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Modified $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ Microwave Dielectric Ceramics

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Abstract

In order to improve the microwave dielectric properties of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solution ceramics, the effects of Bi_2O_3 and $Bi_4Ti_3O_{12}$ additives were determined. The results of SEM and EDS analyses suggested that the present ceramics with $Bi_4Ti_3O_{12}$ additives consisted of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solution matrix phase, and secondary phase of $BaTi_4O_9$, but this was not the situation of Bi_2O_3 added ceramics. XRD analysis also revealed that the unit cell volume of the matrix phase increased with increasing the amount of $Bi_4Ti_3O_{12}$ additive. With addition of $Bi_4Ti_3O_{12}$ into the present ceramics, the dielectric constant increased and the temperature coefficient of resonator frequency decreased, while the Qf value slightly decreased. The excellent microwave dielectric characteristics ($\varepsilon = 94{\cdot}9$, $Qf = 5620\,GHz$, $\tau_f = 21{\cdot}4\,ppm/°C$ could be achieved in the present ceramics through the microstructure control. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: barium neodymium titanate, microwave, dielectric properties.

1 Introduction

Recently, the needs of high quality dielectric resonators have grown rapidly in company with the development of wireless communication. For the materials used in dielectric resonators, the following three properties are generally required: (1) high dielectric constant, ε; (2) high quality factor, Q; and (3) small temperature coefficient of resonant frequency, τ_f, So far five main families of microwave dielectrics have been developed: (1) $Ba_2Ti_9O_{20}$ system,[1] (2) (Zr,Sn) TiO_4 system,[2] (3) $BaO–Ln_2O_3–TiO_2$ (Ln = La,Nd,Sm) system,[3–8] (4) $Ba(B'_{1/3}Ta_{2/3})O_3$ (B′ = Mg,Zn),[9–11] (5) other dielectrics.[12,13]

Among these dielectrics, the ceramics with general formula $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ have special importance due to their high dielectric constant (80–110), high Qf value (above 5000 GHz), and small temperature coefficient. Kolar *et al.*[6,7] made a systematic study on this system first. They reported the dielectric properties and crystal chemistry of three compositions, $BaNd_2Ti_4O_{12}$, $BaNd_2Ti_3O_{10}$, and $BaNd_2Ti_5O_{14}$. Then they found that the relative large temperature coefficient of these ceramics could be decreased by addition of $Bi_4Ti_3O_{12}$. Wakino *et al.*[4] improved the dielectric constant and Q value by substituting Pb for Ba in $BaNd_2Ti_5O_{14}$ compound, they also observed at least three phases which were Ti-rich Nd–Ti binary phase, $BaNd_2Ti_5O_{14}$, and $Nd_2Ti_2O_7$ in this compound. Durand *et al.*[8] reported the excellent microwave dielectric characteristics of $BaO–Bi_2O_3–Nd_2O_3–TiO_2$ ceramics. Subsequently, the researches were extended to other rare-earth oxide, such as Sm_2O_3, La_2O_3, and Pr_2O_3.[3]

In this paper, we report the effects of addition of Bi_2O_3 or $Bi_4Ti_3O_{12}$ upon the microwave dielectric properties and the microstructures of $BaNd_2Ti_4O_{12}$ ($x = 0{\cdot}5$ in $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, hereafter referred to as BNT) ceramics.

2 Experimental Procedures

The starting powders were analytical reagent $BaCO_3$, Nd_2O_3, TiO_2 and Bi_2O_3. Stoichiometric starting powders according to the composition of $BaCO_3{\cdot}Nd_2O_3{\cdot}4\ TiO_2$ were ball milled together in polyethylene jar with ZrO_2 media for 24 h in distilled water. The mixtures were dried and calcined at 1100°C for 3 h in air. The same method was used to prepare $Bi_4Ti_3O_{12}$ powders except for the calcination temperature was 850°C. After adding

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different amounts of Bi_2O_3 or $Bi_4Ti_3O_{12}$, the powders were milled for 24 h again. Then the dry powders with binders were pressed into disks under a pressure of 98 MPa. Samples were sintered in air at temperatures between 1250 and 1340°C for 3 h. The cooling rate from sintering temperature to 1000°C was 2°C/min, and then the samples were cooled with furnace.

The densities of the sintered samples were evaluated by measuring the dimensions and weight, and the microstructures were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), and powder X-ray diffraction (XRD) using Cu-K_α radiation. Microwave characteristics were determined by the dielectric resonator method[14] at the frequencies of about 4·5 GHz.

