

# Microwave dielectric properties of low-firing BiNbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub> substitution

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**Abstract** The effect of V<sub>2</sub>O<sub>5</sub> substitution on the sintering behavior and the microwave dielectric properties of BiNbO<sub>4</sub> ceramics were studied. The sintering temperatures of Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> 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  $\tau_f$  values changes between 0 and +20 ppm/°C between temperature range 25~85°C and decreased with the increasing of  $x$  value.

**Keywords** BiNbO<sub>4</sub> 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

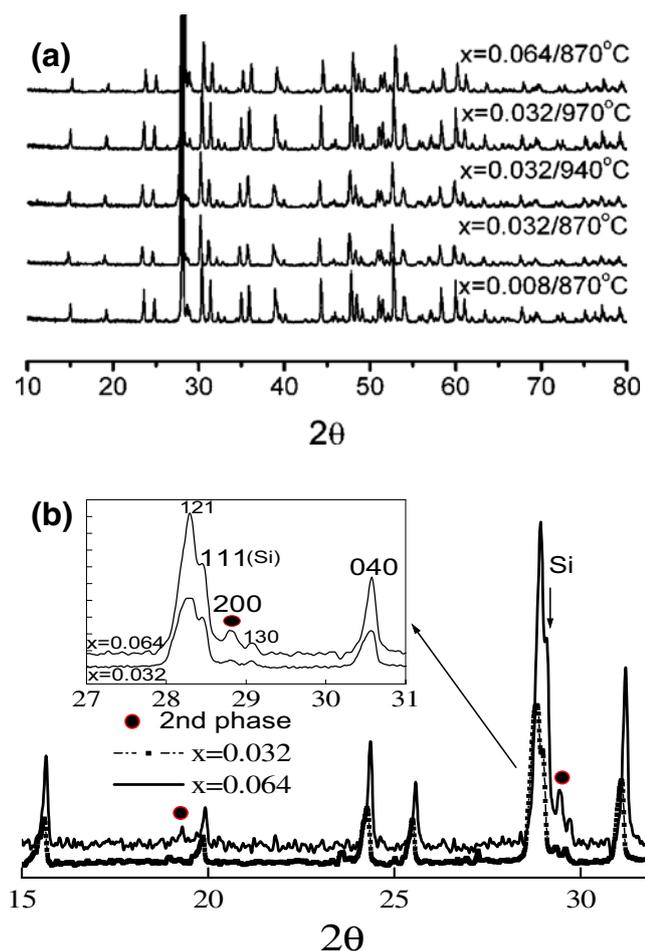
low sintering temperature are needed to co-fire with low loss conductors and melting-point electrode such as silver and brass. Furthermore, high dielectric constant, high quality factor and small temperature coefficient of resonant frequency are the three most important requirements for ceramics used 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 multilayer 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<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub> addition and V<sub>2</sub>O<sub>5</sub>-CuO addition. In their studies, the sintering temperature could be lowered below 960°C to form  $\alpha$ -BiNbO<sub>4</sub>; the dielectric constant stabled between 43 and 44 with different addition and sintering temperature; the temperature coefficients of resonant frequency were positive with V<sub>2</sub>O<sub>5</sub> 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<sup>3+</sup> and Nd<sup>3+</sup> for A site Bi<sup>3+</sup>, the transition temperature could be lowered macroscopically and the dielectric constant could increase with the substitution amount increasing.

In this paper, Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> ceramics were designed with  $x$  from 0.002 to 0.064 by using V<sup>5+</sup> substituting for Nb<sup>5+</sup> 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<sub>4</sub> could appear or the

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**Fig. 1** XRD patterns of  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  ceramics (a) with  $x=0.008$ , 0.032 and 0.064, (b) XRD patterns with the  $\text{BiVO}_4$  phase

transition temperature could be lowered? The microwave dielectric properties of  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  ceramics at different sintering temperature were investigated detailedly.

