

# Temperature dependence of the dielectric dispersion and ferroelectric properties of neodymium doped bismuth titanate ceramics

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**Abstract** Nd-doped bismuth titanate  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  ceramics ( $x = 0\text{--}1.0$ ) were prepared by the solid state reaction method. The temperature dependence of the dielectric dispersion and ferroelectric properties were investigated. With the increase of the Nd substitution for Bi ion, the Curie temperature decreased and the corresponding dielectric constant peak broadened. In addition, the strong low-frequency dielectric dispersions were exhibited. The Nd doping decreases the temperature dependence of the ac conductivity and increases the temperature dependence of the remanent polarization, which is caused by the induced polarization by defects, such as bismuth and oxygen vacancies.

**Keywords** FRAM · BIT · BLSF · Ferroelectric · P-E hysteresis loop · Polarization · Dielectric Property · Conductivity

## 1 Introduction

For the ferroelectric random access memory application, it is necessary to have high remanent polarization, high fatigue endurance, low leakage current and a low processing temperature [1–6]. Ferroelectric properties of Bi-layer structured ferroelectrics (BLSFs), such as  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  (SBN),  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT) and  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT), have been

studied for the purpose of non volatile ferroelectric random access memories (FRAM) [7–15]. The structure of BLSFs can be written with a general formula of  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ , where A can be mono-ions, di-ions, trivalent-ions or a mixture of them, B represents  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Ta}^{5+}$ , and  $n$  can have values of 2, 3, 4, ... One of the BLSFs,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT), is a promising candidate for potential FRAM application. A and B sites are occupied by Bi and Ti ions, respectively, and  $n = 3$  is given in a general formula. Thus, the BIT structure consists of three perovskite-like units  $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ , sandwiched between bismuth oxide  $(\text{Bi}_2\text{O}_2)^{2+}$  layers. It is well known that the ferroelectric properties arise in the perovskite block,  $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ .

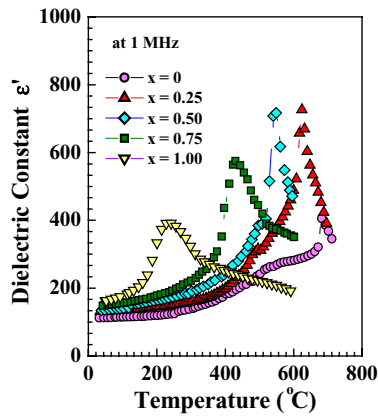
However, the BIT is known to suffer from high leakage current due to defects, leading to polarization fatigue and small remanent polarization. Thus, it is still necessary to develop new ferroelectric materials with high remanent polarization and low conductivity [2]. Recently, the effect of ion doping has been widely studied for polarization fatigue endurance and high remanent polarization [2, 5–15]. In this study, Nd doped BIT (BNdT) ceramics were prepared by the solid state reaction method. The effects of Nd doping on the dielectric dispersion and ferroelectric properties were investigated in the temperature range of 30–700°C.

## 2 Experimental work

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  ceramics (BNdT:  $x = 0.0, 0.25, 0.75$  and  $1.0$ ) were prepared by using the solid-state reaction method. The desired BNdT compositions of the  $\text{Bi}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Nb}_2\text{O}_5$  powders were mixed in methyl alcohol. The mixed BNdT powders were calcined at 750°C

