乌青铜型 $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ 微波介质陶瓷的电导和介电损耗夏海廷^{1,2} 匡小军^{3,*} 王春海¹ 李文先² 荆西平^{1,*} 赵 飞⁴ 岳振星⁴

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摘要: 用固相反应合成了乌青铜型钛酸盐陶瓷 $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$, 并用电化学阻抗和微波介质谐振测试表征了不同热处理和钽掺杂对电导和微波介电损耗的影响. 电导率随退火气氛(空气, 氧气和氮气)的变化与缺陷反应平衡 $2\text{O}_\text{o}^{2-} \leftrightarrow 2\text{V}_\text{o}^{\bullet\bullet} + \text{O}_2\uparrow + 2\text{e}'$ 和 $\text{Ti}_\text{n}^{4+} + \text{e}' \leftrightarrow \text{Ti}'_\text{n}$ 随氧分压的变化一致, 表明 $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ 具有 n 型导电性质. 在空气和氧气中退火有利于减少包括 $\text{V}_\text{o}^{\bullet\bullet}$, Ti'_n 和弱束缚电子在内的本征缺陷因而降低电导. 而在低氧分压的氮气中进行退火处理, 增加了缺陷的浓度, 同时提高了电导率. 在空气/氧气/氮气中的退火处理对微波介电损耗没有明显的影响, 表明本征缺陷对微波介电损耗的影响可以忽略. 空气退火处理样品的电导率和微波介电损耗低于空气淬火处理的样品; 其中电导的变化与缺陷反应平衡相关, 但空气退火降低微波介电损耗可能与退火消除晶格热应力有关. 五价钽的掺杂降低了电导但增大了微波介电损耗. 研究表明空气退火处理能有效地改善 $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ 陶瓷的品质因子 $Q \times f$, 其值提高了约 12%.

关键词: 缺陷; 电导; 微波介电损耗; $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$; 乌青铜结构

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Conductivity and Dielectric Loss of Tungsten-Bronze-Type $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ Microwave CeramicsXIA Hai-Ting^{1,2} KUANG Xiao-Jun^{3,*} WANG Chun-Hai¹ LI Wen-Xian²JING Xi-Ping^{1,*} ZHAO Fei⁴ YUE Zhen-Xing⁴

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Abstract: Tungsten-bronze type titanate $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics were synthesized by solid state reactions. The conductivity and microwave dielectric loss of the samples that were thermally treated under various conditions and Ta-doped were investigated by electrochemical impedance measurement and microwave dielectric resonator measurement. The variation in conductivity with annealing atmospheres of air, O_2 , and N_2 was consistent with the defect equilibria $2\text{O}_\text{o}^{2-} \leftrightarrow 2\text{V}_\text{o}^{\bullet\bullet} + \text{O}_2\uparrow + 2\text{e}'$ and $\text{Ti}_\text{n}^{4+} + \text{e}' \leftrightarrow \text{Ti}'_\text{n}$, suggesting n -type conductance for $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$. Thermal treatment in air/ O_2 was found to favor the elimination of the native defects $\text{V}_\text{o}^{\bullet\bullet}$, Ti'_n and weakly bound electrons thus decreasing the conductivity. Thermal treatment in a N_2 atmosphere, which had a low oxygen partial pressure, increased the defect content and the conductivity. Thermal treatment in air/ O_2 / N_2 did not clearly affect the microwave dielectric loss, suggesting that native

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defects have negligible effects on this property. The air-annealed sample was found to have lower conductivity and lower microwave loss compared with the air-quenched sample. The change in conductivity was found to be related to the equilibrium of the native defects but the change in microwave dielectric loss might be explained by the release of thermally induced lattice strain. Ta doping reduced the conductivity but increased the microwave dielectric loss. This work shows that air-annealing may be an efficient way to improve the $Q \times f$ factor for $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics, which was enhanced by $\sim 12\%$.

