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CeO_2-modified $BiNbO_4$ microwave ceramics sintered under atmosphere

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Abstract

The effects of CeO_2 addition on the sintering behaviors and the microwave dielectric properties of $BiNbO_4$ ceramics were investigated. CeO_2 addition lowered the phase transition temperature (from orthorhombic to triclinic phases) and decreased the sinterability of $BiNbO_4$ ceramics. Low oxygen partial pressure atmosphere were found to enhance the sinterability and accelerate the phase transition procedure of the ceramics. The change of dielectric constants and quality factors with the bulk densities and the phase compositions of the ceramics were reported. The $(Bi_{0.95}Ce_{0.05})NbO_{4.025}$ ceramics sintered at 950 °C had a remarkable microwave dielectric property.

Keywords: Sintering atmosphere; Microwave ceramics

1. Introduction

Multilayer microwave devices have been developed to reduce the size and weight of the components in mobile communications. In multilayer structures, low sintering temperature dielectric materials were needed to co-fire with low melting point base metal electrode (BME) such as copper or silver. Bismuth-based dielectric ceramics were well known as low-fire materials, the microwave dielectric properties of $BiNbO_4$ ceramics were first reported by Kagata et al. [1]. Some research [2] showed that Ag can react with $BiNbO_4$ ceramics, so copper appeared to be the only usable BME for $BiNbO_4$ system.

A major problem of BME was that the devices must be fired under oxygen-free atmosphere to protect Cu from oxidation. Under that atmosphere the $BiNbO_4$ could be slightly reduced, forming point defects in the lattices, and would change the sintering behaviors. Our interest was to clarify the effects of sintering atmosphere and CeO_2 substitution on the microstructures and the microwave dielectric properties of $(Bi_{1-x}Ce_x)NbO_y$ ceramics.

2. Experimental procedures

Pure starting materials CeO_2, Bi_2O_3, Nb_2O_5 (>99.9%) were mixed according to the composition $(Bi_{1-x}Ce_x)NbO_y$ ($x = 0.005, 0.01, 0.02, 0.05, 0.1, 0.2$). A small amount of CuO (0.4 mol%) was added to the powder as a sintering aid after the mixture was calcined at 800 °C for 5 h. Then proper organic binder was added to the powder before pressed uniaxially into one pellet 12 mm in diameter, 1 mm in thickness and another 15 mm in diameter, 6–8 mm in thickness. Protect gas in our study was of high purity N_2 (>99.999%). Samples were sintered at temperatures between 925 and 975 °C under ambient and N_2 atmospheres for 2 h, respectively.

Crystalline phases were analyzed by X-ray diffraction method. Microstructure was observed by a scanning electron microscope. The densities of columns-like specimen sintered at 950 °C were measured by the liquid Archimedes' method. 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. Temperature coefficient of dielectric constant under intermediate frequency (1 MHz) was tested by HP4284 using the smaller samples.

3. Results and discussion

It was known that $BiNbO_4$ had a low-temperature phase (orthorhombic) below 1020 °C, which changed to high-temperature phase (triclinic) gradually as the temperature was increased [3]. The calcined powder exhibited the orthorhombic phase as the main crystalline phase. But CeO_2-doped samples sintered at a temperature above 925 °C showed a mixture of high- and low-temperature phases,

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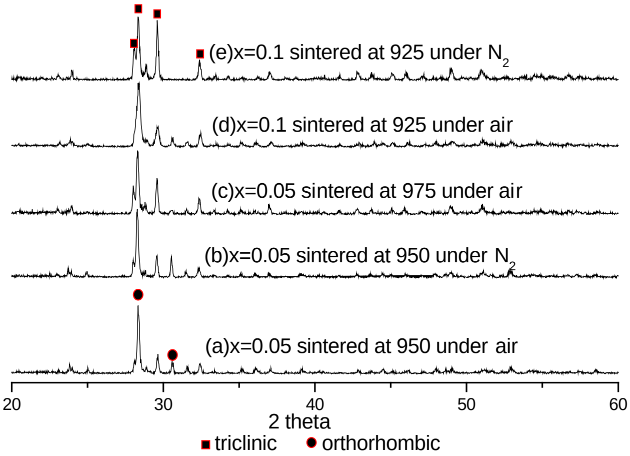