3 Results and Discussion

Addition of Bi_2O_3 or $Bi_4Ti_3O_{12}$ shows virtually no influence on sintering temperature. The ceramics with all the six compositions can be well sintered at the temperatures between 1280 and 1340°C. Figure 1 shows the densities of present ceramics sintered at the optimal temperature of 1300°C. The density of Bi_2O_3 added BNT ceramics decreases with increasing Bi_2O_3, and opposite tendency is

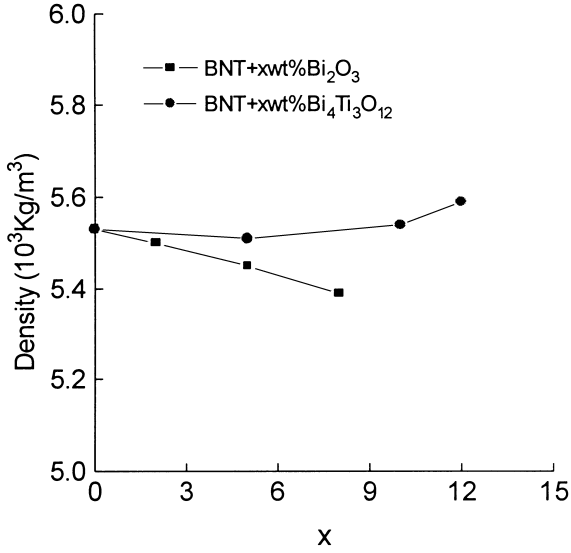

Fig. 1. Densities of $BaNd_2Ti_4O_{12}$ ceramics with Bi_2O_3 or $Bi_4Ti_3O_{12}$ additives, sintered at the optimal temperature of 1300°C in air for 3 h.

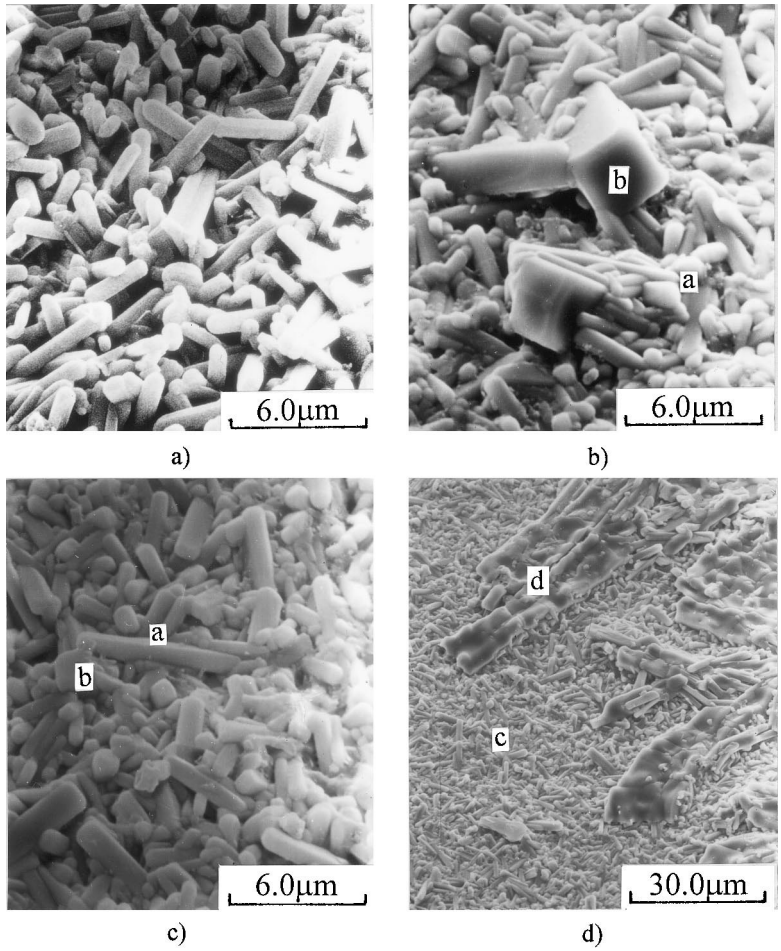

Fig. 2. Microstructures of $BaNd_2Ti_4O_{12}$ ceramics with Bi_2O_3 and $Bi_4Ti_3O_{12}$ additives: (a) 8 wt% Bi_2O_3, 1320°C/3 h; (b) 5 wt% $Bi_4Ti_3O_{12}$, 1320°C/3 h; (c) 10 wt% $Bi_4Ti_3O_{12}$, 1300°C/3 h; (d) 10 wt% $Bi_4Ti_3O_{12}$, 1320°C/3 h.

observed in the situation of $Bi_4Ti_3O_{12}$ addition. This difference is concerned with the different volatilization behavior and the phase constitution.

