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Microwave dielectric properties of low-firing $BiNbO_4$ ceramics with V_2O_5 substitution

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Abstract The effect of V_2O_5 substitution on the sintering behavior and the microwave dielectric properties of $BiNbO_4$ ceramics were studied. The sintering temperatures of $Bi(V_xNb_{1-x})O_4$ ceramics decrease from 990 to 810°C with x value increasing from 0.002 to 0.064. The size of grains increased with the sintering temperature increasing and decreased with the substitution amount increasing. The dielectric properties are affected by the microstructures very much. The quality factor Q value is from 2500 to 4000 at about frequency=5 GHz and reach to the maximum when x= 0.032. With the different x value, the Q_f values change between 15000 to 20000 GHz; the τ_f values changes between 0 and +20 ppm/°C between temperature range 25~85°C and decreased with the increasing of x value.

Keywords $BiNbO_4$ ceramics · Microwave dielectrics · Quality value

1 Introduction

Multilayer microwave devices have been developed to reduce the size of microwave devices in mobile radio communication systems. The microwave dielectrics with low sintering temperature are needed to co-fire with low loss conductors and melting-point electrode such as silver and brass. Furthermore, high dielectric constant, high quality factor and small temperature coefficient of resonant frequency are the three most important requirements for ceramics used in microwave circuit. Addition of low-melting-point oxide, chemical processing and starting materials with smaller particles size are three methods normally used to reduce the sintering temperature of dielectric materials [1], and the first method is popularly applied.

It is well known that bismuth-based dielectric ceramics were low-firing temperature materials and had been studied for piezoelectric materials or multiplayer ceramic capacitors [2]. Tzou WC et al. [3] and Huang CL et al. [4] respectively studied the affection to the sintering and dielectric properties of $BiNbO_4$ ceramics with V_2O_5 addition and V_2O_5–CuO addition. In their studies, the sintering temperature could be lowered below 960°C to form α-$BiNbO_4$; the dielectric constant stabled between 43 and 44 with different addition and sintering temperature; the temperature coefficients of resonant frequency were positive with V_2O_5 addition and negative with CuO addition. Chai and Kim et al. [5] studied the properties of A site substitution. With the substitution of big radius ions like La^{3+} and Nd^{3+} for A site Bi^{3+}, the transition temperature could be lowered macroscopically and the dielectric constant could increase with the substitution amount increasing.

In this paper, $Bi(V_xNb_{1-x})O_4$ ceramics were designed with x from 0.002 to 0.064 by using V^{5+} substituting for Nb^{5+} than simply doping. The XRD and SEM were studied with different x values and different sintering temperatures in detail to find the influence of microstructures to the dielectric properties. When the x value is large enough, whether the second phase like $BiVO_4$ could appear or the

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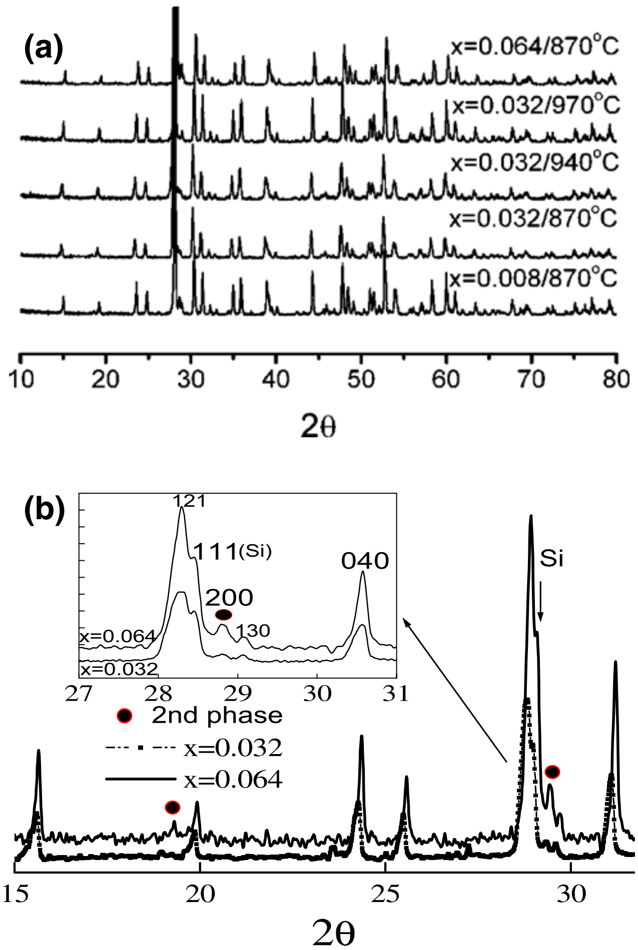

