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Effects of complex substitution of La and Nd for Bi on the microwave dielectric properties of $BiNbO_4$ ceramics

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Abstract

La_2O_3 and Nd_2O_3 were used to substitute Bi_2O_3 and the effects of complex substitution on the sintering behavior and the microwave dielectric properties of $BiNbO_4$ ceramics were studied. With 0.5 wt.% $CuO–V_2O_5$ mixtures addition, all of the $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics could be densified below 920 °C. The triclinic phases are identified in $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0.01$ sintered at 820 °C and the triclinic intensities increase with increasing the x value and sintering temperature. The saturated bulk density slightly decreases from 7.17 to 7.13 g/cm^3 and the ε_r value from 44.24 to 42.76 with increasing x from 0 to 0.07 for $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics. The saturated $Q \times f$ value is between 10,300 and 12,400 GHz depending on the x value. The τ_f values of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics decrease from 28.32 to 12.79 ppm/°C with x varying from 0 to 0.01 and remain almost unchanged with further increasing x.

Keywords: A. Ceramics; C. X-ray diffraction; D. Dielectric properties; D. Microstructure

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1. Introduction

After the utilization of the microwave as a communication media has become popular, the miniaturizations of the terminals for mobile communication systems were pointed out as the important subject. Consequently, the components used in these terminals must be miniaturized. The application of multilayer microwave devices will contribute to this goal [1]. In multilayer structures, dielectric materials are needed to co-fire with low loss and low melting point electrode such as Ag or Cu. Therefore, it is necessary to find the microwave dielectric ceramics with low sintering temperatures and excellent microwave dielectric properties. $(Zr,Sn)TiO_4$, $Ba_2Ti_9O_{20}$, and $Ba(Mg_{1/3}Ta_{2/3})O_3$ systems are the most common ceramics used in dielectric resonators at microwave frequency [2–4]. These ceramics

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possess high dielectric constant (ε_r), high quality value (Q) and low temperature coefficient of resonant frequency (τ_f). But their sintering temperatures are all above 1350 °C and are too high to use the low-melting-point silver and copper electrode. Although several methods of low melting glass addition, chemical processing and smaller particle sizes of the starting materials were usually used to reduce the sintering temperatures of those materials, they also resulted in the deterioration of microwave dielectric properties or required a flexible procedure. The sintering temperatures of those materials were still too high to enable them to co-fire with low melting point electrode.

Bismuth-based dielectric ceramics were well known as low-fired materials and had been investigated for the application as multilayer ceramics capacitors [5,6]. The microwave dielectric properties of $BiNbO_4$ ceramics were first reported by Kagata et al. [7]. The $BiNbO_4$ ceramics with $CuO–V_2O_5$ addition could be densified at 875 °C and had a Q value of 4260 (at 4.3GHz), ε_r value of 43 and a large τ_f value of 38 ppm/°C. In order to lower the τ_f value, Nd_2O_3 and La_2O_3 were used to substitute for Bi_2O_3 and the effects of substitution on sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics were studied by Choi et al. [8] and Huang et al. [9], respectively . The ionic radii of La^{3+}, Nd^{3+} and Bi^{3+} are 1.061, 0.995, and 1.02 Å. The ionic difference between Ln^{3+} ($Ln = La$, Nd) and Bi^{3+} caused the lattice distortion, which lowered the phase transition temperature (orthorhombic to triclinic) of BiNbO4 ceramics. The $Q \times f$ values and τ_f values of Ln-modified $BiNbO_4$ ceramics were assumed to be correlated with the phase transform ratio. Since the ionic difference between Ln^{3+} and Bi^{3+} plays a important role in the phase transition and microwave dielectric properties of $BiNbO_4$ ceramics, we would like to investigate the influence of complex substitution of La_2O_3 and Nd_2O_3 (La^{3+}:Nd^{3+} = 0.38:0.62, the complex ionic radius of $0.38La^{3+}\cdot0.62Nd^{3+}$ is equal to that of Bi^{3+}) for Bi_2O_3 on the sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics. The complex substitute ion of $0.38La^{3+}\cdot0.62Nd^{3+}$ has the same ionic radius with Bi^{3+} and the substitution of $0.38La^{3+}\cdot0.62Nd^{3+}$ for Bi^{3+} might cause less lattice distortion compared with that of La or Nd substitution. The choice of La/Nd ratio used in this study might be benefit to the structure of $BiNbO_4$. The crystalline phases and micrograph of sintered specimens were also be characterized.

