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Chemical Composition, Crystal Structure, and Their Relationships with the Intrinsic Properties of Spinel-Type Crystals Based on Bond Valences

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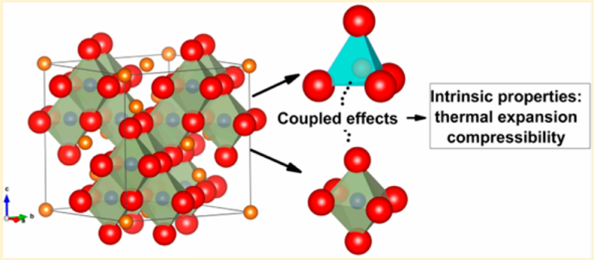
Ⓢ *Supporting Information*



ABSTRACT: Spinel-type crystals may possess complex and versatile chemical composition and crystal structure, which leads to difficulty in constructing relationships among the chemical composition, crystal structure, and intrinsic properties. In this work, we develop new empirical methods based on bond valences to estimate the intrinsic properties, namely, compressibility and thermal expansion of complex spinel-type crystals. The composition-weighted average of bond force constants in tetrahedral and octahedral coordination polyhedra is derived as a function of the composition-weighted average of bond valences, which can be calculated according to the experimental chemical composition and crystal structural parameters. We discuss the coupled effects of tetrahedral and octahedral frameworks on the aforementioned intrinsic properties. The bulk modulus could be quantitatively calculated from the composition-weighted average of bond force constants in tetrahedral and octahedral coordination polyhedra. In contrast, a quantitative estimation of the thermal expansion coefficient could be obtained from the composition-weighted average of bond force constants in octahedral coordination polyhedra. These empirical methods have been validated by the results obtained for a new complex quaternary spinel-type oxynitride $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$ from the literature. Further, these empirical methods have the potential to be extensively applied in other types of complex crystals.

■ INTRODUCTION

The spinel-type crystals comprise a broad group spanning a range of properties including thermoelectricity,[1] the coexistence of transparency and conductivity,[2] electrochemical properties,[3] and catalytic properties.[4] The spinel-type structure consists of an almost ideal cubic-close-packed arrangement of anions in which cations are distributed in tetrahedral and octahedral coordination.[5] There are several spinel-type crystals with complex chemical composition such as $Co_xZn_{1-x}Al_2O_4$ (x = 0.01−0.6),[6] $LiNi_{0.5}Mn_{1.5}O_4$,[3] and γ-Si_2AlON_3,[7] where not only the two cationic sites but also the anionic site can have mixed occupancy. A substantial number of vacancies may reside on the cationic sites as a result of charge balance in nonstoichiometric spinel-type crystals such as $MgO{\cdot}xAl_2O_3$ ($1 < x \leq 3.55$).[8] Moreover, variable degrees of cation disorder between tetrahedral and octahedral sites are possible in spinel-type crystals such as $Zn_{1-x}Cu_xAl_2O_4$ ($0 \leq x \leq 1$),[9] $MgFe_2O_4$,[10] and $CoAl_2O_4$,[11] and the degree of inversion depends on the chemical composition, pressure, temperature, cooling history, etc.[12,13] On the basis of these premises, the chemical composition and crystal structure of spinel-type crystals may have extraordinary complexity and versatility. Because the intrinsic properties of a crystal strongly depend on the chemical composition and crystal structure,[14] understanding the relationships among them is crucial to purposely designing new spinel-type crystals with tunable intrinsic properties. However, these relationships have not been well constructed because of the above-mentioned complex chemical composition and crystal structure in spinel-type crystals.

The intrinsic properties of a crystal, including compressibility and thermal expansion, are generally determined by the bonding properties of constituent coordination polyhedra.[15−18] Until now, few empirical methods have been proposed to relate these intrinsic properties to the bonding properties based on the experimental chemical composition and crystal structure,[17−23] which has been proven to have the advantage of great authenticity and simplicity. Most of these empirical methods apply exclusively to binary crystals with one species of chemical bond and allow one to estimate the intrinsic properties as a function of the accessible parameters, e.g., bond lengths, coordination number, formal charge, and

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ionicity.[19−21] For example, Cohen presented a bulk modulus model for zinc-blende semiconductors using the bond length and empirical ionicity.[19] Hazen and Finger proposed a more general bulk modulus−volume relationship for several structure types such as simple oxides, sulfides, and halides based on the formal charge and empirical ionicity.[20] Moreover, the thermal expansion coefficients of simple oxides were estimated from the cation formal charge and coordination number.[21]

In the aforementioned empirical methods, different quantification schemes are being used for different types of crystals and intrinsic properties.[24] A more suitable and universal parameter to characterize the bonding properties is necessary for empirical methods to have broader applicability. It is noted that the stretching bond force constant of a chemical bond (F_c) is a fundamental parameter to gain insight into the bonding strength and character of a chemical bond.[25,26] The empirical methods based on F_c have been proven to be universal and successful in estimating the thermal expansion and compressibility for different types of binary crystals with one species of chemical bond.[22,23,27−29] However, these empirical methods based on F_c have not been applied to estimate the intrinsic properties of spinel-type crystals with both complex chemical composition and two different coordination sites.

