

Clarification of Phase Diagram in a (Zn, Mg)O Pseudo Binary System by Using Ultra-Fine MgO Source Powder

Courtney Bergstein

Chemistry, Carlow University

NNIN iREU Site: National Institute for Materials Science, Tsukuba, Japan

NNIN iREU Principal Investigator(s): Dr. Naoki Ohashi, Optoelectronics Group, National Institute of Materials Science

Contact: Bergsteincl@gmail.com, ohashi.naoki@nims.go.jp

Abstract:

Zinc and magnesium oxide [(Zn,Mg)O] alloys are appropriate for near ultraviolet (UV) light emitting diodes because of their ability to increase the band gap of ZnO, leading to the tuning of the luminescence wavelength and an increase in the intensity of the light emitted. However, there is no consensus on the solubility limit of MgO in ZnO due to the many difficulties associated with different preparation parameters. This research investigates a small portion of (Zn,Mg)O phase diagram in order to clarify the solubility limit of MgO in ZnO. Grain size measurements, x-ray diffraction measurements, and photoluminescence measurements were used to investigate the composition dependence of lattice parameters as well as energy band gap. All results indicated an increase in the band gap with the increase of concentration and sintering temperature. X-ray diffraction measurements revealed an approximate solubility limit of 18% for samples sintered at 1500°C, 17% for samples sintered at 1400°C, and 15% for samples sintered at 1200°C. Photoluminescence results revealed a solubility limit of approximately 16% for samples sintered at 1400°C. Typical applications are for the use of light-emitting devices.

Introduction:

ZnO is a promising wide gap semiconductor (3.3 eV) in the field of light-emitting devices because of its large band gap and high exciton binding energy. By alloying ZnO with various concentrations of MgO, the luminescence properties in the visible region can be enhanced [1]. High concentrations of (Zn,Mg)O alloy have been obtained by the technique of pulsed laser deposition (PLD) [2]; however the solubility limit has not been clarified, due to many difficulties in sample preparation—such as the stability of both oxides.

In the present study, we investigated the solubility limit of MgO in ZnO, the lattice constants of unstrained (Zn,Mg)O, as well as some intrinsic properties of (Zn,Mg)O. As MgO concentration and reaction temperature increased, we expected changes in the lattice constants and the intrinsic properties of (Zn,Mg)O. Using this information, a phase diagram will be constructed for this pseudo binary system.

Experimental Procedure:

Various samples were prepared using a multi-step process. Samples were prepared of different concentrations of MgO from 5 to 20 atomic %. The nanopowders were mixed using the ball milling process and then pelletized using cold isostatic pressure at 100 Mpa. After the powders were pelletized, they were sintered at various temperatures from 800-1500°C for 3 hours to 20 hours for samples of high concentrations. Homogenous and pure ceramic pellets were produced. The ceramic pellets were characterized using various techniques including scanning electron microscope observations (SEM), x-ray diffraction (XRD), and photoluminescence (PL). SEM characterizations were used to define grain boundaries and perform grain size measurements. The ceramic pellet's

crystallographic features, mainly lattice parameters, were determined by x-ray diffraction with copper (Cu) K α radiation using silicon (Si) standard powder. Luminescence properties of the samples were characterized with photoluminescence using a pulsed laser at 266 nm. All characterizations were performed at room temperature. Calculations were then performed to determine solubility limit in terms of luminescence properties (energy band gap) and lattice parameters (a and c).

Results:

SEM grain size measurements indicated an increase in grain size as temperature increased, but a decrease in grain size as concentration increased. XRD results showed that

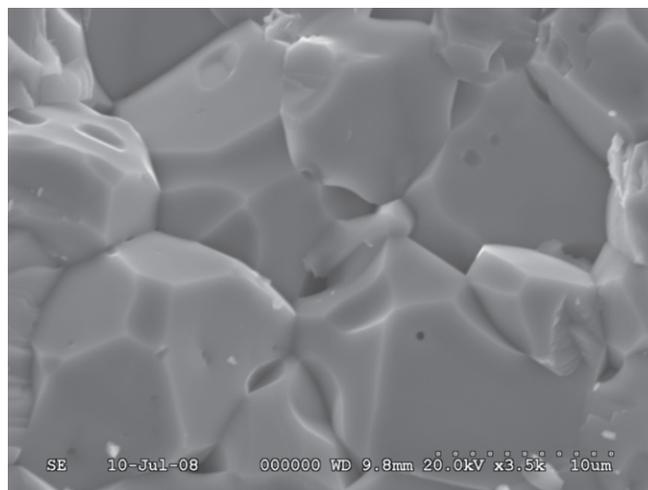


Figure 1: SEM image of 15% (Mg,Zn)O at 1400°C.
Average grain size = 7.095 μ m.

as concentration and temperature increased, diffraction angle decreased (refer to Figure 1). Using the data obtained from XRD, lattice parameters were calculated. The lattice parameter, a , increased as concentration and sintering temperature increased and the lattice parameter, c , decreased as concentration and sintering temperatures increased.

According to Vegard's Law, the plot (Figure 2) shows that the samples with a concentration of 20% MgO did not diffuse into the ZnO lattice. The estimated solubility limit of MgO was 15% for samples prepared at temperatures of 1200°C, 17% at 1400°C, and 18% at 1500°C.

Using the photoluminescence data, the band gap was calculated for all samples. A blue shift of the luminescence occurred with the increase of MgO concentration and reaction temp. Photoluminescence data showed that the band gap had increased to approximately 3.6 eV. As the concentration increased, the band gap should have increased linearly.

