MICROWAVE DIELECTRIC PROPERTIES OF $Ba_{0.75}Sr_{0.25}$ $(Nd_xBi_{1-x})_2Ti_4O_{12}$ SOLID SOLUTION

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This work investigated the influences of Bi content on the phase structure, phase composition, microstructure and microwave properties of tungstenbronze-type like $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ ceramics. XRD patterns showed that the main crystal phase of the ceramics with different Bi content ($0.75 \leq x \leq 0.9$) sintered at 1250°C to 1400°C for 3 h was $BaNd_2Ti_4O_{12}$ with small amount of second phase $Ba_2Ti_9O_{20}$. SEM photographs suggest that Bi could work as sintering aids promoting the densification and grain growth. In the case of the ratio of Nd and Bi (x : (1-x)) is 3:1 namely x is 0.75(B13), this ceramic shows optimum dielectric properties with a high dielectric constant (ε) of 118.5, a quality factor ($Q \times f$) of 4907 (f = 2.8 GHz), and a temperature coefficient of resonant frequency $\tau_f = -1.3$ ppm/°C. As the addition of Bi increased from 0.1 to 0.25, the value of ε markedly increased, the value of $Q \times f$ and τ_f decreased with a τ_f value finally approaching to zero.

INTRODUCTION

$BaO–Nd_2O_3–TiO_2$ (BNT) series materials possess excellent microwave dielectric properties, with a high dielectric $\varepsilon = 80\text{-}110$, high quality factor $Q \times f = 1800\text{-}10000$ GHz and a near zero temperature coefficient of resonant frequency τ_f [1-3]. This kind of materials has great potential for microwave device applications and it has been extensively investigated. Recent studies mainly concerned with the optimization of the dielectric properties by adjusting ionic substitution and modifying structure in a wide range [4]. Masafumi S. et al.[5] reported that, the quality factor $Q{\times}f$ of the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions was improved by substituting Sr ions for Ba ions because of smaller ionic radius of Sr. The substitution of Bi for Nd could decrease the temperature coefficient of resonant frequency and increase the dielectric constant of BNT based ceramics [6]. Yong Z. [7] studied the microwave dielectric properties of $Ba_{6-3x}(Sm_{0.2}Nd_{0.8})_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) doped by Bi_2O_3. When 1wt.% Bi_2O_3 was added, the solid solution had the optimal properties: $\varepsilon = 82.1$, $Q \times f = 8567$ (f = 1 GHz) and $\tau_f = 17.3$ ppm/°C. Qin N. et al. [8] modified the microwave dielectric properties of $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ with different Sm/Bi ratio and it was confirmed that Bi^{3+} ions could increase ε.

In this study, the effect of Bi_2O_3 addition on the microstructure, phase composition and dielectric properties of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ solid solution (x = 0.9, 0.8, 0.75, 0.625) were investigated. In order to adjust the microwave dielectric characteristics, we expected that a new microwave ceramic with a high dielectric constant ε, a high quality factor $Q \times f$ and a near zero temperature coefficient of resonant frequency τ_f can be prepared by changing Bi content.

EXPERIMENTAL

Sample preparation

The samples used in this study were prepared by conventional solid-state reaction technique. The starting materials were reagent grade $BaCO_3$, $SrCO_3$, Bi_2O_3, Nd_2O_3 and TiO_2. They were weighed according to stoichiometric ratio of $Ba_{0.75}Sr_{0.25}$ $(Nd_xBi_{1-x})_2Ti_4O_{12}$ with x=0.9, 0.8, 0.75, 0.625. Initially, the mixtures of the powders were milled in plastic jars using deionized water and zirconia balls for 4h. Then the milled mixtures were dried at 100°C and calcined at 1100°C for 5h with a heating rate of 5°C/min. Subsequently, with 5 wt.% PVA solution as a binder, calcined powders were granulated by an agate and mortar and then they were pressed into cylindrical samples with 18 mm in diameter and 8 mm in thickness by uniaxial pressing under a pressure of 25 MPa with a holding of 30 s. Finally, these samples were sintered at temperature between 1250 and 1400°C in air for 3 h.

Characterization

The bulk densities of the sintered samples were measured by the Archimedes' method. Crystalline phases were identified by X-ray diffraction XRD using Cu K_α radiation (DX-1000CSC). Microstructure observation was conducted by using scanning electron microscopy (SEM, FEI Inspect F). The microwave dielectric characteristics of dielectric constant ε, unloaded $Q \times f$ and temperature coefficient of resonant frequency τ_f were measured by the Hakki-Coleman dielectric resonator method in the TE011 mode using a network analyzer (HP83752A). The sintered samples used for this measurement had the ratio: diameter: height = 1.9-2.3. The τ_f values were measured in a low-temperature Delta Design box furnace at temperatures between 25°C and 85°C.

