Structure, defects, and microwave dielectric properties of Al-doped and Al/Nd co-doped Ba$_4$Nd$_{9.33}$Ti$_{18}$O$_{54}$ ceramics

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Abstract: Low-loss tungsten–bronze microwave dielectric ceramics are dielectric materials with potential application value for miniaturized dielectric filters and antennas in the fifth-generation (5G) communication technology. In this work, a novel Al/Nd co-doping method of Ba$_4$Nd$_{9.33+\frac{z}{3}}$Ti$_{18-\frac{z}{3}}$Al$_{\frac{z}{3}}$O$_{54}$ (BNT–AN, $0 \leq z \leq 2$) was proposed to improve the dielectric properties through structural and defect modulation. Together with Al-doped ceramics ($\text{Ba}_4\text{Nd}_{9.33-\frac{z}{3}}\text{Ti}_{18-\frac{z}{3}}\text{Al}_{\frac{z}{3}}\text{O}_{54}$, BNT–A, $0 \leq z \leq 2$) for comparison, the ceramics were prepared by a solid state method. It is found that Al/Nd co-doping method has a significant effect on improving the dielectric properties compared with Al doping. As the doping amount $z$ increased, the relative dielectric constant ($\varepsilon_r$) and the temperature coefficient of resonant frequency ($\tau_f$) of the ceramics decreased, and the $Q\times f$ values of the ceramics obviously increased when $z \leq 1.5$. Excellent microwave dielectric properties of $\varepsilon_r = 72.2$, $Q\times f = 16,480$ GHz, and $\tau_f = +14.3$ ppm/°C were achieved in BNT–AN ceramics with $z = 1.25$. Raman spectroscopy and thermally stimulated depolarization current (TSDC) technique were firstly combined to analyze the structures and defects in microwave dielectric ceramics. It is shown that the improvement on $Q\times f$ values was originated from the decrease in the strength of the A-site cation vibration and the concentration of oxygen vacancies ($\text{OV}\bullet\bullet\bullet$), demonstrating the effect and mechanism underlying for structural and defect modulation on the performance improvement of microwave dielectric ceramics.

Keywords: microwave dielectric ceramics; Ba$_4$Nd$_{9.33}$Ti$_{18}$O$_{54}$ (BNT); Al and Al/Nd doping; structural and defect modulation

1 Introduction

Nowadays, the fifth-generation (5G) telecommunication technology has been developing rapidly, in which ceramic materials could play important roles [1]. Microwave dielectric ceramics with high $Q\times f$ values ($Q = 1/\tan\delta$, and $f$ is the resonant frequency) and excellent temperature stability are widely used to manufacture 5G antennas and filters [2–5]. In order to meet the requirements of device miniaturization, microwave dielectric ceramics having medium/high relative dielectric constants ($\varepsilon_r$) have been the focus of researches [6,7], including TiO$_2$ [8,9], Ba$_{6-3x}$Ln$_{8+2x}$Ti$_{18}$O$_{54}$ (BLT, where Ln = rare earth element) [10,11], CaO–Li$_2$O–Ln$_2$O$_3$–TiO$_2$ [12,13], Ca$_{1-x}$Ln$_{2x/3}$TiO$_3$ (CLT) [14–16], lead-based perovskite [17,18], etc. In recent years, BLT...
with a tungsten–bronze structure and CLT with a perovskite structure have been extensively studied [19–24]. Meanwhile, novel ceramic systems such as Bi$_5$(Li$_{0.5}$Ta$_{0.5}$)$_6$O$_{19}$ [25,26] and BiVO$_4$ [27,28] have also been developed. However, the above-mentioned ceramic materials either have relatively low $Q\times f$ values or relatively large temperature coefficients of resonant frequency ($\tau_f$), which cannot yet meet the application needs of 5G technology. It is necessary to develop microwave dielectric ceramics with better comprehensive performance.

