Local structure evolution in polycrystalline $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($0 \leq x \leq 0.15$) studied by Raman and by synchrotron x-ray pair distribution analysis

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The local structures of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys have been studied by Raman spectroscopy and by synchrotron x-ray pair distribution function (PDF) analysis. Within the solid solution range ($0 \leq x \leq 0.15$) of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, the wurtzite framework is maintained with Mg homogeneously distributed throughout the wurtzite lattice. The $E_{2}^{\text{high}}$ Raman line of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ displays systematic changes in response to the evolution of the crystal lattice upon the Mg-substitution. The red-shift and broadening of the $E_{2}^{\text{high}}$ mode are explained by the expansion of hexagonal $ab$-dimensions, and compositional disorder of $\text{Zn}/\text{Mg}$, respectively. Synchrotron x-ray PDF analyses of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ reveal that the Mg atoms have a slightly reduced wurtzite parameter $u$ and more regular tetrahedral bond distances than the Zn atoms. For both Zn and Mg, the internal tetrahedral geometries are independent of the alloy composition.

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I. INTRODUCTION

Polar semiconductors such as wurtzite $\text{ZnO}$ and $\text{GaN}$ have great potential for use in the polarization-doped field effect transistors (PolFETs) which exploit a polarization gradient at the channel layer to attain higher mobility and higher concentrations of carriers. The performance of PolFETs depends primarily on the interface quality and the magnitude of the polarization gradient at the heterojunction. Those goals can be approached by interfacing a polar semiconductor with its alloy derivative, as exemplified by the fabrication of a PolFET comprising the interface of $\text{GaN}/\text{Ga}_{1-x}\text{Al}_x\text{N}$ ($x = 0 \sim 0.3$). In designing $\text{ZnO}$-based PolFETs, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys can be considered as the sub-layer component, since Mg-substitution effectively alters the polarization of $\text{ZnO}$ while keeping the lattice dimensions nearly unchanged.

In a previous report we have outlined the prospects for $\text{ZnO}/\text{Zn}_{1-x}\text{Mg}_x\text{O}$ heterojunctions for PolFET applications, based on structural analysis of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys using synchrotron x-ray diffraction. We showed that the ionic polarization can be tuned by $\approx 14\%$ from $\text{ZnO}$ to $\text{Zn}_0.85\text{Mg}_0.15\text{O}$, despite only small changes in the cell volume ($\approx 0.3\%$). Also, it was found that Mg can substitute up to $15\%$ of total Zn in the wurtzite lattice, without any evidence for segregation. While the average crystal structures of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ phases were accurately determined in the above study, there still remain the local structural details of the solid solutions to be understood. Therefore in a continuing effort, we have performed Raman studies and synchrotron x-ray pair distribution function (PDF) analysis of polycrystalline $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ samples. Raman spectroscopy is known to be useful for examining compositional disorder and/or the presence of strain within semiconductor alloys. In previous Raman studies on wurtzite type crystals, the peak position and shape of the $E_{2}^{\text{high}}$ phonon mode have been used to investigate the effects of sample grain size, heterogeneous components, and defects. PDF analysis provides a powerful probe of local non-periodic atomic displacements in the short range, and is a suitable complement to the $k$-space refinement technique. This ability is very relevant to the possible distinction of tetrahedral out-of-center displacements of Zn and Mg, and provides for a better comparison platform with density functional calculations of the crystal structure.

In this study, we provide a complete description of polycrystalline $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys prepared from $\text{Zn}_{1-x}\text{Mg}_x(\text{C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O}$ precursors. We present results of thermogravimetry, ultraviolet/visible diffuse reflectance spectroscopy, infrared, and Raman spectroscopy in addition to examining the distinct tetrahedral geometries of Zn and Mg using synchrotron x-ray PDF analyses based on supercell structure models.