Some studies have shown that the coupled effects of the tetrahedral and octahedral frameworks on the intrinsic properties should be considered in spinel-type crystals.[15,30−33] For instance, Megaw assumed that the thermal expansion of a spinel-type crystal is determined by the thermal expansion of chemical bonds in octahedral coordination polyhedra.[30] Finger et al. suggested that tetrahedral and octahedral coordination polyhedra contribute equally to the total compressibilities in spinel-type crystals.[31] These coupled effects may play an important role in the empirical methods for spinel-type crystals.

In order to develop new empirical methods by F_c for complex spinel-type crystals, the composition-weighted average of bond force constants (F_c^{Ave}) in coordination polyhedra with sites occupied by multiple kinds of mixed anions or cations should be calculated. Until now, most expressions to calculate F_c have been proposed for coordination polyhedra with sites containing a single kind of anion or cation,[25,26] which cannot be used to calculate F_c^{Ave}. It is noted that, on the basis of the bond valence method proposed by Brown,[34,35] the composition-weighted average of bond valence (S_{Ave}) in coordination polyhedra with different kinds of mixed anions or cations can be calculated with the constraint of the chemical composition, which can be used to globally analyze the bonding strength of coordination polyhedra. Furthermore, Brown also has deduced an expression between the bond force constant and bond valence, which has predicted good results in high-symmetry coordination polyhedra with a single kind of anion or cation.[23] On the basis of these premises, we predict that F_c^{Ave} could be well estimated by the aforementioned S_{Ave} parameter. However, so far, there is no report about empirical methods to quantitatively estimate the thermal expansion and compressibility by bond force constants based on bond valences in spinel-type crystals.

Here, we will give a brief introduction of the scheme to present new empirical methods based on bond valences in this paper. First, the complex chemical composition and crystal structure of spinel-type crystals will be determined. Then, F_c^{Ave} in tetrahedral and octahedral coordination polyhedra will be calculated from S_{Ave} values according to the experimental chemical composition and crystal structural parameters. Finally, the coupled effects of the tetrahedral and octahedral frameworks will be further analyzed, and empirical methods using F_c^{Ave} will be proposed to estimate the bulk modulus and thermal expansion coefficients for spinel-type crystals. The performance of the new empirical methods is tested through the results obtained in our recently synthesized complex quaternary spinel-type $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$[36] and validated against literature data on the common ternary spinel-type $MgAl_2O_4$[31,37] and $Al_{2.85}O_{3.45}N_{0.55}$.[37−39]

■ EXPERIMENTAL SECTION

Sample Synthesis. Single-phase $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ powders were prepared by a solid-state reaction process, using high-purity 16.376 mol % MgO (99.99%), 15.377 mol % AlN (~99.9%), and 68.247 mol % α-Al_2O_3 (~99.99%) powders as the raw materials. Elemental analysis of the synthesized powders was performed using a combination of different methods. Quantitative analysis of the O and N contents was performed by the well-established hot gas extraction method (model TC-600; Leco, St. Joseph, MI). Silicon oxide was used as an O calibration standard and tantalum nitride as a N calibration standard. Totals of 42.813 wt % O and 2.681 wt % N were detected. The Mg and Al contents were determined by inductively coupled plasma atomic emission spectroscopy (model Optima 4300DV; PerkinElmer Instruments, Boston, MA). Single element standards of Mg and Al were used as Mg and Al calibration standards. Totals of 4.668 wt % Mg and 49.838 wt % Al were detected. The accuracy is ~1% of the presented content in all cases. The obtained composition can be expressed by the formula $Mg_{0.268(3)}Al_{2.577(26)}O_{3.733(37)}N_{0.267(3)}$. Then, the powders were pressed into disks and annealed at 1875 °C for 24 h. The final products were highly dense and transparent. The detailed preparation and characterization of the powders and disks are available in our recently published paper.[36]

Crystal Structure Refinement. Using an X-ray diffractometer (X'Pert Pro; PANalytical Co., Almelo, The Netherlands), the powder X-ray diffraction (XRD) pattern was collected at room temperature with monochromatized Cu Kα radiation (1.540598 Å, 40 kV, 40 mA). The full measurement range of a 128-channel linear multistrip X′Celerator detector was applied to scan the range from 15° to 145° with a step size of 0.013° and a counting time of 11.22 s for each step. The optics configuration was primary and secondary soller slits of 0.04 rad, a vertical mask of 15 mm, a divergence slit of 0.5°, and antiscatter slits of 8.0 mm. In this paper, we adopted the Rietveld method using the *FULLPROF* program[40] combined with the structure model of spinel-type solid solutions proposed by Lavina et al.[41] to determine the crystal structure of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$. Indeed, because the X-ray scattering factors for Mg and Al are very similar, the cation distribution of Mg and Al cannot be directly obtained from XRD analysis.

Rietveld analysis was performed in the $Fd\bar{3}m$ space group in which Al and cation vacancies (□) were both located on the sites 8a and 16d and O and N on the sites 32e. The Al form factor was used in both cationic sites, with free occupancy to account for the presence of Mg and □. The site occupancies were constrained to the chemical composition $Mg_{0.268}Al_{2.577}\square_{0.155}O_{3.733}N_{0.267}$. The atomic positions of the tetrahedral and octahedral sites were set to (0.125, 0.125, 0.125) and (0.5, 0.5, 0.5) for origin at $\bar{3}m$, respectively. The shapes of the Bragg peaks were quantified by a pseudo-Voigt function. In the final refinement, the following parameters were refined in sequence: $2\theta - 0$; six background parameters; a unit cell parameter; a scale factor; peak-shape parameters; four parameters from asymmetry; three half-width parameters; atomic positions of O and N; isotropic displacement parameters; site occupancies of Al and □.

