

Anion ordering in spinel-type gallium oxonitride

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The specific locations of the anions—nitrogen and oxygen—in the crystallographic sites are not known in the spinel-type gallium oxonitride. We report here on an indirect method for determining the specific location of the light elements N and O in a defect spinel-structured gallium oxonitride, $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$. The locations of elements that are adjacent in the periodic table ($\Delta Z = \pm 1$) are indistinguishable with conventional x-ray diffraction techniques. However, by examining the local electronic structure we show that the anions are spatially ordered such that $R\bar{3}m$ (no. 166) is the most appropriate defect-free space group. Finally, we determined the electronic band gap of $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ experimentally to be 2.95 ± 0.30 , agreeing with our calculated value of 2.79 eV (direct) for $\text{Ga}_3\text{O}_3\text{N}$ using a local density approximation functional including a semilocal potential modified from that of Becke and Johnson (the MBJLDA functional).

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I. INTRODUCTION

Over the last decade, spinel-structured nitrides have been an active area of research spurred by the synthesis of the first spinel-structured nitride, silicon nitride ($\gamma\text{-Si}_3\text{N}_4$).¹ Almost simultaneously, spinel-structured germanium nitride² ($\gamma\text{-Ge}_3\text{N}_4$) was synthesized using similar methods. These nitride phases are synthesized in a high-pressure (15 GPa) and high-temperature (2000 K) environment from their low-pressure trigonal or hexagonal phase ($\alpha\text{-Si}_3\text{N}_4$ or $\beta\text{-Si}_3\text{N}_4$) via shock synthesis experiments³ or diamond anvil cell⁴ and multianvil cell⁵ experiments. Several studies have been carried out regarding ternary nitrides and oxonitrides^{6–15} in an effort to tailor the highly desirable mechanical and electronic properties associated with spinel nitrides to suit specific applications.

Gallium oxonitride ($\text{Ga}_3\text{O}_3\text{N}$) with spinel structure was first predicted by Lowther *et al.*¹⁶ and has since been synthesized recently by several groups.^{12,14,17} The large amount of interest in this material is due to the widespread use of $w\text{-GaN}$ and $\beta\text{-Ga}_2\text{O}_3$. Furthermore, $\text{Ga}_3\text{O}_3\text{N}$ is thought to have robust mechanical and chemical properties similar to the binary phases in the Ga-O-N system, and a predicted direct electronic band gap.^{10–12}

The electronic band gap of a functional material is arguably one of the most important properties. Numerous theoretical studies have focused on the electronic properties and electronic band gaps of compounds with spinel structure.^{6,7,18} Spinel-structured nitrides, in comparison to their respective low-pressure phases, exhibit reduced band gap values allowing these materials to be used in applications that require the device to absorb visible light.^{6,19} With the knowledge that these cubic crystals with large coordination numbers have reduced electronic band gaps, research has expanded further into spinel-type oxonitrides in an effort to engineer the band gap value by varying the N:O ratio. Previously, theoretical studies show that gallium oxonitride with ideal structure ($\text{Ga}_3\text{O}_3\text{N}$) might have a band gap comparable to that of $w\text{-GaN}$ or slightly larger,^{10,12} allowing potentially useful electronic applications.

Direct band gap values calculated using the local density approximation (LDA) and generalized gradient approximation (GGA) are 1.72 and 1.37 eV, respectively.¹³ However, it is well known that LDA and GGA calculations underestimate the band gap²⁰ and the actual band gap value of $\text{Ga}_3\text{O}_3\text{N}$ may be as large as 4 eV.¹⁰ To date, we know of no reports of a measured band gap value for cubic gallium oxonitride.

