The effect of sintering atmosphere on V_2O_5 substituted $BiNbO_4$ microwave ceramics

Lei Zhang · Xi Yao · Hong Wang · Di Zhou

Abstract In multiplayer passive devices, low sintering temperature dielectric materials were needed to co-fire with low melting point inner electrode such as copper or silver, a major problem of base metal electrode (BME) was that the devices must be fired under low oxygen partial pressure atmosphere to protect Cu from oxidation. In this paper, dielectric properties of $Bi(V_xNb_{1-x})O_4$ (x=0.001, 0.004, 0.008, 0.016, 0.048) microwave ceramics sintered under air and N_2 atmosphere have been investigated. The densification temperature sintered in different atmosphere decreased from 1010 to 830°C with the amount of V_2O_5 increasing from 0.001 to 0.048. Due to the increasing vacancy defects, the density of ceramics sintered in N_2 was smaller than that sintered in air. The ceramics sintered under N_2 have similar dielectric constant, and its Qf values are higher while x<0.016.

Keywords Sintering atmosphere · $BiNbO_4$ · V substitution · Microwave properties

1 Introduction

Multilayer microwave devices were developed to reduce the size of band-pass filters and antenna duplexers in mobile radio communication systems. In multiplayer passive devices, low sintering temperature dielectric materials are needed to co-fire with low melting point inner electrode such as copper or silver. It is well known that

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Bismuth-based dielectric ceramics were excellent low-fire materials and had been studied for multilayer ceramics capacitors (MLCC). Up until 1995 most MLCCs were made with expensive inner electrodes of palladium (Pd) or palladium silver alloys. In 2000, more than 60% of MLCCs are manufactured worldwide with Ni base metal electrode (BME) [1].

The microwave dielectric properties of $BiNbO_4$ ceramics were first reported by Kagata et al. [2], BME copper can been applied to $BiNbO_4$ based on the past study on the added CuO sinter additives [3]. Some studies showed that Ag could react with $BiNbO_4$ ceramics [4], so Cu appeared to be a feasible BME for $BiNbO_4$ system.

The major problem of BME was that the devices must be fired under low oxygen partial pressure atmosphere to protect Cu from oxidation. Under that atmosphere the $BiNbO_4$ could be slightly reduced, forming oxygen vacancies and other defects in the lattices. The affects of sintering atmosphere on microwave dielectric properties of $BiNbO_4$ ceramics doped with V_2O_5 have been reported [5]. However, further investigation on the V_2O_5 substituted rather than doped $BiNbO_4$ under different sintering atmosphere is needed to reveal more structure and properties information. This work presents the study results of the sintering behavior and microwave dielectric properties of V_2O_5 substituted $BiNbO_4$ microwave ceramics in N_2 and air. Tentative discussion of the defect influence on the dielectric properties was made.
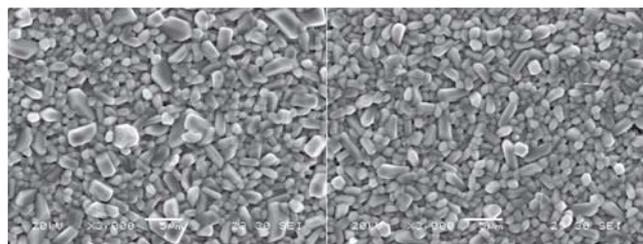
2 Experimental

