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Synthesis, phase transformation and dielectric properties of sol–gel derived $Bi_2Ti_2O_7$ ceramics

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Abstract

Sol–gel derived $Bi_2Ti_2O_7$ ceramic powders have been prepared from methoxyethoxides of bismuth and titanium (molar ratio of Ti/Bi = 1.23 and water/alkoxides = 1.31). The $Bi_2Ti_2O_7$ phase was stable at a low temperature (700 °C), but it then transformed into mixed phases of $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$ at 850–1150 °C. The single phase of $Bi_2Ti_2O_7$ reoccurred at 1200 °C. Dielectric properties and ferroelectric behavior of samples sintered at 1150 and 1200 °C were examined. Under frequency of 1 MHz, samples sintered at 1150 and 1200 °C had a dielectric constant of 101.3 and 104.2, and a loss tangent of 0.0193 and 0.0145, respectively. Only the sample sintered at 1150 °C showed ferroelectric behavior, where remanent polarization is 3.77 $\mu C\,cm^{-2}$ and coercive field is 24 $kV\,cm^{-1}$. Thus, the $Bi_2Ti_2O_7$ did not exhibit ferroelectricity, but the mixed phase of $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$ did.

Keywords: Sol–gel; $Bi_2Ti_2O_7$; Ferroelectricity; Metal alkoxides

1. Introduction

Bismuth titanate ceramics have been studied widely due to their electro-optical property, piezoelectricity, ferroelectricity, ionic conductivity, and low sintering temperature. The materials are useful in the following applications: actuators, capacitors, non-volatile memory devices [1], microwave filters [2], etc. Depending on the chemical compositions and processing conditions, many different phases of bismuth titanate [3–5] were formed such as $Bi_{24}TiO_{38}$(B24T), $Bi_{12}TiO_{20}$(B12T), Bi_8TiO_{14}(B8T), $Bi_4Ti_3O_{12}$(B4T3), $Bi_2Ti_2O_7$(B2T2), $Bi_2Ti_3O_9$(B2T3), $Bi_2Ti_4O_{11}$(B2T4).

Although, the perovskite structure of B4T3 compound has been established as a good ferroelectric material with a high Curie temperature of 675 °C, different results have been reported in the literature concerning the ferroelectricity of B2T2. Shimada et al. [6] grew single crystals of B2T2 from oxide melt process. They posses a cubic structure without piezoelectricity and ferroelectricity. Yordanov et al. [7] prepared B2T2 from corresponding oxides using conventional ceramic technology. They observed dielectric hysteresis, at room temperature, and believed the pyrochlore structure leads to ferroelectricity. Jiang et al. [8] studied the phase transformation behavior of chemically precipitated B2T2. B2T2 transformed into a solid solution of B4T3 and B2T4 after sintering at 975 °C 1 h^{-1}. This solid solution showed good ferroelectricity.

In solid phase reactions between Bi_2O_3 and TiO_2 powders, the separation of Bi_2O_3 or TiO_2 is possible during the transformation of B2T2; this results in composition and structure variations, which may be responsible for the inconsistent results of B2T2 ferroelectricity. A sol–gel process can eliminate these problems since liquid phase reaction provides homogeneous mixing and reaction at an atomic scale for each component of the ceramic materials. Therefore, we synthesized B2T2 ceramics using a sol–gel method and studied their properties. The results are described and discussed in the following sections.

2. Experimental

2.1. Synthesis of metal alkoxide precursors

2.1.1. Sodium methoxyethoxide

Sodium (1.0 g, Aldrich) and tetrahydrofuran (70.0 g, Fisher Scientific Company) were placed in a three-neck reaction flask with stirrer, water condenser and nitrogen purge, then methoxyethanol (3.4 g, Acros Chemical Company) was added into the flask gradually. The reaction was carried out under reflux condition until all the sodium

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had reacted. This produced a sodium methoxyethoxide in tetrahydrofuran solution. By removing the tetrahydrofuran under vacuum, $NaOC_2H_4OCH_3$ was obtained and identified by ^1H NMR ($CDCl_3$, 200 MHz) $\delta = 3.34, 3.37$ ppm, (CH_3); 3.45–3.55 ppm, (CH_2); 3.67–3.71 ppm, (CH_2).