## 2 Experimental

Proportionate amounts of reagent-grade starting materials of  $\text{Bi}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  were mixed according to the composition  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  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  $\text{ZrO}_2$  balls. The mixtures were dried and calcined at  $700^\circ\text{C}$  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  $990^\circ\text{C}$  for 2 h and cylinders being sintered for 4 h.

After surface published, the crystalline structures of the  $\text{BiNbO}_4$  substituted by  $\text{V}_2\text{O}_5$  ceramics were investigated using X-ray diffraction with  $\text{Cu K}\alpha$  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  $\text{TE}_{018}$  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  $\tau_f$  value was calculated by the formula

$$\tau_f = \frac{f_T - f_0}{f_0 \times (T - T_0)}$$

where  $f_T$ ,  $f_0$  were the  $\text{TE}_{011}$  resonant frequencies at the measuring temperature  $T$  ( $55^\circ\text{C}$ ,  $85^\circ\text{C}$  in this paper) and at RT ( $25^\circ\text{C}$ ) respectively.

## 3 Results and discussion

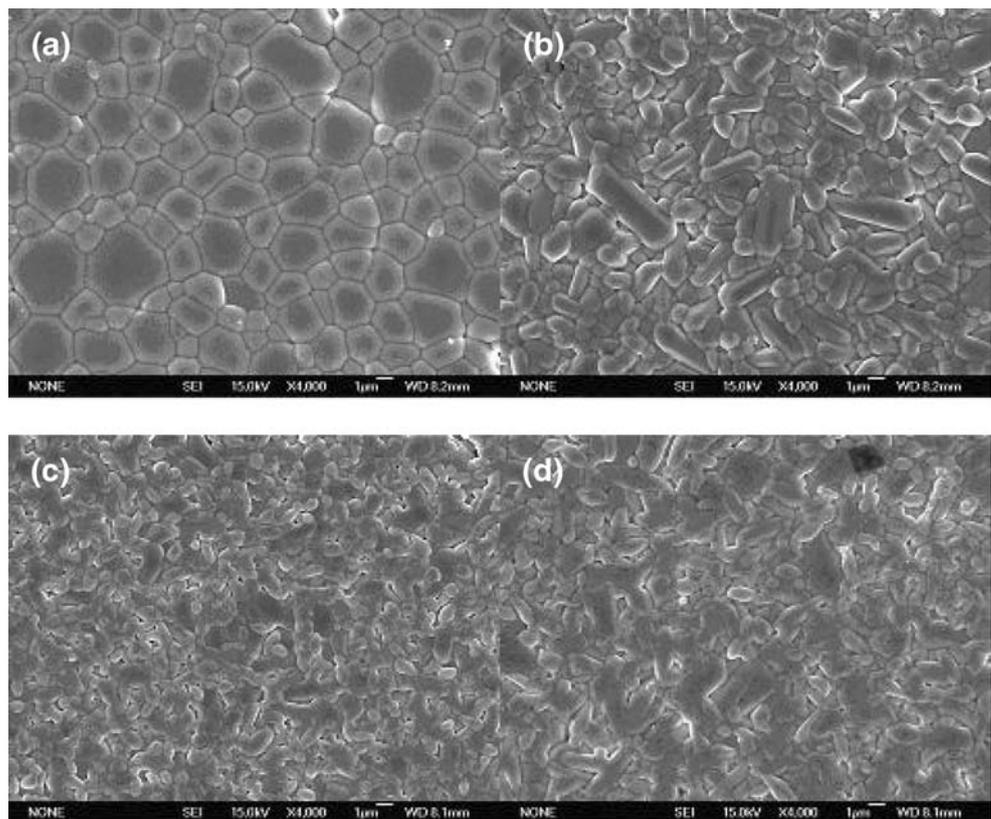
Figure 1(a) shows the XRD patterns of  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  ceramics with different  $x$  value and different sintering temperature. It was known to all that the  $\text{BiNbO}_4$  ceramics formed stable  $\alpha$ - $\text{BiNbO}_4$ , orthorhombic phase closely related to that of  $\text{SbTaO}_4$  type below  $1020^\circ\text{C}$  and then gradually transforms to the triclinic phase  $\beta$ - $\text{BiNbO}_4$  with the temperature increasing [8]. Only the orthorhombic phase was revealed in the sintered  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  ceramics with  $x$  value increasing from 0.008 to 0.064 at the sintering temperature of  $870^\circ\text{C}$  as shown in Fig. 1(a). The  $\beta$ - $\text{BiNbO}_4$  did not appear even at the sintering temperature of  $970^\circ\text{C}$  at  $x=0.032$ .

