The influence of Bi content on dielectric properties of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ceramics

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A kind of lead-free dielectric materials, such as the bismuth layered perovskite-type structure of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$), was prepared by the conventional solid-state method at 800°C and sintered at 1100°C . The variation of structure and electrical properties with different Bi concentration was studied. All the $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) samples exhibited a single structured phase. SEM could be a better approach to present the microstructure of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) ceramics. It could be found that the grain size of $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ sintered at 1100°C was smaller than that of others among the five samples through grain size mechanics. Through impedance spectra analysis, we knew, when the Bi content was fixed, that the dielectric constant and the loss values increased with the decrease of frequency. The Curie temperature of the five samples was about 670°C . In particular, while at the frequency of 100 kHz, the lowest loss was 0.001 when Bi content was 3.98. The $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ ceramics with the minimum grain size had highest dielectric constant and the relatively low loss. Due to its high Curie temperature, high permittivity and low loss, the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) ceramics have a broad application prospect in high density memory, generator, sensor, ferroelectric tunnel junctions and so on.

Keywords: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$; dielectric properties; permittivity; loss.

1. Introduction

The research of materials based on ferroelectric and piezoelectric ceramics has become intense over recent years. Large numbers of studies have shown that dielectric ceramic had been applied in electronic devices such as sensors, actuators,¹ and ultrasonic transducers due to its promising dielectric and piezoelectric properties. However, most conventional piezoelectric and ferroelectric ceramics were lead-containing.² Some of the lead containing materials did not meet the requirements of green environmental protection, which inspired us to study lead-free piezoelectric materials. The lead-free bismuth layered structure ferroelectrics (BLSFs) have surged over recent years, mainly driven by the necessity to reduce or replace $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ -based piezoelectric materials, which often induced ferroelectricity, such as BiFeO_3 .^{3,4} According to the experimental results, we found $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) had maximum relative permittivity of 3,000 at 320°C (T_{max}) and possessed a distorted perovskite structure with extensive chemical, cation-displacement and octahedral tilt disorder.^{5,6} in the application of high-temperature, high-permittivity ceramic capacitors. However, NBT had low operating temperature because of its high leakage

conductivity, and low Curie temperature,⁷⁻⁹ which limited the application of NBT.

In practice, high the constant, high Curie temperature and low loss are necessary. So, we are looking for ceramics to meet the demand of production. As we all know, BIT is widely used in the military, acoustics and modern science and technology fields. BIT is a typical BLSF, known as Aurivillius family of oxides, which has been considered as a candidate for the high-temperature ferro/piezo-electric devices.¹⁰⁻¹² It is composed of pseud-perovskite layers $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{4-}$ and two bismuth oxide $(\text{Bi}_2\text{O}_2)^{2+}$ layers' alternating arrangement along the c-axis. Their formulas are usually expressed as $[(\text{Bi}_2\text{O}_2)^{2+}]_2(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{4-}$ ^{13,14} wherein A cations are in 12-fold coordination, and B cations are in 6-fold coordination. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$) consists of three perovskite-like layers between two fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ layers.

A great deal of scholars had studied its ferroelectric, piezoelectric and photoluminescence properties. Obviously, BIT had become hot in recent years. Jiang *et al.*¹⁵ found that NBT-BIT-0.50 La sample achieved the optimal d_{33} (23 pC/N) measured at room temperature, which was twice more than that of NBT-BIT (10 pC/N). Wei *et al.*¹⁶ found some

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Er^{3+} at $^4\text{F}_{9/2}$ levels produced red upconversion (UC) emissions. $\text{BiTi}_{1-x}\text{SbTi}_x\text{Er}^{3+}$ was also an important FE material. The values of $2P_r$ for $\text{BiTi}_{1-x}\text{SbTi}_x\text{Er}^{3+}$ ($x = 0.04$ and 0.15) reached about $14.7 \mu\text{C}/\text{cm}^2$ and $16.2 \mu\text{C}/\text{cm}^2$ at an applied electric field about $125 \text{ kV}/\text{cm}$. Gu *et al.*¹⁷ found V^{5+} -doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ had a strong optical absorption in both visible and UV wavelength regions. The 10 mol% V-doped BIT showed efficient photocatalytic ability.