2.1.2. Bismuth methoxyethoxide

The bismuth methoxyethoxide was synthesized according to Hubert–Pfalzgraf procedure [9] with modifications. To make a bismuth trichloride solution, bismuth trichloride (4.7 g, Aldrich) was dissolved in tetrahydrofuran (70.5 g); then the solution was added gradually into a flask containing the above sodium methoxyethoxide solution (74.4 g). The reaction was carried out at 35–40 °C for 8 h with stirring and nitrogen purge. The tetrahydrofuran was removed by vacuum. Bismuth methoxyethoxide was obtained by extracting the residue with hexane or isopropyl ether (Aldrich) several times. The extracts were combined and filtered through a 0.5 μm filter in a closed system to avoid contact with moisture. Finally, the extracts were dried using vacuum to remove the solvent. The process yielded 45–80% product that was identified by using MAGNA-IR550 FT-IR (2800 cm^{-1} aliphatic C–H stretching, 1120 cm^{-1} ether stretching, 510–550 cm^{-1} Bi–O stretching) and Bruker DMX-200 ^1H NMR ($CDCl_3$, 200 MHz) $\delta = 3.39$ ppm, (CH_3); 3.49 ppm, (CH_2); 3.82 ppm, (CH_2) and Bruker DMX-200 ^{13}C NMR (58.402, 58.808 ppm (CH_3); 62.184, 62.254, 62.909 ppm (CH_2); 71.396, 77.205 ppm (CH_2, close to Bi–O)). The product was stored in tetrahydrofuran as a 3% solution for long-term stability.

2.1.3. Titanium methoxyethoxide

Titanium isopropoxide (10.0 g, Aldrich) and methoxyethanol (20.0 g) were placed into a three-neck flask equipped with stirrer, nitrogen purge and reflux condenser. Reflux was carried out at 65 °C for 12 h. The reaction by-product, isopropyl alcohol, was removed by vacuum distillation. The product was identified by ^1H NMR ($CDCl_3$, 200 MHz) δ ppm $= 3.18$–3.29 (one H of CH_2), 3.34 (CH_3), 3.5–3.64 (another H of CH_2), 4.28 (CH_2).

2.2. Synthesis of sol–gel B2T2 powder

Titanium methoxyethoxide was mixed with bismuth methoxyethoxide to make an alkoxide mixture with a Ti to Bi molar ratio ranging from 0.95 to 1.25. A 1.14M water solution was prepared by adding water into a 1:1 solvent mixture (by weight) of methoxyethanol and tetrahydrofuran. This water solution was slowly added to the alkoxide mixture to carry out the gel reaction. The amount of water was kept at a 1.31:1 water to alkoxides molar ratio. After the mixture was hydrolyzed for 7 h, gelation began and continued for an additional 19 h at room temperature. The wet gel was aged at 70 °C for 12 h and dried at 145 °C for 17 h to obtain a xerogel. To reduce sodium impurities below 30 ppm, this xerogel was Soxhlet washed with doubled distilled water for 24 h. The washed xerogel was dried at 145 °C for 17 h. The composition of the B2T2 xerogel was identified by EDX (SEM XL30, Philip) and ICP/mass (Sciex Elan 5000, Perkin-Elmer) to have a Ti/Bi molar ratio of 1.23:1. The xerogel has a BET surface area of 210 $m^2\,g^{-1}$ (measured by Micromeritics ASAP2000) and particle size of 0.59 micron (measured by Coulter, LS 230). To make B2T2 powder the xerogel was calcined at 350 °C for 10 h.

2.3. Characterization of B2T2 powders

The thermal properties of B2T2 were monitored with a Du Pont TGA51 Thermogravimetric Analyzer (room temperature to 600 °C at 5 °C min^{-1}) and a Du Pont 1600 differential thermal analyzer (DTA) (room temperature to 900 °C at 5 °C min^{-1}).