The ceramics samples were prepared by the solid-state reaction. Pure starting materials Bi_2O_3, Nb_2O_5, V_2O_5 (>99.0%) were mixed according to the composition Bi
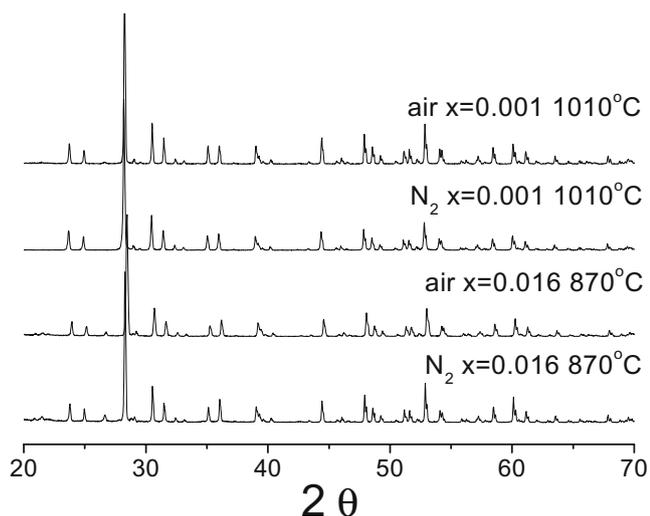
Fig. 1 XRD patterns of Bi(V_xNb_{1-x})O_4 ceramics under different sintering atmosphere

(V_xNb_{1-x})O_4 (x=0.001, 0.004, 0.008, 0.016, 0.048). Mixtures were milled with ZrO_2 balls for 4 h in deionized water. The slurries were dried under an infrared lamp. After drying, the powders were calcined at 750°C for 4 h. The calcined materials were milled with ZrO_2 balls for 4 h in alcohol then dried in infrared lamp. PVA were added as binder before the powder pressed into discs of 12 mm in diameter. The discs were sintered at 550°C for 1 h under air atmosphere. Finally the pallets were sintered under air atmosphere and N_2 at temperatures from 810 to 1020°C. Some samples were re-sintered under different atmosphere
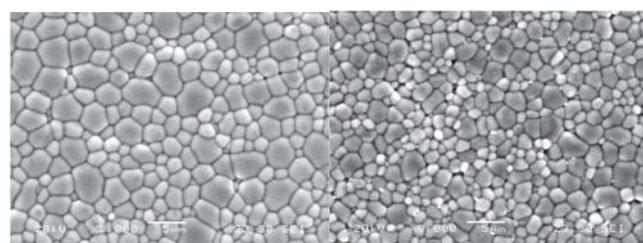
Fig. 2 SEM micrographs of Bi(V_xNb_{1-x})O_4 ceramics at different sinter atmosphere; (**a**) x=0.001, 1010°C, air (**b**) x=0.001, 1010°C, N_2, (**c**) x=0.008, 890°C, air (**d**) x=0.008, 890°C, N_2

Table 1 Sintering temperatures and bulk density (g/cm^3) of Bi (V_xNb_{1-x})O_4 ceramics.

| Sample		x=0.001	x=0.004	x=0.008	x=0.016	x=0.048
air	Sinter temperature	1010°C	910°C	890°C	870°C	830°C
	Density	7.102	7.2	7.058	7.039	7.012
N_2	Sinter temperature	1010°C	910°C	890°C	870°C	830°C
	Density	7.027	7.148	7.032	7.012	7.01

at 850°C for 3 h for study the redox effect on dielectric properties.

The bulk densities were measured by the Archimedes method. Crystalline phases were analyzed by X-ray diffraction method. The X-ray diffraction patterns were obtained using a Rigaku D/MAX-2400 X-ray diffractometer with Cu K$_\alpha$ radiation by 0.02 with 2θsteps width. Microstructure was observed by a scanning electron microscope (SEM).

Measurement of the dielectric constant and the unloaded Q values at 4–7 GHz were completed using a TE$_{01\delta}$ shielded cavity with a HP8720ES network analyzer after polishing the sample's surface.

