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Ceramics International 30 (2004) 1929–1933

CERAMICS INTERNATIONAL

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The effect of sintering atmosphere on the microwave dielectric properties of V_2O_5 doped $BiNbO_4$ ceramics

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Received 4 December 2003; received in revised form 19 December 2003; accepted 22 December 2003

Available online 31 July 2004

Abstract

Sintering behavior and microwave dielectric properties of $BiNbO_4$ doped with V_2O_5 sintered under ambient and N_2 atmosphere were investigated. The densification temperature and dielectric constant of $BiNbO_4$ fired under ambient atmosphere decreased from 975 to 850 °C and 45.6 to 42.2, respectively, as the amount of V_2O_5 increased from 0.1 to 3.2 mol%. $BiNbO_4$ ceramics was very sensitive to low oxygen partial pressure atmosphere and can be severely reduced under H_2 atmosphere. The apparent density of ceramics sintered under high purity N_2 was smaller than that sintered under ambient atmosphere due to the production of vacancies defects. The formation of oxygen vacancies did not change the crystal structure or decay microwave properties. On the contrary, better microwave properties: $\epsilon_r = 42.7$, Qf $= 28{,}500$ were gotten when $BiNbO_4$ ceramics with 0.8 mol% V_2O_5 additives sintered under N_2 atmosphere.

Keywords: Sintering atmosphere; Microwave ceramics; Oxygen vacancies

1. Introduction

Multilayer microwave devices have developed to reduce the size of band-pass filters and antenna duplexers in mobile radio communication systems. In multilayer structures, low sintering temperature dielectric materials were needed to co-fire with low melting point inner electrode such as copper or silver. Bismuth-based dielectric ceramics were well known as low-fire materials and had been studied for multilayer ceramic capacitors; the microwave dielectric properties of $BiNbO_4$ ceramics were first reported by Kagata et al. [1]. Compared to other materials in microwave devices using noble metal electrode, base metal electrode (BME) copper can been applied to $BiNbO_4$ systems due to the added CuO sinter additive in the past study [2]. Some research [3] showed that Ag could react with $BiNbO_4$ ceramics, so Cu appeared to be the only useable BME for $BiNbO_4$ system.

A 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. However the affects of sintering atmosphere on the sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics doped with V_2O_5 were not reported yet. It was interesting to clarify the relationship above. The aim of this paper was just to investigate the influence of sintering atmosphere on the sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics.

2. Experiment procedures

Pure starting materials Bi_2O_3, Nb_2O_5 (>99.95%) were mixed according to the composition $BiNbO_4$. Mixtures were milled with ZrO_2 balls for 24 h in deionized (DI) water then dried. After drying, the powders were ground and calcined at 800 °C for 5 h. The calcined materials were grinded and mixed with V_2O_5 ($x = 0.1$, 0.2, 0.4, 0.8, 1.6, 3.2 mol%, V1–V6) as the sinter aids and then sieved using a 200-mesh screen. PVA were added as binder before the powder pressed uniaxially into one pellet 12 mm in diameter 1 mm in thickness and another 15 mm in diameter and 6–8 mm in thickness. The smaller pellets were sintered at temperatures from 825 to 975 °C for 1 h under ambient atmosphere. Examinations of the shrinkage factors were acted out to determine the proper sintering temperature. Shrinkage factor was defined

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doi:10.1016/j.ceramint.2003.12.039

as:

$$\alpha = \frac{D_0 - D_T}{D_0}$$

where D_0, D_T stand for the diameters of green and fired specimens, respectively.

Protect gas in our study were high purity N_2 (>99.999%). Specimen's color sintered under N_2 were found from light yellow to green with the increase of V_2O_5 content, that very different from the samples sintered under ambient atmosphere, from light yellow to red. This implied the valence of element V had changed due to the low oxygen partial pressure atmosphere.