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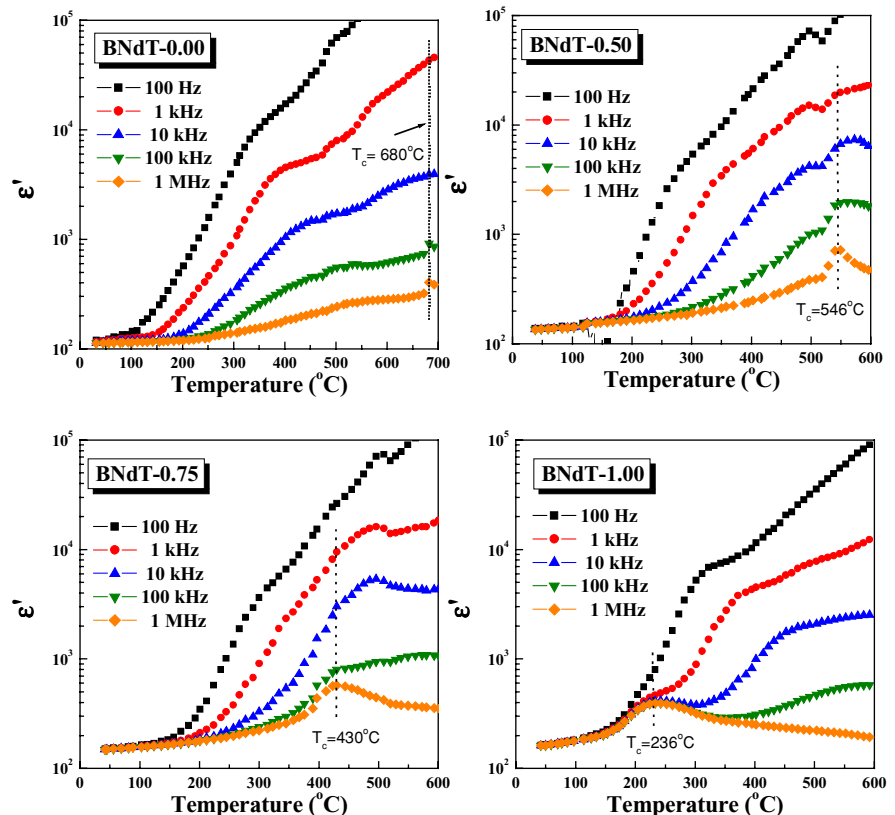
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**Fig. 1** Temperature dependence of the dielectric constants of BNdT ceramics measured at 1 MHz

for 4 h. The calcined powders were pressed into pellets and sintered at 950–1000°C for 5 h. The crystal structure was investigated by X-ray diffraction (XRD) with Cu-K $\alpha$  radiation. To investigate the electrical properties, Pt electrodes were coated onto the polished surface using dc sputtering. The ferroelectric P-E hysteresis loops were measured using a Sawyer-Tower circuit. As the temperature increased from 30° to 600°C, the capacitance and dissipation factors ( $\tan \delta$ ) were measured by an impedance analyzer (HP4194A) in the frequency range of 100 Hz–1 MHz.

**Fig. 2** The dielectric constants of the BNdT ceramics measured at the frequency of 1 k, 10 k, 100 k and 1 MHz



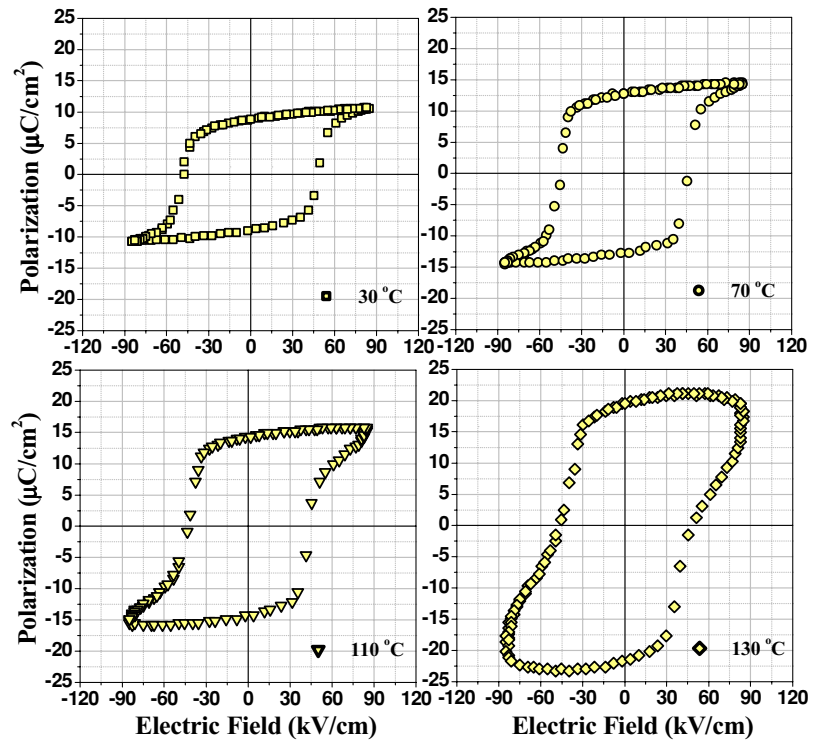
### 3 Result and discussion

Each BNdT ceramic with a different Nd content of  $x = 0$ –1.0 exhibits a similar XRD pattern, which implies that Nd doping does not affect the basic crystal structure [15] of the BIT. The indexed XRD peaks of BNdT ceramics agreed with the peaks of BIT ceramics. The second phase was not observed for Nd doping, which indicates that single phases were formed for all BNdT ceramics.