The B2T2 powder was heat treated at various temperatures and duration in a tube furnace with automated temperature and time controls. The sintering schedule generally followed was 25–150 °C, 2 °C min^{-1}; 150–600 °C, 5 °C min^{-1}; 600 °C 30 min^{-1}; 600-desired temperature, 8 °C min^{-1}; held at desired temperature/desired time. Then, the samples were oven cooled to room temperature. The phase changes of the powder at various process conditions were monitored by X-ray diffraction analysis (X-ray diffractometer (XRD) PW1830, Philip).

The B2T2 ceramic powder was Turbo milled in ethanol using 2 mm zirconia balls for 24 h. The milled powder was dried at 500 °C for 2 h, then pressed into disks of 1 cm (diameter) X 0.6–0.7 mm (thickness) at 55 MPa. Two samples were sintered at 1150 °C 90 min^{-1} and 1200 °C 45 min^{-1}, respectively according to the schedule shown above in the experimental section of phase transformation study. The density of the 1150 °C sample was 6.26 $g\,cm^{-3}$ and the 1200 °C sample was 5.54 $g\,cm^{-3}$. The disk samples were used for dielectric measurements.

The dielectric constants and dissipation factors of samples were measured using a Wayne Kerr Precision Magnetics Analyzer PMA 3260A at 25 °C from 100 to 2×10^6 Hz. The hysteresis loop of samples at 50 $kV\,cm^{-1}$ electric field and 60 Hz frequency were measured by a Sawyer–Tower circuit.

3. Results and discussion

We have prepared sol–gel derived B2T2 ceramics from metal alkoxide precursors. The same alkoxide ligand (methoxyethoxide) was chosen for titanium and bismuth to have similar hydrolysis rates during the formation of the gel. Bismuth methoxyethoxide and titanium methoxyethoxide were synthesized first, and then mixed at a Ti/Bi molar ratio of 1.23:1, and finally the mixture was hydrolyzed at a water/alkoxides molar ratio of 1.31 to obtain B2T2 gel. The dry gel has an average particle size of 0.58 μm and a surface area of 210 $m^2\,g^{-1}$.

Table 1
Phase structures of samples prepared from various solution compositions and sintered at 620 °C for 2 h

Sample	Molar ratio of Ti/Bi		Crystalline phase
	EDX	ICP/mass	
A	1.2	1.23	B2T2
B	1.1	1.02	B2T2 + B4T3 (little)
C	0.9	0.95	B4T3 + B2T2 (minor)

The thermogravimetric analysis showed that the organic ligand of the dry gel was completely decomposed at around 300 °C and the residual weight remained constant from 350 to 600 °C. The differential thermal analysis of the dry gel indicated a crystallization exothermic peak started at 550 °C.

To find out the best composition of sol–gel solution for B2T2 ceramics, we prepared samples with various molar ratios of precursor alkoxides and sintered them at 620 °C for 2 h. Their final chemical compositions were determined by EDX and ICP-Mass and their phase structures were studied by X-ray diffraction. The results are summarized in Table 1. A composition containing approximately equivalent amounts of bismuth and titanium (1.0:1.02), produced a B2T2 phase sample that was contaminated with a small amount of B4T3 phase. A single B2T2 phase sample was obtained from a solution containing a 23% molar excess of titanium. However, as major B4T3 phase sample was obtained from a solution containing a 5% molar excess of bismuth. A high excess amount of Ti is required to obtain B2T2 phase suggests that the formation of B2T2 phase is a probably a kinetically controlled reaction according to the Arrehenius relationship $k = A \exp - (E_a/RT)$. The excess amount of Ti would increase the frequency factor of the reaction at same temperature.

