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Sintering behavior and microwave dielectric properties of $Bi_3(Nb_{1-x}Ta_x)O_7$ solid solutions

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ABSTRACT

Solid solutions of $Bi_3(Nb_{1-x}Ta_x)O_7$ ($x = 0.0, 0.3, 0.7, 1$) were synthesized using solid state reaction method and their microwave dielectric properties were first reported. Pure phase of fluorite-type could be obtained after calcined at $700\,°C\,(2\,h)^{-1}$ between $0 \le x \le 1$ and $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics could be well densified below $990\,°C$. As x increased from 0.0 to 1.0, saturated density of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics increased from 8.2 to $9.1\,g\,cm^{-3}$, microwave permittivity decreased from 95 to 65 while Q_f values increasing from 230 to 560 GHz. Substitution of Ta for Nb modified temperature coefficient of resonant frequency τ_f from $-113\,ppm\,°C^{-1}$ of Bi_3NbO_7 to $-70\,ppm\,°C^{-1}$ of Bi_3TaO_7. Microwave permittivity, Q_f values and τ_f values were found to correlate strongly with the structure parameters of fluorite solid solutions and the correlation between them was discussed in detail. Considering the low densified temperature and good microwave dielectric proprieties, solid solutions of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics could be a good candidate for low temperature co-fired ceramics application.

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1. Introduction

The Bi_2O_3–Nb_2O_5 binary system has good microwave dielectric properties and has attracted much attention in recent years. $BiNbO_4$ in the binary system has excellent microwave dielectric properties (dielectric constant $\varepsilon_r \approx 43$ and Q_f values between 10,000 and 17,000 GHz) and a lot of work on the modification of $BiNbO_4$ ceramics has been broadly carried out [1–4]. Although $BiNbO_4$ ceramics have good properties for microwave application and LTCC, the reaction between $BiNbO_4$ and the important electrode Ag limited its further application [5,6]. Besides $BiNbO_4$ composition, other compounds in the Bi_2O_3–Nb_2O_5 binary system have not been valued and studied roundly for microwave application. But some of them were believed to have potential value in LTCC modules and microwave application such as Bi_3NbO_7 composition with no reaction with Ag electrode [6].

Bi_3NbO_7 has been valued for its ionic conductivities behavior in the recent years. Synthesis, electrical behavior and structure of cubic Bi_3NbO_7 have been studied by many researchers [7–10]. Pure tetragonal phase of Bi_3NbO_7 was first synthesized by Ling et al. and the structure was studied using synchrotron X-ray diffraction and neutron powder diffraction [8]. Valant first reported the microwave dielectric properties of cubic Bi_3NbO_7 (permittivity of 100, $Q_f = 300$ GHz, TCF = $-200\,ppm\,°C^{-1}$) and tetragonal Bi_3NbO_7

(permittivity of 91, $Q_f = 730$ GHz, TCF = $+100\,ppm\,°C^{-1}$) [11,12]. Their study also showed that the cubic incommensurate phase undergoes an order–disorder phase transition into a commensurate tetragonal phase at temperatures below $900\,°C$ and the higher degree of ordering in the tetragonal phase of Bi_3NbO_7 reduces the dielectric losses ($Q_f = 1000$ GHz). Transformation between cubic and tetragonal Bi_3NbO_7 was described as a homogeneous nucleation with temperature-dependent induction time and growth kinetics [13]. Zhou et al reported microwave dielectric properties of cubic Bi_3NbO_7 prepared by high-energy ball milling method and found that stable pure tetragonal Bi_3NbO_7 (permittivity of 79, $Q_f = 640$ GHz, TCF near zero) could be obtained using solid state reaction method with V_2O_5 addition [14]. Ta^{5+} has very similar ion radius and characteristic to Nb^{5+}. Wang et al. ever used Ta^{5+} to substitute for Nb^{5+} in $BiNbO_4$ and pure orthorhombic phase of $BiNb_{1-x}Ta_xO_4$ could be obtained for $0 \le x \le 0.4$ [15]. A solid solution between Bi_9TaO_{16} and Bi_3TaO_7 could be obtained in Bi_2O_3–Ta_2O_5 binary system [8] and pure Bi_3TaO_7 has a smaller cell volume than that of Bi_3NbO_7. (PDF No. 44-0202) Castro reported solid solution of $Bi_3Nb_{1-x}Ta_xO_7$ ($0 \le x \le 1$) synthesized by mechanochemical activation assisted methods and studied their ionic conductivities behavior [16]. Recently, Pirnat and Suvorov [17] studied the incommensurate to commensurate phase transition in $Bi_3(Nb_{1-x}Ta_x)O_7$ system. Their research was focused on the influence from phase transition to dielectric properties.

