IOP Conf. Series: Materials Science and Engineering **381** (2018) 012019 doi:10.1088/1757-899X/381/1/012019

Fabrication, Microstructure and Dielectric Properties of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ Ceramics

Juan Xi and Guohua Chen

School of Materials Science and Engineering, Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, P.R. China
Email: cgh1682002@163.com; 2935635707@qq.com

Abstract. A series of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3(0.4\leq x\leq 0.6)$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 $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ 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 o.4 to 0.6, ε_r decreased from 59.52 to 44.97, $Q\times f$ values decreased from 13736 GHz to 6420 GHz, and the τ_f varied from +57.6 ppm/°C to -21.0 ppm/°C. A near zeroτ_f of -4.8 ppm/°C, dielectric contant 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 τ_f. For instance, $CaTiO_3$ ceramics exhibited dielectric properties of ε_r~162, Q×f value ~12,000 GHz and τ_f ~850 ppm/°C. Even though $CaTiO_3$ ceramics have very low quality factors and a high τ_f values, they have great potential because of their high ε_r. The effective way to achieve near-zero τ_f and optimize Q×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 $A(B'_{1/3}{}^{2+}B''_{2/3}{}^{5+})O_3$ have negative τ_f values[6]. $Ca(Mg_{1/3}Nb_{2/3})O_3$ possesses ε_r~28, Q×f value~58,000 GHz and τ_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×f values, medium ε_r and negative τ_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 $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ 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.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

2. Experimental

2.1 Sample preparation

The $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$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_2O_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 4h, then the powders were mixed with 7wt% 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 4h 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 (τ_f) was measured in the temperature range of 25°C to 75°C using the following equation[7]:

$$\tau_f = \frac{(f_{75} - f_{25}) \times 10^6}{50 \times f_{25}} \quad \text{ppm/°C} \tag{1}$$

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 4h. 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 ^oC.

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 ^oC are given in Figure 1(b). It is found that orthorhombic perovskite structures are obtained for all cases. And the intensity of diffraction peaks increases as the sintering temperature increases.

The comparison of XRD patterns between synthesized powders and sintered ceramics are shown in Figure 2. It indicates that the two perovskite phases, i.e. $CaTiO_3$ and $Ca(Ni_{1/3}Nb_{2/3})_xO_3$, respectively, the single solid-solution phases was obtained after sintered at 1480 ^oC. Figure 3 shows the XRD patterns of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ ($0.4 \le x \le 0.6$) ceramics for all compositions sintered at 1540°C for 4h. All samples exhibited orthorhombic perovskite structures and no secondary phases were observed. These results suggest that the single solid-solution between $CaTiO_3$ and $(Ni_{1/3}Nb_{2/3})_xO_3$ can be obtained at sintering temperature. Moreover, with increasing x, the diffraction peaks in XRD spectra shifted to lower angle, which means that left the lattice parameters of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ 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+} (0.61Å). According to the formula $2d \sin\theta = \lambda$, λ is a constant, with the radius increasing, θ value is decreasing, and the peaks shift left.

