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Short communication

Temperature stable high K microwave dielectric ceramics of Bi_3NbO_7 doped by V_2O_5

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Abstract

Low firing microwave dielectric ceramics $Bi_3(Nb_{1-x}V_x)O_7$ ($x=0.0$, 0.1, 0.2, 0.3, and 0.5) were prepared by the solid state reaction method. Sintering behavior, crystalline structure, microstructure, and microwave dielectric properties were studied. Temperature stable low-firing microwave dielectric ceramics with high permittivity were obtained in the $Bi_3(Nb_{1-x}V_x)O_7$ system when $x=0.1$ and 0.2. The $Bi_3(Nb_{0.9}V_{0.1})O_7$ and $Bi_3(Nb_{0.8}V_{0.2})O_7$ ceramics sintered at 870 °C for 2 h were found to possess high permittivity of 80 and 76, Qf (quality factor) values of 615 and 460 GHz, and TCF (temperature coefficient of frequency) values of −22 and +3.3 ppm/°C, respectively.

Keywords: Sintering; Dielectric properties; Capacitors

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 (ε_r) materials (since the size of resonators is inversely proportional to $\sqrt{\varepsilon_r}$) 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. More recently, by applying low-temperature co-fired ceramic (LTCC) technology, passive elements have been integrated in monolithic, highly reliable, and robust LTCC modules that consist of several layers of ceramic substrates with integrated elements (inductors, capacitors, resonators), which are interconnected with three-dimensional strip-line circuitry [1]. Microwave dielectric ceramics with high permittivity ($\varepsilon_r > 80$) has been widely studied [2–8], such as $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$, Bi_2O_3-TiO_2, $CaTiO_3$-$Li_{1/2-3x}Sm_{1/2+x}TiO_3$ system, while most of them need high sintering temperatures (> 1100 °C). The Bi_3NbO_7 ceramics possess low sintering temperature and good microwave dielectric properties and have attracted much attention in recent years. Valant et al. studied microwave dielectric properties of the Bi_3NbO_7 ceramics and found that the cubic Bi_3NbO_7 (permittivity of 100, Qf=300 GHz, TCF=−200 ppm/°C) and tetragonal Bi_3NbO_7 (permittivity of 91, Qf=730 GHz, TCF=+100ppm/°C) did not react with Ag electrode [9–12], and they were suitable for LTCC modules and microwave application if their TCF value could be modified to near zero.

The quinquevalent ion V^{5+} substitution for Nb^{5+} has improved the sintering behaviors and microwave dielectric properties of some typical Nb-based microwave dielectrics, such as $BiNbO_4$ [13] and $LiNb_{0.6}Ti_{0.5}O_3$ [14]. In addition, based on the similarity of chemical properties with V^{5+} and Nb^{5+}, it can be anticipated that V^{5+} substitution for Nb^{5+} might be a good choice to improve the sintering behavior and microwave dielectric properties of Bi_3NbO_7 compound. In the present work, V_2O_5-doped Bi_3NbO_7 compounds, that is, $Bi_3(Nb_{1-x}V_x)O_7$ ($x=0.0$, 0.1, 0.2, 0.3, and 0.5), were prepared by solid state reaction method. The sintering behavior,

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phase structure, microstructure, and microwave dielectric properties of $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.0, 0.1, 0.2, 0.3 and 0.5) ceramics were studied.

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd, China), Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co, Ltd, China) and V_2O_5 (>99%, Zhu-Zhou Harden Alloys Co, Ltd, China) were mixed according to the composition $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.0, 0.1, 0.2, 0.3, and 0.5) and ball-milled for 5 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) with zirconia balls (2 mm in diameter) and alcohol as milling media. Subsequently, the mixtures were dried at 105 °C and calcined at 700 °C for 4 h to obtained the $Bi_3(Nb_{1-x}V_x)O_7$ compounds. Then, the compounds were re-milled for 5 h with Zirconia balls and deionized water. After being dried, the compounds were granulated into pellets with PVA binder and pressed into cylinders (10 mm in diameter and 4∼5 mm in height) in a steel die under uniaxial pressure of 20 kN/cm^2. Then the cylinder samples were sintered from 810 to 990 °C for 2 h.