The crystal structure of BLT ceramics is composed by three types of large cation sites: A1 rhombic sites, A2 pentagonal sites, and B sites (occupied by Ti$^{4+}$) in the center of TiO$_6$ octahedra [11]. According to Ohsato’s report [11], Ln$^{3+}$ and Ba$^{2+}$ respectively occupy the A1 and A2 sites when $x = 2/3$, and the ordering of Ln$^{3+}$ and Ba$^{2+}$ reduces the internal strain and leads to the largest $Q\times f$ value. To further improve the $Q\times f$ values of BLT ceramics, a large amount of doping modification research was displayed, especially the substitution of low-valence cations for Ti$^{4+}$ at the B sites. Chen et al. [29] and Tao et al. [30] replaced Ti$^{4+}$ with the same amount of Al$^{3+}$ to improve the $Q\times f$ value, while the condition of charge balance was not achieved. In order to meet the condition of charge balance, one method was to use composite ions such as (Cr$_{1/2}$Nb$_{1/2}$)$^{4+}$, (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$, or (Al$_{1/2}$Nb$_{1/2}$)$^{3+}$ to substitute Ti$^{4+}$ [31–33], yet it complicated the synthesis process. The other method is to use excessive trivalent cations (4/3 times in stoichiometry) such as Cr$^{3+}$, Al$^{3+}$, or Ga$^{3+}$ to substitute Ti$^{4+}$ [34–37], yet none of the studies have explained which site these cations entered. Considering that the A1 sites of BLT structure are usually not fully filled, the excessive cations might enter the A1 sites. However, the radii of those cations are much smaller than the size of the A1 sites, which might affect the stability of the crystal lattice and lead to the deterioration of the $Q\times f$ value. Therefore, it is important to conduct a further study on the ion occupancy during these doping processes.

In the present study, Ba$_4$Nd$_{9.33}$Ti$_{18}$O$_{54}$ (BNT) ceramics ($\epsilon_r = 85$, $Q\times f = 10,000$ GHz, and $\tau_f = +60$ ppm/°C) [11] are chosen as matrix. A new strategy, i.e., Al/Nd co-doping in BNT ceramics, is proposed to improve the dielectric properties of tungsten–bronze microwave dielectric ceramics through structural and defect modulation, in which the condition of charge balance was maintained by using the same amount of Al$^{3+}$ to substitute Ti$^{4+}$ and adding Nd$^{3+}$ to fill the vacancies at the A1 site simultaneously, with a chemical formula of Ba$_4$Nd$_{9.33}$Ti$_{18-z}$Al$_z$O$_{54}$ (BNT–AN, $0 \leq z \leq 2$). Correspondingly, Ba$_4$Nd$_{9.33}$Ti$_{18-z}$Al$_z$O$_{54}$ (BNT–A, $0 \leq z \leq 2$) ceramics are also prepared for comparison.

The theoretical solid solubility should be reached when $z = 2$, at which the vacancies at the A1 site could be completely filled. Rietveld refinement, Raman spectroscopy, and thermally stimulated depolarization current (TSDC) are applied to analyze the crystal structure and the strength of the A-site cation vibration. Microwave dielectric ceramics with better comprehensive performance are obtained through Al/Nd co-doping, and the relationship between the structure and the microwave dielectric properties of the ceramics is discussed in the present paper.

### 2 Experimental

The BNT–A and BNT–AN ceramics were prepared through the traditional solid-state processing. High-purity powders including BaCO$_3$ (99.8%, Alfa Aesar), Nd$_2$O$_3$ (99.9%, Aladdin), TiO$_2$ (99.99%, Macklin), and Al$_2$O$_3$ (99.99%, Aladdin) were used as the raw materials. All the raw powders were calcined at 600 °C for 4 h, weighed according to the stoichiometric composition, and ball milled for 4 h in ethanol. After drying, the mixture was calcined at 1150 °C for 4 h, and then re-milled and dried. The dried powders were ground with polyvinyl alcohol solution (PVA, 5 wt%), and uniaxially pressed into cylinders with a diameter of 10 mm and an appropriate thickness. Finally, the specimens were preheated at 600 °C for 4 h to remove the binder and sintered in the range of 1350–1550 °C for 4 h.