In the present work binary systems of $Bi_3(Nb_{1-x}Ta_x)O_7$ ($x = 0.0, 0.3, 0.7, 1$) were synthesized using solid state reaction method. Sintering behavior and phase structure of $Bi_3(Nb_{1-x}Ta_x)O_7$ were

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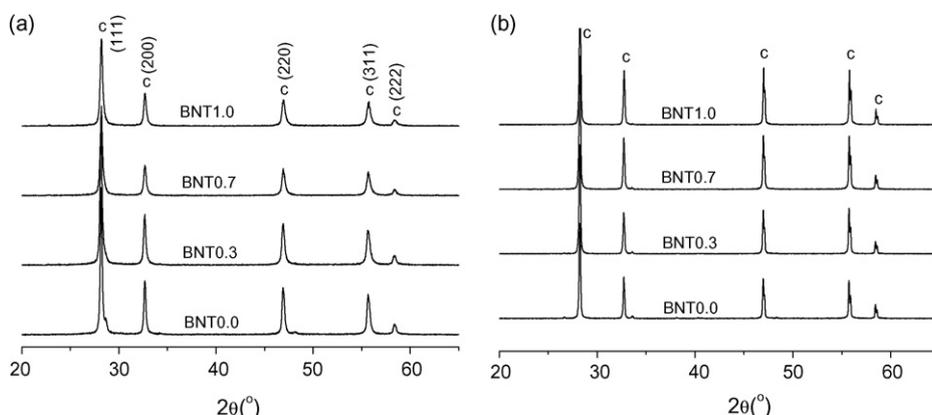*E-mail address:* hwang@mail.xjtu.edu.cn (H. Wang).

Fig. 1. XRD patterns of $Bi_3(Nb_{1-x}Ta_x)O_7$ calcined at $700\,°C(4\,h)^{-1}$ (a) and sintered at $990\,°C(4\,h)^{-1}$ (b) (c—fluorite-type of $Bi_3(Nb_{1-x}Ta_x)O_7$).

studied. Correlation between microwave permittivity, Q_f values, τ_f values and structure parameters of fluorite solid solutions were discussed in detail.

2. Experimental

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd, China), Ta_2O_5 and Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co, Ltd, China) were mixed according to the composition $Bi_3(Nb_{1-x}Ta_x)O_7$ (x = 0, 0.3, 0.7, 1.0) and ball-milled for 5 h with alcohol in a nylon container with ZrO_2 balls. The mixtures were dried and calcined at $700\,°C$ for 4 h. Then the mixtures were remilled with deionized water for 5 h. After drying, the powder with 5 wt.% PVA binder was uniaxially pressed into cylinders in a steel die. Then the cylinder samples were sintered from 870 to $980\,°C$ for 2 h.