The intracrystalline cation distribution was calculated using a model for the spinel-type solid solutions where the chemical and structural parameters were calculated by a function of the cation distribution, using ionic radii for calculation of the bond lengths. The software *SIDR* was modified to calculate the crystal structure of spinel-type oxynitrides. In particular, metal−oxygen bonds were corrected for the presence on N partially substituting for O and using the difference in the ionic radii between tetrahedrally coordinated O^{2-} and N^{3-} reported in Shannon's compilation.[42] Details of the calculation algorithm have been previously described.[41] Briefly, *SIDR* used a least-squares minimization of the following function:

$$D(X_i) = \frac{1}{n}\sum_{1}^{n}{}_{j}\left(\frac{O_j - C_j(X_i)}{\sigma_j}\right)^2 \tag{1}$$

where O_j were observed quantities with their standard deviation σ_j. The j quantities are (i) the four observed crystallographic parameters from Rietveld analysis (cell parameter a, anion position parameter u, the mean atomic number of the tetrahedral (m.a.n.$_T$) and octahedral (m.a.n.$_M$) sites), (ii) the chemical atomic proportions, and (iii) the site occupancies of T and M, and the formula neutrality is treated as discussed Lavina et al. in 2002.[41] $C_j(X_i)$ are calculated as a function of the variable cation fractions X_i (Supporting Information I). $\square$ in $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ was assumed to be located on the octahedral sites according to the octahedral site preference shown by vacancies in other spinel-type crystals.[8,44,45] Because standard deviations from Rietveld analysis are known to underestimate the refined parameter uncertainties, in our cation distribution optimization, we assigned the values of σ = 0.0005, 0.0005, 0.5, and 0.3 to a, u, m.a.n.$_T$, and m.a.n.$_M$, respectively.[41] These values were found to be reasonable average uncertainties in spinel structural refinement based on analysis of a large database of spinel structures. The standard deviations of chemical proportions were assumed within 1% of the measured values. On the basis of doubling of the minimization function, we estimate the uncertainty on the site atomic fractions to be 0.01 afu (atoms per formula unit).

Bond Valence Calculation. According to the bond valence method suggested by Brown,[34,35] the bond valence sum V_i of an atom i was defined as the sum of the bond valence S_{ij} of all the bonds from i to atoms j:

$$V_i = \sum_j S_{ij} \tag{2}$$

$$S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right) \tag{3}$$

where R_0 is the bond valence parameter,[46] R_{ij} is the length of the bond between the two atoms i and j, and b is a universal constant equal to 0.37 Å. The quantity of the overall structure stability could be determined by comparing the calculated bond valence sum (V_i) with the formal valence (v_i), which was referred to the global instability index (GII) according to[43]

$$\mathrm{GII} = \sqrt{\sum_{i=1}^{N}\frac{(V_i - v_i)^2}{N}} \tag{4}$$

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were measured using a spectrometer (VG multilab 2000; ThermoVG Scientific, Southend-on-Sea, Essex, U.K.) with monochromatized Al Kα X-ray radiation in an ultrahigh vacuum ($<10^{-7}$ Pa). The binding energies were calibrated by the C 1s peak (284.64 eV) of carbon impurities as a reference. The peaks were deconvoluted by *Avantage* software after background subtraction, using a mixed Gaussian–Lorentzian function.

Intrinsic Properties. The bulk modulus was determined using ultrasonic equipment (EXPLORE-9000; Matec Instruments, Hookinton, MA) with a fundamental frequency of 15 MHz at 23 °C. The linear coefficient of thermal expansion from 30 to 200 °C at a heating rate of 5 °C·min^{-1} was measured using a dilatometer (DIL 402C; Netzsch, Selb, Germany).

■ RESULTS AND DISCUSSION

Crystal Structure Refinement. The crystal structure of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ is refined by the Rietveld method combined with the structure model of spinel-type solid solutions. From Rietveld analysis, as shown in Table 1, the observed crystallographic parameters containing the cell parameter (a), anion position parameter (u), bond lengths (R_T and R_M), and mean atomic number (m.a.n.$_T$ and m.a.n.$_M$) of the tetrahedral and octahedral sites are obtained. In the last refined cycle (Supporting Information II, Table 1s), the calculated (line) patterns fit well to the experimental (circle) patterns, as shown in Figure 1. The final R values are listed as follows: R_p = 4.61%; R_{wp} = 6.18%; χ^2 = 1.75. Then, according to the structure model of spinel-type solid solutions, the calculated crystallographic parameters and optimized cation distribution are also obtained, as shown in Table 1. The value of $D(X_i)$ is 1.73, which is closed to 1 and indicates good agreement between the calculated and observed data. Minimization leads to the Mg^{2+} cations of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ locating at the tetrahedral sites. This result is consistent with the distribution of Mg^{2+} cations in Mn^{2+}- and Mg^{2+}-codoped γ-AlON.[44]