3 Results and discussion

Pure BiNbO$_4$ has low temperature phase (orthorhombic) below 1020°C, then transformed to high temperature phase (triclinic) gradually as temperature increased [6]. In our experiments, the triclinic phase was not found due to the low sintering temperature. As shown in Fig. 1, the sintering atmosphere do not change the sample's phase structure, it indicates that the amounts of vacancies in the lattice or
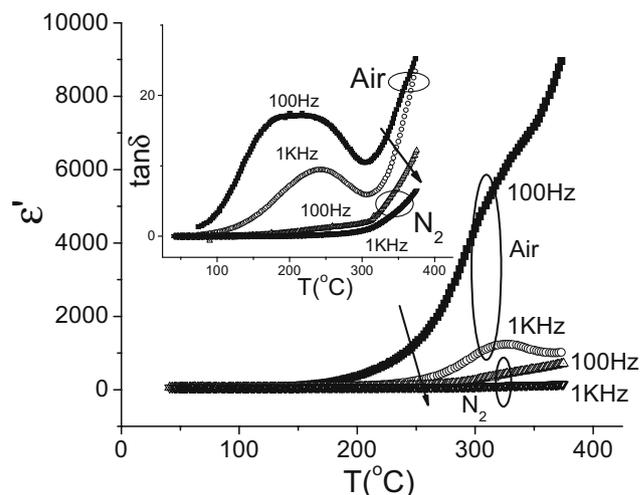
Fig. 3 The change of dielectric constant and loss of the samples sintered in air and re-sintered in N_2 atmosphere, x=0.004
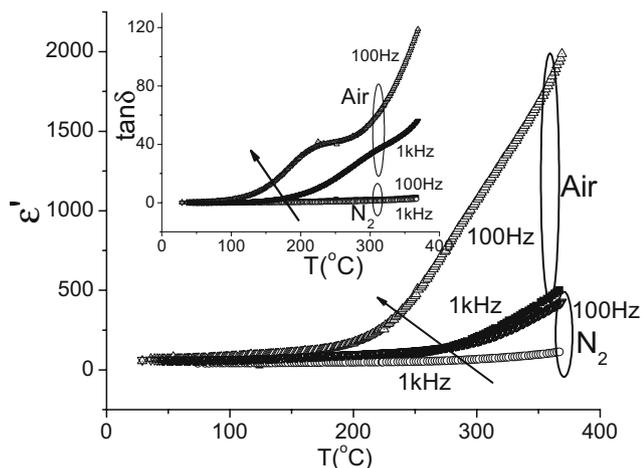
Fig. 4 The change of dielectric constant and loss of the samples sintered in N_2 and re-sintered in air, $x=0.004$

other lattice defects did not reach a level that is enough to change the phase structure.

The SEM of microwave ceramics $Bi(V_xNb_{1-x})O_4$ with different x sintered at different atmosphere are shown Fig. 2. The analysis revealed the dense structure can be obtained after V^{5+} substitution. While $x=0.001$, the grain size is about 2~3 μm in average. The grain size was smaller but more disorder with the x increasing.

Table 1 shows that the densities of the ceramics sintered in N_2 are smaller than those sintered in air atmosphere. In air, there is an increasing of density from $x=0.001$ to 0.004, the density decreases when $x>0.004$. Similar trend can be seen in the samples sintered in N_2.

When the samples were sintered in N_2, the concentration of O_2 decreased dramatically and, according to following defect equation, the thermodynamic balance will move toward the right. Therefore, the concentration of oxygen vacancy will increase when sintering in N_2. The defect equation can be written as

