Microwave Dielectric Properties of Na$_{1/2}$Sm$_{1/2}$Ti$_{1-x}$(Cr$_{1/2}$Nb$_{1/2}$)$_x$O$_3$ Ceramics ($x=0$~$0.025$)

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Abstract: The compound Na$_{1/2}$Sm$_{1/2}$Ti$_{1-x}$(Cr$_{1/2}$Nb$_{1/2}$)$_x$O$_3$ (x =0.00, 0.005, 0.01, 0.015, 0.02, 0.025) (NSTCNx) ceramics were prepared by the conventional solid-state route. The main phase of all NSTCNx ceramics were confirmed as an orthorhombic perovskite structure. The ε$_r$ and Q×f were improved because of improvement of densification and homogeneous fine grained microstructure with proper substitutions (x ≤0.01). The τ$_f$ was able be tuned to a relatively low value of 154.3 ppm/°C because of a continuously decreasing tolerance factors. Typically, the NSTCNx (x =0.01) ceramic fired in air at 1450°C for 2h showed good microwave dielectric characteristics of ε$_r$=104.3, Q×f=9179 GHz and τ$_f$ =171.7 ppm/°C.

1. Introduction

Because of the rapid development of wireless communication industry, microwave dielectric ceramics have been intensively researched and widely used in filters, resonators, EMI (Electro Magnetic Interference) filter, RFID (radio frequency identification) antenna active module and many other microwave devices. Recently, the microwave dielectric with a high dielectric constant (ε$_r$), high quality factor (Q×f) and lower temperature coefficient of resonant frequency (τ$_f$) have been a very active research field [1-3].

The significance of miniaturization and integration cannot be overemphasized in any hand-held communication devices, since inversely proportional relationship between the physical length of a dielectric resonator and $\sqrt{\varepsilon_r}$. The high permittivity compound Na$_{0.5}$Sm$_{0.5}$TiO$_3$ with perovskites type structure has drawn lots of attentions due to its high permittivity (ε$_r$=100.5), high quality factor (Q×f=8,993GHz) and relatively lower τ$_f$ (τ$_f$ =+199ppm/°C[4]). Generally, the dielectric ceramics with high permittivity always have a large positive τ$_f$, which makes them impractical in the electric devices. Two methods are commonly employed to lower the τ$_f$. One easy and common method is to combine two compounds with opposite τ$_f$ values, forming compositional systems, but it always leads to a serious deterioration of ε$_r$ and Q×f value. Another effective approach is changing the tilting of the octahedral by substituting at B site in perovskites [5, 6], and the tilting of the octahedral is explained by the tolerance factor (t): $t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$, where the $r_A$, $r_B$ and $r_O$ represent the radii of ions at A, B, and C sites.

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Great efforts have been made to decrease the $\tau_f$ as well as maintaining a high permittivity and quality factor in many microwave dielectric systems. For example, the $\tau_f$ and $Q\times f$ were improved by doping Ceria (CeO$_2$) because the Ce$^{4+}$ entered the A-site of Na$_{1/2}$Sm$_{1/2}$TiO$_3$ ceramics and changed the lattice structure of perovskites. What’s more, X. Guo and B. Tang claimed that the $\tau_f$ was effectively changed to zero value, and the $Q\times f$ value were significantly improved by Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ substituting for Ti$^{4+}$ owing the continuous decrease of tolerance factor in Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18-y}$Cr$_{y/2}$Nb$_{y/2}$O$_{54}$ [7]. Unfortunately, Cr$_{1/2}$Nb$_{1/2}$$^{4+}$, as an effective aids, hasn’t been researched in the Na$_{1/2}$Sm$_{1/2}$TiO$_3$ system. Therefore, in this study, the method of substitution of Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ for Ti$^{4+}$ is used to enhance the properties of NST systems, and the effects of Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ replacement upon microstructure were researched, as well as dielectric characteristics.

2. Experimental procedures

Specimens of Na$_{1/2}$Sm$_{1/2}$Ti$_{1-x}$Cr$_x$O$_3$ ($x = 0.00, 0.005, 0.01, 0.015, 0.02, 0.025$) ceramics were synthesized by the conventional solid-state ceramic route. High-purity powders (at least 99.9 %) of Na$_2$CO$_3$, Sm$_2$O$_3$, Cr$_2$O$_3$, Nb$_2$O$_5$ and TiO$_2$ were used as the starting materials. The raw oxide materials were weighed according to the stoichiometry proportions with addition of 6 wt. % Na$_2$CO$_3$ powder. The mixture of starting materials was ball-milled in alcohol medium for 5 h in nylon jar using zirconia balls. The mixed slurry was dried, passed through a100-mesh sieve and then calcined in air at 1,150 °C for 3 h. The fine powder was mixed with a 6 wt% of a 10% solution of polyvinyl alcohol (PVA) as a binder. The obtained powders were axially pressed into cylindrical disks with thickness of 0.75 cm and 1.5 cm in a diameter under pressures of 200kg/cm$^2$. These samples were fired at 1450 °C for 2 h.