Table 1. Observed (O_j) and Calculated (C_j) Crystallographic Parameters with the Standard Deviation (σ_j) and Optimized Cation Distribution of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ by the Structure Model of Spinel-Type Solid Solutions

	O_j	σ_j	C_j	$C_j - O_j$
$D(X_i)$ = 1.73				
a (Å)	7.9797	0.0005	7.9794	−0.0003
u	0.3830	0.0005	0.3828	−0.0002
R_T (Å)	1.838	0.007	1.835	−0.003
R_M (Å)	1.933	0.004	1.935	0.002
m.a.n.$_T$	12.705	0.500	12.740	0.035
m.a.n.$_M$	12.141	0.300	12.005	−0.136
Mg^{2+}	0.268	0.003	0.271	0.003
Al^{3+}	2.577	0.026	2.576	−0.001
$\square$	0.155	0.002	0.156	0.001
sum	3.000		3.003	

cation distribution	tetrahedral site	octahedral site
Mg^{2+}	0.271	0.000
Al^{3+}	0.730	1.846
$\square$	0.000	0.156
sum	1.001	2.002

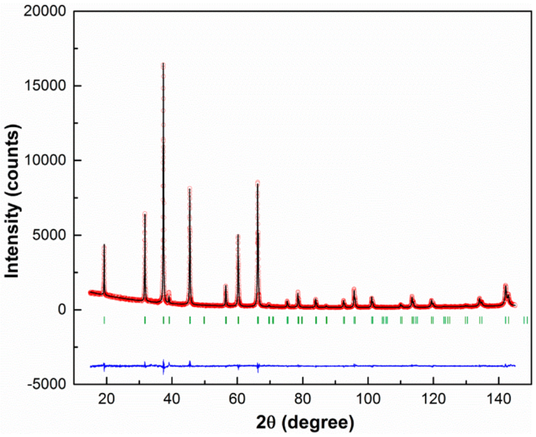

Figure 1. Measured (circles), calculated (line), and differential (bottom line) XRD patterns of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ powders.

To further verify the refined cation distribution, the XPS spectra of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ are interpreted as shown in

Figure 2. No other elements are detected except for the constituent components and contaminated C in the spectrum, as shown in Figure 2a. To analyze the Mg^{2+} and Al^{3+} distributions, the high-resolution XPS spectra of Mg 1s and Al 2p are measured, as shown in parts b and c of Figure 2, respectively. The Mg 1s XPS spectrum is symmetric in our experiment and can be deconvoluted into only one peak. The peak at 1304.06 eV is assigned to the Mg^{2+} ions occupying the tetrahedral sites.[47] The Al 2p XPS spectrum is relatively broad and asymmetric, which indicates that Al^{3+} ions occupy more than one coordination site. The peak at higher binding energy (~74.7 eV) is assigned to the Al^{3+} ions occupying the octahedral sites, while the peak at lower binding energy (~73.6 eV) is due to Al^{3+} ions occupying the tetrahedral sites.[47] The site fraction ratio of Al^{3+} ions in the octahedral and tetrahedral sites is estimated according to the area ratio of these two peaks. This ratio is about 2.52, which agrees well with that calculated from the refined cation distribution.

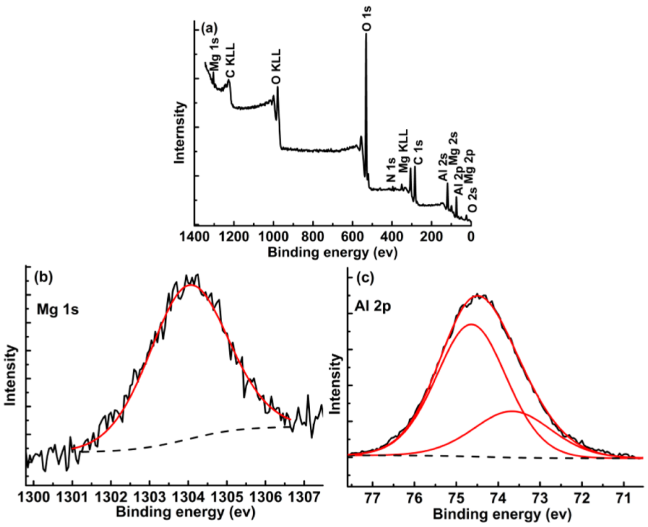

Figure 2. XPS survey spectrum (a) and Mg 1s (b) and Al 2p (c) spectra of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ powders.

On the basis of the crystal structural analysis above, the experimental structural formula of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ could be described as $(Mg_{0.268}Al_{0.732})^{IV}[Al_{1.845}\square_{0.155}]^{VI}O_{3.733}N_{0.267}$. Figure 3 depicts the crystal structure schematic of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$. The basic unit of the structure is the "double rutile" chain, in which a pair of edge-shared octahedra pile up along the [111] directions. Four chains are linked by sharing vertices to form a three-dimensional framework structure. It is suggested that $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ could be defined as a normal spinel-type compound similar to the normal nonstoichiometric magnesium aluminate,[8] because Mg^{2+} and $\square$ may reside exclusively on the tetrahedral and octahedral sites, respectively. Furthermore, the crystal structural parameters of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ (ICSD no. 77583)[31] and $Al_{2.85}O_{3.45}N_{0.55}$ (ICSD no. 70032)[38] are shown in Table 2.