Crystalline phases were analyzed by X-ray diffraction method. Microstructure was observed by a scanning electron microscope. Columns-like specimen were sintered under the optimized sintering temperature under various atmospheres for 2 h. Their densities were measured by the liquid Archimedes method using deionized water as the liquid. Measurements of the dielectric constant and the unloaded Q values on TE_{011} mode at 4–6 GHz were completed by Hakki and Coleman's dielectric resonator method after polishing the samples.

3. Results and discussion

Pure $BiNbO_4$ had a crystal structure similar to $SbTaO_4$ (orthorhombic) below 1020 °C, then transformed to high temperature phase (triclinic) gradually as temperature increased [4]. It was reported that adding proper dopant in this system could lower the phase transforming temperature.

In our experiments, the triclinic phase was not found due to the low sintering temperature, and according to the XRD results, the sample with the highest V_2O_5 content sintered at 850 °C was typically α-$BiNbO_4$ phase without any impurity phase. As shown in Fig. 1, the sintering atmosphere do not change the sample's phase structure, it revealed the amounts of vacancies in the lattice did not reach a level enough to changed the phase structure, but as will mention later did cause the apparent density decrease.

Table 1
Shrinkage factor of samples with various V_2O_5 content sintered at different temperatures under ambient atmosphere

Temperatures (°C)	Samples					
	V1	V2	V3	V4	V5	V6
825						0.124
850					0.132	0.128
875					0.134	0.127
900			0.127	0.134	0.131	0.127
925	0.123	0.131	0.129	0.132	0.13	
950	0.131	0.133	0.126	0.129		
975	0.133	0.133	0.127	0.124		
1000	0.133	0.134				

Shrinkage factor as a function of fire temperature of samples doped with various V_2O_5 contents were listed in Table 1. Shrinkage factor increased first, reached a maximum approximately 0.13, then decreased slightly with the temperature increasing in most samples, thus proper sinter temperature can be drawn at the temperature get maximal shrinkage factor. Optimized sintering temperature decreased from 975 to 850 °C with V_2O_5 content increased from 0.1 to 3.2 mol%.

The SEM revealed the changes in morphology in samples fired under optimized temperature with different content V_2O_5 dopant. As shown in Fig. 2, poles were rarely found on the surface of samples even with very little V_2O_5 dopants. It showed the added V_2O_5 acted as efficient sintering aids. It was also interesting to find that the grain size was larger and more uniform in the samples with lower V_2O_5 contents. Samples sintered under N_2 showed the same micrograph.

From Table 2, we can draw the conclusion that ceramics doped with V_2O_5 were all well densified, got a density higher than 95% theoretical densities (7.35 g/cm^3) (estimated from the standard XRD patterns of $BiNbO_4$). It was

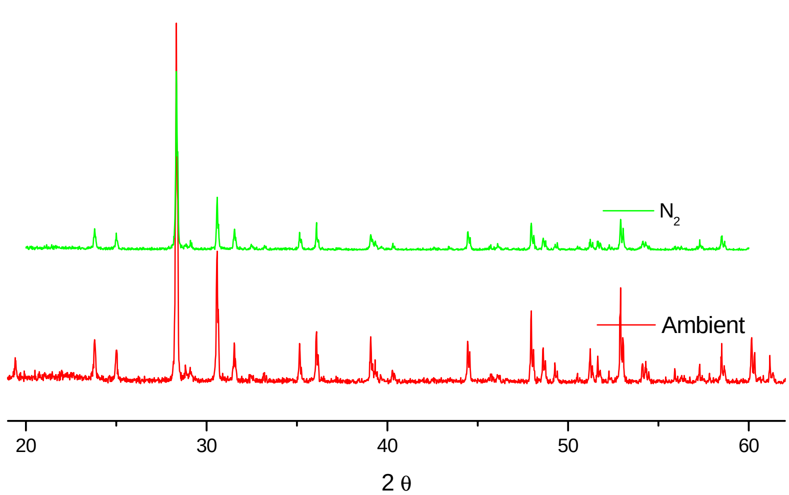

Fig. 1. The XRD patterns of V6 sintered at 850 °C under different atmospheres.

