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Effect of additive $SrWO_4$ on microwave dielectric properties of $SrTiO_3$–$Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract The crystal structure and the properties of a new microwave dielectric ceramics x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ have been investigated. With x=0.025, The new microwave dielectric ceramic achieves the dielectric properties of a dielectric constant ε_r ~27.8, a $Q\times f$ value ~26,800, and a τ_f value ~7.4 ppm/°C. When the $SrWO_4$ is added, the sintering temperature of x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics will fall to 1350 °C, and its $Q\times f$ value can be improved further and the τ_f value becomes smaller. When the $SrWO_4$ is added by 0.07 mol, the specimen acquires the following microwave properties: a dielectric constant ε_r ~30.3, a $Q\times f$ value ~29,500, and a τ_f value of approximately −0.4 ppm/°C.

Keywords Microwave ceramics · Dielectric properties complex perovskites

1 Introduction

The requirement of rapid data transmission has led to an increased interest in the gigahertz region and has prompted research on dielectric materials at microwave frequencies. Communication system relies on dielectric materials with low losses and high-temperature stability. Most recent research of high-Q dielectrics has focused on complex perovskites with permittivity in the range 30–40, and very high $Q\times f$ values (~100,000). For example, the most widely used perovskites, $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) has ε_r~29, $Q\times f$= 165,000 at 11 GHz, and a near zero temperature coefficient of the resonate frequency τ_f [1]. However, the high cost of tantalum oxide has motivated investigations of lower cost replacements for BZT. The niobium-based analogues of the tantalite perovskites constitute one family of candidate materials. In this research, we examine the structures and microwave properties of Mg based niobate perovskite $Sr(Mg_{1/3}Nb_{2/3})O_3$(SMN). $Sr(Mg_{1/3}Nb_{2/3})O_3$ microwave ceramics possesses high dielectric constant (ε_r=30), high-quality factor ($Q\times f$ value ~35,000 GHz), and negative τ_f value (−27 ppm/°C) [2]. It is well known that two or more compounds having negative and positive temperature coefficient values employed to form a solid solution or mixed phase are the most promising method to obtain zero temperature coefficient of resonant frequency. Because $SrTiO_3$ ceramics exhibits dielectric properties of ε_r ~270, $Q\times f$ value ~3,000 GHz and a large positive τ_f value (1,200 ppm/°C), compensation of temperature coefficient of resonant frequency (τ_f) might be obtained by employing solid solution of $SrTiO_3$ and $Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics. In the present study, microwave dielectric ceramics based on the solid solution of $SrTiO_3$ and $Sr(Mg_{1/3}Nb_{2/3})O_3$ were developed, focused in particular on the effect of the $SrWO_4$ additive on the their microwave properties and sintering temperature. The microwave dielectric properties were investigated. In addition, the X-ray diffraction (XRD) pattern and the scanning electron microscopy (SEM) analysis were also employed to study the microstructure of the ceramics.

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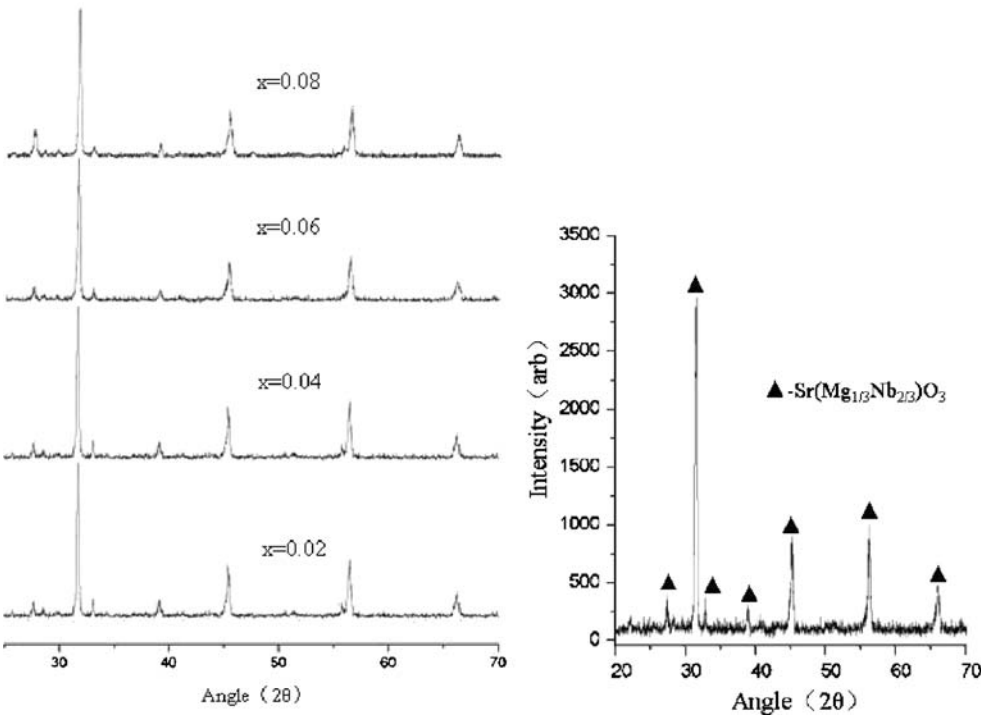

