

Internal pressure effect on cathodoluminescence enhancement of ZnS:Mn²⁺ synthesized by a sealed vessel

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ZnS:Mn²⁺ phosphors were synthesized by a modified solid-state reaction method. In the synthesis method, a sealed vessel is used, where heat and pressure are simultaneously utilized. The effects of various synthesis conditions such as temperature, Mn concentration, and pressure on the cathodoluminescence (CL) were investigated. Among them, pressure had an effect on CL property as much as others. It was observed that CL intensities of ZnS:Mn²⁺ phosphors increased with the increase of pressure and the best sample showed higher intensity than that of a commercial one by 180%. X-ray diffraction (XRD) and electron paramagnetic-resonance (EPR) were used to understand the enhancement. No change of XRD patterns was observed but the full width at half-maximum (FWHM) of the most intense cubic (111) peak of ZnS:Mn²⁺ decreased with the increase of pressure. EPR signal intensity of Mn²⁺ increased with the increase of pressure. The improved crystallinity and more substitution of Zn²⁺ with Mn metal were believed to be responsible for the enhancement.

I. INTRODUCTION

A lot of attention has been paid on ZnS-based materials for various applications such as display, solar cell, and infrared windows because of their large band-gap energy of 3.66 eV, direct recombination properties and high resistance to electric field.¹⁻³ ZnS:Mn²⁺ has been extensively studied as a phosphor material for its exceptional electroluminescent (EL) and cathodoluminescent (CL) properties. As for the EL application, ZnS:Mn²⁺ phosphor has been mostly used as an active layer of both thin-film and powder-type electroluminescent devices driven by alternating or direct current.^{4,5} Many efforts

have been made to enhance its EL property as well as CL via codoping with sensitizer, surface coating, and so on.^{6,7}

Conventional sulfide phosphors are normally prepared by the sulfurization of the corresponding oxides or carbonates with highly purified H₂S or CS₂ gas, which are very toxic and expensive. When CS₂ gas is used, impurity phases that reduce luminescent property can be made. These sulfide phosphors are also prepared by reacting the corresponding oxides or carbonates with sulfur and flux such as Na₂CO₃ and K₂CO₃. In this method, impurity phases can be also made and it is necessary to wash sulfide phosphors to delete remaining flux after firing. During the washing process, the surface of phosphors can be damaged, which can degrade the luminescence property. In addition, those methods need a high firing temperature, long reaction time, and are a complex process.^{8,9}

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In this paper, we made ZnS:Mn²⁺ phosphors by a modified solid-state reaction utilizing a sealed vessel to overcome the problems such as toxic gas, high firing temperature, long reaction time, and complex process. In this method, it was not necessary to use H₂S or CS₂ gas because ZnS was used as a raw material and was fired in a sealed vessel. Even though this method has several advantages, it has not been systematically investigated until now. Thus, we synthesized, a characterized CL property of them, and compared them with ZnS:Mn²⁺ phosphor synthesized by a conventional method. In addition, because pressure was built up by the evaporation of ZnS raw material, pressure effect on CL property was also investigated

II. EXPERIMENTAL

Unlike conventional synthesis processes, ZnS:Mn²⁺ phosphor samples were prepared by a modified solid-state reaction utilizing a sealed vessel in which pressure was added with the temperature increase. High-purity raw materials such as ZnS (99.9%, Aldrich, St. Louis, MO), Mn (99.9%, Aldrich), NaCl (99.9%, Aldrich), and NaBr (99.99%, Aldrich) were weighted in a glove box purged by Ar gas and transferred to a vessel. Afterwards, the vessel was taken out of the glove box and completely sealed by an oxy-propane torch. The vessel with chemicals was fired at different temperatures between 800 and 1000 °C for 3 h. Finally, phosphor samples were recovered from the vessel after heat treatment and prepared for further investigation.