There are two recent reports on the synthesis of a defect structure gallium oxonitride.^{12,14} These studies show that in gallium oxonitride the octahedral site in the spinel structure is not fully occupied and has inherent octahedral gallium vacancies. The two studies report gallium oxonitride with similar stoichiometry, $\text{Ga}_{2.79}\square_{0.21}\text{O}_{3.05}\text{N}_{0.76}\square_{0.19}$ (Ref. 14) and $\text{Ga}_{2.81}\text{O}_{3.24}\text{N}_{0.64}$ (Ref. 12), where $\square$ indicates cationic and anionic vacancies. The occupation of the cation sites, 2.79/3.00 (Ref. 14) and 2.81/3.00 (Ref. 12), was determined through x-ray diffraction (XRD) measurements. However, in order to determine the anion occupations, the ratio of N to O was determined with electron microprobe or electron energy loss spectroscopy measurements and used as a fitting parameter. The complete structural picture (including differentiating between the positions of N and O) of spinel-type gallium oxonitride is not well known. The current experimental results show that the $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ system crystallizes in the spinel-type structure ($Fd\bar{3}m$, no. 227) with tetrahedrally and octahedrally coordinated gallium cations, while the anions are tetrahedrally coordinated. The site occupation of the cations (Ga Wyckoff sites 8a and 16d) is well known, but the positions of the different anions (N and O) are not distinguishable with XRD and are generalized to a single Wyckoff site, 32e.^{14,21} Determination of a complete structural picture of $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ is invaluable for understanding its electronic and mechanical properties. A better understanding of the crystal structure will also facilitate more efficient synthesis methods to produce purer phases with tailored mechanical and electronic properties.

Several theoretical works exist in which the anion ordering in $\text{Ga}_3\text{O}_3\text{N}$ is discussed.^{10,12} In one of these studies,¹² it was

assumed that N and O retain their F arrangements, resulting in three distinct ideal (i.e., defect-free with an N:O ratio of 1:3) crystallographic groups: $Imm2$ (no. 44), $Ima2$ (no. 46), and $R\bar{3}m$ (no. 166). Density functional theory (DFT) calculations based on these structures considering equilibrium energy yielded the $R\bar{3}m$ space group as the likely candidate structure; placing the nitrogen atoms in positions such that they are as far away from other nitrogen atoms as possible minimizes the calculated total energy.¹⁰ An experimental confirmation has not yet been reported however. This motivates the use of x-ray absorption spectroscopy (XAS) measurements, which is a useful tool to examine the local electronic structure. For example, XAS has been employed to determine the local crystal structure of β -SiAlON compounds.²² While this technique does not directly probe the crystal structure, it analyzes the local electronic structure and as such provides a way to indirectly determine the local bonding environment. This technique and the results presented here determine a possible local structure and the band gap of spinel-type gallium oxonitride.

II. METHODS

The spinel-type gallium oxonitride sample was synthesized using a multianvil device based on a Walker-type module and a 1000-ton press (Voggenreiter, Mainleus, Germany). A mixture of w -GaN (99.9%, Alfa Aesar, Karlsruhe, Germany) and β -Ga₂O₃ (99.9%, Sigma Aldrich, Munich, Germany), with the molar ratio of w -GaN: β -Ga₂O₃ = 6:4, was filled into a hexagonal boron nitride capsule (Henze BNP GmbH, HeBoSint S10, Kempten, Germany) and then placed in an 18/11 assembly, which was compressed by eight tungsten carbide cubes (TSM-10 Ceratizit, Reutte, Austria). The peak pressure and temperature values were 5 GPa and 1250 °C. The sample required 15 min to heat and was allowed to cool to 800 °C for a duration of 25 min after the peak temperature was achieved. The sample was then quenched once the temperature reached 800 °C. Final products were separated from the surrounding crucible and XRD was used for the phase analyses of each sample. The data were collected with a Stoe Stadi P diffractometer using monochromatized Cu $K\alpha$ ($\lambda = 1.540\,51$ Å) radiation. The β -Ga₂O₃ in the starting mixtures reacted totally to form the spinel gallium oxonitride, and a Rietveld refinement of the powder diffraction pattern showed the presence of the spinel gallium oxonitride (>95%) next to remaining w -GaN.

