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Short communication

Microwave dielectric properties of $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ $(0.025 \leq x \leq 0.1)$ ceramics

Jiamao Li [a,b], Tai Qiu [a,*]

[a] College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China
[b] School of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, PR China

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Abstract

Microwave dielectric properties of $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ $(0.025 \leq x \leq 0.1)$ ceramics have been investigated. Solid solutions were formed for the ceramic system in the given compositional range. With x increasing from 0.025 to 0.1, dielectric constant value (ε_r) decreased slightly from 33.4 to 32.2, and τ_f value increased from −30.3 to −31.9 ppm/°C. Dielectric loss of the $Nd(Zn_{0.5}Ti_{0.5})O_3$ ceramics could be decreased by the small amount of Co substitution. Excellent microwave dielectric properties of $\varepsilon_r = 32.6$, $Q \times f = 185{,}300$ GHz and $\tau_f = -31.3$ ppm/°C were obtained for the $Nd[(Zn_{0.925}Co_{0.075})_{0.5}Ti_{0.5}]O_3$ ($x = 0.075$) ceramics sintered at 1390 °C for 4 h.

Keywords: $Nd(Zn_{0.5}Ti_{0.5})O_3$; Co substitution; Solid solution; Microwave dielectric properties

1. Introduction

The tremendous growth of the wireless communication industry has created a rapid demand for microwave components such as resonators, filters and oscillators in the past decades. As key materials in microwave circuits, microwave dielectric ceramics should have three characteristics: a high dielectric constant (ε_r), a high quality factor ($Q \times f$) and a near-zero temperature coefficient of resonant frequency (τ_f) [1]. Recently, $Ln(Zn_{0.5}Ti_{0.5})O_3$ (Ln = La, Sm, Nd) ceramics with complex perovskite structures were studied as candidate materials for microwave dielectric components [2–4]. It is found that doping could effectively reduce microwave dielectric loss and other properties of these materials. For example, an ε_r of 31.6, a $Q \times f$ of 170,000 GHz and a τ_f of −42 ppm/°C were obtained for $Nd(Zn_{0.5}Ti_{0.5})O_3$ ceramics sintered at 1330 °C for 4 h [4]. However, the large negative τ_f value limits its practical applications in communication components, where a very small τ_f (less than ±10 ppm/°C) is required to ensure the stability of microwave components at different working temperatures. As a result, some compounds, such as $CaTiO_3$, $Ca_{0.61}Nd_{0.26}TiO_3$ and $SrTiO_3$, with high ε_r and large positive τ_f, were introduced to $Nd(Zn_{0.5}Ti_{0.5})O_3$ to tune τ_f to zero [5–7].

In this study, a small amount of Co $(0.025 \leq x \leq 0.1)$ was introduced to $Nd(Zn_{0.5}Ti_{0.5})O_3$ ceramics, in order to modify its microwave dielectric properties for practical applications.

2. Experimental procedures

Starting materials were high-purity grade (>99%) Nd_2O_3, ZnO, CoO and TiO_2. These starting materials were stoichiometrically weighed and then wet ball milled in distilled water for 12 h in polyethylene bottles with zirconia balls. After dried at 100 °C for about 6 h, the mixtures were calcined at 1200 °C for 2 h. Subsequently, the calcined powder was ground into fine powder for 12 h. Finally, the fine powder with 8 wt.% PVA solution as a binder was pressed into pellets with dimensions of 12 mm in diameter and 6 mm in thickness at a pressure of 300 MPa. With heating rate of 5 °C/min, these pellets were sintered at 1330–1450 °C for 4 h in air.

Bulk densities of the sintered pellets were measured by the Archimedes method. Phase constituents were identified by using an X-ray diffractometer (XRD) using Cu Kα radiation (40 kV and 20 mA, XRD, D8 Advance, Bruker, Germany). Microstructures of the sintered samples were observed by using a scanning electron microscopy (SEM, JEOL JSM 6490,

* Corresponding author. Tel.: +86 25 83587262; fax: +86 25 83587268.
E-mail addresses: lijiamao@ahut.edu.cn (J. Li), qiutai@njut.edu.cn (T. Qiu).

