Chemical preparation and photoluminescence of partially MgO-substituted ZnO powders

K. INOUE*, M. SHOYAMA, M. MURAYAMA, Y. TORII
Industrial Research Division, Mie Science and Technology Promotion Center, Takachaya, Tsu, Mie 514-0819, Japan
E-mail: inoue@mie-iri.tsu.mie.jp

ZnO has a wide band gap of 3.37 eV at room temperature and is a self-activated crystal of hexagonal wurtzite structure. Recently ZnO has attracted some interest because it is considered a promising green light-emitting phosphor for low-voltage luminescence in flat panel displays such as vacuum fluorescent tubes (VFDs) and field emission displays (FEDs). The green emission has been associated with the lattice defects such as interstitial zinc ions [1] or oxygen vacancies [2, 3]. Of them, oxygen vacancies are the most likely candidates for the recombination centers, in other words, the recombination of a free electron with a deeply trapped hole or a delocalized hole with a deeply trapped electron. Zinc sulfides (e.g., ZnS: Ag,Cl) and zinc gallade spinel $ZnGa_2O_4$ are well-known as blue light-emitting cathode phosphors. The former sulfide has relatively high-efficiency phosphor but is unstable under vacuum at high temperatures and include a poisonous element. On the other hand, the latter oxide spinel has the disadvantage of low-efficiency in cathode luminescence and includes high-cost raw material (Ga). It has been increasingly requested to develop blue cathode phosphors with high-efficiency and low-cost. In nanometer-sized semiconductors, the band gap increases with decreasing particle size, and therefore the emission wavelength of semiconductor often becomes shorter owing to the nanometer-sized quantum effect. However, the nanometer-sized powders are not good for handling in manufacturing process. The blue emission luminescence can be expected in hexagonal Mg-doped ZnO because the band gap energy increases under partial substitution of insulating MgO (ca. 8 eV) for ZnO. It is important in photoluminescent application to prepare chemical homogeneous and fine powders of Mg-doped ZnO. Oxalate coprecipitation is relatively low-cost processing and is one of the attractive powder preparation methods because of increased homogeneity, purity, and reactivity over standard ceramic processing. This technique has been adapted to the powder production of multicomponent electronic ceramics such as Ni-Fe-Mn spinel thermistors [4], (Ba, Pb)TiO_3 dielectrics [5], and $BaPbO_3$ thermoelectrics [6].

In the present work, the chemical preparation for hexagonal Zn_{1-x} Mg_xO ($0.0 \leq x \leq 0.2$) solid solution and the effect of partially substituted MgO on the photoluminescence (PL) were investigated.

The PL powders of $(Zn_{1-x}Mg_x)O$ solid solution were prepared by the thermal decomposition of coprecipitated Zn-Mg oxalate. Starting materials were high-purity zinc and magnesium chlorides. The mixed chloride solution of desired molecular ratio was added slowly to an excess of ammonium oxalate solution. The resulting slurry solution was stirred for 2 hr and left overnight. Then the pH of the slurry solution was about 6.5. Next, after stirring again for 1 hr, triply diluted ammonia water was slowly added to the stirred slurry solution of coprecipitated oxalate at pH 7.5. The white precipitate was filtered, washed several times with chilled water, and then dried at 80 °C in air. The products were analyzed by X-ray powder diffraction (XRD) method, using Cu Kα radiation at 60 kV and 40 mA. The hexagonal lattice constants were determined from (100) and (002) reflections with the aim of a 5N Si standard. The reflections were measured at a scanning speed of $(1/8)^\circ$, 2θ min. The PL spectra were measured at room temperature with a 320 nm excitation source from a Xe lamp, using Hitachi F-4500 fluorescence spectrometer.