To study the stability of the B2T2 ceramic, the effects of processing conditions (temperature and time) on phase formation changes were studied for samples prepared with a composition of 23% molar excess of titanium. The results are summarized in Table 2. The B2T2 phase started to form at 550 °C. As shown in Fig. 1, the B2T2 phase was stable up to 700 °C for 2 h. When the temperature was raised to 750 °C, the B4T3 and B2T4 phases began to form. At temperatures between 850 and 1150 °C, the B2T2 phase disappeared completely. However, the B2T2 phase reoccurred at

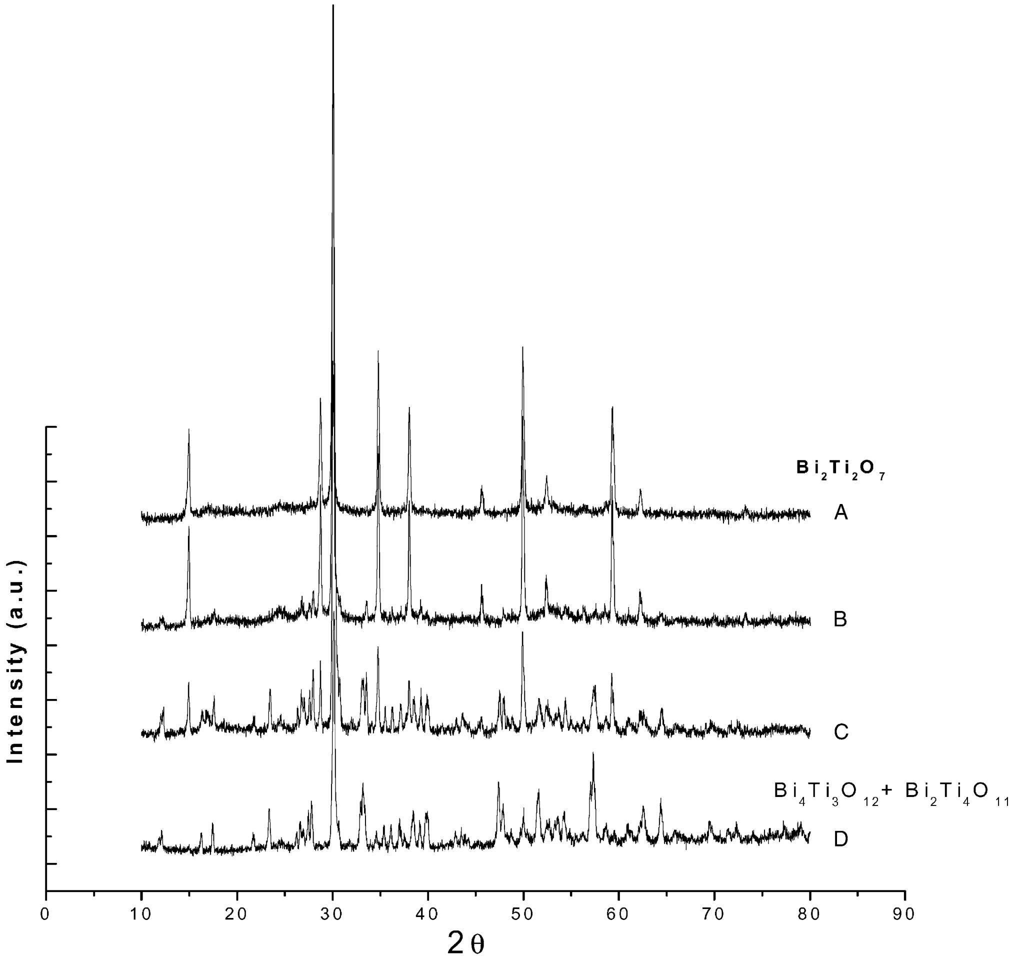

Fig. 1. XRD patterns of B2T2 ceramics sintered at: (A) 700, (B) 750, (C) 800 and (D) 1150 °C for 2 h.

