

Local structures of polar wurtzites $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ studied by Raman and $^{67}\text{Zn}/^{25}\text{Mg}$ NMR spectroscopies and by total neutron scattering

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Local compositions and structures of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys have been investigated by Raman and solid-state $^{67}\text{Zn}/^{25}\text{Mg}$ nuclear-magnetic-resonance (NMR) spectroscopies and by neutron pair-distribution-function (PDF) analyses. The E_2^{low} and E_2^{high} Raman modes of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ display Gaussian- and Lorentzian-type profiles, respectively. At higher Mg substitutions, both modes become broader, while their peak positions shift in opposite directions. The evolution of Raman spectra from $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ solid solutions is discussed in terms of lattice deformation associated with the distinct coordination preferences of Zn and Mg. Solid-state magic-angle-spinning (MAS) NMR studies suggest that the local electronic environments of ^{67}Zn in ZnO are only weakly modified by the 15% substitution of Mg for Zn. ^{25}Mg MAS spectra of $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ show an unusual upfield shift, demonstrating the prominent shielding ability of Zn in the nearby oxidic coordination sphere. Neutron PDF analyses of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ using a $2 \times 2 \times 1$ supercell corresponding to Zn_7MgO_8 suggest that the mean local geometry of MgO_4 fragments concurs with previous density-functional-theory-based structural relaxations of hexagonal wurtzite MgO. MgO_4 tetrahedra are markedly compressed along their c axes and are smaller in volume than ZnO_4 units by $\approx 6\%$. Mg atoms in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ have a shorter bond to the c -axial oxygen atom than to the three lateral oxygen atoms, which is distinct from the coordination of Zn. The precise structure, both local and average, of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ obtained from time-of-flight total neutron scattering supports the view that Mg substitution in ZnO results in increased total spontaneous polarization.

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I. INTRODUCTION

Research in the area of polar semiconductor heterostructures has been growing rapidly, driven in large part by interest in two-dimensional electron-gas (2DEG) systems.¹⁻⁵ 2DEGs are known to form at heterojunction interfaces that bear polarization gradients. They can display extremely high-electron mobilities, especially at low temperatures, owing to spatial confinement of carrier motions.⁶ Recent reports of 2DEG behaviors in $\text{Ga}_{1-x}\text{Al}_x\text{N}/\text{GaN}$ and $\text{Zn}_{1-x}\text{Mg}_x\text{O}/\text{ZnO}$ heterostructures have great significance for the development of quantum Hall devices¹ and novel high-electron-mobility transistors (HEMTs).³⁻⁵

2DEG structures are usually designed by interfacing a polar semiconductor with its less or more polar alloys in an epitaxial manner. Since the quality of the 2DEG depends critically on interface perfection, as well as the polarization gradient at the heterojunction, understanding compositional and structural details of the parent and alloy semiconductors is an important component in 2DEG design and fabrication. The evolution of atomic positions and cell parameters upon alloying can directly affect the magnitude of the polarization gradient and the carrier density at the heterojunction.

$\text{Zn}_{1-x}\text{Mg}_x\text{O}/\text{ZnO}$ is one of the most promising heterostructure types for studies of 2DEGs due to the large polarization of ZnO, the relatively small lattice mismatch, and the large conduction-band offsets in the $\text{Zn}_{1-x}\text{Mg}_x\text{O}/\text{ZnO}$ het-

erointerface. Although 2DEG formation in $\text{Zn}_{1-x}\text{Mg}_x\text{O}/\text{ZnO}$ heterostructures has been researched for some time, a clear understanding of the alloy structure of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ is currently lacking. Recently, we have studied composition-dependent changes in the crystal structures of polycrystalline $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ by synchrotron x-ray diffraction and Raman spectroscopy.^{7,8} For the composition range $0 \leq x \leq 0.15$, we have shown that Mg substitution modifies the aspect ratio of the hexagonal lattice through enhanced bond ionicity and, in parallel, decreases static polarization in the crystal, due to decreased internal distortion in the tetrahedral coordinations.

Here, we conduct a detailed and more precise study of the local structure of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys using Raman and solid-state nuclear magnetic resonance (NMR) in conjunction with neutron-diffraction techniques. Raman and NMR spectroscopies are useful probes for addressing the molecular compositions and structures of solid-solution systems. Peak shapes and widths of the Raman spectra reflect compositional fluctuations and both short- and long-range orders, whereas NMR is sensitive to the local environments around specific nuclei. Thus, both techniques can provide structural information on $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ that is complementary to diffraction analyses. Here, we examine the details of E_2^{low} and E_2^{high} Raman modes for $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x=0, 0.05, 0.10, \text{ and } 0.15$). We have also used spin-echo magic-angle-spinning (MAS) ^{67}Zn and ^{25}Mg NMRs to study separately zinc and/or magnesium species in ZnO and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$. These measure-

ments have been correlated with average and local crystal structures of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and ZnO , as established by Rietveld (diffraction space) and pair-distribution-function (PDF) (real-space) analyses of time-of-flight neutron-diffraction data. Compared with x rays, neutron scattering provides much greater sensitivity to oxygen and Mg positions, as well as larger momentum transfer as measured by the larger maximum Q wave vector.⁹ Using neutron scattering, we are able to isolate the geometry of MgO_4 moieties stabilized in the wurtzite ZnO lattice.

II. EXPERIMENTAL

Polycrystalline powder samples of ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x=0.05, 0.10, 0.125, \text{ and } 0.15$) were prepared from oxalate precursors obtained by coprecipitation using $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{H}_2\text{C}_2\text{O}_4$, all of which had purities of 99.999% from Aldrich. The two metal salts were dissolved together in de-ionized water and added to an oxalic acid solution in the ratio of $[\text{Zn}^{2+}]:[\text{Mg}^{2+}]:[\text{C}_2\text{O}_4^{2-}]=(1-x):x:1.05$. Upon mixing with oxalate, Zn^{2+} and Mg^{2+} immediately coprecipitated as white crystalline oxalate powders, which were washed with de-ionized water and dried at 60°C for 4 h and subsequently heated at 550°C for 20 h in air to decompose the oxalates to the oxides. Powder x -ray diffraction measurements confirmed the formation of $\text{Zn}_{1-x}\text{Mg}_xC_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ after heating at 60°C and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ after decomposing at 550°C . For the NMR experiments, samples were also prepared at different conditions of temperature (900°C) and atmosphere (O_2, N_2).

Raman spectra for ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x=0.05, 0.10, \text{ and } 0.15$) were acquired at room temperature using a Jobin Yvon-Horiba T64000 triple grating (1800 g/mm) spectrometer. The spectra of lightly compressed powders were recorded using micro-Raman sampling in air with 514.5 and 675.5 nm excitations. The spectra reported here are averages of ten acquisitions of 20 s integrations of the charge coupled device (CCD) detector with ≈ 10 mW of laser power focused onto the samples through a $10\times$ objective. There was no evidence of degradation of the samples or associated changes in their spectra under these conditions. The spectrometer was calibrated using a 520.7 cm^{-1} lattice mode of silicon. The Raman features of wurtzite E_2^{low} and E_2^{high} phonon modes were analyzed in detail to determine the peak shape, position, and width. Spectral background was removed following Shirley,¹⁰ and the profile fitting was performed using pseudo-Voigt¹¹ or Breit-Wigner-Fano (BWF) functions.¹²

NMR measurements of the low-gyromagnetic-ratio nuclei ^{67}Zn and ^{25}Mg were conducted at high (19.6 T) magnetic-field strength at the National High Magnetic Field Laboratory in Tallahassee, Florida. These investigations benefited from the enhanced sensitivity and improved resolution for the ^{67}Zn and ^{25}Mg nuclei that result from reduced second-order quadrupolar interactions, which scale inversely with the strength of the applied magnetic field. The experiments were conducted at room temperature at 19.6 T (^1H resonance frequency of 830 MHz), which for ^{67}Zn ($I=\frac{5}{2}$, 4.1% natural

abundance, approximately 1.5 receptivity relative to ^{13}C) and ^{25}Mg ($I=-\frac{5}{2}$, 10.1% natural abundance, approximately 0.7 receptivity relative to ^{13}C) corresponded to Larmor frequencies of 51.88 and 50.76 MHz, respectively. All of the NMR spectra presented here were recorded on a single-resonance 4 mm probehead under MAS conditions at 10 kHz, using a Hahn echo (i.e., $\frac{\pi}{2}-\tau-\pi-\tau$ acquisition) with the delays τ set to one rotor period τ_R . The ^{67}Zn and ^{25}Mg shifts were referenced to the bulk external secondary standards ZnSe [274 ppm relative to 1.0M aqueous $\text{Zn}(\text{NO}_3)_2$] and MgO (26 ppm relative to 3.0M aqueous MgSO_4),¹³ respectively. Pulse lengths of 2 and 4 μs were used for the $\frac{\pi}{2}$ and π pulses, respectively. A recycle delay of 1 s was used in each case using 16 000 transients for the ^{67}Zn MAS spectra (approximately 5 h each) and 160 000 transients for the ^{25}Mg MAS experiments (approximately 46 h each). Second-order quadrupolar MAS line shapes were fitted using the program DMFIT.¹⁴

