



# Phase evolution and dielectric properties of fluorite-type $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$ ceramics ( $\text{M}=\text{Ti}, \text{Zr}, \text{Sn}, \text{W}, \delta=\pm 0.05$ )



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## ABSTRACT

Phase structure and dielectric behavior of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti}, \text{Zr}, \text{Sn}, \text{W}, \delta = \pm 0.05$ ) were discussed. Cubic fluorite solid solutions  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ( $\text{M} = \text{Zr}, \text{Sn}, \text{W}, \delta = \pm 0.05$ ) were obtained through a conventional solid state reaction method. An analysis of the microwave dielectric properties showed that substitution of  $\text{Nb}^{5+}$  by  $\text{W}^{6+}$  was favorable to improving the temperature coefficient of resonant frequency (TCF value). A temperature stable dielectric material  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  was introduced. The  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics sintered at 930 °C for 2 h exhibited a high permittivity of 92.4, a Qf value of 260 GHz and a TCF value of  $-34 \text{ ppm}/^\circ\text{C}$ .

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## 1. Introduction

Modern communication systems have moved to the microwave (MW) frequency region, where advanced dielectric ceramics are frequently used in resonators and filters. Miniaturization requires high relative permittivity ( $\epsilon_r$ ) materials (since the size of resonators is inversely proportional to  $\epsilon_r^{1/2}$ ) with a near zero temperature coefficient of resonance frequency (TCF value). Furthermore, ceramics with low dielectric loss (high Qf value) are needed for the high selectivity and optimized bandwidth of the filters [1]. More recently, an important breakthrough in the telecommunications came with the introduction of low-temperature cofired ceramic (LTCC) technology, which has enabled miniaturization, the integration of passive functions and a reduction in costs, and has led to the production, for example, of the well-known Bluetooth module. LTCC modules are produced by co-firing ceramic layers with a three-dimensional Ag-microstrip circuitry. To avoid melting of the Ag-microstrips, the firing temperature must be lower than 950 °C, which is extremely low for a ceramic material and represents the major problem with this technology [2]. Microwave dielectric ceramics with high permittivity ( $\epsilon_r > 80$ ) has been widely studied [3–8], while most of them need high sintering temperatures. In the

$\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$  system,  $\text{BiNbO}_4$  and  $\text{Bi}_3\text{NbO}_7$  possess low sintering temperatures and good microwave dielectric properties, and have attracted much attention in recent years [9,10].  $\text{BiNbO}_4$  ceramics have good properties for microwave application and LTCC, but the reaction between  $\text{BiNbO}_4$  and the silver electrode limited its further application [11,12]. Valant et al. [12–14] studied the crystalline structure and microwave dielectric properties of  $\text{Bi}_3\text{NbO}_7$  ceramics, and they found that the cubic incommensurate phase  $\text{Bi}_3\text{NbO}_7$  exhibited a high permittivity of 100, a lower Qf value of 300 GHz and a high negative TCF value of 200  $\text{ppm}/^\circ\text{C}$ . The cubic incommensurate phase  $\text{Bi}_3\text{NbO}_7$  underwent an order-disorder phase transition into a commensurate tetragonal phase at temperatures below 900 °C, and the tetragonal phase exhibited a lower permittivity of 91, a higher Qf value of 730 GHz and a positive TCF value of  $+100 \text{ ppm}/^\circ\text{C}$ . Meanwhile, both the cubic incommensurate phase and the commensurate tetragonal phase  $\text{Bi}_3\text{NbO}_7$  ceramics did not react with Ag and they would be suitable for LTCC modules and microwave applications if their TCF value could be modified to near zero.