Fig. 1 shows the TG–DTA curve for the coprecipitated Zn-Mg oxalate with a molar ratio of Zn/Mg=0.9/0.1 as the starting solution. Then the heating rate was 10 °C min^{-1}. Two steps of weight loss were observed at 110–150 °C and at 350–370 °C. They correspond to the dehydration of each oxalate and the decomposition of each anhydrous oxalate, respectively. On the other hand, a sharp exothermic peak appeared at 410 °C, followed by the endothermic peak at 166 °C. In the coprecipitated oxalates with the molar ratio of Zn/Mg=1.0/0.0, 0.8/0.2, and 0.0/1.0, similar TG–DTA curves were observed, except the differences in thermal decomposition temperature. The endothermic and exothermic peaks appeared at 152 °C and 401 °C for Zn/Mg=1.0/0.0, 177 °C and 424 °C, for Zn/Mg=0.8/0.2, 223 °C and 483 °C for Zn/Mg=0.0/1.0, respectively. Consequently, the coprecipitated oxalates seem to behave as a single entity and this is a proof that the zinc and magnesium ions coprecipitate in the solid solution form of (Zn, Mg)$(C_2O_4)2\cdot 2H_2O$. The thermal decomposition of Zn-Mg oxalate salt was found

---

[*] Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-005-4232-5

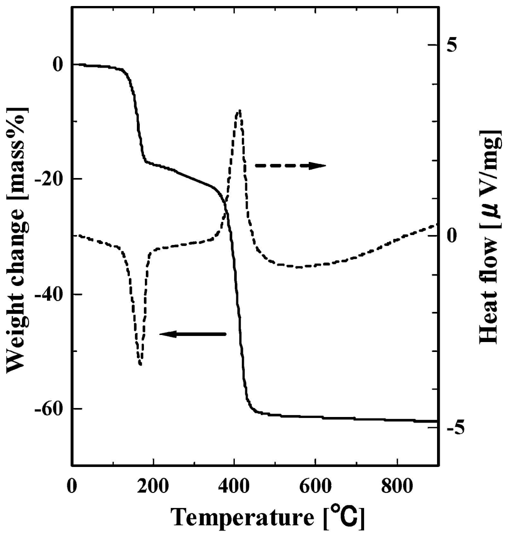

Figure 1 TG–DTA curve for the coprecipitated Zn-Mg oxalate with a ratio of Zn:Mg =0.9:0.1.

to enable the formation of hexagonal ($Zn_{1-x}Mg_x$) O solid solution at low temperatures. A typical example is shown in Fig. 2; which is the XRD pattern for ($Zn_{0.8}Mg_{0.2}$)O (x=0.2) sample decomposed at various temperatures for 2 hr in air. When fired even at 500, the XRD pattern characteristic of wurtzite structure was observed. The X-ray reflections became strong and sharp when fired at higher temperatures than 600 °C, although a small amount of rock-salt-type MgO phase (open circle) was found to exist in the XRD pattern. All the XRD reflections shown by closed circle were clearly indexed as a hexagonal wurtzite-type monophase. In the samples of ($Zn_{1-x}Mg_x$)O with $x \leq 0.12$, the rock-salt-type MgO phase was not detected in the XRD pattern. Fig. 3 shows the change in lattice constants of ($Zn_{1-x}Mg_x$)O solid solution deposited at 800 °C for 3 hr. The *a* axis remains almost unchanged, whereas the *c* axis decreases with MgO concentration (x). The solid solubility of MgO in hexagonal ZnO is estimated as X=0.12. This value is relatively large as compared with that (ca. 2 mol%) reported in high-temperature phase equilibrium of the ZnO-MgO system [7]. This high solid solubility is considered to be due to the powders decomposed directly from the complex oxalate salt. Fig. 4 shows a scanning electron micrograph of ($Zn_{0.9}Mg_{0.1}$)O sample decomposed at 700 °C for 2 hr in air. The decomposed powder is aggregated with the individual particles of about 2 μm size. Thus the oxalate coprecipitation method is effective for producing fine phosphor powders at low temperatures. Fig. 5 shows PL spectra of ZnO and ($Zn_{0.92}Mg_{0.08}$)O (x=0.08) powders annealed at 900 °C for 3 hr in a reduced atmosphere of 5% H_2 gas mixture. In the ZnO sample, a strong green emission band with a peak around 500 nm is seen. Weaker near-band-edge emission at about 400 nm, which can be assigned to exciton emission, is also detected. The visible and near-UV emissions agree well with the spectral data reported previously [2, 3]. On the other hand, in the ($Zn_{0.92}Mg_{0.08}$)O sample, the corresponding emission bands are observed with the maximum around 370 nm and 476 nm, respectively, and the