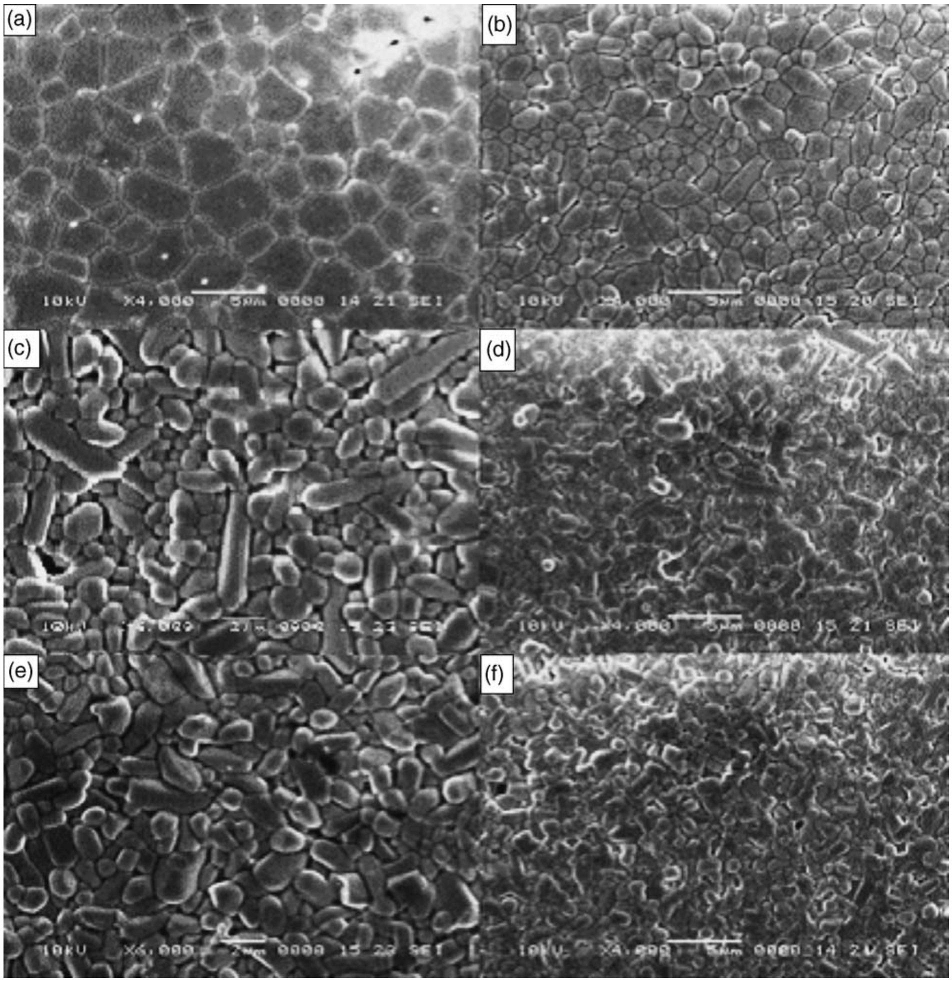

Fig. 2. SEM micrographs of V1 sintered at 950 °C under ambient (a) and N_2 (b); V4 sintered at 900 °C under ambient (c) and N_2 (d); V6 sintered at 850 °C under ambient (e) and N_2 (f).

reported that pure $BiNbO_4$ could not be densified under 1000 °C, so, a little amount of V_2O_5 could be enough to densify $BiNbO_4$. The density of samples sintered at optimized sintering temperature under ambient atmosphere first increased, come to a maximum 7.149 at $x = 0.2$ mol% then decreased slowly as increasing V_2O_5 content. The same trend was found in the samples sintered under N_2 but to our astonishment, all the densities of the samples sintered under N_2 were smaller than that sintered under ambient atmosphere at the same temperature. Excluding experimental error, this can only been explained by the formation of oxygen vacancies in the ceramics when sintered under low oxygen partial pressure atmosphere.