2. Experimental procedures

The samples of $Bi_{(1-x)}(La_{0.38}Nd_{0.62})_xNbO_4$ ($x = 0$, 0.01, 0.03, 0.05, 0.07) were prepared by conventional solid-state reaction methods. The starting materials were high-purity (more than 99.9%) Bi_2O_3, La_2O_3, Nd_2O_3, and Nb_2O_5 powders. These oxides were weighted according to the desired stoichiometry and ball-milled for 24 h with deionized water in a nylon bottle with agate balls. The mixtures were dried and calcined at 800 °C for 3 h. The calcined powder was added with a small amount of $CuO–V_2O_5$ mixtures (0.5 wt.%, $CuO:V_2O_5 = 1:1$ in weight ratio) and then remilled for 24 h. After drying, the powder with 6 wt.% PVA binder was uniaxially pressed into pellets in a steel die. Typical dimensions of the pellets were 16 mm in diameter and 7 mm in thickness. The pellets were sintered from 760 to 920 °C for 3 h under ambient conditions.

The bulk densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were identified by X-ray diffraction patterns using Cu Kα radiation for 2θ from 20 to 60° (Rigaku D/max 2550v X-ray Diffractometer). Microstructure observation of the sintered surface of $Bi_{(1-x)}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics was performed by scanning electron microscopy (SEM) (JEOL JSM-6700F). The average grain sizes were calculated from the line intercept method. The dielectric constants ε_r and the quality values Q at microwave frequency were measured using the Hakki-Coleman's dielectric resonator method, as modified and improved by Courtney [10,11]. An Advantest R3767CG network analyzer was employed in the measurement. The temperature coefficient of resonant frequency τ_f was measured in the temperature range of −25 to +85 °C. The τ_f value was defined as follows:

$$\tau_f = \frac{f_{85} - f_{-25}}{110 \times f_{25}} \times 10^6\ (\mathrm{ppm/^\circ C}) \qquad (1)$$

where f_{85}, f_{-25}, and f_{25} are the resonant frequencies at 85, −25, and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with different x values sintered at different temperatures. Only the orthorhombic phase, the low temperature phase of $BiNbO_4$, is revealed for $Bi_{0.99}(La_{0.38}Nd_{0.62})_{0.01}NbO_4$ ceramics sintered at 780 °C for 3 h, as shown in Fig. 1(a). However, some triclinic phases are identified in the sintered specimens with $x \geq 0.03$ at 860 °C. It is well known that $BiNbO_4$ ceramics have the orthorhombic phase below 1020 °C and then gradually transform to the triclinic phase as temperature increases. The results suggest that the phase transition temperature of $BiNbO_4$ ceramics is also lowered by the complex substitution of La and Nd for Bi, as La or Nd substitution does, respectively [8,9]. To evaluate the degree of phase transition, the triclinic phase intensity ratio (R) is defined as $I_{tri}/[I_{tri} + I_{ortho}]$, where I_{tri} and I_{ortho} are the intensities of triclinic (2 0 2), (−2 1 0) and orthorhombic (0 4 0) peaks [8]. There is no triclinic phase appearing in