Crystalline phases constituting phosphor powders were analyzed by x-ray diffraction (XRD) (D/max-IIIIC, Rigaku, Tokyo, Japan) with Cu-K_α radiation operating at 40 kV and 45 mA. The scan rate was 3°/min and the data were collected between 20° and 80°. CL was measured using a demountable ultrahigh vacuum chamber equipped with a laboratory-built CL spectrometer at room temperature. Kimball Physics (Wilton, NH) FRA-2X1-2/EGPS-2X1 electron gun system was used as an excitation source; energy was 700 eV and beam current density was 40 μA/cm². Inductively coupled plasma-mass spectroscopy (ICP-MS: Perkin Elmer Elan 6100, Waltham, MA) were used for the quantitative analysis. Electron paramagnetic-resonance (EPR) signal was recorded using a Jeol (Tokyo, Japan) X-band EPR spectrometer (JES-RE2X), where the microwave frequency was 9.03 GHz (X-band), the modulation width 0.4 mT, and the modulation frequency 100 kHz.

III. RESULTS

A. CL property of ZnS:Mn²⁺ phosphor

Figure 1 shows CL spectra of various ZnS:Mn²⁺ phosphors that were synthesized with or without flux. The main emission band is at approximately 585 nm, which

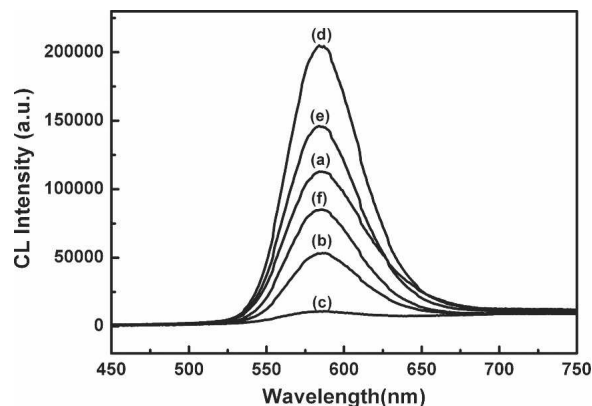


FIG. 1. CL spectra of ZnS:Mn²⁺ phosphors synthesized at 800 °C: (a) commercial ZnS:Mn²⁺, (b) 5 mol% Mn with 5 wt% NaCl, (c) 5 mol% Mn with 5 wt% NaBr, (d) 3 mol% Mn, (e) 5 mol% Mn, and (f) 5 mol% Mn with excess S and 5 wt% NaBr.

results from the Mn: ⁴T₁-⁶A₁ intrashell transition.¹⁰ As shown in Fig. 1, CL intensities of ZnS:Mn²⁺ phosphors synthesized without flux are higher than those with flux and even higher than that of a commercial ZnS:Mn²⁺ field emission display (FED) phosphor by 180%. The result that ZnS:Mn²⁺ phosphors synthesized by our modified solid-state reaction without flux show higher CL intensities than those with flux is different from that of a conventional fabrication process. It means that the washing process can be skipped.¹¹

Besides a large CL increase and simpler process, the modified solid-state reaction has an advantage on manufacturing process that H₂S gas is not necessary to synthesize ZnS:Mn²⁺ phosphors.

B. Optimization of CL property

1. Mn concentration and synthesis temperature

To optimize the process and CL intensity of the product, phosphors were synthesized varying fabrication parameters such as Mn concentration and temperature. As found in Fig. 2, Mn doped the ZnS up to

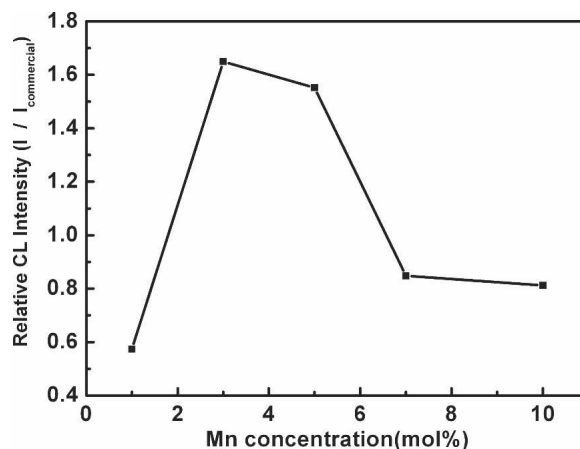


FIG. 2. CL spectra of ZnS:Mn²⁺ phosphors with a different amount of Mn.