Figure 2 shows the microstructures of the as-sintered surface of BNT ceramics with Bi_2O_3 or $Bi_4Ti_3O_{12}$ additives. As expected, the porosity of the $Bi_4Ti_3O_{12}$ added BNT ceramics is less than that of the Bi_2O_3 added BNT ceramics, this may be attributed to the different volatilization behavior of Bi. In the Bi_2O_3 added BNT ceramics, the homogeneous morphology of grains is observed, but two kinds of grains with different morphology exist in the $Bi_4Ti_3O_{12}$ added BNT ceramics. In Fig. 3, the results of EDS analysis suggest that the columnar grains marked 'a' and 'c' are the matrix phase and the grains marked 'b' and 'd' are secondary phase which can be ascertained as barium titanate. This secondary phase can be identified as $BaTi_4O_9$, because that all strong peaks of $BaTi_4O_9$, which overlap the main peaks of the matrix phase can be observed in the XRD pattern, while the peaks of any barium titanate are otherwise never observed. We also find that the amount of the secondary phase is sensitive to the sintering temperature. The aggregates of the secondary phase were observed on the sintered-surface of $Bi_4Ti_3O_{12}$ added BNT ceramics sintered at 1320°C for 3h [Fig. 2(d)]; this suggests that higher sintering temperature lead to increased precipitation of the secondary phase.

On the other hand, the XRD analysis reveals that a matrix phase corresponding to $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ exits in the present ceramics. When $Bi_4Ti_3O_{12}$ additives are added into BNT ceramics, Nd^{3+} ions are partially substituted by Bi^{3+} in forming the solid solution, then the surplus Ti and Ba form the secondary phase, barium-titanate. As shown in Table 1, because of the ionic radius of Bi^{3+} ion is larger than that of Nd^{3+} ion, the unit cell volume of the solid solution increases with increasing $Bi_4Ti_3O_{12}$.

The above analyses suggest that the different phase constitution, $Ba_{6-3x}(Nd,Bi)_{8+2x}Ti_{18}O_{54}$ (s.s.) $+ BaTi_4O_9$ and $Ba_{6-3x}(Nd,Bi)_{8+2x+y}Ti_{18-3y/4}O_{54}$ (s.s.) are expected in $Bi_4Ti_3O_{12}$ and Bi_2O_3 added BNT ceramics, respectively. The dense ceramics are expected for the former because of the formation of liquid phase due to eutectic reaction, and the later includes some vacancies on B sites in the solid solution and then leads to the reduced density.

Figure 4 shows the microwave dielectric properties of BNT ceramics with Bi_2O_3 addition. With increasing the amount of Bi_2O_3, the dielectric constant increases firstly and then decreases due to the volatilization of Bi, while the Qf value slightly decreases. As shown in Fig. 5, the dielectric constant increases with increasing the amount of $Bi_4Ti_3O_{12}$ because the ratio of total polarizability to unit cell volume in $Ba_{6-3x}(Nd,Bi)_{8+2x}Ti_{18}O_{54}$ solid solution increases, while the Qf value also slightly decreases.

Table 1. The lattice parameters of $BaNd_2Ti_4O_{12}$ ceramics with $Bi_4Ti_2O_{12}$ additives

Composite	*Lattice parameters (A)* a	b	c	*Unit cell volume (A^3)*
BNT + 5 wt% BIT	12·214	22·314	3·854	1050·382
BNT + 10 wt% BIT	12·214	22·350	3·859	1053·441
BNT + 12 wt% BIT	12·217	22·354	3·859	1053·888