Time-of-flight neutron-diffraction data for ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ were obtained on the neutron powder diffractometer (NPDF) at the Lujan Neutron Scattering Center at Los Alamos National Laboratory. For ease of structural modeling in the PDF analysis of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, we chose a composition of $x=\frac{1}{8}$ and have used an appropriate 16-atom supercell model of Zn_7MgO_8 . For each sample, ≈ 2 g of powder were packed in a vanadium can, and the data were collected for 3 h at 25°C using four detector banks located at $46^\circ, 90^\circ, 119^\circ, \text{ and } 148^\circ$. Control runs, for the intensity corrections, employed an empty vanadium can, a vanadium piece, and air. The program PDFGETN was used to extract the PDF $G(r)$ from the raw scattering data.¹⁵ First, the coherent scattering intensity $I(Q)$ was obtained from raw data by the intensity corrections for container, background, and incident beam. Then, the $I(Q)$ was converted to the structure factor $S(Q)$ by the corrections for sample absorption, multiple scattering, and inelasticity. Finally, the PDF $G(r)$ was constructed by the Fourier transform of the reduced structure factor $F(Q)=Q[S(Q)-1]$. In the Fourier transform of $F(Q)$ to $G(r)$, Q data were terminated at 35 \AA^{-1} . PDF refinements were performed using the software program PDFGUI.¹⁶ The average crystal structures of ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ were determined by the Rietveld method using the GSAS-EXPGUI software suite.^{17,18}

III. RESULTS AND DISCUSSION

A. Raman spectroscopy

Room temperature Raman spectra for $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x=0, 0.05, 0.10, \text{ and } 0.15$) are shown in Fig. 1 along with mode assignments for the observed peaks.^{19,20} The wurtzite lattice, with space group C_{6v}^4 (Hermann-Mauguin symbol $P6_3mc$), has four Raman-active phonon modes, $A_1+E_1+2E_2$. The two E_2 modes are nonpolar, while the A_1 and E_1 modes are polarized along the z axis and in the xy plane, respectively.¹⁹⁻²¹ The polar modes are further split into longitudinal optical (LO) and transverse optical (TO) components due to the macroscopic electric field associated with the LO modes. Raman spectra of the ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ compounds are

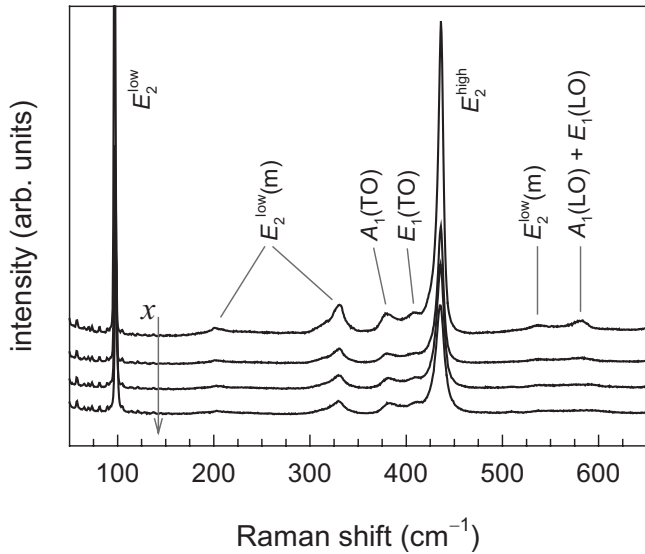


FIG. 1. Raman spectra recorded at room temperature for $Zn_{1-x}Mg_xO$ ($x=0, 0.05, 0.10,$ and 0.15 from top to bottom). The excitation wavelength used was 514.5 nm.

dominated by two intense peaks of E_2^{low} (≈ 98 cm^{-1}) and E_2^{high} (≈ 436 cm^{-1}) modes. Raman-scattering efficiencies of individual modes in ZnO are known to vary with the excitation energy.¹⁹ With 514.5 nm (2.41 eV) excitation, the highest Raman efficiencies are observed from E_2^{high} and E_2^{low} modes. However, the polar LO modes exhibit a strong resonance effect as the excitation energy approaches the electronic transition energies. In cases when ultraviolet lasers are used for excitation, the Raman spectra of ZnO or $Zn_{1-x}Mg_xO$ are dominated by the signals from LO modes.²²

In order to quantify composition-dependent changes in the Raman spectra of $Zn_{1-x}Mg_xO$, the E_2^{low} and E_2^{high} line profiles were analyzed by least-squares fitting with standard peak functions. From the fits, peak position (ω_0), and the full width at half maximum (FWHM, Γ) linewidths were determined. The profile fittings of both E_2 modes are shown in Fig. 2, and the evolutions of peak parameters ω_0 and Γ with Mg substitution x are plotted in Fig. 3. Consistent with the previous study,⁸ the E_2^{high} peaks of $Zn_{1-x}Mg_xO$ are best represented by Lorentzian BWF line shapes with some asymmetry. However, the E_2^{low} line profiles do not fit as well to the Lorentzian-type functions. Instead, the E_2^{low} lines of $Zn_{1-x}Mg_xO$ are found to be pseudo-Voigt type with predominantly Gaussian components of 97%, 83%, 77%, and 81% for $x=0, 0.05, 0.10,$ and 0.15 , respectively.

As shown in Fig. 3(a), the two E_2 modes of $Zn_{1-x}Mg_xO$ exhibit distinct dependences of phonon energy on the composition. With increased concentration of magnesium, the E_2^{low} mode shows a blueshift, while the E_2^{high} mode exhibits a redshift. For explaining these opposing trends, the vibrational eigenvectors of the wurtzite E_2 modes need to be considered. As shown in Fig. 2, both E_2^{low} and E_2^{high} modes are associated with atomic motions in the ab plane. The lower energy branch corresponds mainly ($\approx 85\%$) to the vibrations of heavier components (cations, in case of $Zn_{1-x}Mg_xO$), and conversely the higher energy one corresponds mainly to those of lighter components (oxygen). Consequently, the E_2^{low}

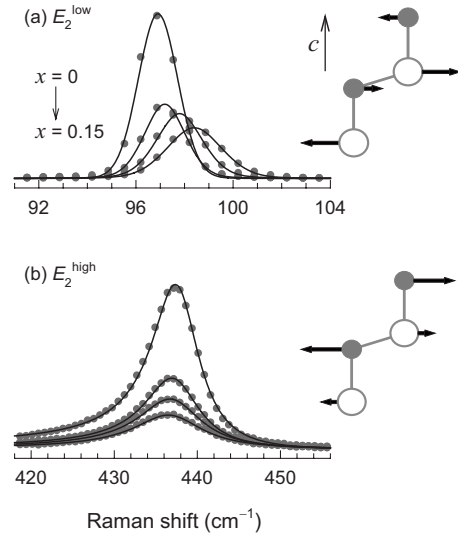


FIG. 2. Line profile fittings for (a) E_2^{low} and (b) E_2^{high} Raman peaks of $Zn_{1-x}Mg_xO$ (observed, gray circles; fit, solid lines; $x=0, 0.05, 0.10,$ and 0.15 from top to bottom). Simplified lattice vibrations are depicted using large open circles for cations (Zn, Mg) and small gray circles for oxygen.

mode energy of $Zn_{1-x}Mg_xO$ is explicitly affected by the cationic substitution, according to the reduced mass effect. Replacement of Zn with Mg will decrease the reduced mass of the oscillator and in turn increase the phonon energy. By comparison, the change in cation mass should have less influence on the E_2^{high} mode energy, and its redshift is adequately attributed to the phonon softening caused by the in-plane lattice expansion. As previously reported, the lattice constant a of $Zn_{1-x}Mg_xO$ increases monotonically with x ,⁷ which appears to account for the observed E_2^{high} mode behavior.

Peak shapes and linewidths of Raman spectra are dictated by the underlying line-broadening mechanisms. Gaussian line broadening is intrinsic to Raman spectra and originates from instrumental resolution. Also, if the sample being ex-

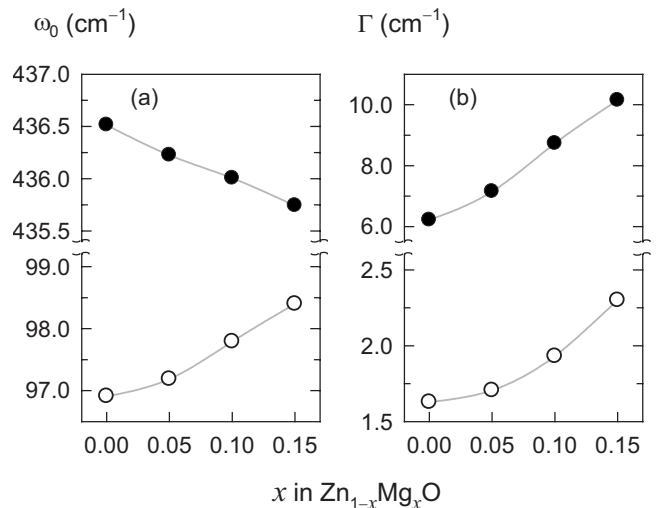


FIG. 3. (a) Raman shifts ω_0 and (b) linewidths Γ for the E_2^{low} (open circles) and E_2^{high} (filled circles) modes of $Zn_{1-x}Mg_xO$.

aminated contains inhomogeneous components with different phonon frequencies, the resulting Raman line shape would have a Gaussian character, reflecting the statistical nature of the spectrum. On the other hand, Lorentzian line broadening is mostly attributed to finite phonon lifetimes (t), according to the energy-time uncertainty relationship $\Gamma/\hbar=1/t$. The phonon lifetime shortening, which will cause linewidth broadening, can occur via two independent phonon decay mechanisms: by anharmonic decay into other Brillouin-zone phonons or by phonon disruption at crystal defects. The latter, involving lattice imperfections, are quite common for alloy and solid-solution systems. Specifically for $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, it is expected that Mg substitution will substantially reduce the size of ordered domains and thereby block the long-range propagation of zone-center phonons.

