Lattice vibrational characteristics and structures-properties relationships of non-stoichiometric Nd\(_{0.5}Mg_{0.5}Sn_{0.5(1+x)}\)O\(_3\) ceramics

Feng Shi\(^1\) · En-Cai Xiao\(^2\) · Guohua Chen\(^3\) · Ying Chen\(^4\)

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Abstract
Non-stoichiometric Nd\(_{0.5}Mg_{0.5}Sn_{0.5(1+x)}\)O\(_3\) (−0.04 ≤ \(x\) ≤ +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. The double perovskite Nd\(_{0.5}Mg_{0.5}Sn_{0.5}\)O\(_3\) with a monoclinic structure was distinguished as the main crystalline phase, and pure phase was obtained when \(x < 0\). 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. The lattice vibrational characteristics were clarified with Raman and infrared active mode spectroscopy. 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 \(\text{F}_{2g}(A)\) and \(\text{F}_{2g}(B)\) 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 \(\text{A}_{1g}(O)\) 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 network [1–3]. 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 improved [4, 5].

Rare-earth based double perovskite MWDCs with formula of \(A(B'_{0.5}B''_{0.5})O_3\) (\(A = \text{La, Nd, Pr, Sm, Dy, Y, etc.}; B' = \text{Mg, Zn, Co, etc.}; B'' = \text{Sn, Ti, etc.}\)) exhibit lower permittivity \(\varepsilon_r\), lower dielectric loss (\(\tan\delta = 1/Q\), i.e., higher quality factor \(Q \times f\) and controllable temperature coefficient of resonant frequency (\(\tau_f\)), and, thus, the materials have potential applications in next-generation communication systems [6, 7]. Babu et al. [8] characterized the crystal structures of \(\text{La}(\text{MgSn})_{0.5}\text{O}_3\) ceramic and achieved dielectric properties (\(\varepsilon_r = 20.1; Q \times f = 63,000\) GHz; and \(\tau_f = -78\) ppm/°C).
Chen et al. [9] lowered the sintering temperature of Nd(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> by adding B<sub>2</sub>O<sub>3</sub> as a sintering aid, and when the amount of B<sub>2</sub>O<sub>3</sub> was 0.25 wt.%, the optimal dielectric properties were achieved (ε<sub>r</sub> = 18.9; Q×f = 32.300 GHz; τ<sub>f</sub> = −52 ppm/°C) after sintered at 1500 °C for 4 h.

Previous researches on rare-earth based A′(B′<sub>0.5</sub>B″<sub>0.5</sub>)O<sub>3</sub>-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 in non-stoichiometric Nd(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> system. The change in composition can significantly affect the structures and properties. The research on the non-stoichiometric Nd(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> ceramics contributes to understanding the compositional control, defect chemistry, crystal structures, dielectric properties, and performance regulation of the rare-earth based A′(B′<sub>0.5</sub>B″<sub>0.5</sub>)O<sub>3</sub>-type MWDCs.

In addition, Raman scattering and far-infrared reflection spectroscopy were often used to investigate the lattice vibrational characteristics of solid-state materials [10–13], which helps to analyze macroscopic properties from a microscopic perspective and provides more innovative perspectives in inherent attribute and structure–property regulation [14–16]. For example, Zhou et al. [17] have examined the structure–property relationships of (Bi<sub>1−x</sub>Y<sub>x</sub>)VO<sub>4</sub> (0.4 ≤ x ≤ 1.0) ceramics based on the Raman spectroscopy and far-infrared spectroscopy. Lu et al. [18] classified the vibrational modes of spinel-structured Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics and also discussed the structure–property relationships. Xing et al. [19] have calculated the intrinsic properties of scheelite structure MWDCs Ba<sub>1+x</sub>MoO<sub>4</sub> (−0.03 ≤ x ≤ 0.03) samples by fitting the far-infrared reflectivity spectra and revealed the internal relationship of the structure–property by changing Ba<sup>2+</sup> content according to the Raman modes.

