

triethylamine or aluminum chloride.<sup>15</sup> Compared with the known procedures, the present method of using cation radicals is simpler and more efficient.

**Acknowledgments.** Financial support from the Organic Chemistry Research Center sponsored by Korea Science & Engineering Foundation (1996) and the Ministry of Education through the Basic Science Research Institute Program (BSRI-96-3433) is gratefully acknowledged.

### References

- (a) Shine, H. J. In *The Chemistry of the Sulfonium Groups*; Stirling, C. J. M.; Patai, S., Eds.; Wiley: New York, 1981; Part 2, pp 523-570. (b) Svanholm, U.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* 1975, 97, 101-106. (c) Svanholm, U.; Parker, V. D. *J. Am. Chem. Soc.* 1976, 98, 997-1001. (d) Kovelesky, A. C.; Shine, H. J. *J. Org. Chem.* 1988, 53, 1973-1979. (e) Kim, K.; Shine, H. J. *J. Org. Chem.* 1974, 39, 2534-2537.
- Hoque, A. K. M. M.; Kovelesky, A. C.; Lee, W. K.; Shine, H. J. *Tetrahedron Lett.* 1985, 26, 5655-5658.
- Chiou, S.; Hoque, A. K. M. M.; Shine, H. J. *J. Org. Chem.* 1990, 55, 3227-3232.
- Shin, S.-R.; Shine, H. J. *J. Org. Chem.* 1992, 57, 2706-2710.
- Park, K. H.; Jun, K.; Shin, S. R.; Oh, S. W. *Tetrahedron Lett.* 1996, 37, 8869-8870.
- Shine, H. J.; Hoque, A. K. M. M. *J. Org. Chem.* 1988, 53, 4349-4353.
- Gilman, H.; Swayampati, D. R. *J. Am. Chem. Soc.* 1955, 77, 3387-3389.
- Schmidt, W.; Stechkan, E. *Chem. Ber.* 1980, 113, 577-585.
- Butler, R. N.; Johnston, S. M. *J. Chem. Soc., Chem. Commun.* 1981, 376-377.
- (a) Naqui, S.; Srinivasan, V. R. *Indian J. Chem.* 1965, 3, 162-164. (b) Crljenak, S.; Tabakovic, I.; Jeremic, D.; Gaon, I. *Acta Chem. Scand.* 1983, B37, 527-535.
- (a) Gibson, M. S. *Tetrahedron* 1963, 19, 1587-1589. (b) Potts, K. T.; Burton, H. R. *J. Org. Chem.* 1966, 31, 251-260. (c) Bower, J. D.; Doyle, F. P. *J. Chem. Soc. Org. Chem.* 1959, 24, 1478-1486. (d) Reynolds, G. A.; VanAllan, J. A. *J. Org. Chem.* 1959, 24, 1478-1486. (e) Case, F. H.; Schilt, A. A.; Fang, T. A. *J. Heterocycl. Chem.* 1974, 11, 463-467. (f) Ito, S.; Kakehi, A.; Matsuno, T.; Yoshida, J.-i. *Bull. Chem. Soc. Jpn.* 1980, 53, 2007-2011.
- Tabakovic, I.; Trkovic, M.; Galijas, D. *J. Electroanal. Chem.* 1978, 86, 241-244.
- (a) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* 1984, 20, 55-189. (b) Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* 1974, 96, 1087-1092.
- Huisgen, R.; Seidel, M.; Wallbillich, G.; Knupfer, H. *Tetrahedron* 1962, 17, 3-29.
- (a) Huisgen, R.; Grashey, R.; Seidel, M.; Wallbillich, G.; Knupfer, H.; Schmidt, R. *Justus Liebigs Ann. Chem.* 1962, 653, 105-113. (b) Conde, S.; Corral, C.; Madronero, R. *Synthesis* 1974, 28-29.