II. EXPERIMENTAL

Powder samples of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x = 0, 0.05, 0.10$, and 0.15) were prepared using an oxalate precursor route as described previously. Aqueous solutions of zinc acetate, magnesium acetate, and oxalic acid were separately prepared and mixed to precipitate zinc magnesium oxalates, which are crystalline, single-phase compounds with $\text{Zn}^{2+}$ and $\text{Mg}^{2+}$ homogeneously mixed at the atomic level. The precipitates were thoroughly washed with deionized water and dried at 60°C for 4 h to produce white powders of $\text{Zn}_{1-x}\text{Mg}_x(\text{C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O}$, as verified by powder x-ray diffraction. Subsequently the oxalate dihydrates were transformed to $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ by heating in air at 550°C for 24 h. The thermal decomposition of $\text{Zn}_{1-x}\text{Mg}_x(\text{C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O}$ was monitored by thermogravimetry using a Cahn ThermMax 400 thermogravimetric analyzer (Thermo Scientific). For each composition, $\approx 60\%$ of powder was heated in air up to 1000°C at 5°C min$^{-1}$. Fourier-transform infrared (FT-IR) spec-
the atomic PDFs $F$ (functions solute electron units to give total scattering structure $I$). In the present work, scattering data with $Q_{\text{max}}$ of 28 Å$^{-1}$ were utilized for extracting PDFs. Sample powders were loaded in Kapton tubes and data were measured in the transmission mode using an amorphous silicon image plate system (General Electric Healthcare). For each sample, 33 images were taken with an exposure time of 16 s per image. The program FIT2D was used to convert images into the corresponding one-dimensional x-ray diffraction (XRD) pattern. The average crystal structures of these samples have been determined by Rietveld method and reported previously. For obtaining the PDF from XRD data, the program PDFGETX2 was used. First the measured scattering intensities were corrected for sample container background, Compton scattering, and Laue diffuse scattering. Next the coherently scattered intensities $I(Q)$ were normalized in absolute electron units to give total scattering structure functions $S(Q)$. Finally the reduced structure functions $F(Q) = Q[S(Q) - 1]$ were Fourier-transformed to produce the atomic PDFs $G(r)$. The refinements of Zn$_{1-x}$Mg$_x$O structures were performed against the above obtained experimental PDFs using the software PDFFIT.

Synchrotron x-ray scattering experiments were carried out at beamline 11-ID-B of the Advanced Photon Source (Argonne National Laboratory) using an x-ray energy of 90.8 keV ($\lambda \approx 0.1365 \text{Å}$) at room temperature. Use of high energy radiation enables data acquisition at high $Q$ ($=4\pi\sin\theta/\lambda$) wave vector, which in turn improves the reliability of the Fourier transformation for obtaining the PDF $G(r)$. In the present work, scattering data with $Q_{\text{max}}$ of 28 Å$^{-1}$ were utilized for extracting PDFs. Sample powders were loaded in Kapton tubes and data were measured in the transmission mode using an amorphous silicon image plate system (General Electric Healthcare). For each sample, 33 images were taken with an exposure time of 16 s per image. The program FIT2D was used to convert images into the corresponding one-dimensional x-ray diffraction (XRD) pattern. The average crystal structures of these samples have been determined by Rietveld method and reported previously. For obtaining the PDF from XRD data, the program PDFGETX2 was used. First the measured scattering intensities were corrected for sample container background, Compton scattering, and Laue diffuse scattering. Next the coherently scattered intensities $I(Q)$ were normalized in absolute electron units to give total scattering structure functions $S(Q)$. Finally the reduced structure functions $F(Q) = Q[S(Q) - 1]$ were Fourier-transformed to produce the atomic PDFs $G(r)$. The refinements of Zn$_{1-x}$Mg$_x$O structures were performed against the above obtained experimental PDFs using the software PDFFIT.