Table 2
List of crystalline phases of bismuth titanate sintered at various temperatures and times

Temperature (°C)	Phases at temperature for 2 h	Phases at temperature for 8 h
550	B2T2	B2T2
600	B2T2	B2T2
650	B2T2	B2T2
700	B2T2	B2T2 + B4T3 (little) + B2T4
750	B2T2 + B4T3 (little) + B2T4	B2T2 + B4T3 + B2T4
800	B2T2 + B4T3 + B2T4	B4T3 + B2T4
850	B4T3 + B2T4	B4T3 + B2T4
900	B4T3 + B2T4	B4T3 + B2T4
950	B4T3 + B2T4	B4T3 + B2T4
1000	B4T3 + B2T4	B4T3 + B2T4
1150	B4T3 + B2T4	–
1200	B2T2 + B2T4 (little) (1200 °C 45 min^{-1})	–
1250	Ceramic melted	

1200 °C (Fig. 2). The observed low stability of B2T2 phase at temperatures higher than 700 °C was consistent with literature reports. Nakamura et al. [10] observed that B2T2 changed to B4T3 at 640 °C when B2T2 was a buffer layer between B4T3 thin film and silicon substrate. Jiang et al. [8] reported the formation of B2T2 at 600 °C from chemical co-precipitation of $Bi(NO_3)_3$ and $(NH_4)_2TiO_4$, and subsequent change into B4T3 and B2T4 after a heat treatment at 975 °C. The B2T2 phase transformed into B4T3 and B2T4 by increasing the sintering temperature and time, indicating that B4T3 and B2T4 are more thermodynamically favored phases than B2T2. This is in agreement with the above chemical composition study. The reoccurrence of B2T2 at the highest studied temperature (1200 °C) may be due to a change in the powder's composition. It is possible that the powder shifted to a Ti rich composition due to the volatilization of bismuth at high temperatures.

Dielectric properties were studied for two samples. One sample was sintered at 1150 °C 90 min^{-1} and exhibited a mixed phase of B4T3 and B2T4. The other sample was sintered at 1200 °C 45 min^{-1} and exhibited a B2T2 phase. The