The solid solutions of  $\text{Bi}_3(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_7$  [15,16] were sensitive to the sintering conditions and the phase structure and microwave dielectric properties can be tailored by changing sintering conditions. The TCF value of  $\text{Bi}_3(\text{Nb}_{0.4}\text{Ta}_{0.6})\text{O}_7$  with tetragonal phase was near to zero but the permittivity decreased greatly to 72 [15]. Our previous work [17] showed that the cubic incommensurate phase  $\text{Bi}_3\text{NbO}_7$  ceramics transmitted into commensurate tetragonal phase

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by means of substitution of  $\text{Nb}^{5+}$  by  $\text{V}^{5+}$ , and the TCF value was tailored to near zero while the dielectric permittivity decreased from 91 to 80. In the present study, we examine substitution of  $\text{Nb}^{5+}$  by tetravalent cations such as  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$  and  $\text{Sn}^{4+}$ , and/or hexavalent cations such as  $\text{W}^{6+}$  in  $\text{Bi}_3\text{NbO}_7$ . The sintering behavior, phase structure, microstructure, and dielectric properties of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ( $M = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) ceramics were studied.

## 2. Experimental procedure

Proportionate amounts of reagent-grade  $\text{Bi}_2\text{O}_3$  (99%, Shu-Du Powders Co. Ltd, China),  $\text{Nb}_2\text{O}_5$  (>99%, Guo-Yao Co, Ltd, Shanghai, China),  $\text{TiO}_2$  (>99%, Linghua Co. Ltd, Zhaoqing, China),  $\text{ZrO}_2$  (>99.5%, Xinxing Co. Ltd, Yixing, China),  $\text{SnO}_2$  (>99.5%, Xinxing Co. Ltd, Yixing, China), and  $\text{WO}_3$  (99%, Tianjin, China) were weighed according to the stoichiometric formulation of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ( $M = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ). Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) with a running speed of 300 r/min. The mixed oxides were then dried and calcined at  $750^\circ\text{C}$  for 4 h. After being crushed and re-milled for 5 h using the  $\text{ZrO}_2$  milling media and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die with 5 wt.% PVA binder addition under a uniaxial pressure of 20 MPa. Samples were sintered in the temperature range from  $850$  to  $950^\circ\text{C}$  for 2 h.

The crystalline structures of samples were investigated using X-ray diffraction with  $\text{Cu K}\alpha$  radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The dielectric properties of ceramic as a function of frequency (1 K–10 MHz) and temperature ( $25$ – $300^\circ\text{C}$ ) were measured by an LCR analyzer (4284, Agilent, Santa Clara, CA) with a self-made high temperature system. Dielectric behaviors at microwave frequency were measured with the  $\text{TE}_{01\delta}$  shielded cavity method with a network analyzer (8720 ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). Temperature coefficient of resonant frequency (TCF value) and temperature coefficient of capacity (TCC value) were calculated with the following formulas:

$$\text{TCF} = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)}, \quad (1)$$

where  $f_{85}$  and  $f_{25}$  are the  $\text{TE}_{01\delta}$  resonant frequencies at 85 and  $25^\circ\text{C}$ , respectively;

$$\text{TCC} = \frac{\varepsilon_{85} - \varepsilon_{25}}{\varepsilon_{25} \times (85 - 25)}, \quad (2)$$

where  $\varepsilon_{85}$  and  $\varepsilon_{25}$  are the permittivity at 100 kHz at 85 and  $25^\circ\text{C}$ , respectively.

## 3. Results and discussions

According to the literature [18,19], there are three types of superstructures in the Nb-doped  $\delta$ - $\text{Bi}_2\text{O}_3$  solid solution system. The structure of cubic  $\text{Bi}_3\text{NbO}_7$  is the so-called type II superstructure, which is an incommensurate superstructure extends from 6.25 to 26.0 mol% of  $\text{Nb}_2\text{O}_5$  in the  $\text{Bi}_2\text{O}_3$ – $\text{Nb}_2\text{O}_5$  system. Fig. 1 presents the XRD patterns of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ( $M = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) ceramics sintered at  $930^\circ\text{C}$  for 2 h. As shown in Fig. 1 (a–c), all peaks can be indexed on a cubic cell with space group  $Fm\bar{3}m$ , except the superlattice ordering diffraction peak at  $2\theta = 33.7$ , which was consistent with the XRD pattern of parent  $\text{Bi}_3\text{NbO}_7$  in the

