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Control of the ferroelectric and electrical properties of Nd substituted bismuth titanate ceramics

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Abstract Nd-doped bismuth titanate $Bi_{4-x}Nd_xTi_3O_{12}$ ceramics were prepared by a solid state reaction method. The effects of Nd doping on ferroelectric and electrical properties were investigated. With Nd substitution for Bi ion, a BNdT single-phase with Bi-layered perovskite was confirmed. The Nd doping decreased the dissipation factor (tanδ) and the dc conductivity, and increased the dielectric constant and the remanent polarization. A small Nd doping on $Bi_4Ti_3O_{12}$ leads to a higher remanent polarization and improves the ferroelectric properties.

Keywords Ferroelectric · Electrical properties · Nd

1 Introduction

Ferroelectric and electrical properties of Bi-layered perovskite ferroelectrics have been studied for the purpose of non volatile ferroelectric random access memories (FRAM) application. It is necessary to have high remanent polarization, high fatigue endurance, low leakage current and low processing temperature [1–6]. Bi-layer structured ferroelectrics (BLSFs) such as $SrBi_2Nb_2O_9$ (SBN), $Bi_4Ti_3O_{12}$ (BIT) and $SrBi_2Ta_2O_9$ (SBT) are known as a ferroelectric material [7–14]. The BLSFs structure can be written with a general formula of $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$ where A can be mono-, di-, trivalent ions or a mixture of them, B represents Ti^{4+}, Nb^{5+}, and Ta^{5+}, etc., and n can have values of 2, 3, 4, ... One of them, $Bi_4Ti_3O_{12}$ (BIT) is a promising candidate for potential FRAM application [1, 5, 11–14]. A and B site is occupied by Bi and Ti ion, respectively, and n=3 are given in the general formula. Thus, the BIT structure consists of three perovskite-like units $(Bi_2Ti_3O_{10})^{2-}$, sandwiched between bismuth oxide $(Bi_2O_2)^{2+}$ layers.

It is well known that the ferroelectric properties arise in the perovskite block, $(Bi_2Ti_3O_{10})^{2-}$. However, the BIT is known to suffer from high leakage current, which leads to polarization fatigue and small remanent polarization. For practical FRAM applications, it is still necessary to develop new ferroelectric materials with an high remanent polarization and a low electrical conductivity [1–9]. Recently, the effect of ion doping on the ferroelectric and electrical properties in BLSFs was widely studied for the improvement of ferroelectric properties [1–5, 9–16]. The nature of the electrical conductivity is of importance in determining the presence of electronic and ionic defects. In this work, for Nd doped BNdT ceramics, effects of Nd doping on the crystal structure, dielectric, ferroelectric and electrical properties were investigated.

2 Experimental work

Nd doped $Bi_4Ti_3O_{12}$ ceramics were prepared by solid-state reaction with a composition of $Bi_{4-x}Nd_xTi_3O_{12}$ (BNdT:x, x= 0, 0.25, 0.50, 0.75 and 1.0). Bi_2O_3, Nd_2O_3 and TiO_2 powders were mixed in methyl alcohol according to the desired BNdT compositions. The mixed BNdT powders

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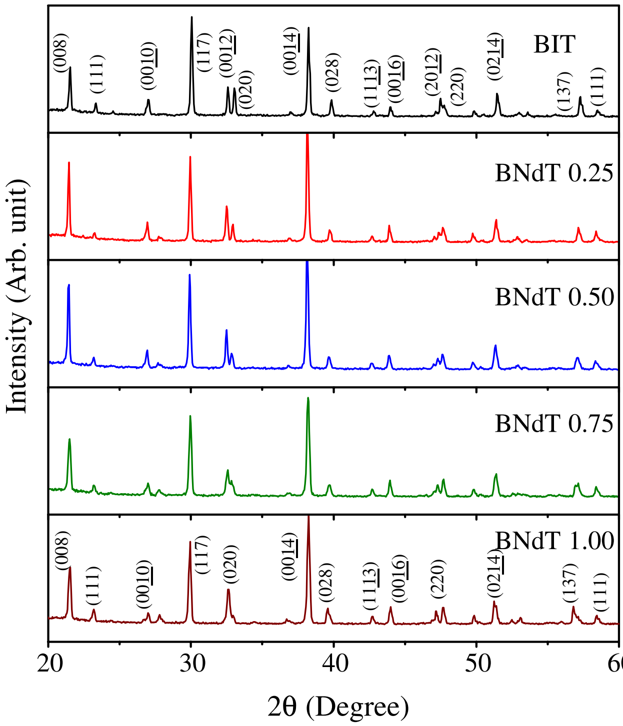