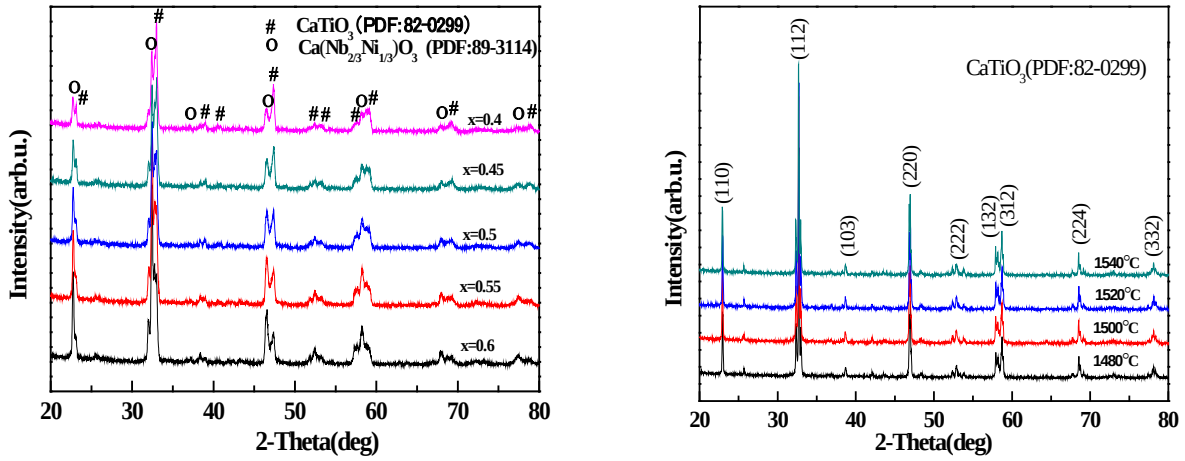


Figure 1. (a)XRD patterns of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ powder synthesized at 1200°C as a function of *x;* (b) XRD patterns for *x*=0.55 composition sintered from 1480 to 1540°C

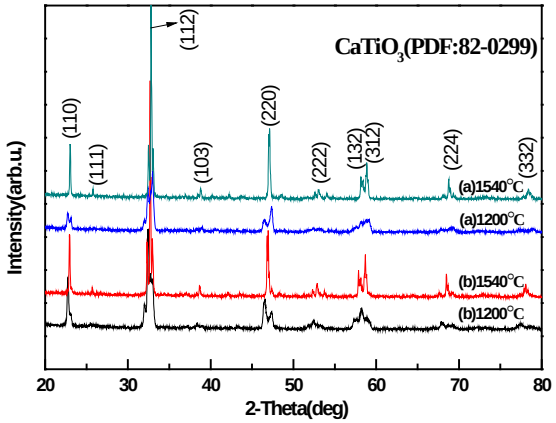


Figure 2. The comparison of XRD patterns between synthesized powders and sintered ceramics: (a)x=0.40, (b)x=0.60

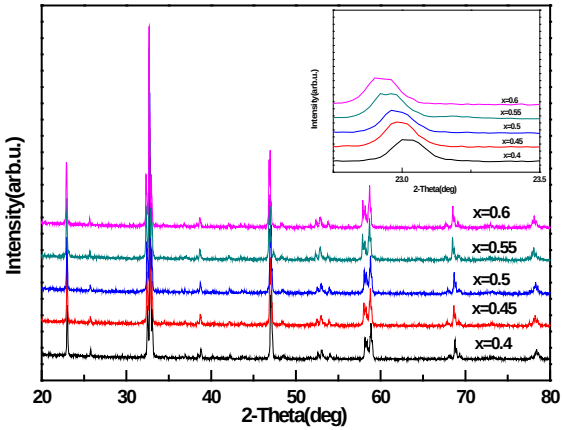
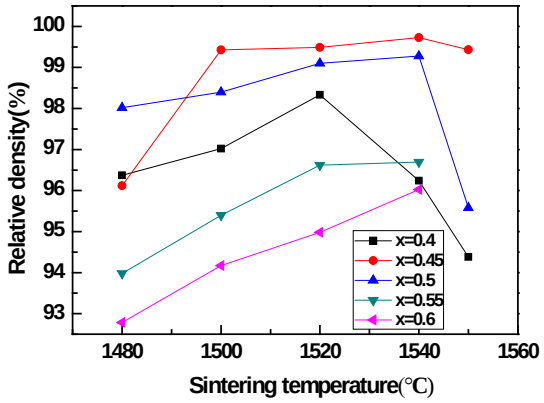


Figure 3. XRD patterns of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3(0.4\leq x\leq 0.6)$ ceramics sintered at 1540°C

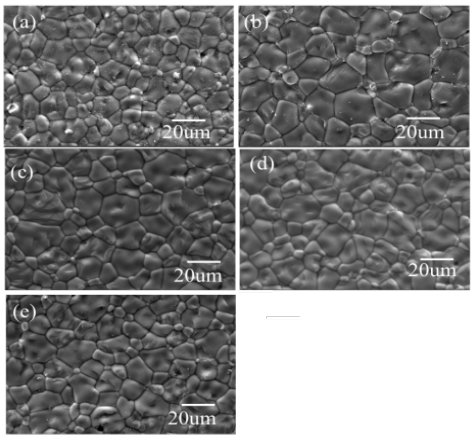
3.2 Microstructure

The relative densities of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ ($0.4\leq x\leq 0.6$) ceramics sintered at different sintering temperature are exhibited in Figure 4(a). When the sintering temperature is above 1540°C, the samples of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ (x=0.55, 0.6) begin to melt. In general, the relative densities of samples ($0.4\leq x\leq 0.5$) 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 ^{o}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).



