ELSEVIER

Ceramics International 30 (2004) 1341–1345

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influences of Fe_2O_3 additives on the dielectric properties of $BiNbO_4$ ceramics under different sintering atmosphere

Yong Yang*, Shihua Ding, Xi Yao

Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China

Received 4 December 2003; received in revised form 18 December 2003; accepted 22 December 2003

Available online 6 May 2004

Abstract

$BiNbO_4$ ceramic is one of the potential low-firing microwave dielectric materials for microwave applications. In this work, Fe oxides were doped into $BiNbO_4$ ceramics. The samples were sintered in air and flowing N_2, respectively. A comparative study of the sintering performance, the crystalline morphology and the dielectric properties (at both low frequency and microwave frequency) of samples sintered under both atmosphere were performed by means of SEM, LCR meter, network analyzer, and thermal environmental test chamber. Material's dielectric performance under microwave frequency is especially considered. Then, the influences of Fe_2O_3 additives on the dielectric properties of $BiNbO_4$ ceramics is investigated. At the same time, the defect influences on the dielectric properties were also discussed.

Keywords: B. Defect; $BiNbO_4$ ceramics; Sintering atmosphere

1. Introduction

The development of dielectric materials for microwave applications has been focused on reducing the size and weight of RF-front end components in mobile communications. Recently, the development of low temperature co-firing ceramics (LTCCs) has attracted much interest because of their application in multilayer integrated circuits (MLICs) such as LC filters [1]. In order to satisfy the devices requirements, the microwave dielectric ceramics with low sintering temperature are needed to co-fire with low-loss conductors such as Ag or Cu. So, finding dielectric ceramic materials with low sintering temperature and excellent dielectric properties has become a major focus.

Bismuth-based dielectric ceramics have been proposed as candidate dielectrics for LTCC due to their low sintering temperature and excellent dielectric properties. $BiNbO_4$ ceramic with practical dielectric properties at microwave frequency was first reported by Kagata et al. [2]. Many researchers have made strong efforts to modify the dielectric properties and the temperature coefficient [3,4]. In this work, we doped Fe^{3+} (the valence may shift to 2+) into $BiNbO_4$ ceramics, and sintered the samples under different atmosphere. By observing the corresponding dielectric properties, the influences of defect on the dielectric properties of $BiNbO_4$ ceramics were discussed.

2. Experimental procedures

Specimen were prepared by conventional solid-state reaction technique. The starting materials to form $BiNbO_4$ compound were high-purity (>99.9%) Bi_2O_3, and Nb_2O_5 powders. The powders were mixed according to the stoichiometric ratio of $BiNbO_4$ and the Fe_2O_3 doping amount of x wt.% ($x = 0.3$, 0.5, 0.8, and 1.0). All mixtures were ball-milled for 24 h with deionized water. After dried, the reagent was calcined at 800 °C for 2 h. Then the powders were uniaxially pressed into pellets in a steel die. Those pellets were sintered in air and flowing N_2 (0.2 l/min) for 2 h, respectively. The sintering temperature ranged from 950 to 980 °C.

By using the Archimedes method, the bulk densities of the sintered ceramics were measured. Crystal structure of these Fe_2O_3 doped $BiNbO_4$ ceramics were investigated by means of the X-ray diffraction (XRD) patterns (BRUKER, D8 advanced). The micrograph observation of the ceramics was performed by a SEM (JEOL, JSM-5510). An HP8753E

* Corresponding author. Fax: +86-21-65985179.
E-mail address: yangyong@fmrl.ac.cn (Y. Yang).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.110

