Lattice Vibrational Characteristics and Structures-Properties Relationships of Non-Stoichiometric Nd[Mg_{0.5}Sn_{0.5}(1+x)]O₃ Ceramics

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Lattice vibrational characteristics and Structures-properties Relationships of non-stoichiometric $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.5(1+x)}]\text{O}_3$ ceramics

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Abstract: Non-stoichiometric $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.5(1+x)}]\text{O}_3$ ($-0.04 \leq x \leq +0.04$) - type samples were prepared using a traditional two-step solid-state sintering process. Their crystal structures, phase compositions, dielectric properties and lattice vibrational characteristics were identified in detail. Double perovskite $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ with a monoclinic structure was distinguished as the main crystalline phase, pure phase was obtained when $x < 0$, and the sample $[\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.49})\text{O}_3]$ at $x = -0.02$ shows the excellent dielectric properties: $\varepsilon_r = 18.74$, $Q \times f = 47,979$ GHz. Lattice vibrational

characteristics were clarified with Raman and infrared active modes assigned and illuminated, accurately. The intrinsic properties were fitted by four-parameter semi-quantum model, which show that the low-frequency infrared modes yield a more significant contribution to permittivity and dielectric loss. Raman shifts of modes $F_{2g}(A)$ and $F_{2g}(B)$ correlate with dielectric constants negatively, which implies that the bond length has a positive correlation with permittivity. Full widths at half maximum of vibrational modes $A_{1g}(O)$ correlate with dielectric loss values positively and correlate with the degree of order (S) negatively.

Keywords: Microwave dielectric ceramics; Double perovskite; Non-stoichiometry; Lattice vibrational characteristics; Structures-properties relationships;

1. Introduction

Microwave dielectric ceramics (MWDCs) have been widely used as application-driven materials for the manufacture of various microwave components, which are also fundamental to modern microwave communication, such as mobile communication, satellite communication, global positioning system, and wireless local area network¹⁻³. With the advent of 5G mobile communication, people expect mobile communication networks to have fast transmission rates and high quality of service. Correspondingly, the properties of MWDCs used in the field of 5G front-end radio frequency devices must be improved⁴⁻⁵.

Rare-earth based double perovskite MWDCs with formula of $A(B'_{0.5}B''_{0.5})O_3$ (A = La, Nd, Pr, Sm, Dy, Y, etc.; B' = Mg, Zn, Co, etc.; B'' = Sn, Ti, etc.) exhibit lower

permittivity ϵ_r , lower dielectric loss ($\tan\delta=1/Q$, *i.e.*, higher quality factor $Q \times f$) and controllable temperature coefficient of resonant frequency (τ_f), and thus have potential applications in next-generation communication systems⁶⁻⁷. Babu *et al*⁸. characterized the crystal structures of $\text{La}(\text{MgSn})_{0.5}\text{O}_3$ ceramic and achieved dielectric properties ($\epsilon_r = 20.1$; $Q \times f = 63,000 \text{ GHz}$; and $\tau_f = -78 \text{ ppm/}^\circ\text{C}$). Chen *et al*⁹. lowered the sintering temperature of $\text{Nd}(\text{Mg}_{1/2}\text{Sn}_{1/2})\text{O}_3$ by adding B_2O_3 as a sintering aid, and when the amount of B_2O_3 was 0.25 wt.%, the optimal dielectric properties were achieved ($\epsilon_r = 18.9$; $Q \times f = 32,300 \text{ GHz}$; $\tau_f = -52 \text{ ppm/}^\circ\text{C}$) after sintered at 1500°C for 4 h.

Previous researches on rare-earth based $\text{A}(\text{B}'_{0.5}\text{B}''_{0.5})\text{O}_3$ -type MWDCs are mostly concentrated on the basic structures of pure phase ceramics, lowering sintering temperature by sintering aid, and enhancing property by doping, but few research focused on the influence of nonstoichiometry on the crystal structures and dielectric properties, especially non-stoichiometric $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ system. In fact, the change in composition can affect the structures and properties significantly. Research on the non-stoichiometric $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ ceramics contributes to understand the composition control, defect chemistry, crystal structures, dielectric properties, and performance regulation of rare-earth based $\text{A}(\text{B}'_{0.5}\text{B}''_{0.5})\text{O}_3$ -type MWDCs.

In addition, Raman scattering spectroscopy and far-infrared reflection spectroscopy were often used to investigate the lattice vibrational characteristics of solid-state materials¹⁰⁻¹³, which helps to analyze macroscopic properties from a microscopic perspective and provides more innovative perspectives in inherent

attribute and structure-property regulation. For example, Zhou *et al*¹⁴. have examined the structure-property relationships of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ($0.4 \leq x \leq 1.0$) ceramics based on the Raman spectroscopy and far-infrared spectroscopy. Lu *et al*¹⁵. classified the vibrational modes of spinel-structured $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ceramics and also discussed the structure-property relationships. Xing *et al*¹⁶. have calculated the intrinsic properties of scheelite structure MWDCs $\text{Ba}_{1+x}\text{MoO}_4$ ($-0.03 \leq x \leq 0.03$) samples by fitting the far-infrared reflectivity spectra and revealed the internal relationship of the structure-property by changing Ba^{2+} content according to the Raman modes.

All in all, the researches on the structures-properties relationships for the non-stoichiometric $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ ceramics based on the analysis of the lattice vibrational characteristics are important both in basic theories and practical application. In our group, Zhang *et al*¹⁷. and Cao *et al*¹⁸ have combined the phonon modes to establish the structure-property relationship of the non- stoichiometric $\text{Nd}(\text{Mg}_{0.5(1+x)}\text{Sn}_{0.5})\text{O}_3$ and $\text{Nd}_{(1+x)}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ ceramics with the change of Mg^{2+} content on the B'-site and Nd^{3+} content on the A-site, respectively. However, quadrivalent Sn^{4+} ions, located on the B''-site in $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ samples, are different from bivalent Mg^{2+} ions and trivalent Nd^{3+} ions in terms of atomic structures and physical properties, which also have great influence on their correlations of structures-properties and also affect their lattice vibrational characteristics. That is, about non-stoichiometric $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.5(1+x)}]\text{O}_3$ ceramics with varying Sn^{4+} content, we know little about their intrinsic properties and inherent attribute, which hinders the deep understanding and practical applications of $\text{A}(\text{B}'_{0.5}\text{B}''_{0.5})\text{O}_3$ -type MWDCs.