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The thermogravimetric profiles of Zn$_{1-x}$Mg$_x$(C$_2$O$_4$)·2H$_2$O ($x = 0$, 0.05, 0.10, and 0.15) are shown in Fig. 1. The stepwise processes of dehydration and oxalate-to-oxide conversion are clearly observed around 130 and 390°C, respectively, with the weight changes in good agreements with calculated estimates. With increase of Mg content, the onset temperatures of both weight loss steps shifted to higher temperature. This could be interpreted as indicative of the extra activation barrier for stabilizing Mg in the wurtzite lattice. For all cases, oxide formation was nearly complete at 500°C without any noticeable weight change at higher temperature. It is therefore assumed that isothermal heating at 550°C for 24 h completely transforms Zn$_{1-x}$Mg$_x$(C$_2$O$_4$)·2H$_2$O to the oxides Zn$_{1-x}$Mg$_x$O.

In Fig. 2, the FT-IR spectra for Zn$_{1-x}$Mg$_x$O are shown, which are consistent with the registered reference data of wurtzite ZnO. A previous report suggested that organic precursors for ZnO synthesis may leave carbonate species strongly bound within the lattice but the samples in this study did not exhibit any spectral feature at around 1300 and 1500 cm$^{-1}$ demonstrating the complete combustion of oxalate. The wurtzite lattice vibrations were observed as broad IR bands at 400–600 cm$^{-1}$. Upon Mg-substitution, these stretching modes shifted to higher wavenumber as a result of the smaller reduced mass of Mg–O compared with that of Zn–O.

The optical band gaps ($E_g$) of Zn$_{1-x}$Mg$_x$O powders were determined from the diffuse-reflectance absorption spectra as shown in Fig. 3. The absorbance ($A$) of the samples were obtained from the measured reflectance ($R$).
FIG. 2: FT-IR spectra of Zn$_{1-x}$Mg$_x$O ($x = 0, 0.05, 0.10$, and 0.15).

FIG. 3: Diffuse-reflectance absorption spectra for Zn$_{1-x}$Mg$_x$O ($x = 0, 0.05, 0.10$, and 0.15). For each spectrum, the band gap energy is indicated by the extrapolated arrow.

according to the Kubelka-Munk relation

$$A = \frac{(1 - R)^2}{2R}$$

In the present measurement setup, the sample analytes are thick enough ($\approx 1.5$ mm) to disallow transmission, and the Kubelka-Munk theory is appropriate. As clearly seen in Fig. 3, the absorption edges are shifted to the higher energy side with the increase of Mg content $x$. Also noticed are slight broadenings of the edge slopes upon the Mg-substitution. The band gap energy gradually increased from 3.24 ($x = 0$) to 3.26 ($x = 0.05$), 3.30 ($x = 0.10$), and 3.35 eV ($x = 0.15$). In previous studies on Zn$_{1-x}$Mg$_x$O thin films grown by pulsed laser deposition, Ohtomo et al. have observed a similar composition dependence of the band gaps; monotonic increases from 3.30 ($x = 0$) to 3.63 eV ($x = 0.14$). Their absolute band gap energies are not exactly reproduced in our polycrystalline samples, but this may be due to the differences in experimental details. The optical band gaps of solids are frequently determined to be different depending on sample type, optical characterization technique, and band gap determination method.

B. Raman spectroscopy

Wurtzite ZnO belongs to the space group $C_{6v}^4$ (Hermann-Mauguin symbol $P6_{3}mc$) and has six lattice phonon modes, $A_1 + 2B_1 + E_1 + 2E_2$, of which the $B_1$ branches are Raman inactive. The $A_1$ and $E_1$ modes are polarized along the $z$-direction and $xy$-plane, respectively, whereas the two $E_2$ modes ($E_{2\text{low}}$ and $E_{2\text{high}}$) are non-polar. Each of the polar modes is split to longitudinal (LO) and transverse optical (TO) components due to the macroscopic electric field associated with the LO phonons.