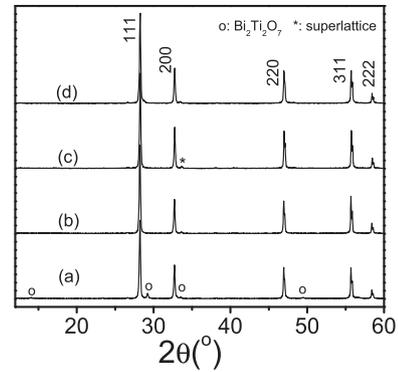


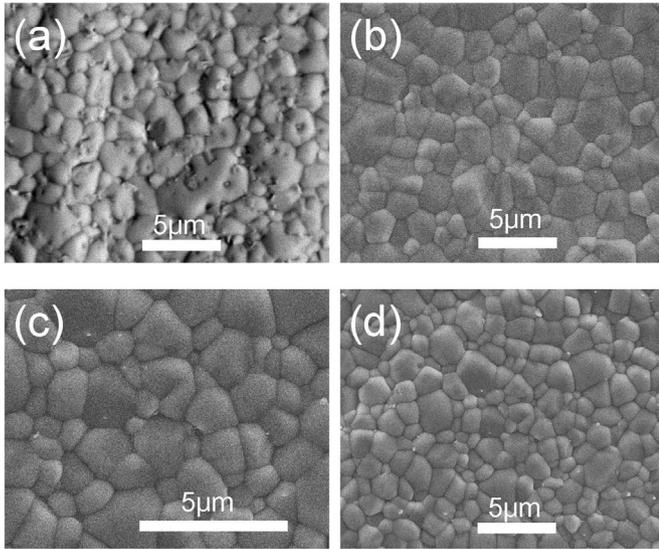
Fig. 1. XRD patterns of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $M = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) sintered at  $930^\circ\text{C}$  for 2 h: (a)  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$ , (b)  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$ , (c)  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$ , (d)  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$ .

literature [14,16,17]. Single phase with incommensurate cubic fluorite-type structure was obtained in the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$ ,  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$ , and  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics, while in the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramics, a small amount of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  phase appeared (as shown in Fig. 1 (d)).

