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Study on the relationship between the defect and dielectric properties of ZnO-doped $BiNbO_4$ ceramic

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Abstract

$BiNbO_4$ ceramic is one kind of potential low-firing microwave dielectric material for microwave applications. ZnO was doped into $BiNbO_4$ ceramics, the dielectric properties of the ceramic as a function of compositional variation, sintering temperature, and sintering atmosphere were studied. By means of the LCR Meter, Network Analyzer and Thermal Environmental Test Chamber, the dielectric properties at various frequencies were tested. Simultaneously, the temperature depended dielectric properties was studied. Then, according to the dielectric behavior under different sintering atmosphere, the relationship between defect and dielectric performance of $BiNbO_4$ ceramic was discussed.

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

1. Introduction

In recent years, the development of low-temperature cofiring ceramics (LTCCs) has been attracting much attention because of the application of multilayer integrated circuit (MLIC) [1]. Most of the well-known commercial microwave dielectric materials possess very high quality factor values and moderate dielectric constant. However, they are not able to compatible with silver or copper electrodes in a multilayer structure because of their high-sintering temperature. So, for the application of the multilayer technology, development of dielectric materials suitable for cofiring with internal conductors has become a major focus.

Recently, bismuth-based dielectric ceramics are becoming attractive due to its relatively low-sintering temperature ($<1000\,^\circ C$) and excellent dielectric properties [2]. Many works have been reported since 1992, which focused on modifying dielectric properties and reducing the temperature coefficient. Many researchers have made efforts to modify the dielectric properties by introducing substitutions for Bi [3,4]. In this work, ZnO was doped into $BiNbO_4$ ceramics. The dielectric properties of the samples sintered under different atmosphere were investigated. The influences of the defect on the dielectric properties were also discussed.

2. Experimental procedures

All the samples were prepared by conventional solid-state reaction method. High purity powders of Bi_2O_3 and Nb_2O_5 were used as the starting materials according to the stoichiometric ratio of $BiNbO_4$ compound. The powders were mixed with different proportion (x wt.%, $x = 0.6$, 0.8, 1.0, 1.2) of ZnO addition. All mixtures were ball-milled for 24 h with deionized water using ZrO_2 balls. After drying, the reagent was calcined at $800\,^\circ C$ 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), respectively, for 2 h. The sintering temperature ranged from 950 to $980\,^\circ C$.

The bulk densities of the sintered ceramics were measured using the Archimedes method. Crystal structure of these ZnO-doped $BiNbO_4$ ceramics were investigated using X-ray diffraction (XRD) patterns (BRUKER, D8 ADVANCED). The micrograph observation of the sintered surface was performed by a SEM (JEOL, JSM-5510). The dielectric constant (ε_r) and the quality values Q at microwave frequency were measured by Hakki and Coleman's dielectric resonator method (modified by Courtney) [5,6]. An HP8753E network analyzer was employed in the microwave property

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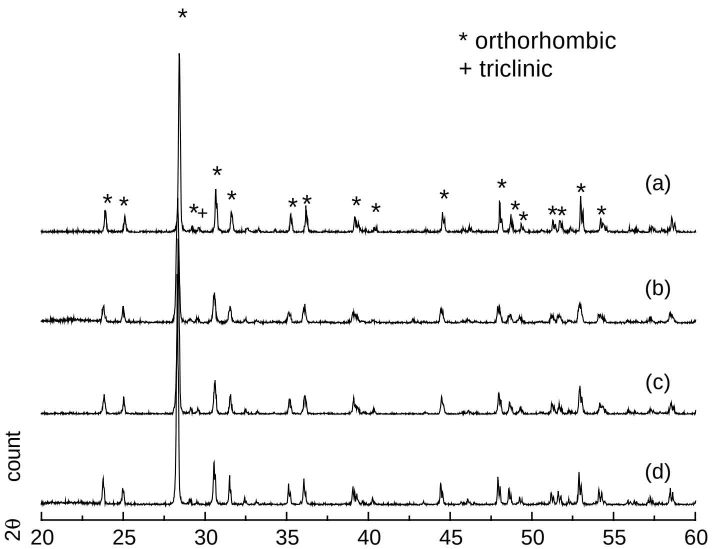