As noted above, the E_2^{low} and E_2^{high} lines of ZnO are, respectively, fitted with Gaussian and Lorentzian functions. It indicates that the E_2^{high} mode of ZnO has anharmonic phonon decay channels, whereas the E_2^{low} phonon does not. The Lorentzian line-broadening behavior of E_2^{high} mode, in Fig. 3(b), further manifests that the Mg substitution increasingly populates the phonon field of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with defect centers. The E_2^{low} mode also undergoes a gradual line broadening with x , and its peak shape changes upon Mg substitution. While unsubstituted ZnO displays a nearly pure Gaussian peak for the E_2^{low} mode, the peaks from $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x > 0$) samples are found to contain $\approx 20\%$ of Lorentzian components. Therefore we conclude that, for the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ system, the same line-broadening mechanism applies to both E_2^{low} and E_2^{high} modes: phonon lifetime shortening by increased crystal defects upon Mg substitution.

B. Solid-state ^{67}Zn and ^{25}Mg NMR spectroscopy

A different view of the disorder induced by Mg substitution in ZnO materials can be obtained from solid-state NMR using the NMR-active isotopes ^{25}Mg (spin $I=-\frac{5}{2}$) and ^{67}Zn ($I=\frac{5}{2}$). These nuclei are challenging to observe because their low natural abundances and low-gyromagnetic ratios (see Sec. II) yield low signal sensitivities and because second-order quadrupolar interactions associated with nuclear spins $|I| > \frac{1}{2}$ can lead to a dramatic broadening of their NMR spectra. Second-order quadrupolar effects, however, scale with the inverse of the static magnetic field B_0 and are therefore mitigated at high magnetic fields, which also increase signal sensitivity.

Solid-state ^{67}Zn MAS NMR spectra acquired at 19.6 T of ZnO and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ are shown in Fig. 4. The materials were prepared by heating at 900 °C in N_2 and yield similar spectra that clearly exhibit scaled second-order quadrupolar powder MAS line-shape features.²³ Associated values for the isotropic ^{67}Zn chemical shift, δ_{iso} , the quadrupolar coupling constant, ν_Q , and the asymmetry parameter, η_Q , can be determined by fitting each resolved second-order quadrupolar MAS line shape. A simulated powder pattern is shown as the dashed line in Fig. 4(a) accompanying the ^{67}Zn MAS spectrum of ZnO and corresponding to the calculated values $\delta_{\text{iso}}=236$ ppm, $\nu_Q=378$ kHz, and $\eta_Q=0.1$. Several discrepancies between the calculated and experimental powder pat-

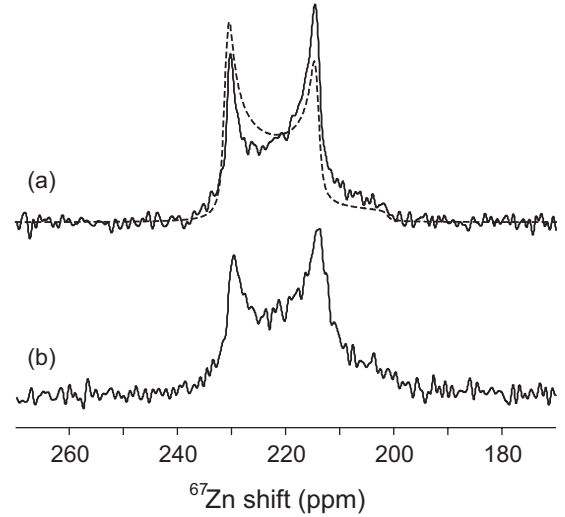


FIG. 4. Solid-state spin-echo ^{67}Zn MAS NMR spectra acquired at 19.6 T, room temperature, and 10 kHz MAS: (a) ZnO and (b) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ powders, both prepared at 900 °C in N_2 . Accompanying the ZnO spectrum in (a) is a fit (dashed line) of the experimental line shape to a simulated second-order quadrupolar powder pattern.

terns may be due to modest anisotropy of the powder particles and/or to uneven excitation of the different crystallite orientations by the radio frequency pulses. The powder pattern and fit parameters are nevertheless consistent with a single crystallographically distinct and relatively symmetric ^{67}Zn site in the wurtzite ZnO structure. The ^{67}Zn MAS spectrum of $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ in Fig. 4(b) exhibits a similar line shape and features, which are broadened by the presumably random incorporation of Mg atoms within the Zn-rich wurtzite lattice.

The close similarity between the ^{67}Zn MAS NMR spectra of ZnO [Fig. 4(a)] and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ [Fig. 4(b)] indicates that the substitution of 15% of Zn atoms by Mg has little influence on the local electronic environments of a majority of the ^{67}Zn nuclei. Assuming that Mg atoms are distributed randomly, the probability of having no Mg atom in the second coordination sphere of a given ^{67}Zn nucleus is only 14% (the first coordination sphere consisting of four O atoms). Significant effects on the ^{67}Zn spectrum would be expected if the quadrupolar interactions were substantially perturbed by the substitution of Mg atoms for 1, 2, 3, and 4 (probabilities of 30%, 29%, 17%, and 7%, respectively) or more of the 12 Zn atoms in the second coordination sphere. However, despite the high probability of modifications of the local chemical environment of the ^{67}Zn nuclei upon 15% Mg substitution, dramatic changes in the ^{67}Zn spectrum are not observed rather only modest broadening that reflects increased disorder. Under these conditions, the differences induced in ZnO or $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ by changing the synthesis atmosphere (e.g., air, O_2 , or N_2) and temperature (over the range of 550–900 °C) were too subtle to be clearly reflected in the corresponding ^{67}Zn MAS NMR spectra (data not shown), which are similar to those in Figs. 4(a) and 4(b). Thus, it appears that ^{67}Zn NMR measurements of these ZnO-related materials are sensitive principally to substitutions that result

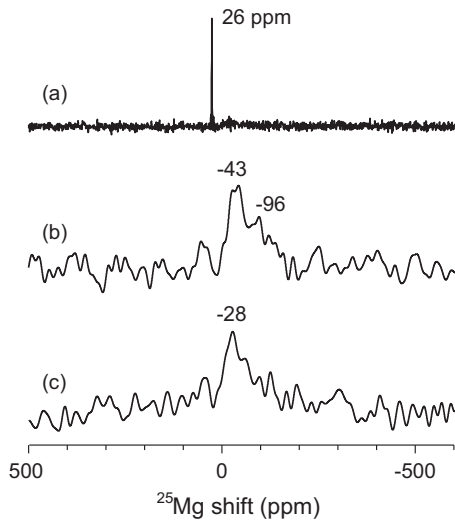


FIG. 5. Spin-echo ^{25}Mg MAS NMR spectra, recorded at 19.6 T, of (a) polycrystalline MgO powder (external reference for ^{25}Mg NMR shift), (b) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ powder prepared at 550 °C in air and (c) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ powder prepared at 900 °C in N_2 .

in modifications of the first coordination sphere of the zinc nuclei (substitution of the anionic species) or to substitutions resulting in larger lattice distortions or increased electronic disorder than observed here.²⁴

Solid-state ^{25}Mg MAS NMR measurements complement the ^{67}Zn NMR results by being sensitive to the structural and electronic perturbations experienced directly by Mg atom incorporated into ZnO lattices. The ^{25}Mg MAS NMR measurements were similarly conducted at 19.6 T and the resulting spectra are shown in Fig. 5 for polycrystalline MgO and different $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ powders prepared at 550 °C in air and at 900 °C in N_2 . The ^{25}Mg MAS spectrum in Fig. 5(a) of MgO shows a narrow well-defined ^{25}Mg peak that reflects the highly symmetric coordination environment of the single type of Mg site in its rocksalt structure.²⁵ By comparison, the ^{25}Mg MAS spectra of the different $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ powders contain broad and relatively unstructured line shapes centered at approximately -30 to -40 ppm that reflect broad distributions of signal intensity and thus broad distributions of local ^{25}Mg environments. The first Mg coordination sphere (MgO_4) in $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ is expected to be significantly distorted from a regular tetrahedral geometry, and the second coordination sphere, composed of $\text{Mg}(\text{Zn},\text{Mg})_{12}$, is expected to have an even larger number of different local configurations, bond distances, and/or bond angles. The ^{25}Mg MAS NMR spectra appear to be more sensitive than the ^{67}Zn NMR results to local material environments in $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$. However, the low signal-to-noise and broad lines observed for natural abundance ^{25}Mg in $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$, even at 19.6 T, preclude a detailed and reliable analysis of the isotropic shift distributions and second-order quadrupolar broadening that would be necessary to extract directly quantitative information on nature of the Mg site distributions and/or their disorder. It is noteworthy that the $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ powders do not display any spectral feature corresponding to bulk MgO, thereby ensuring the phase purity of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x \leq 0.15$) solid solutions, within the sensitivity limit of the ^{25}Mg NMR measurements.²⁶