Key Words: Defect; Conductivity; Microwave dielectric loss; $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$; Tungsten-bronze

1 Introduction

The miniaturization of microwave telecommunication components such as resonators and filters requires dielectric materials with high dielectric permittivity (ϵ), low dielectric loss ($\tan\delta$) or high quality factor ($Q=1/\tan\delta$) and temperature-stable resonance frequency (τ_f) at microwave frequency.¹ These three key parameters are almost always mutually exclusive in dielectric materials,² which complicate the optimization of microwave dielectric properties for developing new microwave dielectrics. Among these three parameters, dielectric loss comprises intrinsic loss from vibration anharmonicity of perfect lattice in materials and extrinsic loss induced by processing, such as porosity, defects, impurities, grain size etc. Optimization of quality factor usually refers to minimization of extrinsic loss, which is still a challenge due to lack of clear understanding on the fundamental physics of microwave dielectric loss and the underlying chemistry on the composition, structure, and defects.

There are considerable interests on titanate-based microwave dielectric ceramics, such as $\alpha\text{-PbO}_2$ -type $\text{Zr}_{1-x}\text{Sn}_x\text{TiO}_4$,³ barium polytitanates $\text{Ba}_2\text{Ti}_9\text{O}_{20}/\text{BaTi}_4\text{O}_9$,⁴ tungsten-bronze-type $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ (R is rare earth elements),⁵⁻⁷ ilmenite-perovskite composite $\text{MgTiO}_3\text{-CaTiO}_3$,⁸ perovskite-type $\text{LaAlO}_3\text{-CaTiO}_3$,⁹ and B-site deficient hexagonal perovskites titanate $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ ¹⁰ because of their excellent microwave dielectric properties. In the titanate-based dielectric ceramics, the occurrence of oxygen loss and Ti^{4+} partial reduction are common during the high temperature sintering process, which hinder the optimization of their Q factors.^{1,2,11,12} Thus the processing of firing the ceramics in the atmosphere with high oxygen partial pressure and doping to eliminate oxygen loss and reduction of Ti^{4+} were employed to improve the Q factors of the titanate-based dielectric ceramics, which were highlighted in the previous publications.^{1,2,11-14} For understanding the correlation between the defects associated with the oxygen loss ($\text{V}_\text{O}^\times$)/titanium partial reduction (Ti'_Ti) and the microwave dielectric loss in titanate-based dielectrics, MgTiO_3 ceramic was chosen as a model material for titanate dielectrics and dielectric loss spectrum of this material was investigated over a wide frequency range in our previous work.¹⁵ We proposed that low frequency conduction arising from electron hopping and relaxation of atomic defect polarization contributes little to the microwave dielectric loss and the atomic defects may affect the microwave dielectric loss *via* modifying

the anharmonicity of lattice vibration. Our recent works on MgTiO_3 ceramics¹⁶ and CaTiO_3 ceramics¹⁷ indicated that native defects, such as $\text{V}_\text{O}^\times$ and Ti'_Ti , and weakly bound electrons, only affected the low frequency conduction, but not the microwave dielectric loss.

Among the titanate-based dielectrics, tungsten-bronze type $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ (R=La, Pr, Nd, Sm, Eu, Gd) have received much attention because of their high permittivity ($\epsilon \sim 70\text{--}150$) and tunable chemical compositions.^{5-7,18} High Q factor was obtained on Nd and Sm analogues at composition around $x=2/3$ due to the A-cation ordering^{7,18} and zero τ_f was achieved by combining Nd analogue with positive τ_f and Sm analogue with negative τ_f , e.g., $\text{Ba}_{4.2}\text{Sm}_{7.36}\text{Nd}_{1.84}\text{Ti}_{18}\text{O}_{54}$, $\epsilon \sim 84$, $Q \times f \sim 9000$ GHz (f is resonance frequency), $\tau_f \sim 0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.⁵ This tungsten-bronze phase was initially reported with a formula $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ by Kolar *et al.*¹⁹ in studying the ternary phase diagram of $\text{BaO-Nd}_2\text{O}_3\text{-TiO}_2$ and its composition was later corrected as $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$.²⁰ Varfolomeev *et al.*²¹ found that this compound formed solid solution as $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ and Ohsato *et al.*²² determined the solid solution limits for Nd and Sm analogues as $0 \leq x \leq 0.7$ and $0.3 \leq x \leq 0.7$, respectively. In the $\text{Ba}_{6-3x}\text{Nd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ solid solution, the material $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ($x=0.5$) exhibited good microwave dielectric property of $\epsilon \sim 85$, $Q \times f \sim 5000\text{--}6000$ GHz except for its high $\tau_f \sim 100 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.⁶ In this study, air-annealing/air-quenching, thermal treatments in various atmospheres (air, O_2 , and N_2) as well as Ta-doping were conducted on $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics. The influences of the various treatments on the conductivity and the microwave dielectric loss of the $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics were investigated and the correlations among the defects, conductivity, and microwave dielectric loss are discussed.