Fig. 1 The XRD patterns of BNdT ceramics with different Nd concentrations

were calcined at 750 °C for 4 h. The calcined powders were pressed into pellets and sintered at 950–1000 °C for 5 h. Crystal structure and surface grain morphologies were investigated by X-ray diffraction (XRD) with Cu–Kα radiation and scanning electron microscopy (SEM), respectively. To investigate the electrical properties, Pt electrodes were coated onto the polished surface using dc sputtering. The ferroelectric P–E hysteresis loops were investigated using Sawyer–Tower circuit. The capacitance and dissipation factor (tanδ) were measured by an impedance analyzer (HP4194A) in the frequency range of 100 Hz–1 MHz and the temperature from 30 to 600 °C. The dc conductivity were investigated by an electrometer (Keithley 236). Then the current of ceramics was measured at the applied electric field of 4 kV/cm.

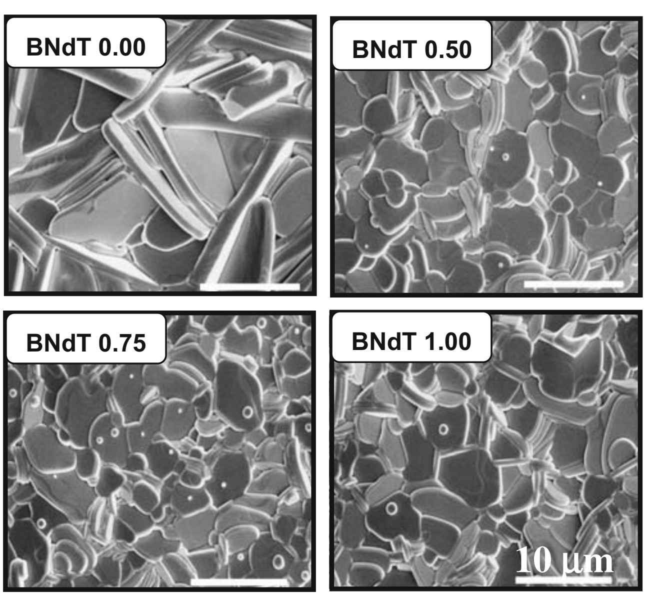

Fig. 2 SEM images of BNdT ceramics with different Nd concentrations

3 Result and discussion

Figure 1 shows the XRD patterns of BNdT ceramics with different Nd contents. The XRD peaks of the BNdT ceramics are similar to that of BIT ceramics [9]. Second

