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Phase evolution and dielectric properties of fluorite-type $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ ceramics (M=Ti, Zr, Sn, W, δ=±0.05)

Li-Xia Pang [a], Di Zhou [b, *], Wei-Guo Liu [a], Zhen-Xing Yue [c]

[a] Laboratory of Thin Film Techniques and Optical Test, Xi'an Technological University, Xi'an 710032, Shaanxi, China
[b] Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China
[c] State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

Phase structure and dielectric behavior of $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ ceramics (M = Ti, Zr, Sn, W, δ = ±0.05) were discussed. Cubic fluorite solid solutions $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ (M = Zr, Sn, W, δ = ±0.05) were obtained through a conventional solid state reaction method. An analysis of the microwave dielectric properties showed that substitution of Nb^{5+} by W^{6+} was favorable to improving the temperature coefficient of resonant frequency (TCF value). A temperature stable dielectric material $Bi_3(Nb_{0.9}W_{0.1})O_{7.05}$ was introduced. The $Bi_3(Nb_{0.9}W_{0.1})O_{7.05}$ 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 ppm/°C.

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 $\varepsilon_r^{1/2}$) 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 threedimensional 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 (ε_r > 80) has been widely studied [3–8], while most of them need high sintering temperatures. In the Bi_2O_3–Nb_2O_5 system, $BiNbO_4$ and Bi_3NbO_7 possess low sintering temperatures and good microwave dielectric properties, and have attracted much attention in recent years [9,10]. $BiNbO_4$ ceramics have good properties for microwave application and LTCC, but the reaction between $BiNbO_4$ and the silver electrode limited its further application [11,12]. Valant et al. [12–14] studied the crystalline structure and microwave dielectric properties of Bi_3NbO_7 ceramics, and they found that the cubic incommensurate phase Bi_3NbO_7 exhibited a high permittivity of 100, a lower Qf value of 300 GHz and a high negative TCF value of 200 ppm/°C. The cubic incommensurate phase Bi_3NbO_7 underwent an order-disorder phase transition into a commensurate tetragonal phase at temperatures bellow 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 ppm/°C. Meanwhile, both the cubic incommensurate phase and the commensurate tetragonal phase Bi_3NbO_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 $Bi_3(Nb_{1-x}Ta_x)O_7$ [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 $Bi_3(Nb_{0.4}Ta_{0.6})O_7$ 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 Bi_3NbO_7 ceramics transmitted into commensurate tetragonal phase

* Corresponding author.
E-mail address: zhoudi1220@gmail.com (D. Zhou).

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by means of substitution of Nb^{5+} by 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 Nb^{5+} by tetravalent cations such as Ti^{4+}, Zr^{4+} and Sn^{4+}, and/or hexavalent cations such as W^{6+} in Bi_3NbO_7. The sintering behavior, phase structure, microstructure, and dielectric properties of $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ (M = Ti, Zr, Sn, W, $\delta = \pm 0.05$) ceramics were studied.

2. Experimental procedure

Proportionate amounts of reagent-grade Bi_2O_3 (99%, Shu-Du Powders Co. Ltd, China), Nb_2O_5 (>99%, Guo-Yao Co, Ltd, Shanghai, China), TiO_2 (>99%, Linghua Co. Ltd, Zhaoqing, China), ZrO_2 (>99.5%, Xinxing Co.Ltd, Yixing, China), SnO_2 (>99.5%, Xinxing Co. Ltd, Yixing, China), and WO_3 (99%, Tianjin, China) were weighed according to the stoichiometric formulation of $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ (M = 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 °C for 4 h. After being crushed and re-milled for 5 h using the 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 °C for 2 h.

The crystalline structures of samples were investigated using X-ray diffraction with Cu Kα 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 °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 $TE_{01\delta}$ 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:

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

where f_{85} and f_{25} are the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively;

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

where ε_{85} and ε_{25} are the permittivity at 100 kHz at 85 and 25 °C, respectively.

3. Results and discussions

According to the literature [18,19], there are three types of superstructures in the Nb-doped δ-Bi_2O_3 solid solution system. The structure of cubic Bi_3NbO_7 is the so-called type II superstructure, which is an incommensurate superstructure extends from 6.25 to 26.0 mol% of Nb_2O_5 in the Bi_2O_3–Nb_2O_5 system. Fig. 1 presents the XRD patterns of $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ (M = Ti, Zr, Sn, W, $\delta = \pm 0.05$) ceramics sintered at 930 °C for 2 h. As shown in Fig. 1 (a~c), all peaks can be indexed on a cubic cell with space group *Fm-3m*, except the superlattice ordering diffraction peak at $2\theta = 33.7$, which was consistent with the XRD pattern of parent Bi_3NbO_7 in the literature [14,16,17]. Single phase with incommensurate cubic fluorite-type structure was obtained in the $Bi_3(Nb_{0.9}Zr_{0.1})O_{6.95}$, $Bi_3(Nb_{0.9}Sn_{0.1})O_{6.95}$, and $Bi_3(Nb_{0.9}W_{0.1})O_{7.05}$ ceramics, while in the $Bi_3(Nb_{0.9}Ti_{0.1})O_{6.95}$ ceramics, a small amount of $Bi_2Ti_2O_7$ phase appeared (as shown in Fig. 1 (d)).