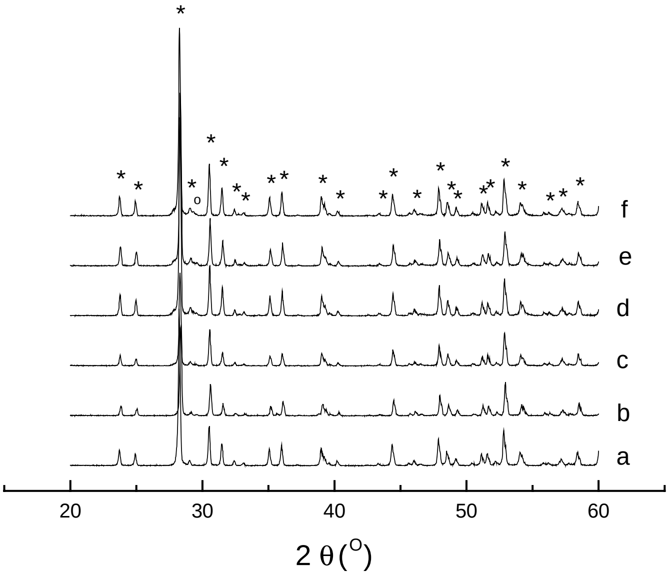


Fig. 1. XRD patterns of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with (a) $x = 0.01$ sintered at 780 °C, (b) $x = 003$, (c) $x = 0.05$, (d) $x = 0.07$ sintered at 860 °C, $x = 0.07$ sintered at (e) 880 °C, and (f) 900 °C. (★) orthorhombic, (○) triclinic.

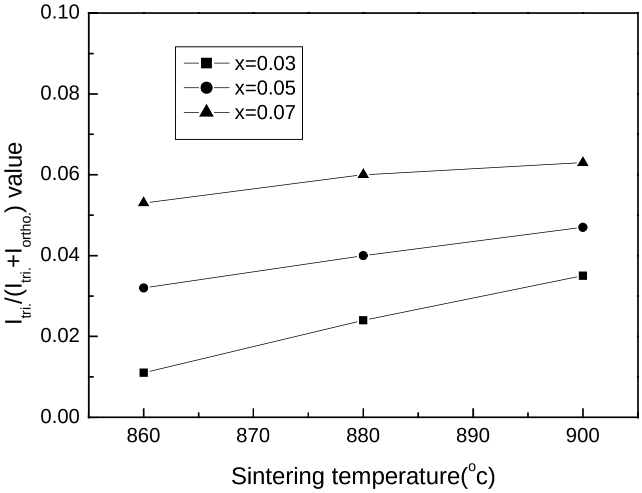
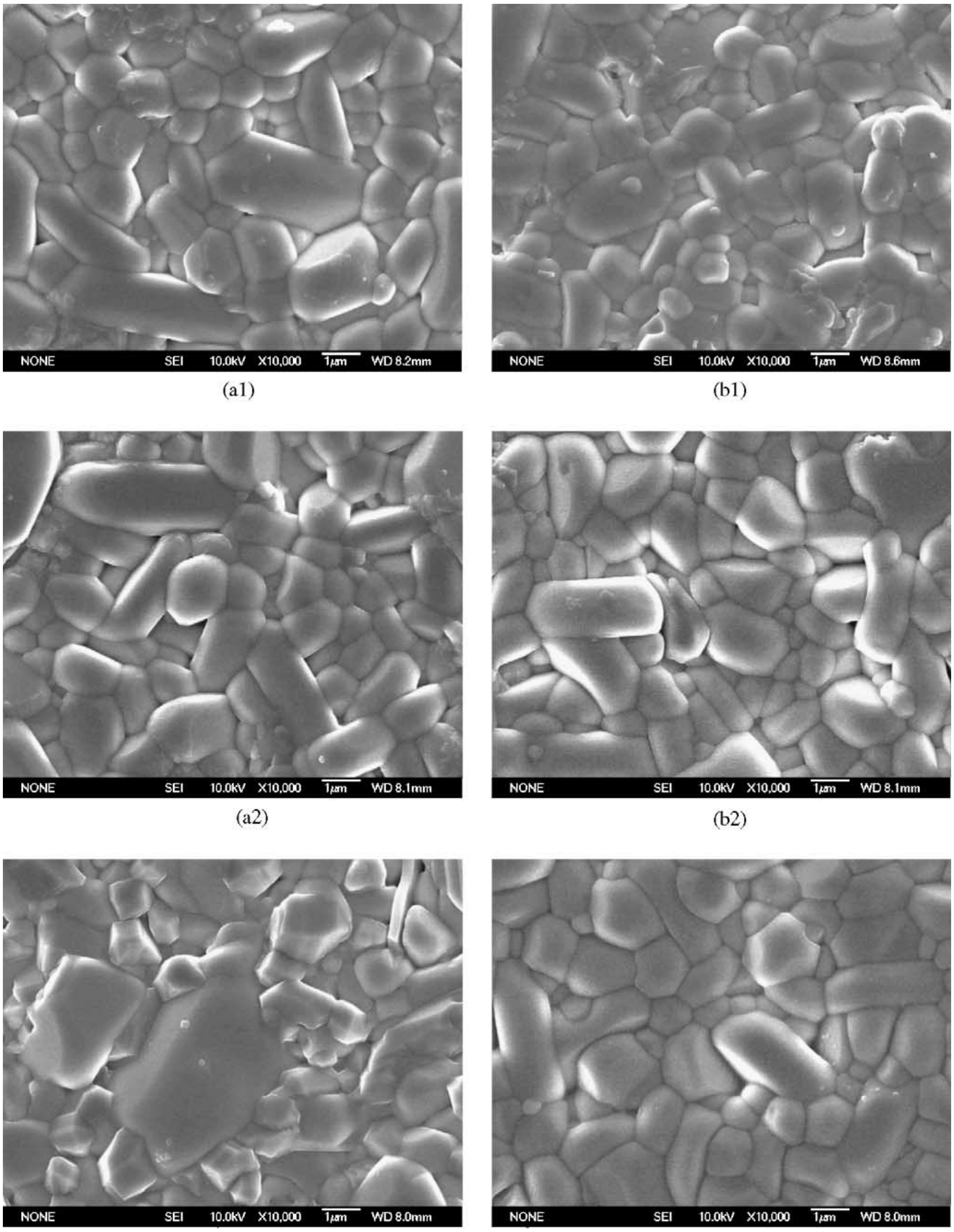