Using this linear relationship, it can be determined that the MgO solubility limit was approximately 16% for samples sintered at 1400°C (Figure 3). These limits are approximations as the actual chemical composition is likely to be different from nominal composition, due to ZnO evaporation during the sintering process.

Conclusions:

A preliminary phase diagram for a pseudo-binary MgO-ZnO system was constructed, as seen in Figure 4. As MgO concentration increased, reaction temperature had to be increased to ensure full diffusivity into the ZnO lattice. By alloying ZnO with MgO, the band gap increased from 3.3 eV to 3.62 eV, causing a blue shift of the luminescence. This allowed for tuning of the luminescence wavelength, making the (Zn,Mg)O alloy a good material for LEDs.

Future Work:

Future work includes performing chemical composition analysis of the samples to determine the actual composition as ZnO can evaporate during the sintering process. The peak photoluminescence wavelengths need to be determined with accuracy. The samples need to be sintered a high temperatures and then annealed at lower temperatures to determine the solubility limit associated with lower reaction temperatures.

Acknowledgements:

The National Nanotechnology Infrastructure Network iREU Program, National Science Foundation, and the National Institute of Materials Science. I want to give a special thanks to Dr. Naoki Ohashi.

References:

- [1] Chawla, S., et al; "Synthesis and optical properties of ZnO/MgO nanocomposite"; Journal of Alloys and Compounds, 459,457-460 (2007).
- [2] Zhuang, L, et al; "Microstructure and optical properties of Mg_xZn_{1-x}O thin films by means of pulsed laser deposition"; Computational Materials Science (2006).

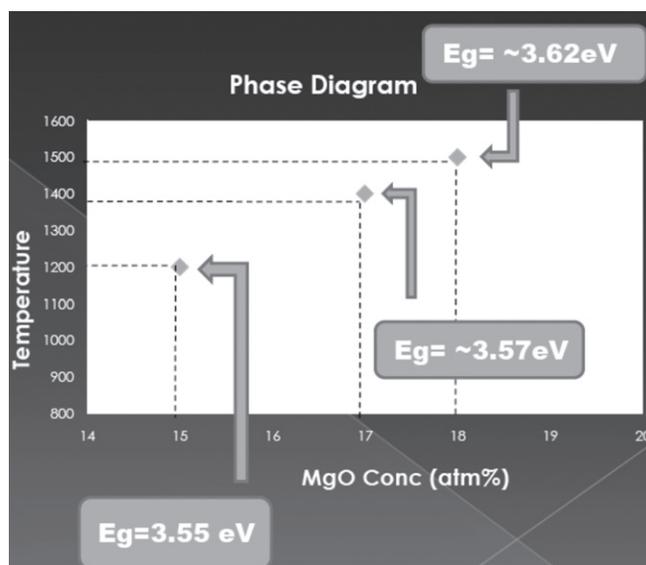
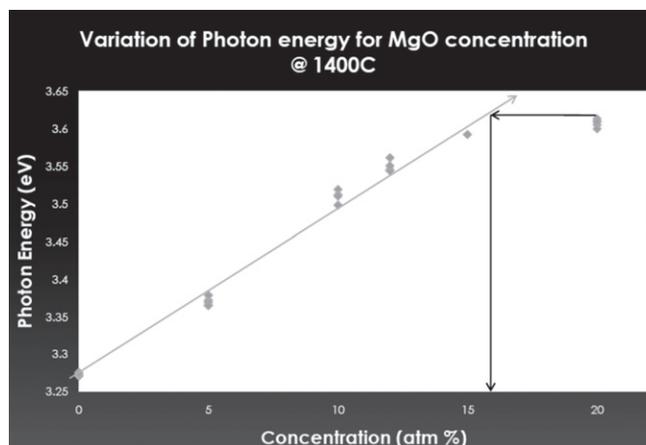
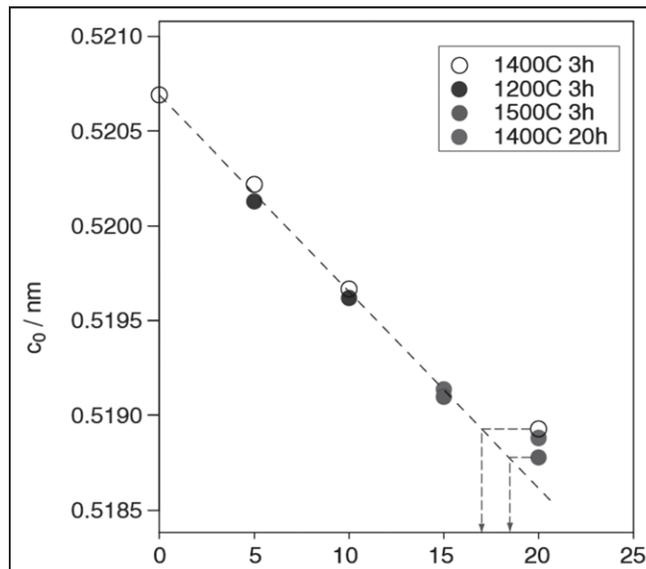


Figure 2, top: Plot of the change of lattice parameters with sintering temperature and increasing concentration.

Figure 3, middle: Graph showing the variation of photon energy with increasing MgO concentration.

Figure 4, bottom: Section of a phase diagram for an (Zn,Mg)O pseudo-binary system.