However, the effect of the A-site doping on the properties is focused on thin films research. There are few reports on their dielectric properties for the influence of Bi content. So we wanted to explore a new dielectric material BIT which can overcome the shortcomings of NBT in experiment.^{18–21} We have conducted an experiment about the dielectric properties of BIT ceramics in order to find the microscopic mechanism of dielectric properties of BIT changes. We all knew that the microscopic mechanism was related to the structure. So, we changed the Bi content ($x = 0.04, 0.02, 0, -0.02, -0.04$). We also tested SEM in order to find out the influence of the structure and grain size on the dielectric properties. Finally, we found that the dielectric constant changed a lot and the loss had little difference at 100 kHz and 1 MHz sintered at 1100°C . The result shows that BIT ceramics are a promising base material for high-temperature capacitor because of their high dielectric properties.^{22–24}

2. Materials and Methods

$\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) ceramics were prepared by traditional solid-state sintering process. Raw materials of Bi_2O_3 (99.9% purity, Alpha) and TiO_2 (99.9% purity, Alpha) powders were mixed together thoroughly with ethanol in agate mortar for no less than 4 h and dried. The dried powders were calcined twice between 800°C and 900°C for 3 h. After each calcination, the powders were ball-milled overnight, re-milled, and shaped into pellets. $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) green bodies were pressed in a uniaxial steel die and pressed isostatically at 200 MPa. The samples were sintered between 1000°C and 1120°C for 2–3 h in a closed alumina crucible to minimize the loss of volatile bismuth oxide. High temperature silver paste was used on both sides of BIT ceramics to perform electric measurements.

Crystal structure of the samples was determined using X-ray diffraction (XRD) pattern analysis recorded by performing on a Japan MAXima_X XRD-7000 system, employing $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1506 \text{ nm}$) at 40 kV and 30 mA, with a step of $2^\circ/\text{min}$ and a range of 10°C – 80°C . The microstructures of the fractured surfaces were examined using a Scanning Electron Microscope (SEM s-4800, Japan). For dielectric measurements, the sintered pellets were ground and polished to 0.9 mm thickness. High temperature impedance spectroscopy (IS) measurements were performed using an impedance analyzer (Agilent 4194A, Agilent) in a non-inductively wound tube furnace. IS data were corrected for

sample geometry (thickness/area of pellet) and analyzed using ZView (Version 2.9c, Scribner Associates Inc., Southern Pines, NC). The relative permittivity and loss tangents were measured by an impedance analyzer (HP Agilent, 4192A Hewlett Packed, Santa Clara, CA) in the temperature range of 20°C – 725°C .

3. Result and Discussion

3.1. Microstructure analysis

X-ray diffraction (XRD) results of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) ceramics are shown in Fig. 1. We can obtain that, from XRD analysis results compared with the standard PDF card, the main peak of these samples was found in the $(\bar{1}17)$ plane position, and there were also peaks in the (111) (200) (0014) (220) positions, which indicated that the new material belonged to bismuth layered perovskite structure. In addition, the difference of Bi content could affect the peak value of the peak position of the ceramic. When $\text{Bi} = 4.04$, the peak value was significantly higher than the other peaks. So we could carry out the next step of testing.

Figure 2 shows the SEM images of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) sintered at 1100°C . When the content of Bi changes, no significant differences were found among five images, which indicated that the Bi^{3+} concentration did not influence the grain growth greatly. However, while the content of Bi was 3.98, the microstructure of the ceramic was relatively better than other samples. Excessive Bi content would lead to abnormal grain growth.

3.2. Effect of Bi content on dielectric properties

In Fig. 3, The relative permittivity (ϵ_r) of the samples sintered at 1100°C was measured under different frequencies (10 kHz, 100 kHz, 250 kHz, and 1 MHz) at 1100°C when the content of Bi was 4.02. The permittivity and the peak value of the

Fig. 1. XRD diffraction patterns of $\text{Bi}_{3.96-4.04}\text{Ti}_3\text{O}_{12}$ ceramic samples sintered at 1100°C .

Fig. 2. The SEM micrographs of (a) $\text{Bi}_{3.96}\text{Ti}_3\text{O}_{11.94}$, (b) $\text{Bi}_{3.98}\text{Ti}_3\text{O}_{11.97}$, (c) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, (d) $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ and (e) $\text{Bi}_{4.04}\text{Ti}_3\text{O}_{12.06}$ sintered at 1100°C .

constant increased with the decrease of the frequency, and every curve exhibited the same shape. The constant almost unchanged when the temperature was below 200°C . When under 10 kHz, the values of the permittivity increased fleetly beyond 200°C . However, at the other frequencies (100 kHz, 250 kHz, and 1 MHz), the curve rose slightly. The greater the frequency was, the lower the line was in the figure.

Figure 4(a) shows the frequency dependence of the constant of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) sintering at 1100°C . The trend of all the curves of samples was similar. Before the temperature rose up to 200°C , the curves nearly had no change, and they rose steadily between 300°C and 500°C , although there were no changes when the temperature was at 500°C – 600°C . Then the constant started

to rise gradually until the temperature was at the Curie temperature. However, over the T_c , the constant decreased quickly. When x was 0.04, 0.02, 0, -0.02 , and -0.04 , the peak of the dielectric constant was, respectively, 1368.8, 2025.6, 1733.9, 2283.6 and 1536.0. In terms of the Curie temperature, $\text{Bi}_{3.98}\text{Ti}_3\text{O}_{11.97}$ ceramic had the biggest value (675°C). But the permittivity of $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ ceramic had the biggest peak value (2283.6).