Fig. 1. X-ray diffraction patterns of $(Bi_{1-x}Ce_x)NbO_y$ sintered under different atmosphere.

without other impurity phase. As shown in Fig. 1, more the CeO_2 dopants and higher the sintering temperature, more is the triclinic phase formed. To determine the degree of phase transition, the triclinic phase intensity ratio (R) was defined as $R = I_{tri}/(I_{tri} + I_{ortho})$, where I_{tri} and I_{ortho} represent the intensities of triclinic $(0\,-1\,2)$ and orthorhombic $(0\,4\,0)$ peaks, respectively. For dopants content $x = 0.005$–0.02, the R-value of the samples showed little variation below 950 °C in spite of the sintering atmosphere. However, the R-value of the samples with $x = 0.05$ sintered under air increased sharply even though the fire temperature was 925 °C, the R-value becomes 0.458 as fire temperature was increased to 950 °C, and the phase transition was completed at 975 °C. It was interesting to find that the sample with $x = 0.05$ sintered at 925 °C under N_2 got a higher R-value of 0.513 compared with the samples sintered under air, and the samples sintered at 925 °C under N_2 were found to be entirely in triclinic phase. It seemed that low oxygen partial pressure atmosphere promoted the phase transition.

The micrographs of samples sintering at 950 °C are shown in Fig. 2. The grain growth was uniform and homogeneous when Ce at a low level of content. But the sinterability of ceramics decreased acutely with increasing the Ce-content as a lot of pores can be found on the surface of the specimen with $x = 0.01$ sintered under air. This led to the decrease of density of the samples with Ce dopant content higher than 0.005. As showed in Fig. 3, the apparent density was only 79% of the theoretical value when the ceramics had a dopant content $x = 0.2$. It seemed that the content of CuO sintering aid did not reach a level enough to densify the ceramics. However, the samples sintered under N_2 showed a different trend. From Figs. 2b and d and 3, we could draw the conclusion that the ceramics were all well densified at 950 °C with various contents of Ce dopants under N_2 atmosphere. It implied that low oxygen partial pressure atmosphere enhanced the sinterability of the Ce-doped $BiNbO_4$ ceramics.