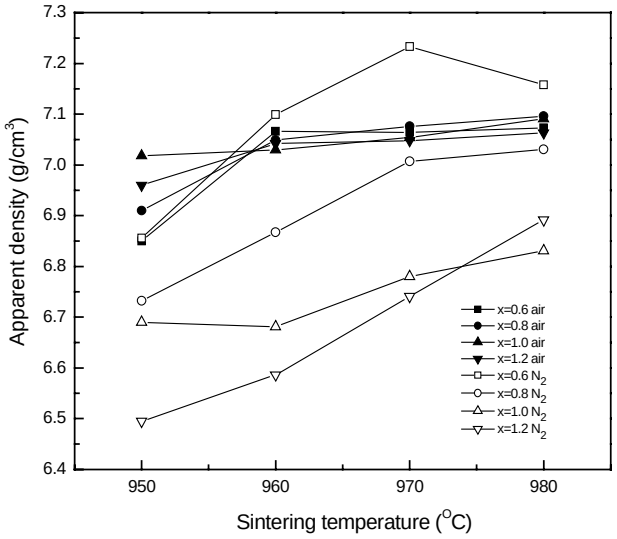

Fig. 1. Bulk densities of Fe_2O_3 doped $BiNbO_4$ ceramics at different sintering atmosphere.

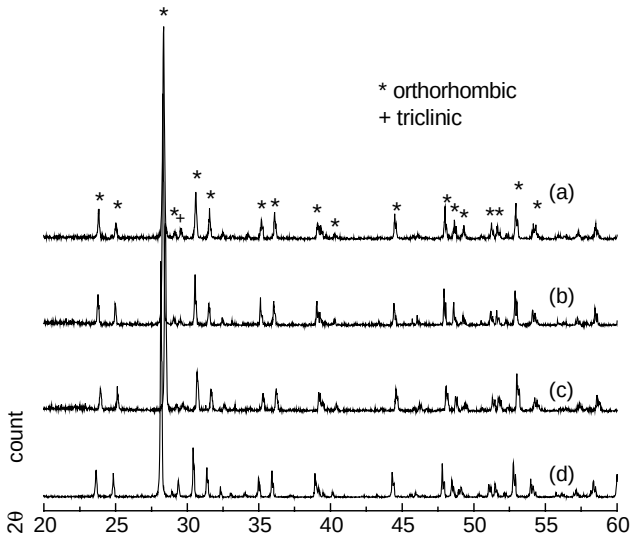

Fig. 2. XRD patterns of Fe_2O_3 doped $BiNbO_4$ ceramics sintered at 980 °C: (a) $x = 0.3$, in air; (b) $x = 1.0$ in air; (c) $x = 03$, in N_2; and (d) $x = 1.0$, in N_2.

network analyzer was used to measure the dielectric constant (ϵ_r) and the quality factor values Q at microwave frequency by Hakki and Coleman's dielectric resonator method [5,6]. The temperature coefficient of resonant frequency τ_f was determined as follows:

$$\tau_f = \frac{f_{80} - f_{20}}{60 \times f_{20}} \times 10^6 \,(\text{ppm}/^\circ\text{C})$$

Simultaneously, the temperature depended dielectric properties at low frequencies (1, 10, and 100 kHz) were also measured by means of a HP4284 precision LCR meter and a thermal environmental test chamber.

3. Results and discussion

The bulk density values of Fe_2O_3 doped $BiNbO_4$ ceramics with different Fe_2O_3 content versus sintering temperatures were showed in Fig. 1. As a result, the bulk densities of the samples sintered in air increased steadily as the sintering