2 Experimental

Polycrystalline $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic samples were prepared using high temperature solid state reactions. Stoichiometric amounts of BaCO_3 (AR), Nd_2O_3 (99.9%), and TiO_2 (AR) as starting materials were weighed and mixed by ball milling in ethanol with agate balls for 24 h. The ethanol was removed by vacuum filtration and the mixed powders were dried in air. The powders were then calcined at $1150 \text{ }^\circ\text{C}$ for 3 h. Further the powders were re-ball-milled in ethanol for 20 h. After filtration and drying processes, a few drops of 3% aqueous solution of polyvinyl alcohol (PVA) was added into the dried powders as

binder and the powders were pressed into pellets by uniaxial pressing. The pellets were then fired at 550 °C for 2 h to remove the PVA binder, followed by sintering at 1350 °C for 4 h in air with a heating rate 20 °C·min⁻¹. After sintering, the pellets were cooled spontaneously in the furnace, leading to as-sintered sample, BNT-0. All the pellets had relative density of ~96%, which was calculated using the weights and dimensions of the pellets as well as the X-ray theoretical density. For the preparation of Ta-doped samples, suitable amount ($\leq 2\%$, molar fraction) of Ta_2O_5 (high purity) was added according to the nominal composition $\text{BaNd}_2\text{Ti}_{4-x}\text{Ta}_x\text{O}_{12-\delta+0.5x}$ and the calcining and sintering processes are the same as those for BNT-0.

For modifying the defect contents, various thermal treatments were conducted on the $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ samples. Air-annealing was performed on a sintered pellet, heated at 1100 °C for 4 h in air and then cooled to 400 °C with a rate of 2 °C·min⁻¹ in a furnace before being taken out to cool down to ambient temperature, resulting in sample BNT-1. The air-quenching was carried out by taking out a sintered pellet quickly from furnace at 1100 °C after being heated at 1100 °C for 4 h then cooling the pellet to ambient temperature in air, producing sample BNT-2. The thermal treatments in air/ O_2 / N_2 atmospheres were performed by heating the sintered pellets in a tube furnace with air, O_2 , or N_2 atmosphere at 650 °C for 4 h. After the treatments, the pellet samples were taken out from the tube furnace quickly, and then cooled down to ambient temperature, leading to samples BNT-3 (air), BNT-4 (O_2), and BNT-5 (N_2).

Phase assemblages were checked by powder X-ray diffraction (XRD, Rigaku D/max 2000 diffractometer, Japan; Cu $K\alpha$ radiation, graphite monochromator). All the ceramic samples studied in this work have pure orthorhombic phase, agreeing with JCPDS file 44-61. Electrochemical impedance spectra were recorded in the frequency range of 5 Hz–13 MHz using an impedance/gain-phase analyzer (Model HP 4192A, USA), which was conducted at various temperature from 200 to 800 °C in air with heating and cooling cycles. The AC impedance measurements were also conducted in different atmospheres at 650 °C and the atmosphere was changed according to the following sequence: air→ O_2 → N_2 → O_2 . The gas flow rate was kept at ~500 mL·min⁻¹ and each atmosphere was maintained for 5–10 h. Prior to the measurements, platinum paste was coated on two opposite surfaces of the pellets and fired at 800 °C for 10 min to burn off the organic components to form electrodes. Microwave measurements in the frequency range of 50 MHz–20 GHz were conducted using a network analyzer (HP 8720ES, USA). The permittivity ϵ was measured using the Hakki and Coleman dielectric resonator method²³ by exciting the TE_{011} resonant mode of the dielectric resonators²⁴ while the unloaded Q factor was measured using the TE_{018} mode.²⁵

3 Results and discussion

3.1 Electrochemical impedance measurements for $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics

Fig.1 Electrochemical impedance plot of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic at 700 °C in air and an equivalent circuit of parallel R_b and C_b for modeling the impedance data

A typical complex impedance plot (Z'' – Z' plot) of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics (BNT-0, measured in air at 700 °C) is shown in Fig.1, in which a single semicircular arc is observed. An equivalent circuit with resistor (R_b) and capacitor (C_b) in parallel is required to model this semicircular arc.²⁶ The associated R_b value can be estimated as the intercept of the semicircular arc at low frequency and the C_b value can be estimated from the equivalent circuit fitting. The C_b value is ~7 pF·cm⁻¹, approximately consistent with the permittivity measured at microwave frequency ($\epsilon=85$) and indicative of bulk response for the semicircular arc. No significant responses from grain boundary and electrode were detected over the measured frequency range and temperature range.