Fig. 2. Triclinic phase intensity ratio R of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0.03$–0.07 as a function of sintering temperature.

$Bi_{0.99}(La_{0.38}Nd_{0.62})_{0.01}NbO_4$ samples sintered at 780 and 800 °C. The R values of these two samples are zero. For $Bi_{0.99}(La_{0.38}Nd_{0.62})_{0.01}NbO_4$ ceramics sintered at 820 °C, the R value is 0.016. The R values of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0.03$–0.07 as a function of sintering temperature are shown in Fig. 2. The R value linearly increases with the increase of sintering temperature and x value. But all of the R values are less than 0.1. The maximum R value for $Bi_{0.93}(La_{0.38}Nd_{0.62})_{0.07}NbO_4$ ceramic sintered at 900 °C is only 0.067. It shows that although the phase transition temperature is lowered by the complex substitution of La and Nd for Bi in $Bi_{(1-x)}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics, the degree of phase transition is smaller than that of with Bi individually substituted by La or Nd [8,9].

The SEM micrographs of $Bi_{(1-x)}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0.03$, 0.05, and 0.07 sintered at 860–900 °C are shown in Fig. 3. The grain morphology of $Bi_{0.97}(La_{0.38}Nd_{0.62})_{0.03}NbO_4$ ceramic sintered at 860 °C is uniform and distinct, as shown in Fig. 3(a1). The average grain size decreases from 1.25 to 1.12 μm with x increasing from 0.03 to 0.05 and even a porous structure is observed in the sintered surface of $Bi_{0.93}(La_{0.38}Nd_{0.62})_{0.07}NbO_4$ ceramic sintered at 860 °C (Fig. 3(b1) and (c1)). This means that the complex substitution of La and Nd for Bi reduces the sinterability of $BiNbO_4$ ceramics and consequently inhibits the grain growth. The pores of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics decrease and the grain sizes gradually increase with increasing the sintering temperatures independent of the x values. However, a large discontinuous grains existing in the fine-grained matrix can be observed for $Bi_{0.97}(La_{0.38}Nd_{0.62})_{0.03}NbO_4$ ceramics sintered at 900 °C, as shown in Fig. 3(a3).