Crystalline structures of $Bi_3(Nb_{1-x}V_x)O_7$ samples were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). The densities of sintered specimens, as a function of sintering temperature, were measured by the liquid displacement method using deionized water as the liquid (Archimedes method). To investigate the morphology of samples, as-fired surface of sintered specimens were observed by scanning electron microscopy (SEM) (JEOL JSM-6460, Japan). Microwave dielectric properties were measured by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA). The temperature coefficients of resonant frequency (TCF) were measured with the 8720ES network analyzer and a DELTA 9023 temperature chamber (Delta Design, Poway, CA) using the $TE_{01\delta}$ shielded cavity method. The TCF value was calculated by the following formula:

$$TCF = \frac{f_{85} - f_{25}}{f_{25} \times (85-25)} ppm/^oC \quad (1)$$

where f_{85}, f_{25} were the $TE_{01\delta}$ resonant frequencies at the measuring temperature 85 °C and at room temperature (25 °C) respectively.

3. Results and discussion

Room temperature X-ray diffraction patterns of the $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.0, 0.1, 0.2, 0.3, and 0.5) ceramics sintered at 900 °C for 2 h are shown in Fig. 1. Pure Bi_3NbO_7 crystallize in a cubic structure after being sintered at 900 °C and this result corresponds well with literatures' reports [10–12]. The $Bi_3(Nb_{0.9}V_{0.1})O_7$ and $Bi_3(Nb_{0.8}V_{0.2})O_7$ ceramics crystallize in a tetragonal structure, as shown in Fig. 1. It indicates that V substitution for Nb in the Bi_3NbO_7 ceramic led the composition to crystallize in a tetragonal phase. The cell

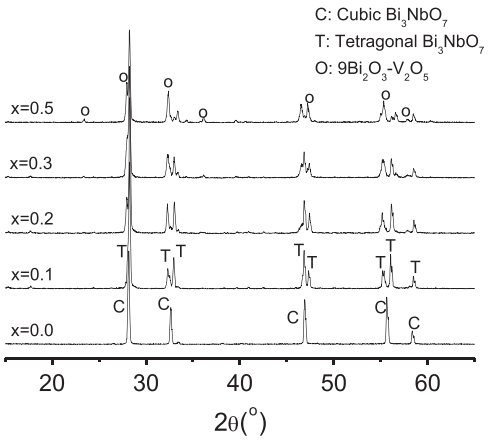

Fig. 1. X-ray diffraction patterns of $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.0, 0.1, 0.2, 0.3, and 0.5) ceramics sintered at 900 °C for 2 h.

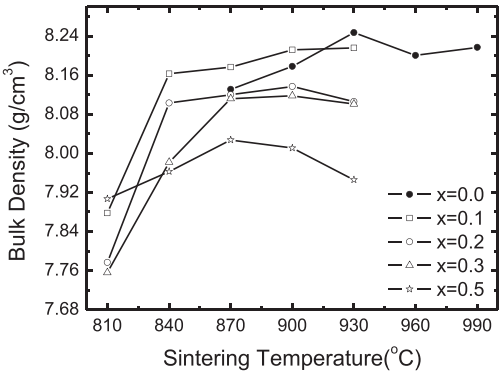

Fig. 2. Bulk densities of $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.0, 0.1, 0.2, 0.3, and 0.5) ceramics as a function of sintering temperature.

parameters of $Bi_3(Nb_{0.9}V_{0.1})O_7$ are $a=b$=5.430 Å, c=5.524 Å, $\alpha=\beta=\gamma$=90 ° (cell parameter of cubic Bi_3NbO_7 are $a=b=c$= 5.478 Å) When the content of V substitution increased to 30 mol% (x=0.3), Bi-rich phase of $9Bi_2O_3$-V_2O_5 [15,16] appeared in the samples.

Bulk densities of the $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.0, 0.1, 0.2, 0.3, and 0.5) ceramics as a function of sintering temperature are shown in Fig. 2. Bulk density of pure Bi_3NbO_7 ceramic reached the maximum value when sintering temperature increased to 930 °C. V substitution for Nb effectively decreased sintering temperature of the Bi_3NbO_7 ceramic. Bulk densities of the $Bi_3(Nb_{0.9}V_{0.1})O_7$ and $Bi_3(Nb_{0.8}V_{0.2})O_7$ ceramics got the saturated values when sintering temperature increased to 840 °C. When the content of V substitution increased to 30 and 50 mol%, the optimal sintering temperature increased to 870 °C, which might be caused by appearance of the secondary phase.