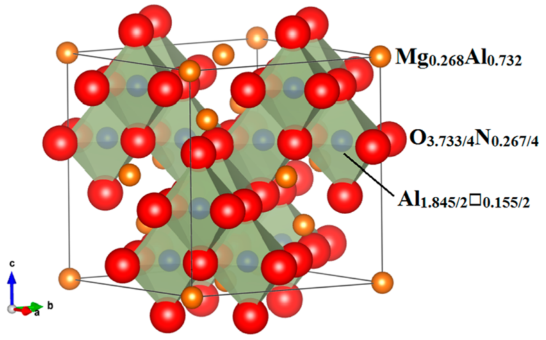

Figure 3. Schematic crystal structure of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$.

Bond Valence Calculation. In order to globally analyze the bonding strength of coordination polyhedra with sites occupied by several kinds of mixed anions or cations, the composition-weighted average of bond valences and bond valence sums could be calculated with the constraint of the chemical composition using the bond valence method.[34,35] On the basis of our previous first-principles study on an atom site preference in γ-AlON,[48] we assume that the clustering of N or $\square$ is also not favorable in complex spinel-type oxynitrides. While anions are randomly distributed at the anionic sites, cations and $\square$ randomly exist at the cationic sites. According to the site assignment ratios of each constituent species in coordination polyhedra, the composition-weighted average of bond valences (S_{Ave}) between cations and anions could be calculated as

$$S_{Ave} = \sum_i [X_i \sum_j (Y_j S_{ij})] \tag{5}$$

where X_i and Y_j are the fractions of one type of cation and anion in coordination polyhedra, respectively. Accordingly, the composition-weighted averages of tetrahedral site bond valences (S_T) and octahedral site bond valences (S_M) could be calculated. The calculated bond valence results of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$ are shown in Table 2 (Supporting Information III, Table 2s).

In addition, the results of bond valence calculations could be used to further validate the newly refined structure.[35,49] V_T (2.57 vu) and V_M (2.68 vu) of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ are about 5% lower than the formal valences of cations in tetrahedral sites (2.73 vu) and octahedral sites (2.77 vu), which shows agreement with the results of other spinel-type crystals.[50] As shown in Table 2, GII of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ (0.10) is lower than 0.2. Consequently, the refined crystal structure of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ could be chemically reasonable.[43]

Bond Force Constant Calculation. The bond force constant in coordination polyhedra with sites containing a single kind of anion or cation could be deduced by the bond valence. The approximate quantitative relationship is given by[23]

$$F_c = \frac{\gamma \left(\frac{8S_{ij}}{3}\right)^{3/2} \left(\frac{1}{b} - \frac{2}{R_{ij}}\right)}{R_{ij}^{\ 2}} \tag{6}$$

where γ = 23 nN Å^2 electrons^{-2}. Further, F_c^{Ave} in coordination polyhedra with sites occupied by different kinds of mixed anions or cations could be estimated by S_{Ave}, which is an important fundamental parameter to characterize the bonding properties of constituent coordination polyhedra in complex spinel-type crystals. According to S_T and S_M, the composition-weighted averages of bond force constants in the tetrahedral (F_c^T) and octahedral (F_c^M) coordination polyhedra could be calculated. The calculated F_c^T and F_c^M in

Table 2. Structural Formulas, Crystal Structural Parameters, and Bond Valence and Bond Force Constant Results of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as Well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$

	$MgAl_2O_4$	$Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$	$Al_{2.85}O_{3.45}N_{0.55}$
structural formula	$(Mg_{0.86}Al_{0.14})^{IV}[Mg_{0.14}Al_{1.86}]^{VI}\ O_4$	$(Mg_{0.268}Al_{0.732})^{IV}[Al_{1.845}\square_{0.155}]^{VI}\ O_{3.733}N_{0.267}$	$(Al_1)^{IV}[Al_{1.85}\square_{0.15}]^{VI}\ O_{3.45}N_{0.55}$
a (Å)	8.0898(9)	7.9797(5)	7.9526(5)
u	0.3883(3)	0.3830(5)	0.3812(2)
R_T (Å)	1.938(4)	1.838(7)	1.807(3)
R_M (Å)	1.921(2)	1.933(4)	1.940(2)
S_T (vu)	0.51(1)	0.64(1)	0.70(1)
S_M (vu)	0.49(1)	0.48(1)	0.49(1)
V_T (vu)	2.05(3)	2.57(4)	2.80(4)
V_M (vu)	2.91(3)	2.68 (3)	2.72(3)
GII	0.04	0.10	0.10
F_c^T (N m^{-1})	162(4)	245(6)	287(6)
F_c^M (N m^{-1})	155(2)	149(2)	153(2)

$Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$ are shown in Table 2. These calculated bond force constants are plotted as a function of the bond valence in Figure 4. The bond force constant quasi-linearly increases with increasing bond valence, which confirms that the bond force constants as well as the bond valences are important parameters to quantitatively investigate the bonding strength of coordination polyhedra in spinel-type crystals. In general, F_c^T and F_c^M in spinel-type crystals can be evaluated by the lattice vibration theory based on Waldron absorption bands developed by Grimes and Collett.[51] It is shown that F_c^T (245 N m^{-1}) and F_c^M (149 N m^{-1}) of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ calculated by S_T and S_M are consistent with F_c^T (~236.72 N m^{-1}) and F_c^M (~130.30 N m^{-1}) calculated by the Waldron absorption bands (Supporting Information IV, Figure 1s), which further confirms that F_c^T and F_c^M calculated based on the weighted average of bond valences are reasonable.