Raman spectra of polycrystalline Zn$_{1-x}$Mg$_x$O powders were examined over the frequency range 90–830 cm$^{-1}$ and part of those spectra are presented in Fig. 4. For all cases of $x = 0 – 0.15$, the measured Raman spectra agree well with the wurtzite ZnO vibration modes, without any new bands arising from Mg-substitution. Raman features characteristic of cubic MgO were not observed. In previous Raman studies on ZnO films or nanophases doped with N, Al, Ga, Sb, Fe, Mn, or Mg, additional bands have been observed and attributed to the induced lattice de-
Each Raman spectrum of Zn
for Zn, the phonon frequency is expected to increase for
Fig. 5. frequency $\omega$
full-width at half-maximum (FWHM), and $\beta$
$I$
where
metry parameter ($\beta$
fect or the dopants’ local vibration. A previous Ra-
m-an study of polycrystalline Zn$_{1-x}$Mg$_x$O has shown that
the Mg-substitution flattens the overall Raman signal. In Fig. 4 the Raman peaks from $A_1$(TO), $E_1$(TO), $E_2^{\text{low}}$
(multiphonon), and $E_2^{\text{high}}$
modes are found. The $A_1$ and $E_1$
modules reflect the strength of the polar lattice bonds,
which are of interest in relation with the c-axial displace-
ments of cations. However the peaks corresponding to
those two modes were not well resolved from the back-
ground and could not be used for a detailed study. Usually Raman signals from polar modes are weaker in in-
tensity due to phonon-plasmon interactions. The $E_2^{\text{high}}$
phonon, which is the most prominent in the ZnO Ra-
man spectra, was used for the peak profile analysis. The
Raman line shape was fitted using the Breit-Wigner func-
tion,

$$I(\omega) \propto \frac{[1 + 2\beta(\omega - \omega_0)/\Gamma]^2}{1 + [2(\omega - \omega_2)/\Gamma]^2} \quad (2)$$

where $I(\omega)$ is the Raman intensity at a given frequency,
$\omega_0$ is the Raman shift, $\Gamma$ is the broadening expressed as
full-width at half-maximum (FWHM), and $\beta$ is an asym-
metry parameter ($\beta = 0$ for the symmetrical peak). For each Raman spectrum of Zn$_{1-x}$Mg$_x$O, the $E_2^{\text{high}}$
phonon frequency $\omega_0$ was determined along with $\Gamma$, as plotted in
Fig. 5.

If we consider the mass change in the Mg-substitution
for Zn, the phonon frequency is expected to increase for
the samples with higher $x$. But the observed trend is
contrary to this: The $E_2^{\text{high}}$ phonon frequency decreases
upon the Mg-substitution. To explain this, it should be
recalled that the $E_2^{\text{high}}$ mode of ZnO corresponds mostly
($\approx 85\%$) to the vibration of oxygen atoms and is insen-
sitive to the mass substitution on the cation site. On the other hand, since the $E_2^{\text{high}}$
mode is associated with atomic motions on the $xy$-plane, its phonon en-
ergy depends on the in-plane lattice dimensions. In the
Zn$_{1-x}$Mg$_x$O solid solution, the hexagonal parameter $a$
monotonically increases with $x$, hence softening the $E_2^{\text{high}}$
phonon mode. The decrease of $E_2^{\text{high}}$
 mode frequency has been similarly observed from ZnO thin films under the
tensile strain along the $xy$-plane.

In addition to the frequency shift, it is also noted that
the $E_2^{\text{high}}$
peaks are markedly broadened upon the Mg-
substitution. The Raman mode frequency and the peak
width can be influenced by the random substitution of Zn
with Mg through the compositional disorder effect. As
inferred from the evolution of average crystal structures in Zn$_{1-x}$Mg$_x$O, the Mg atoms do not have an ident-
tical bonding geometry to that of Zn. In other words the
Mg-substitution alters the translational symmetry of the
wurtzite lattice to modify the phonon oscillation field.
In previous Raman studies on the alloy systems, the spatial
correlation has been regarded an adequate mechanism
responsible for the red-shift of the mode frequency as
well as the peak broadening. The model is based on the
wave vector uncertainty, $\Delta q = 2\pi/L$, where $q$ is the phonon
wave vector range, $L$ is the length scale of phonon con-
finement, and $q$ has the phonon dispersion relation
$\omega(q)$ with the Raman frequency. It predicts that, as the
$L$ becomes smaller, $\Delta q$ becomes larger so that a wider
range of frequencies is allowed for Raman scattering.
In Zn$_{1-x}$Mg$_x$O compounds as well, the presence of the hetero component Mg seems to perturb the wurtzite phonon modes. As shown in Fig. 4 both the frequency shift and the peak broadening become greater for the samples with higher Mg-concentration. However, the
symmetry of $E_2^{\text{high}}$
peak shape did not show significant dependences on the Mg-concentration, which is some-
what unexpected. This is in contrast to the spatial cor-
relation model and also with the experimental examples of
disordered semiconductor crystals, where the Raman
line shapes become more asymmetric as the peak widths
increase.