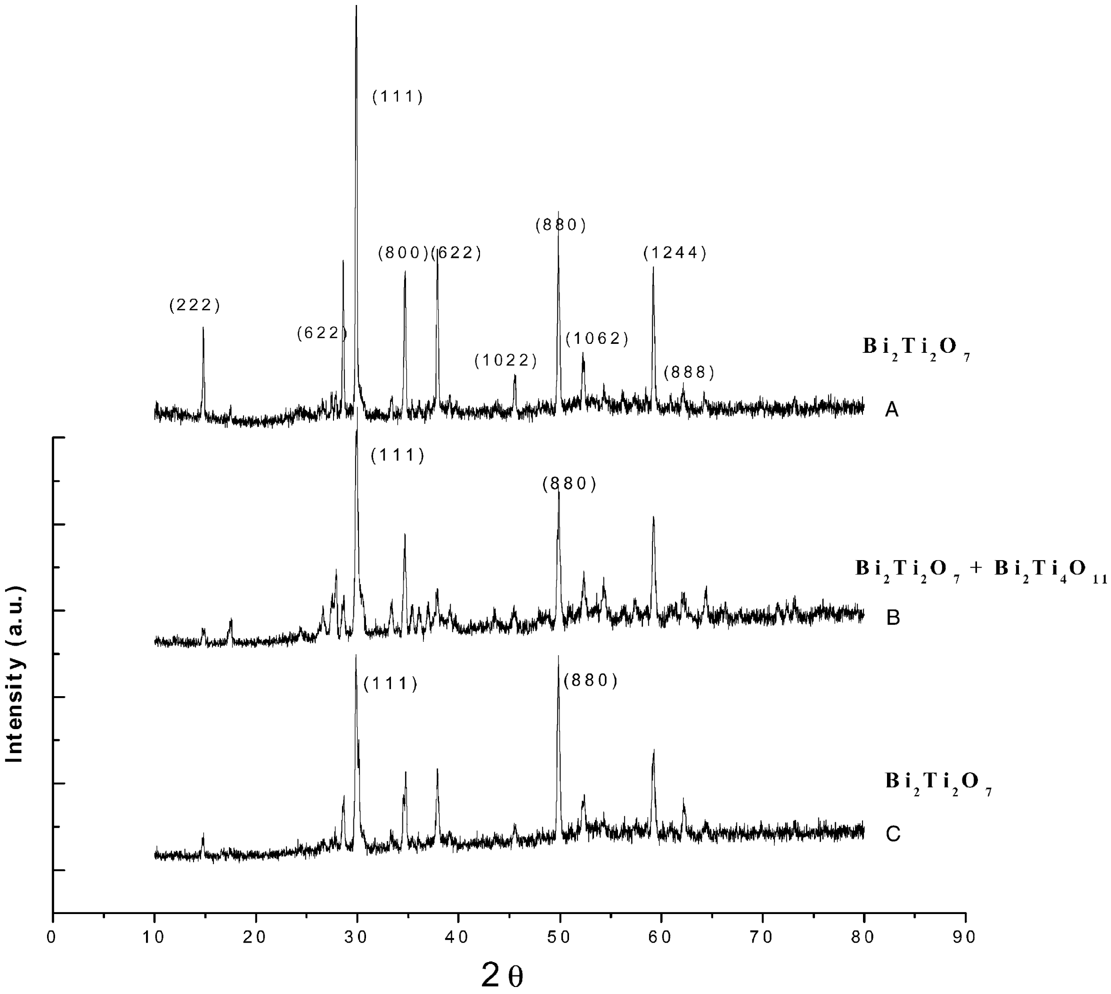

Fig. 2. XRD patterns of B2T2 ceramics sintered at 1200 °C for: (A) 45, (B) 90 and (C) 180 min.

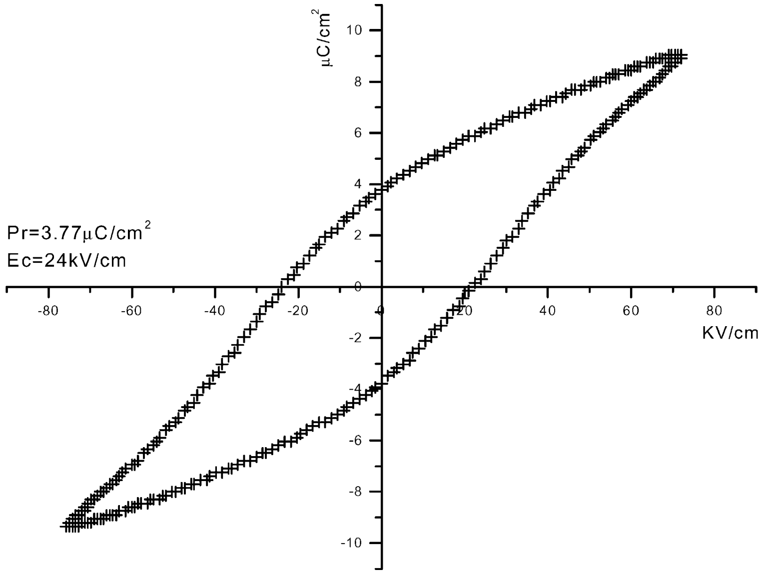

Fig. 3. Hysteresis loop of 1150 °C sample measured at 50 kV and 60 Hz.

dielectric constants of both samples decreased with increasing frequency and leveled off at 10 kHz. The maximum dissipation factor of samples was observed at 10 kHz. These results are consistent with the report by Yordanov et al. The data indicate that main contribution to the dielectric constant of the sample at low frequency was from space charges. [11] The 1150 °C sample showed a higher dielectric constant and a higher dissipation factor than those of the 1200 °C sample at low frequency, indicating that the 1150 °C sample contained more space charges than that of the 1200 °C sample. The high space charges may be from oxygen ion vacancies existing in the layer structure of B4T3 phase of 1150 °C sample. At a high frequency of 1 MHz, the contributions of dielectricity are from the dipoles of the material. Both samples exhibited similar dielectric properties. The 1150 °C sample had a dielectric constant of 101.3 and a loss tangent of 0.0193; and the 1200 °C sample had a dielectric constant of 104.2 and a loss tangent of 0.0145.

