X-ray diffraction of Mg$_x$Zn$_{1-x}$O and ZnO nanocrystals under high pressure

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Mg$_x$Zn$_{1-x}$O ($x=0.15$) and ZnO nanocrystals of about 40 nm in diameter were studied using x-ray diffraction and diamond-anvil cells. The equation of state (EOS) for MgZnO is reported for the first time. Between pressures of 9.45 and 10.7 GPa, MgZnO transforms into the rocksalt (NaCl) structure, which persisted to 1.1 GPa upon decompression. The EOS parameters for ZnO are close to their bulk values and in good agreement with values obtained previously. The bulk modulus for MgZnO was slightly lower than that of ZnO. The pressure-induced decrease in $c/a$ ratio was greater for MgZnO, consistent with the tendency for MgZnO to move toward a cubic structure. From previous photoluminescence measurements [J. Huso et al., Appl. Phys. Lett. 89, 171909 (2006)], the bond-gap volume deformation potentials for ZnO and Mg$_{0.15}$Zn$_{0.85}$O were determined to be $-$3.6 and $-$4.0 eV, respectively. © 2009 American Institute of Physics. [DOI: 10.1063/1.3159036]

I. INTRODUCTION

ZnO and MgZnO are promising materials for future optoelectronic applications. ZnO has been considered one of the best candidates for UV light emission sources, due to its deep excitonic level ($\sim$60 meV). Therefore, its optical and electronic properties are the subject of great interest and have attracted significant research activity over the past decade. ZnO is a wide band-gap semiconductor with $E_g \sim 3.4$ eV. Recently, Mg$_{x}$Zn$_{1-x}$O has been synthesized in both thin-film form and in the form of nanocrystals. Mg$_{x}$Zn$_{1-x}$O heterostructures have been characterized by transmission spectroscopy, x-ray diffraction (XRD), and reflection high-energy electron diffraction. Since MgO has a band gap $E_g \sim 7$ eV, doping of ZnO with Mg atoms allows one to tune the band gap and change optical properties over wide range.

Nanocrystals are known to have properties that are sometimes quite different than those of the bulk materials. In particular, phase transitions in nanomaterials usually occur at pressures higher than the transformation pressures for the respective bulk compounds. This has been found, for example, for CdSe nanocrystals, PbS quantum dots, and ZnO nanocrystals. It is known that bulk ZnO has the wurtzite (B4) crystal structure at ambient pressure and transforms into the rocksalt (B1) structure at about 9 GPa. Nanocrystalline ZnO was probed under high pressure and its transformation pressure was determined to be 15.1 GPa.

The pressure dependence of the photoluminescence (PL) of nanocrystalline ZnO was also investigated and the analogous experiment on Mg$_{0.15}$Zn$_{0.85}$O has only recently been performed. The results for ZnO nanocrystals ($\sim$40 nm diameter) were identical to those for bulk ZnO. The magnitude of the band-gap deformation potential for Mg$_{0.15}$Zn$_{0.85}$O was found to be higher than for ZnO. This result was obtained with the assumption that the bulk modulus for Mg$_{0.15}$Zn$_{0.85}$O was the same as for ZnO. In the present work, we performed x-ray powder diffraction experiments on ZnO and Mg$_{0.15}$Zn$_{0.85}$O and determined their respective EOS. We found that the bulk modulus of Mg$_{0.15}$Zn$_{0.85}$O is slightly lower than that of ZnO. From the PL measurements in Ref. 17, we obtained accurate values for the ZnO and MgZnO deformation potentials.

II. EXPERIMENT

The samples of ZnO and Mg$_{0.15}$Zn$_{0.85}$O nanocrystals ($\sim$40 nm diameter) were synthesized and characterized according to the procedure described elsewhere. Typical PL spectra are shown in Fig. 1. PL spectra were obtained with a cw-Kimmon laser with a wavelength of 325 nm, a JY-Horiba micro-Raman/PL system, and an UV microscope. The Mg$_{0.15}$Zn$_{0.85}$O sample exhibits a blue shift of 0.2 eV relative to ZnO, consistent with previous measurements. The homogeneous line broadening of the Mg$_{0.15}$Zn$_{0.85}$O sample is consistent with a random distribution of alloy components. The samples were loaded into a piston-cylinder-type diamond-anvil cell, equipped with diamonds with 700 $\mu$m culet diameters. A stainless steel gasket was pretrained to a thickness of 25 $\mu$m and a 330 $\mu$m diameter hole was drilled in the center of indentation. The sample was loaded in the hole along with ruby chip for in situ pressure measurements and a 4:1 methanol-ethanol mixture as a pressure transmitting medium. The methanol-ethanol mixture is known to provide a hydrostatic environment up to 10 GPa. The pressure was measured before and after each run and the average of two measurements was taken as the experimental value. We used the Mao pressure scale, which gives pressure according to the formula