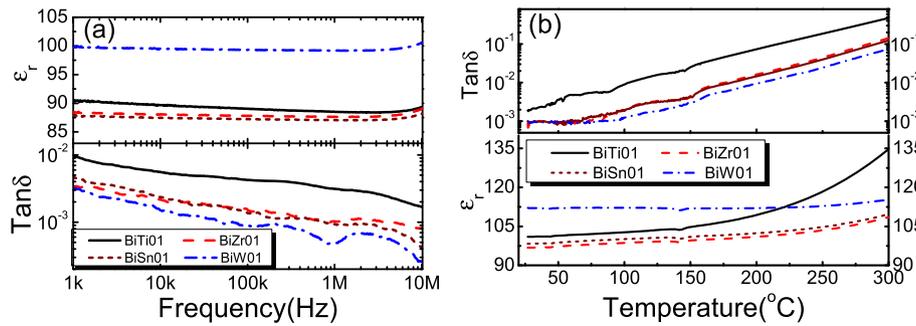
The ionic radii of  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{4+}$  and  $\text{W}^{6+}$  were 0.605, 0.72, 0.69 and  $0.60\text{ \AA}$ , respectively, and the ionic radius of  $\text{Nb}^{5+}$  was  $0.64\text{ \AA}$ , as suggested by Shannon [20]. There was no clear evidence suggesting that the solid solubility of  $\text{Bi}_3\text{NbO}_7$  substituted by  $M$  ( $M = \text{Ti, Zr, Sn}$  and  $\text{W}$ ) is related with ionic radius. As described above, the cubic  $\text{Bi}_3\text{NbO}_7$  is a kind of Nb-doped  $\delta$ - $\text{Bi}_2\text{O}_3$  solid solution with defect fluorite  $\delta$ - $\text{Bi}_2\text{O}_3$  as the basic structure. According to the phase diagrams [21], the structure of  $\delta$ - $\text{Bi}_2\text{O}_3$  can be stabilized at room temperature by doping  $\text{Bi}_2\text{O}_3$  with a large number of metallic cations, such as trivalent rare earth, pentavalent  $\text{V}^{5+}$ ,  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ , or hexavalent  $\text{W}^{6+}$  and  $\text{Mo}^{6+}$ , except tetravalent  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$  and  $\text{Sn}^{4+}$ . I. Abrahams' work [22] showed that  $\text{W}^{6+}$  has a very favorable solution energy for  $\text{Nb}^{5+}$  substitution in  $\text{Bi}_3\text{NbO}_7$  through computer simulation techniques and  $\delta$ - $\text{Bi}_2\text{O}_3$  solid solutions can also be obtained in the  $\text{Bi}_3\text{Nb}_{1-x}\text{W}_x\text{O}_{7+x/2}$  system when  $x \leq 0.2$ . Same result was obtained in the  $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$  system in the composition range  $0.0 \leq x \leq 0.40$  [23], which means that the solution energy of  $\text{Zr}^{4+}$  can be lowered by combining with  $\text{Nb}^{5+}$  substitution. In this work,  $\delta$ - $\text{Bi}_2\text{O}_3$  solid solutions with incommensurate cubic fluorite-type structure were also obtained in the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$  ceramics, as well as in the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$  and  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$ . It means that the solution energy of  $\text{Sn}^{4+}$  can also be lowered by combining with  $\text{Nb}^{5+}$  substitution. In the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramics, the appearance of the secondary phase of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  with face-centered cubic structure (space group  $Fd\bar{3}m$ ) suggests that the solution energy of  $\text{Ti}^{4+}$  is still too high to form a  $\delta$ - $\text{Bi}_2\text{O}_3$  solid solution.

SEM images of as-fired surface of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $M = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) in Fig. 2 shows that all the ceramics can be well densified at sintering temperatures no less than  $870^\circ\text{C}$ . The grain shapes were similar with each other for  $\text{Zr, Sn,}$  or  $\text{W}$  substituted  $\text{Bi}_3\text{NbO}_7$  ceramics because of the same crystalline phase. The grain size lay in  $1$ – $4$  and  $0.5$ – $3\text{ }\mu\text{m}$  for the  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{6.95}$  ceramics ( $M = \text{Zr, Sn}$ ) and the  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics, respectively. In the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic, two kinds of grains were observed. Combining with the XRD results in Fig. 1, it can be declared that the principal part of the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic was fluorite-type  $\text{Bi}_3\text{NbO}_7$  phase which presented as bigger grains, and the smaller grains embedded in the larger ones were corresponding to  $\text{Bi}_2\text{Ti}_2\text{O}_7$  phase.

Fig. 3 (a) shows the dielectric frequency spectrum at room



**Fig. 2.** SEM images of as-fired surface of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  (a),  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$  (b),  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$  (c) and  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  (d) ceramics sintered at 870 °C for 2 h.



**Fig. 3.** Dielectric frequency spectrum at room temperature (a) and temperature characteristics at 100 KHz (b) for  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) sintered at 930 °C for 2 h.

temperature for  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) sintered at 930 °C for 2 h, and Table 1 presents their dielectric properties at 100 KHz. It was seen that  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$  ceramics possessed similar dielectric properties with  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$  ceramics.  $\text{W}^{6+}$  substituted  $\text{Bi}_3\text{NbO}_7$  ceramics possessed much higher dielectric constant (112.1 at 100 KHz) and lower dielectric loss ( $< 1.0 \times 10^{-4}$ ). In the fluorite structure of  $\delta$ - $\text{Bi}_2\text{O}_3$ , a quarter of oxide ion sites is vacant ( $\text{BiO}_{1.5}\text{VO}_{0.5}$ ). The oxide ion vacancies, which results in high dielectric loss, are available for its ion-conducting properties but deleterious for its dielectric