Variations of bulk conductivity σ_b ($=1/R_b$) of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic (BNT-0) with temperatures in a heating and cooling cycle from 420 to 700 °C are represented by Arrhenius plots (Fig.2). The Arrhenius plot of the bulk conductivity on heating shows curvature around 460–500 °C with activation energy (E_a) transition from 0.30 eV in low temperature range (420–460 °C) to 0.76 eV in high temperature range (540–700 °C). Below 540 °C, the conductivity in the heating process is higher than that in the cooling process and conductivities in the both heating and cooling processes are almost identical above 540 °C.

Such conduction behavior is similar to those observed in some other titanates, such as $\text{BaEu}_2\text{Ti}_4\text{O}_{12}$ ²⁷ and MgTiO_3 .¹⁵ De-

Fig.2 Arrhenius plots of the bulk conductivity of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic

fect equilibriums associated with oxygen loss and Ti^{4+} partial reduction may be applied for understanding this phenomenon. During sintering at high temperature, the defects are generated in $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$:

$\text{V}_\text{o}^{\bullet}$ can contribute weakly bound electrons and these electrons can partially reduce Ti^{4+} to Ti^{3+} , i.e.,

The conductance in the $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic is related to the content of the weakly bound electrons that are associated to the defects of $\text{V}_\text{o}^{\bullet}$ and Ti_Ti' (Ti^{3+}), corresponding to n -type conduction. No response of ionic conduction was observed in the AC impedance spectra described above. Above 540°C , E_a consists of two terms: generation energy of the defects/electrons *via* equilibration (1) and potential energy for the trapped electrons hopping over. Below 460°C , the defects generated in the sintering process at elevated temperature are frozen and E_a may only be associated to the potential energy for the trapped electrons hopping over. Therefore, E_a in the high temperature range of $540\text{--}700^\circ\text{C}$ appears higher than that below 460°C . In the heating process, when the temperature increased over 460°C , the defect equilibration takes place, which shifts to the left and reduces the defect content. This accounts for the gradual increase of the conductivity over the range of $460\text{--}540^\circ\text{C}$. Above this range the defect equilibration reaches and the conductivities in the both heating and cooling processes do not show apparent difference. In the cooling process below 540°C , the material contains lower contents of defects than that in the heating process due to annealing effect thus a lower conductivity appears.

Fig.3 shows the conductivity variations with time in various atmospheres at 650°C in an *in-situ* measurement. The initial measurement was conducted in air, followed by a switch sequence: $\text{O}_2 \rightarrow \text{N}_2 \rightarrow \text{O}_2$. When the sample was initially heated in air, the conductivity decreased gradually. After the atmosphere was switched to O_2 , the conductivity decreased continuously. While the atmosphere was switched from O_2 to N_2 , the conductivity increased dramatically. Finally, when we altered the atmosphere back to O_2 again, the conductivity decreased sharply and almost approached to the level after the first O_2 heating. These results support that the equilibriums (1) to (3) occurred in $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics. The initial heating in air reduced the

Fig.3 Bulk conductivity variations with time in various atmospheres in a switching sequence of air $\rightarrow \text{O}_2 \rightarrow \text{N}_2 \rightarrow \text{O}_2$ at 650°C

contents of the intrinsic defects (e.g., $\text{V}_\text{o}^{\bullet}$ and the weakly bound electrons) arising from the high temperature sintering, i.e., the equilibriums (1) to (3) shifted to left during the heating process in air. The following heating in O_2 increased the O_2 partial pressure, leading to the equilibriums further shifting to left and the conductivity was reduced. The conductivity increased during the heating process in N_2 atmosphere due to its low O_2 partial pressure, which drove the equilibriums shifting to right. The n -type conduction behavior of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic was further confirmed by the data in Fig.3.