C. Pair distribution functions

Both Rietveld refinement and PDF analysis utilize one-
dimensional diffraction patterns to extract crystal struc-
ture information. The former focuses on the long range
average structure based on Bragg diffraction, while the
latter focuses on the local structure information over
short length scales from the diffuse scattering in addition
to the Bragg diffraction. Therefore the above
the nearest cation exposes a subtle evolution in the coordination shell of which indicated that the (Zn,Mg) is consistent with the previous Rietveld refinement result. However a close view at the PDF peak at $Q = 0$, $0.05$, $0.10$, and $0.15$. Inset shows the zoomed-in view of the peak corresponding to the first coordination (Zn,Mg)–O shell.

interatomic distances are $(3\times)1.9731\,\text{Å}$ and $1.9941\,\text{Å}$ in ZnO, and $(3\times)1.9756\,\text{Å}$ and $1.9873\,\text{Å}$ in ZnO$_{0.85}$MgO$_{0.15}$. Although small in magnitudes, the above changes correspond to $\approx 45\%$ reduction in the standard deviation of the four bond distances, which result in the discernible peak sharpening. The shifts of peak positions can be ascribed to the lengthening of the three shorter bonds rather than a change in the longer apical bond.

The real space PDF data are therefore useful for directly depicting the bonding geometry in a specific $r$-range. For more detailed and quantitative information, the PDF data were analyzed by full profile refinements using several different models of simple cell as well as supercell. The simple cell models were based on the hexagonal wurtzite structure (space group $P\overline{6}mc$, $Z = 2$, $a \approx 3.25\,\text{Å}$, $c \approx 5.20\,\text{Å}$) with O at $(\frac{1}{4} \frac{4}{4} 0)$ and Zn/Mg at $(\frac{1}{4} \frac{4}{4} u)$. In the analyses using the simple cell, the fractional occupancies of Zn and Mg were set according to the composition of each phase Zn$_{1-x}$Mg$_x$O ($x = 0$, $0.05$, $0.10$, and $0.15$). Supercell model structures were constructed by expanding the wurtzite simple cell to a $3\times3\times1$ size ($Z = 18$, $a \approx 9.75\,\text{Å}$, $c \approx 5.20\,\text{Å}$). By partially replacing the Zn atoms with Mg, the parent Zn$_{18}$O$_{18}$ supercell can be modified to the compositions Zn$_{17}$Mg$_{18}$ (Zn$_{0.944}$Mg$_{0.056}$O), Zn$_{16}$Mg$_{2}$O$_{18}$ (Zn$_{0.889}$Mg$_{0.111}$O), and Zn$_{15}$Mg$_3$O$_{18}$ (Zn$_{0.833}$Mg$_{0.167}$O) to model the $x = 0.05$, $0.10$, and $0.15$ phases, respectively. The Mg atoms in Zn$_{16}$Mg$_{2}$O$_{18}$ and Zn$_{15}$Mg$_3$O$_{18}$ models were separated to be as distant from one another as allowed by the cell. PDF refinements of $G(r)$ were carried out using the variables of scale factor, dynamic correlation factor, resolution factor, lattice constants, independent $u$ of Zn and Mg, and isotropic temperature factors of Zn, Mg, and O.