properties. Substitution of 25 mol% of  $\text{Bi}^{3+}$  by  $\text{Nb}^{5+}$  results in a room temperature-stable cubic  $\delta$ -phase of formula  $\text{Bi}_3\text{NbO}_7$ . This results in a lower number of oxide ion vacancies,  $\text{Bi}_{0.75}\text{Nb}_{0.25}\text{O}_{1.75}\text{VO}_{0.25}$ . The substitution of  $\text{Nb}^{5+}$  by tetravalent cations, such as  $\text{Zr}^{4+}$  and  $\text{Sn}^{4+}$ , would increase the number of oxide ion vacancies, while the substitution of  $\text{Nb}^{5+}$  by hexavalent cations, such as  $\text{W}^{6+}$  would result in a decrease in vacancy concentration [22]. Thus the dielectric loss causing by ion-conducting in  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics is much smaller than that in  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$  and  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$  ceramics. Compared with  $\text{Bi}_3\text{NbO}_7$ , the dielectric loss of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic increased greatly because of the second phase of  $\text{Bi}_2\text{Ti}_2\text{O}_7$ . The dielectric temperature characteristics at 100 KHz for  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) sintered at 930 °C for 2 h are shown in Fig. 3(b), and the TCC values calculated with formula (2) are listed in Table 1. The  $\epsilon_r$  of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Zr, Sn, W, } \delta = \pm 0.05$ ) ceramics increased linearly with measuring temperature in the temperature range from room temperature (RT) to 200 °C, and the TCC values were +252.6, +236.8, and +5.3 ppm/°C, respectively. The TCC value of  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics was near to zero, and it can be used as a new temperature stable dielectric material. The dielectric

losses of the  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Zr, Sn, W, } \delta = \pm 0.05$ ) ceramics increased exponentially with measuring temperature because the ion conductivity increased exponentially with measuring temperature, but they can maintain low values ( $\sim 10^{-3}$ ) when temperature was lower than 100 °C. The  $\epsilon_r$  and  $\text{tan}\delta$  of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic increased greatly when temperature was higher than 100 °C because of the influence of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  phase.

The microwave dielectric properties of  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) sintered at 930 °C for 2 h were shown in Table 1. The  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramic showed a higher

**Table 1**

Dielectric properties at 100 KHz and microwave (MW) region for  $\text{Bi}(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti, Zr, Sn, W, } \delta = \pm 0.05$ ) sintered at 930 °C for 2 h, and microwave dielectric properties of  $\text{Bi}_3\text{NbO}_7$ ,  $\text{Bi}_3(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_7$ ,  $\text{Bi}_3(\text{Nb}_{0.4}\text{Ta}_{0.6})\text{O}_7$  and  $\text{Bi}_3\text{TaO}_7$  ceramics reported by references.

Sample	$\epsilon_r$ (100 KHz)	$\text{Tan}\delta$ ( $10^{-4}$ )	TCC (ppm/°C)	Structure	$\epsilon_r$ (MW)	Qf (GHz)	TCF (ppm/°C)	Ref.
M = Ti	101.0	32.7	+208.5	Cubic	87.1	240	-133	This work
M = Zr	96.8	6.4	+252.6	Cubic	79.2	190	-168	This work
M = Sn	98.3	6.3	+236.8	Cubic	79.5	210	-160	This work
M = W	112.1	1.0	+5.3	Cubic	92.4	260	-34	This work
$\text{Bi}_3\text{N}$	—	—	—	Cubic	100	300	-200	[13,14]
$\text{Bi}_3\text{N}$	—	—	—	Cubic	95	230	-113	[16]
$\text{Bi}_3\text{NV}_{0.1}$	—	—	—	Tetragonal	80	615	-22	[17]
$\text{Bi}_3\text{NT}_{0.6}$	—	—	—	Tetragonal	72	1189	+12	[15]
$\text{Bi}_3\text{T}$	—	—	—	Cubic	65	560	-70	[16]