SEM and BEI images of as-fired surface of the $Bi_3(Nb_{1-x}V_x)O_7$ ceramics are shown in Fig. 3. All the $Bi_3(Nb_{1-x}V_x)O_7$ (x=0.1, 0.2, 0.3, 0.5) ceramics could be well densified when the sintering temperature was around 840 °C and grain size of the $Bi_3(Nb_{1-x}V_x)O_7$ ceramics lay between 1∼3 μm when the V substitution was no higher than 30 mol%. Two kinds of grains were observed obviously in the

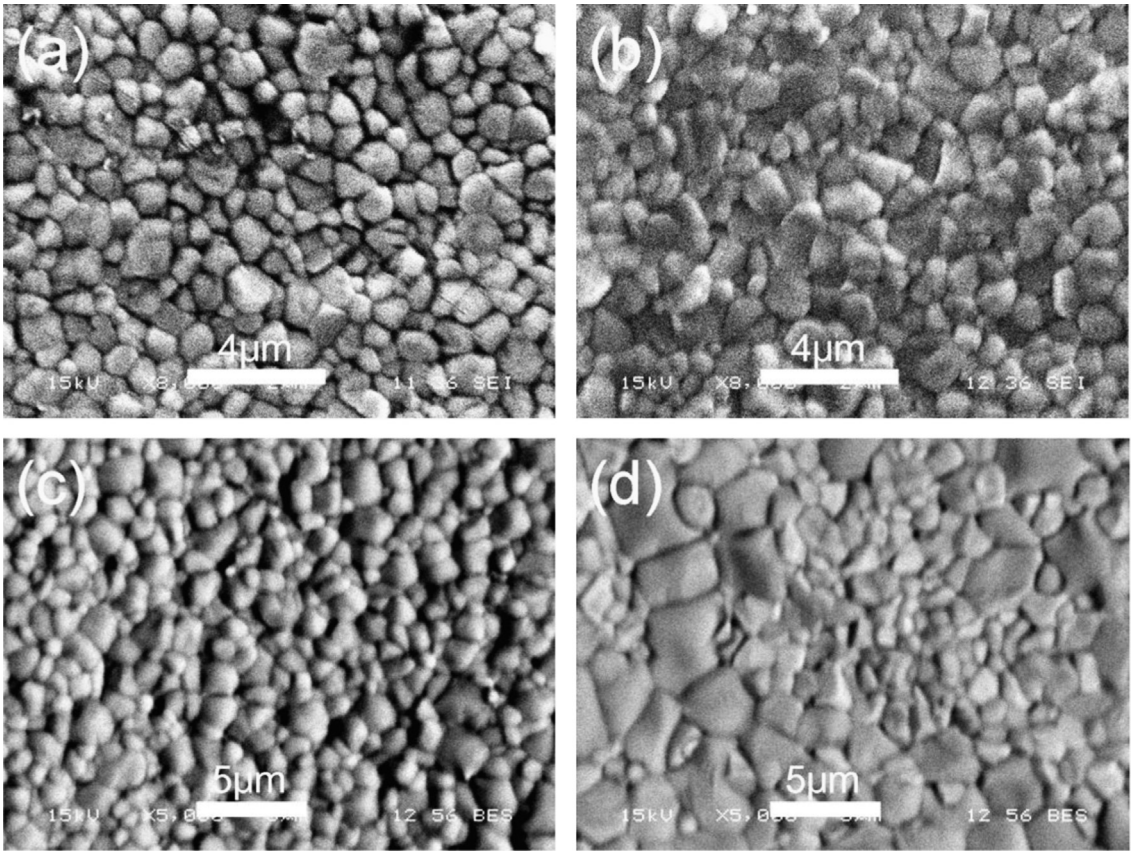

Fig.3. SEM images of as-fired surface of $Bi_3(Nb_{1-x}V_x)O_7$ ceramics sintered at 840 °C for 2 h: (a) $x=0.1$, (b) $x=0.2$; Backscatter electron image (BEI) of as-fired surface of $Bi_3(Nb_{1-x}V_x)O_7$ ceramics sintered at 840 °C for 2 h: (c) $x=0.3$, (d) $x=0.5$.

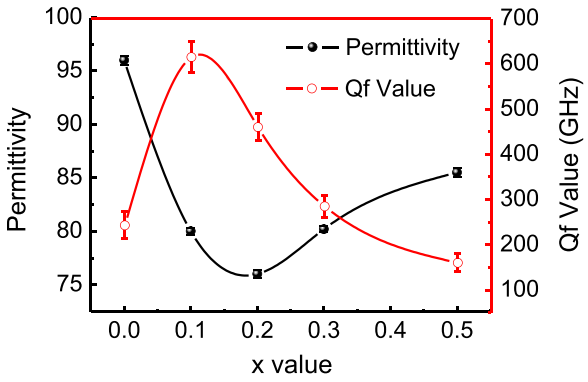

Fig. 4. Microwave permittivity (a) and Qf values (b) of $Bi_3(Nb_{1-x}V_x)O_7$ ceramics.