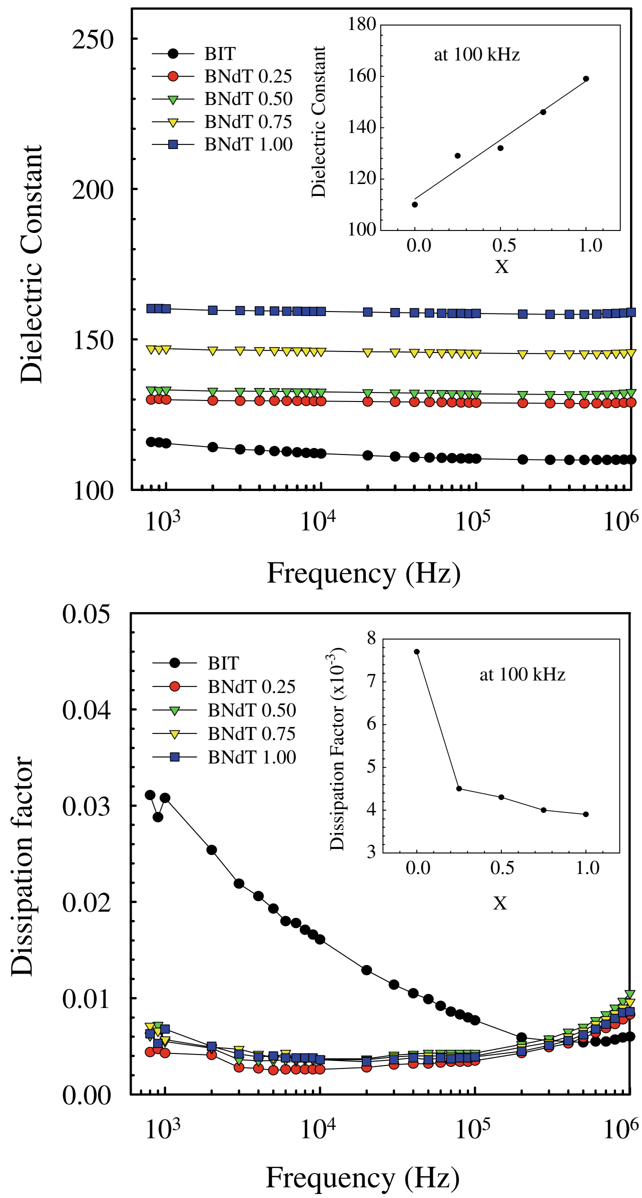

Fig. 3 Dielectric constants and dissipation factor of BNdT ceramics with different Nd concentrations and the inset shows those at 100 kHz

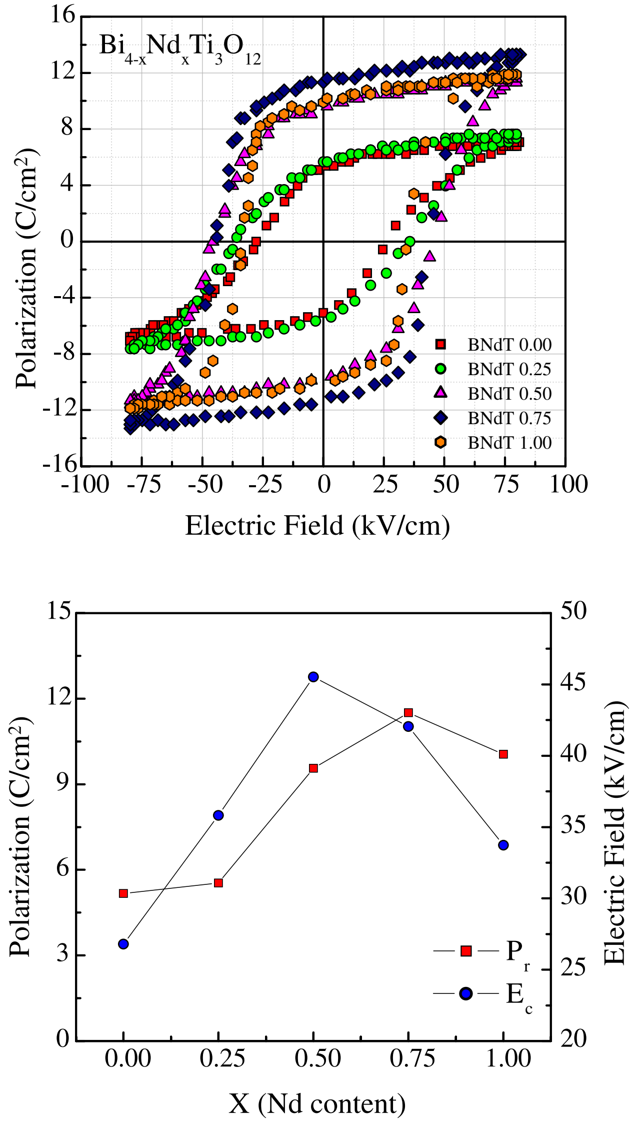

Fig. 4 Hysteresis loops of BNdT ceramics with different Nd concentrations, and remanent polarization P_r and coercive field E_c