In common for ^{29}Si , ^{27}Al , and ^{25}Mg , an increase in the coordination number for a given cationic center counts for enhanced local shielding, resulting in an upfield displacement of the signal(s) to lower shift values.^{13,27} The spinel MgAl_2O_4 containing MgO_4 fragments exhibits a ^{25}Mg shift of 52 ppm, compared to 26 ppm for MgO which is comprised of MgO_6 local units.¹³ By comparison, clay minerals in which Mg atoms are coordinated by six (O,OH) ligands yield ^{25}Mg shifts in the range of 0 to -100 ppm.²⁵ The wurtzite oxide $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ has a four-coordinated geometry of Mg, similar to MgAl_2O_4 , but the former clearly shows a more upfield-shifted ^{25}Mg resonance at -30 to -40 ppm. We infer that ^{25}Mg MAS NMR signals are considerably influenced by the ligand identity beyond the first coordination shell and that Zn has a far stronger shielding contribution than Al, Si, or alkaline earths, thus accounting for the observed resonance values.

C. Neutron diffraction

In previous studies, the crystal structure of ZnO has been reported [space group $P6_3mc$, Zn at $(\frac{1}{3}\frac{2}{3}0)$ and O at $(\frac{1}{3}\frac{2}{3}u)$] with lattice constants of $a=3.2427\text{--}3.2501\text{ \AA}$ and $c=5.1948\text{--}5.2071\text{ \AA}$ and atomic position parameter $u=0.381\text{--}0.3826$.^{28–33} In our previous synchrotron x-ray study on polycrystalline ZnO, we obtained $a=3.2503\text{ \AA}$, $c=5.2072\text{ \AA}$, and $u=0.3829$.⁷ Here, we re-examine the crystal structures of polycrystalline ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ utilizing neutron scattering, which has several advantages over x rays. The coherent neutron-scattering length of O (5.804 fm) is comparable to those of Zn (5.680 fm) and Mg (5.375 fm),³⁴ as distinct from x-ray diffraction, where scattering is strongly weighted by Zn. Moreover, neutron scattering can provide high Q diffraction data with much less attenuation than x rays due to there being no falloff with Q in the form factor.

Rietveld refinements of ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ were carried out on four histograms of data collected at detector locations of 46°, 90°, 119°, and 148°. The highest- Q data from the 148° detector cover the range of $d > 0.25\text{ \AA}$ ($Q < 25\text{ \AA}^{-1}$). The model used for the refinement in space group $P6_3mc$ has Zn/Mg at the $2b$ Wyckoff position $(\frac{1}{3}\frac{2}{3}0)$ and O also at $2b$ position $(\frac{1}{3}\frac{2}{3}u)$. For $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, Zn and Mg were statistically distributed over the common site with fractional occupancies fixed to the respective compositions. The refinement converged with reliability factors of $R_{wp}=2.57\%$, $R_p=1.80\%$, and $\chi^2=2.71$ for ZnO, and $R_{wp}=2.89\%$, $R_p=2.04\%$, and $\chi^2=3.56$ for $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$. The Rietveld refinement profiles and the structural parameters are given in Fig. 6 and Table I, respectively. The present refinement results agree well with the findings from our previous synchrotron x-ray study.⁷ Both studies indicate that Mg substitution expands the a parameter, compresses the c parameter, and decreases the oxygen position parameter u , as summed up in Fig. 7. The two data sets from x-ray and neutron reveal an identical trend in the structural evolution in terms of a , c , and u .

For the composition range up to $x=0.15$, the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ solid solutions remain isostructural with wurtzite ZnO, with

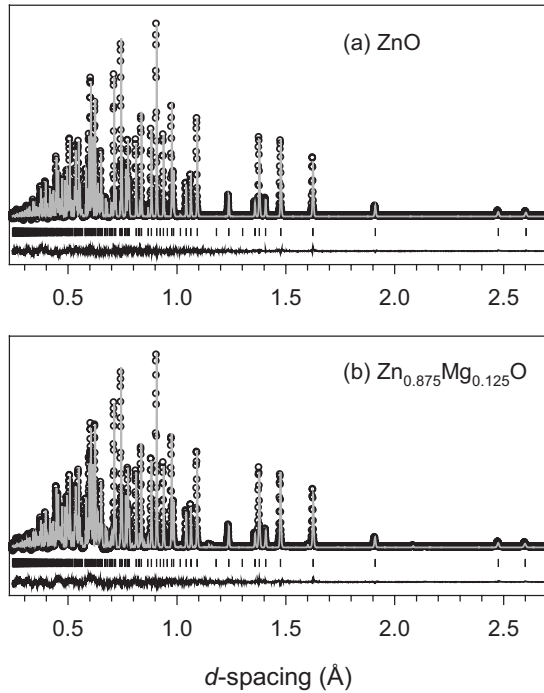


FIG. 6. Rietveld refinement of time-of-flight powder neutron-diffraction profiles of (a) ZnO and (b) $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$. Calculated patterns (gray lines) are superimposed on observed data (open circles), with Bragg positions and difference profiles at the bottom.

both Zn and Mg tetrahedrally coordinated by O atoms. However, since the two cations Zn and Mg have clearly distinct crystal chemistries in oxidic environments, it is conjectured that they may have distinct local geometries within $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ lattices. In order to directly address this question, we have carried out neutron PDF analyses of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ and ZnO. For obtaining an appropriate real-space model for the PDF analysis of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, we estimate as follows the impact of Mg substitution on the chemical environment within the ZnO lattice. Cations in the wurtzite lattice form a hexagonal close-packed sublattice, where each cation has 12 nearest neighbors. At the Mg-

TABLE I. Structural parameters for ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ determined from the Rietveld refinement of time-of-flight neutron-diffraction pattern.

	ZnO	$\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$
V (\AA^3)	47.603(1)	47.578(1)
a (\AA)	3.249 45(1)	3.250 58(2)
c (\AA)	5.205 74(3)	5.197 71(3)
c/a	1.602 04	1.599 40
u	0.382 75(5)	0.382 14(6)
$U_{\text{iso}}(\text{Zn/Mg})$ (\AA^2)	0.006 48(8)	0.0065(2)
$U_{\text{iso}}(\text{O})$ (\AA^2)	0.0101(1)	0.0087(2)
d_{M-O} (\AA)	(1 \times)1.9925(3) (3 \times)1.9729(1)	(1 \times)1.9868(3) (3 \times)1.9743(1)
\angle_{O-M-O} (deg)	108.022(7) 110.881(7)	108.081(9) 110.825(9)

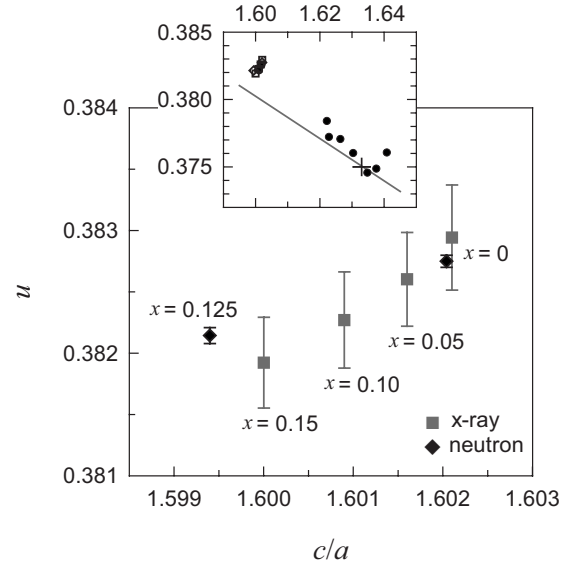


FIG. 7. Average wurtzite parameters c/a and u of ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ determined by Rietveld refinements of neutron (diamonds) and synchrotron x-ray (squares; Ref. 7) diffraction patterns. Note the significantly smaller error bars that emerge from the neutron study. The inset shows the data observed from existing wurtzites (see Ref. 7 for details).

substitution level of $x=0.125$, it is estimated that $\approx 80\%$ of the cations have at least one Mg neighbor in the cation sublattice (Fig. 8). Each cation (whether Zn or Mg) has, as neighbors, 1.5 Mg atoms on average, and the mean Mg-Mg

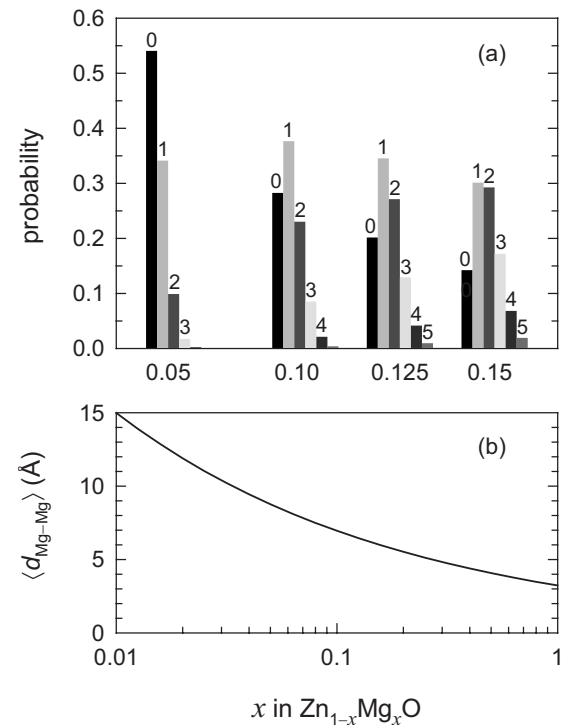


FIG. 8. (a) Probability for a cation in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ to have 0, 1, 2, 3, 4, or 5 Mg neighbors in the 12-membered coordination shell ($r \approx 3.25 \text{ \AA}$) and (b) mean separation between the nearest Mg-Mg pairs.

