged CIE diagram and chromaticity coordinates of $Zn_{1-x}Ga_2S_4:xMn$ phosphors at different values of (A) 0.02, (B) 0.04, (C) 0.06, (D) 0.08, and (E) NTSC red.

The Commission International de l'Eclairage (CIE) chromaticity coordinates of $Zn_{0.96}Ga_2S_4:0.04Mn$ are $x = 0.640$ and $y = 0.355$. $Zn_{1-x}Ga_2S_4:xMn$ are promising candidates as broad red emitting phosphors with excellent chromaticity coordinates. Fig 5 shows photoluminescence spectra of $Zn_{1-x}Ga_2S_4:xMn$ phosphors. The emission intensity of $Zn_{1-x}Ga_2S_4:xMn$ phosphor depends on the Mn concentration. The photoluminescence intensity of $Zn_{1-x}Ga_2S_4:xMn$ with Mn concentration above 4 mol% is gradually decreasing with increasing Mn concentration. This quenching can be explained in terms of the lattice distortion and $Mn^{2+} - Mn^{2+}$ interaction. As shown in Fig 5, there is a red-shift of the photoluminescence peak wavelength in $Zn_{1-x}Ga_2S_4:xMn$ for increasing Mn^{2+} concentration from 2 to 8 mol%. The red shift behavior can be interpreted in terms of the crystal strength in $Zn_{1-x}Ga_2S_4:xMn$ where the Zn^{2+} ion is replaced by the Mn^{2+} ion. The crystal field strength of the Mn^{2+} ion in $Zn_{1-x}Ga_2S_4:xMn$ is proportional to the inverse of the cation to anion distance. The crystal field strength increases with increasing the Mn^{2+} ion in $Zn_{1-x}Ga_2S_4:xMn$. According to the Tanabe-Sugano diagram of the $3d^5$ electron configurations, the position of the 4T_1 emitting level decreases as increasing the crystal field strength (12). Therefore, the emission peaks shift to the red with increasing the Mn^{2+} ion

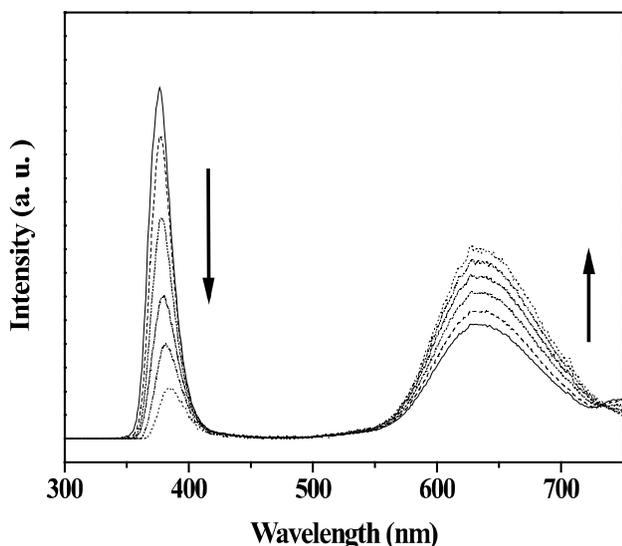


Fig 7. Photoluminescence emission spectra of near-UV and red emitting LEDs. Arrows indicate the changes in the near-UV and red spectra when the amount of $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor is increased.

in $Zn_{1-x}Ga_2S_4:xMn$. The CIE chromaticity coordinates (x , y) of $Zn_{0.98}Ga_2S_4:0.02Mn$, $Zn_{0.96}Ga_2S_4:0.04Mn$, $Zn_{0.94}Ga_2S_4:0.06Mn$, and $Zn_{0.92}Ga_2S_4:0.08Mn$ are (0.639, 0.354), (0.640, 0.355), (0.644, 0.350), and (0.646, 0.347), respectively, as shown in Fig 6. The CIE chromaticity coordinates of red NTSC (National Television Standard Committee) are $x = 0.67$ and $y = 0.33$ (13). The CIE chromaticity coordinates of $Zn_{1-x}Ga_2S_4:xMn$ are close to those of red NTSC. Therefore, $Zn_{1-x}Ga_2S_4:xMn$ have excellent red-emitting color purities.

Fig 7 shows photoluminescence spectra of a near-UV and red emitting LEDs, in which $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor is coated on the near-UV LED. The two distinct emission peaks appear at 380 nm and 635 nm which are the wavelengths of the near-UV LED and red emission from the $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor, respectively. When the amounts of $Zn_{0.96}Ga_2S_4:0.04Mn$ phosphor is increased, the intensity of the 380 nm emission decreases, while that of the 635 nm emission increases simultaneously. Therefore, $Zn_{1-x}Ga_2S_4:xMn$ can be used as red-emitting phosphors pumped by the near-UV LED.

Conclusions

A series of $Zn_{1-x}Ga_2S_4:xMn$ ($x = 0.02-0.08$) were synthe-

sized as a single phase by solid-state reaction. The cell parameters a and b are linearly increased with the concentration of Mn. The photoluminescence emission peaks shift to the red with increasing the Mn^{2+} ion in $Zn_{1-x}Ga_2S_4:xMn$ due to the increase of crystal field strength of $Zn_{1-x}Ga_2S_4:xMn$. $Zn_{1-x}Ga_2S_4:xMn$ have excellent photoluminescence properties, and can be promising red emitting phosphors for applications of white LED excited by the near-UV.

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