The as-fired surfaces of the sintered ceramics were observed by scanning electron microscopy (SEM; MERLIN VP Compact, Carl Zeiss, Germany). The phase compositions and crystal structures of the ceramics were analyzed by X-ray diffraction (XRD; D8 Advance, Bruker, Karlsruhe, Germany) with Cu Kα radiation. Rietveld refinement were executed using the FullProf program [38] with XRD data collected over a 2θ range of 10°–120°. The bulk densities of the ceramics were determined by the Archimedes method, and the relative densities were calculated by the measured and theoretical ones. The $\epsilon_r$ and $\tau_f$ values at microwave range were measured using the Hakki–
Coleman method [39] by exciting the TE$_{011}$ resonant mode [40] using a vector network analyzer (HP8720ES, Hewlett-Packard, Santa Rosa, USA). The $Q$-$f$ values were measured using the TE$_{010}$ mode in the cavity method [41]. Raman spectra (20–1200 cm$^{-1}$) of the ceramics were measured on a high-resolution Raman spectrometer (LabRAM HR800, Horiba Jobin-Yvon, France) with the existing line at 532 nm of a Nd/YAG laser at room temperature.

TSDC measurements were accomplished using a pA meter (6517B, Keithley, Cleveland, USA), and the temperature was controlled by a quarto temperature controller of Novocontrol Technologies (Montabaur, Germany). The ceramic pellets with diameter of ~8.4 mm and thickness of ~0.5 mm were polished, and gold electrodes were sputtered on both sides. The specimens were initially polarized under a DC electric field ($E_p$) at a constant temperature ($T_p$) for a period of time $t_p$ (100 V/mm $\leq E_p \leq$ 350 V/mm, $T_p = 300 ^\circ C$, and $t_p = 10$ min), and then rapidly cooled to $-100 ^\circ C$ with $E_p$ maintained to freeze the polarized defects. After $E_p$ removed and being short-circuited for 10 min, the specimens were heated to 300 $^\circ C$ with a constant heating rate of 5 $^\circ C$/min, with the depolarization currents continually recorded.

3 Results and discussion

Figure 1 presents the SEM photographs of the surface morphology of the ceramic samples. All BNT–A and BNT–AN samples show a single phase of rod-like grains. As shown in Figs. 1(a)–1(c), BNT–A ceramics with different $z$ values could be well-sintered at 1400 $^\circ C$. In comparison, BNT–AN ceramics with $z = 2$ are well-sintered at 1550 $^\circ C$, as shown in Fig. 1(f). The well-sintered samples are selected for subsequent characterization, and the sintering temperature of each composition is listed in Tables S1 and S2 in the Electronic Supplementary Material (ESM). According to Fig. 1 and Tables S1 and S2 in the ESM, it is indicated that the sintering temperature of the BNT–A ceramics is stable at around 1350–1400 $^\circ C$, while that of the BNT–AN ceramics is higher when $z$ values are large. Figures 1(d) and 1(e) show that the grain size of the ceramics with the same composition becomes larger as the sintering temperature gets higher.

The XRD patterns of the ceramic samples are shown in Fig. 2. All samples can be confirmed as a single phase with a tungsten–bronze structure (Ba$_{3.99}$Sm$_{9.34}$Ti$_{18}$O$_{54}$, PDF#89-4356). The detailed XRD data with a 2$\theta$ range of 31$^\circ$–35$^\circ$ are presented in Fig. 2(b), which shows that the peaks shift towards higher degrees as $z$ value increases, indicating that the cell volume decreases. This demonstrates that Al$^{3+}$ with a smaller ionic radius (0.54 Å, CN = 6) successfully enters into the lattice, and substitutes for Ti$^{4+}$ with a larger ionic radius (0.605 Å, CN = 6). Rietveld refinement was performed to further explore the changes of phase composition and lattice parameters with doping amount. Figures 3(a)–3(c) show the refined results of the BNT, BNT–A ($z = 1.25$), and BNT–AN ($z = 1.25$) ceramics as examples, respectively. The fitting results are in good agreement with the experimental XRD patterns. Figure 3(d) shows