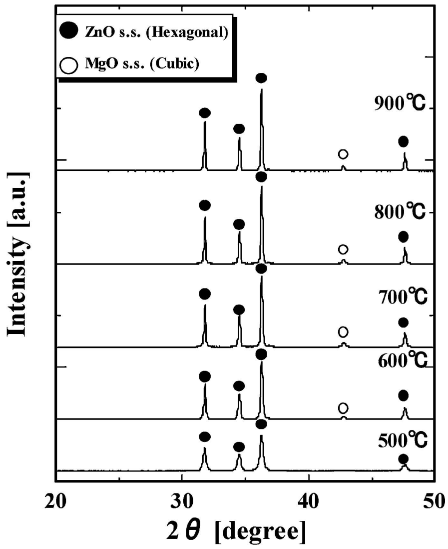

Figure 2 XRD patterns for ($Zn_{0.8}Mg_{0.2}$)O solid solution decomposed at various temperatures for 2 hr in air.

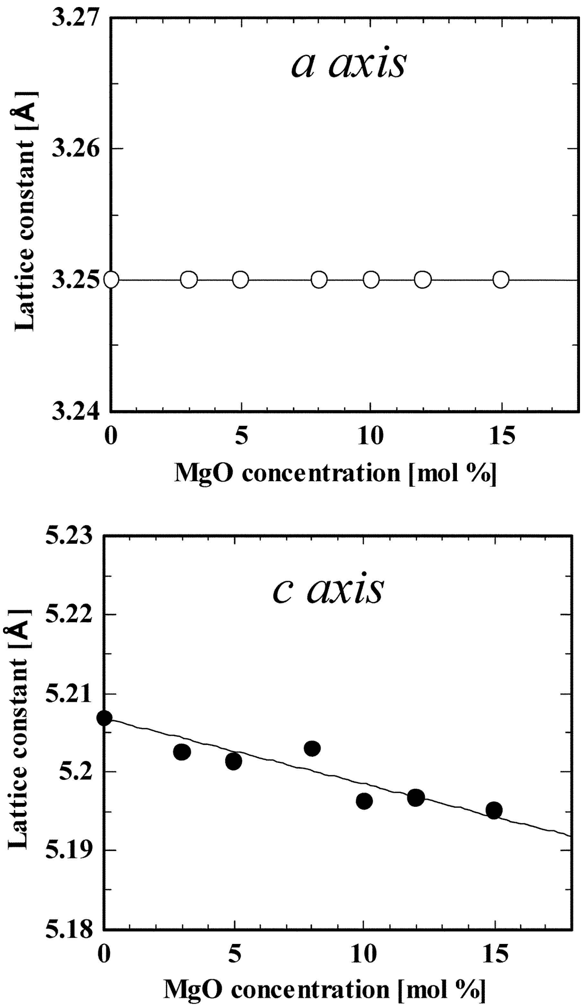

Figure 3 Change in lattice constants of ($Zn_{1-x}Mg_x$)O solid solution deposited at 800 °C for 3 hr.

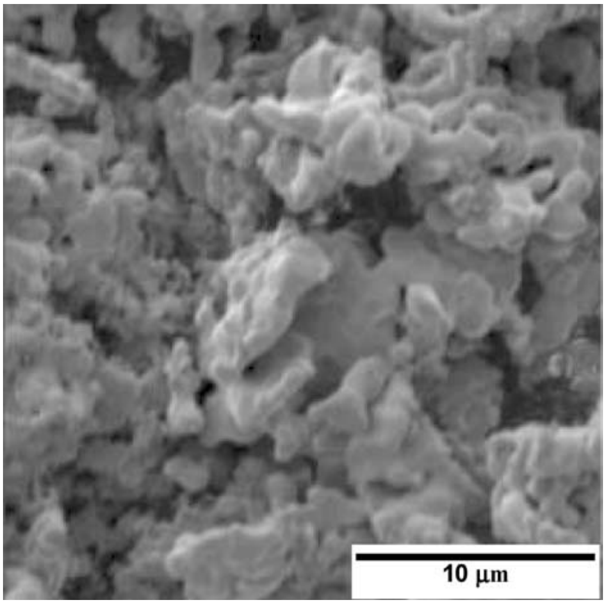

Figure 4 SEM photograph of $(Zn_{0.9}Mg_{0.1})O$ powder decomposed at 700 °C for 2 hr in air.