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Japan). All pellets for SEM observation were polished and thermally etched at a temperature which was 100 °C lower than the sintering temperature. ε_r and unloaded Q values at microwave frequencies were measured by using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [8,9]. τ_f was measured in a temperature range from 25 to 80 °C. τ_f was calculated with the following equation:

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \times 55} \times 10^6 \ \ (\text{ppm}/^{\circ}\text{C}) \quad (1)$$

where f_{25} and f_{80} are the $TE_{01\delta}$ resonant frequencies at 25 and 80 °C, respectively.

3. Results and discussion

Fig. 1 shows XRD patterns of the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ (NZCT) ceramics sintered at 1390 °C for 4 h. All peaks were indexed in terms of monoclinic perovskite. No second phase was detected and complete solid solutions were observed in the whole compositional range. The diffraction peaks slightly shift to a higher angle as x increases, implying that the unit cell volume gradually decreases due to the incorporation of small amount of Co^{2+} (0.65 Å) in place of Zn^{2+} (0.74 Å). Table 1 lists lattice parameters of the NZCT solid solutions. With increasing x, the unit cell volume decreases almost linearly though lattice constants a, b and c vary in different ways. These results also indicate that the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ($0.025 \leq x \leq 0.1$) ceramics are all solid solutions.

Variations in bulk density of the NZCT ceramics with different x values as a function of sintering temperature are illustrated in Fig. 2. It can be found that the bulk density steadily increases first with increasing sintering temperature, and then saturates for all x values. Moreover, the sintering temperature steadily increases with increasing x value. For compositions of $x = 0.025$ and 0.05, the maximum bulk density appears at 1360 °C. In contrast, the maximum bulk density occurs at about 1390 °C for compositions with $x = 0.075$ and $x = 0.1$. These results mean that sinterability of the NZCT solid solutions is decreased with the increase of Co substitution.

Table 1
Lattice parameters and tolerance factors of the NZCT solid solutions.

x	a (Å)	b (Å)	c (Å)	V_m (Å^3)	Tolerance factor
0.025	5.4573	5.62533	7.7733	238.63	0.9115
0.05	5.46283	5.62664	7.76042	238.53	0.9120
0.075	5.45494	5.62813	7.75771	238.17	0.9125
0.1	5.45292	5.62407	7.75467	237.82	0.9130

Fig. 3 illustrates typical SEM micrographs of the NZCT ceramics with different x values. It can be seen that dense and well-developed microstructures are obtained at sintering temperature of 1390 °C for all compositions. All the NZCT ceramics exhibit uniform grain morphology with $x = 0.025$–0.075. However, grain morphology becomes irregular for composition of $x = 0.1$. In addition, average grain size increases steadily from 1.1 μm to 5 μm as the amount of Co^{2+} substitution is increased from 0.025 to 0.1. These results indicate that the substitution of Co^{2+} for Zn^{2+} can promote grain growth of the NZCT solid solutions, which thus affects the microwave dielectric properties.

Fig. 4 shows variations of ε_r and $Q \times f$ value with different x values. As expected, ε_r slightly decreases. With x increasing from 0.025 to 0.1, ε_r value decreases from 33.4 to 32.2. However, the $Q \times f$ value varies remarkably with Co content. It increases almost linearly with the increase of x value first and then saturates at $x = 0.075$. The $Q \times f$ shows a maximum value of 185,300 GHz at $x = 0.075$, which is higher than that of $Nd(Zn_{0.5}Ti_{0.5})O_3$ and is close to that of $Nd[(Zn_{0.8}Co_{0.2})Ti_{0.5}]O_3$. This means that dielectric loss of $Nd(Zn_{0.5}Ti_{0.5})O_3$ ceramics at microwave frequency can be reduced by the small amount of Co substitution. It is well known that there are many factors such as density, secondary phase and grain size to influence microwave dielectric loss of a material. For our NZCT samples, effects of density and secondary phase on $Q \times f$ value can be neglected because there was no secondary phase and relative density of all samples was above 95%. It has been reported that $Q \times f$ value increases with increasing average grain size [10]. As the grain size increases, lattice imperfection becomes less pronounced and then $Q \times f$ value