All in all, the researches on the structures–properties relationships for the non-stoichiometric Nd(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> ceramics based on the analysis of the lattice vibrational characteristics are important both in basic characterization and practical application. In our group, Zhang et al. [20] and Cao et al. [21] have combined the phonon modes to establish the structure–property relationship of the non-stoichiometric Nd(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> ceramics with the change of Mg<sup>2+</sup> content on the B′-site and Nd<sup>3+</sup> content on the A-site, respectively. However, quadrivalent Sn<sup>4+</sup> ions, located on the B″-site in Nd(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> samples, are different from bivalent Mg<sup>2+</sup> ions and trivalent Nd<sup>3+</sup> ions in terms of atomic structures and physical properties, which also have great influence on their structure–property correlations and also affect their lattice vibrational characteristics. That is, we know little about the intrinsic properties of the non-stoichiometric Nd[Mg<sub>0.5</sub>Sn<sub>0.5</sub>(1+x)]O<sub>3</sub> ceramics with varying Sn<sup>4+</sup> content that hinders the deep understanding and practical applications of A′(B′<sub>0.5</sub>B″<sub>0.5</sub>)O<sub>3</sub>-type MWDCs.

In the present work, non-stoichiometric rare-earth based Nd[Mg<sub>0.5</sub>Sn<sub>0.5</sub>(1+x)]O<sub>3</sub> (NMS, −0.04 ≤ x ≤ +0.04) samples were prepared using a conventional two-step solid-state sintering process. The crystal structures and phase component 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 the lattice vibrational characteristics [22]. The intrinsic properties were derived from the FIR peak fitting by a four-parameter semi-quantum (4-P) model, which were compared with the measured values as well as the values predicted from Clausius–Mossotti equation (C-M) based on polarizability. 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 relations were established using Raman active phonon modes to contribute to the design of new-type MWDCs from the perspective of material science as a further study based on the previous results [17, 18].

### 2 Experimental

**Non-stoichiometric Nd[Mg<sub>0.5</sub>Sn<sub>0.5</sub>(1+x)]O<sub>3</sub>**

(−0.04 ≤ x ≤ +0.04) MWDCs were prepared by routine two-step solid-state sintering method with high-purity starting materials of Nd<sub>2</sub>O<sub>3</sub> (99.9%, Aladdin Holdings Group), (MgCO<sub>3</sub>)<sub>4</sub>·Mg(OH)<sub>2</sub>·5H<sub>2</sub>O (99.8%, Aladdin Holdings Group), and SnO<sub>2</sub> (99.8%, Aladdin Holdings Group), 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 h. The calcined powders were milled and next dried for the second time treatment. 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 10×6 mm under 100 MPa, which were finally sintered at 1500 °C for 4 h. All sintered disks were grinded and polished carefully using Al<sub>2</sub>O<sub>3</sub> 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-2000 V, Rigaku, Japan) with Cu-Kα incident radiation was applied to analyze the phase composition and structure of MWDCs, and the XRD data were collected at a range of 10°~80° with the step size of 0.02°. The surface topography of NMS ceramics was characterized by scanning electron microscope (SEM, Nova Nano SEM45). The actual
properties of sintered MWDCs were tested with a network analyzer (E8363B, Agilent). The $\varepsilon_r$ and $Q$ values were determined by the Hakki-Coleman dielectric resonator method [23]. The Raman spectra were obtained applying an Xper-Ram Compact spectrometer (Nanobase) at room temperature, and the 633 nm laser line was used as excitation source. The far-infrared reflectivity spectra were recorded at room-temperature by Fourier-transform infrared spectrometry (IFS 66v/s Vacuum, Bruker Optik GmbH, Ettlingen, Germany). The spectra were collected based on a PE-DTGS (Bruker, Ettlingen, Germany) detector and a Mylar beamsplitter. For the mid-infrared region, a DTGS detector and Ge-coated KBr beamsplitter (Bruker) were used.