According to the results investigated carefully by XRD (as shown in Fig. 1(b)), the second phase  $\text{BiVO}_4$  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  $\text{BiVO}_4$  lines were so

**Table 1** The lattice parameters of the  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  ceramics for  $x=0.032$  and  $x=0.064$ .

$x$ value	Phases	$a$ (Å)	$b$ (Å)	$c$ (Å)
0.032	$\text{BiNbO}_4$	4.9801	5.6788	11.7051
	$\text{BiVO}_4$	5.0819	5.1877	11.7055
0.064	$\text{BiNbO}_4$	4.9814	5.6784	11.7051
	$\text{BiVO}_4$	5.0321	5.1882	11.7079

**Fig. 2** SEM micrographs of Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> 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<sub>4</sub> were not very accurate. However, this evidence indicated that the substitution of V<sub>2</sub>O<sub>5</sub> would lead to the formation of the second phase BiVO<sub>4</sub>.

The densities of sintered Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> 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.

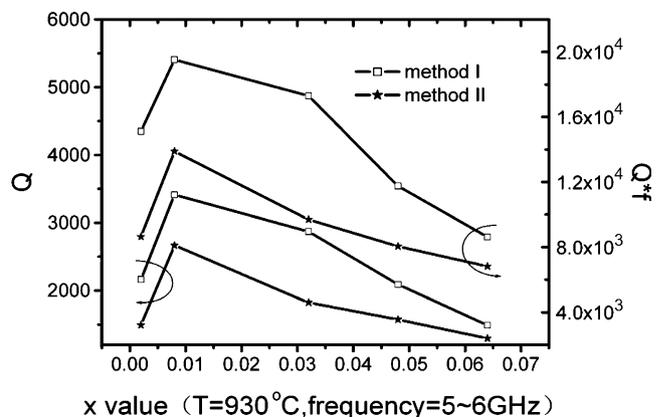
The SEM micrographs of Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> ceramics with various x values sintered at different temperatures are shown in Fig. 2. The homogeneously fine microstructures with almost no pores were revealed for Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> ceramics with x=0.002 sintered at 990°C (Fig. 2(a)). The microstructures of Bi(V<sub>x</sub>Nb<sub>1-x</sub>)O<sub>4</sub> 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<sub>4</sub> grains with more substitution of V<sub>2</sub>O<sub>5</sub>. 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<sub>r</sub> and Q value at microwave frequency were shown in Table 2 measured by method I. The dielectric constant ε<sub>r</sub> varied between 36 and 46 with the x value. The Q value reached above 4673 and the Q<sub>f</sub> value reached 22235G when x=0.032. The Q and Q<sub>f</sub> value of samples with the same S.T.