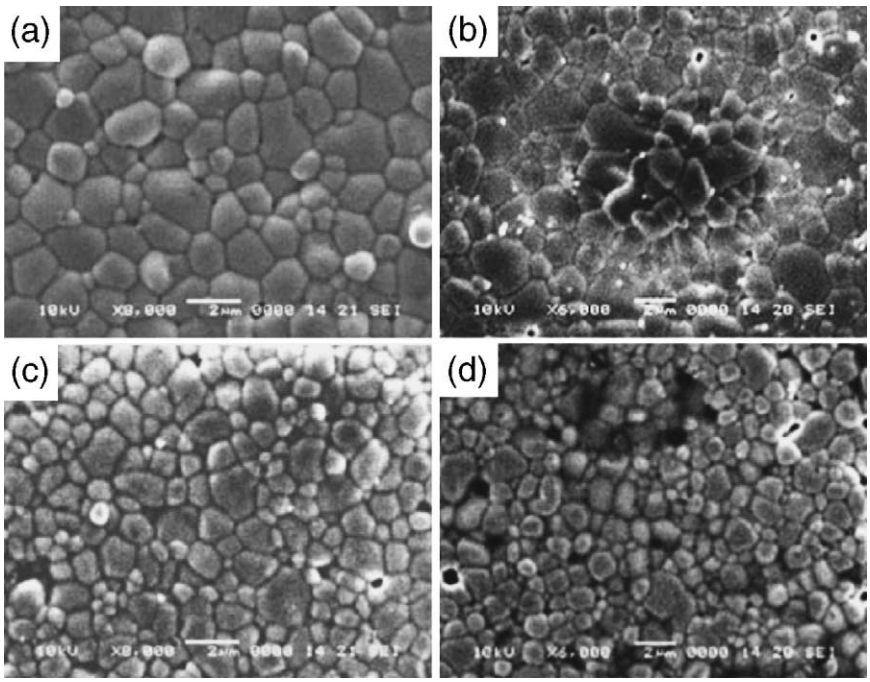

Fig. 3. SEM micrographs of Fe_2O_3 doped $BiNbO_4$ ceramics: sintered at 970 °C: (a) $x = 0.3$, in air; (b) $x = 0.3$, in N_2; (c) $x = 1.0$, in air; and (d) $x = 1.0$, in N_2.

temperature increased from 950 to 980 °C. It can also be seen that the density values of samples sintered in N_2 varied faster than those sintered in air when x value ranged from 0.3 to 1.0.

Fig. 2 showed the XRD patterns of the samples sintered at 980 °C under both air and N_2. It could be seen that all samples exhibited the low temperature phase (orthorhombic $BiNbO_4$) as the main crystalline phase. However, triclinic $BiNbO_4$ phase appeared at $2\theta = 29.3$ for samples sintered in 980 °C. The amount of the triclinic $BiNbO_4$ phase increased with the the increasing of Fe content. The amount of triclinic phase in the samples sintered in N_2 was less than those sintered in air. However, no triclinic phase was found in samples sintered at 970 °C or lower temperature. The results suggested that Fe doping lowered the phase transition temperature, and low oxygen partial pressure atmosphere may hold back the phase transition procedure.

Fig. 3 shows the SEM micrograph of the surface of the sintered samples. It can be seen that as the x value increased, the grain size became smaller, and the ceramics sintered in N_2 were apparently not as dense as those sintered in air. It can also be found that very small pores existed in grain boundary and triple point when the Fe content increased to 1.0 wt.%.

The variation of the microwave dielectric constant (ϵ_r) and Q value at microwave frequency as a function of sintering temperature is shown in Figs. 4 and 5. Generally, dielectric constant increased when sintering temperature ranged from 950 to 980 °C. To the samples sintered in air, ϵ_r values increased with the increasing Fe content. But the rules seemed to be reversed to the samples sintered in N_2. This could be correlated with the valency change of Fe. The Q values of the samples sintered in air firstly increased with the sintering temperature and reached a maximum value at 960 °C and then decreased. Q values of the samples sintered in N_2 showed a similar trend, but the maximum value appeared at

