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Stable dielectric properties of $Na_{1+x}BiTi_6O_{14+0.5x}$ (x = −0.02, − 0.01, 0.01, 0.02) ceramics with low loss and high operating temperature

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A B S T R A C T

New lead-free dielectric ceramics, $Na_{1+x}BiTi_6O_{14+0.5x}$ (x = −0.02, − 0.01, 0.01, 0.02), were prepared by the conventional solid-state method. Micro-structural and electrical properties of $Na_{1+x}BiTi_6O_{14+0.5x}$ were studied. XRD showed all the samples exhibited a single structured phase. Grains decreased at the beginning, then grew with the increasing x content in SEM. Impedance spectra (IS) analysis evidenced the phenomena that the dielectric permittivity increased firstly, then decreased, while the loss had the opposite trend. *Z** plots showed that $Na_{1+x}BiTi_6O_{14+0.5x}$ ceramics were a kind of dielectrics. The activation energy (E_a) could be calculated in the range of 1.53–1.65 eV, which indicated they were dielectric ceramics. $Na_{1+x}BiTi_6O_{14+0.5x}$ ceramics (x = 0.01) sintered at 1040 °C showed prominent dielectric properties with a dielectric constant of 25.76, loss of 0.07%, E_a of 1.65 eV, density of 3.463 g/cm^3, impedance of 0.532 MΩ cm, -Z''_{max} of 0.1958 MΩ cm, capacitance of 5.56 pF/cm (600 °C), which were enhanced much compared with other samples. The existence of dielectric properties with high dielectric constant, low dielectric loss and wide operating temperature range makes it possible to develop the ceramics into high-temperature capacitors.

1. Introduction

In recent years, all kinds of electronic devices are particularly significant in the development of modern technology, such as piezoelectric, ferroelectric and dielectric ceramics. Most of the conventional functional ceramic materials have been widely used in electronic devices like sensors, actuators, ultrasonic transducers, and so on [1–4]. However, PZT-based lead-based piezoelectric ceramics still play an important role in many researchers' daily work as the leading preparation of sensors. The main component of the PZT material, PbO, is a volatile toxic substance that will bring a heavy burden to the environment [5–9]. Therefore, it is extremely urgent for us to find a lead-free piezoelectric ceramic to replace the lead piezoelectric ceramics [10–12]. Fortunately, the science and technology have been developing at a high speed. The discovery of $Na_{.5}Bi_{.5}TiO_3$ (NBT) in 1960 and the development of other lead-free piezoelectric ceramics materials like KNN-based have provided a new direction for the research of ceramics such as KNN-BCW [13], BCT-BMT [14]. For NBT-based ceramics, K. Parmar et al. prepared NBT samples sintered at different temperatures 850, 950, 1050 and 1150 °C to achieve best sintering temperature and get the experimental data ($\mathcal{E}_r$= 132–414, tan δ = 2–5.7%, T_c = 350 °C) [15]. As for KNN-based ceramics, Jiang X.P. et al. reported that crystal structure and electrical properties of $(1–x)K_{.5}Na_{.5}NbO_3–xBaCu_{.5}W_{.5}O_3$ ceramics were investigated with different BCW contents (x = 0%, 0.1%, 0.25%, 0.5%, and 1%, in mole) and got the data of dielectric properties ($\mathcal{E}_r$= 450, tan δ = 3.1%, T_c = 400 °C) [16]. Wang et al. [17] studied the lead-free ceramics $Ba(Cu_{.5}W_{.5})O_3$ and found its great dielectric properties ($\mathcal{E}_r$= 10^3–10^5). The BCW ceramic exhibited two dielectric constant plateaus, at low and high temperature respectively, which can be ascribed to the grain and grainboundary responses. Chen et al. [13] have researched the ceramics $(1\text{-}x)(K_{.5}Na_{.5})NbO_3\text{-}xBi(Cu_{.75}W_{.25})O_3$. Similarly its dielectric properties with $\mathcal{E}_r$= 1121 and tan δ < 0.028