In the current work, non-stoichiometric rare-earth based $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.5(1+x)}]\text{O}_3$ (NMS, $-0.04 \leq x \leq +0.04$) samples were prepared using a conventional two-step solid-state sintering process. The crystal structures and phase components of the ceramics were characterized by X-ray diffraction (XRD) with the surface topographies being observed by scanning electron microscope (SEM). The Raman and far-infrared (FIR) spectra of NMS ceramics were construed at length based on the group theory and the space group information so as to obtain their lattice vibrational characteristics¹⁹. The intrinsic properties were derived from the fitting of FIR peaks by a four-parameter semi-quantum (4-P) model, which were compared with the measured property values as well as the predicted values from Clausius-Mossotti equation (C-M) based on polarizability, respectively. In addition, the reliability of the 4-P model fitting results was confirmed by Kramers–Krönig (K–K) interactive conversion relations, and the influence of the lattice vibration on the dielectric response was evaluated. Finally, the structure-property correlations were established using Raman active phonon modes as a media so as to contribute to the design of new-type MWDCs from the perspective of material science as a further study basen on the previous results^{17,18}.

2. Experimental

Non-stoichiometric $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.5(1+x)}]\text{O}_3$ ($-0.04 \leq x \leq +0.04$) MWDCs were prepared by routine two-step solid-state sintering method with high-purity starting materials of Nd_2O_3 (99.9%), $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (99.8%), and SnO_2 (99.8%), which were first mixed in a polyethylene tank for 6 h, then dried in electric blast

drying oven, and calcined at 1200 °C for 4 hours. The calcined powders were milled and next dried for the second time. Subsequently, 5% polyvinyl alcohol (PVA) solution were added to these powders as a binder, and then the mixed powders were pressed into disks with a size of 10 mm × 6 mm under 100 MPa, which were finally sintered at 1500 °C for 4 hours. All sintered disks were grinded and polished carefully using Al₂O₃ slurry prior to the measurement, which were rubbed off by about 20 μm.

The Archimedes measurement technique was used to determine the bulk density of the samples. X-ray diffraction (XRD, D/max-2000V, Rigaku, Japan) with Cu-K_α incident radiation was applied to analyze the compositions and structures of MWDCs, and the XRD data were collected at a range of 10° ~ 80° with the step size of 0.02°. The surface topographies of NMS cermics were characterized by scanning electron microscope (SEM, Nova Nano SEM45). The actual properties of the sintered MWDCs were tested with a network analyzer (E8363B, Agilent). The ϵ_r and Q values were determined by the Hakki-Coleman dielectric resonator method²⁰. Raman spectra were obtained applying an XperRam Compact spectrometer (Nanobase) at room temperature, and a 633 nm laser line was used as excitation source. Far-infrared reflectivity spectra were recorded at room-temperature by Fourier-transform infrared spectrometry (IFS 66v/s Vacuum, Bruker Optik GmbH, Ettlingen, Germany), which were collected based on a PE-DTGS (Bruker, Ettlingen, Germany) detector and a Mylar beamsplitter. For the mid-infrared region, a DTGS detector and a Ge-coated KBr beamsplitter (Bruker) were used.

3. Results and discussion

Fig. 1 presents the XRD patterns of the NMS samples sintered at 1500 °C for 4 hours. $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ (indexed to JCPDS #16-1439) can be clearly distinguished as the main crystalline phase, which belongs to a monoclinic crystal structure ($\text{P2}_1/\text{n}$ space group) with a double perovskite structure. When $x < 0$, no secondary phase is observed. However, it's worth noting that a small amount of $\text{Nd}_2\text{Sn}_2\text{O}_7$ (indexed to JCPDS #54-1268) is detected as a secondary phase when $x \geq 0$, and the relative intensity of $\text{Nd}_2\text{Sn}_2\text{O}_7$ peaks increases continuously with the increase in the x value, which indicates that the amount of the secondary phase increases with increasing Sn^{4+} content. The reason is that Mg^{2+} can volatilize at higher sintering temperature during the reaction process, but excess Sn^{4+} can promote the generation of the secondary phase. (100) and $1/2(210)$ peaks move to lower angles from -0.04 to -0.02 and then to higher angles from -0.02 to +0.04, as shown in the inset figure, which indicates that the lattice volume of the samples increases first from -0.04 to -0.02 and then decreases from -0.02 to +0.04.

Some additional peaks, such as $1/2(111)$, are illustrated by half-integer Miller indices, which are closely related to the ordered arrangement of the B-site cations²¹ and belong to superlattice reflection peaks. The ordered parameter (S) can be calculated using the following formula (1)²².

$$S = \sqrt{\frac{\left(\frac{I_{1/2(210)}}{I_{110}}\right)_{exp.}}{\left(\frac{I_{1/2(210)}}{I_{110}}\right)_{theo. S=1}}} \quad (1)$$

Where I_i is the intensity of a given peak, the “*exp*” and “*theo*” represents the experimental and theoretical value, respectively. The lattice structure is fully ordered when $S = 1$.

TOPAS software was used to perform Rietveld refinement so as to obtain the fine structural parameters of NMS systems. Table 1 shows the detailed structural parameters after Rietveld refinement, including lattice parameters, space group information, R-factors and ordered parameters (S) of NMS ceramics.

The refinement pattern of $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.49})\text{O}_3$ ($x = -0.02$) is presented in Fig. 2a as an example. The refined and collected diffraction profiles are coincident, as proved by the low amplitude of the difference line (green line in Fig. 2a). The effects of the Rietveld refinement could be mirrored by reliable factors (R_{wp} , R_{p} , and GOF were 6~10%, 4~6%, and 1.1~1.6, respectively), which indicates a satisfied reliability for the fine structural data. Moreover, the curves of the lattice parameters of the main crystal phase vary with x is provided in Fig. 2b.