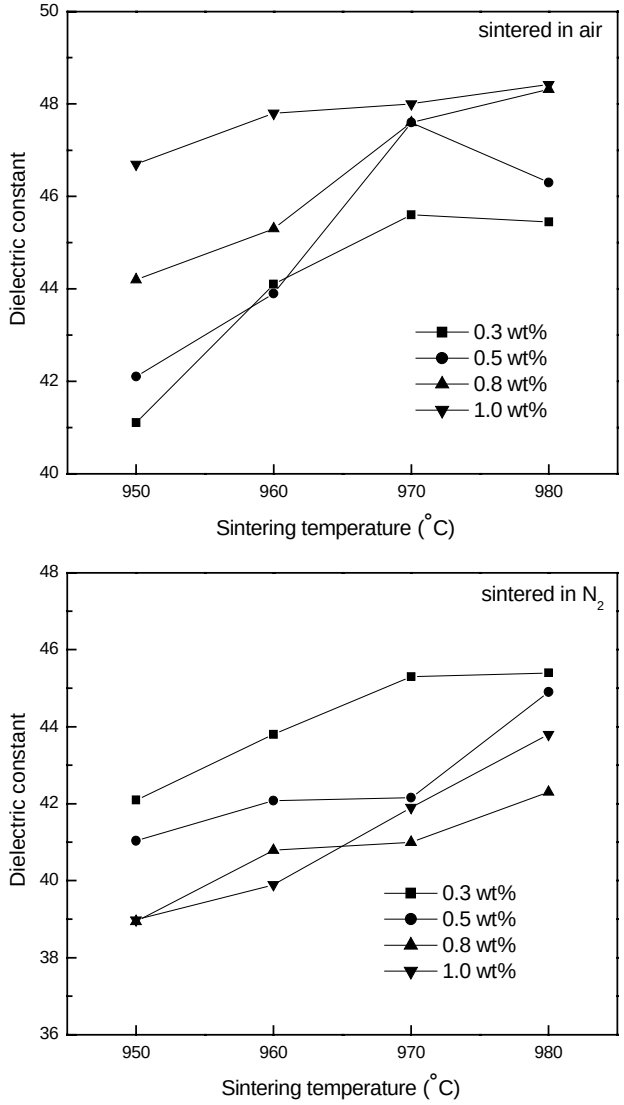

Fig. 4. Dielectric constants of $BiNbO_4$ ceramics with $x = 0.3$–1.0 as a function of sintering temperature.

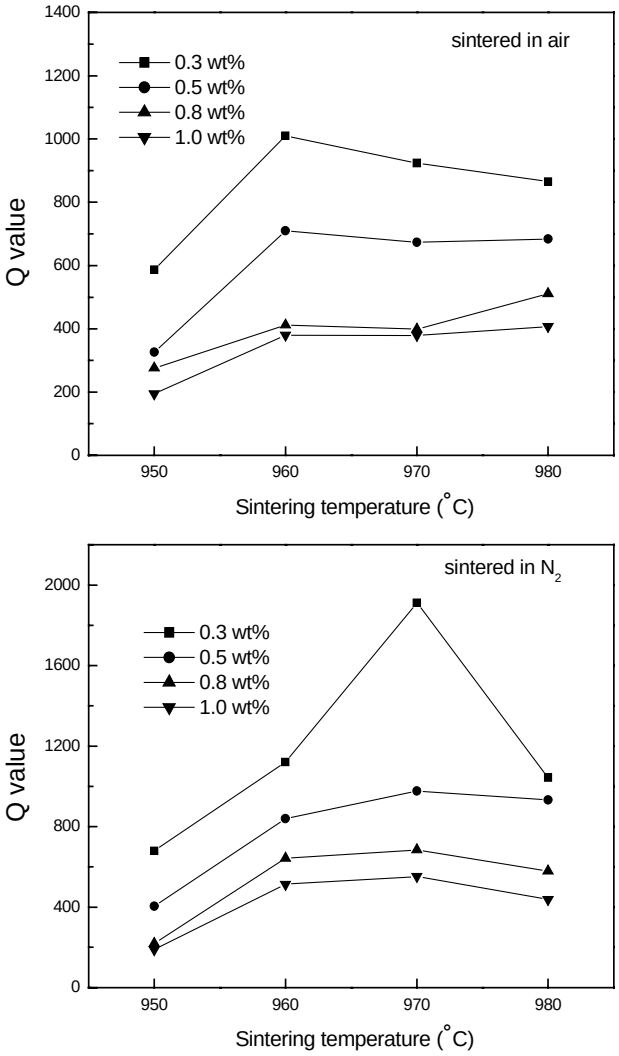

Fig. 5. Q values of $BiNbO_4$ ceramics with $x = 0.3$–1.0 as a function of sintering temperature.