Fig. 1 XRD patterns of Bi($V_x Nb_{1-x}$)O_4 ceramics (**a**) with x=0.008, 0.032 and 0.064, (**b**) XRD patterns with the $BiVO_4$ phase

transition temperature could be lowered? The microwave dielectric properties of Bi($V_x Nb_{1-x}$)O_4 ceramics at different sintering temperature were investigated detailedly.

2 Experimental

Proportionate amounts of reagent-grade starting materials of Bi_2O_3, Nb_2O_5 and V_2O_5 were mixed according to the composition Bi($V_x Nb_{1-x}$)O_4 in which the x value was 0.002, 0.008, 0.032, 0.048, 0.064, and ball-milled for 4 h with alcohol in a nylon container with ZrO_2 balls. The mixtures were dried and calcined at 700°C for 4 h. Then the mixtures were re-milled, and after drying, the powder with 5 wt.% PVA binder was uniaxially pressed into pellets and cylinder in a steel die. The pellets were sintered from 790 to 990°C for 2 h and cylinders being sintered for 4 h.

After surface published, the crystalline structures of the $BiNbO_4$ substituted by V_2O_5 ceramics were investigated using X-ray diffraction with Cu Kα radiation. To find out whether the second phase occurred, the samples were then carefully investigated by powder X-ray diffraction using Guinier–Hägg camera and a Guinier–Si (NBS #640c, a= 5.431195) as internal standard for accurately determining unit cell parameters through the “Unitcell” software package. To investigate the morphology of the samples, the sintered surface of the specimens were observed by SEM.

Dielectric behaviors at microwave frequency were measured by Hakki–Coleman's dielectric resonator method improved by Kobayashi et al. (method I) [6], and **TE**$_{0\ 1\delta}$ shielded cavity method (method II) [7]. A 8720ES network analyzer was used in both the above methods for the microwave measurement.

The resonant frequencies as the function of temperature T were measured with the 8720ES network analyzer and a DELTA 9023 Chamber using the shielded cavity method. The τ_f value was calculated by the formula

$$\tau_f = \frac{f_T - f_o}{f_o \times (T - T_o)}$$

where f_T, f_0 were the TE_{011} resonant frequencies at the measuring temperature T (55°C, 85°C in this paper) and at RT (25°C) respectively.

3 Results and discussion

Figure 1(a) shows the XRD patterns of Bi($V_x Nb_{1-x}$)O_4 ceramics with different x value and different sintering temperature. It was known to all that the $BiNbO_4$ ceramics formed stable α-$BiNbO_4$, orthorhombic phase closely related to that of $SbTaO_4$ type below 1020°C and then gradually transforms to the triclinic phase β-$BiNbO_4$ with the temperature increasing [8]. Only the orthorhombic phase was revealed in the sintered Bi($V_x Nb_{1-x}$)O_4 ceramics with x value increasing from 0.008 to 0.064 at the sintering temperature of 870°C as shown in Fig. 1(a). The β-$BiNbO_4$ did not appear even at the sintering temperature of 970°C at x=0.032.