As shown in Fig. 2b, the fine structural parameters of the main crystal phases vary with the Sn^{4+} content, which maybe caused by the vacancy defects due to the volatilization of Mg^{2+} ions and the replacement of Mg^{2+} ions by Sn^{4+} ions. With increasing Sn^{4+} content from -0.04 to -0.02, Sn^{4+} occupies some Mg^{2+} vacancies, the number of Mg^{2+} vacancy defects decreases, and the lattice parameters as well as the unit cell volumes raise, they next slightly decrease from -0.02 to 0.01. A possible explanation is that the Mg^{2+} ions may be replaced by excess Sn^{4+} ions to form a solid

solution, because the radius of Sn^{4+} (0.69 Å) is slightly smaller than that of Mg^{2+} (0.72 Å), and the difference between these two radii is about 4.2%, less than 15%, and accordingly, the slight lattice distortion is formed own to this subtle difference. That is, the maximum cell volume appears at $x = -0.02$. When $x \geq 0.01$, more secondary phases are formed, which causes excessive Sn^{4+} ions to be consumed, so the lattice parameters and unit cell volumes show no significant change.

Table 2 lists all atomic Wyckoff positions of single phase NMS sample, and Fig. 3a shows its unit cell representation, based on the refined lattice parameters in Table 1 and the atomic Wyckoff positions in Table 2. As shown in Fig. 3a, Sn and Mg atoms are distributed along $B':B'' = 1:1$ order in the unit cell, and as a result, form an Sn/Mg-oxygen octahedron structure with the adjacent six oxygen atoms. Fig. 3b shows the Mg^{2+} ions vacancy and the substitution of the Mg^{2+} ions by excess Sn^{4+} ions in the surface (001), respectively. Figs. 3c–3d exhibit the surface (010) of single phase NMS ceramic and the secondary phase of $\text{Nd}_2\text{Sn}_2\text{O}_7$.

The ball-and-stick model in Fig. 3a shows the three kinds of O with six kinds of Mg/Sn–O bond. The deviation of the octahedron in the crystal structure from a regular octahedron (Δ) can be estimated from the individual bond length (R_i) by using the following equation (2)²³:

$$\Delta = \frac{1}{6} \sum \left(\frac{R_i - \bar{R}}{\bar{R}} \right)^2 \quad (2)$$

where $\bar{R}$ denotes the average bond length of oxygen octahedron. To explain the preceding analysis, the bond information, the average bond length and the calculated

Δ was obtained and listed in Table 3.

To better analyze the results, the bond length and deviation of the octahedron variation curves were generated in Fig. 4, which shows no significant changes in the lengths of Mg/Sn-O3(1) and Mg/Sn-O3(2); thus, the fluctuation in the average bond length is mainly attributable to the changes of the other four bond lengths.

The average bond length increases from -0.04 to -0.02, slightly decreases from -0.02 to +0.02, and eventually remains stable after $x = +0.02$, however, the change for the distortion of octahedron is opposite to the variation of bond length. Moreover, considering the correlation between the bond length and the polarizability, the binding force weakens between the nucleus and electron in a chemical bond with the bond length increasing, at the same time, the polarizability increases²⁴, which results in an increasing dielectric constant, correspondingly.

Fig. 5 presents the scanning electron micrographs of the fractured surfaces of the NMS ceramics, which show fine crystal grains with clearly distinguished grain boundaries. When $x \leq -0.02$, the grains are fine and uniform with an average size of about 2–3 μm . When $x \geq -0.02$, the grain size slightly increases with micropores formed. That is, the sample when $x = -0.02$ possesses the highest crystalline quality.

Fig. 6 shows the change of relative density, permittivity, and quality factor of NMS ceramics with different Sn^{4+} content.

All samples, as shown in Fig.6, exhibit high densification, *i.e.*, relative density exceeding 96% when $x < 0$. The relative density markedly decreases with the

appearance of the secondary phase at $x \geq 0$ (Fig. 6a), which is consistent with the microstructure observed by SEM in Fig. 5. The change in the permittivity and the quality factor complies with the density as a function of x , and the sample exhibits the best dielectric properties at $x = -0.02$. Table 4 lists both the relative density values and the dielectric property values of the NMS ceramics.

As shown in Table 4, the corrected dielectric constant, $\varepsilon_{r(cor)}$, can be calculated using formula (3)²⁵⁻²⁶ based on the measured ε_r and the porosities (P) of the samples, where the porosity can be obtained according to the relative density value of each sample.

$$\varepsilon_r = \varepsilon_{r(cor)} \left(1 - \frac{3P(\varepsilon_{r(cor)} - 1)}{2\varepsilon_{r(cor)} + 1} \right) \quad (3)$$

According to the equation (3), the porosity affects the dielectric constant values of the material, *i.e.*, the larger the porosity, the smaller the dielectric constant.

Changes in the interior of ceramic crystals, such as the distortion of oxygen octahedron and the variation in the degree of order, can be reflected in their lattice vibrational spectra. Detailed information about the vibrational modes can be expressed as equation (4) according to the group theory as well as the crystallographic data of ceramics.

$$\Gamma_{\text{optic}} = 12A_g + 23A_u + 12B_g + 22B_u \quad (4)$$

Fig. 7 presents the Raman scattering spectra of NMS ceramics from 50 cm⁻¹ to

800 cm^{-1} . As shown in Fig. 7a, the Raman spectra of the samples are similar, the baseline is flat, and the vibrational peaks can be easily distinguished. Depending on the results of group theory analysis, ceramic crystals with the space group $P2_1/n$ should have 24 Raman active vibrational modes ($12A_g+12B_g$). However, in the actual Raman spectra, only 12 vibrational modes are observed because of the interaction of Raman active peaks as well as the influence of the facility resolution.