(a)



(b)

Figure 4.(a) Relative density values of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$specimens; (b)SEM micrographs of the sintered specimens: (a)*x*=0.4, 1520°C, (b)*x*=0.45,1540°C, (c)*x*=0.5, 1540°C, (d)*x*=0.55, 1540°C, (e)*x*=0.6,1540°C

3.3 Sintering and dielectric properties

The permittivity of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ with different compositions as a function of sintering temperatures are presented in Figure 5(a). For fixed *x* value, the ε_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 ε_r is slightly affected by sintering temperature. Although the total polarizabilities due to the substitution increase from 2.93 to (1.23+2×3.97)/3 $Å^3$ in reality the effective ionic polarizabilities decrease with the increase of *x*. It is probable that the tilting of octachedra increased with the increase of *x* has a much stronger effect on ionic polarizabilities.

Figure 5(b) shows the Q×*f* values of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ with different compositions (x=0.40~0.60) as a function of sintering temperatures. The Q×*f* values are affected by the sintering temperature. Generally, the Q×*f* value depends on the secondary phase, density, and microstructure. Since there is no secondary phase, its effect on the Q×*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×*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×*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 τ_f value of the samples as a function of *x* value is shown in Figure 6. It is observed that the τ_f decreases from positive to negative with increasing *x*. As a result, a near-zero τ_f ceramic with dielectric constant of 48.5 and Q×f value of 11873 GHz can be obtained at *x*=0.55 in the present experiment.

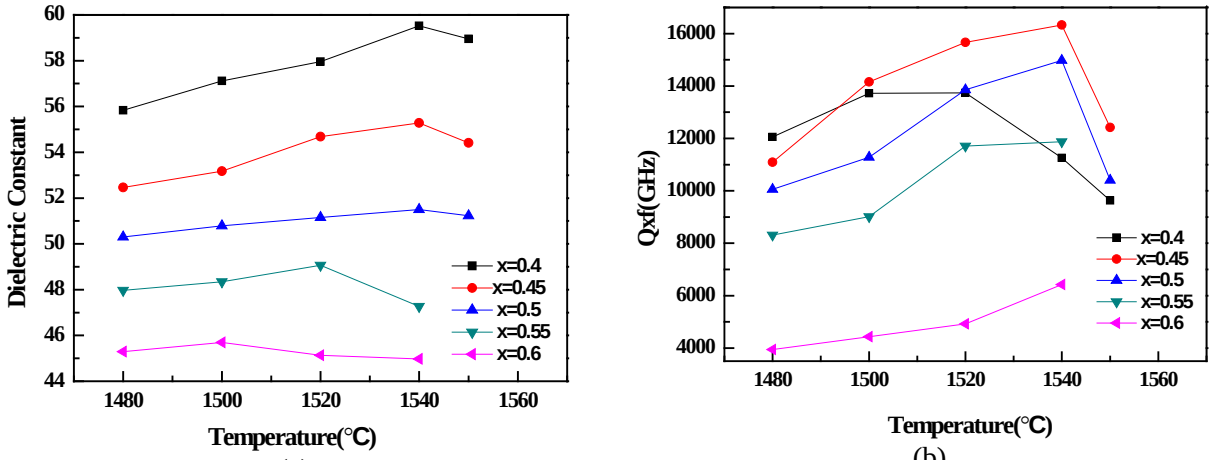


Figure 5. (a) Permittivity of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ as a function of sintering temperature; (b) $Q\times f$ values of specimens as a function of sintering temperature

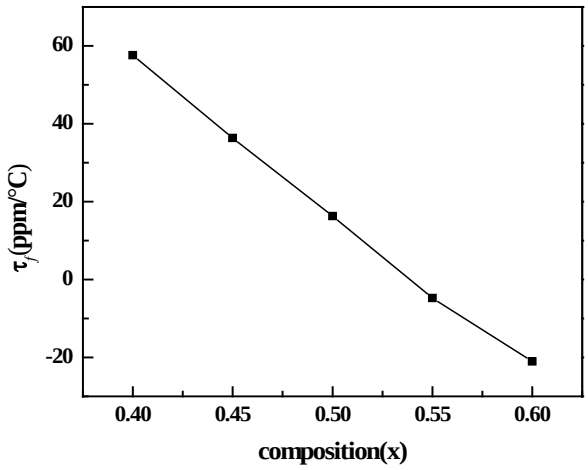


Figure 6. τ_f of the specimens sintered at 1540 °C for 4h as a function of *x* value