According to the results investigated carefully by XRD (as shown in Fig. 1(b)), the second phase $BiVO_4$ began to appear at x=0.032 with very weak peaks and became obvious at x=0.064. The lattice parameters were calculated and shown in the Table 1. Since the $BiVO_4$ lines were so

Table 1 The lattice parameters of the Bi($V_x Nb_{1-x}$)O_4 ceramics for x= 0.032 and x=0.064.

x value	Phases	a (Å)	b (Å)	c (Å)
0.032	$BiNbO_4$	4.9801	5.6788	11.7051
	$BiVO_4$	5.0819	5.1877	11.7055
0.064	$BiNbO_4$	4.9814	5.6784	11.7051
	$BiVO_4$	5.0321	5.1882	11.7079

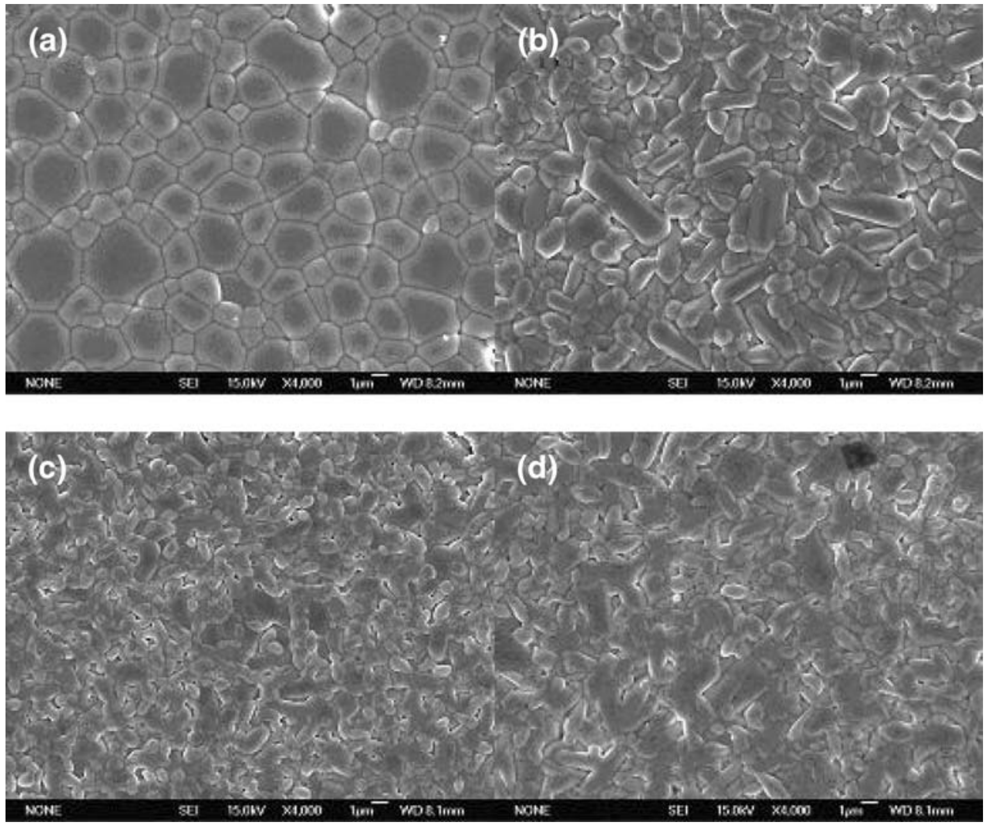

Fig. 2 SEM micrographs of $Bi(V_xNb_{1-x})O_4$ ceramics (**a**) x=0.002, 990°C/2 h; (**b**) x=0.032, 850°C/2 h; (**c**) x=0.064, 810°C/2 h; (**d**) x=0.064, 850°C/2 h

weak that the lattice parameters of $BiVO_4$ were not very accurate. However, this evidence indicated that the substitution of V_2O_5 would lead to the formation of the second phase $BiVO_4$.

