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Crystal structure, Raman spectroscopy and microwave dielectric properties of $Ba_{3.75}Nd_{9.5}Ti_{18-z}(Al_{1/2}Nb_{1/2})_zO_{54}$ ceramics

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ABSTRACT

The influences of substitution of $(Al_{1/2}Nb_{1/2})^{4+}$ on the crystal structure, Raman spectroscopy and microwave dielectric properties in $Ba_{3.75}Nd_{9.5}Ti_{18}O_{54}$ (BNT) ceramics were investigated in this work. The sintering samples were mainly measured by SEM, XRD and Raman spectrometer. The results showed that all $Ba_{3.75}Nd_{9.5}Ti_{18-z}(Al_{1/2}Nb_{1/2})_zO_{54}$ (BNT-(AN)z) samples formed the orthorhombic tungsten-bronze type like structure. Lattice parameters of BNT-(AN)z samples were refined by Rietveld method, and unit cell volume of samples decreased as z increased. The blue shift of Raman spectral peaks was confirmed to the result of Rietveld refinement. Moreover, Raman spectra revealed that flexible oxygen octahedra networks became stressed-rigid and oxygen octahedra became more tilted, which was ascribed to Al^{3+} and Nb^{5+} occupational disorder when $(Al_{1/2}Nb_{1/2})^{4+}$ substituted for Ti^{4+}. With increase of z value, the dielectric constant (ε_r) and temperature coefficient of resonant frequency (τ_f) decreased. The BNT-(AN)2 ceramic sintered at 1375 °C for 4 h exhibited excellent microwave dielectric properties: ε_r = 73.9, $Q\times f$ = 13,177 GHz, and τ_f = +0.3 ppm/°C. The relationship of the bond valence of the B-site to Raman shift of the A_g mode, dielectric constant (ε_r) and τ_f were analyzed.

1. Introduction

In recent years, the rapid progress of modern wireless communication applications, such as wireless charging, Virtual Reality (VR) and self-driving technology has stimulated the development of microwave dielectric ceramics to meet the demand of microwave device including resonators, oscillator and wave guides [1,2]. With respect to microwave applications, the materials should have high relative permittivity (ε_r), high quality factor ($Q\times f$) and near zero temperature coefficient of resonant frequency (τ_f), which are necessary to achieve high miniaturization, integration and reliability in microwave communication system [3].

For decades, $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solution-based ceramics have drawn an increasing interest for their high ε_r and high $Q\times f$ value, and they have attracted many scientific research personnel to study them. In 1996, Negas [4] studied the microwave dielectric properties of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ceramics as x value changes. What's more, many senior scientists have investigated the structure of $BaO\text{-}Nd_2O_3\text{-}TiO_2$ ternary compounds by various analysis methods, and they all announced that the crystal structure of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ceramics contained elements of tungsten–bronze [5–8]. As shown in Fig. 1, the 2 × 2 perovskite block took shape in tungsten-bronze type like structure, Ti^{4+} and O^{2-} formed titanium-oxygen octahedra [TiO_6], then Ba^{2+} and Nd^{2+} occupied A1, A2 site respectively in titanium-oxygen octahedra [TiO_6] interstice. It was reported that the τ_f value of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solution series were affected by tilting of the TiO_6 octahedra [9–11]. But their large positive τ_f value (+65 to +130 ppm/°C) always retarded their wide utilization [8,12,13]. Among $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions series, the excellent properties of $Ba_{3.75}Nd_{9.5}Ti_{18}O_{54}$($x$ = 3/4) (BNT) ceramics ($\varepsilon_r \geq 80$, $Q\times f \geq 9000$ GHz, τ_f ~70 ppm/°C) deserves further attention [13,14]. Many researchers have studied modified $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions. For example, Nenasheva et al. determined the Zr^{4+}substitution was in favour of lower τ_f in $BaNd_2Ti_4O_{12}$ ceramics but resulted in deteriorative ε_r and $Q\times f$ values [15]. Later, the $Ba_4(Sm_{0.5}Nd_{0.5})_{28/3}Ti_{18}O_{54}$ and $Ba_4Nd_{9.33}$-