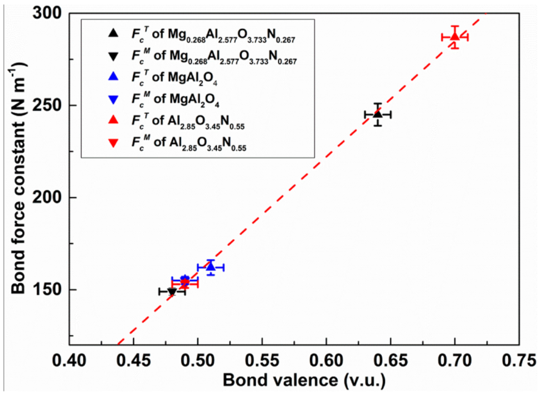

Figure 4. Calculated composition-weighted averages of bond force constants in the tetrahedral (F_c^T) and octahedral (F_c^M) coordination polyhedra of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$, $MgAl_2O_4$, and $Al_{2.85}O_{3.45}N_{0.55}$ as a function of the bond strength.

Bulk Modulus Calculation. The bulk modulus of a crystal is roughly dependent on the compressibility of constituted polyhedral structures.[17,18,23,52] An expression by the bond force constant has been developed to estimate the bulk modulus of a chemical bond (B_v) given by[23]

$$B_v = \frac{F_c}{3gR_{ij}} \tag{7}$$

where g is a geometric factor that represents the ratio of the effective area supported by the bond to the square of the bond length. Values of g for a number of simple structures have been obtained.[23] The bulk modulus of different simple high symmetry structures with a single-coordinate framework can be quantitatively estimated by B_v derived from F_c and was found accurate to around 95%.[23] However, because spinel-type crystals have complex crystal structure, the interactive effect of the tetrahedral and octahedral frameworks on the compressibility of a crystal should be analyzed. In general, the spinel-type structure can be viewed as a combination of two kinds of simple high symmetry polyhedral structures with a single-coordinate framework, the tetrahedrally bonded blende-type structure and the octahedrally bonded rock salt structure. Moreover, cation vacancies may reside on cationic sites, leading to a decrease in the number of bonds, which can influence the bulk modulus of the polyhedral structure in the spinel-type structure. The bulk modulus of the tetrahedral (B_T) and octahedral (B_M) coordinate structure can be calculated from

$$B_T = pB_v^T = p\frac{F_c^T}{3g_1R_T} \tag{8}$$

$$B_M = qB_v^M = q\frac{F_c^M}{3g_2R_M} \tag{9}$$

where p and q are the total cation fractions in the tetrahedral and octahedral sites, respectively. The values of g_1 and g_2 are 2.31 and 1, respectively.[23] It is noted that some studies have shown that tetrahedra and octahedra contribute equally to the total compressibilities in spinel-type crystals.[31−33] As a result, the bulk modulus (B_{Cal}) of a complex spinel-type crystal could be calculated by the average of B_T and B_M, which is written as

$$B_{Cal} = \frac{B_T + B_M}{2} \tag{10}$$

As shown in Table 3, the calculated and experimental bulk moduli of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$ are listed, which shows good agreement between the calculated and experimental values. The calculated results have proven that $MgAl_2O_4$ has a possibly similar bulk modulus of about 200 GPa.[31,33]

Thermal Expansion Coefficient Calculation. The thermal expansion of a crystal is closely related to the thermal expansion of constituted chemical bonds.[17,18,22,30] Because the thermal expansion of a bond is related to the increase in the

Table 3. Experimental and Calculated Bulk Moduli and Thermal Expansion Coefficients of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ Compared with Those of $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$

	$MgAl_2O_4$		$Mg_{0.268}Al_{2.577}O_{3.733}$-$N_{0.267}$		$Al_{2.85}O_{3.45}N_{0.55}$	
property	exp[31,37]	cal	exp	cal	exp[37,39]	cal
B_v^T (GPa)		121(3)		192(5)		229(5)
B_v^M (GPa)		269(4)		257(4)		262(4)
B_T (GPa)		121(3)		192(5)		229(5)
B_M (GPa)		269(5)		237(4)		243(4)
B_{Cal} (GPa)	~190	195(3)	201(3)	215(3)	~215	236(3)
α_v^T (10^{-6} K^{-1})		5.9(1)		4.1(1)		3.6(1)
α_v^M (10^{-6} K^{-1})		6.3(1)		6.5(1)		6.3(1)
α_{Cal} (10^{-6} K^{-1})	~6.97	6.3(1)	6.1(2)	6.0(1)	~5.66	5.8(1)

amplitude of the atomic vibrations along the direction of the bond, the expression for the thermal expansion coefficient of a chemical bond (α_v) can be deduced according to the distortion theorem based on the bond valence method given by[22,34]