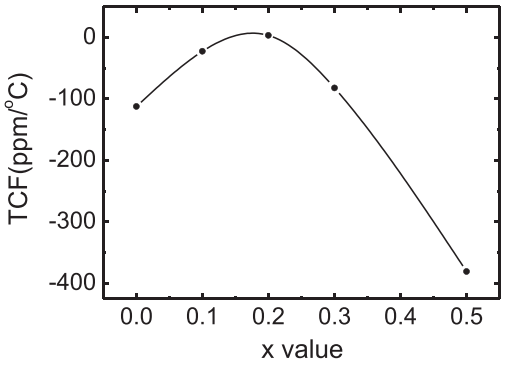

Fig. 5. TCF value of $Bi_3(Nb_{1-x}V_x)O_7$ ceramics as a function of x values.

BEI image of $Bi_3(Nb_{0.5}V_{0.5})O_7$ ceramic, as shown in Fig.3 (d). The grains with brighter color and those with darker color and bigger size were corresponding to the Bi-rich phase of $9Bi_2O_3$-V_2O_5 and $Bi_3(Nb_{1-x}V_x)O_7$ phase, respectively.

Microwave dielectric permittivity and Qf values of the $Bi_3(Nb_{1-x}V_x)O_7$ ceramics are show in Fig. 4. Permittivity and Qf value of pure Bi_3NbO_7 ceramic were 96 and 243 GHz respectively, which agreed well with those reported by Valant et al. [10,11]. Permittivity of the $Bi_3(Nb_{0.9}V_{0.1})O_7$ ceramic decreased to about 80, and the Qf value increased to 615 GHz. There are two main factors that are responsible for this result. One is the phase transformation from cubic phase to tetragonal phase caused by V substitution (as shown in Fig. 1), and the other is the smaller ionic polarizability of V^{5+} (2.92 $Å^3$) than that of Nb^{5+} (3.97 $Å^3$) [17]. When the content of V substitution increased to 30 and 50 mol%, dielectric permittivity increased and Qf value decreased seriously, which was mainly caused by the secondary phase of $9Bi_2O_3$-V_2O_5.

TCF value of the $Bi_3(Nb_{1-x}V_x)O_7$ ceramics shifted from −112 to 3.3 ppm/°C when the content of V substitution increased from 0 to 20 mol%, as shown in Fig.5. Then, it shifted to negative value when the content of V substitution

increased further. Temperature stable (-30 ppm/°C < TCF < 30 ppm/°C) low-firing microwave dielectric ceramics were obtained in the $Bi_3(Nb_{1-x}V_x)O_7$ system when $x=0.1$ and 0.2. The $Bi_3(Nb_{0.9}V_{0.1})O_7$ and $Bi_3(Nb_{0.8}V_{0.2})O_7$ ceramics sintered at 870 °C for 2 h possessed high permittivity of 80 and 76, Qf values of 615 and 460 GHz, and TCF values of -22 and $+3.3$ ppm/°C, respectively.

4. Conclusions

$Bi_3(Nb_{1-x}V_x)O_7$ ceramics were prepared by solid state reaction method. All the ceramics could be well densified when the sintering temperatures were 840∼930 °C The V substitution for Nb in the Bi_3NbO_7 ceramic led the composition to crystallize in a tetragonal phase. When the content of V substitution increased to 30 mol% ($x=0.3$), the Bi-rich phase of $9Bi_2O_3$-V_2O_5 appeared in the samples. Correspondingly, permittivity of the $Bi_3(Nb_{1-x}V_x)O_7$ ceramics decreased from 96 to 76 and the TCF value shifted from -112 to 3.3 ppm/°C when the content of V substitution increased from 0 to 20 mol % ($x=0.2$), while the permittivity increased and the TCF value shifted towards negative because of the appearance of secondary phase when the content of V substitution increased further. Temperature stable low-firing microwave dielectric ceramics with high permittivity were obtained in the $Bi_3(Nb_{1-x}V_x)O_7$ system when $x=0.1$ and 0.2. The $Bi_3(Nb_{0.9}V_{0.1})O_7$ and $Bi_3(Nb_{0.8}V_{0.2})O_7$ ceramics sintered at 870 °C for 2 h possessed high permittivity of 80 and 76, Qf values of 615 and 460 GHz, and TCF values of -22 and $+3.3$ ppm/°C, respectively.

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