Microwave Dielectric Properties of $Na_{0.5+x}Nd_{0.5}TiO_3$ Ceramics (x=-0.05~0.1)

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Abstract: The influence of nonstoichiometry of Na on micronmicrowave dielectric properties of $Na_{0.5+x}Nd_{0.5}TiO_3$ (NxNT) ceramics was systematically investigated in this research. The main phase of samples was indexed as cubic perovskite structure, and $Nd_{0.667}TiO_3$ was detected as secondary phase$(-0.05 \leq x \leq 0)$, which was caused by the evaporation of Na ions. As x was increased from 0 to 0.05, the $Nd_{0.667}TiO_3$ phase was effectively eliminated and the densification process was improved. Therefore, the ε_r and $Q\times f$ initially increased, later they decreased, which was accordance to the change of density. The τ_f value didn't show a dramatic change, and a relatively low value of 248.2 ppm/°C was obtained at x=0.05. Excellent microwave dielectric properties of ε_r=110, $Q\times f$=8115 GHz and τ_f=248.2 ppm/°C) were

1. Introduction

With the wireless communication technology evolving from 3G to 4G, microwave dielectric ceramics have always been studied and utilized as key components of filter, oscillator and antenna components[1]. The search of ceramics with high dielectric constant (ε_r), high quality factor ($Q\times f$) and tunable temperature coefficient of resonant frequency (τ_f) and the research on improving the comprehensive properties have attracted considerable attention. To date, lots of microwave ceramic systems have been extensively researched, such as $CaO\text{-}Li_2O\text{-}Ln_2O_3\text{-}TiO_2$ and $BaO\text{-}Ln_2O_3\text{-}TiO_2$ (Ln=rare earth) [2, 3]. But their dielectric permittivities were mainly distributed from 80 to 100, which are not competitive to satisfy the requirements of miniaturization sufficiently. As a result, many efforts were made to develop microwave ceramics with higher dielectric constant.

Takahashi et al. first investigated the microwave dielectric properties of $Na_{0.5}Nd_{0.5}TiO_3$ ceramics with perovskite structure, as well as its special super-lattice structure[4]. Zhou et al. [5] reported that the Sn doped $Na_{0.5}Nd_{0.5}TiO_3$ ceramics possessed a good combination properties of ε_r >100, $Q\times f$ >7000 GHz and τ_f=260 ppm/°C. However, in the Na containing compounds, the Na contents can seriously evaporate at high temperature. And the phase composition and microwave dielectric properties of NST ceramics are highly dependent on the Na contents[6]. As is known to all, the microwave properties would be greatly affected by the variation of microstructure and phase composition. The present study of NST ceramics are mainly focus on how to tune their τ_f by the compositional method and few studies are devoted to deal with the nonstoichiometry of Na ion at A-sites. Thus, it is quite necessary to optimize the concentrations of Na_2CO_3 to accommodate evaporation of Na ion. In the present work, the densification, microstructure and microwave dielectric properties were systematically investigated with the variation of Na content in A-site cation.

2. Experimental Procedure

In this work, the samples were conventionally synthesized by using solid state methods.
The raw materials were Na_2CO_3, Nd_2O_3 and TiO_2 with at least 99.9% purity. After drying, the starting materials were weighed corresponding to nonstoichiometric ratio of $Na_{0.5+x}Nd_{0.5}TiO_3$ (N*x*ST), where *x*= -0.05, 0, 0.05 and 0.1. They were milled in a nylon jar with zirconia balls in ethanol for 10 h, and the mixtures were dried and calcined at 1000 °C for 3 h. Later, the calcined powders were mixed with a 6 wt% of a 10% solution of PVA as a binder and granulated. The resulting powder was axially pressed into cylindrical disks with a thickness of 6.5 mm and a diameter of 14 mm under a pressure of 200 kg/cm^2. The pellets of N*x*NT were sintered at 1300 °C for 2 h in air.