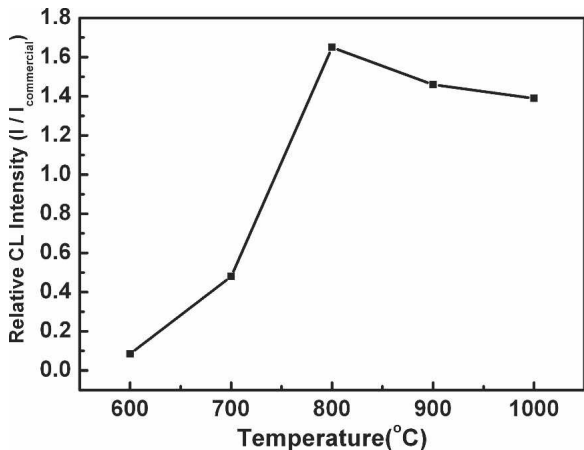


FIG. 3. CL spectra of 3 mol% Mn doped ZnS phosphors with different synthesis temperature.

10 mol% and each CL intensity was normalized to that of the commercial one while maintaining other fixed conditions. As the concentration of Mn increased, CL intensity increased up to 3 mol% of Mn and then gradually decreased by concentration quenching, as shown in Fig. 2.

CL intensities of ZnS:Mn²⁺ phosphors synthesized at various temperatures were also measured. As depicted in Fig. 3, the maximum CL intensity of 3 mol% Mn doped ZnS phosphor was detected when the phosphor was fired at 800 °C. The origin of the intensity decrease above 800 °C has been investigated with XRD analysis. As shown in Fig. 4, ZnS:Mn²⁺ phosphors consist of cubic phase only up to the synthesis temperature of 800 °C.

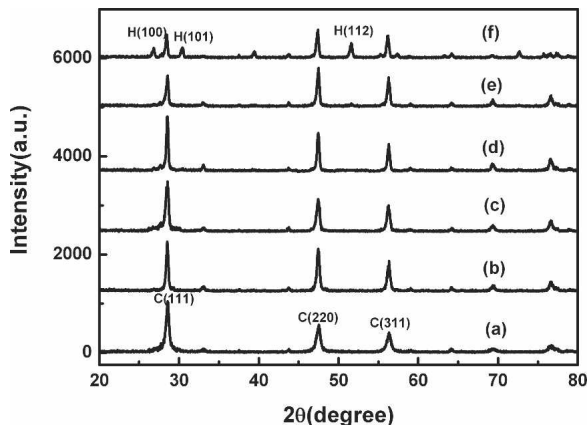


FIG. 4. XRD patterns of 3 mol% Mn doped ZnS phosphors with different synthesis temperature: (a) raw ZnS, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, and (f) 1000 °C.

However, cubic (111) peak becomes smaller and hexagonal phase is about to appear at 900 °C. This behavior is similar to that of phosphors prepared by a conventional solid-state reaction method.¹² The appearance of a hexagonal phase was also investigated by scanning electron microscopy (SEM) images of ZnS:Mn²⁺ phosphors. As shown in Fig. 5, a grainy surface of the ZnS:Mn²⁺ powders at 800 °C starts to agglomerate and powders with crystallographic planar surfaces appear at 900 °C. The change of the ZnS:Mn²⁺ powders can be more clearly observed when synthesized at 1000 °C. Therefore, it is believed that the morphological change of the powders along with the growth of hexagonal phase is responsible for the CL intensity decrease over 800 °C.