3.2 Microwave properties of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics

The microwave dielectric property measurements were carried out for the $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic samples, which had been thermally treated in various conditions. The permittivity was insensitive to the thermal treatments and all samples gave ϵ about 85. The quality factors represented by $Q \times f$ are listed in Table 1. The conductivity data for the related samples are also listed for comparison. The air-annealing reduces the conductivity by $\sim 76\%$ and improves the $Q \times f$ value by $\sim 12\%$, while the air-quenching increases the conductivity by $\sim 61\%$ and deteriorates the $Q \times f$ value by $\sim 3\%$. These results might support the idea that increasing the contents of the native defects damages the quality factor and reducing the contents of the defects improves the quality factor. However the data from the samples thermally treated in various atmospheres do not support this idea. When thermally treated in various atmospheres, the conductivity value changes several tens percent, which can be understood by the equilibriums (1) to (3), but the $Q \times f$ value is al-

Table 1 $Q \times f$ values ($f \sim 4.6$ GHz) at room temperature and conductivities of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics with various thermal treatments

Sample No.	Thermal treatment	$(Q \times f)/(\text{GHz})$	$\Delta(Q \times f)/(Q \times f)_0^*$	$10^6 \sigma_b / (\Omega^{-1} \cdot \text{cm}^{-1})$	$\Delta \sigma_b / \sigma_{b0}^*$
BNT-0	as-sintered	6762	0	0.107 (440 $^\circ\text{C}$) 7.53 (650 $^\circ\text{C}$)	0
BNT-1	air-annealing	7576	12%	0.0262 (440 $^\circ\text{C}$)	-76% ^a
BNT-2	air-quenching	6494	-3%	0.172 (440 $^\circ\text{C}$)	61% ^a
BNT-3	in air	6724	-0.6%	6.73 (650 $^\circ\text{C}$)	-11% ^b
BNT-4	in O_2	6793	0.5%	5.35 (650 $^\circ\text{C}$)	-29% ^b
BNT-5	in N_2	6700	-0.9%	8.97 (650 $^\circ\text{C}$)	19% ^b

* The relative variations on the $Q \times f$ and σ_b values were calculated in comparison with $(Q \times f)_0$ and σ_{b0} values for the as-sintered BNT-0. ^a The $\Delta \sigma_b / \sigma_{b0}$ values were calculated using the data at 440°C . ^b The conductivities were taken from Fig.3 and the $\Delta \sigma_b / \sigma_{b0}$ values were calculated using the data at 650°C .

most of no change. The above results suggest that the conductivity measured in low frequency range has no direct relation with the Q factor. It seems that other factor rather than the native defects affects the Q factor here.

Yoo *et al.*²⁸ investigated the mechanism responsible for the reduction in microwave dielectric loss during the slow cooling of MgTiO₃ ceramics. They proposed an acceptable mechanism using precise XRD data, which showed that the reduction on the $Q \times f$ was due to the release of thermally induced lattice strain. The $Q \times f$ deterioration for the air-quenched BaNd₂Ti₄O₁₂ in this work can be explained by Yoo's proposal²⁸ as air-quenching may induce more strain in the lattice. On the other hand, air-annealing may release the lattice strain thermally induced during high temperature sintering, which leads to the clear improvement on the $Q \times f$ value.

3.3 Ta-doping effect on the conductivity and microwave properties of BaNd₂Ti₄O₁₂ ceramics

Not only the native defects, but doping defects also affect the electric properties of ceramics. Ferreira and Baptista's work²⁹ indicated that alio-valence doping of Nb to MgTiO₃ dielectric ceramics resulted in the elimination of oxygen vacancies in the lattice and the improvement of Q factor. Similar results were obtained for Zr_{0.8}Sn_{0.2}TiO₄ systems.³⁰ Our previous research^{16a} also showed that Ta-doping enhanced the Q factor of MgTiO₃. In this work, the conductivity and microwave properties of Ta-doped BaNd₂Ti₄O₁₂ were studied. It is assumed that Ta-doping (Ta₂O₅ as dopant) introduces oxygen to fill the oxygen vacancies, thus the composition of the doped ceramic samples can be represented as the formula BaNd₂Ti_{4- x} Ta _{x} O_{12- δ +0.5 x} .