The local electronic structure around the anions was probed with a combination of x-ray emission spectroscopy (XES) and x-ray absorption near-edge spectroscopy (XANES) measurements. XES and XANES were used to probe both the valence band (VB) and conduction band (CB) in Ga_{2.79}O_{3.05}N_{0.76}. The unoccupied and occupied states that were probed with N 1s and O 1s excitations were limited to N and O p states due to the dipole selection rule ($\Delta l = \pm 1$); thereby XES and XANES probe the local partial occupied and unoccupied density of states (LPDOS), respectively.

The XES measurements were performed on beamline 8.0.1 at the Advanced Light Source (Berkeley, CA, USA),²³ and were recorded with the grating spectrometer permanently affixed to the beamline. The sample was set to an incidence

angle of 30° (between the normal surface vector and incident beam). The XANES measurements were performed on the SGM beamline at the Canadian Light Source (Saskatoon, SK, Canada).²⁴ The XANES measurements were recorded in total fluorescence yield mode with a high-voltage channel plate detector with the sample surface perpendicular to the incident beam. The XANES measurements were normalized during the experiment using the photocurrent from a highly transparent gold mesh to monitor changes in the incident photon flux. XES and XANES spectra were energy calibrated using the reference compounds h -BN and bismuth germanate, and the energy locations of the spectra used were the same as those in Ref. 25.

The sample synthesis and structural characterization proceeded similarly to those described in Ref. 14, and as such the structural parameters described therein were used to create the structural models presented here. The structural models (see Table I), nos. 1–3, were created using the lattice parameters and fractional coordinates found in Ref. 14. In the refinement of the spinel-type structured gallium oxonitride within the space group $Fd\bar{3}m$, all of the anions and vacancies are placed on the Wyckoff position $32e$ possessing an F symmetry, and thus an ordering of the anions would lead to a reduction of the symmetry. Three different space groups were identified in which an ordering of the anions could be described. It is important to note that these structures only differ by the

TABLE I. The structural details of all crystal structures used in this study are listed. Please note that the fractional coordinates for structure 3 are given in rhombohedral coordinates and the lattice parameters are given using hexagonal lattice vectors. All structures were created from the structural details of Ref. 14.

Atom	Wyckoff	Fractional x	Fractional y	Fractional z
Structure 1 ^a				
Ga1	4a	1/2	0	3/4
Ga2	4b	3/4	3/8	3/4
Ga3	4b	1/4	1/4	0
N	4b	1/4	0.0069	0.5138
O1	4b	1/4	0.4931	0.4862
O2	8c	0.4862	0.2569	1/4
Structure 2 ^b				
Ga1	2a	0	0	0
Ga2	2b	0	1/2	1/4
Ga3	4c	3/4	0	3/8
Ga4	4d	0	1/4	5/8
N	4c	0.2638	0	0.1319
O1	4c	0.7638	0	0.6181
O2	4d	0	0.7638	0.3819
O3	4d	0	0.7362	0.8681
Structure 3 ^c				
Ga1	1a	0	0	0
Ga2	2c	0.3750	0.3750	0.3750
Ga3	3d	1/2	0	0
N	2c	0.2431	0.2431	0.2431
O	6h	0.2431	0.2431	0.7707

^aStructure 1 $Ima2$ (no. 46): $a, c = 5.8534$ Å, $b = 8.2780$ Å.

^bStructure 2 $Imm2$ (no. 44): $a, b = 5.8534$ Å, $c = 8.2780$ Å.

^cStructure 3 $R\bar{3}m$ (no. 166): $a, b = 5.8534$ Å, $c = 14.3379$ Å.

placement of the N and O atoms in the anion sites. If the N and O were indistinguishable, the space group would revert back to $Fd\bar{3}m$. The N:O ratio was a 2:6 occupation of the eight available anionic sites in the F lattice. In contrast, the structure determination of a single crystal (Ref. 14) showed vacancy rates of 7% (cation) and 5% (anion), but these were not included in the model structures used herein as they would not contribute significantly to the experimental measurements due to the limited available resolution, and therefore would not affect any comparison to the experimental data (but would increase the complexity of the calculations significantly).