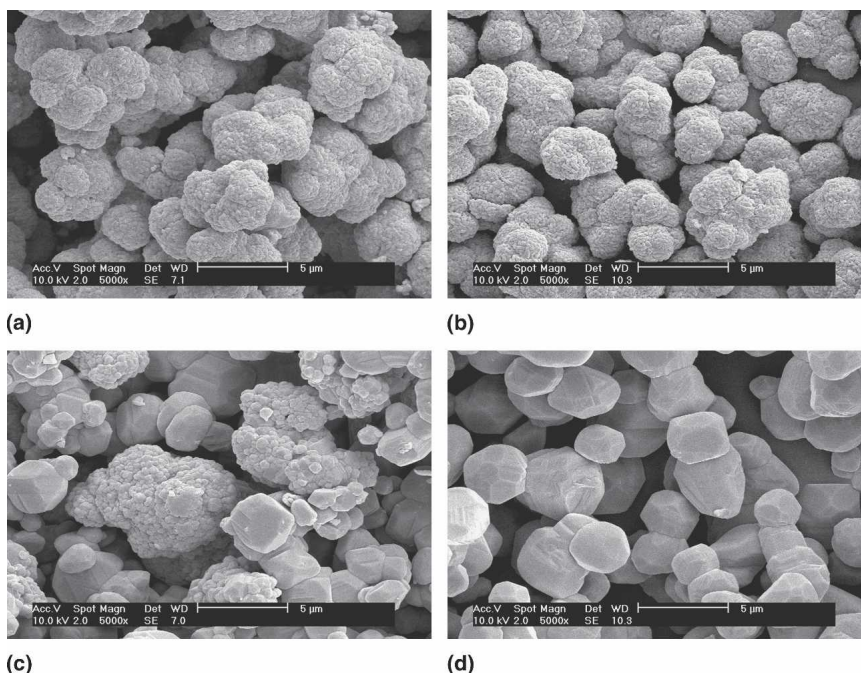


FIG. 5. SEM images of 3 mol% Mn doped ZnS phosphors with different synthesis temperature: (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C.

2. Internal Pressure

In a conventional sulfide-phosphor synthesis process, pressure on the phosphor materials is not usually taken into consideration as the synthesis normally takes place in open environment. In addition, to compensate the degassed sulfur out of sulfide host materials, excess sulfur is generally added to raw materials. However, because the chemicals react in a closed vessel in the present method, the evaporated sulfur gas can induce a pressure in it.

The contribution of internal pressure to CL property was studied varying the vessel volume with a fixed amount of raw materials and firing temperature. Different sized vessels with volumes of 324 mm³ (sample 1), 1080 mm³ (sample 2), 1920 mm³ (sample 3), and 4320 mm³ (sample 4) mm³ were prepared and CL properties of ZnS:Mn²⁺ phosphors synthesized with them were measured. As shown in Fig. 6, the intensity of CL spectra gradually increases as the size of the vessel decreases.

Vapor pressure depends on temperature and type of molecule as expressed in Antoine's equation.¹³ Because all of the vessels used in the experiment contain the same amount of raw materials and were fired at 800 °C, it is reasonable to assume that all the vessels contain the same amount of evaporated gas molecules. Furthermore, because sulfur is the most volatile, it is believed that evaporated gas consists of mostly sulfur gas molecules that are the origin of internal pressure. Thus, the internal pressure of the vessel is inversely proportional to the volume of vessel under the condition of the same amount of sulfur gas molecules and same firing temperature. The relative internal pressure of the vessels can be derived based on the volume of vessels and the pressure ratio of sample 1 to sample 4 (P_1/P_4) is about 13. This supports the effect of induced gas pressure on the synthesized phosphor powders and their CL properties.

We also measured CL efficiency of ZnS:Mn²⁺ phosphors synthesized with different sized vessels using the

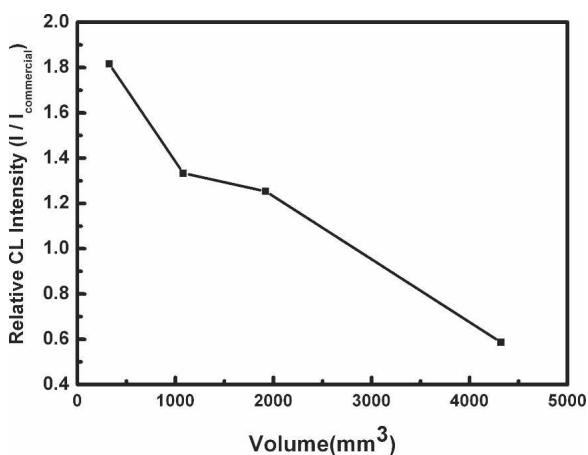


FIG. 6. CL spectra of 3 mol% Mn doped ZnS phosphors synthesized in different vessels.