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also exhibits good dielectric performance. From the context given above, we can see NBT-based and KNN-based piezoelectric ceramics materials don't have prominent dielectric properties such as loss not low enough. In addition, NBT (T_c = 320 °C) and KNN (T_c = 400 °C) have low Curie temperature and narrow operational temperature range. It's easy to cause Bi leakage for NBT. After large number of investigations and experiments around NBT-based, we found a new type of the NBT-based lead-free ceramics, $NaBiTi_6O_{14}$. To satisfy the need of industry, it is required to have excellent electrical properties, low dielectric loss, and wide operational temperature range (25–600 °C). Besides that, we have done a lot of researches around $NaBiTi_6O_{14}$ ceramics over the past period of time. For example, Mg-doping on the Ti-site is an important try, the experiment shows that the minimum dielectric loss of $NaBiTi_6O_{14}$ is about 1.417% (25–600 °C), and for $NaBi(Ti_{.98}Mg_{.02})_6O_{13.88}$, the dielectric loss is low to 0.0104% (25–600 °C). This work indicated that micro doping has great influence on the microstructure [18].

In this study, we prepared nanometer $NaBiTi_6O_{14}$ powders by ball milling, and made ceramic samples by the conventional solid-state sintering method. After that, we tried to explore the dielectric properties of $NaBiTi_6O_{14}$ ceramics by changing the non-stoichiometric ratio of sodium content at A site to discuss the effect on the electrical properties and explore micro-mechanism. Preliminary experimental results show that $NaBiTi_6O_{14}$ ceramics probably have a good application prospect of high- temperature ceramic capacitors because of stable relative permittivity, lower dielectric loss and wide operational temperature range.

2. Experimental procedure

$NaBiTi_6O_{14}$ ceramics have been fabricated by the conventional solid-state sintering method, and oxides of Na_2CO_3, Bi_2O_3, and TiO_2 with a mole ratio of 1:1:12 were weighted stoichiometrically and accurately, mixed with alcohol ball-milled in polyethylene bottles with ZrO_2 balls for 4 h. And then, the dried mixture was calcined in air at 800 °C for 3 h to synthesize the $NaBiTi_6O_{14}$ phase. After the second ball milled, dried and milled, the powders mixed with the binder of 9 wt% PVA were pressed into disks with 10 mm in diameter and 1.5 mm in thickness under a pressure of 8 MPa. After burning out the PVA at 550 °C for 5 h, the samples were sintered between 1000 and 1080 °C for 3 h in a closed alumina crucible to minimize the loss of volatile bismuth oxide.

X-ray diffraction (XRD) (Bruker D8 Advanced, Bruker, Germany) was used to analyze the crystalline structure of the obtained samples.

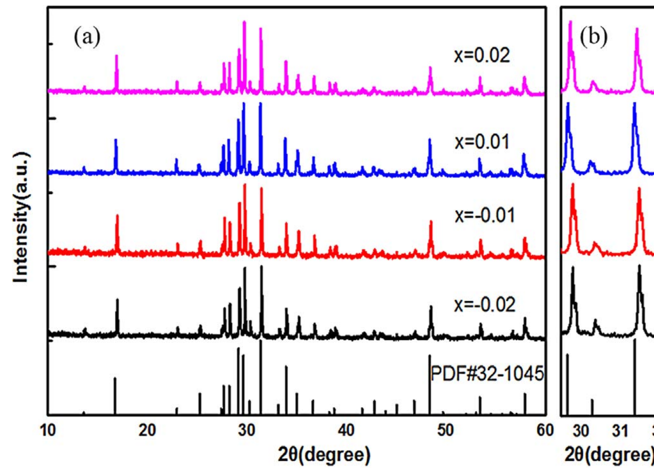

Fig. 1. X-ray diffraction patterns of $Na_{1+x}BiTi_6O_{14+0.5x}$ (x = −0.02, − 0.01, 0.01, 0.02) samples sintered at 1040 °C (a) 10–70°, (b) 29.5–32°.