The software package WIEN2K was used for all DFT calculations.²⁶ The exchange correlation functionals used were the generalized gradient approximation of Perdew-Burke-Ernzerhof²⁷ (PDE) and a LDA functional including a semilocal potential modified from that of Becke and Johnson (the MB-JLDA functional).²⁰ A $12 \times 12 \times 12$ k -point mesh was employed for a unit cell with plane wave energy cutoff of -6.0 Ry and an $R_{k\text{max}}$ of 7.0. The sphere sizes used to enclose the core electron wave functions were 2.000, 1.5600, and 1.5600 bohrs for Ga, N, and O, respectively. A $1 \times 2 \times 1$ supercell incorporating a full core hole was used to simulate the XANES, and the k -point mesh was reduced to $8 \times 4 \times 8$. Four important aspects need to be taken into account when comparing XES and XANES measurements directly to theoretical LPDOS calculations. These are final-state considerations, lifetime broadening, instrumental broadening, and nonequivalent-site contributions. Further details pertaining to simulating XANES and XES with this method are described elsewhere.^{15,25}

The band gap or energy gap of a material is the difference in energy between the highest occupied DOS (or the top of the VB probed by XES) and the lowest unoccupied DOS (or the bottom of the CB probed by XANES). The band gap can therefore be determined by combining XES and XANES measurements on a common energy scale. There are three important experimental effects that need to be accounted for when using XES and XANES to determine the band gap. Core hole effects can shift the CB states to lower energies, effectively decreasing the measured band gap. Nonequivalent sites will have different core level binding energies, resulting in splitting of the spectral contributions and effectively decreasing the measured band gap. The VB and CB are affected by experimental broadening and the VB and CB locations are determined using the second derivative of the corresponding spectrum.²⁸ Corrections for these three effects help provide more reliable and accurate band gap estimates.

III. RESULTS AND DISCUSSION

A. Anion ordering

The anion ordering in spinel-type gallium oxonitride is a pertinent question. Ascertaining the exact nature of the bonding allows for further study of the electronic and mechanical properties. As mentioned previously, each unique crystal structure produces a unique electronic structure. While we cannot directly measure the local anion ordering (the location of the N and O atoms), we can probe the electronic structure and indirectly determine the specific location of the anion atoms.