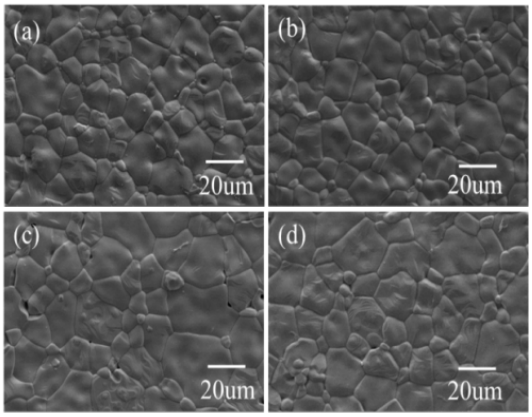


Figure 7. SEM micrographs of $CaTi_{0.45}(Ni_{1/3}Nb_{2/3})_{0.55}O_3$ ceramics annealed at different temperatures for 4 h:(a) before annealing, (b)1200°C, (c)1300°C, (d)1400°C

Table 1. Microwave dielectric properties of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})xO_3$ (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
ε_r	47.3	47.1	48.4	48.5
$Q\times f$ (GHz)	11873.2	12236.3	13802.1	16130.6
τ_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 4h 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 ε_r and τ_f values is observed after annealing. However, $Q\times f$ values are affected strongly by annealing process. The sample annealed at 1400 °C exhibits the maximum $Q\times f$ 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 ε_r ~48.5, $Q\times f$ ~16130.6 GHz, τ_f ~-4.81 ppm/°C can be obtained.

4. Conclusions

The structure, microstructure and microwave dielectric properties of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ ($0.4\leq x\leq 0.6$) ceramics have been investigated in this work. XRD results show $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ is pure phase for all sintered compositions, adopting an orthorhombic $CaTiO_3$ perovskite structure. The unit cell volume of $CaTi_{1-x}(Ni_{1/3}Nb_{2/3})_xO_3$ 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 ε_r ~ 48.5, $Q\times f$ ~16130.6 GHz, τ_f ~ -4.81 ppm/°C, which can be considered applying to microwave wireless communication field.

5. Acknowledgments

This work was supported by the Research funds of The Guangxi Key Laboratory of Information Materials (Nos.131018-Z and 131004-Z)

6. References

[1] H Zheng, S H Yu, L X Li, X S Lyu, Z Sun and S L Sun, Crystal structure, mixture behavior, and microwave dielectric properties of novel temperature stable (1-x) MgMoO4-xTiO2 composite ceramics 2017 J. Eur. Ceram. Soc. 37 4661-4665.
[2] C H Shen, C L Huang, C F Shih and C M Huang, Dielectric properties of Mg0.95Ni0.05TiO3 ceramic modified by Nd0.5Na0.5TiO3 at microwave frequencies 2009 Curr. Appl. Phys. 9 1042-1045.
[3] D Liu, X M Chen and X Hu, Microwave dielectric ceramics in (Ca1−x Bax) (Zn1/3Nb2/3)O3 system 2007 Mater. Lett. 61 1166–1169.
[4] W Lei, W Z Lu, J H Zhu and X H Wang, Microwave dielectric properties of ZnAl2 O4–TiO2 spinel-based composites 2007 Mater. Lett. 61 4066–4069.
[5] F Liu, C L Yuan, X Y Liu and G H Chen, Effects of Bi3+ substitution for Nd3+ on microwave dielectric properties of Ca0.61(Nd1-xBix)0.26 TiO3 ceramics 2015 Mater. Lett. 159 436-438.
[6] H Kagata and J Kato, Dielelctric properties of Ca-based complex perovskite at microwave frequencies 1994 Jpn. J. Appl. Phys. 33 5463–5465.
[7] T Nishikawa, K Wakino, H Tamura and Y Ishikawa, 1987 in IEEE MTT-S International Microwave Symposium Digest. 87 277-280.