Fig. 1 XRD pattern of x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics at 1600 °C for 4 h

2 Experimental procedure

2.1 Samples preparation

Specimen powders were prepared by a conventional solid-state reaction technique. High purity (99.9%) $SrCO_3$, TiO_2, MgO, and Nb_2O_5 were weighed according to the composition x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$, where $0.01 \leqslant x \leqslant 0.1$, and were ground in ethyl alcohol for 4 h in a balling mill with zirconia balls, dried at 80 °C. Prepared powders were calcined at 1200 °C for 4 h in air. After calcinations, the calcined powders were mixed according to the molar fraction $(1-x)SrTiO_3$–x $Sr(Mg_{1/3}Nb_{2/3})O_3$ +$y$$SrWO_4$ and re-milled for 4 h with a 5% solution of PVA as a binder. The dried power were isostatically pressed into pellets 20 mm in diameter and 13–16 mm in height under the pressure of 2×10^7 Pa. After being fired to remove an organic binder, these samples were sintered at temperature 1350–1600 °C for 4 h in air.

2.2 Measuring methods

The crystalline phase of the prepared samples was identified by D/MAX-RB X-ray diffraction pattern (XRD). The microstructure observation of the sintered ceramics was performed by means of JSM-5610LV scanning electron microscopy (SEM). The dielectric constants ε_r and an unloaded quality values Q in microwave frequency (2–6 GHz) were measured using the parallel-plate method combined with a work analyzer(Advantest R3767C) and a computer. The temperature coefficient of resonant frequency was obtained by measuring the $TE_{01\delta}$ resonant coefficient at temperatures −20 °C(f_{-20}) and 60 °C(f_{60}).

3 Results and discussions

Figure 1 shows the XRD patterns of x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics. It is observed that as the x value increased, the XRD patterns of x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics have not apparent changes and are very similar to that of $Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics, which is mainly owing to small $SrTiO_3$ mol fraction. Most the peaks from x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics could be indexed based on the 1:2 ordered structure, and complex perovskite structures were observed for all compositions [3].

Table 1 Dielectric properties of the x $SrTiO_3$ −$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ system ceramic.

x value	d (g/cm^3)	ε_r	$Q\times f$ (GHz)	τ_f (ppm)
0.01	4.38	26.5	29,500	−23
0.02	4.33	27.2	27,700	−16.3
0.025	4.37	27.8	26,800	7.4
0.03	4.28	29.3	25,800	17.2
0.04	4.29	30.2	23,400	25.8
0.05	4.17	31.5	22,600	36.3
0.06	4.16	32.8	20,200	47.6
0.07	4.19	33.7	19,400	58.9
0.08	4.15	35.2	18,900	70.6

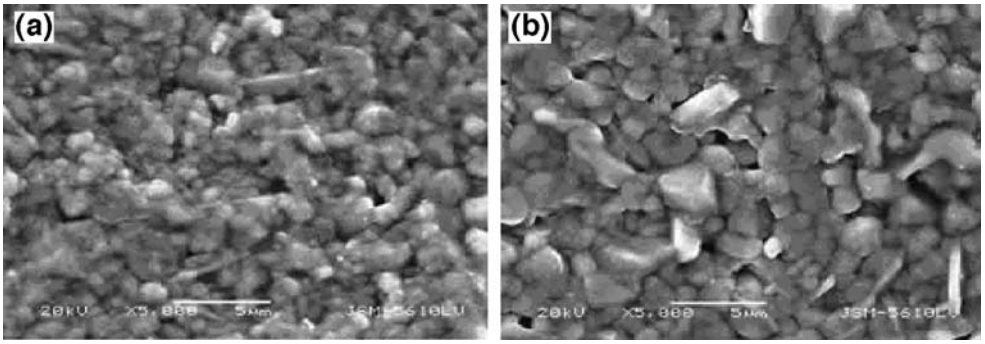

Fig. 2 SEM of $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$: (**a**) without $SrWO_4$ addition at 1600 °C for 4 h, (**b**) with $SrWO_4$ addition at 1350 °C for 4 h

Therefore, the above results indicate that x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics ($0.01 \leqslant x \leqslant 0.08$) has 1:2 ordered perovskite structure, which is mainly for that most complex perovskite structure ceramics have high quality factor.