The vibrational modes in the 100–270 cm^{-1} are attributed to A-site cations (Nd^{3+}), which are similar to the results in Refs²⁷⁻²⁸, the modes $F_{2g}(B)$ in the 270–460 cm^{-1} represent the 1:1 ordered phase on B-site, whereas modes 11 and 12 belong to the oscillation of oxygen atoms. When $x \geq 0$, a new Raman peak around 530 cm^{-1} (named new mode) appears and the intensity increases as increasing Sn^{4+} content, which maybe related to the formation of the secondary phase. Peak 12 near 660 cm^{-1} is assigned to the $A_{1g}(O)$ mode, which conforms with the symmetrical breathing of oxygen octahedron. In addition, the full width at half-maximum value (FWHM) of the $A_{1g}(O)$ mode depends mainly on the ordered degree of the B-position cation.

To further observe the distinct change in Raman modes, the local variation in each peak is exhibited in Figs. 7b–7d. To analyze the vibrational modes accurately, peak fitting was conducted with the Lorentz function in LabSpec software, as shown in Fig. 7e, and the related frequency/FWHM parameters of the representative modes are listed in Table 5. As shown in Figs. 7b–7e and Table 5, the Raman shifts of mode 1 and mode 9 as well as the FWHM of mode 12 after Lorentz fitting have the lowest values for the sample at $x = -0.02$.

According to the space group analysis²⁹, the space group P2₁/n has 45 infrared active modes (23A_u+ 22B_u) and 7 available effective modes, as shown in Fig. 8. The peaks near 100–200, 200–550, and 620 cm⁻¹ can be attributed to the A–BO₆ translation modes, M–O–B stretching modes (octahedron external modes) and B–O₆ bending modes (octahedron internal modes), respectively. The intensities of F₁ modes near 110 cm⁻¹ increase with increasing Sn⁴⁺ content, and the modes in the 200–550 cm⁻¹ range verify the presence of ion ordering on the B-site in the samples.

Infrared spectroscopy provides a deep insight into the dielectric response mechanism. Fig. 8 also presents the fitted IR spectra according to the 4-P model. The correlation between the IR spectrum [R(ω)] and the complex permittivity (ε*) is described in Formula (5). Besides, the intrinsic properties can be fitted efficiently according to the 4-P model, and the complex permittivity is defined in Equation (6)³⁰:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon^*} - 1}{\sqrt{\varepsilon^*} + 1} \right|^2 \quad (5)$$

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty \prod_{j=1}^n \frac{\Omega_{jLO}^2 - \omega^2 + i\omega\gamma_{jLO}}{\Omega_{jTO}^2 - \omega^2 + i\omega\gamma_{jTO}} \quad (6)$$

where the optical permittivity (ε_∞) only arises from electronic polarization at extremely high frequencies; *n* indicates the number of phonon modes; the frequency and damping factors of the *j*_{th} transverse mode are denoted by Ω_{*j*TO} and γ_{*j*TO}, respectively. Ω_{*j*LO} means the frequency of the longitudinal mode, and γ_{*j*LO} shows the damping factor of the longitudinal mode⁶. The calculated parameters based on 4-P model are shown in Table 6, taking the ceramic where *x* = -0.02 as an example.

The measured and fitted IR spectra of the sample $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.49})\text{O}_3$ are presented in Fig. 9a. To confirm the results obtained using FOCUS software, the real part (ϵ'), imaginary part (ϵ''), and $(\epsilon^{-1})''$ are independently calculated using the Kramers–Krönig (K–K) relationship³¹. The transverse optical mode (TO) and the longitudinal optical mode (LO) can be obtained using ϵ'' and $(\epsilon^{-1})''$ and then compared with the original fitting values. As shown in Fig. 9b, 9c, the K–K conversion results with $x = -0.02$ are given, all peaks of the sample maintain good consistency, which confirms the feasibility of the 4-P model and the reliability of the fitted results.

Based on the results of infrared spectrum fitting, the values (the real part and the imaginary part of the dielectric constants) calculated by extrapolating conform with the measured values, as shown in Fig. 9d, implying that the absorption of phonons in the IR region can cause the dielectric polarization. When the infrared spectrum is extrapolated to the microwave region, the fitting results comply well with the actual measured values. As shown in Fig. 9d, the calculated $Q \times f$ (49404 GHz, $f=12.6$ GHz) value of sample $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.49})\text{O}_3$ ($x = -0.02$) is similar to the measured value (47979 GHz, 12.6 GHz).

The dielectric contribution of the j_{th} modes can be calculated applying the following equation¹⁹.

$$\epsilon_j = \frac{\epsilon_\infty}{\Omega_{jTO}^2} \frac{\prod_{k=1}(\Omega_{kLO}^2 - \Omega_{jTO}^2)}{\prod_{k \neq j}(\Omega_{kTO}^2 - \Omega_{jTO}^2)} \quad (7)$$

$$\tan \delta_j / \omega = \frac{\epsilon_j \gamma_{jTO} / \Omega_{jTO}^2}{\epsilon_\infty + \sum_j \epsilon_j} \quad (8)$$

On the basis of the calculation results (as shown in Table 6), the low-frequency infrared active modes yield a more significant effect to the permittivity and dielectric loss, for example, the peak F_5 has the greatest contribution to the former property value, *i.e.*, dielectric constant, while the peak F_3 possesses the greatest contribution to the latter property value, *i.e.*, dielectric loss.

Permittivity and dielectric loss values fitted by 4-P mode agree well with the tested values, as compared with Table 4 and Table 7, which also prove the reliability of the fitting results.

Generally speaking, Raman mode is only relative to the crystal structure of the material, but the previous research can indirectly reflect the dielectric properties³². That is, Raman active modes can be applied as a media to bulid a structure-property relationship³³. The relationships between the average length ($\bar{R}$) of Mg/Sn-O bonds, the Raman shifts (frequencies) of the $F_{2g}(A)$ and $F_{2g}(B)$ active modes and the dielectric constants (ϵ_r) are presented in Fig. 10. With increasing Sn^{4+} content, the Raman modes initially shift to a lower wavenumber from -0.04 to -0.02 and then shift to higher wavenumber from -0.02 to +0.04, that is, the ϵ_r value has a remarkable negative relationship with Raman shift of $F_{2g}(A)/F_{2g}(B)$ mode, respectively, which perhaps is caused by the positive relationship between the Raman shifts of the $F_{2g}(A)/F_{2g}(B)$ modes and the bond energies of Mg/Sn-O¹⁵. When Raman active modes turn to left side, *i.e.*, lower shifts, the bond lengths of the Mg/Sn-O bonds increase and their bond energies decrease accordingly, which make the cell volume and the

electron mobility space increase. Subsequently, larger polarizabilities exist in the Mg/Sn-O dipoles, and therefore, the permittivities also increase¹⁵.