## Preparation and Photoluminescence Properties of the ZnGa<sub>2</sub>O<sub>4</sub>:Mn Phosphor by Polymerized Complex Precursor

Du-Hwan Jo, Ha-Kyun Jung, Sang-Il Seok, and Do-Soon Park\*

Korea Research Institute of Chemical Technology, Taejon 305-600, Korea  
Received February 19, 1997

The preparation and photoluminescence properties of ZnGa<sub>2</sub>O<sub>4</sub>:Mn phosphor are presented. Under 254 nm excitation Zn<sub>1-x</sub>Mn<sub>x</sub>Ga<sub>2</sub>O<sub>4</sub> exhibits the green emission band at 506 nm wavelength and maximum intensity where  $x=0.005$ . The manganese activated ZnGa<sub>2</sub>O<sub>4</sub> phosphor prepared by the polymerized complex method shows a remarkable increase in the emission intensity and is smaller particle size than that prepared by conventional method. Also, electron paramagnetic resonance study on ZnGa<sub>2</sub>O<sub>4</sub>:Mn powders indicates that the increase in emission intensity after firing treatment in mild hydrogen reducing atmosphere is due to the conversion of the higher valent manganese to Mn<sup>2+</sup>.

### Introduction

In the past few years special attention has been paid to ZnGa<sub>2</sub>O<sub>4</sub> based phosphors due to their potential applications as luminescent materials in flat panel displays (FPDs), electroluminescent (EL) devices and AC plasma (ACP) panels.<sup>1</sup> A current research interest in the area of luminescence and display technologies is the development of both novel and improved phosphor synthesis techniques. High resolution,

short decay time, high brightness, and high efficiency are the major requirements of phosphors used in flat panel display devices such as field emission displays (FEDs).<sup>2</sup>

The ZnGa<sub>2</sub>O<sub>4</sub> phosphor has been studied for its good luminescent characteristics at low voltage. The ZnGa<sub>2</sub>O<sub>4</sub> is a compound oxide of ZnO and Ga<sub>2</sub>O<sub>3</sub> as the spinel structure, and optical band gap is about 4.4 eV. Also, the results of high temperature operating lifetime test have been proven to show the excellent stability of this phosphor. In addition,

$\text{ZnGa}_2\text{O}_4$  phosphor shows emission from green to red when it is doped with Mn and Cr, and also shows blue emission even without being doped with impurity. The luminescent properties of phosphors are strongly dependent on the particle size and crystal structure, and the preparing conditions may be controlled to achieve better luminescent properties. Conventional phosphor synthesis techniques cannot always achieve these requirements. Conventional however, powder process has some disadvantages such as high temperature firing, need for mechanical particle size reduction and longer heating schedules. This leads to defects in the system and no doubt affects the efficiency of the phosphor powder.

Therefore, in this paper the "polymerized complex method", a novel ceramic synthesis technique, was introduced to produce the manganese activated  $\text{ZnGa}_2\text{O}_4$  with improved luminescent properties. Polymerized complex method, was first documented by Pechini,<sup>3</sup> appeared promising for ceramics because of its success in producing fine particle size, multicomponent, homogeneous ceramics at considerably lower temperatures and with reduced processing time.<sup>4</sup>

### Experimental

**Preparation of phosphor.** Phosphors with the general formulas  $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{O}_4$  ( $\text{ZnGa}_2\text{O}_4:\text{Mn}$ ) with  $x$  ranging from 0.003 to 0.008 were prepared by polymerized complex method.  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.00992-0.00997 mole) and  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (0.01 mole) were first dissolved into 4 mole of ethylene glycol (EG), and then 0.1 mole of anhydrous citric acid (CA) was added into this solution followed by an addition of the stoichiometric amount of  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . The mixture was stirred until it became transparent. The solution was refluxed for 2 hrs to promote the ester reaction between CA and EG. As the solution became concentrated, it turned to be highly viscous indicating the formation of a polymeric gel. The viscous polymeric product was dried at about 200 °C to remove residual solvent. The precursor thus obtained was ground followed by calcination in air at 1000 °C for 8 hrs., then fired in a reducing atmosphere of 95% $\text{N}_2$ -5% $\text{H}_2$  at 900 °C for 1 hr with a flow rate of 10 mL/min.