In Fig. 4(b), the frequency was 1 MHz. The curve rose slowly while the temperature was below 300°C , but when the temperature was beyond 300°C , the permittivity increased sharply, and there was a ‘Λ’ shape of the curve at T_c . When x was 0.04, 0.02, 0, -0.02 , and -0.04 , $\epsilon_{r\text{max}}$ was, respectively, 503.3, 763.3, 872.8, 982.0 and 760.2. $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ ceramic still had the maximum dielectric constant.

Fig. 3. (Color online) The dielectric constant (ϵ_r) of $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ sintered at 1100°C under 10, 100, 250 KHz and 1 MHz.

3.3. Effect of Bi content on dielectric loss

In this research, we set up five different samples sintered at the same temperature (1100°C) to obtain the effect of the variation of Bi content on the dielectric loss ($\tan\delta$) of the $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) ceramics. As we could see from Fig. 5, every sample had a common observation that the lower the frequency was, the greater the loss was. It was not difficult to find that the trend of all the curves of samples was roughly the same. When the test temperature was below 200°C , the loss was relatively small, almost zero. Then the $\tan\delta$ showed a steady rise as the temperature increased until the maximum peak was reached. After the slightly decrease in loss, the curve started to rise sharply. When the frequency was 100 kHz, the minimum

Fig. 4. (Color online) The dielectric constant of the five ceramic samples under (a) 100 kHz and (b) 1 MHz sintered at 1100°C.

dielectric loss was 0.0019 when Bi content was 3.98. Under frequency at 1 MHz, the minimum loss was 0.0033 with Bi content at 3.98.

Scanning Figs. 4 and 6, by comparison, we could find that, at same frequency (100 kHz) and temperature, $\text{Bi}_{3.98}\text{Ti}_3\text{O}_{11.97}$ ceramic had the least value of the $\tan\delta$, when the content of Bi was 4.02, the greatest constant was 2283.6 and its minimum loss was 0.0033. When at T_c , $\text{Bi}_{3.98}\text{Ti}_3\text{O}_{11.97}$ had the maximum loss, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ had the minimum loss. In summary, as shown in Table 1, $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ ceramic had high permittivity and the low loss. It met the required permittivity for ferroelectric ceramics. The ceramics with high T_c can be applied to high-temperature field such as high-temperature capacitors.

When the A position of the Bi^{3+} ion is excessive, the excess positive charge mainly forms A vacancy to compensate. The formation of A vacancies enables lattice relaxation, and ion arrangement is not tight, which leads to easy production interstitial defects. In addition, the internal friction of material increases, which would increase the

dielectric loss. At the same time, due to the charge compensation, the vacancy of the A position leads to the production of oxygen vacancies, which would influence the dielectric properties.^{25–28}

(a)

(b)

Fig. 5. (Color online) The dielectric loss of $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ sintered at 1100°C under 10, 100, 250 KHz and 1 MHz.

Fig. 6. (Color online) The dielectric loss of the five ceramic samples under (a) 100 kHz and (b) 1 MHz sintered at 1100°C.

Table 1. Dielectric properties of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-15x}$ ceramic samples under 100 KHz and 1 MHz sintered at 1100°C.

Sample	Bulk density (g/cm ³)	$\epsilon_{r\max}$		tan $\delta_{\min}$	
		100 kHz	1 MHz	100 kHz	1 MHz
$\text{Bi}_{3.96}\text{Ti}_3\text{O}_{11.94}$	7.7536	1368.8	503.3	0.0466	0.1834
$\text{Bi}_{3.98}\text{Ti}_3\text{O}_{11.97}$	7.8137	2025.6	763.3	0.0019	0.0033
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	7.8037	1733.9	872.8	0.0062	0.0056
$\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$	7.8552	2283.6	982.0	0.0033	0.0052
$\text{Bi}_{4.04}\text{Ti}_3\text{O}_{12.06}$	7.1334	1536.0	760.2	0.0038	0.0051

4. Conclusion

- (1) All the samples were synthesized by conventional solid-state method and well sintered at an intermediate temperature (1100°C). Single-phase perovskite-type structure was successfully observed by XRD.
- (2) In this paper, electrical properties of $\text{Bi}_{4-x}\text{Ti}_3\text{O}_{12-1.5x}$ ($x = 0.04, 0.02, 0, -0.02, -0.04$) ceramics had been investigated by IS over a wide temperature range under different frequencies. The plots as a function of temperature indicated that the samples possess high constant and low loss. The highest permittivity reached 2283.6 ($x = -0.02$) and the lowest loss was 0.0019 ($x = 0.02$) under 100 kHz sintered at 1100°. With the increasing of frequency, relative permittivity and the loss decreased.
- (3) The tendency of the constants of the five ceramic samples with different Bi content was similar. Curie temperature is almost 670°C. $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ has the largest dielectric constant, the smaller dielectric loss, which indicated the $\text{Bi}_{4.02}\text{Ti}_3\text{O}_{12.03}$ ceramic was a promising base material.

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