Crystalline structures of $Bi_3(Nb_{1-x}Ta_x)O_7$ samples were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). Calculation of lattice parameters of sintered samples was based on X-ray powder diffraction data using Si as the internal standard. The densities of sintered specimens, as a function of sintering temperature, were measured by the liquid displacement method using deionized water as the liquid (Archimedes method). To investigate the morphology of samples, natural surface and broken surface of sintered specimens were observed by scanning electron microscopy (SEM) (JEOL JSM-6460, Japan). Microwave dielectric properties were measured by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA). The temperature coefficients of resonant frequency τ_f were measured with the 8720ES network analyzer and a DELTA 9023 temperature chamber (Delta Design, Poway, CA) using the $TE_{01\delta}$ shielded cavity method. The τ_f was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \tag{1}$$

where f_{85}, f_{25} were the $TE_{01\delta}$ resonant frequencies at the measuring temperature $85\,°C$ and at RT ($25\,°C$), respectively.

3. Results and discussions

Fig. 1 shows the XRD patterns of $Bi_3(Nb_{1-x}Ta_x)O_7$ samples calcined at $700\,°C(4\,h)^{-1}$ and sintered at $960\,°C(4\,h)^{-1}$. Solid solutions of fluorite-type could be obtained in all $Bi_3(Nb_{1-x}Ta_x)O_7$ compositions in samples calcined at $700\,°C(4\,h)^{-1}$ and sintered at $960\,°C(4\,h)^{-1}$ as shown in Fig. 1(a) and (b). Cell parameters and volumes of $Bi_3(Nb_{1-x}Ta_x)O_7$ solid solutions could be calculated from XRD data as shown in Fig. 2. As x value increased, both volume and a decreased approximately linearly.

Fig. 3 shows bulk density of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics sintered at different temperatures. Pure Bi_3NbO_7 could be well densified at $900\,°C$ with density of about 8.2 g cm^{-3}. As x value increased, densified temperatures of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics increased and pure Bi_3TaO_7 ceramic sintered at $990\,°C$ got its saturated density of about 9.1 g cm^{-3}. All of the solution of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics could get a relative density larger than 96% at their densified temperatures. (Relative density equals apparent density/absolute density and absolute density was calculated from cell parameters.)
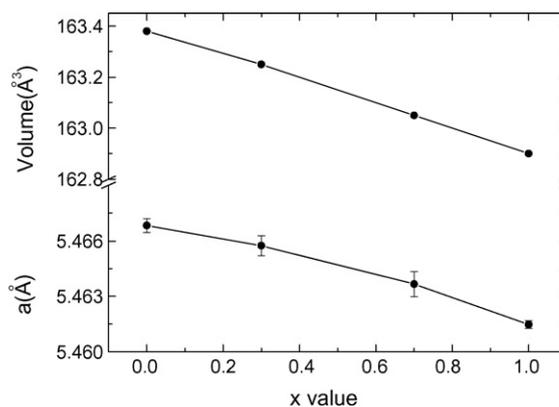

Fig. 2. Cell parameter and volume of $Bi_3(Nb_{1-x}Ta_x)O_7$ solid solutions.

Microwave dielectric properties of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics as a function of temperature were shown in Fig. 4. Microwave permittivity ε_r of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics first increased as sintering temperature increasing because of decrease of pores in ceramics. Then they reached their saturated values and this corresponded well with the trend of density as a function of sintering temperature. As x value increasing from 0.0 to 1.0, ε_r of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics decreased from 95 to 65 while Q_f values increasing from 230 to 560 GHz as shown in Fig. 4(a) and (b). The change of both permittivity and Q_f value in $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics should only be attributed to the substitution of Ta for Nb because of the similar structure and composition.

