J Mater Sci (2007) 42:7052–7055
DOI 10.1007/s10853-007-1641-7

LETTER

Effects of Gd doping on the sintering and microwave dielectric properties of $BiNbO_4$ ceramics

Yue Pang · Chaowei Zhong · Shuren Zhang

Received: 7 December 2006 / Accepted: 26 February 2007 / Published online: 8 June 2007

Abstract Gd^{3+} was chosen as a substitute for Bi^{3+} in $BiNbO_4$ ceramics, and the substitution effects on the sintering performance and microwave dielectric properties were studied in this paper. The high temperature triclinic phase was observed only in the $Bi_{0.98}Gd_{0.02}NbO_4$ ceramics when sintered at 920 °C. Both bulk den'sities and dielectric constant (ε_r) increased with the sintering temperature, while decreased with the Gd content. The quality factor (Q) exhibited a correlation to the Gd content and the microstructures of $Bi_{1-x}Gd_xNbO_4$ ceramics. At the sintering temperature of 900 °C, $Bi_{0.992}Gd_{0.008}NbO_4$ ceramics exhibited microwave dielectric properties of $\varepsilon_r \sim 43.87$, $Q \times f \sim 16{,}852$ GHz (at 4.3 GHz), and its temperature coefficient of resonant frequency (τ_f) was found to be near-to-zero.

Introduction

The development of multilayer devices for microwave applications has been paid an increasing attention since they have promising applications for reducing the size and the weight of mobile communication components. To meet the requirements of such small sized devices, dielectric materials sintered at low temperatures were intensively studied to be co-fired with highly conductive metal electrode, such as silver or copper, which has a low melting point of 961 °C and 1064 °C, respectively. Bismuth-based dielectric ceramics have been proposed as one of the most promising candidates for low temperature co-fired ceramics (LTCCs) due to the lower sintering temperatures. Kageta et al. [1] reported the dielectric properties of $BiNbO_4$ ceramics at microwave frequency for the fist time, i.e., dielectric constant $\varepsilon_r \sim 43$, quality factor $Q \sim 4260$ (at 4.3 GHz). However, their temperature coefficient of resonant frequency (τ_f) is too high (+38ppm/°C) for practical use. Accordingly, many efforts have been made to improve the microwave dielectric properties and the temperature coefficient. In addition, CuO, V_2O_5 or their mixtures are often used as sintering aids to lower the sintering temperature [2–8]. Several researchers attempted to modify the dielectric properties of $BiNbO_4$ ceramics, especially the τ_f value, by introducing La^{3+}, Sm^{3+} or Y^{3+} as a substitute for Bi^{3+} [9–11]. For La, Sm or Y substitution, the optimum microwave properties were achieved with $Q \times f = 10600$, 13000, 11579 GHz, and $\tau_f = -2$, -4.2, 8.93 ppm/°C, respectively. The phase-transition temperature of $BiNbO_4$ ceramics got decreased due to the lattice distortion caused by the ionic size difference between Ln^{3+} (Ln = La, Sm, Y) and Bi^{3+}.

In this work, Gd^{3+} will be selected as a substitute for Bi^{3+} since they have the same valency charge and small ionic size difference (Bi^{3+}: 1.02 Å [9], Gd^{3+}: 0.938 Å [12]). A $CuO–V_2O_5$ mixture (0.3 wt%) is used as a sintering aid. The main purpose of our work is to clarify the effects of Gd^{3+} substitution on the sintering and microwave dielectric characteristics of $Bi_{1-x}Gd_xNbO_4$ ceramics. The correlation between the microstructures and the $Q \times f$ values will also be investigated.

Experimental

$Bi_{1-x}Gd_xNbO_4$ ceramics samples ($x = 0.003$, 0.005, 0.008, 0.01, 0.015, 0.02) were prepared by conventional

---

Y. Pang (✉) · C. Zhong · S. Zhang
State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronics Science & Technology of China, Chengdu 610054, China
e-mail: cynthia0061@126.com

solid-state reaction method. High-purity oxide powers, i.e. Bi_2O_3 (>99.99%), Gd_2O_3 (>99.99%), and Nb_2O_5 (>99.99%), were used as raw materials. These oxide powders were mixed according to stoichiometry of the ceramics to be prepared, and ball-milled for 24 h. The milled mixtures were collected, dried and calcined. The resulting powders were mixed with a mixture of $CuO–V_2O_5$ (0.3 wt%), and then re-milled for 24 h. After drying, the powders with 8 wt% polyvinyl alcohol (PVA) binder were uniaxially pressed into pellets with a steel die at a pressure of 17 MPa and then sintered at various temperatures from 850 °C to 920 °C in air for 3 h.