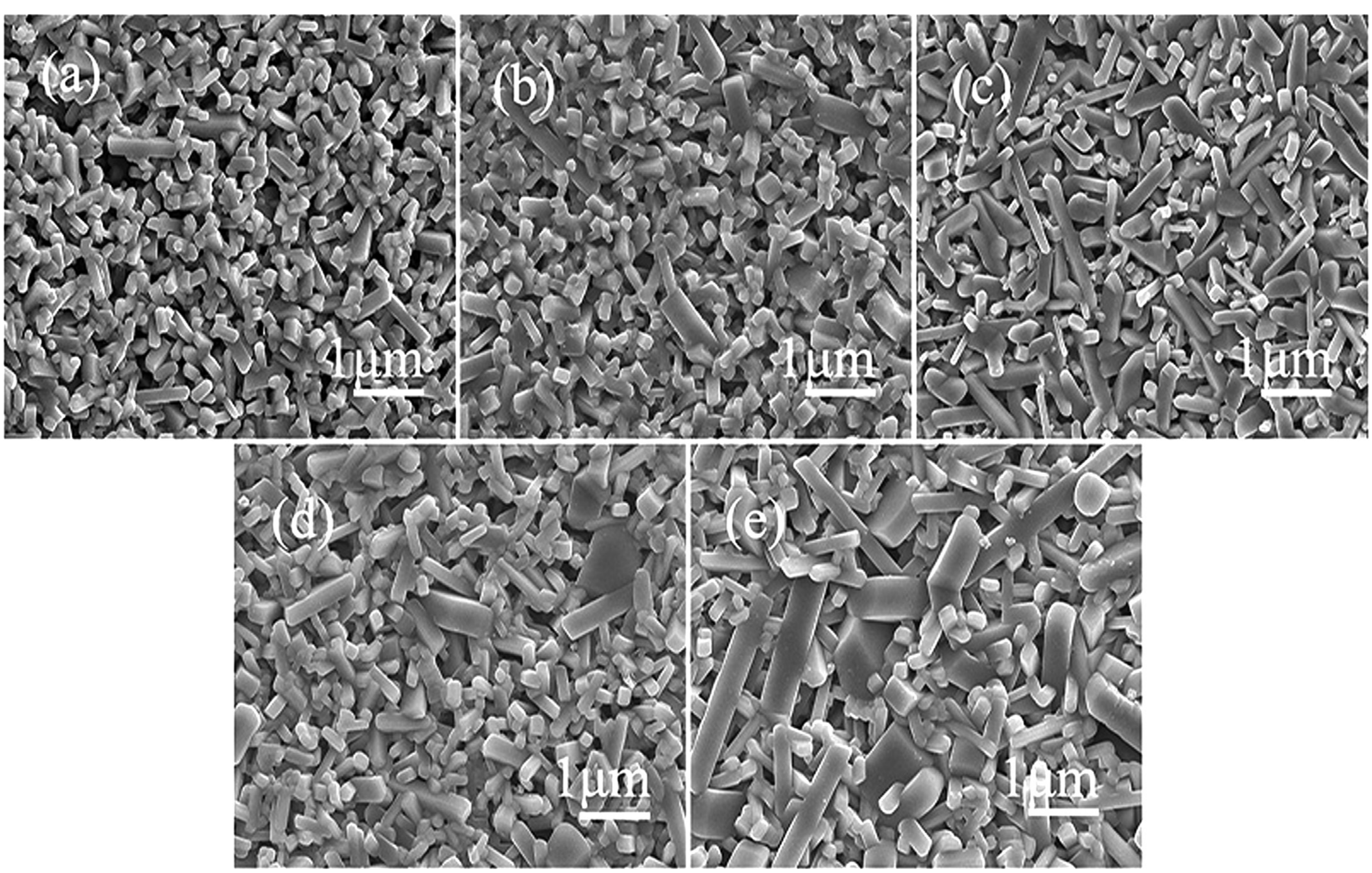

Fig. 2. SEM of different samples (A) SEM of $Na_{1+x}BiTi_6O_{14+0.5x}$ (x = 0.01) ceramics sintered at various sintering temperature (T = 1000, 1020, 1040, 1060, 1080 °C), (B) SEM of $Na_{1+x}BiTi_6O_{14+0.5x}$ (x = −0.02, − 0.01, 0.01, 0.02) ceramics sintered at 1040 °C.,.