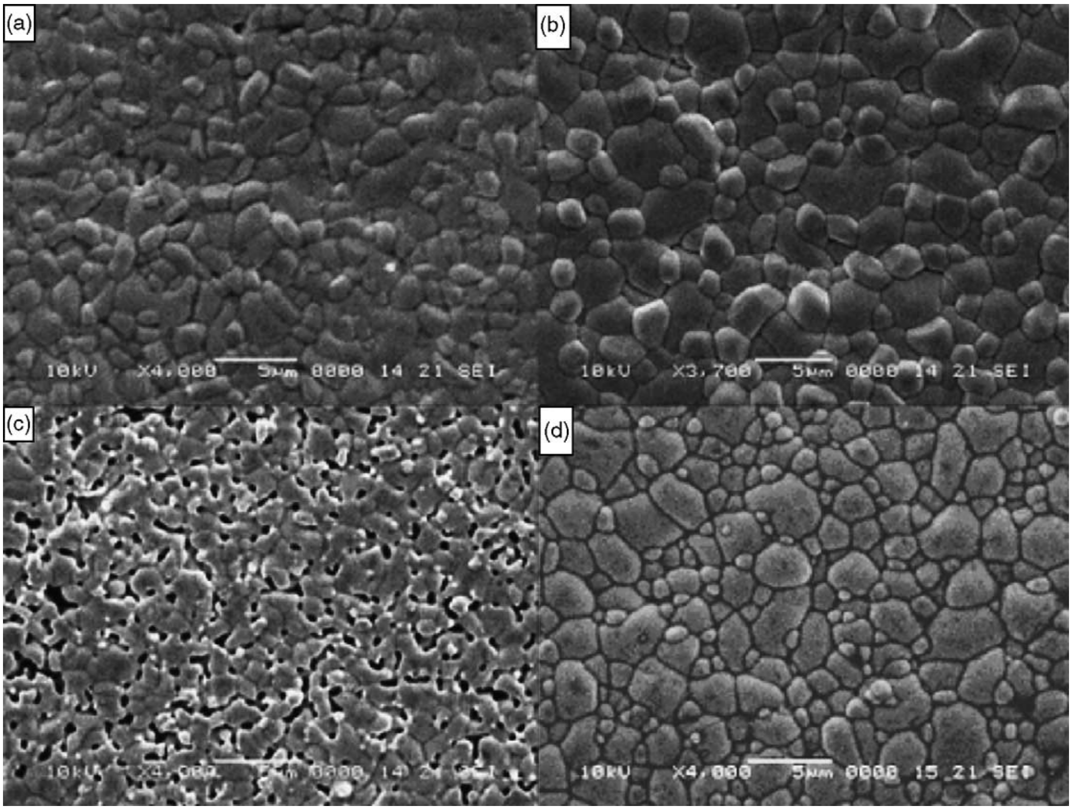

Fig. 2. Micrograph of samples sintered at 950 °C: (a) $x = 0.005$ under ambient atmosphere, (b) $x = 0.005$ under N_2, (c) $x = 0.2$ under ambient atmosphere, (d) $x = 0.2$ under N_2.

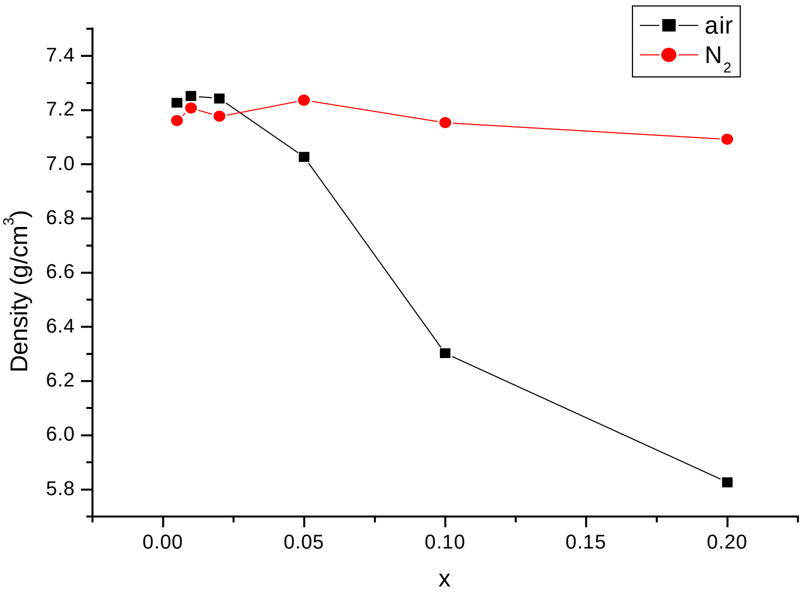

Fig. 3. Densities of $(Bi_{1-x}Ce_x)NbO_y$ ceramics sintered at 950 °C under ambient and N_2 atmosphere.

This could be explained by the increase of volume diffusion due to introduction of oxygen vacancies when oxide ceramics were sintered under N_2 atmosphere.

As we have mentioned earlier, there was a phase transition as samples with dopants content higher than 0.05 were sintered at a temperature higher than 925 °C under N_2, this might cause an increase of the density due to the pure triclinic $BiNbO_4$ getting a higher theoretical density 7.5 g/cm^3 compared with orthorhombic 7.35 g/cm^3. However, this effect might be weakened by the descendant current of density owning to the substitution of heavier Bi atoms by lighter Ce atoms. This resulted in a lower density, 7.092 g/cm^3, when ceramics with dopant $x = 0.2$ were sintered under N_2, which was assumed to be well densified from Fig. 3.

Fig. 4 illustrates the dielectric constant of $(Bi_{1-x}Ce_x)NbO_y$ ceramics sintered at 950 °C. The trend was similar to the bulk density. The dielectric constants of samples sintered under air increased from 44.32 to 46.42 as Ce-content increased from 0.005 to 0.05, then decreased rapidly to 33.51 as Ce-content attained 0.2. However, the dielectric constants of the samples sintered under N_2 increased stably from 44.28 to 48.96 as Ce-content increased from 0.005 to 0.2. It implied that the triclinic phase of ceramics has a higher dielectric constant than the orthorhombic phase. The decrease of dielectric constants of samples sintered under air can only be explained by the existence of high levels of porosity.