The correlation between the FWHM value of mode $A_{1g}(O)$ at about 658 cm^{-1} and the dielectric loss of the NMS system was established as shown in Fig. 11. With increasing Sn^{4+} content, the minimum FWHM value is obtained at $x = -0.02$. The smaller the FWHM value is, the higher the degree of order (S) on the B-site cation is, and also the smaller the dielectric loss. That is, the dielectric loss correlates with the FWHM value of mode $A_{1g}(O)$ positively and with the degree of order (S) negatively.

In short, the dielectric properties of the NMS sample at $x = -0.02$ achieve the best dielectric property values of $\varepsilon_r = 18.74$, $Q \times f = 47979\text{ GHz}$, $f = 12.6\text{ GHz}$.

Conclusion

Non-stoichiometric NMS systems were prepared by a traditional two-step solid-state sintering method, whose dielectric properties, phase composition, crystal structures and vibrational modes were identified and measured in particular. The secondary phase $\text{Nd}_2\text{Sn}_2\text{O}_7$ appears in the ceramics when $x \geq 0$ with an increase in pore number, whereas the pure phase $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ is obtained when $x < 0$. Rietveld refinement of XRD data shows that the lack of Sn^{4+} introduces vacancy defects in the crystal, and with increasing Sn^{4+} content, Sn^{4+} occupies some vacancies. The Mg^{2+} may be replaced by some Sn^{4+} ions to form solid solution and excess Sn^{4+} ions also promote the formation of the secondary phase, and the slight lattice distortion is formed. Analysis of bonding information for the oxygen octahedron

indicates that the lowest lattice distortion of oxygen octahedron is obtained at $x = -0.02$, which exhibits the excellent dielectric properties ($\epsilon_r = 18.74$, $Q \times f = 47,979$ GHz, $f = 12.6$ GHz). Both Raman and FIR active modes were assigned and illuminated, accurately. The dielectric properties were fitted and calculated according to the infrared spectra base on the 4-P model. The reliability of the fitted results was verified by K–K interaction. When the infrared spectrum is extrapolated to the microwave region, the fitting results agree well with the tested values. Both the Raman shifts of modes $F_{2g}(A)$ and $F_{2g}(B)$ negatively correlate with the dielectric constant values, which implies that the bond length correlates with dielectric constant. The FWHM values of modes $A_{1g}(O)$ positively correlate with the dielectric loss values and negatively correlate with the S values.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References

1. Sebastian, M. T.; Ubic, R.; Jantunen, H., Low-loss dielectric ceramic materials and their properties. *International Materials Reviews* **2015**, *60* (7), 392-412.
2. Liu, B.; Li, L.; Liu, X. Q.; Chen, X. M., Structural Evolution of $\text{SrLaAl}_{1-x}(\text{Zn}_{0.5}\text{Ti}_{0.5})_x\text{O}_4$ Ceramics and Effects on Their Microwave Dielectric Properties. *Journal of Materials Chemistry C* **2016**, *4* (21), 4684-4691.
3. Jie, Z.; Yue, Z.; Li, L., Crystal Structure, Defect Relaxation and Microwave Dielectric Properties of $\text{Ba}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Hf}_x]\text{O}_3$ Solid Solutions. *Journal of the American Ceramic Society* **2018**, *101* (5), 1974-1981.
4. Zhou, D.; Pang, L. X.; Wang, D. W.; Li, C.; Jin, B.; Reaney, I. M., High permittivity, low loss microwave dielectrics suitable for 5G resonator and low temperature co-fired ceramic architecture. *Journal of Materials Chemistry C* **2017**, *5* (38), 1094-1098.
5. Ullah, B.; Lei, W.; Yao, Y. F.; Wang, X. C.; Wang, X. H.; Muneeb-UR-Rehman; Lu, W. Z., Structure and Synergy Performance of $(1-x)\text{Sr}_{0.25}\text{Ce}_{0.5}\text{TiO}_3$ - $x\text{La}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ based microwave dielectric ceramics for 5G architecture. *Journal of Alloys & Compounds* **2018**, *763*, 990-996.
6. Diao, C. L.; Wang, C. H.; Luo, N. N.; Qi, Z. M.; Shao, T.; Wang, Y. Y.; Lu, J.; Wang, Q. C.; Kuang, X. J.; Fang, L., First-principle calculation and assignment for vibrational spectra of $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ microwave dielectric ceramic. *Journal of Applied Physics* **2014**, *115* (11), 787-791.
7. Jo, H. J.; Kim, E. S., Effects of structural characteristics on microwave dielectric properties of $\text{MgTi}_{1-x}(\text{Mg}_{1/3}\text{B}_{2/3})_x\text{O}_3$ (B= Nb, Ta). *Journal of the European Ceramic Society* **2016**, *36* (6), 1399-1405.
8. Babu, S.; SUBRAMANIAN; MURTHY; V., R. K., Structure determination and microwave dielectric properties of $\text{La}(\text{MgSn})_{0.5}\text{O}_3$ ceramics. *Journal of the European Ceramic Society* **2007**, *27* (8), 2973-2976.
9. Chen, Y. C.; Chang, Y. H., Dielectric properties of B_2O_3 -doped $\text{La}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ ceramics at microwave frequencies. *Journal of Alloys & Compounds* **2009**, *477* (1), 450-453.
10. Jing, G.; Di, Z.; Lu, W.; Hong, W.; Tao, S.; Qi, Z. M.; Xi, Y., Infrared spectra, Raman spectra, microwave dielectric properties and simulation for effective permittivity of temperature stable ceramics $\text{AMoO}_4\text{-TiO}_2$ (A = Ca, Sr). *Dalton Transactions* **2013**, *42* (5), 1483-1491.
11. Jiang, S.; Yue, Z.; Feng, S., Effects of BaWO_4 additive on Raman phonon modes and structure-property relationship of $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ microwave dielectric ceramics. *Journal of Alloys & Compounds* **2015**, *646*, 49-55.