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$Ti_{18}O_{54}$ with Al_2O_3 addition were synthesized by Chang [16] and Yao [17] respectively. Huang et al. [18]. Reported that $(Ba_{1-x}Sr_x)4(Sm_{0.4}Nd_{0.6})_{28/3}Ti_{18}O_{54}$ composition showed properties of $\varepsilon_r = 93.2$, $Q\times f = 9770$ GHz, $\tau_f = +4.56$ ppm/°C when $x = 0.08$. In addition, there were many papers about properties and structure of impure BNT ceramics by other cations substituting for B-site (Ti^{4+}), such as $(Cr_{1/2}Nb_{1/2})^{4+}$ [14], Al^{3+} [9], $(Mg_{1/3}Nb_{2/3})^{4+}$ [19] and so on.

All these works didn't investigate the relationship between structure of BNT ceramics and their microwave dielectric properties by using Raman spectroscopy. Raman spectrum analysis of BNT-(AN)z ceramics would be momentous for BNT ceramics and set a model for the modified ceramic investigation.

2. Experimental procedures

2.1. Preparation of BNT-(AN)z

The starting raw powders: $BaCO_3$, Al_2O_3, Nd_2O_3 Nb_2O_5 and TiO_2 were high-purity (99.0%) powders and weighed according to the ratio of $Ba_{3.75}Nd_{9.5}Ti_{18-z}(Al_{1/2}Nb_{1/2})_zO_{54}$ (BNT-(AN)z) where z = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0. And milled in plastic jars using deionized water for 8 h. The resulting mixtures were calcined at 1100 °C for 5 h in air with 5°C/min heating rate. Then these calcined powders were produced with 7 wt% of a 10% solution of PVA added in the size of 15 mm in diameter and 8 mm in thickness under the pressure of 200 kg/cm^2. At last, the samples were preheated at 600 °C for 3 h to exclude the organic binder, and sintered at 1350–1425 °C for 4 h in air.

2.2. Characterization

After sintering completely, the bulk densities of samples were measured by the Archimedes method. The crystalline phases of the samples were determined with XRD using CuK<alpha> radiation (Philips x'pert Pro MPD, Netherlands). The visualization of crystal structure of ceramics was acquired by VESTA software with ceramics crystallography data [20]. The refinement of crystal unit cell parameters of samples was calculated by analyzing XRD data using the "Material Analysis Using Diffraction" (MAUD) based on the Rietveld method [21,22]. The microstructure of the samples was investigated by scanning electron microscopy(SEM) (FEI Inspect F, United Kingdom) coupled with energy dispersive spectrometer(-EDS) which detected the main chemical composition of specimens. Raman spectra of the samples were measured on Nicolet ALMEGA Raman spectrometer with the existing line at 523 nm of a Nd/YAG laser at room temperature, and collected in the range of 100–1000 cm^{-1}. The dielectric characteristics at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method in the TE011 mode using a network analyzer (Agilent Technologies HP83752A) and a temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficient of resonant frequency (τ_f) of specimens was determined from the difference between the resonant frequency (2 ~ 3 GHz) obtained at 25 °C and 85 °C using Eq. (1):

$$\tau_f = \frac{\Delta f}{f_0 \cdot \Delta t} \times 10^6 = \frac{f_{85°C} - f_{25°C}}{f_{25°C} \times (85-25)} \times 10^6 \ (\text{ppm}/°\text{C}) \quad (1)$$

In Eq. (1), $f_{25\ °C}$ and $f_{85\ °C}$ represent the resonant frequency at 80 °C and 25 °C, respectively. All cylindrical samples were untreated after sintering when they were made to do dielectric measurements.