$$O_o \rightleftarrows V\ddot{o} + \frac{1}{2}O_2 + 2e \qquad (1)$$
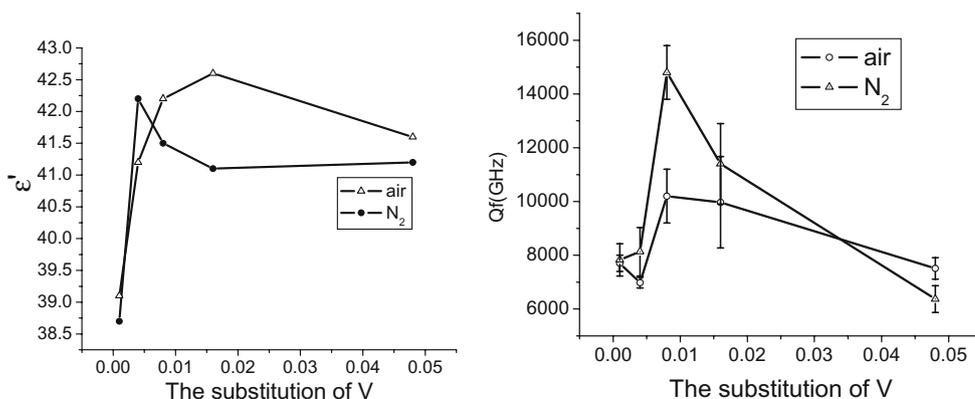
After measuring the properties of the samples which were first sintered in air, we re-sintered them again in reduced atmosphere N_2. Figure 3 shows the dielectric constant and loss of the $x=0.004$ samples first sintered in air then re-sintered in N_2 atmosphere. The dramatic increasing of dielectric constant from 150°C in air sintered samples now decreases after the samples re-sintered in N_2. The corresponding dielectric loss peaks in air sintered samples disappeared and the loss value decreases about 10~40% after the samples sintered in N_2.

And the N_2 sintered samples were re-sintered in air again. The change of dielectric properties just in the reverse direction, i.e. the abnormal increased dielectric constant and deteriorated loss "recovered" again (Fig. 4). This means the polarization being responsible to this process is reversible.

Dielectric constants of $BiNbO_4$ substituted by V_2O_5 at microwave region were shown in Fig. 5. It increase from 39.1 at $x=0.001$ to 42.6 at $x=0.016$, then decrease to 41.6 at $x=0.048$ under air atmosphere. In N_2 atmosphere, dielectric constant increases from 38.7 at $x=0.001$ to its maximum of 42.2 at $x=0.004$ then decreases to 41.1 at $x=0.016$ and 41.2 at $x=0.048$.

The Qf values were strongly dependent on the content of V_2O_5. As shown in Fig. 4, the maximum of Qf is nearly 15000 at $x=0.008$, in N_2 atmosphere. From $x=0.001$ to 0.016, the Qf value of samples sintered in N_2 is higher than that of the sampled sintered in air. However, when $x=0.048$, a slightly higher value is obtained from the samples under air.

In low-frequency region, the difference of the dielectric properties of the samples sintered in air and in N_2 could be supposed to attribute to the appearance of localisation [7]. The localisation can be regarded as "traps" in ceramics. The density of these traps increases with increasing oxygen vacancies. It is known that the concentration of oxygen vacancies of samples in N_2 is larger than it in air, thus making the difference of the dielectric properties for increasing dielectric loss.

Fig. 5 Microwave dielectric behavior of $Bi(V_xNb_{1-x})O_4$ ceramics

Generally speaking, people regard that the existence of defects like oxygen vacancies will lead to the increasing loss and decreasing Qf value. However, the experimental data we acquired in this work do not support such an opinion. The effect of increasing oxygen vacancies of samples sintered in N_2 on Qf values seems unobvious and irregular. In some cases ($x=0.004, 0.008, 0.016$), the Qf values of samples in N_2 are bigger than that sintered in air while in some cases ($x=0.048$) the Qf value of samples in N_2 are lower than that in air. The maximum of Qf value was obtained at $x=0.008$ in the samples both sintered in air and in N_2 but the divergence of the Qf values in air and N_2 reached to maximum too. Since the Qf values in microwave region are affected by many variation factors, present experimental data are not enough to draw a conclusion for explaining such an anomaly reasonably. Further works need to be done for answering this question.

4 Conclusion

V^{5+} substitution for Nb^{5+} is help to reduce the sinter temperature. Sintering atmosphere has little effect on the phase structure for $Bi(V_xNb_{1-x})O_4$, and the bulk density of samples sintered under air atmosphere is a little bigger than it under N_2. The Qf reaches its maximum at $x=0.008$ under N_2 atmosphere.

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