12. Babu, G. S.; Subramanian, V.; Murthy, V. R. K.; Lin, I.; Chia, C. T.; Liu, H. L., Far-infrared, Raman spectroscopy, and microwave dielectric properties of $\text{La}(\text{Mg}_{0.5}\text{Ti}_{0.5-x}\text{Sn}_x)\text{O}_3$ ceramics. *Journal of Applied Physics* **2007**, *102* (6), 064906.
13. Hsiang-Lin, L.; Hung-Chung, H.; I-Nan, L.; Ming-Ti, Y.; Wei-Chung, L.; Yi-Chun, C.; Chia-Ta, C.; Hsiu-Fung, C., The dielectric properties of $\text{La}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics studied by Raman-scattering, infrared reflectivity spectroscopy, and first-principles calculations. *Journal of Physics Condensed Matter An Institute of Physics Journal* **2011**, *23* (22), 225901.
14. Zhou, D.; Li, J.; Pang, L. X.; Chen, G. H.; Qi, Z. M.; Wang, D. W.; Reaney, I. M., Crystal Structure, Infrared Spectra, and Microwave Dielectric Properties of Temperature-Stable Zircon-Type (Y, Bi) VO_4 Solid-Solution Ceramics. **2016**, *1* (5), 963–970.
15. Lu, X.; Zheng, Y.; Huang, Q.; Dong, Z., Structural dependence of microwave dielectric properties of spinel-structured $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ceramic: crystal structure refinement and Raman spectroscopy study. *Journal of Electronic Materials* **2016**, *45* (2), 940-946.
16. Xing, C.; Li, J.; Wang, J.; Chen, H.; Qiao, H.; Yin, X.; Wang, Q.; Qi, Z.-m.; Shi, F., Internal Relations between Crystal Structures and Intrinsic Properties of Nonstoichiometric $\text{Ba}_{1+x}\text{MoO}_4$ Ceramics. *Inorganic chemistry* **2018**, *57* (12), 7121-7128.
17. Zhang, J.; Chen, G.; Wang, J.; Li, J.; Xing, C.; Qi, Z.-M.; Shi, F., Crystal structures, intrinsic properties and phonon characteristics of non-stoichiometric $\text{Nd} [\text{Mg}_{1/2(1+x)}\text{Sn}_{1/2}]\text{O}_3$ ceramics. *Journal of Materials Science: Materials in Electronics* **2019**, *30* (3), 2450-2458.
18. Cao, Z.; Xiao, E.-C.; Li, X.-H.; Yue, Z.; Chen, G.; Chen, Y.; Song, K.; Zhou, H.; Qi, Z.; Shi, F., Lattice vibrational characteristics, crystal structures and dielectric properties of non-stoichiometric $\text{Nd}_{(1+x)}(\text{Mg}_{1/2}\text{Sn}_{1/2})\text{O}_3$ ceramics. *Journal of Materiomics* **2020**, *6* (3), 476-484.
19. Li, J.; Wang, J.; Fu, G.; Xing, C.; Yin, X.; Qiao, H.; Chen, H.; Qi, Z.; Wang, Q.; Shi, F., Crystal structure characteristics, intrinsic properties, and vibrational spectra of non-stoichiometric $\text{Ca}_{1+x}\text{WO}_4$ ceramics. *Journal of Applied Physics* **2018**, *124* (4), 044104.
20. Courtney, W. E., Analysis and Evaluation Method of Measuring the Complex Permittivity and Permeability of Microwave Insulators. **1970**, *18* (8), 476-485.
21. Glazer, A. M., Simple Ways of Determining Perovskite Structure. *Acta Crystallographica* **2010**, *31* (6), 756-762.
22. Farber, L.; Valant, M.; Akbas, M. A.; Davies, P. K., Cation Ordering in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PMN-PSN) Solid Solutions. *Journal of the American Ceramic Society* **2010**, *85* (9), 2319-2324.

23. Zhang, J.; Zuo, R., Octahedral distortion, phase structural stability and microwave dielectric properties in equivalently substituted LaTiNbO_6 ceramics. *Journal of the American Ceramic Society* **2017**, *100* (11), 5249-5258.
24. Liu, Z.; Wu, G., Asymmetric environment around the thiourea molecule in aqueous solution as evidenced by the bond polarizability derivatives from Raman intensity. *Chemical Physics* **2005**, *316* (1), 25-28.
25. Wang, Y.; Zuo, R.; Zhang, C.; Zhang, J.; Zhang, T., Low-Temperature-Fired ReVO_4 (Re = La, Ce) Microwave Dielectric Ceramics. *Journal of the American Ceramic Society* **2015**, *98* (1), 1-4.
26. Huang, C. L.; Tseng, Y. W.; Chen, J. Y., High- Q dielectrics using ZnO-modified Li_2TiO_3 ceramics for microwave applications. *Journal of the European Ceramic Society* **2012**, *32* (12), 3287-3295.
27. Qiao, H.; Sun, H.; Li, J.; Chen, H.; Xing, C.; Yang, J.; Dong, H.; Wang, J.; Yin, X.; Qi, Z. M., Structure, Intrinsic properties and Vibrational Spectra of $\text{Pr}(\text{Mg}_{1/2}\text{Sn}_{1/2})\text{O}_3$ Ceramic Crystal. *Scientific Reports* **2017**, *7* (1), 13336.
28. Babu, G. S.; Subramanian, V.; Murthy, V. R. K.; Moreira, R. L.; Lobo, R. P. S. M., Crystal structure, Raman spectroscopy, far-infrared, and microwave dielectric properties of $(1-x)\text{La}(\text{MgSn})_{0.5}\text{O}_3$ - $x\text{Nd}(\text{MgSn})_{0.5}\text{O}_3$ system. *Journal of Applied Physics* **2008**, *103* (8), 2063.
29. Ayala, A. P.; Guedes, I.; Silva, E. N.; Augsburger, M. S., Raman investigation of A_2CoBO_6 (A= Sr and Ca, B= Te and W) double perovskites. *Journal of Applied Physics* **2007**, *101* (12), 385.
30. Diao, C. L.; Wang, C. H.; Luo, N. N.; Qi, Z. M.; Tao, S.; Wang, Y. Y.; Jing, L.; Wang, Q. C.; Kuang, X. J.; Liang, F., First-Principle Calculation and Assignment for Vibrational Spectra of $\text{Ba}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ Microwave Dielectric Ceramic. *Journal of the American Ceramic Society* **2013**, *96* (9), 2898-2905.
31. Siqueira, K. P. F.; Moreira, R. L.; Dias, A., Synthesis and Crystal Structure of Lanthanide Orthoniobates Studied by Vibrational Spectroscopy. *Chemistry of Materials* **2010**, *22* (8), 2668-2674.
32. Shi, F.; Dong, H.-L.; Zhou, D.; Wang, C.-H.; Tan, Q.-L.; Xiong, J.-J.; Wang, Q., Lattice dynamics and phonon characteristics of complex perovskite microwave ceramics. *IET Nanodielectrics* **2019**, *2* (1), 11-26.
33. Achary, S. N.; Patwe, S. J.; Krishna, P. S. R.; Sindhe, A. B.; Tyagi, A. K., Crystal structure analysis of Scheelite and Zircon type thorium germanates: A neutron diffraction study. *Cheminform* **2007**, *438* (1), 274-278.

