Fabrication, Microstructure and Dielectric Properties of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ Ceramics

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Abstract. A series of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ (0.4 ≤ x ≤ 0.6) ceramics were prepared through conventional solid-state reaction method. The effects of doping, sintering temperature and annealing process on the phase composition, microstructure and dielectric properties of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics were investigated. The X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis results indicated that all the sintered samples adopted single perovskite phase. As x increased from 0.4 to 0.6, $\varepsilon_r$ decreased from 59.52 to 44.97, $Q\times f$ values decreased from 13736 GHz to 6420 GHz, and the $\tau_f$ varied from +57.6 ppm/°C to -21.0 ppm/°C. A near zero $\tau_f$ of -4.8 ppm/°C, dielectric constant of 47.3 and $Q\times f$ value of 11873.2 GHz were obtained at the sintering temperature of 1540 °C. Moreover, by annealing at 1400°C, the $Q\times f$ value was improved to 16130.6GHz.

1. Introduction

Due to the increasing use of multimedia function and the advance in high frequency wireless communication industry, it is essential that electronic device miniaturized, lightweight, and highly efficient. In order to meet the requirements, the materials should possess high permittivity, high quality factor value and near zero temperature coefficient of resonant frequency [1-4]. Most of the microwave dielectric ceramics with high dielectric constant have positive $\tau_f$. For instance, CaTiO$_3$ ceramics exhibited dielectric properties of $\varepsilon_r$~162, $Q\times f$ value ~12,000 GHz and $\tau_f$ ~850 ppm/°C. Even though CaTiO$_3$ ceramics have very low quality factors and a high $\tau_f$ values, they have great potential because of their high $\varepsilon_r$. The effective way to achieve near-zero $\tau_f$ and optimize $Q\times f$ value is compensating the large positive temperature coefficient values using the compounds having negative temperature coefficient values with high quality factors [5].

Several complex perovskites having the general formula A(B$^{1/3}$B$^{2/3}$)$^{3+}$O$_3$ have negative $\tau_f$ values [6]. Ca(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ possesses $\varepsilon_r$~28, $Q\times f$ value~58,000 GHz and $\tau_f$ ~-48 ppm/°C. It is known that Ni$^{2+}$ and Mg$^{2+}$ ions have the same valence state and similar ionic radius as well as ion dielectric polarizabilities. It can be inferred that Ca(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ also possesses high $Q\times f$ values, medium $\varepsilon_r$ and negative $\tau_f$. Considering the quality factor and the dielectric constant, Ca(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ can be selected to be the compensating compounds.

In this work, the microstructure and microwave dielectric properties of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics were investigated as a function of sintering temperature and composition. Moreover, the effects of annealing treatment on the microstructure and microwave dielectric properties of the sintered ceramics were investigated.
2. Experimental

2.1 Sample preparation
The CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics were synthesized by conventional solid-state method by reagent-grade raw material of CaCO$_3$ (≥99.0%), TiO$_2$ (≥99.0%), NiO (≥98.0%), and Nd$_2$O$_5$ (≥99.5%) powders. According to the stoichiometry, the powders were weighed to ball milled in agate balls with ethanol for 24 h and then dried at 80°C. After calcining at 1200°C in air for 4 h, then the powders were mixed with 7 wt% PVA binder. The granulated powders were pressed into disks of 12 mm diameter and 6 mm in thickness. These specimens were heated to 600°C for 4 h to remove the organic binder and sintered at 1480~1550°C for 4 h in air.

2.2 Performance measuring
The phase structure was analyzed by X-ray diffraction (XRD, D8-ADVANCE, Bruker, Karlsruhe, Germany) with CuKa radiation in the 2θ range 20°-80°. The scanning electron microscope (FE-SEM; Quanta FEG450, America) was used for observing the microstructures of the sintered samples. The bulk density was measured using the Archimedes method. The microwave dielectric properties were measured by a Vector Network Analyzer (N5230C, Agilent Technologies, Palo Alto, CA). The temperature coefficient of resonant frequency ($\tau_f$) was measured in the temperature range of 25°C to 75°C using the following equation:\[7]\:

$$\tau_f = \frac{(f_{75} - f_{25}) \times 10^6}{50 \times f_{25}} \text{ ppm/°C}$$

where $f_{75}$ and $f_{25}$ were the resonant frequencies at 75°C and 25°C, respectively.