First the PDF refinements were performed for Zn$_{1-x}$Mg$_x$O ($x = 0$, $0.05$, $0.10$, and $0.15$) using the four-atom simple cell models, in which the cation composi-

FIG. 6: XRD patterns of Zn$_{0.95}$Mg$_{0.05}$O, used for (a) PDF analysis and (b) Rietveld refinement. Sample-to-detector distances were 150 mm for (a) and 660 mm for (b).
FIG. 8: PDF refinement profiles for (a) ZnO and (b) Zn$_{0.85}$Mg$_{0.15}$O, using four-atom simple cell models. Experimental (open circles) and calculated (solid lines) data are plotted in the bottom panels, along with the difference patterns ($G_{\text{expt}} - G_{\text{calc}}$) in the top panels.

TABLE I: Summary of PDF refinements for Zn$_{1-x}$Mg$_x$O ($x = 0, 0.05, 0.10$, and $0.15$) using simple cell models, over the $r$-range of 1.5–10 Å.

| $x$ | 0    | 0.05 | 0.10 | 0.15 |
|-----|------|------|------|------|
| $R_w$ (%) | 13.4 | 17.0 | 17.2 | 17.8 |
| $a$ (Å)  | 3.2500(2) | 3.25028(5) | 3.2504(1) | 3.2506(1) |
| $c$ (Å)  | 5.2101(4) | 5.2109(1) | 5.2115(3) | 5.2119(3) |
| $u$(Mg)  | -   | 0.380(4) | 0.379(4) | 0.380(3) |
| $u$(Zn)  | 0.3819(4) | 0.3817(1) | 0.3815(3) | 0.3813(3) |

Refinements over wider $r$-ranges tended to yield higher $R_w$ factors but the fit results were similar to those given in Table I. It can be mentioned that the obtained $R_w$'s near 20% are common for PDF refinements, even for well-crystallized materials. The $R_w$'s from the PDF and Rietveld refinements cannot be directly compared, but they serve the same purpose of finding out the best structure solution from a number of competing models with similar numbers of refinable parameters. The inherently higher $R_w$ in the PDF analysis stems from the greater sensitivity to the local atomic ordering, imperfect data correction, and systematic errors. The $R_w$'s for the Zn$_{1-x}$Mg$_x$O ($x > 0$) samples are significantly higher than that for ZnO ($x = 0$). It implies the presence of irregular Mg/Zn distribution in the alloy phases, which may not be well portrayed by simple structure models.

For all the four compositions, the lattice constants from the PDF agree well with the Rietveld refinement results, although the precision is slightly lower in PDF. Moreover the Zn atomic position and the Zn–O bond distances in ZnO are well reproduced in the PDF analysis, when compared with Rietveld refinement results. For the Zn$_{1-x}$Mg$_x$O phases, the $z$-coordinates of Zn and Mg were independently refined to investigate the distinct local geometries of the two cation types. Interestingly the refined $u$(Mg) is smaller than $u$(Zn) for all the three solid solutions with $x = 0.05, 0.10$, and $0.15$ (Fig. 9). This trend is consistently repeated in the supercell model analyses detailed below. The $u$(Mg) parameters have rather large estimated deviations together with weak variations depending on $x$, but the observation $u$(Mg) < $u$(Zn) was quite robust regardless of the refinement $r$-range or the choice of constraints.

We recognize that in the above simple cell model for Zn$_{1-x}$Mg$_x$O, only the cation sub-lattices can be distorted while the anion framework remains undistorted. The wurtzite structure is its own antitype where the cation and anion sublattices are interchangeable. Depending on which of the two is distorted the resulting PDFs will be slightly different from each other, although the corresponding average crystal structures are practically indis-
FIG. 10: (Color online) Local structural distortions in \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) supercells of (a) cation-lattice deformation, \( u(\text{Mg}) \neq u(\text{Zn}) \), \( u(\text{O}_{\text{Mg}}) = u(\text{O}_{\text{Zn}}) \) and (b) anion-lattice deformation, \( u(\text{Mg}) = u(\text{Zn}) \), \( u(\text{O}_{\text{Mg}}) \neq u(\text{O}_{\text{Zn}}) \). \( ax \) and \( eq \) denote the cation–anion distances with different bond orientations, \( ||c \) and \( \perp c \), respectively. As resulted from local distortions, \( ax' \neq ax \) and \( eq' \neq eq \).