Table and Figure captions

Table 1. Crystallographic data of NMS ceramics derived from the Rietveld refinement of XRD data.

Table 2. The Wyckoff positions of atoms in the unit cell of $\text{Nd}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$

Table 3. The bond information, the average bond length and the calculated in octahedra of NMS ceramics.

Table 4. Densities and dielectric properties of the NMS samples.

Table 5. Frequency/FWHM parameters obtained from the Lorentz fitting of Raman spectra.

Table 6. Parameters of the IR-Active Modes of $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.49}]\text{O}_3$ ($x = -0.02$) ceramic.

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Table 1. Crystallographic data of NMS ceramics derived from the Rietveld refinement of XRD data.

Formula	<i>x</i> = -0.04	<i>x</i> = -0.03	<i>x</i> = -0.02	<i>x</i> = -0.01	<i>x</i> = 0	<i>x</i> = 0.01	<i>x</i> = 0.02	<i>x</i> = 0.03	<i>x</i> = 0.04
Main crystal phase (wt%)	100	100	100	100	94.76	89.71	84.40	81.19	72.91
Crystal system	Monoclinic								
Space group	P2 ₁ /n								
Lattice parameter <i>a</i> in Å	5.531	5.534	5.537	5.536	5.536	5.535	5.536	5.536	5.535
Lattice parameter <i>b</i> in Å	5.723	5.724	5.726	5.726	5.726	5.725	5.725	5.725	5.726
Lattice parameter <i>c</i> in Å	7.925	7.926	7.928	7.928	7.927	7.927	7.927	7.927	7.928
Lattice parameter <i>beta</i> in °	90.094	90.179	90.182	90.198	90.169	90.163	90.158	90.147	90.163
Cell volume in Å ³	250.818	251.100	251.326	251.303	251.253	251.212	251.253	251.234	251.254
Formula units per cell Z	4								
Second phase (wt%)	0	0	0	0	5.24	10.29	16.52	18.81	27.09
Space group	Fd-3m								
Lattice parameter <i>a</i> in Å	—	—	—	—	10.550	10.551	10.558	10.562	10.563
Cell volume in Å ³	—	—	—	—	1174.37	1174.58	1176.92	1178.29	1178.75
Formula units per cell Z	8								
Structure refinement	Topas3								
Radiation	Cu K _α								
Temperature in K	293								
Profile range in degree	10°≤2θ≤80°								
R-factors									
<i>R</i> _p	6.00	5.35	4.47	4.79	5.67	5.45	5.89	5.85	5.35
<i>R</i> _{wp}	9.36	8.50	7.14	7.61	8.07	7.89	6.93	8.57	7.71
<i>R</i> _{exp}	6.00	6.08	5.90	6.07	6.00	6.08	4.56	5.89	5.89

<i>R</i> -Bragg	0.492	0.378	0.190	0.253	0.536	0.523	0.305	0.558	0.471
GOF	1.56	1.40	1.21	1.25	1.35	1.30	1.18	1.47	1.31
<i>S</i>	0.937	0.950	0.986	0.985	0.966	0.957	0.955	0.957	0.960

Table 2. The Wyckoff positions of atoms in the unit cell of Nd(Mg_{0.5}Sn_{0.5})O₃

Atom	Site	x	y	z	Ion	occupancy
Nd1	4e	0.48590	0.55350	0.25020	Nd ³⁺	1
Mg1	2c	0.00000	0.50000	0.00000	Mg ²⁺	0.94
Mg2	2d	0.50000	0.00000	0.00000	Mg ²⁺	0.06
Sn1	2d	0.50000	0.00000	0.00000	Sn ⁴⁺	0.94
Sn2	2c	0.00000	0.50000	0.00000	Sn ⁴⁺	0.06
O1	4e	0.29800	0.29500	0.05000	O ²⁻	1
O2	4e	0.19900	0.80800	0.06100	O ²⁻	1
O3	4e	0.60600	-0.03200	0.25700	O ²⁻	1

Table 3. The bond information, the average bond length and the calculated Δ in octahedra of NMS ceramics.

