

Fabrication and Cathode Luminescence of Partially MgO-Substituted ZnO Powders

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酸化マグネシウムを部分固溶した酸化亜鉛粉末の作製とカソードルミネセンス

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Recently, the development of new nonsulfide phosphors with high efficiency is urgently needed for VFDs and FEDs. The fabrication for hexagonal $Zn_{1-x}Mg_xO$ ($0.0 \leq x \leq 0.15$) solid solution and the effect of partially substituted MgO on the cathode luminescence (CL) were investigated in this research. 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. 15%. In the samples annealed at 1373 K for 2 h in a reduced atmosphere, green to blue cathode luminescence was observed. It is evident that the partial substitution of MgO results in the shift of green emission band at low wavelength side. The CL material is expected as a low-cost and blue light-emitting phosphor for low-voltage luminescence in flat panel displays.

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1. Introduction

Field emission displays (FEDs) have been developed as a next-generation flat-panel displays, which can replace some liquid-crystal displays (LCDs) and plasma display panels (PDPs), recently. When compared with phosphors for cathode-ray tubes (CRTs), phosphors for FEDs are required to work at lower voltage and higher current density.¹⁾ Highly efficient sulfide phosphors widely used in CRTs are not suitable for FEDs, mainly because they emit sulfur and sulfur oxide gas, which damages a cathode of FED under a high current density.²⁾ Thus, the development of new nonsulfide phosphors with high efficiency is urgently needed for FEDs. ZnO has a wide band gap of 3.37 eV at room temperature and is a self-activated crystal of hexagonal wurtzite structure.^{3),4)} 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 tube (VFDs) and FEDs. The green emission has been associated with the lattice defects such as interstitial zinc ions⁵⁾ or oxygen vacancies.^{6),7)} 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 gallate 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 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 phos-

phors 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 cathode-luminescent application to prepare chemical homogeneous and fine powders of Mg-doped ZnO. Oxalate co-precipitation is relatively low-cost processing and is one of 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 multi-component electronic ceramics such as Ni–Fe–Mn spinel thermistors,⁸⁾ (Ba, Pb) TiO₃ dielectrics⁹⁾ and BaPbO₃ thermoelectrics.¹⁰⁾

In the present work, the fabrication for hexagonal $Zn_{1-x}Mg_xO$ ($0.0 \leq x \leq 0.15$) solid solution and the effect of partially substituted MgO on the cathode luminescence (CL) were investigated.

2. Experimental procedure

The CL powders of $(Zn_{1-x}Mg_x)O$ solid solution were prepared by the thermal decomposition of co-precipitated 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 h and left overnight. Then the pH of the slurry solution was about

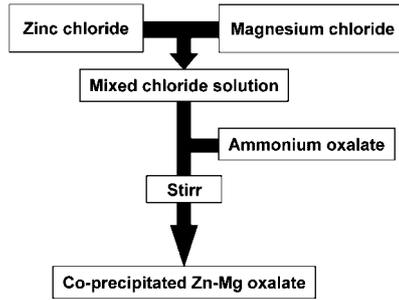


Fig. 1. A typical flowchart for the powder preparation-process of partially MgO-substituted ZnO powder.

6.5. Next, after stirring again for 1 h, triply diluted ammonia water was slowly added to the stirred slurry solution of co-precipitated oxalate at pH = 7.5. The white precipitate was filtered, washed several times with chilled water and then dried at 353 K in air. A typical flowchart for the powder preparation-process of partially MgO-substituted ZnO powder is shown in Fig. 1. The obtained powders were heated in the range of 773 K to 1373 K in a reduced atmosphere of 3% H₂-Ar gas mixture. The products were analyzed by X-ray powder diffraction (XRD) method, using Cu K α radiation at 60 kV and 40 mA. The hexagonal lattice constants were determined from (100) and (002) reflections with the aim of a 5 N Si standard. The reflections were measured at a scanning speed of (1/8) $^\circ$, 2 θ min. The CL spectra were measured at room temperature with a cathode-ray source of a 3 kV excitation, using Horiba Jobin Yvon MP-32SP cathode luminescence spectrometer with Hitachi S-3500H scanning electron microscope. The emission and probe current were 120–140 μ A and 300–600 pA, respectively.