**Table 2** The resonant frequency and ε<sub>r</sub> at microwave frequency.

x value	D (mm)	L (mm)	S.T. (°C)	f <sub>0</sub> (GHz)	ε <sub>r</sub>	Q	Q <sub>f</sub> (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<sub>f</sub> value as a function of substitution amount x

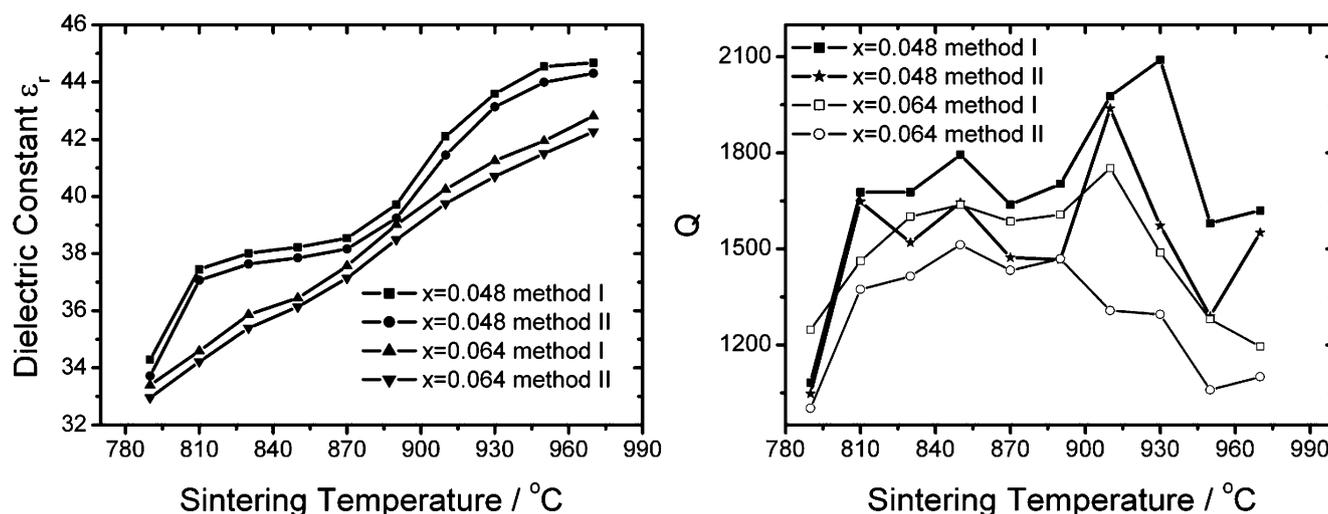


Fig. 4 The microwave properties of  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  ceramics with  $x=0.048$  as a function of sintering temperatures

(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  $\text{BiVO}_4$  phase.

The dielectric constant  $\epsilon_r$  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  $\epsilon_r$  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  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  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  $\tau_f$  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  $T=85^\circ\text{C}$  (shown in Table 3). The influence to  $\tau_f$

Table 3 The  $\tau_f$  of different  $x$  value at  $T=55^\circ\text{C}$  and  $T=85^\circ\text{C}$ .

$T/^\circ\text{C}$	$x=0.002$	$x=0.032$	$x=0.048$	$x=0.064$
55	8.86	14.12	15.94	16.00
85	4.77	9.44	11.69	12.27

of the expansion of the shielded cavity must be considered in the further studies.

#### 4 Conclusion

The densified temperature of  $\text{BiNbO}_4$  ceramics could be lowered to  $810^\circ\text{C}\sim 990^\circ\text{C}$  by the substitution of  $\text{V}_2\text{O}_5$  for  $\text{Nb}_2\text{O}_5$ . The trace of second phase  $\text{BiVO}_4$  was found with the  $\text{V}_2\text{O}_5$  substitution for  $\text{BiNbO}_4$  ceramics and no transition from  $\alpha\text{-BiNbO}_4$  to  $\beta\text{-BiNbO}_4$  was found at  $970^\circ\text{C}$ . With  $x$  value between 0.002 and 0.064, the dielectric constant  $\epsilon_r$  of  $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$  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  $\tau_f$  is between 0 and +20 ppm between 25 and  $100^\circ\text{C}$ . The  $Q$  and  $Q_f$  values measured by both methods above correspond very well.

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