$$\alpha_v = \frac{1.35k}{F_c R_{ij}} \tag{11}$$

where k is the Boltzmann constant. According to the calculated bond force constants F_c^T and F_c^M, the thermal expansion coefficients of constituted tetrahedral (α_v^T) and octahedral (α_v^M) site chemical bonds could be obtained in spinel-type crystals, respectively. However, the coupled effects of the tetrahedral and octahedral frameworks on the thermal expansion of crystals need to be considered in spinel-type crystals. In spinel-type structures, the majority of cations occur in octahedra, which shares edges to form a continuous framework. The octahedral bond length thus determines the size of the framework, and the thermal expansion of a spinel-type crystal is mainly determined by the thermal expansion of chemical bonds in the octahedrally coordinated sites.[30,32] In addition, cation vacancies in the octahedral sites also have an impact on the thermal expansion. The thermal expansion coefficient (α_{Cal}) of a spinel-type crystal is closely related to α_v^M and could be calculated by

$$\alpha_{Cal} = q{\alpha_v}^M = q\frac{1.35k}{F_c^M R_M} \tag{12}$$

The calculated and experimental thermal expansion coefficients of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$ are shown in Table 3. There is good agreement between the calculated and experimental values, which indicates the validity of this method to quantitatively estimate the thermal expansion coefficients of complex spinel-type crystals.

CONCLUSIONS

In summary, new empirical methods by the bond force constants based on bond valences are developed to estimate the compressibility and thermal expansion of complex spinel-type crystals, which is successful in $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ as well as $MgAl_2O_4$ and $Al_{2.85}O_{3.45}N_{0.55}$. The simple and feasible scheme is proposed to present these empirical methods. First, the chemical composition and crystal structure are determined. Then, the composition-weighted average of bond valences and bond force constants in tetrahedral and octahedral coordination polyhedra are calculated. Finally, for spinel-type crystals, the bulk modulus is quantitatively calculated by the average of B_T and B_M derived from S_T and S_M, and the thermal expansion coefficient is quantitatively estimated by α_v^M derived from S_M. Further, our scheme to present the empirical methods could also have potential use in other types of complex crystals such as perovskites and garnets, in which it is critical to analyze the coupled effects of frameworks with different coordination polyhedra. These empirical methods would contribute to setting up relationships among the composition, structure, and intrinsic properties of complex crystals and give useful clues for material design.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Rietveld refinement results of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ from X-ray data, detailed introduction of the structure model of spinel-type solid solutions, detailed computational formula of the composition-weighted average of bond valences and bond valence sums for $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$, and IR absorption spectra of $Mg_{0.268}Al_{2.577}O_{3.733}N_{0.267}$ powders. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Ishida, Y.; Baba, T.; Eguchi, R.; Matsunami, M.; Taguchi, M.; Chainani, A.; Senba, Y.; Ohashi, H.; Okamoto, Y.; Takagi, H. *Phys. Rev. B* **2009**, *80*, 081103.

(2) Dekkers, M.; Rijnders, G.; Blank, D. H. *Appl. Phys. Lett.* **2007**, *90*, 021903.

(3) Xiao, J.; Chen, X.; Sushko, P. V.; Sushko, M. L.; Kovarik, L.; Feng, J.; Deng, Z.; Zheng, J.; Graff, G. L.; Nie, Z. *Adv. Mater.* **2012**, *24*, 2109−2116.

(4) Scheffe, J. R.; Li, J.; Weimer, A. W. *Int. J. Hydrogen Energy* **2010**, *35*, 3333−3340.

(5) Sickafus, K. E.; Wills, J. M.; Grimes, N. W. *J. Am. Ceram. Soc.* **1999**, *82*, 3279−3292.

(6) Duan, X.; Yuan, D.; Yu, F. *Inorg. Chem.* **2011**, *50*, 5460−5467.

(7) Schwarz, M.; Zerr, A.; Kroke, E.; Miehe, G.; Chen, I. W.; Heck, M.; Thybusch, B.; Poe, B. T.; Riedel, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 789−793.

(8) Sheldon, R. I.; Hartmann, T.; Sickafus, K. E.; Ibarra, A.; Scott, B. L.; Argyriou, D. N.; Larson, A. C.; Dreele, R. B. *J. Am. Ceram. Soc.* **1999**, *82*, 3293−3298.

(9) Le Nestour, A.; Gaudon, M.; Villeneuve, G.; Andriessen, R.; Demourgues, A. *Inorg. Chem.* **2007**, *46*, 2645−2658.

(10) Stevanovic, V.; d'Avezac, M.; Zunger, A. *J. Am. Chem. Soc.* **2011**, *133*, 11649−11654.

(11) Nakatsuka, A.; Ikeda, Y.; Yamasaki, Y.; Nakayama, N.; Mizota, T. *Solid State Commun.* **2003**, *128*, 85−90.

(12) Andreozzi, G. B.; Princivalle, F.; Skogby, H.; Della Giusta, A. *Am. Mineral.* **2000**, *85*, 1164−1171.

(13) Hazen, R. M.; Navrotsky, A. *Am. Mineral.* **1996**, *81*, 1021−1035.

(14) Buchanan, R. C.; Taeun, P. *Materials Crystal Chemistry*; Marcel Dekker, Inc.: New York, 1997.

(15) Ching, W.; Mo, S. D.; Tanaka, I.; Yoshiya, M. *Phys. Rev. B* **2001**, *63*, 064102.

(16) Ouyang, L.; Ching, W. *Appl. Phys. Lett.* **2002**, *81*, 229−231.