Table 2
Densities of samples with various V_2O_5 contents sintered at optimized sintering temperature under ambient and N_2 atmosphere (ST: sintering temperature)

	Samples					
	V1	V2	V3	V4	V5	V6
ST (°C)	975	950	925	900	875	850
Air	7.093	7.149	7.143	7.128	7.104	7.047
N_2	7.089	7.131	7.139	7.121	7.099	7.032

It was known that metal oxide ceramics could be slightly reduced when sintered under reducing atmosphere. This procedure can been described as:

$$O_O - 2e \rightarrow V_{\ddot{O}} + \frac{1}{2}O_2 \uparrow$$

The formation of oxygen vacancies responds for many related properties changes in specimen sintered under low oxygen partial pressure atmosphere, such as conductance, density, and so on. In the case of density, the theoretical value of perfect $BiNbO_4$ can be calculated by:

$$\rho = [Bi_{Bi}]M_{Bi} + [Nb_{Nb}]M_{Nb} + [O_O]M_O$$

where M stands for the atomic weight. The sum is determined by both metal and oxygen contents, so the formation of large amounts of oxygen vacancies at the oxygen sites in the lattice can reduce the apparent density detectably.

Dielectric constants of $BiNbO_4$ doped with V_2O_5 under microwave region were shown in Fig. 3. It decreased sharply

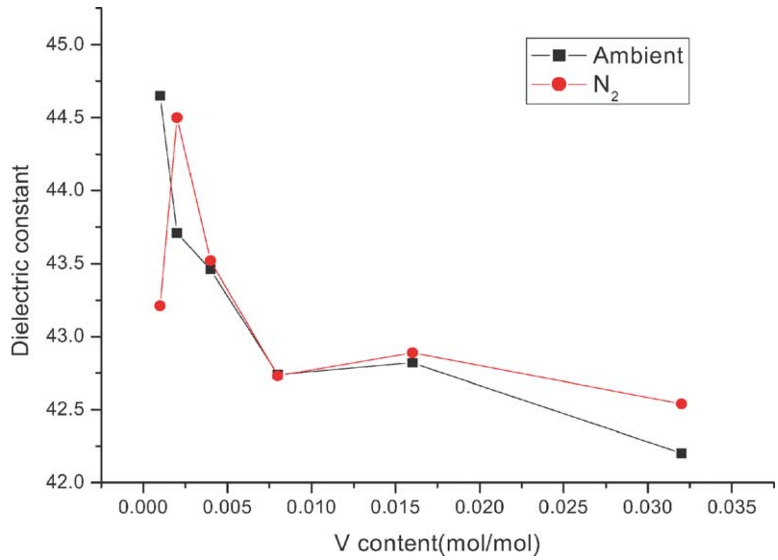

Fig. 3. Dielectric constant of $BiNbO_4$ sintered at optimized sintering temperature under different atmospheres as a function of V_2O_5 contents.

from 44.7 at $x = 0.1$ mol% to 42.7 at $x = 0.8$ mol%, and then saturated at 42 with more V_2O_5 additives when samples sintered under ambient atmosphere. The same trend was found in the samples sintered under N_2 atmosphere. Their permittivity appeared to be a little higher than that of the samples fired under ambient atmosphere, especially V_2O_5 additives reached a higher level of contents.

The Qf values were strongly dependent on the amounts of V_2O_5 additives and had the same trend as the bulk density of ceramics. As shown in Fig. 4, the Qf values increased from 4530 to 22,100 as the amount of V_2O_5 additive increased from 0.1 to 0.8 mol% when the samples sintered under ambient atmosphere, then followed by a decrease to 1600 as V_2O_5 content reached 3.2 mol%.