3 Results and discussion

The XRD patterns of the NMS samples sintered at 1500 °C for 4 h are presented in Fig. 1. Nd(Mg$_{0.5}$Sn$_{0.5}$)O$_3$ (JCPDS #16-1439) can be clearly identified as the main crystalline phase, which belongs to a monoclinic double perovskite structure (space group P21/n). When $x < 0$, no secondary phase is observed. However, a small amount of Nd$_2$Sn$_2$O$_7$ (JCPDS #54-1268) is detected as a secondary phase at $x \geq 0$, and the relative intensity of Nd$_2$Sn$_2$O$_7$ peaks increases continuously with the $x$ value increase, 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 the Sn$^{4+}$ excess can promote the secondary phase generation. The (100) and 1/2(210) peaks move to lower angles on the $x$ variation from $-0.04$ to $-0.02$ and then to higher angles from $-0.02$ to $+0.04$, as shown in the inset Fig. 1, and it indicates that the cell volume increases first at $x$ from $-0.04$ to $-0.02$ and then decreases at $x$ 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 cations [24] and belong to superlattice reflection peaks. The ordered parameter ($S$) can be calculated using the following formula (1) [25].

$$S = \sqrt{\frac{I_{1/2(210)}}{I_{110}} \text{exp} - \frac{I_{1/2(210)}}{I_{110}} \text{theoS}}$$

where $I_i$ is the intensity of a given peak, and the “exp” and “theo” notations represent the experimental and theoretical values, respectively. The lattice structure is fully ordered when $S = 1$.

The TOPAS (3.0 version) software was used to perform Rietveld refinement so as to obtain the fine structural parameters of NMS systems. The main structural parameters obtained by Rietveld refinement, including cell parameters, space group information, R- factors and ordered parameters ($S$) of NMS ceramics, are listed in Table 1.

As an example, the difference Rietveld pattern of Nd(Mg$_{0.5}$Sn$_{0.49}$)O$_3$ ($x = -0.02$) is presented in Fig. 2a. The refined and collected diffraction profiles are coincident, as proved by the low amplitude of the difference line (green line in Fig. 2a). The obtained factors ($R_{wp}$, $R_p$, and GOF were 6 ~ 10%, 4 ~ 6%, and 1.1 ~ 1.6, respectively) indicate a satisfactory reliability of the refinement. Besides, the dependences of cell parameters of the main crystal phase on $x$ are provided in Fig. 2b.

As seen in Fig. 2b, the cell parameters of the main crystal phases vary with $x$ variation, which may be caused by the vacancy defects due to the volatilization of Mg$^{2+}$ ions and replacement of Mg$^{2+}$ ions by Sn$^{4+}$ ions. With increasing $x$ content from $-0.04$ to $-0.02$, Sn$^{4+}$ occupies some Mg$^{2+}$ vacancies, the number of Mg$^{2+}$ vacancy defects decreases, and the cell 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

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

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$\varepsilon_r$ and $Q$ values were determined...
Table 1 Crystallographic data of NMS ceramics derived from the Rietveld refinement of XRD data