(17) Li, H.; Zhang, S.; Zhou, S.; Cao, X. *Inorg. Chem.* **2009**, *48*, 4542−4548.

(18) Zhang, S.; Zhou, S.; Li, H.; Li, L. *Inorg. Chem.* **2008**, *47*, 7863−7867.

(19) Cohen, M. L. *Phys. Rev. B* **1985**, *32*, 7988−7991.

(20) Hazen, R. M.; Finger, L. W. *J. Geophys. Res.: Solid Earth* **1979**, *84*, 6723−6728.

(21) Hazen, R. M.; Prewitt, C. T. *Am. Mineral.* **1977**, *62*, 309−315.

(22) Brown, I. D.; Dabkowski, A.; McCleary, A. *Acta Crystallogr., Sect. B: Struct. Sci.* **1997**, *53*, 750−761.

(23) Brown, I. D.; Klages, P.; Skowron, A. *Acta Crystallogr., Sect. B: Struct. Sci.* **2003**, *59*, 439−448.

(24) Xu, B.; Wang, Q.; Tian, Y. *Sci. Rep.* **2013**, *3*, 3068.

(25) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128−131.

(26) Gordy, W. *J. Chem. Phys.* **1946**, *14*, 305−320.

(27) Hill, F.; Gibbs, G.; Boisen, M. B., Jr. *Struct. Chem.* **1994**, *5*, 349−355.

(28) Waser, J.; Pauling, L. *J. Chem. Phys.* **1950**, *18*, 747−753.

(29) Sirdeshmukh, D.; Subhadra, K. *J. Mater. Sci.* **2005**, *40*, 1553−1570.

(30) Megaw, H. D. *Mater. Res. Bull.* **1971**, *6*, 1007−1018.

(31) Finger, L. W.; Hazen, R. M.; Hofmeister, A. M. *Phys. Chem. Miner.* **1986**, *13*, 215−220.

(32) Jiang, J.; Lindelov, H.; Gerward, L.; Ståhl, K.; Recio, J.; Mori-Sanchez, P.; Carlson, S.; Mezouar, M.; Dooryhee, E.; Fitch, A. *Phys. Rev. B* **2002**, *65*, 161202.

(33) Recio, J.; Franco, R.; Pendás, A. M.; Blanco, M.; Pueyo, L.; Pandey, R. *Phys. Rev. B* **2001**, *63*, 184101.

(34) Brown, I. D. *the Chemical Bond in Inorganic Chemistry: the Bond Valence Model*; Oxford University Press: New York, 2006.

(35) Brown, I. D. *Chem. Rev.* **2009**, *109*, 6858−6919.

(36) Liu, X.; Wang, H.; Tu, B. T.; Wang, W. M.; Fu, Z. Y. *J. Am. Ceram. Soc.* **2014**, *97*, 63−66.

(37) Bass, M. *Handbook of Optics, Vol. II: Devices, Measurements and Properties*; McGraw-Hill, Inc.: New York, 1995.

(38) Willems, H.; De With, G.; Metselaar, R.; Helmholdt, R.; Petersen, K. *J. Mater. Sci.* **1993**, *12*, 1470−1472.

(39) Willems, H.; Van Hal, P.; Metselaar, R. *J. Mater. Sci.* **1993**, *28*, 6185−6189.

(40) Rodriguez-Carvajal, J. *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr*; Toulouse, France, 1990; IUCr: Bordeaux, France, 1990; p 127.

(41) Lavina, B.; Salviulo, G.; Della Giusta, A. *Phys. Chem. Miner.* **2002**, *29*, 10−18.

(42) Shannon, R. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751−767.

(43) Salinas, S. A.; Garcia, M. J.; Rodriguez, C. J.; Saez, P. R.; Martinez, J. *J. Solid State Chem.* **1992**, *100*, 201−211.

(44) Xie, R. J.; Hirosaki, N.; Liu, X. J.; Takeda, T.; Li, H. L. *Appl. Phys. Lett.* **2008**, *92*, 201905.

(45) Takeda, T.; Xie, R. J.; Hirosaki, N.; Matsushita, Y.; Homma, T. *J. Solid State Chem.* **2012**, *194*, 71−75.

(46) Brese, N. E.; O'keeffe, M. *Acta Crystallogr., Sect. B: Struct. Sci.* **1991**, *47*, 192−197.

(47) Duan, X.; Wang, X.; Yu, F.; Liu, X. *Mater. Chem. Phys.* **2012**, *137*, 652−659.

(48) Tu, B. T.; Wang, H.; Liu, X.; Wang, W. M.; Fu, Z. Y. *J. Am. Ceram. Soc.* **2013**, *96*, 1937−1943.

(49) Nfor, E. N.; You, X. Z.; Wei, L.; Iniama, G. *Acta Crystallogr., Sect. E: Struct. Rep.* **2006**, *62*, 379−381.

(50) Lufaso, M. W.; Woodward, P. M. *Using Bond Valences to Model the Structures of Ternary and Quaternary Oxides*; Springer-Verlag: Berlin, 2013.

(51) Grimes, N.; Collett, A. *Phys. Status Solidi B* **1971**, *43*, 591−599.

(52) Li, K.; Ding, Z.; Xue, D. *Phys. Status Solidi B* **2011**, *248*, 1227−1236.