following method.^{14,15} Luminescence efficiency(η) is defined by the ratio of the luminance to the input power:

$$\eta = \frac{\text{output power}(lm)}{\text{input power}(W)}$$

Luminescence efficiency under electron beam excitation(η) can be rewritten by the following equations:

$$\eta = \frac{\pi L}{W} = \pi \frac{L}{VjD_u}$$

where, L is luminance(cd/m²), V is acceleration voltage(V), j is current density(A/cm²) and D_u is duty cycle. Luminance was measured at 700 V and 40 μ A/cm². Thus, CL efficiency was calculated and summarized in Table I. As shown in Fig. 6, CL efficiency also increases as the internal pressure increases.

IV. DISCUSSION

To understand how pressure improved CL intensity, host material (ZnS) and activator (Mn) were investigated. In the case of host material, XRD and SEM analyses were performed because crystallinity and morphology of ZnS could affect CL property. Because characteristics of Mn ions could also alter the CL property, EPR signals of Mn²⁺ were analyzed to figure it out.

A. Improved crystallinity

Figure 7 represents XRD patterns of ZnS:Mn²⁺ phosphors synthesized in varying vessel sizes. As shown in Fig. 7, all XRD patterns are nearly the same and it is quite difficult to identify the improvement of crystallinity. However, full width half-maximum (FWHM) is related to crystallinity and particle size. In other words, FWHM of XRD peaks becomes narrower if phosphor particles are aligned to the same direction and have better crystallinity, or if particle size becomes increased. Thus, one of the main peaks was selected for comparison, i.e., C (111) at $2\theta = 28.5^\circ$ and FWHM was measured. From Fig. 8, FWHM gradually increases as the size of the vessel decreases.

TABLE I. Luminescence efficiency: Samples 1, 2, 3, and 4 are synthesized in different vessels whose volume is 324, 1080, 1920, and 4320 mm³, respectively.

Phosphor	Luminance (cd/m ²)	Luminescence efficiency (lm/W)
Commercial	220	2.47
Sample 1	305	3.42
Sample 2	240	2.69
Sample 3	230	2.58
Sample 4	205	2.30

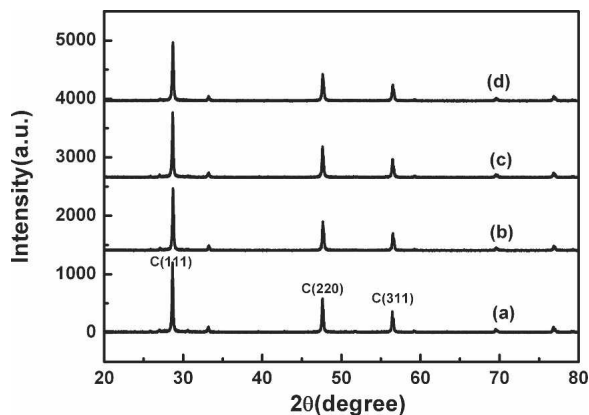


FIG. 7. XRD patterns of 3 mol% Mn doped ZnS phosphors synthesized in different vessels: (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.