Fig. 4 shows the plots of the bulk densities of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with different x values as a function of sintering temperature. The effects of La and Nd complex substitution for Bi on the sinterability of $BiNbO_4$ ceramics are apparent in Fig. 4. The densities of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with different x values rapidly increase and reach saturated values with the increase of sintering temperatures, and then slightly decrease with further increasing the temperatures. The sintering temperatures of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics required for obtaining their maximum densities increase from 780 to 920 °C as the x values increase from 0 to 0.07. The decrease of low-firing-temperature Bi-based contents may account for this result [8,9]. The saturated bulk densities of

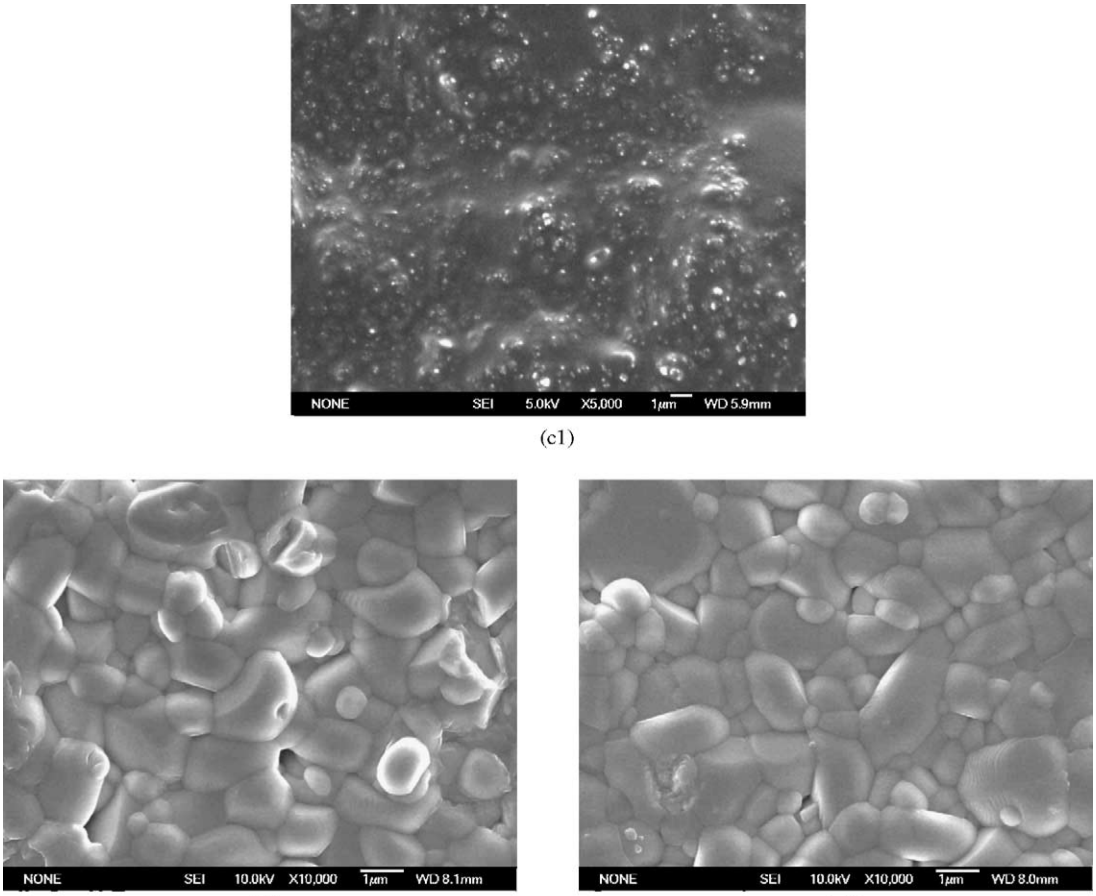


(a1) (b1)

(a2) (b2)

(a3) (b3)

Fig. 3. SEM micrographs of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with (a) $x = 0.03$, (b) $x = 0.05$, and (c) $x = 0.07$ sintered at temperatures of (1) 860 °C, (2) 880 °C, and (3) 900 °C.