RESULTS AND DISCUSSION

The bulk densities of the sintered samples with various x values as a function of sintering temperatures are shown in Figure 1. Generally, the more Bi_2O_3 was doped; a slightly higher density was obtained at the same sintering temperature. The bulk densities of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ ceramics with x = 0.9 and 0.8 namely a low Bi content were increased monotonously with increasing sintering temperature, but for samples with x = 0.75 and 0.625, there were maximum values for bulk densities appeared at 1350°C. Because Bi_2O_3 is a kind of flux formers which possesses low melting temperatures, it can be thought that the densification temperature tended to shift down with increasing Bi_2O_3 content. During sintering, the immediate products formed liquid phase for flux former, in which ions transferred easily, so the densification was improved with Bi addition. The above results implied that Bi additions are effective in lowering the sintering temperature of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$.

Figure 2 shows the X-ray diffraction (XRD) patterns of the $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ ceramics with different x sintered at 1400°C for 3h. From the XRD patterns, the diffraction peaks indexed to orthorhombic tungsten-bronze type like $BaNd_2Ti_4O_{12}$ solid solution as the main crystalline phase, the peaks of secondary phase $Ba_2Ti_9O_{20}$ also appeared. The Sr^{2+} substituted for Ba^{2+} and Bi^{3+} substituted for Nd^{3+} to form solid solution. Wu Y. J. et al. [3] found that the addition of Bi_2O_3 addition tended to give a single-phase material. With x deceasing to 0.625, $Ba_2Ti_9O_{20}$ turned to be one of the main crystal phases from a minor one. Takashi O. et al [9] reported that the appearance of the second phases $Ba_2Ti_9O_{20}$ was due to substantial amount vaporization of Bi changing the initial stoichiometric proportion of the material.

Figure 3 shows the influence of sintering temperature and Bi content on the microwave dielectric properties of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ solid solution. With the decreasing of x in the range of 0.625 to 0.75, the value of ε increased from 83.7 to 118.5, while $Q \times f$ decreased from 6187 GHz to 3470 GHz with increasing Bi content. And the modification of τ_f was quite obvious by doping Bi, it continuously decreased and finally approached to zero.

The samples with x = 0.75 sintered at 1350°C had the optimum τ_f = -1.3 ppm/°C. While x decreased to 0.625, ε began to decrease, the value of τ_f shifted to more negative values. The τ_f values are mainly determined by the phase composition of the ceramics and the degree

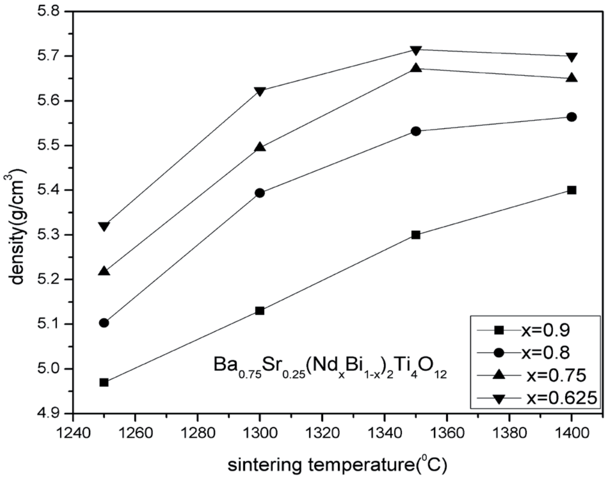


Figure 1. Bulk densities of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ ceramics with different x sintered at 1250, 1300, 1350, 1400°C.

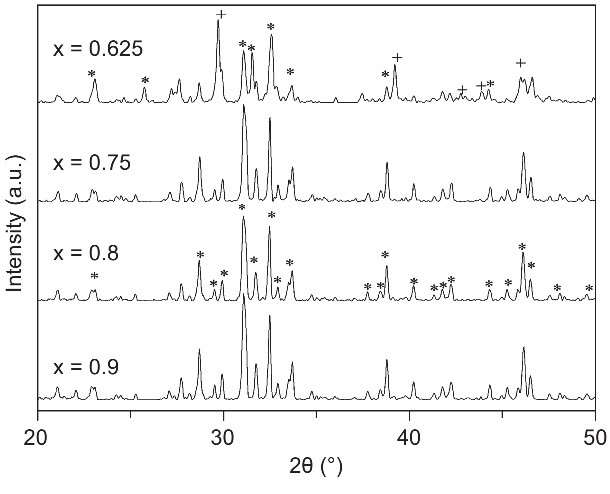


Figure 2. XRD patterns of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ samples with different x sintered at 1400°C (∗ - $BaNd_2Ti_4O_{12}$; + - $Ba_2Ti_9O_{20}$).