970 °C. According to the XRD and the density result, the decrease in the Q values may be caused by the amount variation of the triclinic phase. With the Fe content increase from 0.3 to 1.0 wt.%, the Q values decreased to a very low value. It could be explained as: when the ceramics were sintered in N_2, much more Fe ions changed their valence from 3^+ to 2^+. When the Fe^{2+} substituted the Bi^{3+} at A site of the lattice, oxygen vacancies appeared to keep electrical neutrality. The amount of these oxygen vacancies increased with the x value. This could make the Q value decreased. The dielectric constants and dielectric loss at low frequencies (1, 10, and 100 kHz) versus testing temperature were measured by means of HP4284 LCR meter and the thermal test chamber. The curves are shown in Fig. 6 ($x = 0.3$, sample sintered at 960 °C). As expected, the dielectric constants and loss increased to very high values as the result of thermal ionic polarization when temperature was above 100 °C. The details between 60 and 250 °C were magnified in the small

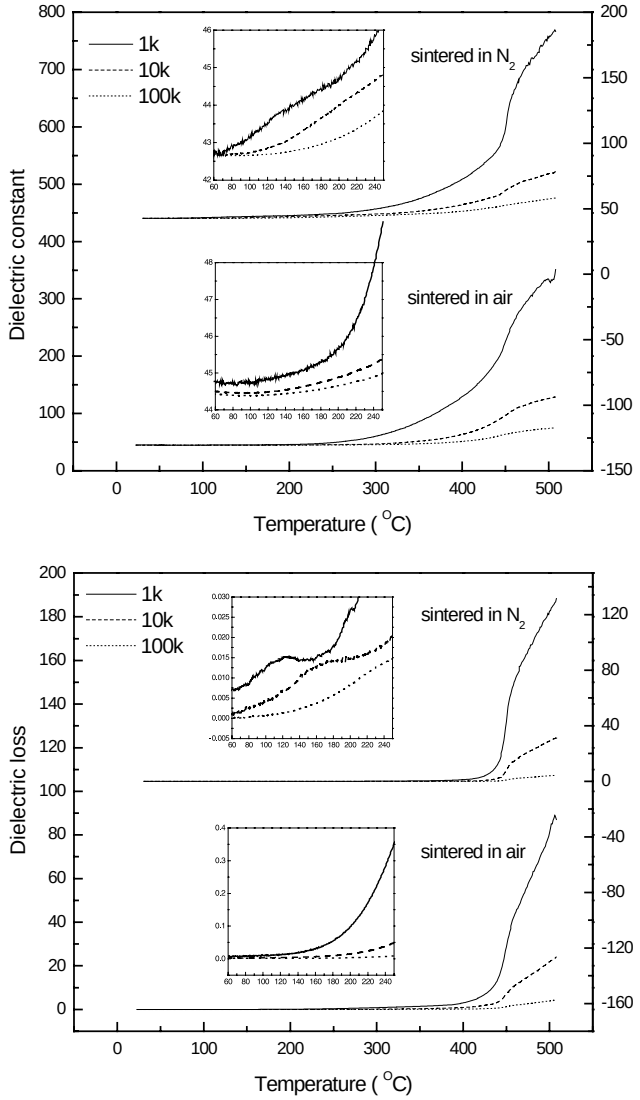

Fig. 6. Dielectric properties of $BiNbO_4$ ceramics with 0.6 wt.% ZnO addition sintered at 970 °C as a function of temperature.