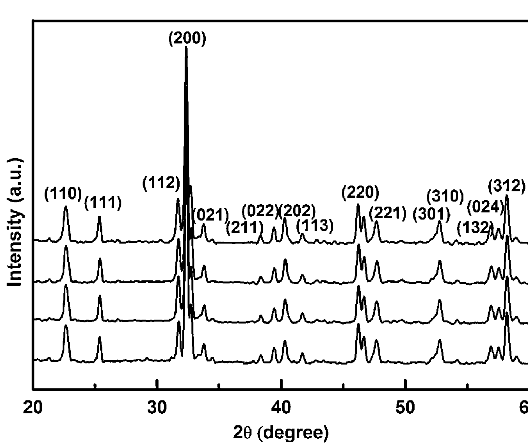

Fig. 1. XRD patterns of the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ($0.025 \leq x \leq 0.1$) ceramics sintered at 1390 °C for 4 h.

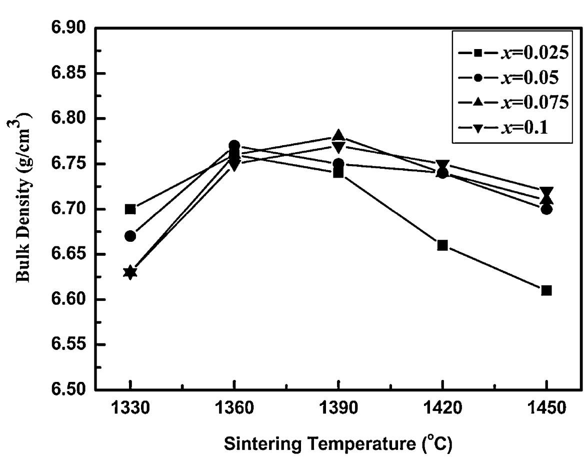

Fig. 2. Density variation of the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ceramics with sintering temperature.