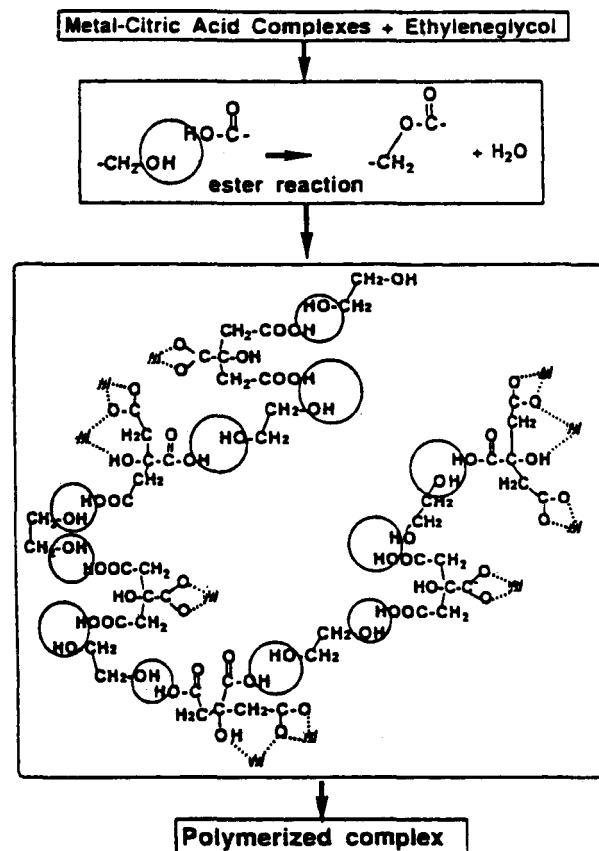
**Identification and Photoluminescence measurements.** The phosphors were characterized by X-ray diffraction analysis using a Rigaku Model DMAX-33 X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation operating at 35 kV, 15 mA, and 4° of 2 $\theta$ /min scanning rate. The morphology of the phosphor was observed by scanning electron microscopy (SEM). The photoluminescence measurements of polycrystalline samples were obtained using a Perkin-Elmer LS 50 luminescence spectrometer. Samples were excited with 254 nm radiation from pulsed xenon discharge lamp. The emission wavelength was scanned from 300 to 700 nm at a scanning rate of 480 nm/min. For measurements of excitation spectra the excitation wavelength was scanned from 200 to 700 nm at the same scanning rate, and the emission wavelength was fixed at 506 nm. EPR spectra were recorded on a Bruker ESP-300E and referenced to DPPH as the g-value standard.

### Results and Discussion

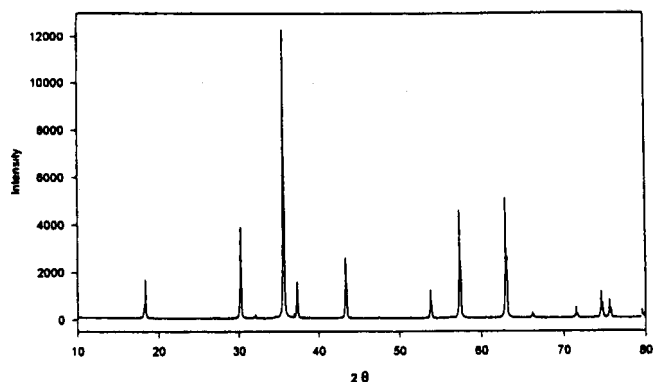
$\text{ZnGa}_2\text{O}_4$  with the general formula  $\text{AB}_2\text{O}_4$  has a spinel