Figure 1 shows the temperature dependence of the dielectric constants measured at the frequency of 1 MHz. With the increase of temperature, the dielectric constant increased and had a dielectric maximum peak at Curie temperature  $T_c$ . With the increase of the Nd substitution for Bi ion in A site, the  $T_c$  decreased and the degree of broadness increased. Therefore, the dielectric constant peak changed from a sharp peak with a normal dielectric anomaly to a diffusive peak with a broad dielectric anomaly. Therefore, the diffuse phase transition behaviors indicated a departure from the Curie-Weiss law [16].

Figure 2 shows the frequency dependence of the dielectric constants of the BNdT ceramics as a function of temperature. The BIT ceramics show a strong low-frequency dielectric dispersion above 100°C. Next, the humps depending on frequency were observed and shifted to a higher temperature. Previously, it was understood that the temperature

**Fig. 3** Temperature dependence of the hysteresis loops of BNdT0.75 ceramics



dependence of the dielectric dispersion was caused by the space charge and ionic motion [13, 17], contributed by defects within BIT. Similarly, the low-frequency dielectric dispersions of the BNdT ceramics were observed, which caused by the space charge and ionic motion.

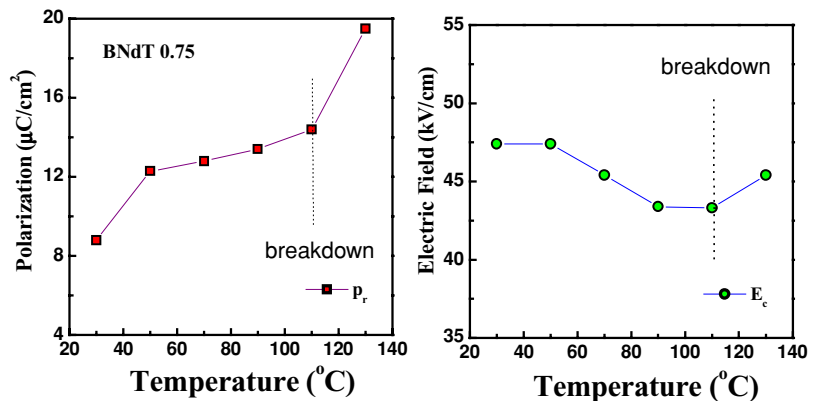
Figure 3 shows the temperature dependence of the ferroelectric P-E hysteresis loops of the BNdT:0.75 ceramics measured at the electric field of 60 kV/cm. At the room temperature, the remanent polarization of the BNdT:0.75 ceramics increased and the maximum  $P_r$  value was  $8.0 \mu\text{C}/\text{cm}^2$ , which is higher than that of BIT ceramics of  $4.20 \mu\text{C}/\text{cm}^2$ . It indicated that the Nd doping improved the ferroelectricity.

As the temperature increased, well-saturated ferroelectric P-E hysteresis loops were observed up to  $110^\circ\text{C}$ . However, the ferroelectric P-E hysteresis loops exhibited the leaky behavior above  $110^\circ\text{C}$ , which is caused by the increase of