| Formula         | $x = -0.04$ | $x = -0.03$ | $x = -0.02$ | $x = -0.01$ | $x = 0$ | $x = 0.01$ | $x = 0.02$ | $x = 0.03$ | $x = 0.04$ |
|-----------------|-------------|-------------|-------------|-------------|---------|------------|------------|------------|------------|
| Main crystal phase (wt%) | 100         | 100         | 100         | 100         | 94.76   | 89.71      | 84.4       | 81.19      | 72.91      |
| Crystal system  | Monoclinic  |             |             |             |         |            |            |            |            |
| Space group     | P2_1/n      |             |             |             |         |            |            |            |            |
| Cell parameter $a$ in Å | 5.531       | 5.534       | 5.537       | 5.536       | 5.536   | 5.535      | 5.536      | 5.536      | 5.535      |
| Cell parameter $b$ in Å | 5.723       | 5.724       | 5.726       | 5.726       | 5.726   | 5.725      | 5.725      | 5.726      | 5.726      |
| Cell parameter $c$ in Å | 7.925       | 7.926       | 7.928       | 7.928       | 7.927   | 7.927      | 7.927      | 7.927      | 7.928      |
| Cell parameter $\beta$ in ° | 90.094      | 90.179      | 90.182      | 90.198      | 90.169  | 90.163     | 90.158     | 90.147     | 90.163     |
| Cell volume in $\text{Å}^3$ | 250.818     | 251.1       | 251.326     | 251.303     | 251.253 | 251.212    | 251.234    | 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-3 m      |             |             |             |         |            |            |            |            |
| Lattice parameter $a$ in Å | –           | –           | –           | –           | –       | 10.55      | 10.551     | 10.558     | 10.562     |
| Cell volume in $\text{Å}^3$ | –           | –           | –           | –           | –       | 1174.37    | 1174.58    | 1176.92    | 1178.29    |
| Formula units per cell $Z$ | 8           |             |             |             |         |            |            |            |            |
| Structure refinement | Topas3     |             |             |             |         |            |            |            |            |
| Radiatation     | Cu K$_\alpha$ |             |             |             |         |            |            |            |            |
| Temperature in K | 293         |             |             |             |         |            |            |            |            |
| Profile range in degree | $10^\circ \leq 2\theta \leq 80^\circ$       |             |             |             |         |            |            |            |            |
| $R$-factors     |             |             |             |             |         |            |            |            |            |
| $R_p$           | 6           | 5.35        | 4.47        | 4.79        | 5.67    | 5.45       | 5.89       | 5.85       | 5.35       |
| $R_{wp}$        | 9.36        | 8.5         | 7.14        | 7.61        | 8.07    | 7.89       | 6.93       | 8.57       | 7.71       |
| $R_{exp}$       | 6           | 6.08        | 5.9         | 6.07        | 6       | 6.08       | 4.56       | 5.89       | 5.89       |
| $R$-Bragg       | 0.492       | 0.378       | 0.19        | 0.253       | 0.536   | 0.523      | 0.305      | 0.558      | 0.471      |
| GOF             | 1.56        | 1.4         | 1.21        | 1.25        | 1.35    | 1.3        | 1.18       | 1.47       | 1.31       |
| $S$             | 0.937       | 0.95        | 0.986       | 0.985       | 0.966   | 0.957      | 0.955      | 0.957      | 0.96       |

Fig. 2 a Rietveld refinement plots of Nd[Mg$_{0.5}$Sn$_{0.49}$]O$_3$ ($x = -0.02$) ceramic. b The cell parameters as a function of the $x$ value.
appears at \( x = -0.02 \). When \( x \geq 0.01 \), more secondary phases are formed, which causes excessive \( \text{Sn}^{4+} \) ions to be consumed, so the cell parameters and unit cell volumes show no significant change.

The atom positions refined for the \( \text{Nd(Mg}_{0.5}\text{Sn}_{0.5})\text{O}_{3} \) sample are given in Table 2, and the unit cell representation, based on the structural parameters listed in Tables 1, 2, is shown in Fig. 3a. As shown in Fig. 3a, Sn and Mg atoms are distributed along \( \text{B′:B″}=1:1 \) order in the unit cell, and as a result, form an Sn/Mg-oxygen octahedron structure with the adjacent six oxygen atoms. Two ions’ positions are shown in Fig. 3b, which belong to the site due to the substitution of the \( \text{Mg}^{2+} \) ions by the excess \( \text{Sn}^{4+} \) ions in (001) plane and the site of the \( \text{Mg}^{2+} \) ions vacancy, respectively. The (010) plane of single phase NMS and the structure of secondary phase \( \text{Nd}_{2}\text{Sn}_{2}\text{O}_{7} \) are exhibited in Fig. 3c, d.

As shown in Fig. 3a, there are three kinds of O and six kinds of Mg/Sn–O bonds. The deviation \( (\Delta) \) of distorted octahedron from regular octahedron can be estimated by the individual bond lengths \( (R_i) \) using the following Eq. (2) [26]:

\[
\Delta = \frac{1}{6} \sum \left( \frac{R_i - R}{R} \right)^2 ,
\]