The bulk densities of the fired samples were tested using the Archimedes' principle. The phase composition were examined by X-ray diffraction (XRD) using CuKα radiation (DX–1000 CSC, Japan) and the lattice parameters of samples were collected from XRD data using the Rietveld method by using the "Material Analysis Using Diffraction" (Maud). To examine surface morphology, scanning electron microscopy (SEM) (FEI Inspect F, United Kingdom) was utilized to study the thermally etched surface morphology of the specimens. The dielectric properties at microwave frequencies were tested by the Hakki–Coleman dielectric resonator method in the $TE_{01\delta}$ mode utilizing a network analyzer (Agilent Technologies E5071C, USA) and a temperature chamber (DELTA 9023, Delta Design, USA). The $\tau_f$ were obtained by equation: 

$$\tau_f = \frac{(f_2 - f_1)}{(f_1 \times (t_2 - t_1))},$$

where $f_1$ and $f_2$ were the resonant frequencies at the measuring temperature $t_1$ (25 °C) and $t_2$ (85 °C), respectively.

3. Results and discussions

The XRD patterns of NSTCN$_x$ ($x = 0.00–0.025$) ceramics fired at 1450°C are presented in Fig. 1. The orthorhombic solid solutions in space group Pmn$\overline{3}m$ are obtained and there is no secondary phase is determined for all compositions. The weak superlattice reflections were also detected. And these weak peaks can be indexed as (1, 1/2, 0), (1,1,1/2), (3/2, 1/2, 1/2), (2, 1/2, 0), (3/2, 3/2, 1/2), (2, 1, 1/2) and (2, 1, 2/3), which were in doubled index superlattice reflections (an even-even-odd and odd-odd-odd manner) and assigned as the space group Pmn$\overline{3}m$[4, 8, 9]. The diffraction peaks slightly shift to lower 2θ angles as Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ content increases, reflecting the increments in the cell volumes on the substitution of Ti$^{4+}$ (0.605 Å) by the larger Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ (r=0.6275 Å[10]). The refinements were performed using Maud based on the XRD of all NSTCN$_x$ ceramics.
Fig. 2(a) shows the results of the observed and calculated XRD patterns for \( x = 0.01 \). The refined parameters for this orthorhombic perovskite phase in the \( \text{Na}_{1/2}\text{Sm}_{1/2}\text{Ti}_{0.99}(\text{Cr}_{1/2}\text{Nb}_{1/2})_{0.01}\text{O}_3 \) were \( a = 3.83406 \) Å, \( b = 3.8429 \) Å and \( c = 3.8386 \) Å with a space group \( Pm\overline{3}m \). The lattice parameters for all NSTCN\( x \) ceramics are also described in Fig. 2(b). With increasing \( x \), the unit cell volumes expanded. These refined results also confirmed that the \( (\text{Cr}_{1/2}\text{Nb}_{1/2})^{4+} \) could partially substitute for \( \text{Ti}^{4+} \).

Figure 3 shows the back scattered electron images for thermally etched surface of the NSTCN\( x \) ceramics fired at 1450 °C for 2 h with (a) \( x = 0.00 \) to (f) \( x = 0.025 \). Obviously, large amounts of pores around the boundaries were observed with \( x = 0.00 \), and the pores could be effectively eliminated with addition of \( \text{Cr}_{1/2}\text{Nb}_{1/2}^{4+} \) content. But when the \( \text{Cr}_{1/2}\text{Nb}_{1/2}^{4+} \) content exceeded 0.01, a certain amount of pores was detected again. On the other hand, the grain growth was promoted with the assistance of \( (\text{Cr}_{1/2}\text{Nb}_{1/2})^{3+} \) content, and when \( x \leq 0.01 \), the microstructure gradually became uniform. It was apparent that the densest and most uniform microstructure was obtained at \( x = 0.01 \).
Fig. 4 illustrates the microwave dielectric characteristics of NSTCN$_x$ ($x=0.00$ to $0.025$) fired at $1450 \, ^\circ C$ for 2 h. For the apparent density and permittivity shown in Fig. 4(a) and 4(b), they presented a similar varying trend, which was attributable to the same reason that density and permittivity were much affected by the densification and pores. It was clear that there is a big drop of permittivity from 104.3 to 95.6 as superfluous Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ contents ($x \geq 0.015$) were added. The decrease of density was the main reason. On the other hand, the decrease of permittivity should be related to the decrease of microscope polarizability and expansion of molar volume correlated to ionic radius[11]. And in this work, the average ion polarizability of Cr$_{1/2}$Nb$_{1/2}$$^{4+}$ ($\alpha = 2.73 \, \text{Å}^3$) is much weaker than the ion polarizability of Ti$^{4+}$ ($\alpha = 2.94 \, \text{Å}^3$)[12], and the cell volume increased with the substitution of larger Cr$_{1/2}$Nb$_{1/2}$$^{4+}$.