Fig. 1. XRD patterns of ZnO-doped $BiNbO_4$ ceramics sintered at 980 °C: (a) $x = 0.6$ in air; (b) $x = 1.2$ in air; (c) $x = 0.6$ in N_2; and (d) $x = 1.2$ in N_2.

measurements. The temperature depended dielectric properties were also investigated using an HP4284 precision LCR meter and a Thermal Environmental Test Chamber.

3. Results and discussion

Fig. 1 showed the X-ray diffraction patterns of ZnO-doped $BiNbO_4$ ceramics sintered at 980 and 970 °C for 2 h. According to the XRD result, some high temperature phase (triclinic $BiNbO_4$) appeared in the samples sintered in air at 980 °C, the amount of triclinic phase increased as x ranged from 0.6 to 1.2. When samples were sintered at 970 °C or lower temperature, the amount of high temperature phase (triclinic $BiNbO_4$) was much less than those sintered at 980 °C. However, samples sintered in N_2 at even 980 °C didn't exhibit any triclinic $BiNbO_4$ phase. The result suggested that ZnO may lowered the phase transition temperature, and low oxygen partial pressure sintering atmosphere may hold back the phase transition.

Fig. 2 showed the plots of the bulk densities of ZnO-doped $BiNbO_4$ ceramics with different x values versus their sintering temperatures. As the sintering temperatures varied from 950 to 980 °C, the bulk densities of samples sintered in air increased and reached the saturated values at 970 °C. The bulk densities of the samples sintered in N_2 demonstrated a increasing trend as the sintering temperature increased. The density values of the samples sintered in air were lower than those sintered in N_2.

The SEM micrographs of ZnO-doped $BiNbO_4$ ceramics sintered at 970 °C are shown in Fig. 3. The grain growth was uniform in spite of the Zn content and the sintering atmosphere. The samples sintered in air were apparently denser than those sintered in N_2.

Fig. 4 showed the microwave dielectric constant (ε_r) with different x values versus the sintering temperatures. As a result, ε_r values of the samples sintered in air increased with the sintering temperature and reached its maximum value at 970 °C and then decreased. The ε_r values of the samples sintered in N_2 increased steadily till 980 °C. According to the XRD and the bulk density results, the increase of the triclinic phase amount and the decrease of the densities at 980 °C caused the decrease of ε_r value.

The Q values of ZnO-doped $BiNbO_4$ ceramics at microwave frequencies with various ZnO content under different sintering atmosphere were showed in Fig. 5. The Q values of $BiNbO_4$ ceramic decreased dramatically as x values increased from 0.6 to 1.2. Q values of the samples sintered in air increased with sintering temperature and then decreased at 970 °C. According to the XRD and the density results, the decrease in Q values at 970 °C may be caused by

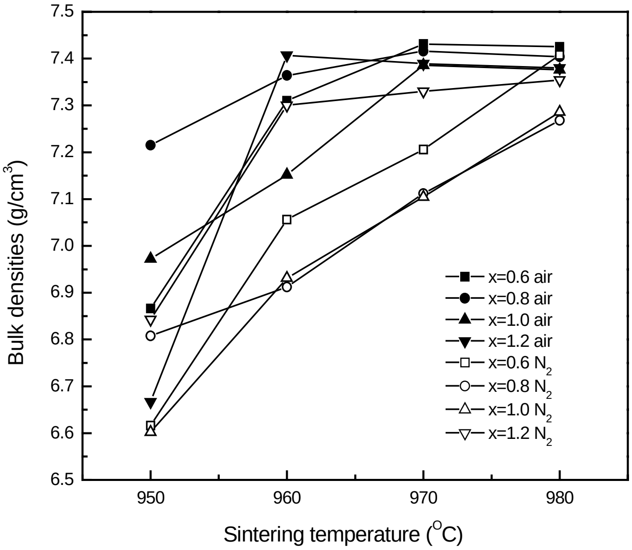

Fig. 2. Bulk densities of ZnO-doped $BiNbO_4$ ceramics at different sintering atmosphere.