$\text{Bi}_3\text{N}$ :  $\text{Bi}_3\text{NbO}_7$ ;  $\text{Bi}_3\text{NV}_{0.1}$ :  $\text{Bi}_3(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_7$ ;  $\text{Bi}_3\text{NT}_{0.6}$ :  $\text{Bi}_3(\text{Nb}_{0.4}\text{Ta}_{0.6})\text{O}_7$ ;  $\text{Bi}_3\text{T}$ :  $\text{Bi}_3\text{TaO}_7$ .

permittivity of 92.4, a Qf value of 260 GHz, and a near zero TCF value of  $-34$  ppm/ $^{\circ}$ C. Comparing with  $\text{Bi}_3\text{NbO}_7$  ceramics [16], the TCF value was improved greatly by W substitution for Nb, and the dielectric loss (Qf value) maintained the same level. Structure analysis with neutron diffraction profiles shows that  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramic exhibits a defect fluorite structure with evidence of superlattice ordering of the oxide ion sublattice, and  $\text{Nb}^{5+}$  and  $\text{W}^{6+}$  are believed to exhibit six-coordinate geometry [22]. The higher cation charge of  $\text{W}^{6+}$  compared to  $\text{Nb}^{5+}$  results in reduced ionic mobility. The structure of  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramic is beneficial to its Qf value and the stability of permittivity with frequency. The dielectric permittivity of  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics maintained a high value in comparison to V or Ta substituted  $\text{Bi}_3\text{NbO}_7$  ceramic [15,16], because the  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramics crystallized as a cubic structure instead of a tetragonal structure. It means that it was a great success to improve the microwave dielectric properties of  $\text{Bi}_3\text{NbO}_7$  ceramic by proper amount of W substitution for Nb. The permittivities of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Zr}_{0.1})\text{O}_{6.95}$  and  $\text{Bi}_3(\text{Nb}_{0.9}\text{Sn}_{0.1})\text{O}_{6.95}$  ceramics decreased to 79.2 and 79.5, respectively, and their Qf values were a little lower than pure  $\text{Bi}_3\text{NbO}_7$  ceramics. Although the dielectric loss of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic was much higher at low frequency, the Qf value in the microwave region of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic was comparable to that of  $\text{Bi}_3\text{NbO}_7$  ceramic. Dielectric loss is a function of frequency. Usually, dielectric loss decreases with frequency, which is related with polarization. When the frequency increases to microwave region, the dipolar and space charge polarization are weakened, and the dielectric loss decreases greatly correspondingly. In the  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic, the dielectric loss from  $\text{Bi}_2\text{Ti}_2\text{O}_7$  phase decreased greatly in the microwave region, which result in the relatively higher Qf value of  $\text{Bi}_3(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_{6.95}$  ceramic.

#### 4. Conclusions

$\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Ti}, \text{Zr}, \text{Sn}, \text{W}$ ,  $\delta = \pm 0.05$ ) ceramics were fabricated by solid state reaction method. Fluorite-type solid solutions were obtained in the  $\text{Bi}_3(\text{Nb}_{0.9}\text{M}_{0.1})\text{O}_{7+\delta}$  ceramics ( $\text{M} = \text{Zr}, \text{Sn}, \text{W}$ ,  $\delta = \pm 0.05$ ) with sintering temperatures about  $900$   $^{\circ}$ C. The dielectric properties were studied and the results showed that the dielectric properties of  $\text{Bi}_3\text{NbO}_7$  ceramics were modified by 10 mol% W substitution for Nb. A temperature stable dielectric material of  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramic was introduced.

The  $\text{Bi}_3(\text{Nb}_{0.9}\text{W}_{0.1})\text{O}_{7.05}$  ceramic sintered at  $930$   $^{\circ}$ C for 2 h possessed good microwave dielectric properties with a high permittivity of 92.4, a Qf value of 260 GHz, and a near zero TCF value of  $-34$  ppm/ $^{\circ}$ C.

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