$P = \frac{1}{3} \left( \frac{E_{\text{el}}} {\text{amu}} \right)^{\frac{3}{2}} \left( \frac{D_{\text{el}}} {\text{amu}} \right)^{\frac{1}{2}} \left( \frac{E_{\text{ion}}} {\text{amu}} \right)^{\frac{1}{2}} \left( \frac{D_{\text{ion}}} {\text{amu}} \right)^{\frac{1}{2}}$
Here \( A = 1904 \), \( B = 7.665 \), and \( \lambda_0 \) is the zero-pressure wavelength (\( \lambda_0 = 694.2 \) nm in this study). The ruby lines remained well resolved, indicating hydrostatic conditions.

The XRD experiment was performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, beamline 12.2.2. The beam was collimated to 10 \( \times 15 \) \( \mu \)m\(^2\) and spectra (\( \lambda = 0.3543 \) \( \AA \)) were collected by a high-resolution MAR3450 image plate detector. All diffraction images were integrated by the FIT2D program,\(^21\) and the detailed analysis was performed using the GSAS program.\(^22\) Pressure-volume (\( P-V \)) data were fit to the third-order Birch–Murnaghan EOS,

\[
P(GPa) = A/B \left[ \left( \frac{\lambda}{\lambda_0} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left[ 1 + \frac{3}{4}(K' - 4) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right],
\]

using the EOS-FIT (V5.2) least-squares package.\(^23\) Here, \( K_0^{\prime} \) is the zero-pressure bulk modulus and \( K' \) is its derivative with respect to pressure.

The \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) sample was taken through compression and decompression cycles, whereas the \( \text{ZnO} \) sample was not decompressed.

### III. RESULTS

#### A. \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \)

The sample of \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) was loaded to 8.4 GPa, compressed to 10.7 GPa and then decompressed to 0.8 GPa, after which it was compressed to 8.05 GPa. Typical integrated XRD spectra are shown in Fig. 2. It shows four peaks corresponding to (100), (002), (101), and (102) reflections from the wurtzite \( B4 \) structure (space group \( P6_3mc \)). Upon compression to 10.7 GPa, an extra peak at \( 2\theta = 9.68^\circ \) appeared, which we believe corresponds to the rocksalt \( B1 \) phase of \( \text{MgZnO} \). This peak persisted upon decompression all the way to 1.1 GPa and back up in pressure to 8 GPa. We fitted the spectra assuming two phases and obtained excellent fits for all the peak positions. The (111) peak of the rocksalt phase is masked by the (101) peak of the wurtzite phase, as indicated in Fig. 2.

Pressure-volume data for the wurtzite phase of \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) are presented in Fig. 3, both for the compression and decompression cycles. The errors in volume are from the GSAS fits of the spectra and the pressure errors were estimated as the difference between pressure before and after the runs. The data were fitted to the third-order Birch–Murnaghan EOS and we obtained the following EOS parameters: \( V_0 = 47.81 \pm 0.03 \) \( \text{Å}^3 \); \( K_0 \) \( = 136.5 \pm 2.1 \) GPa; \( K' = 4 \) (fixed). Similar values resulted from the fit to the Vinet EOS,\(^24\,25\) which we do not present here. Our results are similar to those obtained for bulk \( \text{ZnO} \).\(^26\,29\) The appearance of an extra peak was detected between pressures 9.45 and 10.7 GPa, which is explained as the phase transition from \( B4 \) wurtzite into the \( B1 \) cubic (\( \text{NaCl} \)) structure. It is known that bulk \( \text{ZnO} \) undergoes a phase transition at pressures about 9 GPa.\(^3\)

![FIG. 1. (Color online) PL spectra of \( \text{ZnO} \) and \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) at room temperature.](image1)

![FIG. 2. (Color online) Typical integrated XRD spectra of \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) at two different pressures. Reflection peaks are indexed to the wurtzite structure \( B4 \). The higher-pressure spectrum shows an extra peak corresponding to the (200) reflection from the rocksalt \( B1 \) phase.](image2)

![FIG. 3. (Color online) \( P-V \) data for the wurtzite \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) sample. Solid squares indicate compression; solid circles indicate decompression. The solid line is the fit to the third-order Birch–Murnaghan EOS.](image3)
We also monitored the pressure dependence of the lattice constants $a$ and $c$. Their extrapolated zero-pressure values are $a=3.2568 \pm 0.0006$ Å and $c=5.2056 \pm 0.002$ Å. In Ref. 7 it was determined that, for Mg$_{x}$Zn$_{1-x}$O, $a$ increases and $c$ decreases with increasing Mg content. The formula describing the increase in $a$ is given by\cite{20}

$$a(\text{Å}) = 3.25 + 0.036x,$$

(3)

Where $x$ is the Mg content ($0 \leq x \leq 1$). Using Eq. (3), we estimated the Mg content in our sample to be $x=0.19$. Considering the large scatter in XRD data for MgZnO alloys, this value is in satisfactory agreement with $x=0.15$.