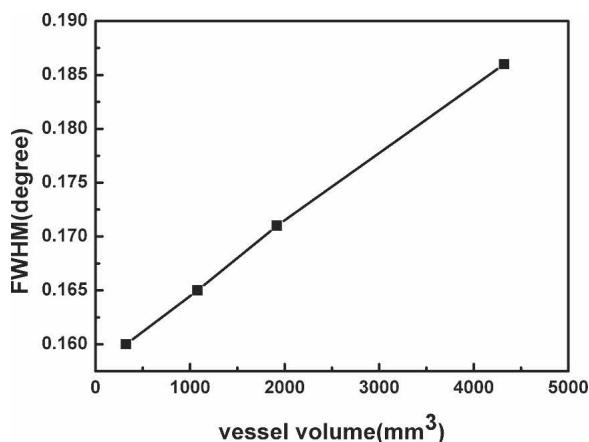


FIG. 8. FWHM of C(111) peak of 3 mol% Mn doped ZnS phosphors synthesized in different vessels.

B. Surface morphology

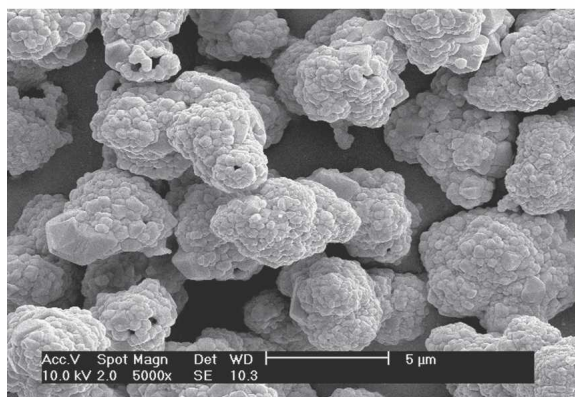
Morphology of the powders was examined by SEM to elucidate its correlation with pressure and CL enhancement. Figure 9 is SEM images of ZnS:Mn²⁺ phosphors synthesized in different size of vessels whose volume are 324 mm³ and 4320 mm³, respectively. As shown in Fig. 9, radical change of the powder morphology like Fig. 5 is hardly observed with vessel volume change, but particle size is slightly increased with vessel volume. However, the increase of particle size is relatively small compared with that of the particle size shown in Fig. 5. This means that the increase of particle size hardly has an effect on FWHM, and thus, the decrease of FWHM with the increase of internal pressure is mainly attributed to the improvement of crystallinity.

C. EPR of Mn²⁺ luminescent center

Before EPR analysis, change in the amount of Mn, Zn, and S was examined before and after heat treatment by ICP-MS and summarized in Table II. The amount of Mn,



(a)



(b)

FIG. 9. SEM images of 3 mol% Mn doped ZnS phosphors synthesized in different vessels: (a) sample 1 and (b) sample 3.

TABLE II. ICP-MS result.

Phosphor	Mn (wt%)	Zn (wt%)	S (wt%)
Starting material ^a	1.72	65.95	32.33
Commercial phosphor	1.65	65.46	33.81
Sample 1	1.87	65.69	33.97
Sample 4	1.85	65.40	31.76
% RSD	0.48	0.26	3.1

^aWeight percent of starting material was calculated.

Zn, S has not been changed except for a slight change in sulfur, which was only within % RSD. Because there is no change in the amount of Mn, CL enhancement by internal pressure can not be explained by ICP-MS result. Thus, a more accurate examination on luminescent center of Mn²⁺ has been made by EPR.

EPR is a well-known technique for determination of charge state of Mn ions and useful to estimate their concentration. EPR signals from ZnS:Mn²⁺ phosphors synthesized in different size of vessels were recorded at room temperature. Figure 10 shows that Mn ions present two characteristic EPR signals. One is the typical hyperfine six-lines signal from the fine structure transition $|1/2 \rangle$ to $|1-1/2 \rangle$ for Mn²⁺ ions and the other one is the

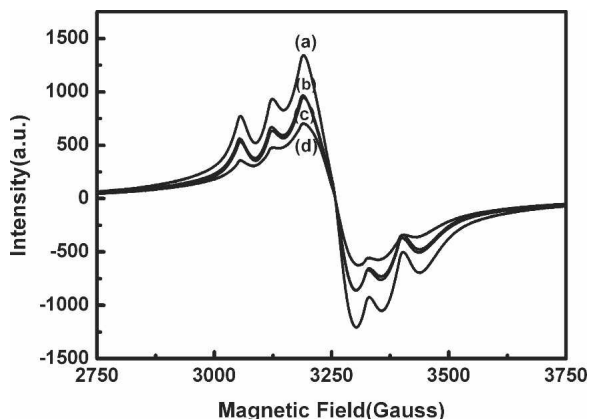


FIG. 10. EPR spectra of 3 mol% Mn doped ZnS phosphors synthesized in different vessels: (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.