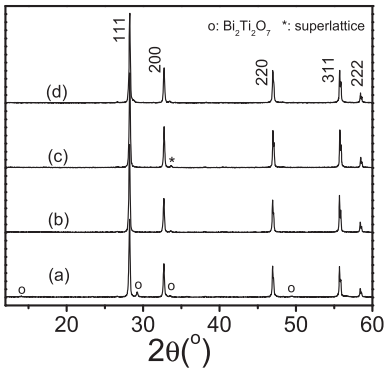

Fig. 1. XRD patterns of $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ ceramics (M = Ti, Zr, Sn, W, $\delta = \pm 0.05$) sintered at 930 °C for 2 h: (a) $Bi_3(Nb_{0.9}Ti_{0.1})O_{6.95}$, (b) $Bi_3(Nb_{0.9}Zr_{0.1})O_{6.95}$, (c) $Bi_3(Nb_{0.9}Sn_{0.1})O_{6.95}$, (d) $Bi_3(Nb_{0.9}W_{0.1})O_{7.05}$.

The ionic radii of Ti^{4+}, Zr^{4+}, Sn^{4+} and W^{5+} were 0.605, 0.72, 0.69 and 0.60 Å, respectively, and the ionic radius of Nb^{5+} was 0.64 Å, as suggested by Shannon [20]. There was no clear evidence suggesting that the solid solubility of Bi_3NbO_7 substituted by M (M = Ti, Zr, Sn and W) is related with ionic radius. As described above, the cubic Bi_3NbO_7 is a kind of Nb-doped δ-Bi_2O_3 solid solution with defect fluorite δ-Bi_2O_3 as the basic structure. According to the phase diagrams [21], the structure of δ-Bi_2O_3 can be stabilized at room temperature by doping Bi_2O_3 with a large number of metallic cations, such as trivalent rare earth, pentavalent V^{5+}, Nb^{5+} and Ta^{5+}, or hexavalent W^{6+} and Mo^{6+}, except tetravalent Zr^{4+}, Ti^{4+} and Sn^{4+}. I. Abrahams' work [22] showed that W^{6+} has a very favorable solution energy for Nb^{5+} substitution in Bi_3NbO_7 through computer simulation techniques and δ-Bi_2O_3 solid solutions can also be obtained in the $Bi_3Nb_{1-x}W_xO_{7+x/2}$ system when $x \leq 0.2$. Same result was obtained in the $Bi_3Nb_{1-x}Zr_xO_{7-x/2}$ system in the composition range $0.0 \leq x \leq 0.40$ [23], which means that the solution energy of Zr^{4+} can be lowered by combining with Nb^{5+} substitution. In this work, δ-Bi_2O_3 solid solutions with incommensurate cubic fluorite-type structure were also obtained in the $Bi_3(Nb_{0.9}Sn_{0.1})O_{6.95}$ ceramics, as well as in the $Bi_3(Nb_{0.9}Zr_{0.1})O_{6.95}$ and $Bi_3(Nb_{0.9}W_{0.1})O_{7.05}$. It means that the solution energy of Sn^{4+} can also be lowered by combining with Nb^{5+} substitution. In the $Bi_3(Nb_{0.9}Ti_{0.1})O_{6.95}$ ceramics, the appearance of the secondary phase of $Bi_2Ti_2O_7$ with face-centered cubic structure (space group *Fd-3m*) suggests that the solution energy of Ti^{4+} is still too high to form a δ-Bi_2O_3 solid solution.

SEM images of as-fired surface of $Bi_3(Nb_{0.9}M_{0.1})O_{7+\delta}$ ceramics (M = 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 °C. The grain shapes were similar with each other for Zr, Sn, or W substituted Bi_3NbO_7 ceramics because of the same crystalline phase. The grain size lay in 1–4 and 0.5–3 um for the $Bi_3(Nb_{0.9}M_{0.1})O_{6.95}$ ceramics (M = Zr, Sn) and the $Bi_3(Nb_{0.9}W_{0.1})O_{7.05}$ ceramics, respectively. In the $Bi_3(Nb_{0.9}Ti_{0.1})O_{6.95}$ 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 $Bi_3(Nb_{0.9}Ti_{0.1})O_{6.95}$ ceramic was fluorite-type Bi_3NbO_7 phase which presented as bigger grains, and the smaller grains embedded in the larger ones were corresponding to $Bi_2Ti_2O_7$ phase.

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