![Fig. 1](https://www.springer.com/journal/40145)
Fig. 2 (a) XRD patterns of the BNT, BNT–A, and BNT–AN ceramics (z = 0, 0.25, 0.75, 1.25, and 1.75). (b) XRD peak shifts in the range of $31^\circ \leq 2\theta \leq 35^\circ$.

that there are a few peaks that cannot be fitted in the experimental data of the BNT–A ceramics, together with $\chi^2$ rising as $z$ value increases, indicating that a small amount of unknown secondary phase appears. In contrast, Fig. 3(e) shows that there is no secondary phase peak in the experimental data of the BNT–AN ceramics. The above-mentioned unknown secondary phase may have an impact on the microwave dielectric properties of the BNT–A ceramics.

The lattice parameters and cell volumes calculated by Rietveld refinement are shown in Fig. 4. The lattice parameters and cell volumes of the BNT–A and BNT–AN ceramics both decrease with the increase in $z$ value, and basically shows the same linear decrease trend as $z \leq 1.25$. This indicates that the type of trivalent cations (Al$^{3+}$ or Nd$^{3+}$) filling the vacancies at the A1 sites has less influence on the lattice parameters in the doping process of the BNT ceramics. When $z \geq 1.25$, the lattice parameters and cell volumes of the BNT–AN ceramics continuously show a linear decreasing trend, while the decreasing trend of those of the BNT–A ceramics deviates from linearity. Combining with Figs. 3(d) and 3(e), it can be demonstrated that such a deviation is caused by the secondary phase in the BNT–A ceramics. Therefore, the BNT–A ceramics cannot form a complete solid solution phase when more Al$^{3+}$ ions are added, while the BNT–AN ceramics can form a continuous solid solution in the range of $0 \leq z \leq 2$. The detailed results of the structural parameters and reliability factors obtained by Rietveld refinement are shown in Tables S1 and S2 in the ESM.

Figure 5 presents the relative densities and microwave dielectric properties of the BNT–A and BNT–AN ceramics. According to Fig. 5(a), the relative densities of almost all ceramic samples have reached higher than 97%, indicating the ceramics are all well densified. When
The relative densities of the BNT–AN ceramics are lower than those of BNT–A ceramics with the same doping amount. In addition, the sintering temperature of the BNT–AN ceramics is higher with large \( z \) values as illustrated in SEM results. Therefore, the BNT–AN ceramics are more difficult to be well-sintered than the BNT–A ceramics. Figures 5(b) and 5(d) show that the \( \varepsilon_r \) and \( \tau_f \) values of the ceramics decrease in a similar trend with the increase in \( z \) value, which is consistent with the reports of low-valence cations doping at the B sites in the BLT system \[29–37\]. According to Shannon’s rule \[42\], \( \varepsilon_r \) is related to the ionic polarizability (\( \alpha_D \)) and the molecular volume (\( V_m \)):

\[
\alpha_D = \frac{V_m(\varepsilon_{rc} - 1)}{b(\varepsilon_{rc} + 2)} 
\]

(1)