FIG. 11: Atomic positions in \( \text{Zn}_{0.85}\text{Mg}_{0.15}\text{O} \) as functions of the length of the vector \( r_{\text{max}} \). PDF refinements were carried out using the supercell model structures based on (a) anion-lattice deformation and (b) cation-lattice deformation. Gray lines are best linear fits.
IV. DISCUSSION

For various AX-type compounds including ZnO and MgO, the relative stabilities of wurtzite, zinc blende, and rock salt structures have been a long-standing and intriguing subject. The correlations between the binary composition and the favored structure type have been proposed in several different ways, but commonly using the bond ionicity and the ion sizes of A and X as the principal parameters. If we limit our attention to ZnO and MgO, the observed crystal structures can be explained simply by the ionicity consideration, in other words, electronegativities of Zn and Mg. With intermediate electronegativity, Zn can achieve the tetrahedrally directed valence orbital via facile $sp^3$-hybridization. On the other hand, Mg is more electropositive and its valence orbital is dominated equally by the $3p_x$, $3p_y$, and $3p_z$ components, by which the nearest oxide ions are oriented in the octahedral geometry. Hence Zn and Mg adopt the four- and six-fold coordinations, respectively, in their binary oxides. Given those coordination preferences, the alloying with MgO should destabilize the host ZnO lattice. Indeed the thermodynamic solubility limit in Zn$_{1-x}$Mg$_x$O is reached at a low Mg-concentration, $\approx$15%.

The ZnO has wurtzite parameters of $c/a = 1.6021$ and $u = 0.3829$, which are ideally 1.633 and 0.375, respectively. Considering the range of $c/a$ (1.600~1.645) observed from the binary wurtzites, ZnO is near the borderline of wurtzite stability. On the other hand, the wurtzite MgO structure is not available experimentally. Instead, the first-principle methods based on density functional theory (DFT) have predicted that the wurtzite MgO will have much smaller $c/a$ than those of existing wurtzite phases. An earlier DFT study has reported an extremely distorted hexagonal structure ($c/a = 1.20, u = 0.5$) for the wurtzite MgO, in which Mg sits on a mirror plane and has a bi-pyramidal coordination. However recent studies, independently conducted by Janotti et al. and Gopal and Spaldin, have reported $c/a = 1.51$ and $u = 0.398$. More relevant to our experimental work, Malashevich and Vanderbilt performed the geometry optimization of Zn$_{1-x}$Mg$_x$O supercells ($x = 0, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}$, and $\frac{1}{7}$). They showed that the $c/a$ decreases with increase of Mg content, and $u$(Mg) is larger than $u$(Zn) in all the supercell compositions. Therefore those DFT studies on MgO and Zn$_{1-x}$Mg$_x$O consistently surmise that the Mg-substitution in ZnO would result in the decrease of $c/a$, in agreement with the previously established idea that the Mg-substitution in ZnO would destabilize the host ZnO lattice. Indeed the thermodynamic solubility limit in Zn$_{1-x}$Mg$_x$O is reached at a low Mg-concentration, $\approx$15%.