of the densification. The τ_f values declined as the proportion of Bi_2O_3 increased, which was strongly attributed to the improvement of densification. It suggested that the τ_f values could be adjusted by adding different proportion of Bi. However, the practicability of this method was weak as the addition of Bi had significant influences on the microstructure and other microwave properties as well. Associating Figure 1, we can draw a conclusion that the variation trend of ε and $Q \times f$ values of samples with the composition $x = 0.625$ was accorded with the tendency between bulk density and temperature. In this composition the highest value of ε, $Q \times f$ and the optimum τ_f came from the high bulk density. As $Ba_2Ti_9O_{20}$ became one of the main crystalline phases for the samples with $x = 0.625$ from the XRD patterns in Figure 2, dielectric constant decreased significantly for the low dielectric constant (ε=38.8 [7]) of $Ba_2Ti_9O_{20}$.

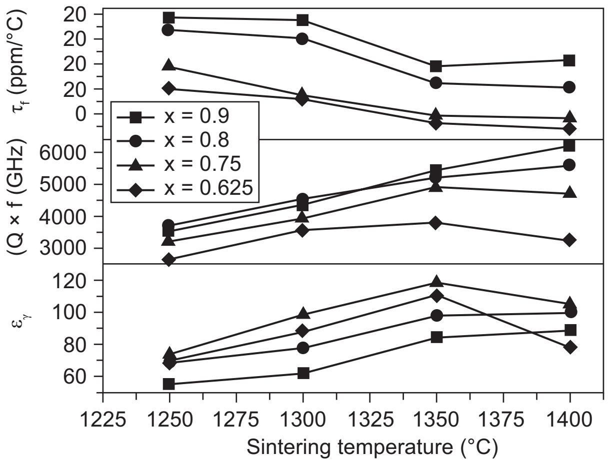


Figure 3. microwave dielectric properties of $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ ceramics with different x at different sintering temperatures.