The densities of sintered $Bi(V_xNb_{1-x})O_4$ ceramics with different x values, as a function of sintering temperature, were measured by Archimedes method. The proper sintering temperature was determined for certain x value when its density reached maximum at this temperature.

The SEM micrographs of $Bi(V_xNb_{1-x})O_4$ ceramics with various x values sintered at different temperatures are shown in Fig. 2. The homogeneously fine microstructures with almost no pores were revealed for $Bi(V_xNb_{1-x})O_4$ ceramics with x=0.002 sintered at 990°C (Fig. 2(a)). The microstructures of $Bi(V_xNb_{1-x})O_4$ ceramics with x=0.032 sintered at 850°C with good densification was shown in Fig. 2(b). The densification temperature and grain size reduced with the increasing of x value. The bar shape grains emerged and became more and more with x value increasing. This indicates the growth anisotropies of $BiNbO_4$ grains with more substitution of V_2O_5. The size of all shapes of grains, the amount of bar shape and other abnormal grains all increased with the sintering temperature increasing from 810°C to 850°C for x=0.064. (Fig. 2(c)–(d)).

The resonant frequency, dielectric constant ε_r and Q value at microwave frequency were shown in Table 2 measured by method I. The dielectric constant ε_r varied between 36 and 46 with the x value. The Q value reached above 4673 and the Q_f value reached 22235G when x= 0.032. The Q and Q_f value of samples with the same S.T.

Table 2 The resonant frequency and ε_r at microwave frequency.

x value	D (mm)	L (mm)	S.T. (°C)	f_0 (GHz)	ε_r	Q	Q_f (GHz)
0.002	12.64	11.02	990	3.9656	40.7	3774	14966
0.008	10.08	9.12	890	4.7602	43.2	3704	17632
0.032	10.14	8.84	850	4.7582	44.0	4673	22235
0.048	10.10	8.50	830	4.7866	45.0	3817	18270
0.064	8.46	7.86	810	6.0904	36.7	1965	11968