structure, where A and B are metal cations which occupy the tetrahedral and octahedral interstices of the unit cell. The  $\text{ZnGa}_2\text{O}_4$  is a normal spinel with all of the  $\text{Zn}^{2+}$  ions in A sites,  $\text{Ga}^{3+}$  ions in B sites. Zinc gallate is a promising phosphor material for field emission display with low excitation voltage.<sup>5</sup> Blue emitting  $\text{ZnGa}_2\text{O}_4$  and green emitting manganese activated  $\text{ZnGa}_2\text{O}_4$  phosphors are a possible alternative to the ZnS-based low voltage cathodoluminescent phosphors currently used in FEDs.<sup>6</sup> ZnS-based phosphors have been optimized for operation at high voltages and low current densities, but this cause severe saturation and degradation of phosphor at low voltage operation.<sup>7</sup> This causes not only the decrease of luminous efficiency of the phosphors but also the deterioration of cathode filament, which are serious problems in FEDs. At present, when compared with ZnS-based phosphors for FED, the overall luminous output of zinc gallate phosphors is less.

Fine particle phosphor is fundamental requirement for high resolution displays. We believe that this requirement can only be met by improved synthetic methods which would yield fine particles of good crystallinity, so that the high efficiency obtainable with large particle size is retained in the system with much high resolution. "Polymerized complex method" is to obtain a polyester resin comprising randomly coiled macromolecular chains in which various metal ions can be uniformly distributed, as is schematically shown in Figure 1. Many of metal ions except monovalent cations form very stable chelate complexes with citric acid, in



**Figure 1.** Formation of polymerized complex precursor based upon ester reaction between metal citric acid complexes and ethylene glycol.

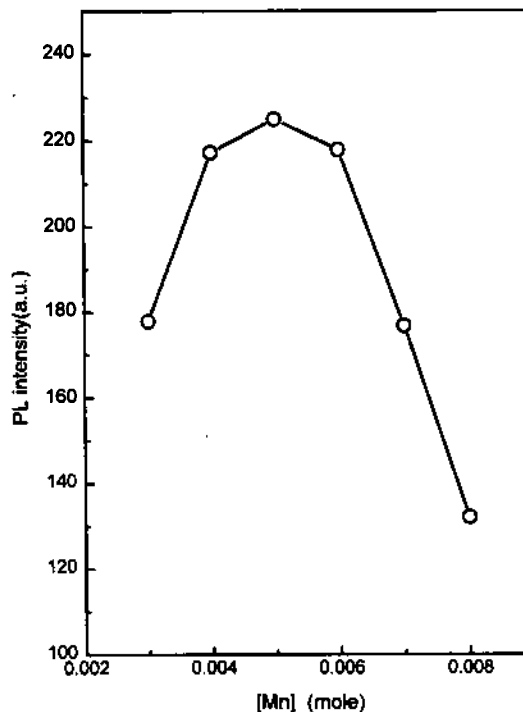


**Figure 2.** X-ray diffraction pattern of the  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor prepared from the polymeric complex precursor.