Fig.4 shows that the conductivity measured by the electrochemical impedance analyzer decreases with an increase of Ta content in the range $x < 0.01$, which can be understood by the equilibrium (4)

Ta-doping reduces the contents of $\text{V}_\text{O}^{\bullet\bullet}$ and electrons, resulting in the reduction of the conductivity. In fact, Ta_Ti^+ can also contribute weakly bound electrons:

The reduction of the conductivity with Ta content suggests that the bonding between electrons and $\text{V}_\text{O}^{\bullet\bullet}$ is weaker than that

Fig.4 Correlation between conductivity and Ta doping content for the BaNd₂Ti_{4- x} Ta _{x} O_{12- δ +0.5 x} ceramics at 600 °C

Fig.5 Correlations between $Q \times f$ factor / relative density and Ta doping content for the BaNd₂Ti_{4- x} Ta _{x} O_{12- δ +0.5 x} ceramic system

between electrons and Ta_Ti^+ . When x is beyond 0.01, the conductivity keeps almost constant, which might imply a narrow solid solution range ($x \leq 0.01$) for the system BaNd₂Ti_{4- x} Ta _{x} O_{12- δ +0.5 x} .

The microwave measurements indicated that the permittivity ϵ was also insensitive to the Ta-doping in the content range studied, which was about 85–86. The $Q \times f$ decreased dramatically with the doping content of Ta (Fig.5). The appearance of Ta_Ti^+ in the lattice might be a detrimental factor to the $Q \times f$ value, which may enhance the anharmonicity of the lattice vibrations. Fig.5 also shows that with Ta-doping content increase, the relative density of the ceramic samples decreases and this might be another reason responding to the deterioration of the $Q \times f$ factor. The above results further support the idea that the decrease of the conductivity is not directly related to the Q factor improvement.

4 Conclusions

We measured electrochemical impedance spectra and microwave properties of BaNd₂Ti₄O₁₂ ceramic samples that had been thermally treated under various conditions. The properties of Ta-doped samples were also investigated. The AC impedance data showed that BaNd₂Ti₄O₁₂ had n -type conduction and the native defects $\text{V}_\text{O}^{\bullet\bullet}$, Ti'_Ti , and weakly bound electrons are probably the main intrinsic defects in the lattice. The conductivity clearly increases in N₂ atmosphere and decreases in O₂ atmosphere, which can be understood by changes in the contents of the native defects. With a change in atmosphere, the quality factor $Q \times f$ varies little. Our results reveal that the native defects only influence the low frequency conductivity but not the microwave dielectric loss. Air-annealing may be an effective way to improve the $Q \times f$ value (enhanced by ~12%) but air-quenching clearly reduces the $Q \times f$ factor, which implies that the release of the thermally induced lattice strain might be involved in the $Q \times f$ improvement. Ta-doping reduces the conductivity associated with the reduction of the native defects, but deteriorates the $Q \times f$ factor, which further supports that the native defects are not the main detrimental factors to the $Q \times f$ factor. Some previous research believed that the native defects contribute to the dielectric loss in titanate materials but our da-

ta indicate otherwise. Our recent research results on MgTiO_3 and CaTiO_3 ceramics also support our idea.