It was known that the dielectric loss of ceramics in the microwave region had an intrinsic and an extrinsic origin. Anharmonic phonon decay processes in the pure crystal lattice caused the intrinsic losses while crystal defects and microstructures caused the extrinsic losses. The XRD patterns showed us the $BiNbO_4$ ceramic had a single phase with various V_2O_5 additives, it implied the extrinsic loss dominated the dielectric loss of the ceramics. From Fig. 2 minimum poles can been found on the surface of specimen doped with 0.1 mol% V_2O_5, this answered for the lower Qf of the sample. More V_2O_5 additive more compact samples can be gotten, thus resulted in higher Qf value. The ceramics got a better figure of merit Qf $= 22{,}100$ at $x = 0.8$ mol%. However, on increasing the amount of V_2O_5 from 0.8 to

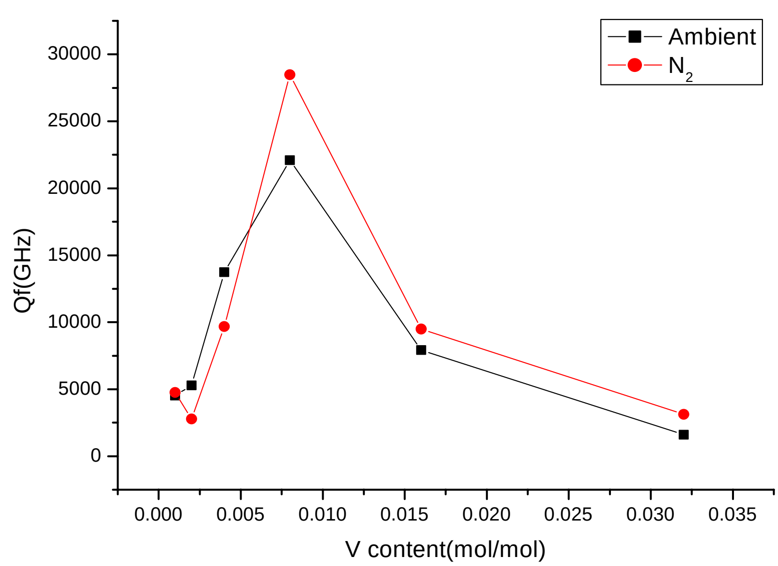

Fig. 4. Qf of $BiNbO_4$ sintered at optimized sintering temperature under different atmospheres as a function of V_2O_5 contents.

3.2 mol%, Qf values were degraded abruptly. The reason might be the grain boundary phase or second phase in the ceramics caused by too many additives, and thus degraded the dielectric properties.

The Qf values of samples sintered under N_2 showed the same trend. The maximum was about 28,500 and was gotten at $x = 0.8$ mol%. It was interesting to find that the Qf values were much higher when the samples sintered under N_2 than that sintered under ambient atmosphere. It was opposite to the trend of density. Since the XRD and SEM results showed us little difference between them, this can only be explained by the decrease of densities, i.e. the formation of oxygen vacancies. So it seems that proper content of oxygen vacancies can enhance the microwave dielectric properties of the ceramics.

4. Conclusion

V_2O_5 was an employable sintering aid for $BiNbO_4$ ceramic. $BiNbO_4$ can be densified below 1000 °C under ambient atmosphere with very little V_2O_5, and the ceramic with 0.8 mol% V_2O_5 got better microwave dielectric properties: $\epsilon_r = 42.7$, Qf = 22,100. But V_2O_5 doped $BiNbO_4$ ceramics were very sensitive to low oxygen partial pressure sintering atmosphere. And the ceramics were severely reduced under H_2 atmosphere, metal bismuth was found on the surface of the samples. A lot of oxygen vacancies formed in the lattices when $BiNbO_4$ sintered under high purity N_2 atmosphere, and thus changed the apparent density detectably. But the formations of oxygen vacancies in the samples sintered under N_2 atmosphere did not reach a level enough to decay the microwave dielectric properties. On the contrary, proper content oxygen vacancies enhanced the Qf values of the $BiNbO_4$ ceramics doped with moderate content of V_2O_5, the $BiNbO_4$ with 0.8 mol% V_2O_5 sintered under N_2 atmosphere showed excellent microwave dielectric properties: $\epsilon_r = 42.7$, Qf = 28,500.

Acknowledgements

This work was supported by the Ministry of Science and Technology of China through 863-project under grant 2001AA325110, 973-project under grant 2002CB613302.

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