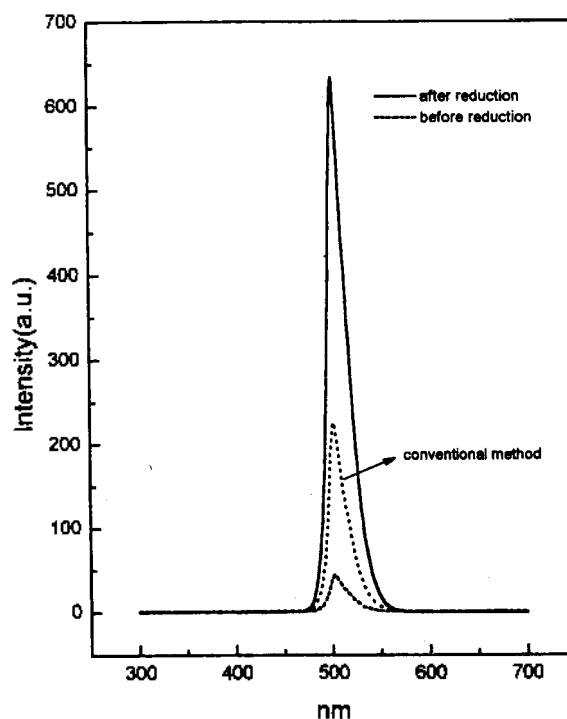
which has three carboxylic acid groups and one alcoholic group. Esterification of metal complexes of citric acid occurs readily in the presence of ethylene glycol at an appropriate temperature ( $\sim 130^\circ\text{C}$ ), and prolonged heating of the mixed solution promotes polyesterification yielding a transparent polymerized complex precursor. A matter of vital importance is to have a homogeneous polymeric precursor with exactly the same metal stoichiometry as that of the final multicomponent oxides. These remarkable characters in the polymerized complex route provide an advantage particularly in the synthesis of complicated multi-component oxides, in which it is crucial to obtain a homogeneous precursor with well interspersed elements for a successful outcome.

Single spinel phase of manganese activated  $\text{ZnGa}_2\text{O}_4$  phosphor was prepared by firing the polymerized complex precursor in air at  $1000^\circ\text{C}$  for 8 hrs. The phosphor prepared by this method was examined by X-ray powder diffraction (see Figure 2). All of the lines indicated in JCPDS data files<sup>8</sup> are shown in the XRD spectrum. The sample had a peach body color and weak green emission (Figure 3, arbitrary unit=45) due to highly oxidized manganese(III, IV) species, and the second firing in mild hydrogen reducing atmosphere for 1hr at  $900^\circ\text{C}$  produced powder with a white body color and strong green emission intensity (a.u.=645). Manganese activated  $\text{ZnGa}_2\text{O}_4$  shows a remarkable increase in the 506 nm emission intensity by firing in a reducing atmosphere. In  $\text{ZnGa}_2\text{O}_4:\text{Mn}$ , the increase in emission intensity after reduction is possibly a result of the conversion of the highly oxidized manganese(III, IV) species to  $\text{Mn}^{2+}$  in the four-coordinated position of the spinel lattice.

Figure 3 exhibits the 506 nm emission intensities on Mn contents of the  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphors prepared by the conventional method. The emission intensity increased with the addition of manganese ions, with  $x=0.005$  being the concentration at maximum intensity. Figure 4 shows the emission spectra of the  $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{O}_4$  ( $x=0.005$ ) phosphors prepared by polymerized complex method and by the conventional method. Although both the methods resulted in the 506 nm emission from  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphors, the emission intensity of the phosphor obtained by polymerized complex method was much stronger than that (a.u.=225) prepared by the conventional method.<sup>9</sup> In general, the emission intensity of phosphor tends to decrease as the particle



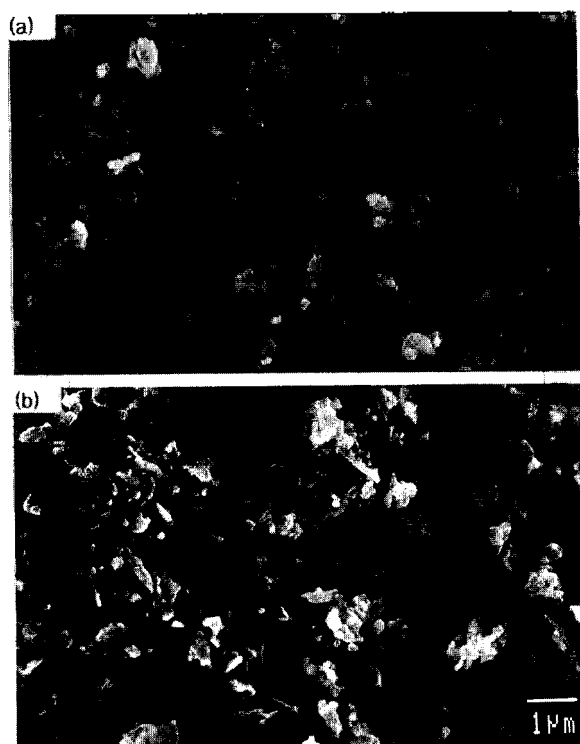
**Figure 3.** The 506 nm emission intensities of the  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  as a function of Mn contents.