The bulk densities of the sintered ceramics were measured using the Archimedes' method. Phase identification was carried out using an X-ray diffractometer (Philips X'Pert Pro MPD) with a CuK_α radiation and an X'Pert software. Microstructures of the samples were observed by a scanning electron microscopy (S-530, Hitachi). A network analyzer (E8363A, Agilent Technologies) was employed to measure the dielectric constant ε_r and the quality value Q according to the Hakki-Coleman dielectric resonator methods [13]. In order to obtain the temperature coefficient of resonant frequency, the $TE_{01\delta}$ resonant frequency at 25 °C and 100 °C was measured, respectively, and the temperature coefficient can thus be calculated by the equation as follows:

$$\tau_f = \frac{f_{100} - f_{25}}{75 \times f_{25}} \times 10^6 \quad (\text{ppm/°C}) \tag{1}$$

where τ_f is temperature coefficient of resonant frequency, and f_{100}, f_{25} is the $TE_{01\delta}$ resonant frequency at 25 °C and 100 °C, respectively.

Results and discussion

Figure 1 shows the typical XRD patterns of $Bi_{1-x}Gd_xNbO_4$ ceramics sintered at different temperatures. As known, a $SbTaO_4$-type orthorhombic phase could be developed with $BiNbO_4$ ceramics below 1020 °C, and gradually transforms to a triclinic phase as temperature increases. As shown in Fig. 1, the sintered $Bi_{1-x}Gd_xNbO_4$ powders mainly exhibit the low temperature orthorhombic phase, and nearly no triclinic phase is found except for the sample shown in Fig. 1e. When doping La^{3+}, the ionic radii differences could induce a lattice distortion, and a lower phase-transition temperature could thus be achieved [9]. In present work, the phase-transition is not as evident as that with La doping although the ionic size difference between Gd^{3+} (0.938 Å) and Bi^{3+} (1.02 Å) is bigger than that between La^{3+} (1.061 Å) and Bi^{3+} [9, 12]. The small amount of Gd doping appears to count for this observation.

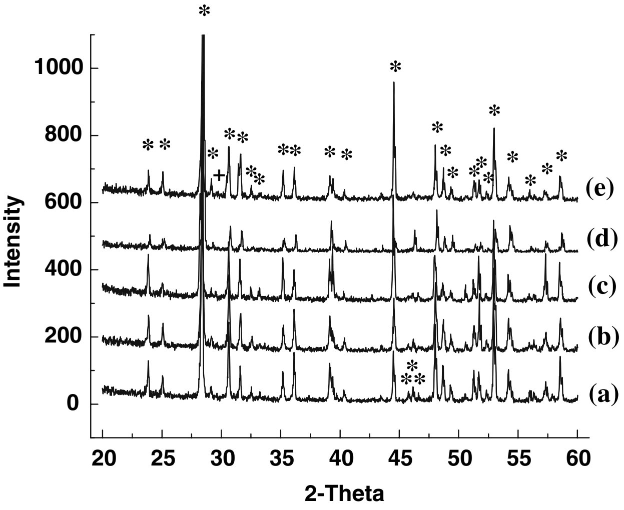


Fig. 1 XRD patterns of $Bi_{1-x}Gd_xNbO_4$ ceramics with different x values sintered at different temperatures. (a) $x = 0.003$, 860 °C, (b) $x = 0.008$, 860 °C, (c) $x = 0.008$, 880 °C, (d) $x = 0.008$, 920 °C, (e) $x = 0.020$, 920 °C (*: orthorhombic; +: triclinic)

Presumably, the diffraction of the triclinic phase was too weak to be effectively identified by XRD.

The correlation of the bulk densities to the sintering temperatures is shown in Fig. 2. It can be seen that the densities increase with the sintering temperature initially, and then decrease lightly. The maximum densities decrease from 7.21 g/cm^3 (98.1% TD) to 7.15 g/cm^3 (97.3% TD) while x increases from 0.003 to 0.02. This could be ascribed to that the lighter Gd atoms were substituted for the heavier Bi atoms. It is also found that such Gd substitution for Bi causes poor sinterability mostly due to the decrease in the amount of Bi-based low-firing-temperature oxides. This finding is in accordance with that in the case of Ta substitution for Nb, reported by Huang [14].