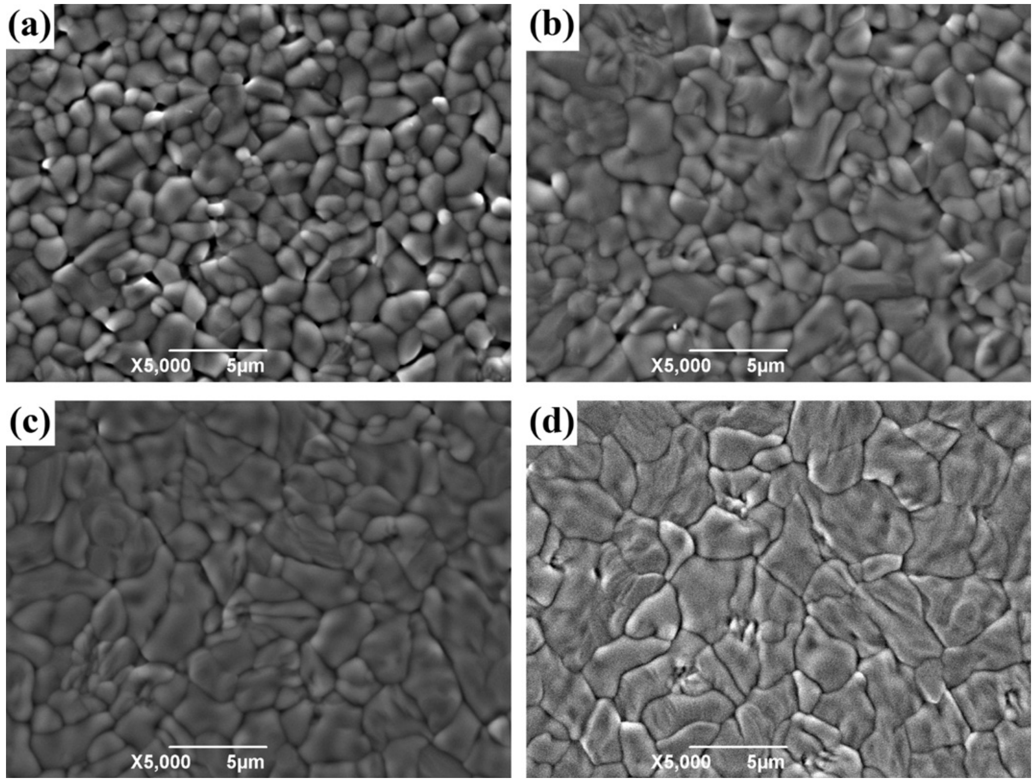

Fig. 3. SEM micrographs of the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ceramics with different x values: (a) $x = 0.025$; (b) $x = 0.05$; (c) $x = 0.075$ and (d) $x = 0.1$.

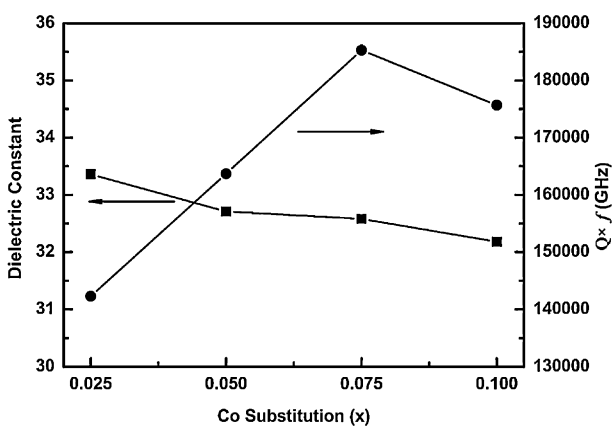

Fig. 4. Variations in ε_r and $Q \times f$ with x of the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ceramics.

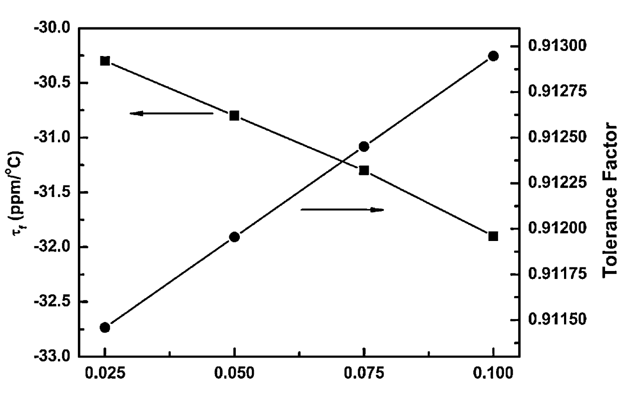

Fig. 5. Variations in τ_f and t with x of the $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ceramics.

increases. Therefore, the increase in $Q \times f$ value of our NZCT ceramics should be attributed to the increase in grain size.

Variation of τ_f value of the NZCT ceramics as a function of composition (x) is shown in Fig. 5. The τ_f value changes from -30.3 ppm/°C to -31.9 ppm/°C as x varies from 0.025 to 0.1. In general, τ_f is related to composition, additives and secondary phase. Clearly, the τ_f of our NZCT ceramics is mainly governed by composition, since no additive was introduced and no secondary phase was detected. With increasing x value, the tolerance factor value (shown in Table 1 and Fig. 5) increases slightly, which makes the τ_f value slightly negative.

4. Conclusions

In this paper, $Nd[(Zn_{1-x}Co_x)_{0.5}Ti_{0.5}]O_3$ ceramics with a small amount of Co substitution ($0.025 \leq x \leq 0.1$) were prepared by conventional solid state reaction method. Microwave dielectric properties as a function of composition were investigated. Complete solid solutions with monoclinic perovskite structure were obtained in the given compositional range. ε_r and τ_f were not significantly affected with increasing x. However, $Q \times f$ value varied remarkably. Excellent microwave dielectric properties of $\varepsilon_r = 32.6$, $Q \times f = 185{,}300$ GHz and -31.3 ppm/°C were obtained in $Nd[(Zn_{0.925}Co_{0.075})_{0.5}Ti_{0.5}]O_3$ ($x = 0.075$) ceramics sintered at 1390 °C for 4 h.

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