Table 2: The Wyckoff positions of atoms in the unit cell of \( \text{Nd(Mg}_{0.5}\text{Sn}_{0.5})\text{O}_{3} \)

| Atom  | Site | Site | Site | Ion  | Occupancy |
|-------|------|------|------|------|-----------|
| Nd_1  | 4e   | 0.48590 | 0.55350 | 0.25020  | Nd^{3+}  | 1 |
| Mg_1  | 2c   | 0.00000 | 0.50000 | 0.00000  | Mg^{2+}  | 0.94 |
| Mg_2  | 2d   | 0.50000 | 0.00000 | 0.00000  | Mg^{2+}  | 0.06 |
| Sn_1  | 2d   | 0.50000 | 0.00000 | 0.00000  | Sn^{4+}  | 0.94 |
| Sn_2  | 2c   | 0.00000 | 0.50000 | 0.00000  | Sn^{4+}  | 0.06 |
| O_1   | 4e   | 0.29800 | 0.29500 | 0.05000  | O^{2−}   | 1 |
| O_2   | 4e   | 0.19900 | 0.80800 | 0.06100  | O^{2−}   | 1 |

Fig. 3 a Unite cell representation of \( \text{Nd[Mg}_{0.5}\text{Sn}_{0.5}]\text{O}_{3} \) ceramic, b the schematic representations of surface (001), c the schematic representations of surface (010) and d the unit cell representation of secondary phase \( \text{Nd}_{2}\text{Sn}_{2}\text{O}_{7} \).
where $R$ denotes the average bond length of oxygen octahedron. To explain the preceding analysis, the bond information, average bond length, and $\Delta$ values are calculated and listed in Table 3.

To better analyze the results, the bond length and octahedron deviation as functions of $x$ are generated in Fig. 4, which shows no significant changes in the lengths of Mg/Sn-O3(1) and Mg/Sn-O3(2). Thus, the average bond length fluctuation is mainly attributable to the changes of the other four bond lengths.

The average bond length increases with $x$ variation from $-0.04$ to $-0.02$, slightly decreases in the $x$ range 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, and, at the same time, the polarizability increases [27], which results in higher dielectric constant.

The fine crystal grains with clearly distinguished grain boundaries are observed in the SEM patterns recorded for the fractured surfaces of NMS ceramics, as shown in Fig. 5, and the faceted microcrystals are observed [28–30] [J. Cryst. Growth 318 (2011) 683–686; J. Phys. Chem. C 118 (2014) 15,404–15,411; ACS Appl. Mater. Interfaces 7 (2015) 26,235–26,243]. When $x \leq -0.02$, the grains are fine and uniform with an average size of about 2–3 $\mu$m. When $x \geq -0.02$, the grain size slightly increases and micropores form. That is, the sample when $x=-0.02$ has the highest microstructural quality.

The composition dependences of relative density, permittivity, and quality factor of NMS ceramics are shown in Fig. 6. 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) that is consistent with the microstructure changes observed by SEM (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 $x=-0.02$. The relative density and the dielectric property values of NMS ceramics are summarized in Table 4.

As shown in Table 4, the corrected dielectric constant, $\varepsilon_{r(\text{cor})}$, can be calculated using formula (3) [31, 32] based on the measured $\varepsilon_r$ and porosity (P) of the samples, where the porosity can be obtained according to the relative density value.

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

According to the Eq. (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 crystallinity variation, can be reflected in their lattice vibrational spectra. The detailed information about the vibrational modes can be expressed by Eq. (4) according to the group theory and crystallographic data of NMR crystal.

Table 3 The bond information, the average bond length and the calculated $\Delta$ 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-O2 (Å)      | 2.0632| 2.0643| 2.065 | 2.0649| 2.0647| 2.0645| 2.0646| 2.0645| 2.0647|
| Mg/Sn-O3 (Å)      | 2.053 | 2.0546| 2.0555| 2.0554| 2.0551| 2.0549| 2.0550| 2.0549| 2.0549|
| Mg/Sn-O4 (Å)      | 2.1263| 2.126 | 2.1263| 2.1263| 2.1264| 2.1264| 2.1264| 2.1265| 2.1266|
| Mg/Sn-O5 (Å)      | 2.1263| 2.126 | 2.1263| 2.1263| 2.1264| 2.1264| 2.1264| 2.1265| 2.1266|
| $R$ (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|