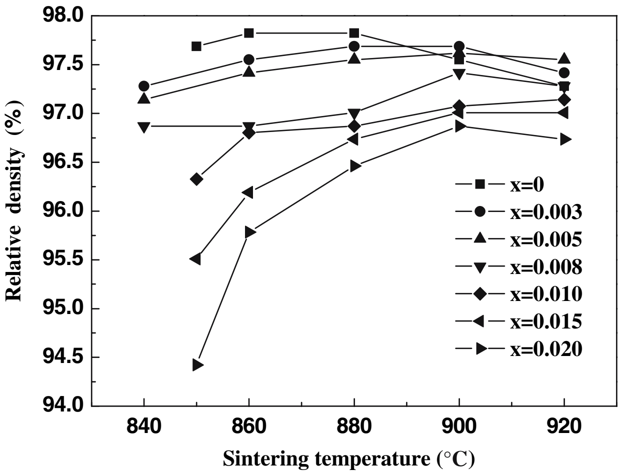


Fig. 2 Relative densities of $Bi_{1-x}Gd_xNbO_4$ ceramics with different x values versus sintering temperature

Figure 3 shows the SEM micrographs of $Bi_{1-x}Gd_xNbO_4$ ceramics, with $x = 0.003, 0.008, 0.015$, sintered at different temperatures. As shown in Fig. 3a, the grains morphology of the sample ($x = 0.003$) when sintered at 850 °C is uniform, exhibiting a homogeneous growth. It however becomes worse with increasing the content of Gd and the sintering temperature. The average grain size decreases from 1.24 μm to 1.07 μm as the substitution amount of Gd increases. However, it appears to increase with the sintering temperature, which can be seen clearly from Fig. 3b–d. When the ceramics are sintered at 920 °C, an abnormal grain growth occurs, which may cause a deterioration of the dielectric properties. In Fig. 3f, acicular grains appear at the main grain boundaries. Unfortunately, these impurity phases were not identified precisely mainly due to their complex compositions and probably low crystallinity. A further local area analysis is therefore suggested.

Figure 4 shows plots of the dielectric constant (measured at 4.3 GHz) as a function of the sintering temperature. Significantly, the curves are similar to those for the bulk density. It is much understandable that the ε_r of all the samples initially increase with the sintering temperature, and reach a maximum at either 860 °C or 920 °C (dependent on x), and then get decreasing smoothly when further increasing the sintering temperature. The first stage of the increase of ε_r is undoubtedly due to the grain growth and the decrease of porosity. The next step of abnormal grain growth should be the reason for the decrease of ε_r All in all, the dielectric constant of $Bi_{1-x}Gd_xNbO_4$ ceramics decreases gently while Gd content increases. Nevertheless, this decrease is not very remarkable.

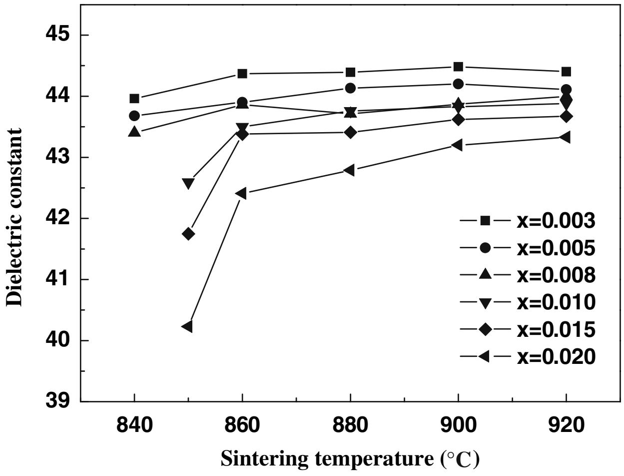


Fig. 4 Dielectric constants of $Bi_{1-x}Gd_xNbO_4$ ceramics as a function of sintering temperature