TABLE III. EPR parameters of 3 mol% Mn doped ZnS phosphors synthesized in different vessels.

Phosphor	Symmetry	g_0	A_0 (Gauss)	Reference
Sample 1	Cubic	2.0024	64.08	This work
Sample 2	Cubic	2.0027	63.37	This work
Sample 3	Cubic	2.0023	63.31	This work
Sample 4	Cubic	2.0025	63.59	This work
ZnS:Mn ²⁺	Cubic	2.0025	68.4	15

broad resonance line signal, which is attributed to the clustering of Mn²⁺ ions.¹⁶ Other signals from Mn³⁺ and Mn⁴⁺ ions were not detected. The typical hyperfine six-lines signal originated from the interaction between Mn²⁺ electron cloud and ⁵⁵Mn nucleus (99.98% natural abundance) of spin $I = 5/2$. The hyperfine lines can be analyzed using the following equation¹⁷:

$$H_m = H_0 - A_0 m - \{(A_0/8H_0)(35 - 4m^2)\} \quad ,$$

where $H_0 = hv/g_0\beta$ and $m = -5/2, -3/2, \dots, +5/2$. g_0 is the isotropic g factor and A_0 is the isotropic hyperfine interaction parameter.

The g_0 and A_0 value of each typical hyperfine six-lines signal were calculated from Fig. 10 and summarized in Table III. They are almost similar to $g_0 = 2.0025$ and $A_0 = 6.84$, which was calculated from cubic phase of ZnS:Mn²⁺ phosphors where Mn²⁺ is substituted in the octahedral site.¹⁸ As mentioned earlier, ZnS: Mn²⁺ phosphor synthesized at 800 °C shows only cubic phase. Because ZnS:Mn²⁺ phosphors for EPR experiment were also synthesized at 800 °C, the result is in agreement with the XRD analysis.

The intensity of EPR signal is normally proportional to the number of resonance centers because EPR signal arises only from luminescent ions.¹⁹ From Fig. 10, the relative peak-to-peak intensities of two signals increase

as the volume of vessel decreases even though the Mn concentrations of all phosphors are the same. The increase of EPR signal intensity indicates the increased number of Mn ions that substitute Zn²⁺. It is reasonable to assume that Mn metal easily substitutes Zn²⁺ in a vessel with small volume, i.e., under high internal pressure. The increased Mn²⁺ concentration in the phosphor is, therefore, responsible for the enhanced CL intensity as the vessel volume decreases in Fig. 6.

It is found that the change of internal pressure via vessel volume in the present synthesis process improves crystallinity and spurs Mn²⁺ formation in the produced powders that promoted the CL intensity. Because the activator concentration directly influences the emission intensity, it is believed that the increased Mn²⁺ concentration would be the major origin of the enhanced CL intensity in the modified solid-state reaction compared with other mechanisms that bring marginal improvement.

V. CONCLUSIONS

ZnS:Mn²⁺ phosphor which showed ~180% higher CL intensity than that of a commercial one was obtained by a modified solid-state reaction. To optimize the synthesis condition, temperature and Mn concentration were investigated and 3 mol% Mn doped ZnS phosphor synthesized at 800 °C showed the best CL property. The mechanism of the CL enhancement was investigated and the pressure induced by the evaporation of ZnS during the synthesis was responsible for the improvement. XRD, SEM, and EPR signals were collected and analyzed to find the mechanism and its role for the CL intensity. The built-in pressure within the sealed vessel improved the crystallinity of the powders. It also increased the Mn²⁺/Zn²⁺ substitution ratio resulting in the increased population of the activator, which practically enhanced the CL intensity.

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