3. Results and discussion

3.1. Crystalline structure and microstructure

The X-ray diffractograms of BNT-(AN)z ($z = 0$–3) ceramics sintered at 1375 °C for 4 h in air are shown in Fig. 2 (a). All samples were crystalized as a tungsten-bronze type like structure phase $BaNd_2Ti_5O_{14}$ (JCPDS No. 33–0166) and no peaks for secondary phase were detected, which implied that it did form a single phase and composite ions $(Al_{1/2}Nb_{1/2})^{4+}$ had entered into crystal cell. Furthermore, Fig. 2 (b) depicts that the diffraction peaks of all samples shift towards the higher angle with the increase of z value. The intensity of the splitting peak (as shown in Fig. 2 (b)) gradually increased when z value increased 0 to 3. We can see from the XRD patterns of the JCPDS No. 33–0166 in Fig. 2 (a), the strongest diffraction peak of (151) face ($2\theta = 31.57°$) was very close to diffraction peak (270) face ($2\theta = 31.63°$). So the splitting peak

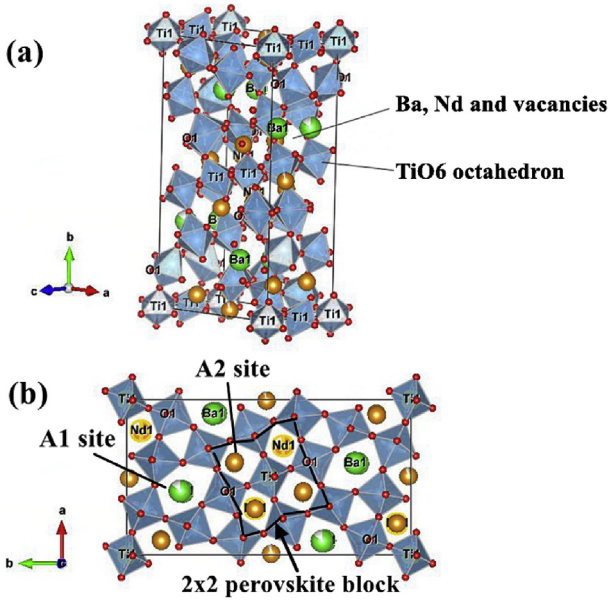

Fig. 1. Schematic representation of (a) $Ba_{3.75}Nd_{9.5}Ti_{18}O_{54}$ with tungsten-bronze type like structure and (b) the c-axis was chosen as the short axis.

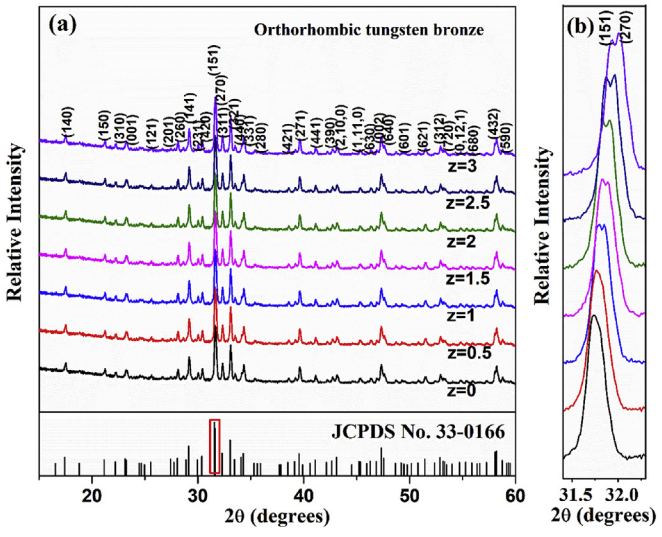

Fig. 2. (a) XRD patterns of BNT-(AN)z ($z = 0$–3) ceramics sintered at 1375 °C for 4 h in air. (b) The characteristic peaks of (270) and (151) for BNT-(AN)z phase of corresponding samples.