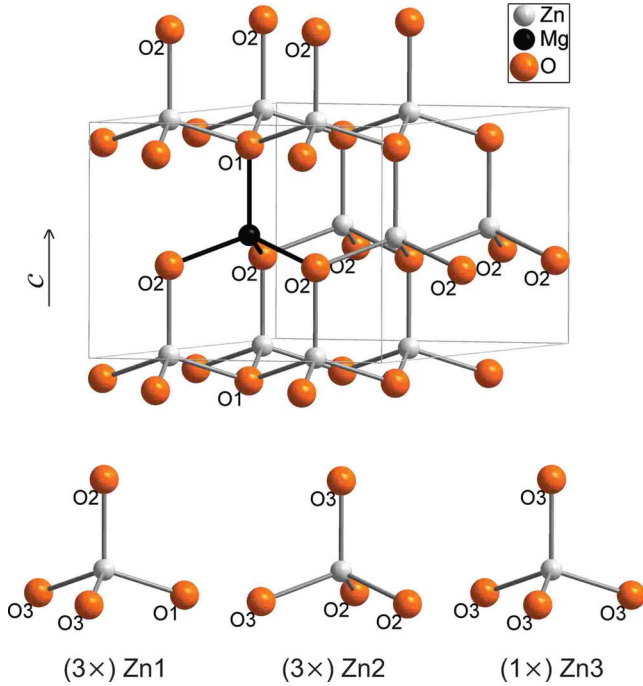


FIG. 9. (Color online) Zn_7MgO_8 supercell model structure used for neutron PDF analyses of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ and coordination environments for three distinct Zn sites therein. In the top part, unlabeled oxygen atoms belong to the O3 type (see text).

distance is as short as 6.5 Å. Therefore the coordination geometry of MgO_4 will serve a substantial structural factor in the PDF of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ and needs to be treated with independent parameters in the PDF refinement.

On the basis of the above considerations, the structural model for $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ was designed as follows. To distinguish the Mg and Zn atoms in the unit cell, while maintaining the composition, a $2 \times 2 \times 1$ supercell of the primitive wurtzite structure was selected, with the cell parameters $a = b \approx 6.5$ Å, $c \approx 5.205$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, and the unit content Zn_7MgO_8 . In the average structure scheme, in which the atomic positions are set as $(\frac{1}{3}\frac{2}{3}0)$ for cations and $(\frac{1}{3}\frac{2}{3}u)$ for anions, the external and internal geometries of all the tetrahedra are uniformly defined by the c/a ratio and u , respectively. However in the supercell model, we allowed the MgO_4 unit to have its own coordination geometry, irrespective of the ZnO_4 geometry. As a result, the eight O atoms in the supercell unit are divided into three groups: one O atom bonded to Mg along the c axis (O1), three O atoms bonded to Mg laterally (O2), and the remaining four O atoms (O3). The seven Zn atoms are also grouped according to their proximities to the Mg atom: three Zn atoms having an apical O2 oxygen atom (Zn1), three Zn atoms bonded to O2 atoms laterally (Zn2), and one Zn bonded to only O3 atoms (Zn3). Figure 9 illustrates the supercell configuration and the three different types of ZnO_4 geometries.

The PDF of ZnO was analyzed using a simple wurtzite cell (Zn_2O_2) obeying the symmetry requirements of the $P6_3mc$ space group. However, for the supercell refinement of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, several symmetry constraints were lifted from the average structure description. The z coordinates of

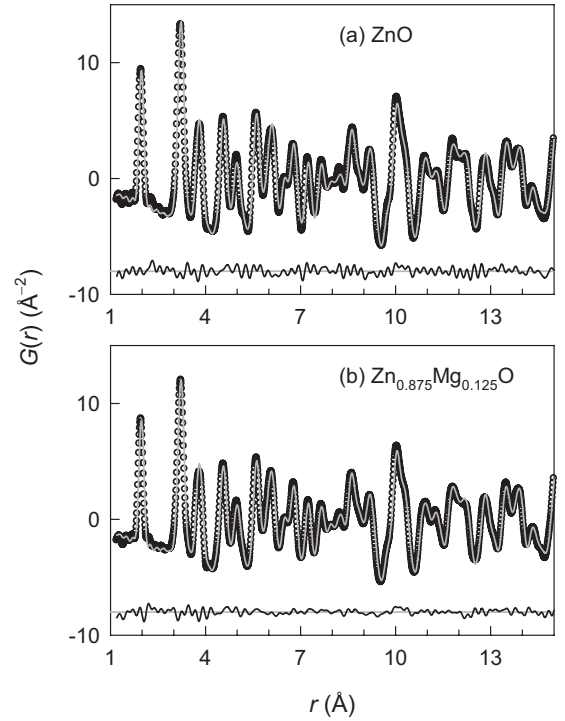


FIG. 10. Neutron PDF refinements for (a) ZnO and (b) $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, parts of the 1.2–22 Å fittings. Calculated PDFs (gray lines) are superimposed on experimental data (open circles), with the differences shown at the bottom of each.

the O1, O2, and O3 types of oxygen atoms were independently varied, and the z coordinate of Mg was also refined. We also attempted in-plane displacements of the O2 atoms but found that these were unstable in the refinement. Therefore, the refinement for $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ included three more position parameters than those for ZnO. For both ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, the refinements of $G(r)$ used the variables of lattice constants, atomic position parameters, isotropic temperature factors, structure scale factor, and peak sharpening coefficients.

Figure 10 shows the neutron PDF refinements for ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, carried out in the r range of 1.2–22 Å. The refinement parameters are summarized in Table II. For both structures, the refinements were achieved with satisfac-

TABLE II. Structural parameters from the neutron PDF refinements of ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ over the r range of 1.2–22 Å.

	ZnO	$\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$
a (Å)	3.2514(3)	$3.2527(4) \times 2$
c (Å)	5.2089(6)	5.2015(8)
c/a	1.6020	1.5991
$z(\text{O})$	0.3824(4)/0.8824(4)	0.3825(8)/0.8825(8) (O3) 0.386(3) (O2) 0.858(5) (O1)
$z(\text{Mg})$		0.486(8)
$U_{\text{iso}}(\text{Zn/Mg})$ (Å ²)	0.0086(8)	0.0063(6)
$U_{\text{iso}}(\text{O})$ (Å ²)	0.0070(6)	0.0081(8)

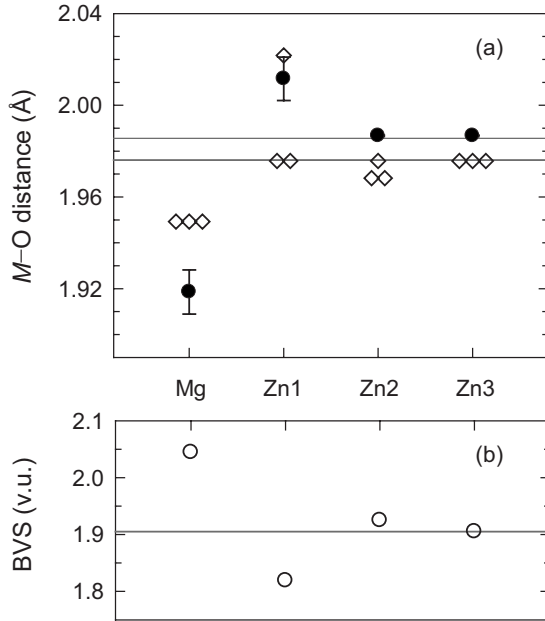


FIG. 11. (a) Mg-O and Zn-O bond distances in $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, as analyzed by the neutron PDF refinement of a Zn_7MgO_8 supercell model (c -axial bonds, circles; lateral bonds, diamonds), and (b) bond valence sums for each cation site. Horizontal lines indicate the Zn-O bond distances (in the upper panel) and BVS for Zn (in the lower panel) in ZnO.

torily low R_w 's of 7.9% (ZnO) and 8.3% ($\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$). In comparison with the Rietveld results, the PDF-refined lattice constants are systematically larger by $\approx 0.06\%$, but good agreements are observed for the c/a ratios. Also, the oxygen atom position in ZnO is reasonably well reproduced from the PDF and Rietveld refinements. An interesting finding emerges from the atomic coordinates of Mg and its adjacent oxygen atoms (O1 and O2) in $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$. As found in Table II, the three groups of O atoms have clearly distinct z coordinates from one another. Both the O1 and O2 groups are vertically shifted toward their respective Mg atoms. Mg itself also moves toward the basal plane formed of O2 atoms. The resulting MgO_4 unit has a squashed tetrahedral geometry (point group C_{3v}), with a much shorter height than those of ZnO_4 tetrahedra. However the O3 atoms, which are not directly bonded to Mg, have similar z coordinates to those found in ZnO. Therefore, the $(\text{Zn3})(\text{O3})_4$ tetrahedra retain the unperturbed geometry of ZnO. The other types of ZnO_4 tetrahedra share corners with MgO_4 and are likely to undergo intermediate distortion.