The dielectric properties of x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics are illustrated in Table 1. As the x value increased from 0.01 to 0.08, the dielectric constants ε_r increased from 26.5 to 35.2 while the $Q\times f$ values gradually decreased, it is because that $SrTiO_3$ ceramics has lower Q value. The τ_f value varied from −23 to 70.6 as the x value increased from 0.01 to 0.08 for x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics. It implied that near zero τ_f value can be obtained by properly adjusting the x value. After optimization, a new microwave dielectric material $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$ was suggested and exhibited the dielectric constant ε_r ~27.8, the $Q\times f$ values ~26,800 and the τ_f value ~7.4 ppm/°C.

It was found that it was difficult to obtain high density x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics even by sintering at temperature as high as 1600 °C. However, the addition of $SrWO_4$ additives could effectively promote densification by sintering at 1350 °C and high density. The (a) and (b) of Fig. 2 show respectively SEM of $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$ without $SrWO_4$ addition at 1600 °C for 4 h and with $SrWO_4$ addition at 1350 °C for 4 h. From the Fig. 2, it was seen that without $SrWO_4$ addition, even if the $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$ was sintered on 1600 °C for 4 h, the crystal size was small and the sintered ceramic was not dense. While the $SrWO_4$ was added, the size of ceramics crystal grew larger and the ceramics became more dense.

Figure 3 shows the changes in dielectric constant of $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics with the addition of $SrWO_4$ at 1350 °C for 4 h. The $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics has a dielectric constant of about 27.8, and when $SrWO_4$ was added, the dielectric constant increased initially because of increasing density. Over 0.07 mol $SrWO_4$, the dielectric constant decreased steadily with increasing $SrWO_4$ because of increasing $SrWO_4$ phase whose dielectric constant (ε ~9) is lower than that of $Sr(Mg_{1/3}Nb_{2/3})O_3$ and $SrTiO_3$.

Figure 4 shows changes in $Q\times f$ values with different $SrWO_4$ mol fraction at 1350 °C for 4 h. From the Fig. 4, the $Q\times f$ values slowly increased with the $SrWO_4$ addition firstly up to the 0.03 $SrWO_4$ mol fraction. It is mainly because that the density was increased due to better sinterability with $SrWO_4$. When the addition of $SrWO_4$ is over 0.03 mol, the $Q\times f$ values rapidly increase, which may