where \( \varepsilon_{rc} \) is the corrected dielectric constant, and \( b \) is a constant equal to \( 4\pi/3 \). According to Eq. (1), \( \varepsilon_{rc} \) increases when \( \alpha_D \) increases or \( V_m \) decreases. Although the cell volume of the ceramics decreases slightly when \( z \) value increases as shown in Fig. 4, the decrease in \( \alpha_D \) (\( \alpha(Al^{3+}) = 0.78 \ \text{Å}^3 \), \( \alpha(Ti^{4+}) = 2.94 \ \text{Å}^3 \)) mainly dominates the decrease in \( \varepsilon_r \). Reaney and Iddles \[6\] reported that \( \tau_f \) is usually determined by \( \varepsilon_r \), and the change trends of \( \varepsilon_r \) and \( \tau_f \) are often similar in the same ceramic system. When \( z \geq 1.25 \), the decrease in \( \varepsilon_r \) of the BNT–A ceramics slows down, and it is related to the small amount of secondary phase, consistent with the previous results of Al-doping in the BLT system \[36\]. Figure 5(c) shows that when \( z \leq 1.5 \), the \( Q\times f \) values of the ceramics significantly increase as \( z \) value increases, which may be related to the decline in the activity of \( \text{OV} \) illustrated by TSDC technique in our past research \[36\]. As \( z \geq 1.5 \), the continuous doping makes the \( Q\times f \) values of the ceramics decrease slightly. It can be indicated that the decrease in the \( Q\times f \) values of the BNT–A ceramics is affected by the secondary phase, and that of BNT–AN ceramics is related to the decline of densification. BNT–AN ceramics with \( z = 1.25 \) have reached excellent microwave dielectric properties: \( \varepsilon_r = 72.2 \), \( Q\times f = 16,480 \ \text{GHz} \), and \( \tau_f = +14.3 \ \text{ppm/}^\circ\text{C} \).
It is noticed from Figs. 5(b) and 5(c) that when \( z \leq 1.5 \), the \( \varepsilon_r \) and \( Q \times f \) values of the BNT–AN ceramics are both higher than those of the BNT–A ceramics with the same doping amount, indicating that Al/Nd co-doping is a superior strategy for the substitution in the BNT ceramics. The comparison of the \( \varepsilon_r \) and \( Q \times f \) values of these ceramics is visually presented in Fig. 6. This important difference in microwave dielectric properties may be related to the factors such as the composition, structure, and defects of the ceramics. The trivalent cations filling the vacancies at the A1 sites have different polarizabilities (\( \alpha(\text{Al}^{3+}) = 0.78 \text{ Å}^3 \), \( \alpha(\text{Nd}^{3+}) = 5.01 \text{ Å}^3 \)), which results in higher \( \varepsilon_r \) values of BNT–AN ceramics according to Shannon’s rule [42]. As for the \( Q \times f \) values, the determinants may become more complicated: In addition to the secondary phase and porosity that have been discussed, the defects and stability of crystal lattice may also play an important role [6,43]. Bond length, bond valence, and bond energy are important factors that reflect the stability of crystal lattice, and have been used to explore the relationship between the structure and properties of microwave dielectric ceramics [44–46]. However, according to the results of Rietveld refinement, the variation of the average bond length of the ceramics related to \( z \) value is less than 0.01 Å, which is roughly equivalent to the uncertainty of Rietveld refinement method (~0.006 Å). The average bond length of A1–O is shown in Fig. S1 in the ESM as an example. These data could hardly be used for further analysis. Therefore, Raman spectroscopy and TSDC technique are performed to further explore the relationship among the crystal structure, defects, and \( Q \times f \) values of the ceramics.

Raman spectroscopy can reflect the lattice vibration information of the materials. The polarization mechanism of dielectrics in the microwave frequency band is mainly ion displacement polarization [47], which is closely related to the vibration of ions in the crystal lattice. Therefore, Raman spectroscopy is a powerful tool for studying the relationship between the structure and properties of microwave dielectric ceramics [21,33,48–54]. The space group of the BLT superlattice with tungsten–bronze structure is \( \text{Pbnm} \) (No. 62), and there are 24 Raman active vibration modes: \( 7A_g + 7B_g + 5B_2g + 5B_3g \) [55]. The Raman spectrum results of the BNT–A and BNT–AN ceramics are presented in Fig. 7. A total of 17 Raman vibration modes were observed in the experimental data. As the Raman spectra of the BLT system are excessively complex, previous studies had different opinions on the identification of Raman modes. Nevertheless, most studies considered that the Raman vibration modes in the region of 100–200 cm\(^{-1}\) correspond to A-site cation translation. The vibration modes in the regions of 200–400 and 400–600 cm\(^{-1}\) were attributed to the rotation and the internal vibration of the TiO\(_6\) octahedra, respectively. The mode at 757 cm\(^{-1}\) might correspond to the second order scatter [21,33,52–54]. Limited by the test conditions, vibration modes between 50 and 100 cm\(^{-1}\) in the BLT system have not been reported yet. Previous studies on perovskite systems such as SmAlO\(_3\), NdNiO\(_3\), LaGaO\(_3\), and BaCeO\(_3\), which also have the space group symmetry \( \text{Pbnm} \), reported Raman modes in the region of 50–100 cm\(^{-1}\), and identified all those modes as A-site cation translation [55–60]. Therefore, in the BNT–A and BNT–AN systems, the vibration modes between 50 and 100 cm\(^{-1}\) are identified as A-site cation translation as well as the vibration modes between 100 and 200 cm\(^{-1}\). It is reported that the mode at 234 cm\(^{-1}\) was considered as the tilting vibration of the TiO\(_6\) octahedra when the A sites are occupied by...
Ba$^{2+}$ [49,55]. The doping methods in the present work have not made any changes to the Ba$^{2+}$ cations occupying the A2 sites, so it can be considered that this mode does not change significantly. In order to compare the intensities of the Raman modes, the relative intensities of the Raman spectra in Fig. 7 were obtained by normalizing the experimental intensities based on the peak values of the Raman mode at 234 cm$^{-1}$.