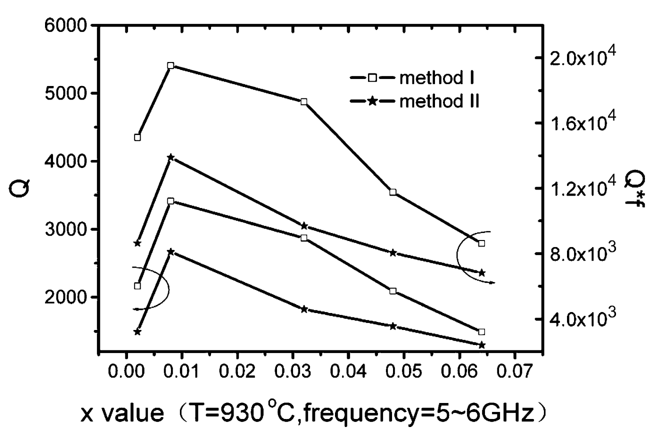

Fig. 3 Q and Q_f value as a function of substitution amount x

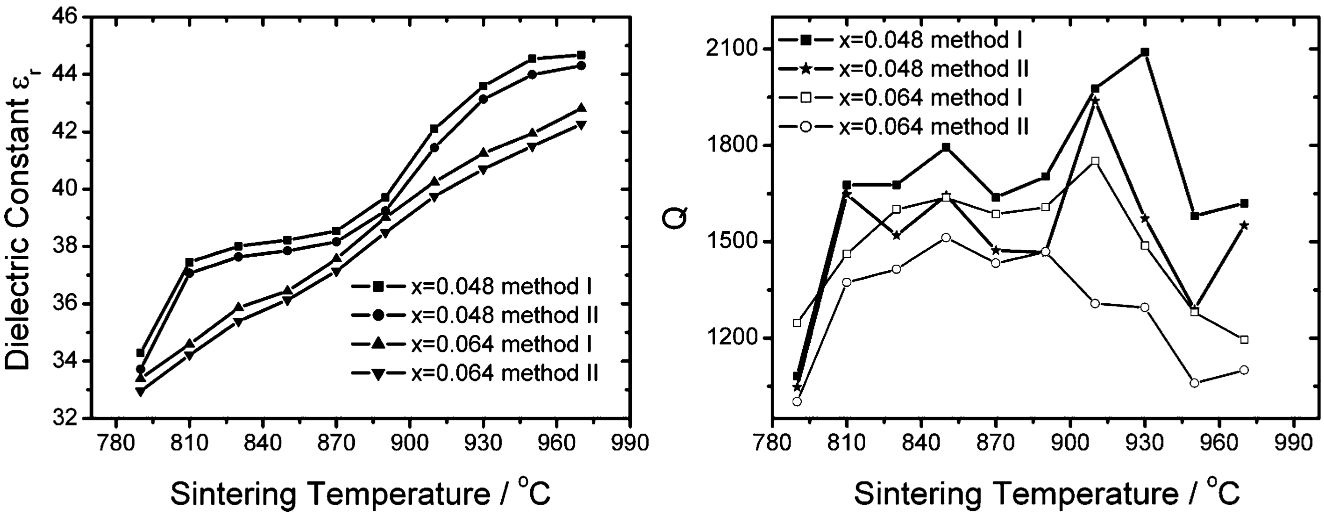

Fig. 4 The microwave properties of $Bi(V_xNb_{1-x})O_4$ ceramics with x=0.048 as a function of sintering temperatures

(930°C) were measured with resonant frequency= 5~6 GHz, as shown in Fig. 3. The results and the trends measured by the two methods were similar to each other. When x=0.008 and 0.032, the Q and Q_f had relative higher values. The microwave dielectric properties deteriorated much when x>0.032, this can be attributed to the appearance of $BiVO_4$ phase.

The dielectric constant ε_r and quality value Q were strongly dependent on the sintering temperature as shown in Fig. 4. The same trends were shown by both measurement methods. The dielectric constant ε_r increased with the increasing sintering temperature which mainly attributed to the grain growth in the corresponding samples. The Q values firstly increased quickly with increasing sintering temperatures and then reached a saturation value between a certain wide temperature range for different x value. Because the pores and grain boundary area decreased as the grain size increasing, the lattice imperfections were reduced and Q value thus increased. But the abnormal grain growth occurring in $Bi(V_xNb_{1-x})O_4$ ceramics with further increasing in sintering temperatures above the densified temperatures caused the increasing of the crystal defects and decreasing of Q value. So Q could remained a saturation value between a wide temperature range then deteriorated again.

The temperature coefficient τ_f decreased with the increasing of the measuring temperature for different x value, and increased with the x value and changed from +4.77 to +12.27 ppm/°C with x value increasing from 0.002 to 0.064 at T=85°C(shown in Table 3). The influence to τ_f of the expansion of the shielded cavity must be considered in the further studies.

Table 3 The τ_f of different x value at T=55°C and T=85°C.

T/°C	x=0.002	x=0.032	x=0.048	x=0.064
55	8.86	14.12	15.94	16.00
85	4.77	9.44	11.69	12.27

4 Conclusion

The densified temperature of $BiNbO_4$ ceramics could be lowered to 810°C~990°C by the substitution of V_2O_5 for Nb_2O_5. The trace of second phase $BiVO_4$ was found with the V_2O_5 substitution for $BiNbO_4$ ceramics and no transition from α-$BiNbO_4$ to β-$BiNbO_4$ was found at 970°C. With x value between 0.002 and 0.064, the dielectric constant ε_r of $Bi(V_xNb_{1-x})O_4$ ceramics is between 38 and 46, the quality factor Q is between 1000 and 4000 (3~6 GHz) and the Q_f lies between 15000 and 20000 GHz. The temperature coefficient of resonant frequency τ_f is between 0 and +20 ppm between 25 and 100°C. The Q and Q_f values measured by both methods above correspond very well.

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