As illustrated in Fig. 4 (c), the $Q \times f$ value firstly increased to 9179 GHz at $x=0.01$, but sharply decreased to 8038 GHz at $x=0.025$ thereafter. The average grain size increased and homogeneous microstructure was obtained with a proper substitutions ($x \leq 0.01$), which enhanced the quality factor[13]. And the substitution of Cr$^{3+}$ for Ti$^{4+}$ restrained Ti$^{3+}$ reduction which was attributable to improvement of $Q \times f : \text{Cr}_2\text{O}_3 \rightarrow 2\text{Cr}_2\text{Ti} + V_0 + 3O_2^\circ$. However, the inhomogeneous microstructure would lead to a deterioration of $Q \times f$ values when excessive substitutions ($x \geq 0.015$) were carried out.
According to the formula: \( \frac{\text{Nb}_5\text{O}_5^{TiO_2}}{\text{Ti}_2\text{O}_5} \rightarrow 2\text{Nb}_{Ti} + \frac{1}{2} \text{O}_2 \uparrow + 4\text{O}_0^{X} + 2e' \), the substitution of Nb\(^{5+}\) for Ti\(^{4+}\) resulted in the accumulation of electron and damaged the \( Q\times f \) \( [11, 14] \). Finally, the appearance of pores shown in Fig. 3(c) and 3(f) should also be attributable to the reduction of \( Q\times f \) value.

Fig. 3(d) presents the \( \tau_f \) of NSTCN\(_x\) (\( x = 0.00~0.025 \)) ceramics fired at 1450\(^\circ\)C for 2h. Remarkably, the \( \tau_f \) was changed from 199.1 to 154.3 ppm/\(^\circ\)C with substitutions increased. In perovskites type ceramics, the change of \( \tau_f \) was closely related to the tilting of Ti-O octahedral which could be strongly explained by the variation of \( t \). The changing trend of \( \tau_f \) was consistent with the \( t \) decreasing from 0.9575 to 0.95738 \( [2, 6, 15] \), as the substitutions rose sequentially. Therefore, the \( \tau_f \) was effectively changed to a relatively low 154.3 ppm/\(^\circ\)C owing to a continuous decrease in tolerance factors.

4. Conclusions
The microwave dielectric characteristics and microstructures of NSTCN\(_x\) ceramics (\( x=0~0.025 \)) have been researched. The XRD patterns associated with the refined data confirmed that all samples were indexed as the orthorhombic perovskites structure in a in space group \( Pm\bar{3}m \). The proper amount of B-site substitutions of Cr\(_{1/2}\)Nb\(_{1/2}\)\(^{4+}\) for Ti\(^{4+}\) adjusted the \( \tau_f \) for the decreasing tolerance factor, as well as improving permittivity and \( Q\times f \). The improvement of densification mainly contributed to increasing permittivity, and \( Q\times f \) was enhanced because of the homogeneous fine grained microstructure at \( x=0.01 \). Ultimately, good microwave dielectric properties of NSTCN\(_x\) were achieved at 1450\(^\circ\)C for 2h when \( x=0.01 \): \( \varepsilon_r=104.3 \), \( Q\times f=9179 \) GHz, and \( \tau_f=171.7 \) ppm/\(^\circ\)C.

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References
[1] Sebastian M T 2010 Dielectric materials for wireless communication Elsevier.
[2] Fang Z, Tang B, Li Y, Si F and Zhang S 2015 Journal of Elec Materi 44 4236-4242
[3] Zhou D, Pang L X and Qi Z M 2014 Inorganic Chemistry 53 9222-9227
[4] Fang Z X, Tang B, Si F and Zhang S R 2015 J Mater Sci: Mater Electron, 1-7
[5] Yu S, Zhang S, Tang B, Zhou X and Fang Y 2012 Ceramics International 38 613-618
[6] Liu T, Zhao X Z, Chen W 2006 Journal of the American Ceramic Society 89 1153-1155
[7] Guo X, Tang B, Liu J, Chen H and Zhang S 2015 J Alloys Compd 646 512-516
[8] Glazer A 1972 Crystallographica Section B 28 3384-3392
[9] Sun, Pai-Hsuan, Nakamura T O, Shan Y J, Inaguma Y, Itoh M 1997 Ferroelectrics 200 93-107
[10] Shannon R D and Prewitt C T 1969 Acta Crystallographica Section B 25 925-946
[11] Zhang S L, Ma P P, Liu X Q and Chen X M 2015 Journal of the American Ceramic Society 98, 3185-3191
[12] Shannon R T 1976 Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography 32 751-767
[13] Chazono H and Kishi H 2000 Journal of the American Ceramic Society 83, 101-106
[14] Nakayama Hiroyuki and Hiroshi Katayama Y 2001 Jap J Appl Phys 40 L1355
[15] Tseng C F, Wei T C and Lu S C 2014 Ceramics International 40, 7081-7085