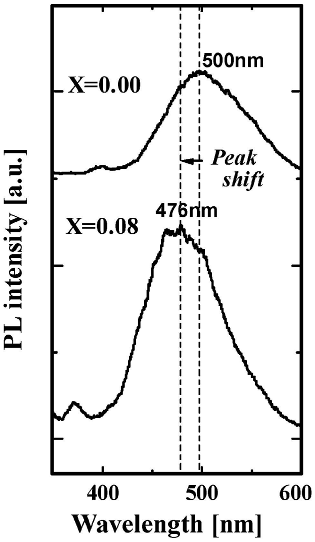

Figure 5 PL spectra of ZnO and $(Zn_{0.92}Mg_{0.08})O$ powders annealed at 900 °C for 3 hr in a reduced atmosphere.

two peak intensities are stronger than those observed in the ZnO sample. As shown in Fig. 6, the maximum of visible emission band was found to shift at low wavelength side with MgO-substituted concentration. The origin of the green–blue emission is based on the oxygen vacancies reduced in partially MgO-substituted ZnO powders. Our data indicates that the green–blue photoluminescence is attributed to the recombination of donor electrons in singly occupied oxygen vacancies (V_O^+) with photoexcited holes in the valence band, according to the green PL mechanism proposed by K. VANHEUSDEN *et al.* [2]. The partial substitution of MgO for ZnO results in expanding the band gap of ZnO semiconductor. In fact, the near-band-edge emission band is observed to shift at lower wavelength, as shown in Fig. 5. Therefore, the energy difference between the donor level and the valence band would become larger because the donor level based on oxygen vacancies is considered to remain unchanged as compared with the change of band gap. Consequently, partial substitution of MgO for ZnO is estimated to make it possible to generate the blue–green photoluminescence.

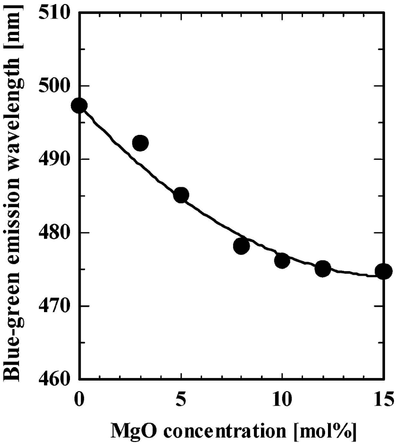

Figure 6 Change in blue–green emission wavelength observed for $(Zn_{1-x}Mg_x)O$ solid solution.

In conclusion, a limited range of $(Zn_{1-x}Mg_x)O$ solid solution was prepared using the thermal decomposition of complex Zn-Mg oxalate. The solubility of Mg in ZnO was estimated to be ca. 12%. In the samples annealed at 900 °C for 3 hr in 5% H_2 gas mixture, green to blue photoluminescence was observed. It is evident that the partial substitution of MgO results in the shift of green emission band at low wavelength side. The PL material is expected as a low-cost and blue light-emitting phosphor for low-voltage luminescence in flat panel displays.

References

1. S. A. M. LIMA, F. A. SIGOLI, M. JAFELICCI, JR.. and M. R. DEVOLOS, *Int. J. Inorg. Mater.* **3** (2001) 749.
2. K.VANHEUSDEN, W. L.WARREN, C. H. SEAGER, D. R.TALLANT, J. A.VOIGT and B. E.GNADE, *J. Appl. Phys.* **79** (1096) 7983.
3. A. V.DIJKEN, E. A. MUELENKAMP, D. VANMAEKELBERGH and A. MEIJERINK, *J. Lumin.* **90** (2000) 123.
4. Y. TORII, A. TSUZUKI, K. KATO, Y. UWANINO, B. H. CHOI and M. J. LEE, *J. Mater. Sci.* **31** (1996) 2603.
5. B. H. CHOI, M. J. LEE, S. M. KIM and Y. TORII, *J. Korean Ceram. Soc.* **33** (1996) 743.
6. Y. KODAMA, N. MURAYAMA, Y. TORII and M. YASUKAWA, *J. Mater. Sci. Lett.* **17** (1998) 1999.
7. E. R. SEGNIT and A. E.HOLLAND, *J. Amer. Ceram. Soc.* **48** (1965) 412.

Received 6 June
and accepted 12 July 2005