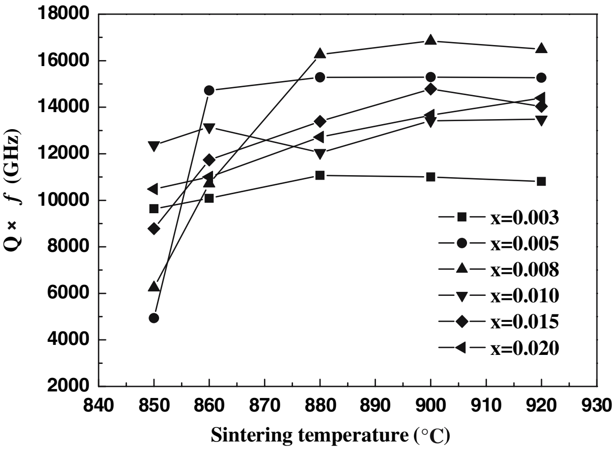
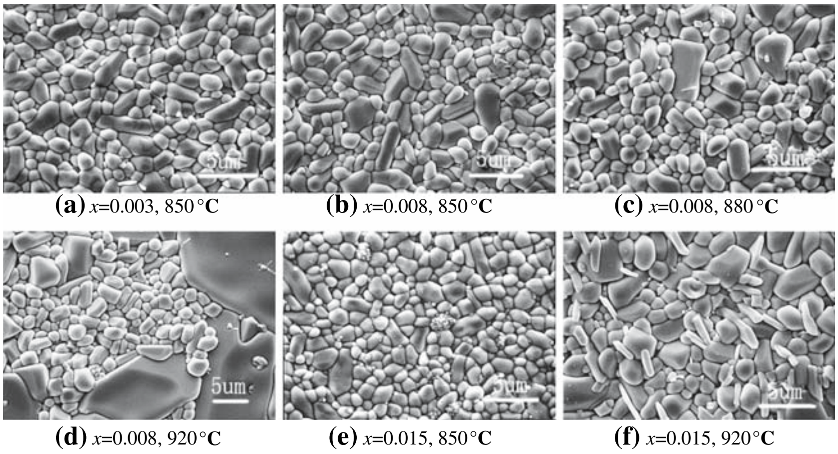


Fig. 5 $Q \times f$ values of $Bi_{1-x}Gd_xNbO_4$ ceramics with various x values sintered at different temperatures

Presented in Fig. 5, is the $Q \times f$ values (measured at 4.3 GHz) of $Bi_{1-x}Gd_xNbO_4$ ceramics sintered at different temperatures. The correlation of the $Q \times f$ values to the sintering temperatures are quite similar for all samples. The $Q \times f$ values increase initially as the sintering temperature increases, and then decrease gently. Basically, there are two loss components for dielectric ceramics at microwave frequency, i.e., intrinsic loss and extrinsic loss. The intrinsic loss is caused by an anharmonic phonon decay process in a pure crystal lattice while the extrinsic

Fig. 3 SEM micrographs of $Bi_{1-x}Gd_xNbO_4$ ceramics with $x = 0.003, 0.008, 0.015$ sintered at different temperature (a) $x = 0.003$, 850 °C (b) $x = 0.008$, 850 °C (c) $x = 0.008$, 880 °C (d) $x = 0.008$, 920 °C (e) $x = 0.015$, 850 °C (f) $x = 0.015$, 920 °C temperatures



(a) x=0.003, 850°C **(b)** x=0.008, 850°C **(c)** x=0.008, 880°C

(d) x=0.008, 920°C **(e)** x=0.015, 850°C **(f)** x=0.015, 920°C loss is presumably correlated to the existence of crystal defects, grain boundaries, secondary phases and pores in the bulk ceramics [15]. As mentioned above, the grain size of the $Bi_{1-x}Gd_xNbO_4$ ceramics is observed to increase with sintering temperature, as shown in Fig. 3(b–d). The grain growth could lead to a decrease of the number of pores and boundary areas. Probably, this decrease could result in a higher density and a lower dielectric loss. As the sintering temperature is further increasing to a higher one than the densification temperature, the abnormal grain growth occurs. Consequently, it is possible to cause an increase in the crystal defects and a decrease in the density. Therefore, it is reasonable that the $Q \times f$ values decease after reaching a maximum, denoted as the saturated value. The saturated $Q \times f$ values of the $Bi_{1-x}Gd_xNbO_4$ ceramics strongly depend on the x values. It increases steadily from 10,070 GHz to 16,852 GHz while x increases from 0.003 to 0.008, and then decreases to 14,394 GHz while x increases to 0.02. The maximum $Q \times f$ value appears with the sample ($x = 0.008$) when sintered at 880 °C. The decrease in the saturated $Q \times f$ values with the increasing of x could be attributed to the existence of a small amount of triclinic mass in the sintered samples, which may cause some extra extrinsic losses.