Fig. 4 Normalized $d_{B-O}$ information in octahedra of NMS ceramics
The Raman scattering spectra of NMS ceramics from 50 to 800 cm$^{-1}$ are presented in Fig. 7. As shown in Fig. 7a, the Raman spectra of the samples are similar, the baseline is flat, and the vibrational peaks are sharp. According to the results of group theory analysis, the crystal with space group P2$_1$/n should have 24 Raman active vibrational modes ($12A_g + 12B_g$). However, in the actual Raman spectra, only 12 peaks are observed because of superposition of Raman active peaks as well as the influence of the facility resolution.

In the 100–270 cm$^{-1}$, the modes are attributed to the vibrations of the A-site cations (Nd$^{3+}$), which are similar to the results in Refs [33, 34]. In the 270–460 cm$^{-1}$, the $F_{2g}(B)$ modes represent the 1:1 ordered phase in B-site. However, modes 11 and 12 belong to the oscillation of oxygen atoms. When $x \geq 0$, a new Raman peak around 530 cm$^{-1}$ appears and the intensity increases as increasing Sn$^{4+}$ content, and this peak may be related to the secondary phase formation. 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 Fig. 7b–d. To analyze the vibrational modes accurately, the peak fitting was conducted with the Lorentz function in LabSpec software, as shown in Fig. 7e, and the related wavenumber/FWHM parameters of the representative modes are listed in Table 5. As shown in Fig. 7b–e and Table 5, the Raman shifts of mode 1 and mode 9 as well as the FWHM of mode

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

(4)
Table 4 Densities and dielectric properties of the NMS samples

| $x$   | Density (g/cm$^3$) | Relative density (%) | $\varepsilon_r$ | Q × f (GHz) | $\tan\delta \times 10^{-4}$ | $\varepsilon_{r\text{corr}}$ |
|-------|-------------------|----------------------|-----------------|-------------|-----------------------------|---------------------------|
| +0.04 | 6.42              | 92.21                | 17.74           | 45,719      | 3.02                        | 18.82                     |
| +0.03 | 6.43              | 92.34                | 17.76           | 46,013      | 2.94                        | 18.83                     |
| +0.02 | 6.45              | 92.60                | 17.81           | 46,461      | 2.91                        | 18.87                     |
| +0.01 | 6.50              | 93.33                | 18.02           | 46,722      | 2.82                        | 18.91                     |
| 0     | 6.54              | 93.99                | 18.11           | 46,828      | 2.78                        | 18.96                     |
| −0.01 | 6.75              | 96.92                | 18.52           | 47,542      | 2.67                        | 19.09                     |
| −0.02 | 6.76              | 97.07                | 18.74           | 47,979      | 2.63                        | 19.23                     |
| −0.03 | 6.77              | 97.20                | 18.61           | 47,146      | 2.66                        | 19.17                     |
| −0.04 | 6.74              | 96.82                | 18.56           | 46,889      | 2.70                        | 19.14                     |

Fig. 7 a Raman spectra of NMS Ceramics. b, c, d Locally magnified view of the Raman spectra for ceramics and e Fitting curves of Raman spectra for Nd[Mg$_{0.5}$Sn$_{0.49}$]O$_3$ ($x = −0.02$) ceramic

12 after Lorentz fitting have the lowest values for the sample at $x = −0.02$.

According to the space group analysis [35], the space group P2$_1$/n has 45 infrared active modes (23A$_u$ + 22B$_u$) and seven 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–BO$_6$ translation modes, M–O–B stretching modes (octahedron external modes) and B–O$_6$ bending modes (octahedron internal modes), respectively. The intensity of F$_1$ mode near 110 cm$^{-1}$ increases with increasing Sn$^{4+}$ content, and the modes in the 200–550 cm$^{-1}$ range verify the presence of ion ordering on the B-site.