As shown in Fig. 7, with the increase in $z$ value, most of the Raman modes present a blue-shift, which indicates that the cell volume decreases [21,33,47,50,53,54,61], consistent with the XRD results. The relative intensities of the vibration modes in the region of 300–400 cm$^{-1}$ increase slightly as $z$ value increases, implying that the tilting vibration of the TiO$_6$ octahedra becomes stronger, and the decline of $\tau_I$ is related to this phenomenon [49,52,54]. More obvious changes appear in the vibration modes between 50 and 200 cm$^{-1}$, which are identified as A-site cation translation. As $z$ value increases, the relative intensities of these Raman modes are significantly reduced, where the variation of relative intensities of the Raman modes at 80 and 94 cm$^{-1}$ is shown in Fig. 8 as an example. It represents that the A-site cation translation is weakened, indicating that the binding force towards the A-site cations is strengthened, and accordingly the contribution to the microwave dielectric loss is reduced and the $Q$-$\tau_f$ values increase. Comparing the Raman spectra of BNT–A and BNT–AN ceramics with the same $z$ value, it is found that the relative intensities of the Raman modes at 80 and 94 cm$^{-1}$ of the BNT–AN ceramics are lower than those of the BNT–A ceramics, as shown in Fig. 8. It is implied that the strength of the A-site cation vibration in the BNT–AN ceramics is weaker, so the contribution to the microwave dielectric loss is lower, and the $Q$-$\tau_f$ values are higher. Briefly, the relationship between the $Q$-$\tau_f$ values and the strength of the A-site cation vibration in the BNT–A and BNT–AN systems has been established through Raman spectroscopy.

TSDC technique can provide valuable information on the types and concentrations of defects in dielectrics, and has been widely used to explore the dielectric response mechanism of ceramics [36,62–69]. Liu and Randall [62] firstly reported the method for determining the types of defects in inorganic dielectrics through the changes in peak position ($T_m$, the temperature at which the absolute value of current density is maximized) and peak intensity ($J_m$, the maximum of the absolute value of current density) of the TSDC curves with various polarization conditions ($T_p$ and $E_p$), and Zhang et al. [67] applied this method to microwave dielectric ceramics for the first time. Figure 9 shows the TSDC curves of the BNT, BNT–A ($z = 1.25$), and BNT–AN ($z = 1.25$) ceramics. The curves of all samples show three or four TSDC peaks, indicating that there are at least three or four defect relaxation mechanisms. In the range of 50 $^\circ$C $< T_m < 150$ $^\circ$C, there is a weak peak (referred to as peaks A$_1$, A$_2$, and A$_3$) in each figure. And peaks similar to each other (referred to as peaks B$_1$, B$_2$, and B$_3$) are displayed in the range of 160 $^\circ$C $< T_m < 200$ $^\circ$C. The TSDC curves of different samples are quite different in the high temperature section above 200 $^\circ$C. The curves of the undoped sample exhibit a very strong peak (referred to as peak D$_1$), and its $T_m$ values have exceeded the test range. The curves of the two doped samples both show peaks with similar changes (referred to as peaks C$_2$ and C$_3$) at around 240 $^\circ$C. The TSDC curves of the BNT–A ($z = 1.25$) ceramics also show a weak peak (referred to as peak D$_3$) with $T_m > 280$ $^\circ$C.