3. Results and discussion

Figure 2 shows the TG-DTA curve for the co-precipitated Zn-Mg oxalate with a molar ratio of Zn/Mg = 0.85/0.15 as the starting solution. Then, the heating rate was 5 K min⁻¹. Two steps of weight loss were observed at 383–423 K and at 623–643 K. 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 683 K, followed by the endothermic peak at 439 K. In the co-precipitated oxalates with the molar ratio of Zn/Mg = 1.0/0.0, 0.85/0.15 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 425 K and 674 K for Zn/Mg = 1.0/0.0, 450 K and 697 K, for Zn/Mg = 0.85/0.15, 296 K and 756 K for Zn/Mg = 0.0/1.0, respectively. Consequently, the co-precipitated oxalates seem to be behaved as a single entity and this is a proof that the zinc and magnesium ions co-precipitate in the solid solution form of (Zn, Mg)(C₂O₄)₂·2H₂O. The thermal decomposition of Zn-Mg oxalate salt was found to enable the formation of hexagonal (Zn_{1-x}Mg_x)O solid solution at low temperatures. A typical example is shown in Fig. 3; which is the XRD patterns for (Zn_{0.85}Mg_{0.15})O ($x=0.15$) sample decomposed at various temperatures for 2 h in a reduced atmosphere of 3% H₂-Ar gas mixture. When fired even at 773 K, the XRD pattern characteristic of wurtzite structure was observed. The X-ray reflections became to be strong and sharp when fired at higher temperatures than 973 K, although a small amount of rock-salt type MgO phase (open circle) was

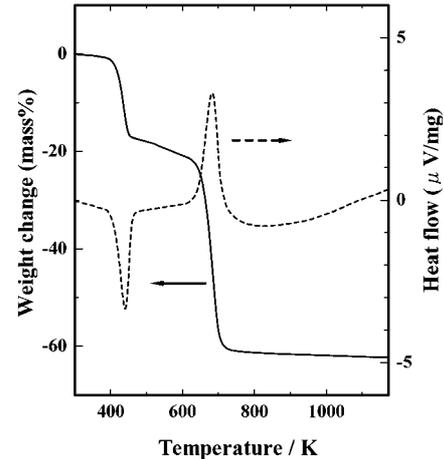


Fig. 2. TG-DTA curve for the co-precipitated Zn-Mg oxalate with a ratio of Zn : Mg = 0.85 : 0.15.

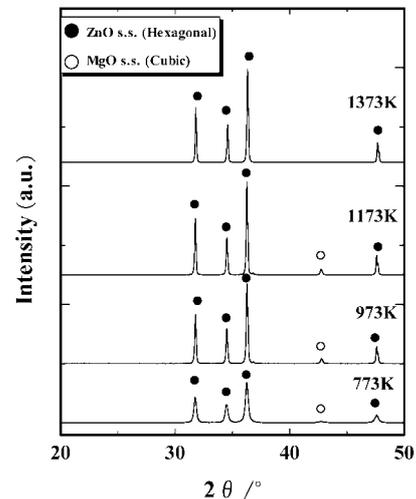


Fig. 3. XRD patterns for (Zn_{0.85}Mg_{0.15})O powder decomposed at various temperatures for 2 h in a reduced atmosphere of 3% H₂-Ar gas mixture.

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 0.00 ≤ x ≤ 0.15, the rock-salt type MgO phase was not detected in the XRD pattern when fired at 1373 K. Figure 4 shows the change in lattice constants of (Zn_{1-x}Mg_x)O solid solution deposited at 1373 K for 2 h in a reduced atmosphere of 3% H₂-Ar gas mixture. 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 $X=0.15$. This value is relatively large as compared with that (ca. 2 mol%) reported in high-temperature phase equilibrium of the ZnO-MgO system.¹¹⁾ Periclase (MgO) is cubic, whereas zincite (ZnO) is hexagonal. However, the similarity in ionic radius of Mg²⁺ and Zn²⁺ allows some replacement in either structure.¹²⁾ This high solid solubility is considered to be due to powders decomposed directly from the complex oxalate salt. Figure 5 shows a scanning electron micrograph of (Zn_{1-x}Mg_x)O (0.00 ≤ x ≤ 0.15) samples decomposed at 1373 K for 2 h in a reduced atmosphere of 3%

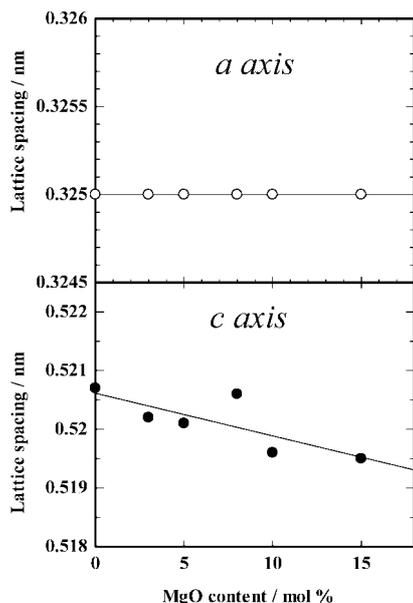


Fig. 4. Change in lattice constants of $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ solid solution deposited at 1073 K for 3 h in a reduced atmosphere of 3% H_2 -Ar gas mixture.