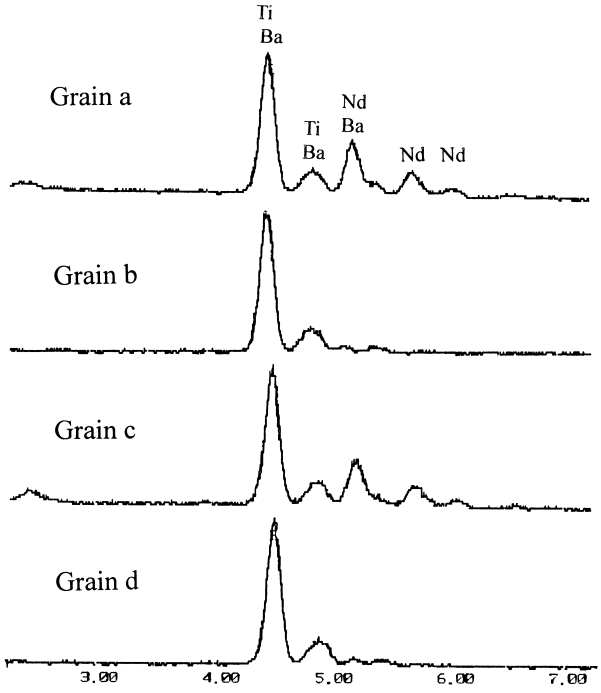

Fig. 3. EDS results of the different grains marked in Fig. 2.

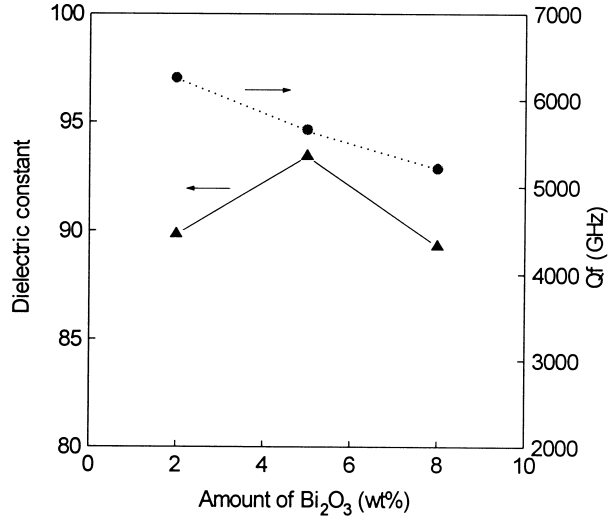

Fig. 4. Microwave dielectric properties of $BaNd_2Ti_4O_{12}$ ceramics with Bi_2O_3 additives.

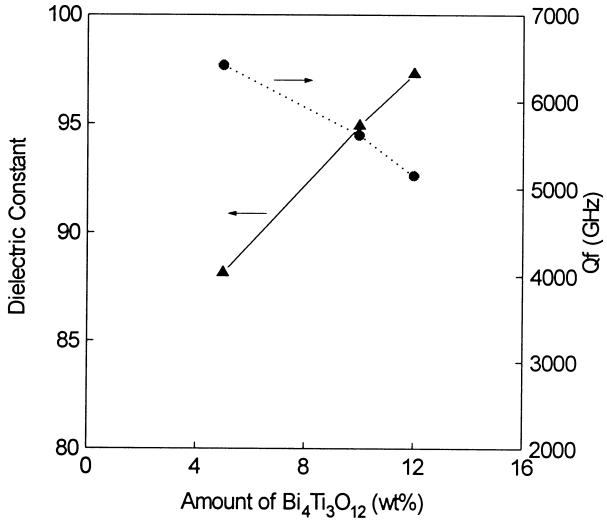

Fig. 5. Microwave dielectric properties of $BaNd_2Ti_4O_{12}$ ceramics with $Bi_4Ti_3O_{12}$ additives.

Both of these two additions can decrease the temperature coefficient of resonator frequency. The BNT ceramics with 10 wt% $Bi_4Ti_3O_{12}$ additions sintered at 1300°C for 3 h in air have the excellent microwave dielectric properties, $\varepsilon = 94{\cdot}9$, Qf = 5620 GHz, and $\tau_f = 21{\cdot}4$ ppm/°C.

4 Conclusion

The effects of Bi_2O_3 or $Bi_4Ti_3O_{12}$ additions upon the microstructures and the microwave dielectric properties of BNT ceramics were investigated. The BNT ceramics with Bi_2O_3 or $Bi_4Ti_3O_{12}$ additions were easy to be sintered. The results of SEM and EDS analyses revealed that the $Bi_4Ti_3O_{12}$ added BNT ceramics have two phases, $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solution and barium titanate phase, but there are no secondary phase exits in the Bi_2O_3 added BNT ceramics. The unit cell volume of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solution increased with increasing the amount of $Bi_4Ti_3O_{12}$, and the amount of barium titanate phase increased with increasing the sintering temperature. Both Bi_2O_3 and $Bi_4Ti_3O_{12}$ addition could increase the dielectric constant and decrease the temperature coefficient of resonator frequency, while the Qf value was slightly decreased. Through controlling the microstructures of present ceramics, the excellent microwave dielectric properties could be achieved.

Acknowledgements

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