The apparent densities of the sintered samples were measured using the Archimedes' method. The powder phase composition was examined by X-ray diffraction (XRD) using CuKα radiation (Philips x'pert Pro MPD, Netherlands). Scanning electron microscopy (SEM) (FEI Inspect F, United Kingdom) was employed to study the thermally etched surface morphology of the specimens. The dielectric characteristics at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method in the TE011 mode using a network analyzer (Agilent Technologies E5071C, USA) and temperature chamber (DELTA 9023, Delta Design, USA). The τ_f measured at 2~3 GHz were obtained by the equation: $\tau_f = (f_{t2} - f_{t1}) \times 10^6 / (f_{t1} \times 60)$ (1), where f_{t2} and f_{t1} are the resonant frequencies at the measuring temperature $t1$ (25 °C) and $t2$ (85 °C).

3. Results and discussion

The XRD patterns of powdery N*x*NT ceramics with different *x* values sintered at 1300°C for 2h are presented in Fig. 1. In the whole compositional range, the main phase of samples was indexed as cubic perovskite structure (JCPDS# 39-0880). However, the $Nd_{0.667}TiO_3$ (JCPDS# 49-0244) as secondary phase was detected in the range of *x*=-0.05~0.0 for N*x*NT ceramics. The appearance of $Nd_{0.667}TiO_3$ was attributable to the evaporation of Na contents when the samples were sintered in an extremely high temperature of 1300°C. The intensity of secondary phase became weaker as the x value increased. When the Na concentrations changed from 0.05 to 0.1, only the cubic perovskite structured phase could be observe, and the secondary phase disappeared. Meanwhile, the weak superlattice peaks were also observed. The double index of the above reflections are in an even–even–odd plus odd–odd–odd manner, and these weak reflections can be assigned to space group Pnma [7]. As a result, a pure NNT phase could be obtained when the Na contents was superfluous$(x > 0)$.

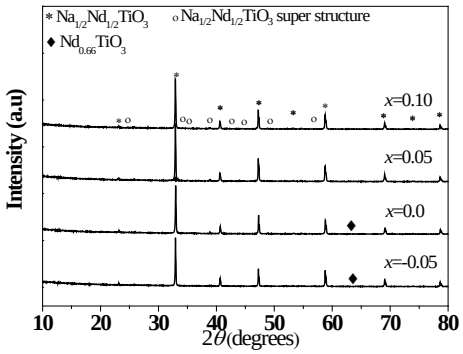

Figure 1. The XRD patterns of powdery N*x*NT ceramics with different *x* values sintered at 1300°C for 2h.

Fig. 2 displays the SEM image of N*x*NT ceramics with different *x* values sintered at 1300°C for 2h with (a) *x*=-0.05, (b) *x*=0.0, (c) *x*=0.05 and (d) *x*=0.1. As shown in Fig. 2(a), the ceramic presented a porous and inhomogeneous microstructure, had a grain size of 2 to 3 μm and two types of grains can be observed. When *x* was increased to 0.05, the grains grew to an average size of 5μm, and the pores

around the grain boundaries were effectively eliminated. Obviously, the specimens showed a dense and compact microstructure with additional Na_2CO_3 dopants added (x=0.05). However, when excessive Na contents were doped $(x > 0.05)$, the porous and inhomogeneous microstructure appeared again.

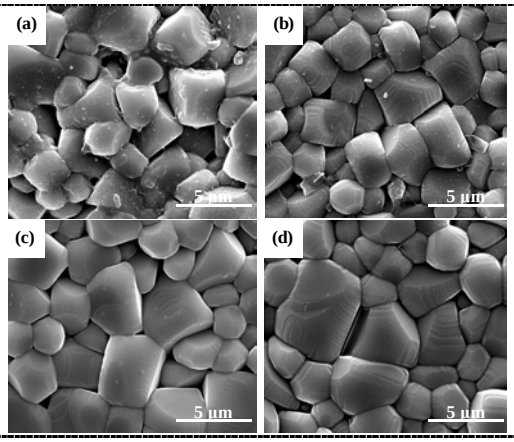

Figure 2. The SEM image of N*x*NT ceramics with different *x* values sintered at 1300°C for 2h with (a) *x*=-0.05, (b) *x*=0.0, (c) *x*=0.05 and (d) *x*=0.1