(c1)

(c2) (c3)

Fig. 3. (*Continued*).

$Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics slightly decrease from 7.17 to 7.13 g/cm^3 with increasing x from 0 to 0.07 due to the substitution of heavier Bi atoms by lighter La and Nd atoms.

The dependence of dielectric constant of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics on sintering temperature for $x = 0$–0.07 is illustrated in Fig. 5. The ε_r values of all $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics increase with the sintering temperatures and saturate at 780–900 °C depending on the x values and then decrease with further increasing the temperatures. The relationships between ε_r values and sintering temperatures exhibit the same trend with those between densities and sintering temperatures. This suggests that the increase of dielectric constant with temperature is due to the increase of density and grain growth. But it is noting that the saturated ε_r values and densities for $x \geq 0.03$ occur at different sintering temperatures, i.e. 860, 880, and 900 °C for ε_r values, 880, 900, and 920 °C for bulk densities of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0.03$, 0.05, and 0.07, respectively. Compared with Figs. 2 and 3, the triclinic intensity ratios (R) of $Bi_{0.97}(La_{0.38}Nd_{0.62})_{0.03}NbO_4$ ceramics increase from 0.011 to 0.024 and the average grain sizes remain almost unchanged with the sintering temperature increasing form 860 to 880 °C. The theoretical density of triclinic phase $BiNbO_4$ ceramics is higher than that of orthorhombic phase $BiNbO_4$ ceramics [12,13]. So the increase of bulk density of

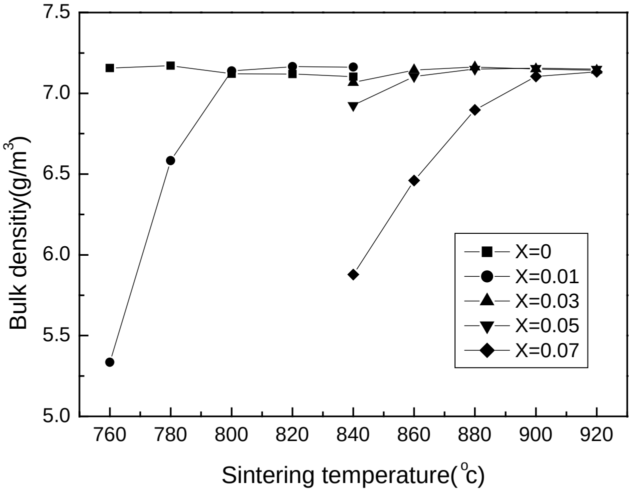


Fig. 4. Bulk densities of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0–0.07$ as a function of sintering temperature.

$Bi_{0.97}(La_{0.38}Nd_{0.62})_{0.03}NbO_4$ ceramics from 860 to 880 °C is owing to the increase of the triclinic phases. The saturated ε_r values of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics are also correlated to the x values and decrease from 44.24 for $x = 0$ to 42.76 for $x = 0.07$.

The $Q \times f$ values of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with various x values as a function of sintering temperature are plotted in Fig. 6. The change of $Q \times f$ values of all samples with the sintering temperatures shows the similar trend as that for bulk densities. It is known that there are intrinsic loss and extrinsic losses for dielectric ceramics at microwave region. The intrinsic loss is caused by anharmornic phonon decay process in the pure crystal lattice while the extrinsic losses are caused by crystal defects, grain boundaries and second phases [14]. The pores and grain boundary area decrease with the increase of the density and grain size and then the lattice imperfections and dielectric losses

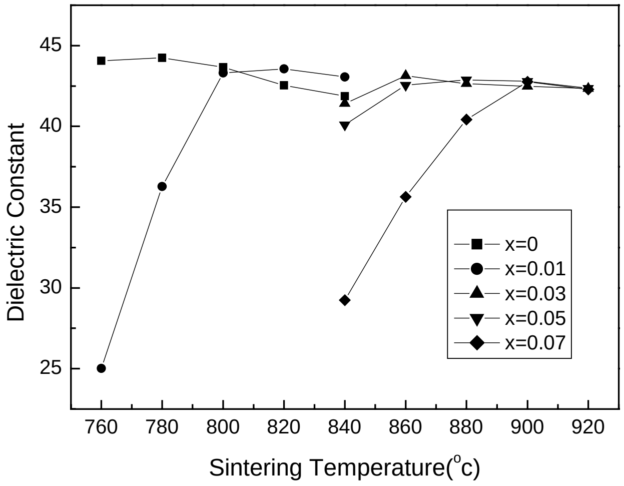


Fig. 5. Dielectric constants of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0–0.07$ as a function of sintering temperature.