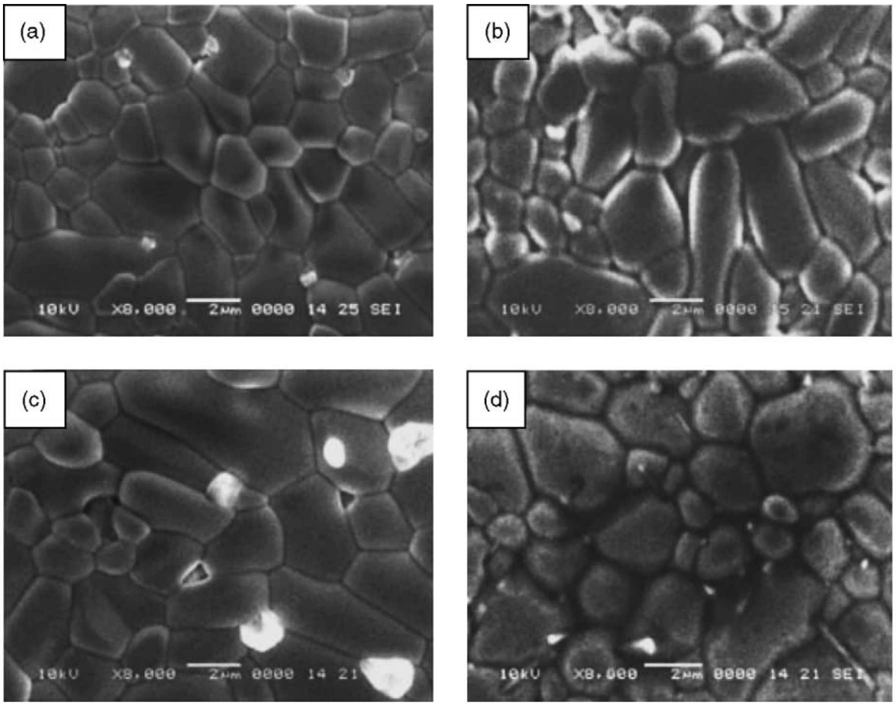

Fig. 3. SEM micrographs of ZnO-doped $BiNbO_4$ ceramics sintered at 970 °C: (a) $x = 0.6$ in air; (b) $x = 0.6$ in N_2; (c) $x = 1.2$ in air; and (d) $x = 1.2$ in N_2.

the increase of the triclinic $BiNbO_4$ phase amount and the decrease of the densities. The dielectric constant and the dielectric loss of ZnO-doped ceramics ($x = 0.6$ wt.%) at low frequencies (1, 10, 100 kHz) as a function of testing temperature (20–500 °C) were measured using a LCR meter and a thermal test chamber. The result was showed in Fig. 6. As the temperature rises from 20 to 500 °C, both the dielectric constant and dielectric loss soared to a very high value. This was caused by thermal ionic polarization. The small graphs in the figure is the magnification of the curves between 60 and 250 °C. It could be seen that relaxation peaks appeared at about 80 °C on the curves of the samples sintered in N_2. When $x = 0.8$, 1.0 and 1.2, the same phenomenon appeared. According to the results mentioned above, the decrease of the Q value with the increase of x values can be explained as: when ZnO was doped into $BiNbO_4$ ceramics, the Zn^{2+} was supposed to substitute the Bi^{3+} at A site of the lattice. Because the Zn^{2+} has a different valance with the Bi^{3+}, oxygen vacancies appeared in order to keep electrical neutrality. These oxygen vacancies could make the dielectric loss increase remarkably. At the same time, low oxygen partial pressure could also cause oxygen vacancies, this also made the Q value decreased. Consider the curves showed in Fig. 5, the relaxation phenomenon at about 80 °C could also be a