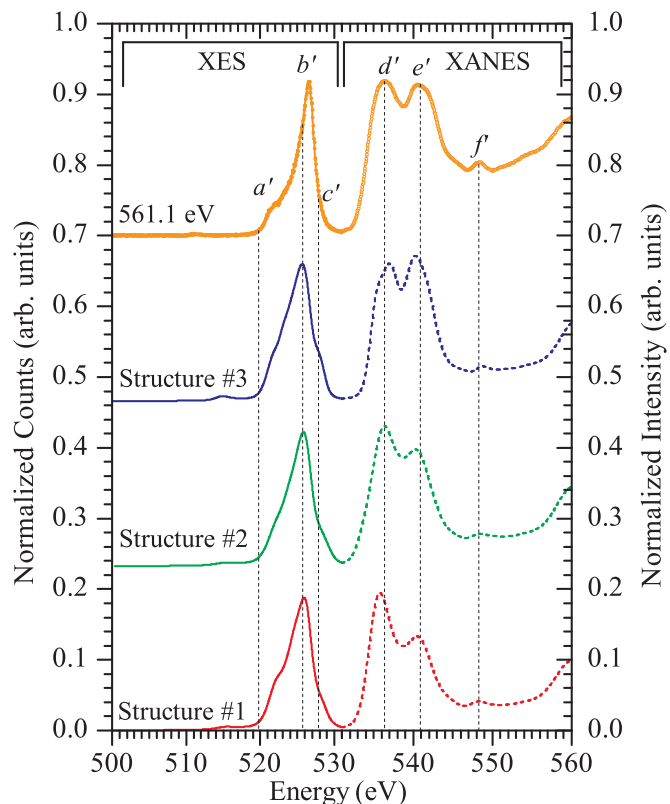


FIG. 1. (Color online) The measured (points) and simulated (solid and dashed lines) O $K\alpha$ XES and O $1s$ XANES spectra probe the occupied and unoccupied O p states, respectively. A comparison of the simulated and measured data determines which structural model best reproduces the experiment. Vertical dashed lines indicate spectral features and are used to guide the eye to the comparable features of the simulated and measured spectra. The annotation to the left of the spectrum indicates the corresponding structural model outlined in Table I or the excitation energy of the measured O $K\alpha$ XES spectra.

Figure 1 shows a comparison of the measured and simulated O $1s$ XANES spectra, which suggest that structure 3 exhibits the most correct anion ordering. The unoccupied O p states have three features labeled d' , e' , and f' , but only two features, d' and e' , change among the different structures. The measured unoccupied O p states suggest that the relative intensity of these features, d' and e' , should be approximately the same. The origin of these features may be elucidated with the partial density of states (PDOS). Figure 2 shows the PDOSs for structures 1, 2, and 3; they are used to look at the detailed electronic structure information since simulation of the XES and XANES spectra requires significant broadening, resulting in a loss of detail. Here, the PDOSs clearly show that feature d' can be attributed to Ga s -O p hybridization, while feature e' can be attributed to Ga p -O p hybridization. Examining Fig. 1, we see that of the structures 1–3, no. 3 has the largest amount of Ga p -O p hybridization and best reproduces the measured unoccupied O p states.

Figure 1 also shows a comparison of the measured and simulated O $K\alpha$ XES spectra, which also suggest that structure 3 has the most appropriate anion ordering. The simulated occupied O p states have a similar shape between the different structures. There is, however, one key distinguishing feature,

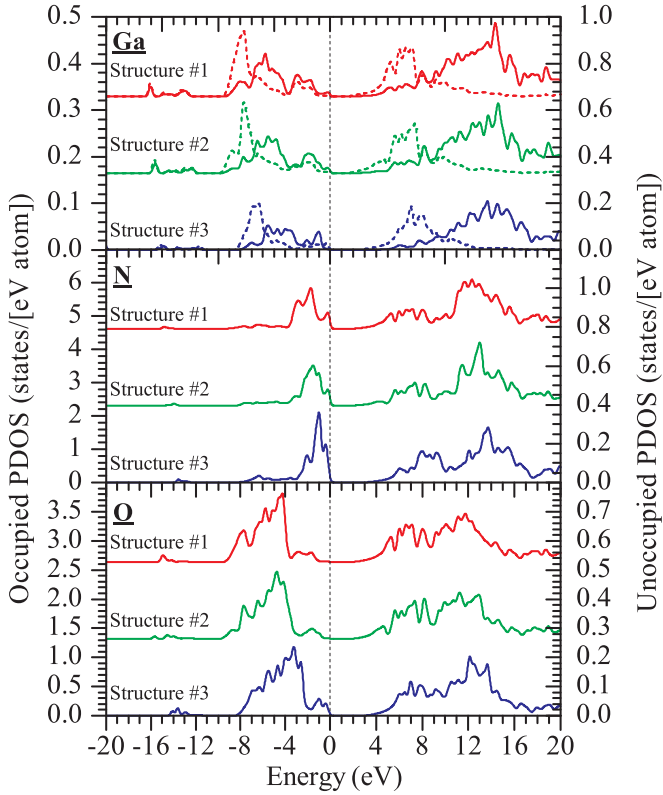


FIG. 2. (Color online) The partial densities of states of $\text{Ga}_3\text{O}_3\text{N}$ including Ga s states (dashed) and Ga, N, and O p states (solid) for structures 1, 2, and 3 (displayed in red, blue, and green, respectively). The PDOS has been broadened to allow for easy comparisons. The top of the valence band is set to 0.0 eV and is indicated with a vertical dashed line. The colors of the PDOSs correspond to specific structural models as in Figs. 1 and 3.