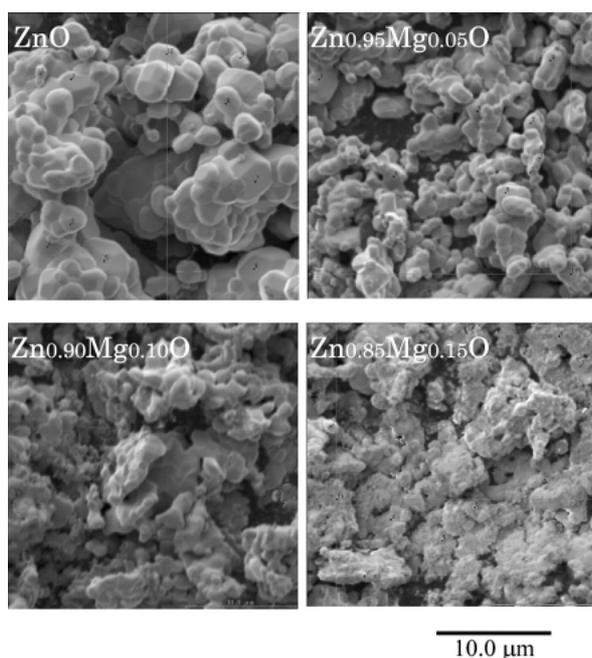


Fig. 5. SEM photographs of $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ solid solution powders decomposed at 1373 K for 2 h in a reduced atmosphere of 3% H_2 -Ar gas mixture.

H_2 -Ar gas mixture. The decomposed powder is aggregated with the individual particles of about $2\ \mu\text{m}$ size in the ZnO sample. The plate particles similar to ZnO ceramic are also observed in the SEM photographs. Then, the particle size of $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ ($0.00 \leq x \leq 0.15$) samples was decreased with the rich of MgO-substituted concentration. Thus the oxalate co-precipitation method is effective for producing fine phosphor powders at low temperatures. **Figure 6** shows CL spectra of ZnO and $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ ($0.00 \leq x \leq 0.15$) powders annealed

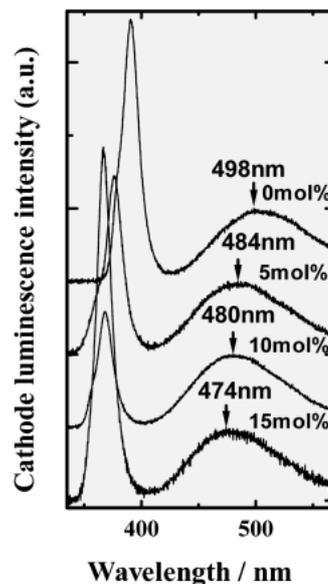


Fig. 6. CL spectra of $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ solid solution powders annealed at 1373 K for 2 h in a reduced atmosphere of 3% H_2 -Ar gas mixture.

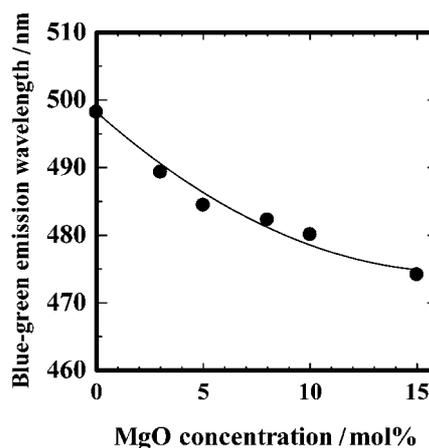


Fig. 7. Change in blue-green emission wavelength observed for $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ solid solution.

at 1373 K for 2 h in a reduced atmosphere of 3% H_2 -Ar gas mixture. In the ZnO sample, a strong green emission band with a peak around 498 nm is seen. Stronger 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^(6,7) reported previously. On the other hand, the green emission in the ZnO sample is observed to shift at low wavelength side with the rich of MgO-substituted concentration. Consequently, the corresponding emission band of $(\text{Zn}_{0.85}\text{Mg}_{0.15})\text{O}$ ($x=0.15$) sample is observed with the maximum around 474 nm. As shown in **Fig. 7**, 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 luminescence is attributed to the recombination of donor electrons in singly occupied oxygen vacancies (V_{O}^+) with cathode-excited holes in the valence band, according to the green-luminescence mechanism

reported by Vanheusden et al.⁶⁾ 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. 6. 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, partially substitution of MgO for ZnO is estimated to make it possible to generate the blue-green cathode luminescence.

4. Conclusion

A limited range of $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ solid solution was prepared using the thermal decomposition of complex Zn-Mg oxalate. The solubility of Mg in ZnO was estimated to be ca. 15%. In the samples annealed at 1373 K for 2 h in 3% H_2 -Ar gas mixture, green to blue cathode luminescence was observed. It is evident that the partial substitution of MgO results in the shift of green emission band at low wavelength side. The CL material is expected as a low-cost and blue light-emitting phosphor for low-voltage luminescence in flat panel displays.

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