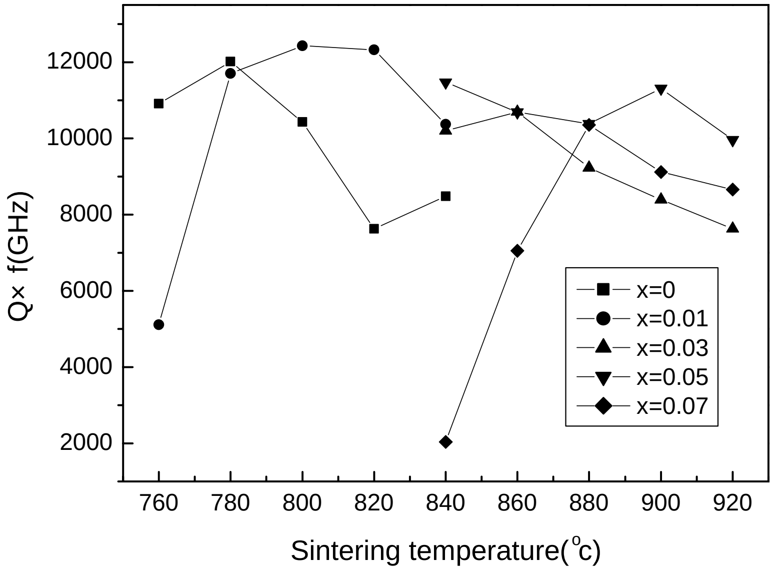


Fig. 6. $Q \times f$ values of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with $x = 0$–0.07 as a function of sintering temperature.

are reduced. The abnormal grain growth occurs and the amount of triclinic phases increases in sintered $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with further increasing the sintering temperatures above the densified temperatures, which leads to the increase in the crystal defects and the second phases and the decrease in the $Q \times f$ values. The slight increase in $Q \times f$ values of pure $BiNbO_4$ ceramics with the sintering temperature increasing from 820 to 840 °C might be related with the error-sensitivity of measurement. According to the results reported by Choi et al. and Huang et al., the $Q \times f$ values of $BiNbO_4$ ceramics rapidly increase as the triclinic transition ratio (R value) is 0.4–0.6 with Bi individually substituted by La and Nd [8,9]. However, all the R values of $BiNbO_4$ with La and Nd complex substitution for Bi ceramics are less than 0.1 and the abrupt increase in the $Q \times f$ values with the change of R value is not observed in this study. The saturated $Q \times f$ values of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics are distributed in the range from 10,300 to 12,400 GHz depending on the x values. The slight decrease of saturated $Q \times f$ values with increasing x values might be attributed to the existence of small amount of triclinic phases, which maybe have similar effect as second phase in sintered samples and cause some extra extrinsic losses.

Fig. 7 shows the τ_f values of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics with various x values. As x value changes from 0 to 0.01, the τ_f value critically decreases from 28.32 to 12.79 ppm/°C. With further increasing x from 0.01 to 0.07, the τ_f values remain almost unchanged. For the $BiNbO_4$ ceramics with the substitution of Nd for Bi, the τ_f values first gradually increase in the positive direction with the increase of x value at the sintering temperature up to 950 °C and then rapidly decrease in the negative direction with x increasing at the temperatures above 950 °C [8]. The decrease of τ_f values appears to be associated with the rapid increase of R values in Nd-modified $BiNbO_4$ ceramics. The τ_f values of La substituted $BiNbO_4$ ceramics continuously decrease with the increase of x value and sintering temperature and all the τ_f values exhibit negative values, which is also caused by the increase of phase transition from orthorhombic to triclinic [9]. But all the τ_f values of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics is revealed to possess similar positive values with x increasing from 0.01 to 0.07 although the