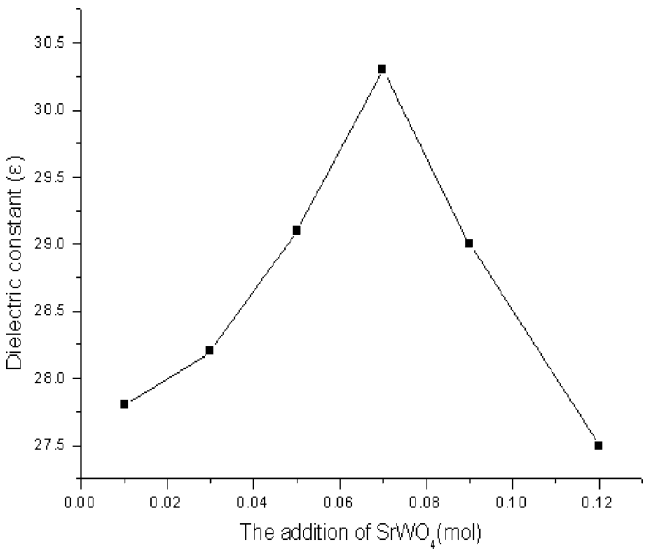

Fig. 3 Dielectric constant vs $SrWO_4$ mol fraction

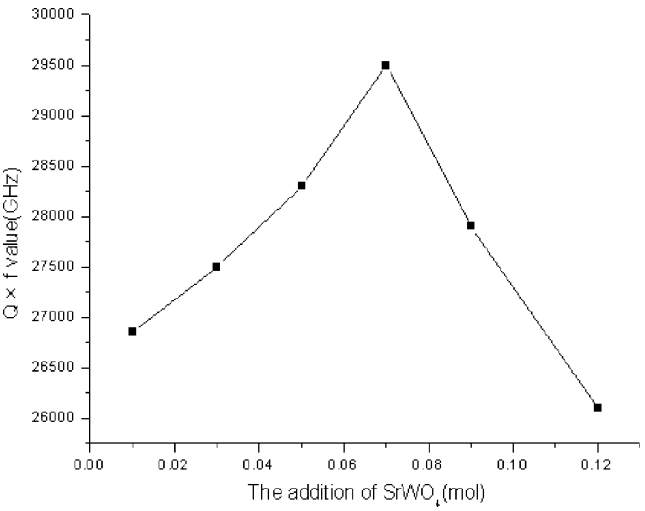

Fig. 4 The $Q\times f$ value as a function of $SrWO_4$ mol fraction

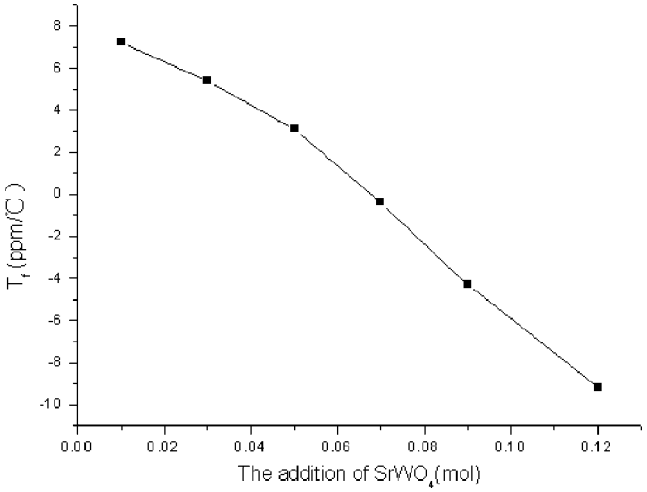

Fig. 5 The τ_f value as a function of addition of $SrWO_4$

be due to the increasing of the B-site ions order because of substituting for the Nb^{5+} ions of $Sr(Mg_{1/3}Nb_{2/3})O_3$ by the W^{6+} ions of $SrWO_4$. Due to the substitution, the charge difference of the B-site ions in $Sr(Mg_{1/3}Nb_{2/3})O_3$ increases from 3+, between Mg^{2+} and Nb^{5+}, to 4+, between Mg^{2+} and W^{6+}. Also, the ionic radius difference and the B-site ions increase from 0.04 Å, between Mg^{2+}(=0.72 Å) and Nb^{5+}(=0.68 Å) to 0.14 Å, between Mg^{2+}(=0.72 Å) and W^{6+}(=0.58 Å). So the W^{6+} ions substitution effectively promoted the charge and ionic radius differences between the B-site ions simultaneously so that the ordering of the B site increased, it is similar to the findings of Galasso and Pyle [4] and Ki Hyun Yoon [5]. In addition, the oxygen vacancies of $Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics are eliminated by the 6+ ion substitution of the 5+ ion, Because the oxygen vacancies absorb the electromagnetism wave energy, when the oxygen vacancies were reduced , the $Q\times f$ values of $Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics can increase as well. This can be explained by the following defect Eq. 1:

$$\begin{aligned} &2M_fO_3 \xrightarrow{M_2O_5} 2M^{\bullet}_{Mf} + 2e^- + 5O_o + \tfrac{1}{2}O_2 \\ &\tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e^- \rightarrow O_O \\ &2M_fO_3 + V_O^{\bullet\bullet} \xrightarrow{M_2O_5} 2M^{\bullet}_{Mf} + 6O_O \end{aligned} \quad (1)$$

Beyond the 0.07 mol $SrWO_3$, the $Q\times f$ values decreases with the increasing $SrWO_3$, which is because of the lower $Q\times f$ value (2,020 at 8.2 G) of $SrWO_4$ ceramics.

Figure 5 illustrates the τ_f (temperature coefficient of resonant frequency) of the specimens sintered at 1350 °C for 4 h as a function of $SrWO_4$ mol fraction. According to Fig. 5, with increasing $SrWO_4$ mol fraction, the $SrWO_4$ phase(τ_f approximately −50 ppm/°C) increased, the τ_f value of the specimen became continuously smaller by the volume mixture rule [6], When the mol fraction of $SrWO_4$ addition is 0.07 mol, the TCF becomes −0.4 ppm/°C.

4 Conclusions

Microwave dielectric properties of x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics system have been investigated. As the x value increased from 0.01 to 0.08 , the dielectric constants increase from 26.5 to 35.2, while the $Q\times f$ values gradually decreased and the temperature coefficient of resonant frequency (τ_f) varies in a wide range from −23 to 70.6 ppm/°C. When the $SrWO_4$ was added, the x $SrTiO_3$–$(1-x)Sr(Mg_{1/3}Nb_{2/3})O_3$ ceramics is easier to be sintered at lower sintering temperature(1350 °C). In addition, With increasing $SrWO_4$ mol fraction, the dielectric constant ε_r and the $Q\times f$ values increased initially. Over 0.07 mol $SrWO_4$, the dielectric constant ε_r and the $Q\times f$ values decreased steadily with increasing $SrWO_4$. The TCF value of the specimen decreased with addition of $SrWO_4$. As a new microwave dielectric material, $0.025SrTiO_3$–$0.975Sr(Mg_{1/3}Nb_{2/3})O_3$–0.07 $SrWO_4$ can acquire the following microwave properties: a dielectric constant ε_r~30.3, a $Q\times f$ value ~29,500, and a τ_f value~−0.4 ppm/°C.

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