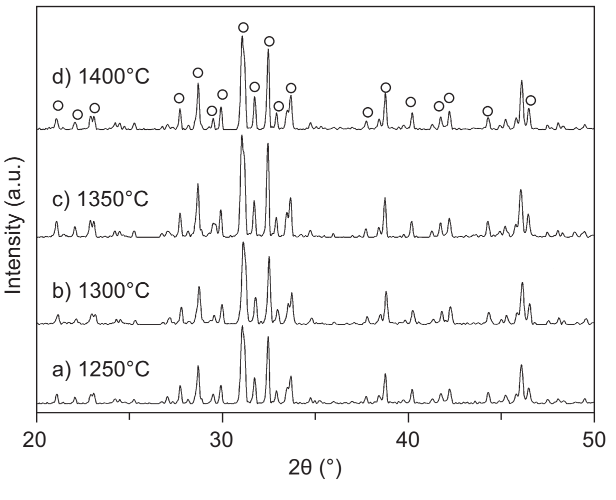


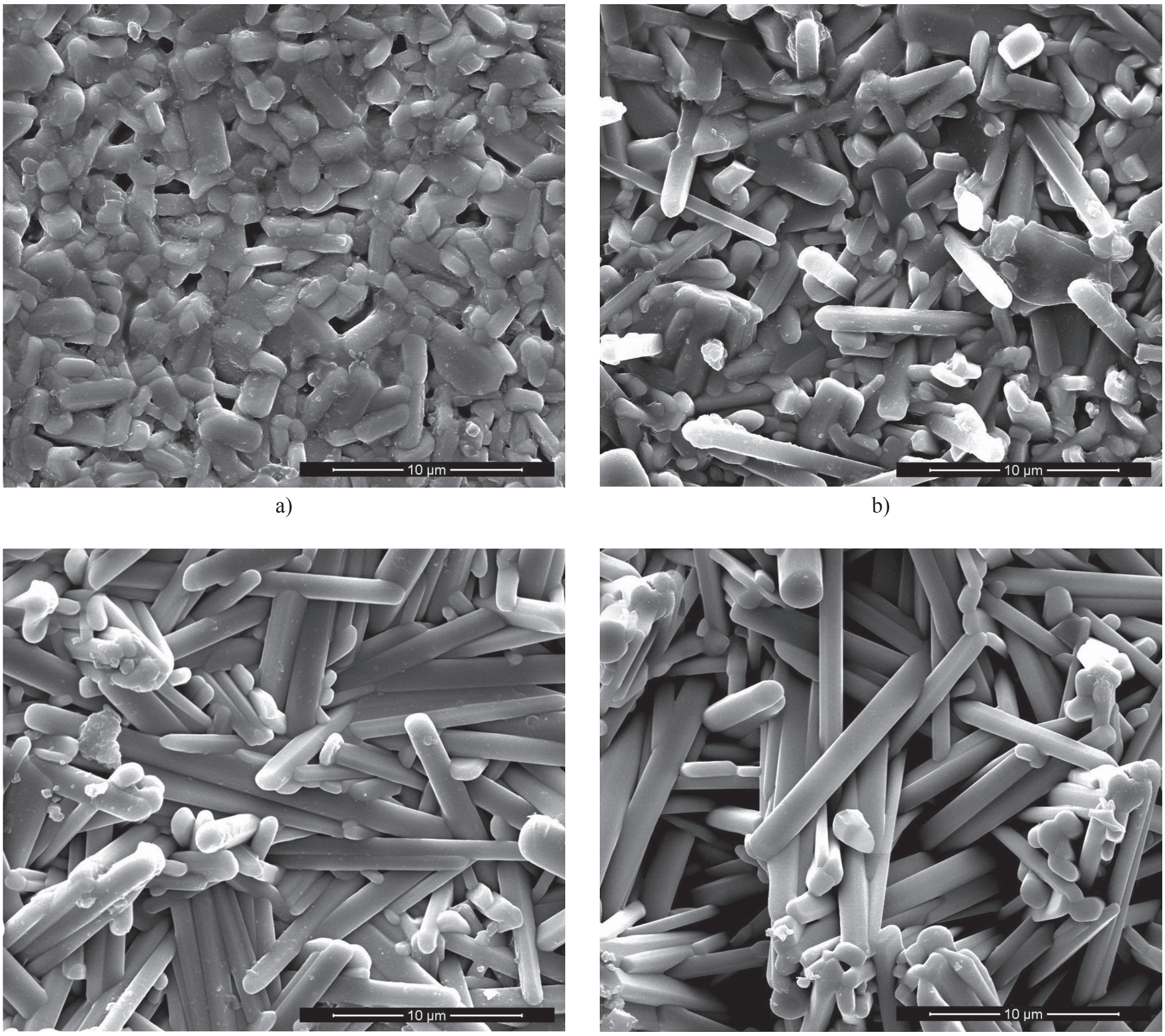
Figure 4. XRD patterns of B13 samples sintered at 1250, 1300, 1350 and 1400°C (○ - $BaNd_2Ti_4O_{12}$).

$Ba_{0.75}Sr_{0.25}(Nd_{0.75}Bi_{0.25})_2Ti_4O_{12}$ (B13) ceramics sintered at 1350°C had the optimum microwave dielectric properties: $\varepsilon = 118.5$, $Q \times f = 4907$ ($f = 2.8$ GHz) and temperature coefficient of resonant frequency $\tau_f = -1.3$ ppm/°C. When the sintering temperature continued to increase to 1400°C, microwave dielectric properties began to deteriorate. The composition of B13 was chosen for further study on account of its optimum value of τ_f among these compositions in Figures 3 and 4 shows XRD patterns of B13 samples as a function of sintering temperatures. The ceramics are consisted of single tungstenbronze-type like $BaNd_2Ti_4O_{12}$ solid solution and a small amount of secondary phase $Ba_2Ti_9O_{20}$. The diffraction peaks of B13 sintered at 1350°C are slightly stronger than those sintered at 1250°C and 1300°C. It means that $BaNd_2Ti_4O_{12}$ crystals grown better with the increasing of sintering temperature. Yet the temperature continuously increased up to 1400°C, the intensity of the peaks showed no growth any more.

The scanning electronic micrographs (SEM) recorded from the surface of B13 samples sintered at 1250, 1300, 1350 and 1400°C for 3 h are displayed in Figure 5. We can find that the grains are long-column-like, and they are more than 15 μm in length when the sintering temperatures were 1350°C and 1400°C. These graphs also indicate that the increase of sintering temperature led to a somewhat aligned growth. We could get the best-sintered samples at 1350°C with relatively perfect grown grains and few pores. In the case of 1400°C, a few pores are observed in the (d) graph. Then associating Figures 3 and 5, there was a substantial connection between microstructure and $Q \times f$ values.