**Figure 4.** Effect of reduction treatment on the emission spectra of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor under 254 nm excitation.

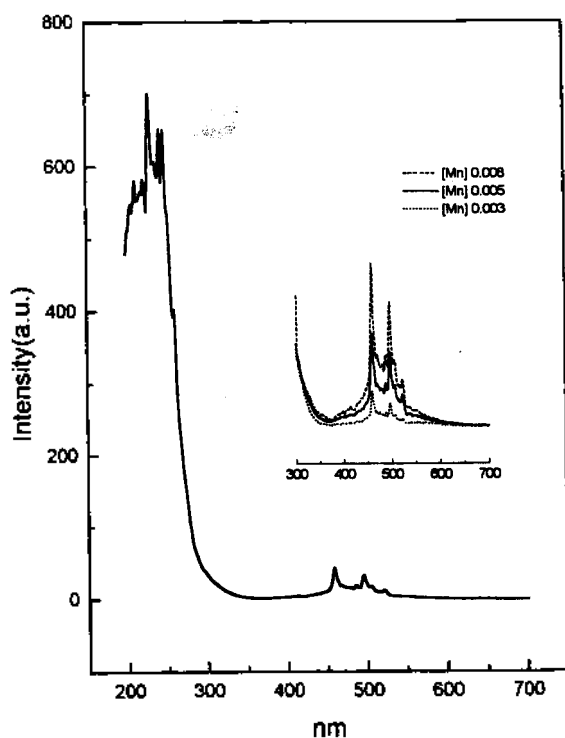
size of phosphor decreases.<sup>10</sup>

Scanning electron micrograph (SEM) of the phosphor prepared by polymerized complex method and conventional method are shown in Figure 5. It can be seen, that the particles of the phosphor prepared by polymerized complex method are smaller and more homogeneous than those by

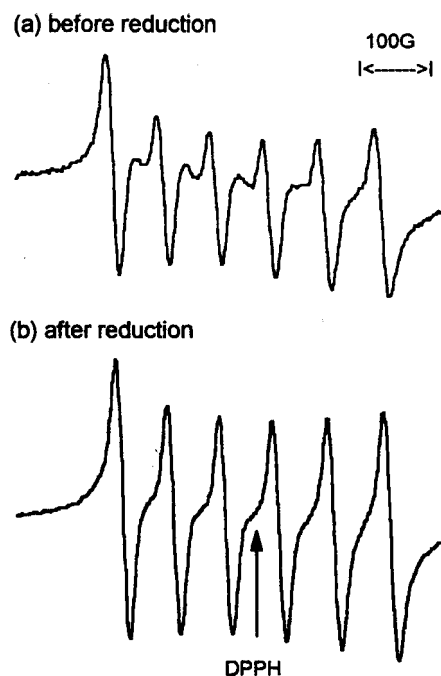


**Figure 5.** SEM photographs of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor prepared by polymerized complex method(a) and by conventional method(b).

conventional method. This difference in the emission intensities due to particle size could arise from the difference in the damage of phosphor surface and the minimization of



**Figure 6.** Excitation spectra of the 506 nm emission from  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  prepared by polymerized complex precursor.