In Fig. 4 we show the ratio of $c$ to $a$ as a function of pressure. It is clearly seen from Fig. 4 that the axis ratio, $r=c/a$, decreases with pressure linearly. A least-squares fit yields

$$r = (1.5973 \pm 0.0004) - (9.1 \times 10^{-4} \pm 6 \times 10^{-5}) 
\times P(\text{GPa}).$$

(4)

The value of $r$ at zero pressure is smaller, and the magnitude of its pressure coefficient is higher, than the values obtained for pure ZnO.\cite{27,26}

Pressure-volume data for the rocksalt $B1$ phase of Mg$_{0.15}$Zn$_{0.85}$O are presented in Fig. 5. The fit to the third-order Birch–Murnaghan EOS resulted in the following EOS parameters: $V_0=19.55 \pm 0.02$ Å$^3$; $K_0T=172 \pm 6$ GPa; $K'=4$ (fixed). These results are, within experimental errors, in agreement with those for cubic ZnO.\cite{31,32,27} the zero-pressure volume being in excellent agreement with prior work.\cite{27,31}

B. ZnO

The ZnO sample was loaded according to the same procedure described in Sec. III A for the Mg$_{0.15}$Zn$_{0.85}$O sample. The sample was compressed from 0.6 to 9.9 GPa. No phase change was observed, and the sample was not decompressed. The integrated XRD spectra were similar to the upper spectrum in Fig. 2. The $P$-$V$ data for ZnO sample are shown in Fig. 6, along with the fit to the Birch–Murnaghan EOS. The EOS parameters are $V_0=47.74 \pm 0.02$ Å$^3$; $K_0T=144 \pm 2$ GPa; $K'=4$ (fixed). These results are in close agreement with those obtained earlier for bulk ZnO.\cite{26,29} No phase transition was detected up to the highest pressure achieved. We also plotted the pressure dependence of the ratio of two lattice constants, $a$ and $c$ (Fig. 7). For ZnO, the ratio $r=c/a$ is linearly decreasing with pressure, consistent with previous observations.\cite{26,28} The linear fit resulted in the following functional dependence:
\[ r = (1.6043 \pm 0.0004) - (6.4 \times 10^{-4} \pm 7 \times 10^{-5}) \times P \text{(GPa)}. \] (5)

This is, within experimental errors, in agreement with values obtained before.\textsuperscript{26-28}

IV. CONCLUSIONS

Using XRD, we determined the EOS for Mg\textsubscript{0.15}Zn\textsubscript{0.85}O and ZnO nanocrystals. We obtained the bulk modulus and the pressure dependence of \( r = c/a \) for both materials. It was determined that the bulk modulus for Mg\textsubscript{0.15}Zn\textsubscript{0.85}O is 136.5 GPa and for ZnO it is 144 GPa. The result for ZnO is in excellent agreement with earlier studies. The ratio of \( c/a \) is valid. A similar result was obtained for PbSe nanocrystals, where the effect of the compressibility on the band-gap shift was shown to be negligible.\textsuperscript{33}

In the study of the PL energy response to pressure, \textsuperscript{17} the volume deformation potentials were calculated under the assumption that the bulk moduli for ZnO and MgZnO nanocrystals were equal. As shown in Sec. III, however, that assumption was incorrect. The volume deformation potential is given by \( \alpha_v = \partial E/\partial \ln V \). From the PL data of Ref. 17 and the EOS data of the present study, we obtained \( \alpha_v = -3.6 \pm 0.1 \) eV and \(-4.0 \pm 0.2 \) eV for ZnO and MgZnO, respectively. Hence, the difference in PL shifts cannot be explained merely by differences in compressibility. The difference in deformation potentials suggests that the model proposed in Ref. 17, which explained the lower deformation potential of ZnO as a result of \( d \) orbitals in the valence band, is valid. A similar result was obtained for PbSe nanocrystals, where the effect of the compressibility on the band-gap shift was shown to be negligible.\textsuperscript{33}

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