References

- (1) Reaney, I. M.; Iddles, D. J. *Am. Ceram. Soc.* **2006**, *89*, 2063.
- (2) Cava, R. J. *J. Mater. Chem.* **2001**, *11*, 54.
- (3) Wolfram, G.; Gobel, H. E. *Mater. Res. Bull.* **1981**, *16*, 1455.
- (4) Negas, T.; Yeager, G.; Bell, S.; Coats, N.; Minis, I. *Am. Ceram. Soc. Bull.* **1993**, *72*, 80.
- (5) Ohsato, H.; Kato, K.; Mizuta, M.; Nishigaki, S.; Okuda, T. *Jpn. J. Appl. Phys.* **1995**, *34*, 5413.
- (6) Valant, M.; Suvorov, D.; Rawn, C. J. *Jpn. J. Appl. Phys.* **1999**, *38*, 2820.
- (7) Ohsato, H. *J. Eur. Ceram. Soc.* **2001**, *21*, 2703.
- (8) Wakino, K. *Ferroelectrics* **1989**, *91*, 69.
- (9) Nenashva, E. A.; Mudroliubova, L. P.; Kartenko, N. F. *J. Eur. Ceram. Soc.* **2003**, *23*, 2443.
- (10) Okawa, T.; Kiuchi, K.; Okabe, H.; Ohsato, H. *Jpn. J. Appl. Phys.* **2001**, *40*, 5779.
- (11) Kuang, X.; Allix, M. M. B.; Claridge, J. B.; Niu, H. J.; Rosseinsky, M. J.; Ibberson, R. M.; Iddles, D. M. *J. Mater. Chem.* **2006**, *16*, 1038.
- (12) Templeton, A.; Wang, X.; Penn, S. J.; Webb, S. J.; Cohen, L. F.; Alford, N. M. *J. Am. Ceram. Soc.* **2000**, *83*, 95.
- (13) Lee, M. J.; Kim, C. Y.; You, B. D.; Kang, D. S. *J. Mater. Sci. Mater. Electron.* **1995**, *6*, 173.
- (14) Lee, M. J.; You, B. D.; Kang, D. S. *J. Mater. Sci. Mater. Electron.* **1995**, *6*, 165.
- (15) Kuang, X.; Jing, X.; Tang, Z. *J. Am. Ceram. Soc.* **2006**, *89*, 241.
- (16) (a) Kuang, X.; Xia, H.; Liao, F.; Wang, C.; Li, L.; Jing, X.; Tang, Z. *J. Am. Ceram. Soc.* **2007**, *90*, 3142.
- (b) Zhu, H.; Kuang, X.; Wang, C.; Xia, H.; Li, L.; Hu, P.; Jing, X.; Tang, Z.; Zhao, F.; Yue, Z. *Jpn. J. Appl. Phys.* **2011**, *50*, 065806.
- (17) Hu, P.; Jiao, H.; Wang, C. H.; Wang, X. M.; Ye, S.; Jing, X. P.; Zhao, F.; Yue, Z. X. *Mater. Sci. Eng. B* **2011**, *176*, 401.
- (18) Ohsato, H. *J. Ceram. Soc. Jpn.* **2005**, *113*, 703.
- (19) Kolar, D.; Gaberscek, S.; Volavsek, B.; Parker, H. S.; Roth, R. S. *J. Solid State Chem.* **1981**, *38*, 158.
- (20) Takahashi, J.; Ikegami, T.; Kageyama, K. *J. Am. Ceram. Soc.* **1991**, *74*, 1873.
- (21) Varfolomeev, M. B.; Mironov, A. S.; Kostomarov, V. S.; Golubtsova, L. A.; Zolotova, T. A. *Russ. J. Inorg. Chem.* **1988**, *33*, 607.
- (22) Ohsato, H.; Ohhashi, T.; Nishigaki, S.; Okuda, T.; Sumiya, K.; Suzuki, S. *Jpn. J. Appl. Phys.* **1993**, *32*, 4323.
- (23) Hakki, B. W.; Coleman, P. D. *IEEE Trans. Microwave Theory Tech.* **1960**, *8*, 402.
- (24) Courtney, W. E. *IEEE Trans. Microwave Theory Tech.* **1970**, *18*, 476.
- (25) Krupka, J.; Derzakowski, K.; Riddle, B.; Baker-Jarvis, J. *Meas. Sci. Technol.* **1998**, *9*, 1751.
- (26) Irvine, J. T. S.; Sinclair, D. C.; West, A. R. *Adv. Mater.* **1990**, *2*, 132.
- (27) Jing, X. P.; West, A. R. *Acta Phys.-Chim. Sin.* **2003**, *19*, 109. [荆西平, West, A. R. 物理化学学报, **2003**, *19*, 109.]
- (28) Yoo, S.; Yoon, K. H.; Choi, J.; Yoon, S. *Jpn. J. Appl. Phys.* **2004**, *43*, L343.
- (29) Ferreira, V. M.; Baptista, J. L. *J. Am. Ceram. Soc.* **1996**, *79*, 1697.
- (30) Michiura, N.; Tatekawa, T.; Higuchi, Y.; Tamura, H. *J. Am. Ceram. Soc.* **1995**, *78*, 793.