phases were not observed up to x=1.0. Thus, the XRD peaks of the BNdT ceramics were indexed according to the previous XRD data. The layered perovskite (117) peak and other perovskite (00l) peaks were found in XRD patterns, which agreed with peaks of BIT ceramics. This indicates that BNdT single phases having BLSF crystal structure were confirmed for the different Nd contents.

Figure 2 shows the surface grain microstructure of BIT and BNdT ceramics. The grain morphologies of the BIT ceramic were plate-like shapes and oriented preferred orientation along the c-axis, which were agreed with that of previous results [15]. The average grain sizes of BIT were around 15 μm, while the grain size of BNdT was 4–7 μm. Thus, Nd doping results in the decrease of grain size.

Figure 3 shows the dielectric constants and dissipation factor measured at the frequency range of 1 kHz–1 MHz and at room temperature. The inset shows the dielectric constant and dissipation factor of the BNdT ceramics measured at a frequency of 100 kHz. The dielectric constant of BNdT ceramics is a constant value with increasing frequency. In addition, the dielectric constant increased with increasing Nd concentration. The dissipation factor of BIT ceramics decreased with increasing frequency, however, that of BNdT was decreased by Nd doping and had a constant value. As seen in the inset, the dissipation factor of BNdT ceramics was decreased by the Nd doping. The contribution of the dissipation factor of BIT is caused by the defects. Compared to that of BIT ceramics, the dissipation factor of BNdT ceramics was decreased at a small doping of x=0.25–1.0. Thus, the decrease of dissipation factor and the increase of the dielectric constant can be explained by the decrease of defects such as oxygen and bismuth vacancies [12–14].

Figure 4 shows the ferroelectric P–E hysteresis loops measured at 80 kV/cm (50 °C). Well saturated ferroelectric P–E hysteresis loops were observed and the polarization was increased by Nd doping. The variation of the remanent