3. Results and discussion

3.1 Phase analysis
In order to synthesize the phase pure perovskites, the mixed powders were calcined at 1200°C for 4 h. Figure 1(a) displays the XRD patterns of the as-synthesized powders. All samples show two perovskite phases, CaTiO$_3$ and Ca(Ni$_{1/3}$Nb$_{2/3}$)O$_3$. With the increase of $x$ value, the (Ni$_{1/3}$Nb$_{2/3}$)$^{4+}$ complex ions replace more Ti$^{4+}$, thus the peak intensity of Ca(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ phase obviously enhances and that of CaTiO$_3$ phase decreases. This result indicates that two perovskites formed for all compositions after calcination at 1200°C.

To study the effects of sintering temperature on the microstructure and phase transition of Ca[Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$]O$_3$ ceramics, XRD patterns for $x=0.55$ composition sintered at temperature range of 1480~1540°C are given in Figure 1(b). It is found that orthorhombic perovskite structures are obtained for all cases. The comparison of XRD patterns between synthesized powders and sintered ceramics are shown in Figure 2. It indicates that the single solid-solution between CaTiO$_3$ and (Ni$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ can be obtained at sintering temperature. Moreover, with increasing $x$, the diffraction peaks in XRD spectra shifted to lower angle, which means that the lattice parameters of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics linearly increase, as shown in the inset in Figure 3. It is due to that the ionic radii of Ni$^{2+}$ (0.69 Å) and Nb$^{5+}$ (0.78 Å) are larger than that of Ti$^{4+}$ (0.61 Å). According to the formula $2d \sin \theta = \lambda$, $\lambda$ is a constant, with the radius increasing, $\theta$ value is decreasing, and the peaks shift left.
Figure 1. (a) XRD patterns of CaTi\textsubscript{1-x}(Ni\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{x}O\textsubscript{3} powder synthesized at 1200°C as a function of \(x\); (b) XRD patterns for \(x=0.55\) composition sintered from 1480 to 1540°C

Figure 2. The comparison of XRD patterns between synthesized powders and sintered ceramics: (a)\(x=0.40\), (b)\(x=0.60\)

Figure 3. XRD patterns of CaTi\textsubscript{1-x}(Ni\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{x}O\textsubscript{3}(0.4≤\(x\)≤0.6) ceramics sintered at 1540°C

3.2 Microstructure
The relative densities of CaTi\textsubscript{1-x}(Ni\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{x}O\textsubscript{3} (0.4≤\(x\)≤0.6) ceramics sintered at different sintering temperature are exhibited in Figure 4(a). When the sintering temperature is above 1540°C, the samples of CaTi\textsubscript{1-x}(Ni\textsubscript{1/3}Nb\textsubscript{2/3})\textsubscript{x}O\textsubscript{3} \((x=0.55, 0.6)\) begin to melt. In general, the relative densities of samples (0.4≤\(x\)≤0.5) reach a maximum value, and then decrease with the further increment of temperature. The optimum sintering temperatures of the solid-solutions can be determined. It clearly reveals that the density saturation occurs at the temperature range of 1520~1540 °C.

Figure 4(b) presents the SEM micrographs of the surface of specimens with various compositions. The compact microstructures are obtained and almost no porosity is observed in the sintered samples. With the increase of \(x\) (0.4~0.5), the porosity is reduced and the grain size is increased. When \(x\) exceeds 0.5, the porosity is somewhat increased. This is well agreement with the relative density shown in Figure 4(a).
3.3 Sintering and dielectric properties

The permittivity of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ with different compositions as a function of sintering temperatures are presented in Figure 5(a). For fixed $x$ value, the $\varepsilon_r$ of ceramics first increases and then decreases with increasing temperature, which is in agreement with the variation trend shown in Figure 4(a). However, in general, the $\varepsilon_r$ is slightly affected by sintering temperature. Although the total polarizabilities due to the substitution increase from 2.93 to $1.23+2\times3.97)/3$ Å$^3$ in reality the effective ionic polarizabilities decrease with the increase of $x$. It is probable that the tilting of octahedra increased with the increase of $x$ has a much stronger effect on ionic polarizabilities.