Fig. 3 illustrates the apparent density and microwave dielectric properties N*x*NT ceramics with different *x* values sintered at 1300°C for 2h: (a) apparent density, (b) dielectric constant, (c) quality factor and (d) temperature coefficient of resonant frequency. As shown in Fig.3 (a), the apparent density steadily increased with rising Na contents from -0.05 to 0.05, later it sharply decreased. Generally, the density was influenced by pores and secondary phase [8, 9]. Since the theoretical density of $Nd_{0.667}TiO_3$ (5.8 g/cm^{-3}) was larger than that of NNT (5.28 g/cm^{-3}), the decrease of secondary phase was not attributable to the increase of density. Thus, the improvement of densification should mainly be caused by the elimination of pores. However, with $(x > 0.05)$, the appearance of pores led to the decrease of density. For the dielectric constant and quality factor, both of the dielectric constant and quality factor showed a similar varying trend to that of apparent density. This is because density, dielectric constant and quality factor are affected by the same reason, such as densification process. These changes were considered to correlate with the compactness of the samples; a higher ε_r and $Q\times f$ value were usually related to a denser microstructure, which was also confirmed by the SEM images. Fig. 3(d) depicts the variation of the τ_f as a function of Na contents. The τ_f value didn't show a dramatic change, and a relatively low value of 248.2 ppm/°C was obtained at *x*=0.05.

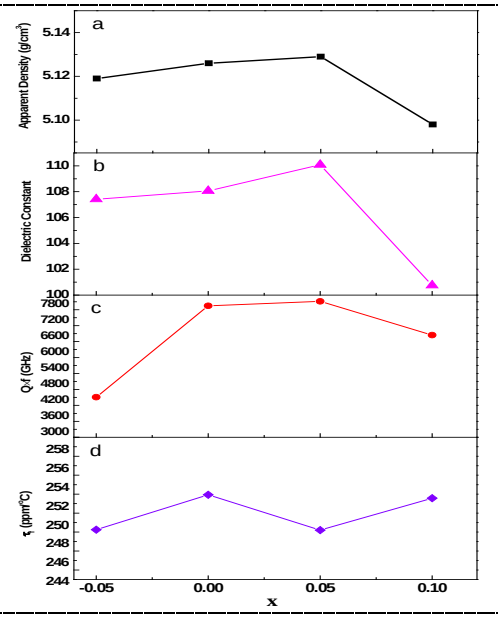

Figure 4. The apparent density and microwave dielectric properties N*x*NT ceramics with different x values sintered at 1300°C for 2h: (a) apparent density, (b) dielectric constant, (c) quality factor and (d) temperature coefficient of resonant frequency

4. Conclusion

The influence of nonstoichiometry of Na on micronmicrowave dielectric properties of N*x*NT ceramics were strongly determined by the Na contents. The main phase of samples was indexed as cubic perovskite structure, and $Nd_{0.667}TiO_3$ was detected as secondary phase($-0.05 \leq x \leq 0$), which was caused by the evaporation of Na ions. As *x* was increased from 0 to 0.05, the $Nd_{0.667}TiO_3$ phase was effectively eliminated and the densification process was improved. Therefore, the ε_r and $Q\times f$ initially increased, later they decreased, which was accordance to the change of density. The τ_f value didn't show a dramatic change, and a relatively low value of 248.2 ppm/°C was obtained at x=0.05. Excellent microwave dielectric properties of ε_r=110, $Q\times f$=8115 GHz and τ_f=248.2 ppm/°C) were achieved when x = 0.05 sintered in air at 1300 °C for 2h.

Acknowledgments

This work is supported by National Natural Science Funds of China (Grant No. 51402039)

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