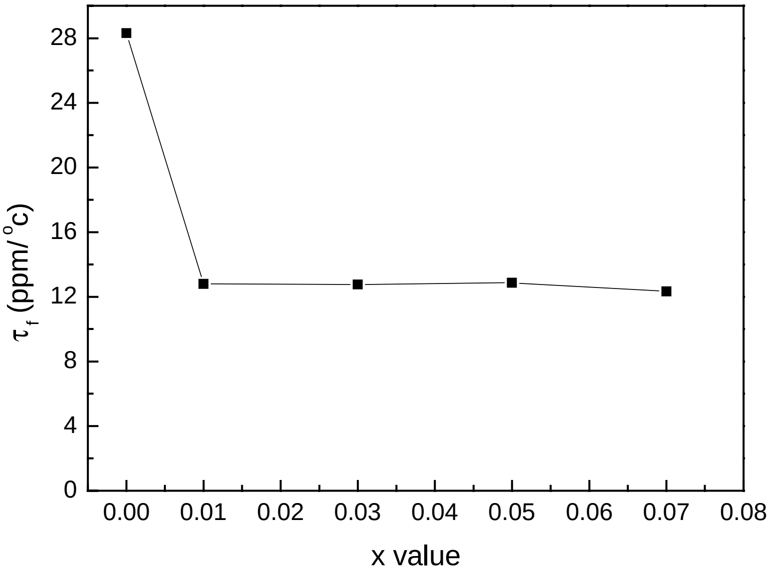


Fig. 7. τ_f values of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics as a function of x value.

R values increase from 0.016 to 0.067 in the same condition. The maximum R value of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics in this study is 0.067, which is far less than the R values of $Bi_{1-x}Nd_xNbO_4$ ceramics and $Bi_{1-x}La_xNbO_4$ ceramics reported by Choi et al. and Huang et al. This suggests that the small triclinic phase transition ratio has no apparent influence on the τ_f values of $BiNbO_4$ ceramics with complex substitution of La and Nd for Bi. It was reported that an almost linear correlation between the temperature coefficients of resonant frequency (τ_f) and the unit-cell volume was revealed for MNb_2O_6 compounds (where M = Ca, Mn, Co, Ni or Zn) [15]. The complex ionic radius of $0.38La^{3+}\cdot 0.62Nd^{3+}$ is equal to that of Bi^{3+} and the unit-cell volumes of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics might be almost unchanged by the complex substitution of La and Nd for Bi in the conditions of phase transition ratio being small. That might be the reason that the τ_f values of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics keep nearly constant with increasing x value from 0.01 to 0.07. However, the reason for the decrease of τ_f values of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics from 28.32 to 12.79 ppm/°C with x increasing from 0 to 0.01 is still unclear and is needed to be further investigated.

4. Conclusions

The microwave dielectric properties and the microstructure of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics doped with 0.5 wt.% $CuO–V_2O_5$ mixtures were investigated. The phase transition temperature of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics is lowered below 900 °C by the complex substitution of La and Nd for Bi. The densified temperatures increase from 780 to 920 °C with the x value increasing from 0 to 0.07. The bulk densities and ε_r values increase with the sintering temperatures, reach the maximum values and then decrease with further increasing the temperatures. The saturated bulk densities and ε_r values of $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics slightly decrease with the increase of x values. The $Q \times f$

values are also dependent on the x values. But the τ_f value of dense $Bi_{1-x}(La_{0.38}Nd_{0.62})_xNbO_4$ ceramics remain almost unchanged with x increasing from 0.01 to 0.07. The $Bi_{0.99}(La_{0.38}Nd_{0.62})_{0.01}NbO_4$ ceramics shows good microwave dielectric properties of $\varepsilon_r \sim 43.57$, $Q \times f \sim 12{,}323$ GHz and $\tau_f \sim 12.79$ ppm/°C even sintered at the low temperature of 820 °C.

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