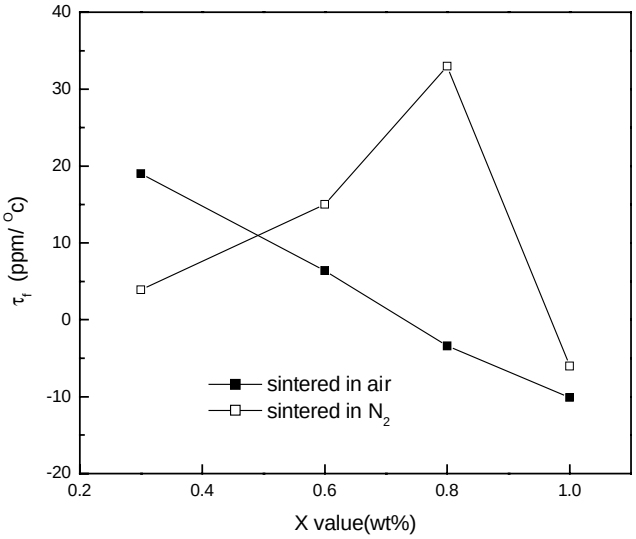

Fig. 7. τ_f values of Fe_2O_3 doped $BiNbO_4$ ceramics sintered at 970 °C as a function of x value.

graphs in the figure. It can be seen that there were some differences between the curves of the samples sintered under different atmosphere. When the temperature ranged from 60 to 250 °C, relaxation phenomenon could be recognized on the curves of those samples sintered in N_2. But such phenomenon did not appeared on those samples sintered in air. It is known that low oxygen partial pressure could create large amount of oxygen vacancies in the lattice. The relaxation phenomenon could be regarded as a proof of the existence of the vacancies. Oxygen vacancies and doping cation at A site of the lattice (Bi^{3+} substituted by Fe^{2+}) could be associated by Coulomb force and form defect dipoles, that caused the relaxation phenomenon at about 120 °C. It could be decided that the oxygen vacancies were the main cause of the relaxation of the samples sintered in N_2.

The microwave temperature coefficients (τ_f) of Fe_2O_3 doped $BiNbO_4$ ceramics sintered at 970 °C under both atmosphere are shown in Fig. 7. As a result, τ_f values of the samples sintered in air decreased from about 20 to –10 ppm/°C as the x value increased. τ_f of those samples sintered in N_2 varied between −5 and 35 ppm/°C, reached a maximum value when $x = 0.8$.

4. Conclusion

Fe_2O_3 addition made the microwave properties of $BiNbO_4$ ceramics poor (Q value < 2000). The Fe addition lowered the phase transition temperature. As the Fe amount increased, the Q values decreased dramatically. The sintering atmosphere also had a remarkable effect on the dielectric properties. The oxygen vacancies created by low oxygen partial pressure atmosphere could decrease the Q value, and the vacancies also could cause the relaxation phenomenon at about 120 °C at low frequencies (1, 10, and 100 kHz).

Acknowledgements

This work was supported by the Ministry of Sciences and Technology of China through 863-project under grant 2001AA325110, 973-project under grant 2002CB613302 and the University Key Studies Project of Shanghai.

References

[1] S.T. Ishizaki, M. Fujita, H. Kagata, T. Uwano, H. Miyake, A very small dielectric planar filter for portable telephones, IEEE Trans. Microwave Theory Tech. MTT-42 (1994) 2017–2022.

[2] H. Kagata, T. Inoue, J. Kato, I. Kameyama, Low-fire bismuth-based dielectric ceramics for microwave use, Jpn. J. Appl. Phys. 31 (1992) 3152–3155.

[3] H.C. Ling, M.F. Yan, W.W. Rhodes, High dielectric constant and small temperature coefficient bismuth-based dielectric compositions, J. Mater. Res. 5 (1990) 1752–1762.

[4] C.L. Huang, W.H. Weng, The microwave dielectric properties and the microstructures of $Bi(Nb,Ta)O_4$ ceramics, Jpn. J. Appl. Phys. 38 (1999) 5949–5952.

[5] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IEEE Trans. Microwave Theory Tech. MTT-8 (1960) 402–410.

[6] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators, IEEE Trans. Microwave Theory Tech. MTT-18 (1970) 476–485.