The figures of merit of ceramics with various contents of CeO_2 dopants sintered at 950 °C under different atmospheres were shown in Fig. 5. In the case of samples sintered under air, the quality factor increased first, reached a maximum $Q_f = 15\,000$ at $x = 0.05$, then followed by a sharp decrease. Excluding the exceptional data point at $x = 0.02$, the Q_f as a function of Ce dopant was rather simple.

But we must remember the existence of phase transition in the ceramics with the increase of Ce-content sintered at a fixed sintering temperature. Huang et al. [4] reported that the maximum Q_f values of $(Bi_{1-x}Ce_x)NbO_4$ ceramics occur at a phase transform ratio (orthorhombic to triclinic) $R = 0.3$ and then rapidly decreased, and the procedure was dominated by many factors. So, in this study, the maximum Q_f values occurred at phase transform ratio $R = 0.458$. One different thing was that lower phase transform ratio can also decay the Q_f value, because a relatively higher $Q_f = 14\,000$ achieved in the sample had almost a pure orthorhombic phase with $x = 0.01$ before decreased to $Q_f = 9600$ with $x = 0.02$, which was assumed to be a composition of orthorhombic and triclinic phase.

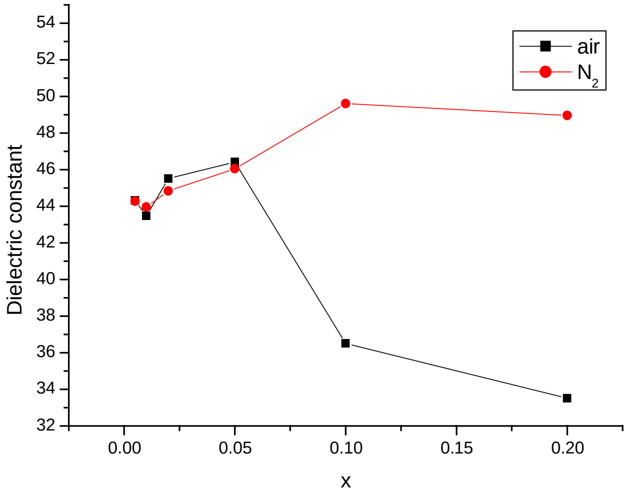

Fig. 4. Dielectric constants of $(Bi_{1-x}Ce_x)NbO_y$ ceramics sintered at 950 °C under ambient and N_2 atmosphere.

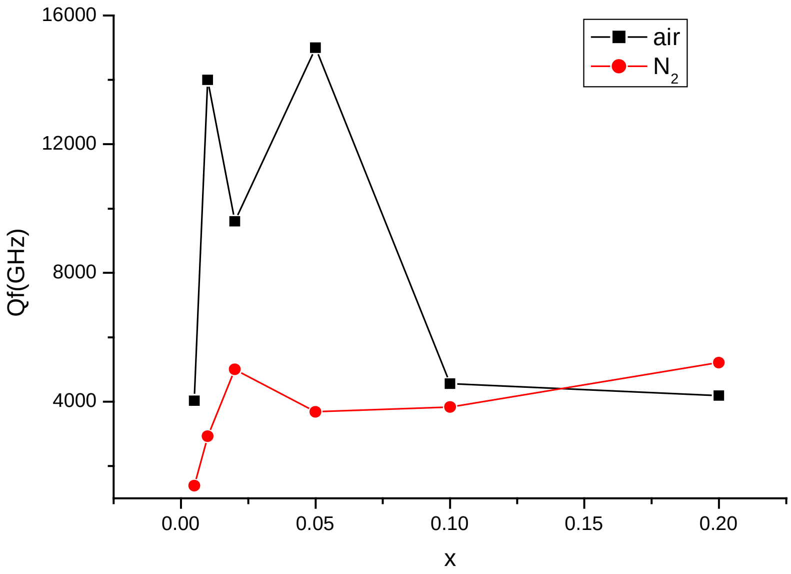

Fig. 5. Figure of merit of $(Bi_{1-x}Ce_{x)})NbO_y$ ceramics sintered at 950 °C under ambient and N_2 atmosphere.