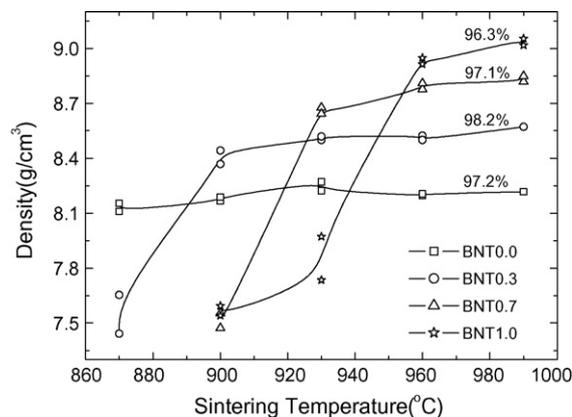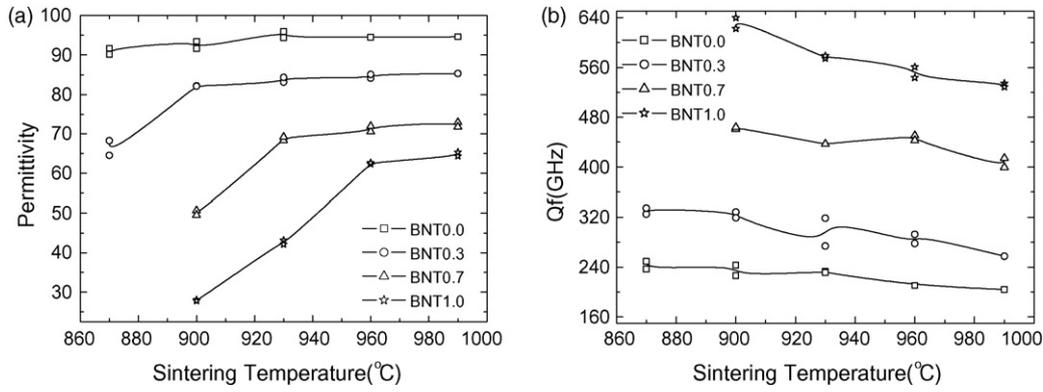**Fig. 3.** Density of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics as a function of sintering temperature.

Fig. 4. Microwave permittivity and Q_f values of $Bi_3(Nb_{1-x}Ta_x)O_7$ (a) and (b) ceramics as a function of sintering temperature.

At microwave region, the polarizability is the sum of both ionic and electronic components [18]. Shannon [19] suggested that molecular polarizabilities of complex substances could be estimated by summing the polarizabilities of constituent ions. Then the polarizabilities ε_x could be got as follows:

$$\alpha_x = 3\alpha_{Bi^{3+}} + (1-x)\alpha_{Nb^{5+}} + x\alpha_{Ta^{5+}} + 7\alpha_{O^{2-}} \quad (2)$$

where α_x is the polarizability of $Bi_3(Nb_{1-x}Ta_x)O_7$. Considering the Clausius–Mosotti relation as follow:

$$\varepsilon_x = \frac{3V_x + 8\pi\alpha_x}{3V_x - 4\pi\alpha_x} \quad (3)$$

where V_x is the cell volume of $Bi_3(Nb_{1-x}Ta_x)O_7$, we could obtain the following result:

$$\alpha_{Nb^{5+}} - \alpha_{Ta^{5+}} = \frac{\alpha_{x_1} - \alpha_{x_2}}{x_2 - x_1} = 0.634 \pm 0.074\,\text{Å} \quad (4)$$

This result meant that in fluorite structure polarizability of Nb^{5+} was bigger than that of Ta^{5+}. The difference was about 0.634 Å and it was relative a very big value, which was different from the results reported by Shannon [19]. Assuming Bi^{3+} and O^{2-} ions in $Bi_3(Nb_{1-x}Ta_x)O_7$ had the same chemical and physical properties, the smaller polarizability of Ta^{5+} than Nb^{5+} could be attributed to the decrease of cell volume. The smaller volume decreased the librations space of Ta^{5+}. Subsequently, polarizability and dielectric losses caused by ion librations decreased. This could explain results of microwave dielectric constant and Q_f values as shown in Fig. 4.