**Figure 7.** Effect of reduction treatment on the EPR spectra of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor at room temperature. The DPPH standard value is denoted by the arrow.

contamination of impurities in the preparation process of phosphor. These agree to the fact that the emission intensity of phosphor under UV excitation is dependent on the surface condition of phosphor.<sup>11</sup>

The excitation spectra of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor are shown in Figure 6. The emission has been fixed at 506 nm. The first part, between 200 nm and 300 nm, corresponds to the host lattice absorption of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  spinel. In addition, various weak bands are observed around 460, 500, 506, and 520 nm due to the manganese transitions. These band intensities tend to increase as the manganese contents in the phosphor increase. According to report by A. Morell and N. El Khiati<sup>12</sup> for divalent manganese, these transitions occur by splitting of the  $^4\text{D}$  and  $^4\text{G}$  levels due to the crystal field.

Figure 7 shows the effect of reduction treatment on the EPR spectra of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor prepared by polymerized complex method. The spectrum of fired raw phosphor (see Figure 7(a)) seems to consist of two manganese species with  $g$  values close to 2.00, each coupled to the manganese nuclei ( $^{55}\text{Mn}$ ,  $I=5/2$ ). The strong sextet and weak multiplet hyperfine signals in the spectrum (a) indicate that the majorities of manganese species could be  $\text{Mn}^{2+}$  and the small portions be  $\text{Mn(III)}$  or  $\text{Mn(IV)}$ . While, the trivalent manganese species show EPR-silent at room temperature due to short spin-lattice relaxation time.<sup>13</sup> Therefore the weak hyperfine signals in the spectrum seem to couple unpaired  $d$  electron of  $\text{Mn}^{4+}$  with the manganese nuclei. Thus, the spectrum also supports the presence of highly oxidized manganese(IV) species in the  $\text{ZnGa}_2\text{O}_4$  host lattice. The effect of reducing atmosphere in the spectrum Figure 7(b) is the increased  $\text{Mn}^{2+}$  signals with disappearing weak  $\text{Mn}^{4+}$  signals. This spectra indicate that  $\text{Mn}^{4+}$  in the raw phosphor after a reducing firing could changed to  $\text{Mn}^{2+}$ , causing a remarkable increase in the emission intensity.

## Conclusions

The manganese activated  $ZnGa_2O_4$  phosphor was prepared by the polymerized complex method to improve the photoluminescence properties of the phosphor. The  $ZnGa_2O_4:Mn$  phosphor prepared by this method shows a remarkable increase in the emission intensity than that prepared by conventional method. Therefore, the polymerized complex method is an available process for the preparation of phosphor since homogeneous particles in a small size level can be easily prepared without pulverizing process. Also, the increase in emission intensity after a reducing firing is a result of the conversion of the highly oxidized manganese (IV) to  $Mn^{2+}$ .