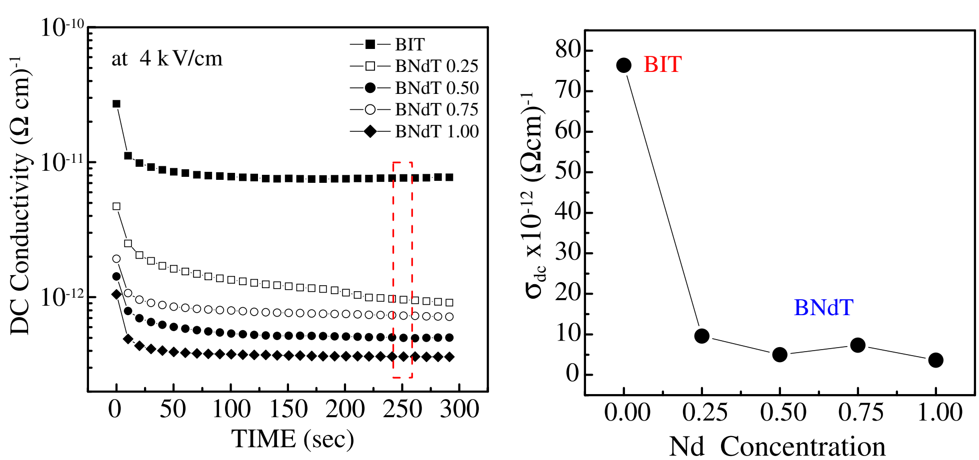

Fig. 5 DC conductivity of BNdT ceramics with different Nd concentrations

polarization (P_r) and coercive field (E_c) were obtained from the ferroelectric P–E hysteresis loops. As the Nd content increases, the P_r increases and then decreases, reaching the maximum value at $x=0.75$. Thus, the Nd doping results in the increase of the remanent polarization. With increasing Nd content, also the E_c increased and then decreased. The BNdT 0.75 ceramics has the maximum P_r value of 11.05 μC/cm^2, which was higher than that of BIT ceramic of 5.20 μC/cm^2. It indicates that the Nd doping with proper content improved the ferroelectric properties. The spontaneous polarization, P_s, of BIT single crystals [10] along the *a*-axis was 45–50 μC/cm^2 and that along the *c*-axis was 4.5 μC/cm^2. In this work, the order of the *c*-axis orientation of the BNdT ceramic was decreased, as shown in XRD analysis [14]. Thus, the polarization of BNdT ceramics was thought to be increased by the increase of the random grain orientation and by a decrease of defects.

Figure 5 shows the dc conductivity of BNdT ceramics as a function of time and the saturated dc conductivity after 200 s. With increasing time, the dc conductivity of BNdT ceramics decreased and saturated after about 200 s. Then the saturated dc conductivity was compared with other BNdT ceramics. The saturated dc conductivity was decreased by Nd doping at $x=0.25$–1.0. Thus, the small Nd doping decreases the dc conductivity.

In oxide ferroelectrics, doubly charged oxygen vacancies ($V_O^{\cdot\cdot}$) are the most mobile charges and play an important role in the conduction process [11], which is attributed to the thermal motion of the oxygen ion or the formation of associations between oxygen vacancies and residual cations in the grain boundary. Ti and Bi ions in BIT are known to be unstable. Bi ions easily evaporate during the sintering process. Thus, defects, such as bismuth and oxygen vacancies, may exist in the perovskite layers and play an important role in polarization fatigue and conducting process. Defects get trapped at sites like grain boundaries and grain-electrode interfaces, and space charges are created. For PZT thin film, oxygen vacancies move and reach the interface/electrodes, and are trapped at trap sites. Thus, space charges are created at the boundaries/interfaces, and polarization fatigue occurs.

On the other hand, the BIT suffers from high leakage current and domain pinning due to defects, leading to a small remanent polarization after read/write cycles. Bi ions easily evaporate during the sintering process and then defects are generated by Bi vacancies. Previously, it is known that role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies accompanied with oxygen vacancies which act as space charge [1]. For the BNdT ceramics, the dielectric constant was increased and the dissipation factor was decreased, which indicates that Nd doping reduces defects such as bismuth and oxygen vacancies. Then the remanent polarization increased and the electrical conductivity decreased, and the improvement of ferroelectric properties can be explained by the decrease of defects. Therefore, Nd doping in BIT could be effective for a decrement of charge carriers, it could be improve the ferroelectric properties.

4 Conclusions

The effect of Nd doping on ferroelectric and electrical properties of $Bi_{4-x}Nd_xTi_3O_{12}$ ceramics (BNdT, $x=0$, 0.25, 0.50, 0.75 and 1.0) were investigated. BNdT single phases having BLSF crystal structure were formed for the different Nd contents. The average grain sizes of BIT ceramics were around 15 μm, while the grain size of BNdT ceramics was 4–7 μm. The dielectric constant was increased and the dissipation factor was decreased by the Nd doping. The maximum remanent polarization of the BNdT 0.75 ceramics ($P_r \approx 11.2$ μC/cm^2) is higher than that of BIT ceramic ($P_r=5.2$ μC/cm^2). The conductivity was decreased and exhibited the minimum conductivity at the $x=0.75$. Therefore, the small Nd doping leads to a higher remanent polarization, and improves ferroelectric properties.

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