which is the prevalence of occupied O p states near the Fermi level (feature c'). The origin of this effect is explained by examining the calculated unbroadened PDOS. The occupied O p states near the Fermi level change significantly between structural models. The difference in c' between the different structures is that in structures 1 and 2, the occupied O p states are withdrawn from the Fermi level and do not contribute at the top of the VB. This is in contrast to structure 3 in which the occupied O p states do contribute at the top of the VB. Now in the measured O $K\alpha$ XES spectra, the O p states contribute greatly to the top of the VB, best corresponding to the occupied O p states of structure 3, which is the only model where the occupied O p states are at the top of the VB. This small but definite difference suggests that structure 3 is the appropriate structure since the measurements suggest that O p states do contribute to the top of the VB. This suggests the structure 3 is the most appropriate model for the $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ compound studied here.

Figure 3 shows a comparison of the measured and simulated N $1s$ XANES spectra, which further elucidates the appropriate anion ordering, but these measurements are contaminated with remaining h -BN that was used as the crucible material during the synthesis of $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$. We therefore need to take into account the effect the h -BN impurity will have on the measured N p states making it not readily apparent which

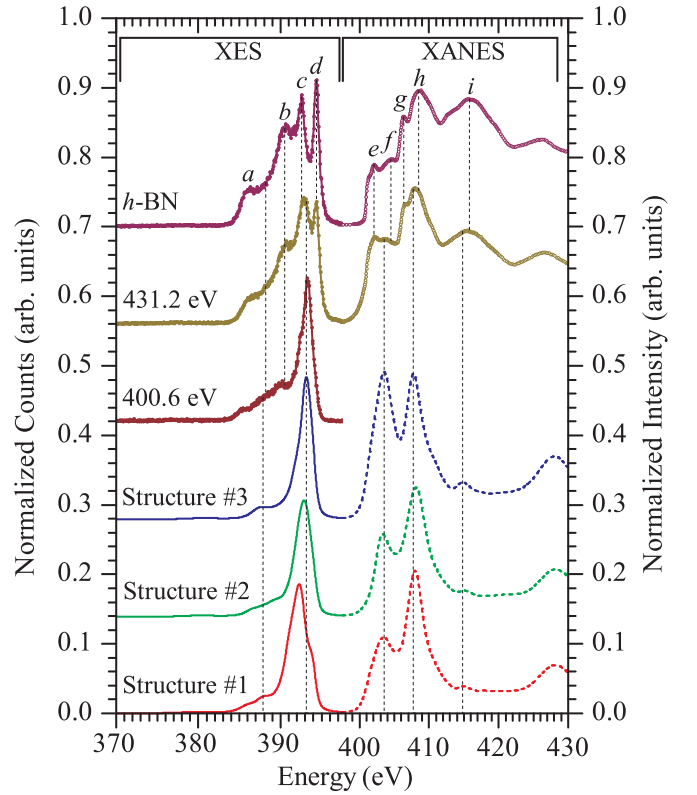


FIG. 3. (Color online) The measured (points) and simulated (solid and dashed lines) N $K\alpha$ XES and N $1s$ XANES spectra probe the occupied and unoccupied N p states, respectively. A comparison of the simulated and measured data determines which structural model best reproduces the experiment. Vertical dashed lines indicate spectral features and are used to guide the eye to the comparable features of the simulated and measured spectra. The annotation to the left of the spectrum indicates the corresponding structural model outlined in Table I or the excitation energy of the measured N $K\alpha$ XES spectra.

structural model best reproduces the measured N p states. The measured unoccupied N p states of $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ bear a striking resemblance to the h -BN unoccupied N p states, but with a few subtle differences. These differences are that the relative intensity ratio of the features f and h is smaller for h -BN and that the unoccupied N p states of $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ extend lower in energy, indicating a smaller band gap than in h -BN, which we expect from theoretical calculations presented here. With a difference in the intensity of features f and h in mind, we would expect that for our simulated unoccupied N p states the relative intensity ratio of $f:h$ would be larger than the measured value in $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$, since the addition of an h -BN spectrum will reduce the relative intensity.