Infrared spectroscopy provides a deep insight into the dielectric respond mechanism. The fitted IR spectra according to the 4-P model are presented in Fig. 8. The correlation between the IR spectrum [R($\omega$)] and the complex
permittivity ($\varepsilon^*$) can be described in Formula (5). Besides, the intrinsic properties can be fitted efficiently according to the 4-P model, and the complex permittivity is defined by Eq. (6) [36]:

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

(5)

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

(6)

where the optical permittivity ($\varepsilon_\infty$) 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 $\Omega_{jTO}$ and $\gamma_{jTO}$, respectively. $\Omega_{jLO}$ means the frequency of the longitudinal mode, and $\gamma_{jLO}$ shows the damping factor of the longitudinal mode [6]. The calculated parameters on the base of 4-P model are shown in Table 6, taking the ceramic with $x = -0.02$ as an example.

The measured and fitted IR spectra of the sample $\text{Nd(Mg}_{0.5}\text{Sn}_{0.49})\text{O}_3$ are presented in Fig. 9a. To confirm the results obtained using FOCUS software, the real part ($\varepsilon'$), imaginary part ($\varepsilon''$), and ($\varepsilon^*$)$''$ are independently calculated using the Kramers–Krönig (K–K) relationship [37].
The transverse optical mode (TO) and the longitudinal optical mode (LO) can be obtained using $\varepsilon''$ and $(\varepsilon - 1)''$ and then compared with the original fitting values. As shown in Fig. 9b, c, where 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 $Q \times f$ (49,404 GHz, $f = 12.6$ GHz) value of sample Nd(Mg$_{0.5}$Sn$_{0.49}$)O$_3$ ($x = -0.02$) is similar to the measured value (47,979 GHz, 12.6 GHz).

The dielectric contribution of the $j$th modes can be calculated applying the following equation [22]:

$$
\varepsilon_j = \frac{\varepsilon_\infty}{\varepsilon_\infty + \sum \varepsilon_j} + \sum \varepsilon_j
$$

On the basis of the calculation results 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.

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

| $x$   | -0.04 | -0.03 | -0.02 | -0.01 | 0     | +0.01 | +0.02 | +0.03 | +0.04 |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\varepsilon_r$ | 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  | 3.44  | 3.46  | 3.67  |

Generally speaking, Raman mode is only relative to the crystal structure of the material, but the previous research can indirectly reflect the dielectric properties [38]. That is, the Raman active modes can be applied as a media to build a structure–property relationship [39]. The relationships between the average length ($R$) of Mg/\(\text{Sn}–\text{O}\) bonds, Raman shifts (frequencies) of the $F_{2g}(A)$ and $F_{2g}(B)$ active modes and dielectric constants ($\varepsilon_r$) are presented in Fig. 10. With increasing Sn$^{4+}$ content, the Raman modes initially shift to lower wavenumber from $-0.04$ to $-0.02$ and then shift to higher wavenumber from $-0.02$ to $+0.04$. That is, the $\varepsilon_r$ 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 bond energies of Mg/\(\text{Sn}–\text{O}\)\textsuperscript{18}. When Raman active modes turn to lower wavenumbers, the bond lengths of Mg/\(\text{Sn}–\text{O}\) bonds increase and their bond energies decrease accordingly, which make the cell volume and electron mobility space increase. Subsequently, the larger polarizabilities exist in the Mg/\(\text{Sn}–\text{O}\) dipoles, and therefore, the permittivities also increase [18].

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, 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 $\varepsilon_r = 18.74$, $Q \times f = 47,979$ GHz, $f = 12.6$ GHz.

## 4 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 $Nd_2Sn_2O_7$ appears in the ceramics when $x \geq 0$ with an increase in pore number, whereas the pure phase $Nd(Mg_{0.5}Sn_{0.5})O_3$ is obtained when $x < 0$. The Rietveld refinement of XRD data shows that the lack of $Sn^{4+}$ introduces vacancy defects in the crystal, with increasing $Sn^{4+}$ content, $Sn^{4+}$ occupies some vacancies. $Mg^{2+}$ 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 appeared. 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 ($\varepsilon_r = 18.74$, $Q \times f = 47,979$ GHz, $f = 12.6$ GHz). Both Raman and FIR active modes were accurately assigned. The dielectric properties were fitted and calculated according to the infrared spectra, as 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.

### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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