Temperature coefficients of resonant frequency τ_f of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics as a function of x value were shown in Fig. 5. τ_f of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics increased from -113 to $-70\,\text{ppm}\,^\circ\text{C}^{-1}$ approximate linear to x value as shown in Fig. 4(a). Substitution of Ta for Nb improved the τ_f of fluorite-type $Bi_3(Nb_{1-x}Ta_x)O_7$ and made it more suitable for microwave application. Temperature coefficients of resonant frequency τ_f could be defined as following:

$$\tau_f = -\alpha_l - \frac{1}{2}\tau_\varepsilon \quad (5)$$

where α_l is the linear thermal expansion coefficient and τ_ε is the temperature coefficient of permittivity. Since α_l of microwave dielectrics is known to be in the range of $10\,\text{ppm}\,^\circ\text{C}^{-1}$, τ_f mainly depends on τ_ε. Using the Clausius–Mosotti equation, Bosman and Havinga [20] derived and expression for τ_ε at constant pressure, as follows:

$$\tau_\varepsilon = \frac{1}{\varepsilon}\left(\frac{\partial \varepsilon}{\partial T}\right)_P = \frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}(A+B+C) = \left(\varepsilon - \frac{2}{\varepsilon} + 1\right)(A+B+C) \quad (6)$$

$$A = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P, \quad B = \frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P, \quad C = \frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial T}\right)_V$$

The sum of the A and B terms is approximately $6 \pm 1\,\text{ppm}\,^\circ\text{C}^{-1}$. For term C, the suggested value is in the range of -1 to $-10\,\text{ppm}\,^\circ\text{C}^{-1}$. Since the variation in term C is much larger than the sum of A and B terms, it is expected that τ_ε will largely depend on C. The term C represents the direct dependence of the polarizability on temperature. For $Bi_3(Nb_{1-x}Ta_x)O_7$ solid solutions, A, B and C had very similar values and absolute value of τ_ε largely depended on ε_r values. As x value increased, ε_r decreased and this caused absolute value of τ_ε and τ_f decreased. Lee et al. [21] reveal that the unit-cell volume was inversely proportional to the lattice energy if compounds were the same structure. Then they found that τ_ε of $M^{2+}Nb_2O_6$ compounds increased linearly as unit-cell volume increasing and this could correlate the τ_ε values with lattice energy, provided crystal structure was unchanged. Our results also gave the very similar law: τ_f of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics increased from -113 to $-70\,\text{ppm}\,^\circ\text{C}^{-1}$ as cell volume decreased from 163.4 to 162.9 Å linearly.

4. Conclusions

Solid solutions of $Bi_3(Nb_{1-x}Ta_x)O_7$ ($x = 0.0$, 0.3, 0.7, 1) were synthesized using solid state reaction method and could be well densified below 990 °C. As x value increased from 0.0 to 1.0, microwave permittivity of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics decreased from 95 to 65, Q_f values increased from 230 to 560 GHz and

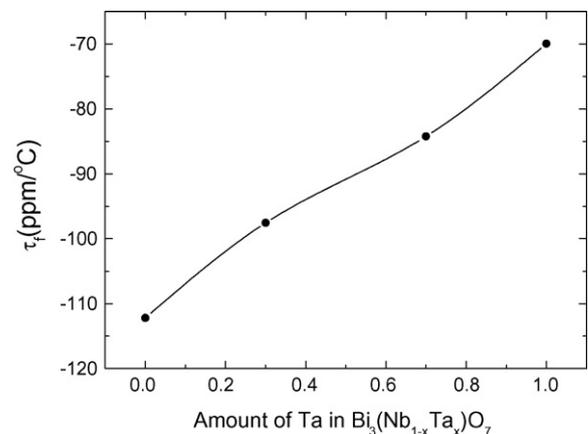**Fig. 5.** Temperature coefficient of resonant frequency of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics sintered at 960 °C (2 h)$^{-1}$.

temperature coefficient of resonant frequency increased from -113 to -70 ppm $^{\circ}$C^{-1}. Considering the low densified temperature and good microwave dielectric proprieties, solid solutions of $Bi_3(Nb_{1-x}Ta_x)O_7$ ceramics could be a good candidate for low temperature co-fired ceramics application.

Acknowledgements

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