The $T_m$ and $J_m$ of peaks A$_1$ and A$_2$ both increase with an increase in $E_p$, indicating that these peaks are related to the relaxation of $V_{O^\circ}$. As $E_p$ increases, the $J_m$ of peak A$_2$ increases while the $T_m$ decreases, indicating that peak A$_2$ is related to the relaxation of trapped charges. Using the initial rise method [67,70], the activation energies of peaks A$_1$, A$_2$, and A$_3$ are calculated as 0.43–0.50, 0.14–0.17, and 0.24–0.36 eV, respectively. Based on the previous results from Refs. [36,65,66], the activation energies of peaks A$_1$ and A$_3$ are close to those of the in-grain $V_{O^\circ}$, and it can be inferred that these peaks are related to the relaxation of the in-grain $V_{O^\circ}$. The $T_m$ and activation energy of peak

![Fig. 8](https://www.springer.com/journal/40145)
A2 are similar to those of peaks A1 and A3, and it is speculated that peak A2 may correspond to trap charges associated with the in-grain $V_O^\Gamma$. Peaks B1, B2, B3, C2, and C3 have $T_m$ values which basically unchanged with polarization conditions, while their $J_m$ values increase with an increase in $E_p$, indicating that they are related to the relaxation of defect dipoles. The calculated activation energies of peaks B1, B2, and B3 are 0.58–0.80, 0.64–0.75, and 0.59–0.75 eV, respectively. According to the results from Refs. [36,64,71], it can be inferred that peak B is related to the relaxation of the Ti$^{IV}_B$ – $V_O^\Gamma$ defect dipoles. Although the activation energies of peaks C2 and C3 are difficult to calculate by the initial rise method, the type of defects related to peak C could be determined by the defect reactions in the doping process, considering that peak C appears only after doping. During the substitution process of Al$^{III}$ for Ti$^{IV}$ at the B sites, Al$^{III}_B$ point defects are formed. Meanwhile, excess trivalent cations (Al$^{III}$ or Nd$^{III}$) were added to fill the vacancies at the A1 sites, forming Al$^{III}_A$ or Nd$^{III}_A$ point defects. Thus the condition of charge balance could be ensured, without ion valence changing or $V_O^\Gamma$ producing. Therefore, peaks C2 and C3 are considered as the relaxation peaks of the Al$^{III}_B$ – Al$^{III}_A$ and Al$^{III}_B$ – Nd$^{III}_A$ defect dipoles, respectively. As for peak D1, the current density rises slower when $E_p$ is higher, indicating that it will reach a peak value at a higher temperature with higher $E_p$, which signifies that peak D1 is related to the relaxation of $V_O^\Gamma$. The calculated activation energy of peak D1 is 0.98–1.19 eV, similar to that of the across-grain-boundary $V_O^\Gamma$ (1.1 eV) [36,63]. It is implied that peak D1 is related to the relaxation of the across-grain-boundary $V_O^\Gamma$. Since the position of peak D2 is similar to that of peak D1, it is speculated that the relaxation mechanisms of the two are the same, so that it can be considered that peak D2 is also related to the relaxation of the across-grain-boundary $V_O^\Gamma$.