The Rietveld study on Zn$_{1-x}$Mg$_x$O has also shown that $c/a$ is gradually decreased with the Mg-substitution. The Mg-substitution in ZnO is not disfavored from packing considerations, but may reduce the electrostatic stabilizations in the long range through the change in $c/a$ ratio. At the solubility limit Zn$_{0.85}$Mg$_{0.15}$O, the $c/a$ is as low as 1.600, and this value seems to represent the lowest

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![Graph showing Zn–O and Mg–O bond distances in Zn$_{0.85}$Mg$_{0.15}$O, obtained from the PDF refinements using the cation-lattice deformation supercell model. Gray lines are guides to the eye.](image-url)
c/a that can be sustained by the wurtzite lattice. The energy-minimized Zn$_{1-x}$Mg$_x$O supercells of Malashevich and Vanderbilt\textsuperscript{21} have $u$(Mg) in the range 0.387$\sim$0.390, and the $u$(Zn), 0.378$\sim$0.382, which is not in agreement with the PDF results shown in Figs.\textsuperscript{9} and \textsuperscript{11}. As a consequence of $u$(Mg) $>$ $u$(Zn), the spontaneous polarization in the computed Zn$_{1-x}$Mg$_x$O supercells become larger for the compositions with higher Mg content\textsuperscript{22},\textsuperscript{23} while the Rietveld analysis indicated that the $u$ parameter of Zn$_{1-x}$Mg$_x$O average structures and therefore the spontaneous polarization in the Clausius-Mosotti limit decrease upon Mg-substitution.\textsuperscript{15} The above discrepancies are in fact connected with a more fundamental question of how the tetrahedral geometries of ZnO$_4$ and MgO$_4$ would differ in the extended solids. Understanding of cation local geometries in Zn$_{1-x}$Mg$_x$O is important also for the application of ZnO/Zn$_{1-x}$Mg$_x$O heterojunction devices. While tetrahedral MgO$_4$ is found in a few minerals such as MgAl$_2$O$_4$, Ca$_2$MgSi$_2$O$_7$\textsuperscript{24,25} and K$_2$MgSi$_2$O$_5$\textsuperscript{26} Zn$_{1-x}$Mg$_x$O provides an opportunity to explore its equilibrated tetrahedral geometry. However the computational and experimental results on the internal tetrahedral geometry of Zn$_{1-x}$Mg$_x$O do not agree well. In the supercell structures of Malashevich and Vanderbilt\textsuperscript{21} the ZnO$_4$ tetrahedra are more regular than the MgO$_4$ tetrahedra (as judged from the differences of the cation$-$anion bond distances), in contrast to the PDF findings presented in Fig.\textsuperscript{12}. These points may be further clarified by using alternative techniques such as neutron PDF or extended x-ray absorption fine structure. It is equally possible that the DFT methods must be re-examined, with inclusion of perhaps more accurate exchange functionals.

V. CONCLUSION

Raman and synchrotron x-ray PDF have been employed to probe the local structures of Zn and Mg atoms that occupy the common crystallographic site in the wurtzite alloys Zn$_{1-x}$Mg$_x$O ($x = 0$, 0.05, 0.10, and 0.15). Regardless of the Mg concentration, structure model, and $r$-range, the PDF refinements consistently show that the Mg atoms have smaller out-of-center tetrahedral displacements than the Zn atoms. Even for the Zn$_{0.95}$Mg$_{0.05}$O that has only 5 mol\% MgO, the atomic coordinates of Zn and Mg were similarly obtained as those for Zn$_{0.90}$Mg$_{0.10}$O and Zn$_{0.85}$Mg$_{0.15}$O, thereby demonstrating the fidelity of PDF technique. It is understood that the lessened tetrahedral distortion of MgO$_4$, compared with ZnO$_4$, leads to the decrease of wurtzite $u$ parameters in the Zn$_{1-x}$Mg$_x$O average structures. The hexagonal $c/a$ ratio of Zn$_{1-x}$Mg$_x$O decreases with the increase of Mg concentration, which is ascribed to the ionic character contributed from MgO. Therefore, from both ionicity and dipole strength viewpoints, we expect that the Zn$_{1-x}$Mg$_x$O alloys will have smaller spontaneous polarizations than ZnO. It is noted that in terms of ZnO$_4$ and MgO$_4$ local geometries, our experimental results are somewhat contrary to the descriptions obtained from DFT-based studies.

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