This ratio again can be correlated with the electronic structure, and Fig. 2 shows the PDOS for the unoccupied N p states. These figures show that feature f is a result of N p -Ga s hybridization and feature h is due to N p -Ga p hybridization. The unoccupied N p states in structure 3 have the largest relative intensity ratio of these features, suggesting that it is the appropriate structural model for $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$. While the reduced band gap of $\text{Ga}_{2.79}\text{O}_{3.05}\text{N}_{0.76}$ is not useful for the comparison of the unoccupied N p states it does prove fruitful in the comparison of the occupied N p states.

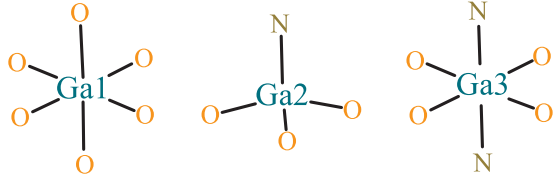


FIG. 4. (Color online) The bonding polyhedra of structure 3 are Ga-O₆ (left), Ga-O₃N (center), and Ga-O₄N₂ (right). These highly symmetric polyhedra represent the local bonding environment that is responsible for the bond hybridization.

Figure 3 also shows a comparison of the measured and simulated N $K\alpha$ XES spectra, which confirm that the anion ordering in structure 3 best reproduces the measured occupied N p states. The band gap difference of Ga_{2.79}O_{3.05}N_{0.76} in comparison to h -BN allows us to tune the XES spectrum excitation energy to the lowest value possible in order to avoid photons being absorbed by h -BN. Thus, we predominantly probe the occupied N p states of the Ga_{2.79}O_{3.05}N_{0.76} present in the sample as opposed to both h -BN and Ga_{2.79}O_{3.05}N_{0.76}. The corresponding XES spectrum is labeled as 400.6 eV in Fig. 3. The measured occupied N p states change drastically and look almost identical to those calculated for structure 3, confirming our previous conclusion drawn from the comparison of the measured and simulated unoccupied N p states: that the appropriate structure is no. 3.

So far, structure 3 is determined to provide the most correct model of the anion ordering out of the three structures tested. This is largely based on the nature of the bond hybridization that is seen in the experimental measurements. The cause of this large degree of hybridization of the Ga-O and Ga-N bonds may be the highly symmetric nature of the bonding polyhedra; see Fig. 4. As discussed earlier, the nitrogen atoms substitute such that they increase their separation as much as possible; however, the increased stability may be due to the symmetry of the polyhedra that occur. This is not uncommon for spinel structure compounds; for example, in the solid solutions γ -(Si,Ge)₃N₄ Ge occupies the tetrahedral sites because that allows the most symmetric N-(Ge,Si) tetrahedra to exist.^{8,9} With the notion that the anions would prefer to be distributed as symmetrically as possible in bonding polyhedra, it seems unlikely that a random distribution of anions would achieve better results.