To examine the presence of short-range structural characteristics, the PDF refinements were carried out from 1.2 Å to different values of r_{max} between 10 and 30 Å. The lattice constants and position parameters showed insignificant variations with r_{max} , and the R_w values had shallow minima at $r_{\text{max}} \approx 22$ Å for both ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$. The Mg-O and Zn-O bond distances plotted in Fig. 11 represent the averaged results of multiple refinements over $1.2-r_{\text{max}}$ (Å), where r_{max} was increased from 10 to 30 Å in 2 Å steps. From Fig. 11(a), we find a meaningful distinction between the MgO_4 and ZnO_4 bonding structures. The Mg-O bonds are shorter than the Zn-O bonds, and the former set consists of

one short and three longer bonds, in contrast to the latter. These results are consistent with the greater sensitivity of the ^{25}Mg NMR spectra [Figs. 5(b) and 5(c)] to Mg substitution into ZnO-rich lattices, compared to the ^{67}Zn NMR results (Fig. 4). For Mg and the three Zn atom types in $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, bond valence sums (BVSs) (Ref. 35) are evaluated, as shown in Fig. 11(b). The valence sums for all of the cation and anion sites in $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ are within a reasonable range around the ideal magnitude of 2 valence units (v.u.). The relatively underbonded situation for Zn1 atoms and the slight overbonding of the Mg atom are the results of a rather drastic shift of the bridging O1 atom. The global instability index (GII) (Ref. 35) of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ is calculated as 0.116 v.u., which is significantly larger than that of ZnO (0.067 v.u.). The GII value is often used as a measure of the residual bond strain and is known not to exceed 0.2 v.u. for ordinary structures in the standard state.^{35,36} It is worth mentioning, in light of the above GII considerations, that the increased microstrain upon Mg substitution results in characteristic optical and x-ray line-broadening behavior of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ that we have previously reported.^{37,38}

The solid solution of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ has the thermodynamic solubility limit of $x \approx 15\%$ on the ZnO-rich side. Obviously the distinct coordination preferences of Mg and Zn prevent the formation of a continuous solid solution across the entire composition range, x . While Mg has a point symmetry of O_h in its binary oxide MgO, wurtzite ZnO possesses only a C_{3v} environment. Here, we rationalize the neutron PDF result for the MgO_4 tetrahedral geometry in several ways. Both bond valence³⁹ and ionic radii⁴⁰ compilations are useful to explain the smaller tetrahedral volume of MgO_4 , as compared with ZnO_4 . The bond valence parameter of Mg-O ($R_0 = 0.693$ Å) is smaller than that of Zn-O ($R_0 = 0.704$ Å), implying that in general Mg-O bonds are shorter than Zn-O bonds for the same coordination numbers. Similarly, the four-coordinate ionic radius of Mg^{2+} (0.57 Å) is smaller than that of Zn^{2+} (0.60 Å). In order for the MgO_4 tetrahedron to have a smaller volume than ZnO_4 , either the tetrahedral height or the base area should shrink or an isotropic volume change could occur. From the PDF analysis, the c parameter around Mg showed a clear decrease, whereas the a parameter appears to be nearly unchanged. The c -axial parameter contraction of MgO_4 unit can be deduced also from the composition-dependent changes in the average structure of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$.

The variable u is the only position parameter in the wurtzite structure. It corresponds to the ratio of the apical bond distance to the c length, d_{apical}/c or $d_{\text{apical}}/2h$, where h is the height of the tetrahedron. For $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, $u(\text{Mg})$ is determined to be 0.395, a value that finds no correspondence to the experimental structures of pure wurtzites. Existing wurtzites have u values within the range of 0.374–0.383. Such a high u found for MgO_4 is closely linked with its extremely small aspect ratio ($2h/a = 1.509$, as compared to the ideal value 1.633). To compare the potential fields within the tetrahedral spaces of MgO_4 and ZnO_4 , the valence sums of Mg and Zn were calculated as functions of u (Fig. 12). In ZnO, the tetrahedral cavity is slightly oversized for Zn, and the BVS(Zn) has a minimum of ≈ 1.9 v.u. at $u \approx 0.382$. The

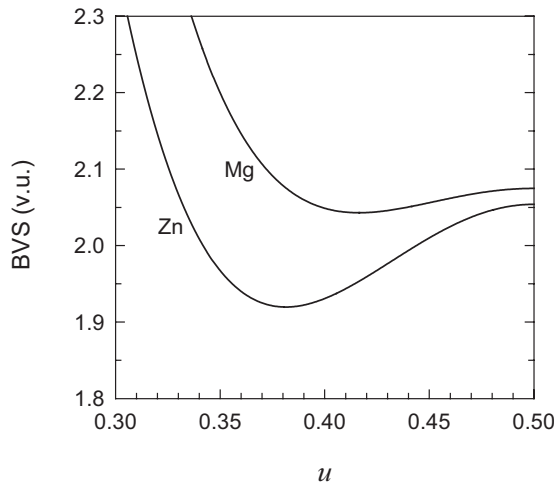


FIG. 12. u -dependent bond valence sums for Mg and Zn in the tetrahedral spaces of their oxides. The dimensions of MgO_4 and ZnO_4 tetrahedra are from the neutron PDF refinements of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ and ZnO , respectively. For u near 0.5, a fifth oxygen atom was added to the coordination shell to account for the pseudobipyramidal configuration.

potential minimum suggested by $\text{BVS}(\text{Zn})$ is in a good agreement with the experimental u for ZnO . However, the MgO_4 shell in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ is rather small for Mg, resulting in a global overbonding situation. The $\text{BVS}(\text{Mg})$ is minimized at a markedly higher u range than for $\text{BVS}(\text{Zn})$, making it clear why the experimental $u(\text{Mg})$ is conspicuously larger than $u(\text{Zn})$.

Several authors have used first-principles density-functional theory (DFT) to predict the relaxed structure of hypothetical wurtzite MgO .^{41–43} An earlier DFT study attempted to relax the energy-minimized wurtzite MgO structure but only to obtain a hexagonal structure corresponding to the limit of c -axis compression ($c/a=1.20$, $u=0.5$).⁴¹ However in later studies, the energy minimizations for wurtzite MgO were achieved within appropriate boundary conditions: $c/a=1.514$, $u=0.398$ by Janotti *et al.*⁴² and $c/a=1.520$, $u=0.395$ by Gopal and Spaldin.⁴³ Therefore, wurtzite MgO , if it ever occurs, is expected to have an abnormally small c/a ratio and large u value, compared with common wurtzites including ZnO . Interestingly, the above computational approximations of the hexagonal MgO structure agree well with our PDF analyses of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, which underscores that the MgO_4 fragment has smaller c/a and larger u than ZnO_4 . Malashevich and Vanderbilt⁴⁴ and Fan *et al.*⁴⁵ performed DFT computations of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ supercell models, also deriving consistent conclusions that c/a decreases with Mg substitution and that $u(\text{Mg}) > u(\text{Zn})$. The results from the neutron PDF refinement and the above DFT computations are plotted together in Fig. 13, in which the distinct internal or external geometries of MgO_4 and ZnO_4 are contrasted. As a general trend, isolated MgO_4 tetrahedra always have larger u parameters than ZnO_4 units. The extremely good agreement between the *local* coordination of Mg in $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ determined here from PDF studies and DFT calculations on end-member wurtzite MgO is remarkable. This is in part attributed to our use of the ratio c/a as a

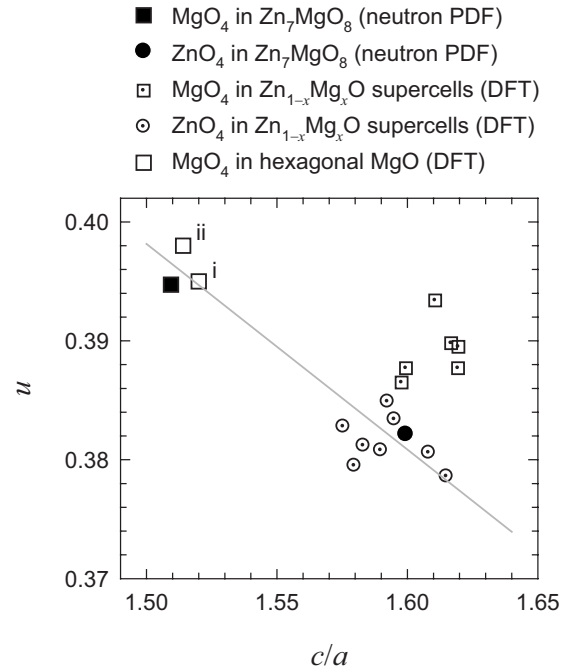


FIG. 13. Aspect ratio c/a and internal position parameter u for MgO_4 (filled square) and ZnO_4 (filled circle) tetrahedra in $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, as analyzed by neutron PDF refinements. DFT results for wurtzite MgO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ supercells are compared together: open squares correspond to the MgO_4 geometry in hexagonal MgO [(i) Ref. 42; (ii) Ref. 43] and the dotted open squares and dotted open circles represent the MgO_4 and ZnO_4 geometries found in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ supercells (Ref. 46), respectively. The gray line defines the border where the axial cation-anion bond along c and three lateral bonds become equidistant.

comparison parameter. This ratio has fewer systematic errors than do the values of the lattice parameters taken separately.