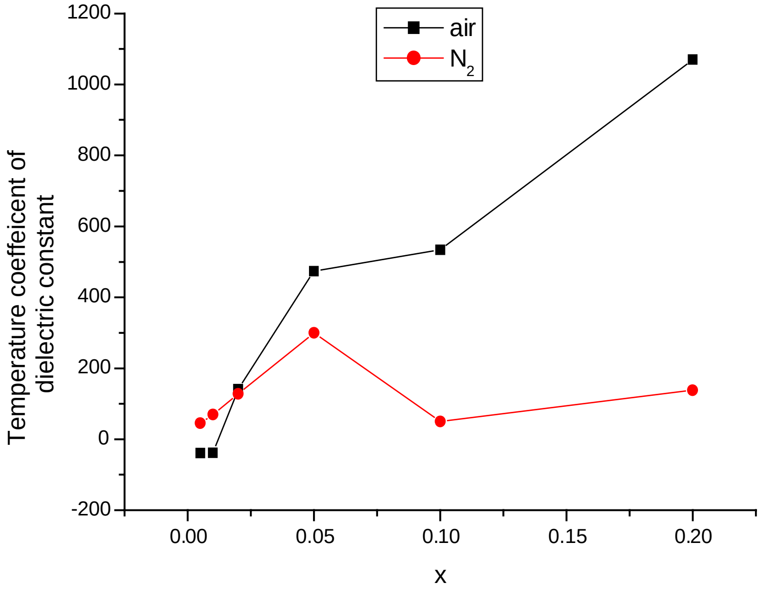

Fig. 6. $\tau_{\varepsilon,80}$ of $(Bi_{1-x}Ce_x)NbO_y$ ceramics sintered at 950 °C under ambient and N_2 atmosphere.

The quality factors of samples sintered under N_2 atmosphere were much smaller than that sintered under air. It increased first, reached a maximal $Q_f = 5000$ at $x = 0.02$, and then followed by a decrease, reached a minimum $Q_f = 3680$ at $x = 0.05$, at last it increased slightly again. The formation of oxygen vacancies might contribute to the decay of Q_f compared with the higher Q_f of the samples sintered under air. Since the triclinic-phase ceramics were well densified, the poor dielectric properties might also be due to the high intrinsic loss of high-temperature phase.

Fig. 6 shows the temperature coefficient of dielectric constant of $(Bi_{1-x}Ce_x)NbO_y$ ceramics sintered at 950 °C under air and N_2 atmospheres. For $x > 0.02$, the temperature coefficients were much higher $\tau_{\varepsilon,80} > +100$ ppm/°C in spite of the sintering atmosphere. But it was worthwhile to note that the ceramics with dopant content $x = 0.01$ had $\tau_{\varepsilon,80} = -38$ ppm/°C when sintered under air, $\tau_{\varepsilon,80} = 70$ ppm/°C when sintered under N_2.

4. Conclusions

$(Bi_{1-x}Ce_x)NbO_y$ ceramics with 0.4 mol% CuO sintering additives were found well densified for $x < 0.05$ sintered at 950 °C under air, but the ceramics were a mixture of triclinic and orthorhombic phases, though the phase transition remained very low. As more Ce substituted the Bi sites in $BiNbO_4$ ceramics, i.e. $x > 0.05$, low sinterability and rapid phase transition were observed when samples were fired at a temperature of 950 °C under ambient atmosphere. However, low oxygen partial pressure atmosphere was found to enhance the sinterability and accelerate the phase transition procedure. The dielectric constants of $(Bi_{1-x}Ce_x)NbO_y$ ceramics sintered at 950 °C under ambient atmosphere were strongly dependent on the bulk density and dopant content, while those of the ceramics sintered under high purity N_2 atmosphere at 950 °C were found to be saturated in the range of 44–49. Unloaded quality factors of samples sintered under ambient atmosphere were much higher than that of the samples sintered under N_2. The τ_ε of ceramics were quite higher regardless of the sintering atmosphere for $x > 0.02$. The microwave dielectric properties of the $(Bi_{0.95}Ce_{0.05})NbO_{4.025}$ ceramics sintered at 950 °C under ambient atmosphere were $\varepsilon_r = 46.42$, $Q_f = 15\,000$, while the dielectric properties of those sintered under N_2 were: $\varepsilon_r = 46.05$, $Q_f = 3700$.

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