As we know, besides the lattice vibration modes mainly cause the microwave dielectric loss, the additional phases, the porosity, the crystal defects and the average grain size contribute to the microwave dielectric loss. The composition providing the best microstructure such as few pores, concentrated grain size distribution and well crystallization can possess a high $Q \times f$ value. The existence of inhomogeneous pores of the samples sintered at 1400°C caused a decrease of $Q \times f$ values, for the pores increased the extrinsic loss. Thus the ceramics with the composition $Ba_{0.75}Sr_{0.25}(Nd_{0.75}Bi_{0.25})_2Ti_4O_{12}$ sintered at 1350°C exhibited optimum microwave dielectric properties with $\varepsilon = 118.5$, $Q \times f = 4907$ ($f = 2.8$ GHz) and $\tau_f = -1.3$ ppm/°C.

For different amount of Bi vaporization in high sintering temperature and the complexity of the structure of tungstenbronze-type like $BaNd_2Ti_4O_{12}$, it is difficult to precisely control the stoichiometric ratio and investigate the mechanism of Bi-doping [10,11]. However, as this series of material possesses high dielectric constant ε, high quality factor $Q \times f$ and a near zero temperature coefficient of resonant frequency τ_f, Ba–Nd–Bi–Ti system still is one of the most popular candidate used for microwave dielectric application.



a) b) c) d)

Figure 9. SEM of B13 samples sintered at 1250, 1300, 1350 and 1400°C.

CONCLUSION

The $Ba_{0.75}Sr_{0.25}(Nd_xBi_{1-x})_2Ti_4O_{12}$ ceramics with $x = 0.9, 0.8, 0.75, 0.625$ have been prepared by the conventional solid-state ceramic route for the purpose of investigating the effect of Bi_2O_3 ratio on the sintering behavior and microwave dielectric properties. As the sintering temperature increased from 1250 to 1400°C, tungstenbronze-type like $BaNd_2Ti_4O_{12}$ appeared as the main crystalline phase accompanied by a small amount of secondary phase $Ba_2Ti_9O_{20}$ with x between 0.9 and 0.75. However, when x decreased to 0.625, namely Bi content reaching to the maximum, for samples sintered at 1400°C, the content of $Ba_2Ti_9O_{20}$ was more than that of $BaNd_2Ti_4O_{12}$. The primary cause is Bi vaporization at high temperature. And furthermore, Bi_2O_3 functioned as a sintering aid, which promoted the densification and grain growth, thus influenced the microwave dielectric properties. Moreover, high temperature and Bi vaporization lead to excessive growth of column-like grain and the appearance of porosity in the material. With the increasing of Bi proportion, the dielectric constant increased monotonically, quality factor $Q \times f$ decreased and τ_f approached to the value of zero. Samples with the formula $Ba_{0.75}Sr_{0.25}(Nd_{0.75}Bi_{0.25})_2Ti_4O_{12}$ sintered at 1250°C to 1350°C for 3 h had compact and homogeneous structure which exhibited the excellent microwave dielectric properties: $\varepsilon = 118.5$, $Q \times f = 4907$ ($f = 2.8$ GHz), and the temperature coefficient of resonant frequency $\tau_f = -1.3$ ppm/°C.

References

1. Nenasheva E.A., Kartenko N.F.: J. Eur. Ceram. Soc. *21*, 15 (2001).
2. Cheng C.C., Hsieh T.E., Lin I.N.: Mater. Chem. Phys. *79*, 2 (2003).
3. Wu Y.J., Chen X.M.: J. Eur. Ceram. Soc.*19*, 6 (1999).
4. Choi J.H., Kim J. H., Lee B. T., Kim Y. M., Moon J. H.: Mater. Lett. *44*, 1 (2000).
5. Suzuki M., Ohsato H., Kakimoto K.I., Nagamoto T., Otagiri T.: J. Eur. Ceram. Soc. *26*, 10 (2006).
6. Wu Y.C., Wang S.F., Wang Y.R., Wu J.W.: J. Alloys Compd. *468*, 1 (2009).
7. Yong Z., Xing Z.Z., Wen L.: Mater. Lett. *60*, 4 (2006).
8. Qin N., Chen X.M.: Mater. Sci. Eng. B *111*, 1 (2004).
9. Takashi O., Masaki I., Hitoshi O. Mater. Sci. Eng. *88*, 1 (2002).
10. Wu Y.J., Chen X. M.: J. Am. Ceram. Soc. *83*, 7 (2000).
11. Rick U., Ian M.R., William E.L.: Ferroelectr. *223*, 1 (1999).