Fig. 3 shows the 1150 °C sample to be a ferroelectric material that exhibits a remanent polarization of 3.77 μC cm^{-2} and a coercive field of 24 kV cm^{-1}. The ferroelectricity of the sample is from the B4T3 phase. Jiang et al. [8] reported that heat treated B2T2 samples exhibited a remanent

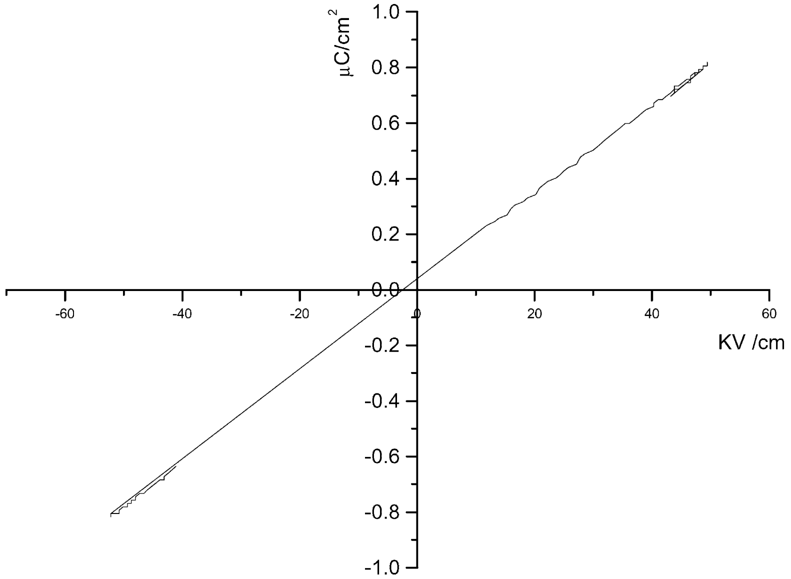

Fig. 4. Hysteresis loop of 1200 °C sample measured at 50 kV and 60 Hz.

polarization of 5.5 μC cm^{-2} and a coercive field of 26 kV cm^{-1}, values similar to our results. However, a completely closed hysteresis loop was obtained for our sample whereas Jiang's loop was not closed. This indicates that our sample was of good ferroelectric quality and had a minimal leakage current to the hystersis loop. The B2T2 material exhibited no evidence of ferroelectric behavior since a hysteresis loop was not observed in the 1200 °C sample (Fig. 4). This is in contrast with Yordanov et al., who reported B2T2 to be a ferroelectric material. They made B2T2 by mixing equivalent amounts of Bi_2O_3 and TiO_2 and sintered them at 1150–1200 °C for 2–3 h, but they did not have X-ray data to support the completed formation of B2T2 phase in their material. The observed ferroelectricity of their sample was most likely from the B4T3 phase, rather than from the B2T2 phase due to high sintering temperatures and equivalent amounts of Bi and Ti.

4. Conclusions

B2T2 ceramics were made from sol–gel method using bismuth methoxyethoxide and titanium methoxyethoxide at a Ti/Bi molar ratio of 1.23:1. The formation of B2T2 is possible a kinetically controlled reaction.

The B2T2 phase was stable at 700 °C for 2 h, but it changed into a thermal dynamically favored mixed phase of B4T3 and B2T4 at increased sintering temperatures and times.

The ferroelectric behavior of B2T2 ceramics is due to the B4T3 phase rather than from the B2T2 phase. The material sintered at 1150 °C 90 min^{-1} exhibited a mixed phase of B4T3 and B2T4. It exhibits a remanent polarization of 3.77 μC cm^{-2} and coercive field of 24 kV cm^{-1}; while, the material sintered at 1200 °C 45 min^{-1} exhibited a B2T2 phase, which did not exhibit ferroelectric hystersis behavior.

Acknowledgements

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