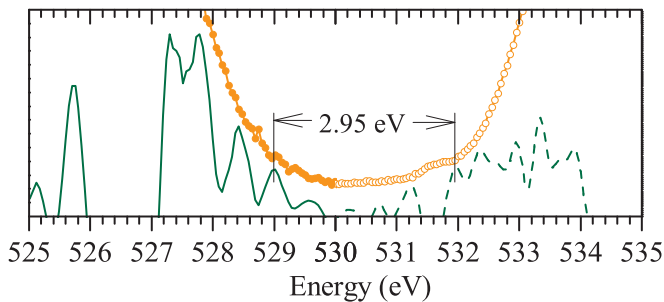


FIG. 5. (Color online) The second derivatives (solid and dashed) of the measured (points) nonresonant O $K\alpha$ XES and O $1s$ XANES spectra determine the top of the VB and bottom of the CB. The first peak above the background noise level is used to determine the VB and CB edges.

TABLE II. The calculated band gap values using the PDE (E_g^{PDE}) and MBJLDA (E_g^{MBJLDA}) functionals are compared to the experimentally determined value (E_g^{expt}). The type of band gap transition that can occur is indicated in parentheses. The calculated band gap values using the same method for w -GaN and β -Ga₂O₃ illustrate the reliability of the calculated values.

Material	E_g^{PBE} (eV)	E_g^{MBJLDA} (eV)	E_g^{expt} (eV)
Ga _{2.79} O _{3.05} N _{0.76}	1.14 (direct)	2.79 (direct)	2.95 ± 0.30
w -GaN	1.94	3.23	3.4 ± 0.1
β -Ga ₂ O ₃	2.50	4.96	4.8 ± 0.1

B. Electronic band gap

Now that we have determined the most probable model for the anion ordering to be structure 3, we turn our attention to the electronic band gap of Ga_{2.79}O_{3.05}N_{0.76}. The measured oxygen data are not affected by h -BN impurities and are used to evaluate the electronic band gap.

The band gap is determined by combining the measured occupied and unoccupied O p states on the same energy scale as in Fig. 1. Figure 5 displays the second derivative of the measured occupied and unoccupied O p states and is used to determine the location of the VB and CB edges. There is no significant core hole shift (0.0 ± 0.1 eV) as determined from our DFT calculations by comparing the calculations with and without a core hole. This places the measured band gap of Ga_{2.79}O_{3.05}N_{0.76} at 2.95 ± 0.30 eV with no corrections necessary since there is only one oxygen site in structure 3. The error associated with this band gap value is evaluated by including three considerations: the error in the experimental precision in energy (± 0.20 eV), the error in the relative calibration (± 0.20 eV), and the error in the core hole shift (± 0.1 eV).

The electronic band gap values were also implicitly calculated from the DFT results. Table II lists the band gap values calculated with both the PBE and MBJLDA functionals. It is well known that conventional GGA (PBE) calculations underestimate the band gap, but including a semilocal screening potential provides significantly more accurate values.²⁰ The calculated band gap values for structure 3 are used as the theoretical values for Ga_{2.79}O_{3.05}N_{0.76}. The reliability of MBJLDA band gap calculations of similar compounds, w -GaN and β -Ga₂O₃, suggests that the value should be within 0.2 eV, which is what we see when we compare the calculated and measured values.

IV. CONCLUSIONS

Here we tested three structural models for Ga₃O₃N in which there is a significant level of anion ordering, in contrast to XRD measurements, which generalize the anions to a single site. We confirm that of the three possible structure types tested, the appropriate structural model is that which adopts the $R\bar{3}m$ space group. This structure provides the appropriate hybridization of Ga s and p with N and O p states. The high level of hybridization stems from the increased symmetry of the Ga-O₆ and Ga-O₄N₂ octahedra and Ga-O₃N tetrahedra. The measured band gap of Ga_{2.79}O_{3.05}N_{0.76} is 2.95 ± 0.30 eV using the O $K\alpha$ XES and O $1s$ XANES spectra and agrees

with the calculated value of 2.79 eV. We used a combination of DFT calculations along with XES and XANES measurements to experimentally determine both the band gap and anion ordering in spinel-type gallium oxonitride. This technique is not limited to this material but may be applied to any material where the locations of the elements, differing by $\Delta Z \pm 1$, are not easily determined with XRD.

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