TSDC peaks with higher $J_m$ imply a higher concentration of the corresponding defects [69,72]. Comparing the TSDC curves of the three ceramic samples, the BNT ceramics with peak D1 in Fig. 9(a) show extremely high concentration of the across-grain-boundary $V_O^\Gamma$, while the BNT–A ($z = 1.25$) ceramics with peak D2 in Fig. 9(b) show only a small amount of the across-grain-boundary $V_O^\Gamma$, and the BNT–AN ($z = 1.25$) ceramics show no peaks corresponding to the across-grain-boundary $V_O^\Gamma$ in Fig. 9(c). It is generally believed that oxygen vacancies could cause the extrinsic loss of dielectric ceramics, and affect the $Q\times f$ values at microwave frequency bands [6]. The TSDC results in the present work are consistent with it. It is noticed that each O$^{2-}$ in the crystal lattice is adjacent to several A-site cations in the BLT system. Associating the results of TSDC with the aforementioned Raman spectroscopy of the BNT–A and BNT–AN ceramics, it can be found that with the strengthening of binding force between the A-site cations and O$^{2-}$, the formation of $V_O^\Gamma$ becomes difficult, indicating that the results of TSDC and Raman spectroscopy are consistent. It is demonstrated
for the first time that in the structural and defect modulation of the BNT ceramics, the formation of $V_0$ in the crystal lattice is closely related to the strength of the A-site cation vibration, $\varepsilon_r$ affects the lattice vibration, and then affects the microwave dielectric loss.

The microwave dielectric properties ($Q\times f$ value vs. $\varepsilon_r$) of medium/high $\varepsilon_r$ ceramics reported after 2010 with high $Q$ and near-zero $\tau_f$ are summarized in Fig. 10 [25,26,29,33,36,37,54,73–78]. The current BNT–AN ceramics obviously exhibit superior microwave dielectric properties. Using the structural and defect modulation strategy, the novel doping strategy developed in this paper could provide new ways on the modification of medium/high $\varepsilon_r$ ceramics, and the ceramics could have outstanding application prospects in the 5G technology.

![Fig. 10 Summary of $Q\times f$ value vs. $\varepsilon_r$ plot for microwave dielectric ceramics reported after 2010 with 65 < $\varepsilon_r$ < 85, $Q\times f$ > 10,000 GHz, and $-20 \text{ ppm/}^\circ C < \tau_f < 20 \text{ ppm/}^\circ C$. The data are collected from Refs. [25,26,29,33,36,37,54,73–78].](image)

4 Conclusions

The Al-doped and Al/Nd co-doped BNT ceramics are prepared through the solid state processing. The microwave dielectric properties of the BNT–A and BNT–AN ceramics are compared, and the relationship among the composition, structure, defects, and microwave dielectric properties of the ceramics was explored through Rietveld refinement, Raman spectroscopy, and TSDC technique. As the doping amount increases, the $\varepsilon_r$ and $\tau_f$ values of the ceramics decrease, and the $Q\times f$ values first increase and then slightly decrease. The $\varepsilon_r$ and $Q\times f$ values of BNT–AN ceramics are both higher than those of BNT–A ceramics, indicating that Al/Nd co-doping is a novel and superior doping method that maintains the condition of charge balance. The results of Rietveld refinement show that there is a small amount of unknown secondary phase in the BNT–A ceramics, and the relative density data show that the BNT–AN ceramics are more difficult to densify, which may result in the deterioration of microwave dielectric performance when $z \geq 1.5$. Raman spectroscopy and TSDC measurement together show that the $Q\times f$ values of the BNT–A and BNT–AN ceramics are closely related to the strength of the A-site cation vibration and the concentration of $V_0$. With the strengthening of binding force between the A-site cations and $O^{2−}$, the contribution of the A-site cations to the microwave dielectric loss reduces, the $Q\times f$ values decrease, and the formation of $V_0$ becomes difficult. It is also proved that in microwave frequency bands, oxygen vacancies affect the dielectric loss by affecting the lattice vibration. Microwave dielectric ceramics with excellent performance in the field of medium/high $\varepsilon_r$ were obtained by the structural and defect modulation strategy: $\varepsilon_r = 72.2$, $Q\times f = 16,480 \text{ GHz}$, and $\tau_f = +14.3 \text{ ppm/}^\circ C$, which could have outstanding application prospects in the 5G technology.

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