Bond in Octahedra	-0.04	-0.03	-0.02	-0.01	0	+0.01	+0.02	+0.03	+0.04
Mg/Sn-O1 (Å)	2.0632	2.0643	2.065	2.0649	2.0647	2.0645	2.0646	2.0645	2.0647
Mg/Sn-O1 (Å)	2.0632	2.0643	2.065	2.0649	2.0647	2.0645	2.0646	2.0645	2.0647
Mg/Sn-O2 (Å)	2.053	2.0546	2.0555	2.0554	2.0551	2.0549	2.0550	2.0549	2.0549
Mg/Sn-O2 (Å)	2.053	2.0546	2.0555	2.0554	2.0551	2.0549	2.0550	2.0549	2.0549
Mg/Sn-O3 (Å)	2.1263	2.126	2.1263	2.1263	2.1264	2.1264	2.1265	2.1266	2.1265
Mg/Sn-O3 (Å)	2.1263	2.126	2.1263	2.1263	2.1264	2.1264	2.1265	2.1266	2.1265
$\bar{R}$ (Å)	2.0808	2.0816	2.0823	2.0822	2.0821	2.0819	2.0820	2.0820	2.0820
$\Delta (\times 10^{-3})$	1.456	1.384	1.362	1.367	1.381	1.390	1.390	1.398	1.391

Table 4. Densities and dielectric properties of the NMS samples.

x	Density (g/cm ³)	Relative density (%)	Tested			
			ε_r	$Q \times f$ (GHz)	$\tan\delta$ ($\times 10^{-4}$)	$\varepsilon_{r(cor)}$
+0.04	6.42	92.21	17.74	45719	3.02	18.82
+0.03	6.43	92.34	17.76	46013	2.94	18.83
+0.02	6.45	92.60	17.81	46461	2.91	18.87
+0.01	6.50	93.33	18.02	46722	2.82	18.91
0	6.54	93.99	18.11	46828	2.78	18.96
-0.01	6.75	96.92	18.52	47542	2.67	19.09
-0.02	6.76	97.07	18.74	47979	2.63	19.23
-0.03	6.77	97.20	18.61	47146	2.66	19.17
-0.04	6.74	96.82	18.56	46889	2.70	19.14

Table 5. Frequency/FWHM parameters obtained from the Lorentz fitting of Raman spectra.

Modes	F _{2g} (A)-Mode1		F _{2g} (B)-Mode9		A _{1g} (O)-Mode12	
	Frequency	FWHM	Frequency	FWHM	Frequency	FWHM
	(cm ⁻¹)		(cm ⁻¹)		(cm ⁻¹)	
+0.04	106.81	3.411	364.20	15.133	658.82	23.907
+0.03	106.80	3.402	364.28	16.756	658.98	23.900
+0.02	106.74	3.346	364.04	15.663	658.80	23.797
+0.01	106.54	3.304	363.88	16.113	658.78	23.680
0	106.48	3.271	363.51	16.458	658.78	23.456
-0.01	106.36	3.197	362.44	16.625	658.69	23.013
-0.02	106.31	3.170	362.04	16.753	658.45	22.670
-0.03	106.42	3.186	362.66	16.341	658.75	22.894
-0.04	106.61	3.215	363.15	16.468	658.82	23.022

Table 6. Parameters of the IR-Active Modes of Nd(Mg_{0.5}Sn_{0.49})O₃ ($x = -0.02$) ceramic.

Modes	$\Omega_{\text{TO}} (\text{cm}^{-1})$	$\gamma_{\text{TO}} (\text{cm}^{-1})$	$\Omega_{\text{jLO}} (\text{cm}^{-1})$	$\gamma_{\text{jLO}} (\text{cm}^{-1})$	$\Delta\epsilon_{\text{j}}$	$\tan\delta_{\text{j}}/\omega$
F ₁	108.73	6.43	112.65	6.69	1.555	0.459
F ₂	152.29	14.27	155.44	29.13	1.076	0.359
F ₃	180.28	21.38	199.34	7.38	3.259	1.163
F ₄	282.23	15.74	303.86	26.86	2.501	0.268
F ₅	380.54	16.39	428.15	34.52	4.436	0.272
F ₆	428.28	23.38	509.74	38.13	0.008	0.001
F ₇	590.15	33.57	671.64	40.78	0.596	0.031

Note: $\epsilon_{\infty} = 5.01$, $\epsilon_r = \epsilon_{\infty} + \text{Sum} (\Delta\epsilon_{\text{j}}) = 18.44$, $\tan\delta = \text{Sum} (\tan\delta_{\text{j}}/\omega) = 2.553 \times 10^{-4}$.

Table 7. The dielectric properties calculated by 4-P mode of the NMS samples.

x	-0.04	-0.03	-0.02	-0.01	0	+0.01	+0.02	+0.03	+0.04
ε_r	18.31	18.39	18.44	18.28	18.07	17.90	17.73	17.53	17.48
$\tan\delta (\times 10^{-4})$	3.97	3.29	2.55	2.85	3.31	3.17	3.44	3.46	3.67

Fig. 1. XRD patterns of NMS ceramics sintered at 1500 °C for 4 h.

Fig. 2. (a) Rietveld refinement plots of $\text{Nd}[\text{Mg}_{0.5}\text{Sn}_{0.49}]\text{O}_3$ ($x = -0.02$) ceramic, (b) The lattice parameters as a function of the x value.

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Figures

Figure 1

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Figure 2

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Figure 4

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Figure 5

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(a) Measured and fitted infrared reflectivity spectra for Nd(Mg_{0.5}Sn_{0.49})O₃ (x = -0.02) ceramic, (b) (c) ϵ' , ϵ'' and $(\epsilon'⁻¹)''$ (the imaginary parts of reciprocal dielectric functions) of the complex dielectric function, obtained from K-K analysis and 4-P model as indicated, (d) The real parts (ϵ') and imaginary parts (ϵ'') of the complex permittivity of the sample are calculated by the 4-P model and extrapolated to the microwave region.

Figure 10

Relationship of the Raman shift of the $F_{2g}(A)$ and $F_{2g}(B)$ phonon mode, the experimental dielectric constant and the average length of Mg/Sn-O bonds as a function of x values.

Figure 11

Relationship among A1g(0) phonon mode, FWHM values, degree of order S and the experimental dielectric loss as a function of x values.

Supplementary Files

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