The total polarization P_s of polar oxides can be broken down into electronic, ionic, and piezoelectric contributions, related, respectively, to the polarizability of component ions, ionic arrangements, and lattice parameters. Mg substitution decreases the electronic polarization (P_{el}) of ZnO because of its greater ionic character, whereas the concomitant c -axis compression is expected to increase the piezoelectric polarization (P_{pz}). Quantitative estimation of the above two contributions, P_{el} and P_{pz} , requires sophisticated theoretical analyses and cannot be provided here for ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$. Meanwhile, the ionic polarization (P_{ion}) of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ can be approximated by a simple electrostatic model using the c -axial positions of Zn, Mg, and O. We calculated P_s of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ and ZnO , assuming point charges ($q=+2$ for Zn and Mg and -2 for O) and using the atomic coordinates as determined by neutron PDF analysis (see Appendix). Separate reference structures were used for ZnO and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, with the corresponding experimental a and c values, but with $u=0.375$, so that within isolated $(\text{Zn,Mg})\text{O}_4$ moieties the net centers of the cation and anion charges coincide. The calculated P_s values ($=P_{ion}$ here), along c , are $-5.18 \mu\text{C}/\text{cm}^2$ for ZnO and $-5.25 \mu\text{C}/\text{cm}^2$ for $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ ($\Delta P_{ion} = -0.07 \mu\text{C}/\text{cm}^2$). For comparison, Malashevich and Vanderbilt⁴⁴

employed the Berry-phase approach to obtain electric polarization of a Zn_5MgO_6 ($x=\frac{1}{6}$) supercell. They find $\Delta P_{\text{ion}} = -0.22 \mu\text{C}/\text{cm}^2$, $\Delta P_{\text{el}} = +0.01 \mu\text{C}/\text{cm}^2$, and $\Delta P_{\text{pz}} = -0.81 \mu\text{C}/\text{cm}^2$, relative to $P_s(\text{ZnO}) = -3.22 \mu\text{C}/\text{cm}^2$. In fact, the following relations hold true in general for other $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ supercells ($x=\frac{1}{4}, \frac{1}{3}, \frac{1}{2}$) studied by them: $\Delta P_{\text{el}} > 0$, $\Delta P_{\text{ion}} < 0$, $\Delta P_{\text{pz}} < 0$, and $|\Delta P_{\text{el}}| \ll |\Delta P_{\text{ion}}| < |\Delta P_{\text{pz}}|$. We therefore expect that the total polarization of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ should be larger than that of ZnO, with the increases in piezoelectric and ionic polarizations dominating the decrease in the electronic contribution. The $P_s(\text{ZnO})$ calculated by Malashevich and Vanderbilt⁴⁴ differs somewhat from the results of other DFT studies^{43,47–49} where $P_s(\text{ZnO}) = -5.0$ to $-5.7 \mu\text{C}/\text{cm}^2$. But since we are primarily interested in the signs and relative magnitudes of ΔP_{el} , ΔP_{ion} , and ΔP_{pz} , induced by the Mg substitution in ZnO, we disregard the small discrepancies in the absolute values of P_s .

The result, an increase in P_{ion} upon Mg substitution, differs from our previous estimates based solely on synchrotron x-ray diffraction analyses.^{7,8} This inconsistency arises mostly from the improved models for the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ supercell structures that are permitted by the present neutron-scattering data. It is noteworthy that the structure modeling for the PDF or Rietveld analyses can confine the range of structural information that is sought. For example, Rietveld refinement of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ used only one positional parameter, and therefore MgO_4 and ZnO_4 tetrahedra are characterized by the same c/a and u . In the previous x-ray PDF refinement, two position parameters were refined, so that we could differentiate $u(\text{Mg})$ and $u(\text{Zn})$ but not their local c/a ratios.⁸ However, for the neutron PDF refinement, we used four positional parameters as variables and were able to distinguish the MgO_4 and ZnO_4 geometries through both c/a and u . Present neutron data showed sufficient integrity for testing various structure models, which were not possible for the x-ray data alone. In Fig. 14, we compare the best fit PDF profiles obtained from three different refinements of the $2 \times 2 \times 1$ supercell of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, using 1, 2, or 4 positional variables. While those refinements result in very similar fit patterns to one another, a close examination reveals non-negligible variations in $G(r)$ at several regions including $r \approx 6 \text{ \AA}$ and $r \approx 9 \text{ \AA}$. As shown in Table III, the cell dimensions do not depend on the structure model. However the goodness parameter R_w is smallest when we distort both the cation and anion sublattices, implying that the increased degree of freedom led to improved PDF refinements of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$. It is important to note that the Mg substitution in ZnO will certainly cause the local distortions that cannot be properly modeled by using only one or two positional variables. Our $2 \times 2 \times 1$ supercell with four positional variables is the simplest structure model that can account for such local phenomena. Perhaps the more accurate structural description of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ alloy might require even larger degrees of freedom but we found that if too many (i.e., more than 4) positional variables are employed, reliable refinements cannot be achieved using the present neutron PDF data.

IV. CONCLUSION

Detailed structural analyses of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($0 \leq x \leq 0.15$) solid solutions, focusing on the dissimilar local geometries of

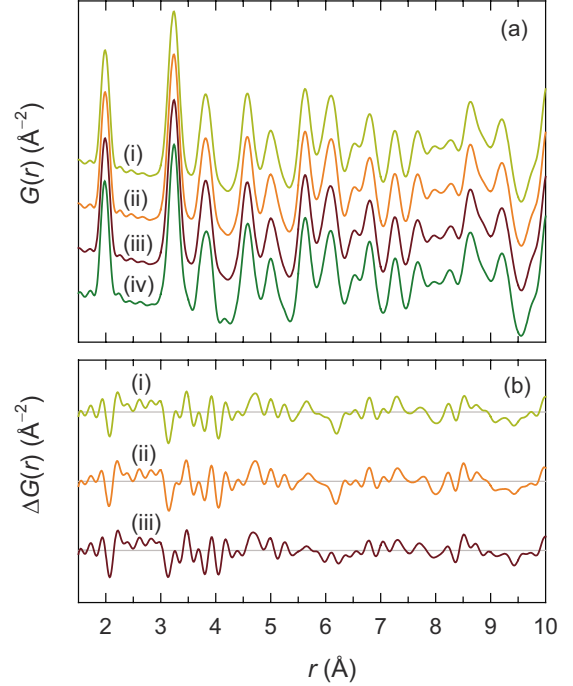


FIG. 14. (Color online) Best fit results for the neutron PDF refinement of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ using a supercell model with different degrees of structural freedom. (a) $G(r)$, (i) refined using one variable $u(\text{O})$, (ii) refined using two variables $u(\text{Mg})$ and $u(\text{O})$, (iii) refined using four variables $u(\text{Mg})$, $u(\text{O1})$, $u(\text{O2})$, and $u(\text{O3})$, and (iv) experimentally observed; and (b) corresponding difference profiles ($G_{\text{obs}} - G_{\text{calc}}$) for the data in (a). For clarity, data are vertically shifted to adjacent spacings of 4 \AA^{-2} in (a) and 2 \AA^{-2} in (b).

Mg and Zn, have been performed by using Raman scattering, $^{67}\text{Zn}/^{25}\text{Mg}$ NMR spectroscopy, and neutron Rietveld/PDF analyses. Line broadenings of the Raman and $^{67}\text{Zn}/^{25}\text{Mg}$ NMR spectra imply that Mg substitution into a ZnO-rich lattice gradually increases the configurational disorder and crystal defects in the lattice. Rietveld refinement of time-of-flight neutron-diffraction patterns and Raman peak profile analyses show that the macroscopic lattice distortions in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ wurtzites develop in a way such that the c/a ratio decreases with Mg content x . A real-space neutron PDF analysis using a supercell model of Zn_7MgO_8 reveals that the

TABLE III. Neutron PDF refinement results of $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$ using a $2 \times 2 \times 1$ supercell model having 1, 2, or 4 positional variables (see caption for Fig. 14).