Figure 5(b) shows the $Q\times f$ values of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ with different compositions ($x=0.40$~$0.60$) as a function of sintering temperatures. $Q\times f$ values are affected by the sintering temperature. Generally, the $Q\times f$ value depends on the secondary phase, density, and microstructure. Since there is no secondary phase, its effect on the $Q\times f$ value can be neglected. With increasing sintering temperature, the relative density increases slightly, and grain size increases obviously, which leads to the decrease of grain boundaries and structural defect. For fixed $x$ value, $Q\times f$ value gradually is increased to the maximum value and then decreased as the sintering temperature increases. The result is in consistent with the variation trend shown in Figure 4(a). At the same sintering temperature (1540 °C), with the increase of $x$, more (Ni$_{1/3}$Nb$_{2/3}$)$^{4+}$ complex ions can replace Ti$^{4+}$, which results in the lattice distortion, therefore the $Q\times f$ values decrease from 16325.7 GHz to 6420.4 GHz. The optimum sintering temperature is 1540 °C for All specimens except $x=0.4$.

The $\tau_f$ value of the samples as a function of $x$ value is shown in Figure 6. It is observed that the $\tau_f$ decreases from positive to negative with increasing $x$. As a result, a near-zero $\tau_f$ ceramic with dielectric constant of 48.5 and $Q\times f$ value of 11873 GHz can be obtained at $x=0.55$ in the present experiment.
Figure 5. (a) Permittivity of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ as a function of sintering temperature; (b) Q×f values of specimens as a function of sintering temperature.

Figure 6. $\tau_f$ of the specimens sintered at 1540 °C for 4 h as a function of $x$ value.

Figure 7. SEM micrographs of CaTi$_{0.45}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.55}$O$_3$ ceramics annealed at different temperatures for 4 h: (a) before annealing, (b)1200°C, (c)1300°C, (d)1400°C.

Table 1. Microwave dielectric properties of CaTi$_{1-x}$(Ni$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ($x$=0.55) annealed at various temperatures for 2 h.

|                  | Before annealing | 1200 °C | 1300 °C | 1400 °C |
|------------------|------------------|---------|---------|---------|
| $f_0$ (GHz)      | 4.43             | 4.44    | 4.38    | 4.37    |
| $\varepsilon_r$  | 47.3             | 47.1    | 48.4    | 48.5    |
| Q×f (GHz)        | 11873.2          | 12236.3 | 13802.1 | 16130.6 |
| $\tau_f$ (ppm/°C)| -4.80            | -4.84   | -4.85   | -4.81   |

The SEM photographs of CaTi$_{0.45}$(Ni$_{1/3}$Nb$_{2/3}$)$_{0.55}$O$_3$ sintered at 1540 °C for 4 h and after annealing are shown in Figure 7. The microwave dielectric properties are listed in Table 1. It is found that no obvious variation in $\varepsilon_r$ and $\tau_f$ values is observed after annealing. However, Q×f values are affected strongly by annealing process. The sample annealed at 1400 °C exhibits the maximum Q×f value compared with other conditions. Firstly, the less porosity and uniform large grain size after annealing...
can reduce the number of grain boundaries, which decreases the crystal defects. Secondly, for the samples sintered at high temperatures, the reduction of valence state for Ti\(^{4+}\) increases the dielectric loss. However, after annealing, the change in valence state could be suppressed effectively and dielectric loss decreases. Hence, the optimum microwave dielectric properties with \(\varepsilon_r \sim 48.5\), \(Q\times f \sim 16130.6\) GHz, \(\tau_f \sim -4.81\) ppm/°C can be obtained.

4. Conclusions
The structure, microstructure and microwave dielectric properties of CaTi\(_{1-x}\)(Ni\(_{1/3}\)Nb\(_{2/3}\))\(_x\)O\(_3\) (0.4≤\(x\)≤0.6) ceramics have been investigated in this work. XRD results show CaTi\(_{1-x}\)(Ni\(_{1/3}\)Nb\(_{2/3}\))\(_x\)O\(_3\) is pure phase for all sintered compositions, adopting an orthorhombic CaTiO\(_3\) perovskite structure. The unit cell volume of CaTi\(_{1-x}\)(Ni\(_{1/3}\)Nb\(_{2/3}\))\(_x\)O\(_3\) increases with the increment of (Ni\(_{1/3}\)Nb\(_{2/3}\))\(^{4+}\) contents. The microwave dielectric properties are mainly related to doping (Ni\(_{1/3}\)Nb\(_{2/3}\))\(^{4+}\) contents, densification and annealing temperature. Optimized microwave dielectric properties are achieved at \(x = 0.55\) with \(\varepsilon_r \sim 48.5\), \(Q\times f \sim 16130.6\) GHz, \(\tau_f \sim -4.81\) ppm/°C, which can be considered applying to microwave wireless communication field.

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6. References
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