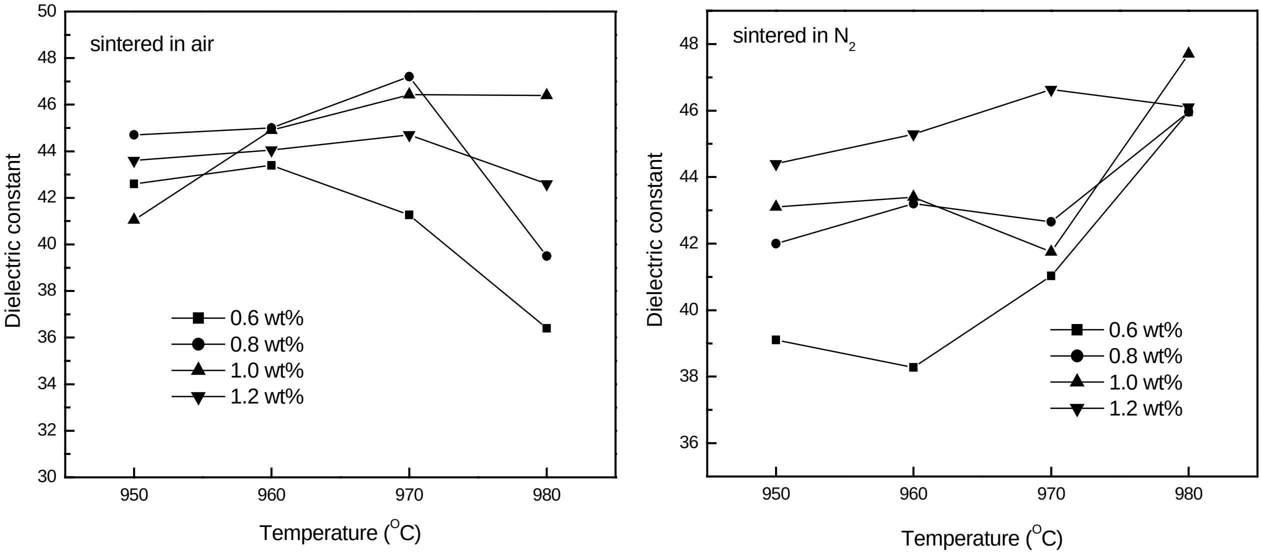

Fig. 4. Dielectric constants of ZnO-doped $BiNbO_4$ ceramics as a function of sintering temperature.