**Acknowledgment.** This research was supported financially by the Ministry of the Science and Technology in Korea.

## References

- (a) Kobayashi, H.; Tanaka, S. *Journal of the SID* 1996, 4/3, 157. (b) Minami, T.; Maeno, T.; Kuroi, Y.; Takata, S. *Jpn. J. Appl. Phys.* 1995, 34, L684. (c) Minami, T.; Takata, S.; Kuroi, Y. *SID Intl. Symp. Digest Tech. Papers* 1995, 724.
- Yamamoto, H. *Journal of the SID* 1996, 4/3, 165.
- Pechini, M. P. *U.S. Patent* 1967, July No.3, 330, 697.
- (a) Anderson, H. U.; Pennell, M. J.; Guha, J. P. *Advances in Ceramics, Ceramic Powder Science*; edited by Messing, G. L.; Mazdizyasni, J. W.; McCauley & R. A. Haber (Am. Ceram. Soc. 21 Westerville OH, 1987), p 91. (b) Lessing, P. A. *Am. Ceram. Soc. Bull.* 1989, 168, 1002. (c) Tai, L. W.; Lessing, P. A. *J. Mater. Res.* 1992, 7, 511. (d) Cho, S. G.; Johnson, P. F.; Condrate, R. A. *J. Mater. Sci.* 1990, 25, 4738. (e) Kakihana, M.; Borjesson, L.; Eriksson, S.; Svedlindh, P. *J. Appl. Phys.* 1991, 69, 867. (f) Kakihana, M.; Yoshimura, M.; Mazaki, H.; Yasuoka H.; Borjesson *J. Appl. Phys.* 1992, 71, 3904. (g) Berastegui, P.; Kakihana, M.; Yoshimura, M.; Mazaki, H.; Yasuoka, H.; Johanssen, L. G.; Eriksson, S.; Borjesson, L.; Kall, M. *J. Appl. Phys.* 1993, 73, 2424.
- Hsieh, I. J.; Chu, K. T.; Yu, C. F.; Feng, M. S. *J. Appl. Phys.* 1994, 76, 3735.
- Shmulovich, J.; Kocian, D. F. *Proc. SID.* 1989, 30, 200.
- (a) Itoh, S.; Kimizuka, T.; Tonegawa, T. *J. Electrochem. Soc.* 1989, 138, 1819. (b) Itoh, S.; Toki, H.; Sato, Y.; Morimoto, K.; Kishino, T. *J. Electrochem. Soc.* 1991, 138, 1509.
- JCPDS data file, 1986, No. 3-1155.
- Jo, D.-H.; Jung, H.-K.; Kim, C.-H.; Seok, S.-I.; Park, D.-S. *J. Kor. Chem. Soc., manuscript for publication.*
- Jpn. Phosphor Research Society, Phosphor handbook, 1987.
- Chang, I. F.; Brownlow, J. W.; Sun, T. I.; Wilson, J. S. *J. Electrochem. Soc.* 1989, 136, 3532.
- Morell, A.; El Khiati, N. *J. Electrochem. Soc.* 1993, 140, 2019.
- Kutty, T. R. N.; Devi, L. G. *Mater. Res. Bull.* 1986, 21, 1093.

## Preparation and Characterization of $LiMn_2O_4$ Powder by Combustion of Poly(ethylene glycol)-Metal Nitrate Precursor

Hyu-Bum Park, Young-Sik Hong, Ji-Eun Yi\*, Ho-Jin Kweon\*\*, and Si-Joong Kim<sup>†</sup>

*Department of Chemistry, Korea University, Sungbuk-Gu, Seoul 136-701, Korea*

*\*Korea Basic Science Institute, Sungbuk-Gu, Seoul 136-701, Korea*

*\*\*Samsung Display Devices Co., Hwasung-Gun, Kyungki-Do 445-970, Korea*

*Received February 25, 1997*

$LiMn_2O_4$  powders were prepared by burning and subsequent calcination of PEG-metal nitrate precursor. After the burning stage of the precursor, some minor phases such as  $Mn_2O_3$  (or  $Mn_3O_4$ ),  $MnO$ , and carbonate were formed and single phases of  $LiMn_2O_4$  were obtained by further calcinations above 400 °C. From thermal analysis of the precursor, a violent thermal decomposition, which was indicated by a drastic weight loss accompanied by a sharp and strong exothermic peak, was observed and probably caused by an oxidation-reduction reaction between oxidizer and fuel. The formation of the minor phases could be explained in terms of the burning behavior of the precursor by employing valence concepts of propellant chemistry. The calcined powders were composed of sub-micron-sized but highly agglomerated particles and showed very broad particle size distribution.

## Introduction

The spinel  $LiMn_2O_4$  and the layered compounds  $LiCoO_2$

and  $LiNiO_2$  are the most widely studied cathode materials for Li ion rechargeable batteries.<sup>1,2</sup> Among these lithium transition metal oxides,  $LiMn_2O_4$  has attracted a good deal of research because of its economical and environmental advantages; Mn is abundant and significantly cheaper than Co

<sup>†</sup>To whom correspondence should be addressed