No. of variables	1	2	4
R_w (%)	8.86	8.93	8.26
a (Å)	6.5049(9)	6.5047(8)	6.5053(8)
c (Å)	5.2019(9)	5.2017(9)	5.2015(8)
$u(\text{Zn})$	0	0	0
$u(\text{Mg})$	0	-0.002(38)	-0.014(8)
$u(\text{O})$	0.3824(6)	0.382(5)	0.3825(8)(O1) 0.386(3) (O2) 0.358(5) (O3)

Mg and Zn atoms in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ have markedly distinct local geometries: MgO_4 tetrahedra are smaller in height and volume and have a larger internal parameter u . The wurtzite structural parameters c/a and u for MgO_4 deviate from their ideal values, in agreement with computational predictions of wurtzite MgO structures. Previous DFT studies on $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ supercells and the present neutron PDF analysis strongly suggest that Mg substitution will increase the spontaneous polarization of ZnO .

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TABLE IV. Complete list of atomic coordinates for the 16-atom wurtzite supercell Zn_7MgO_8 ($a=b=6.5054$ Å, $c=5.2015$ Å, $\alpha=\beta=90^\circ$, and $\gamma=120^\circ$), as determined by the neutron PDF analysis.

Atom	x	y	z	Type
Zn	0.1667	0.3333	0	Zn1
	0.6667	0.3333	0	Zn3
	0.1667	0.8333	0	Zn1
	0.6667	0.8333	0	Zn1
	0.3333	0.1667	0.5	Zn2
	0.8333	0.1667	0.5	Zn2
	0.8333	0.6667	0.5	Zn2
	0.3333	0.6667	0.5	Zn2
Mg	0.3333	0.6667	0.486(8)	Mg
O	0.1667	0.3333	0.386(3)	O2
	0.6667	0.3333	0.3825(8)	O3
	0.1667	0.8333	0.386(3)	O2
	0.6667	0.8333	0.386(3)	O2
	0.3333	0.1667	0.8825(8)	O3
	0.8333	0.1667	0.8825(8)	O3
	0.3333	0.6667	0.858(5)	O1
	0.8333	0.6667	0.8825(8)	O3

APPENDIX

See Table IV for the complete list of atomic coordinates as determined by the neutron PDF analysis.

- ¹A. Tsukazaki, A. Ohtomo, T. Kita, Y. Ohno, H. Ohno, and M. Kawasaki, *Science* **315**, 1388 (2007).
- ²K. Koike, K. Hama, I. Nakashima, G. Takada, M. Ozaki, K. Ogata, S. Sasa, M. Inoue, and M. Yano, *Jpn. J. Appl. Phys.*, Part 2 **43**, L1372 (2004).
- ³S. Rajan, H. Xing, S. DenBaars, U. K. Mishra, and D. Jena, *Appl. Phys. Lett.* **84**, 1591 (2004).
- ⁴S. Sasa, M. Ozaki, K. Koike, M. Yano, and M. Inoue, *Appl. Phys. Lett.* **89**, 053502 (2006).
- ⁵H. Tampo, H. Shibata, K. Matsubara, A. Yamada, P. Fons, S. Niki, M. Yamagata, and H. Kaine, *Appl. Phys. Lett.* **89**, 132113 (2006).
- ⁶J. H. Davies, *The Physics of Low-Dimensional Semiconductors: An Introduction* (Cambridge University Press, New York, 1998).
- ⁷Y.-I. Kim, K. Page, and R. Seshadri, *Appl. Phys. Lett.* **90**, 101904 (2007).
- ⁸Y.-I. Kim, K. Page, A. M. Limarga, D. R. Clarke, and R. Seshadri, *Phys. Rev. B* **76**, 115204 (2007).
- ⁹Th. Proffen, T. Egami, S. J. L. Billinge, A. K. Cheetham, D. Louca, and J. B. Parise, *Appl. Phys. A: Mater. Sci. Process.* **74**, S163 (2002).
- ¹⁰D. A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- ¹¹P. Thompson, D. E. Cox, and J. B. Hastings, *J. Appl. Crystallogr.* **20**, 79 (1987).
- ¹²M. Yoshikawa, *Mater. Sci. Forum* **52-53**, 365 (1989).
- ¹³R. Dupree and M. E. Smith, *J. Chem. Soc., Chem. Commun.* **1988**, 1483.
- ¹⁴D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, and G. Hoatson, *Magn. Reson. Chem.* **40**, 70 (2002).
- ¹⁵P. F. Peterson, M. Gutmann, Th. Proffen, and S. J. L. Billinge, *J. Appl. Crystallogr.* **33**, 1192 (2000).
- ¹⁶C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Bozin, J. Bloch, Th. Proffen, and S. J. L. Billinge, *J. Phys.: Condens. Matter* **19**, 335219 (2007).
- ¹⁷A. C. Larson and R. B. von Dreele, Los Alamos National Laboratory Report No. LAUR 86-748, 1994.
- ¹⁸B. H. Toby, *J. Appl. Crystallogr.* **34**, 210 (2001).
- ¹⁹J. M. Calleja and M. Cardona, *Phys. Rev. B* **16**, 3753 (1977).
- ²⁰T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.* **142**, 570 (1966).
- ²¹J. M. Zhang, T. Ruf, M. Cardona, O. Ambacher, M. Stutzmann, J.-M. Wagner, and F. Bechstedt, *Phys. Rev. B* **56**, 14399 (1997).
- ²²H.-M. Cheng, K.-F. Lin, H.-C. Hsu, C.-J. Lin, L.-J. Lin, and W.-F. Hsieh, *J. Phys. Chem. B* **109**, 18385 (2005).
- ²³E. Kundla, A. Samoson, and E. Lippmaa, *Chem. Phys. Lett.* **83**, 229 (1981).
- ²⁴E. S. Toberer, J. D. Epping, B. F. Chmelka, and R. Seshadri, *Chem. Mater.* **18**, 6345 (2006).
- ²⁵K. J. D. MacKenzie and R. H. Meinhold, *Am. Mineral.* **79**, 250 (1994).
- ²⁶K. J. D. MacKenzie and R. H. Meinhold, *Thermochim. Acta*

- 230**, 331 (1993).
- ²⁷M. Magi, E. Lippmaa, A. Samoson, G. Engelhardt, and A.-R. Grimmer, *J. Phys. Chem.* **88**, 1518 (1984).
- ²⁸H. Sawada, R. Wang, and A. W. Sleight, *J. Solid State Chem.* **122**, 148 (1996).
- ²⁹T. M. Sabine and S. Hogg, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **25**, 2254 (1969).
- ³⁰S. C. Abrahams and J. L. Bernstein, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **25**, 1233 (1969).
- ³¹P. Harrison, G. A. Jeffrey, and J. R. Townsend, *Acta Crystallogr.* **11**, 552 (1958).
- ³²J. Albertsson, S. C. Abrahams, and A. Kvik, *Acta Crystallogr., Sect. B: Struct. Sci.* **45**, 34 (1989).
- ³³E. H. Kisi and M. M. Elcombe, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **45**, 1867 (1989).
- ³⁴V. F. Sears, *Neutron News* **3**, 26 (1992).
- ³⁵I. D. Brown, *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model* (Oxford University Press, Oxford, 2002).
- ³⁶I. D. Brown, *Acta Crystallogr., Sect. B: Struct. Sci.* **48**, 553 (1992).
- ³⁷Y.-I. Kim and R. Seshadri, *Inorg. Chem.* **47**, 8437 (2008).
- ³⁸Y.-I. Kim and R. Seshadri, *J. Korean Phys. Soc.* (to be published).
- ³⁹N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.* **47**, 192 (1991).
- ⁴⁰R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **32**, 751 (1976).
- ⁴¹S. Limpijumnong and W. R. L. Lambrecht, *Phys. Rev. B* **63**, 104103 (2001).
- ⁴²A. Janotti, D. Segev, and C. G. Van de Walle, *Phys. Rev. B* **74**, 045202 (2006).
- ⁴³P. Gopal and N. A. Spaldin, *J. Electron. Mater.* **35**, 538 (2006).
- ⁴⁴A. Malashevich and D. Vanderbilt, *Phys. Rev. B* **75**, 045106 (2007).
- ⁴⁵X. F. Fan, H. D. Sun, Z. X. Shen, J.-L. Kuo, and Y. M. Lu, *J. Phys.: Condens. Matter* **20**, 235221 (2008).
- ⁴⁶A. Malashevich and D. Vanderbilt (private communication).
- ⁴⁷A. Dal Corso, M. Posternak, R. Resta, and A. Baldereschi, *Phys. Rev. B* **50**, 10715 (1994).
- ⁴⁸F. Bernardini, V. Fiorentini, and D. Vanderbilt, *Phys. Rev. B* **56**, R10024 (1997).
- ⁴⁹Y. Noel, C. M. Zicovich-Wilson, B. Civalleri, Ph. D'Arco, and R. Dovesi, *Phys. Rev. B* **65**, 014111 (2001).