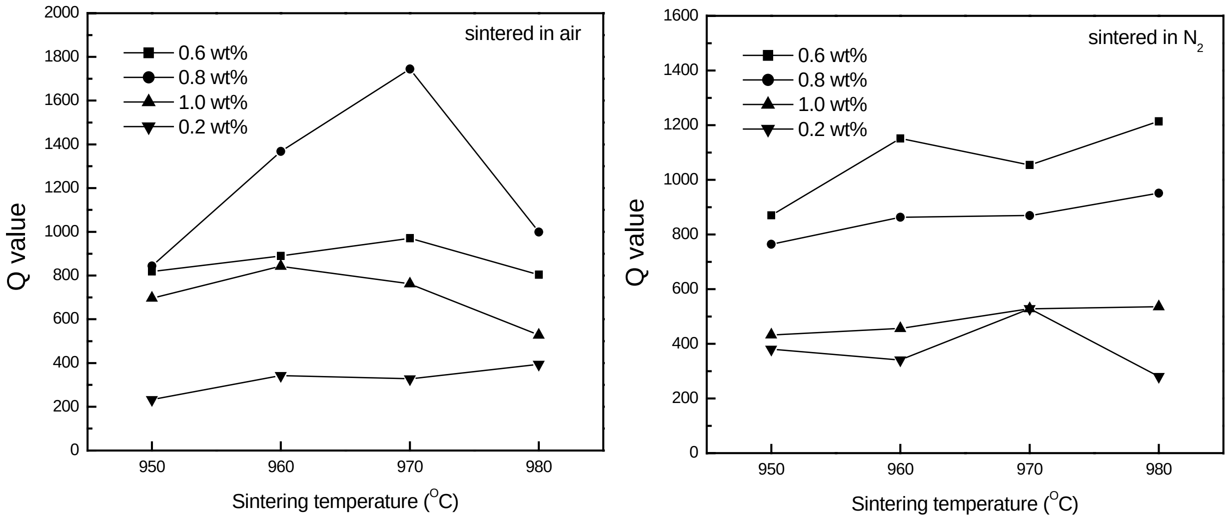

Fig. 5. Q values of ZnO-doped $BiNbO_4$ ceramics as a function of sintering temperature.

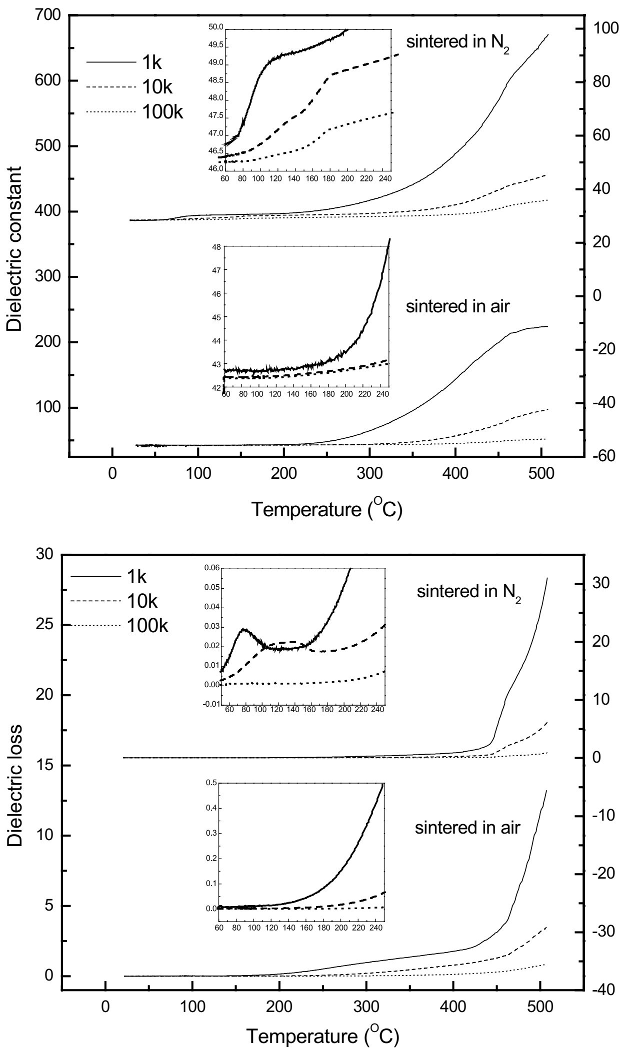

Fig. 6. Dielectric properties of $BiNbO_4$ ceramics ($x = 0.6$) sintered at 970 °C as a function of temperature.

proof of the existence of these vacancies. Oxygen vacancies and Zn^{2+} in A site (substitution for Bi^{3+}) could associate and form defect dipoles, which could be seen as the main cause of the relaxation. Compare to curves of the samples sintered in air, it could be decided that the oxygen vacancies created by sintering atmosphere caused the relaxation of $BiNbO_4$ ceramics at about 80 °C.

4. Conclusion

The dielectric properties were remarkably affected by the sintering atmosphere. Sintering in N_2 can hold back the phase transition (orthorhombic to triclinic, $BiNbO_4$) of $BiNbO_4$ ceramics. Oxygen vacancies caused by substitution and sintering atmosphere made Q value low. Obvious at low frequencies (1, 10, 100 kHz), relaxation phenomenon could be observed on the dielectric constant\loss—temperature curves of the samples sintered in N_2. Vacancies caused by the sintering atmosphere could be considered as the main cause of the relaxation.

Acknowledgements

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