The τ_f values of well-densified $Bi_{1-x}Gd_xNbO_4$ ceramics as well as that of the $Bi_{0.992}Gd_{0.008}NbO_4$ ceramics sintered at different temperatures are presented in Fig. 6. The τ_f values of the $Bi_{1-x}Gd_xNbO_4$ ceramics samples are 29.31 ppm/°C, 3.63 ppm/°C, 0.26ppm/°C and 4.57 ppm/°C, in regard to $x = 0$, 0.005, 0.008 and 0.015, respectively. When sintered over a wide temperatures range from 860 °C to 900 °C, the $Bi_{0.992}Gd_{0.008}NbO_4$ ceramics exhibited a near-to-zero resonant frequency coefficient. It suggests that an appropriate Gd doping can make the value of τ_f down toward zero, which means that the obtained $Bi_{0.992}Gd_{0.008}NbO_4$ ceramics in this work behave the optimum frequency stability and could be suitable for practical applications.

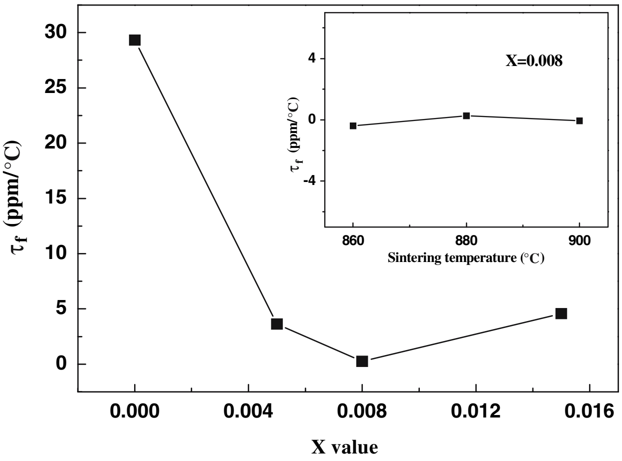


Fig. 6 τ_f values of fully dense $Bi_{1-x}Gd_xNbO_4$ ceramics with various x values and that of the $Bi_{0.992}Gd_{0.008}NbO_4$ ceramics sintered at different temperatures

Conclusion

The microstructures and the microwave dielectric properties of $Bi_{1-x}Gd_xNbO_4$ ceramics with 0.3 wt% $CuO–V_2O_5$ doping were studied in detail in this work. The well-densified $Bi_{1-x}Gd_xNbO_4$ ceramics can be obtained at different temperatures corresponding to the specific Gd contents. The dielectric constant ε_r increases with the increase of sintering temperature, but decreases with the increase of x value. The $Q \times f$ values of $Bi_{1-x}Gd_xNbO_4$ ceramics are significantly related to the Gd contents and the samples' microstructures, and a maximum is thus obtained with the sample of $Bi_{0.992}Gd_{0.008}NbO_4$ when sintered at 900 °C. Interestingly, a near zero temperature coefficient of the resonant frequency was also observed. The $Bi_{0.992}Gd_{0.008}NbO_4$ ceramics sintered over the temperatures range from 880 °C to 900 °C show good dielectric properties, i.e., $\varepsilon_r = 43.71$~43.87, $Q \times f = 16{,}270$~16,852 GHz (at 4.3 GHz), $\tau_f \sim 0$ppm/°C. These prepared modified ceramics are promising for being co-fired with low cost conductors for the fabrications of multi-layers microwave devices.

References

1. Kageta H, Kato J, Kameyama I (1992) Jpn J Appl Phys 31:3152
2. Huang CL, Weng MH, Yu CC (2001) Ceram Int 27:343
3. Wang ZW, Yao X, Zhang LY (2004) Ceram Int 30:1929
4. KambaS, Wang H, Berta M et al (2006) J Eur Ceram Soc 26:2861
5. Lee HR, Yoon KH, Kim ES (2003) Jpn J Appl Phys 42:6168
6. Wang ZW, Yao X, Zhang LY (2004) Ceram Int 30:1329
7. Yang CF (1999) Jpn J Appl Phys 38:6797
8. Wang N, Zhao MY, Yin ZW, Li W (2004) Mater Res Bull 39:439
9. Huang CL, Weng MH, Wu CC (2000) Jpn J Appl Phys 39:3506
10. Huang CL, Weng MH, Wu CC, Lion CT (2001) Mater Res Bull 36:827
11. Wang N, Zhao MY, Li W, Yin ZW (2003) Jpn J Appl Phys 42:3514
12. Tsur Y, Hitomi A, Scrymgeour I et al (2001) Jpn J Appl Phys 40:255
13. Hakki BW, Coleman PD (1960) IEEE Trans Microwave Theory Tech MTT-8:402
14. Huang CL, Weng MH, (1999) Jpn J Appl Phys 38:5949
15. Tamura H (1994) Am Ceram Soc Bull 73:92