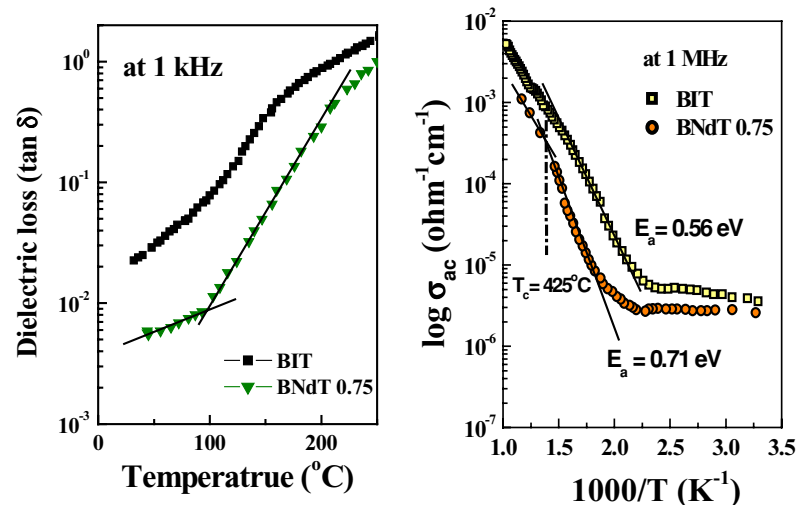
electrical conductivity. Afterwards, the leaky current remarkably increased and the dielectric breakdown occurred.

Figure 4 shows the temperature dependences of the remanent polarization ( $P_r$ ) and coercive field ( $E_c$ ). With the increase of the temperature, the  $E_c$  decreased and the  $P_r$  increased. However, the increase of  $P_r$  was different from that of normal ferroelectrics, such as  $\text{BaTiO}_3$  and TGS (triglycine sulfate) [18], since the ferroelectric polarization of normal ferroelectrics decreases with an increase in temperature. Thus, the increase of the  $P_r$  is explained by the induced polarization. As seen in the temperature dependence of the dielectric constant measured at a frequency of 1 k–1 MHz, the space charge and ionic motion caused the low-frequency dielectric dispersion and the electrical conductivity. In addition, the space charge and the ionic motion caused the induced polarization with the increase of the thermal energy.

**Fig. 4** Temperature dependence of the remanent polarization  $P_r$  and coercive field  $E_c$



**Fig. 5** Dielectric loss and electrical conductivity of BIT and BNdT0.75 ceramics



In spite of the decrease of the ferroelectric polarization, the increase of the induced polarization increased the total polarization with an increase in the temperature.

Figure 5 shows the temperature dependences of dielectric loss at the frequency of 1 kHz and ac conductivity vs. the reciprocal temperature,  $1/T$ , measured at the frequency of 1 MHz. Compared to that of BIT ceramics, the dielectric loss of BNdT0.75 ceramics decreased. The dielectric loss of BNdT ceramics abruptly increased over  $100^{\circ}\text{C}$ , which was caused by the contribution of increased defects. Next, the leakage current was measured at  $100^{\circ}\text{C}$  [19], however, it is difficult to measure the leakage current over  $110^{\circ}\text{C}$  due to increased electrical conductivity.

Thus, as shown in Fig. 4, the dielectric breakdown was explained by the increase of defect charge carriers. Compared to that of BIT ceramics, the ac conductivity of BNdT0.75 ceramics decreased in low and high temperatures at the boundary of  $230^{\circ}\text{C}$ . In the low temperature region, the ac conductivity of BNdT ceramics is independent of temperature and steadily increased above  $230^{\circ}\text{C}$ . From the slope of the  $\ln \sigma_{ac}$  vs.  $1000/T$  curve, the activation energy of BIT and BNdT0.75 ceramics was 0.56 eV and 0.71 eV. In oxide ferroelectrics, doubly charged oxygen vacancies ( $V_{\text{O}}^{\bullet\bullet}$ ) are the most mobile charges and play an important role in the conduction process. The motion of oxygen vacancies is well known to give rise to an activation energy of about 1 eV [9] at high temperatures. Thus, the calculated activation energy of 0.56–0.71 eV 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 [9].

Ti and Bi ions 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 conduction. Defects get trapped at sites like grain bound-

aries and grain-electrode interfaces, and space charges are created. Therefore, the defects influenced the dielectric and ferroelectric properties. Currently, the role of doping of lanthanoid elements such as La, Nd and Sm elements [2, 5, 8, 10–16], is to displace the volatile Bi to suppress the A-site vacancies accompanied with oxygen vacancies which act as space charges. From the results of decreased conductivity by Nd doping, Nd ion doping reduced defects act as space charges. With an increase in temperature, however, the space charge and the ionic motion is activated with the increase of the thermal energy. Consequently, the low-frequency dielectric dispersion and induced polarization is caused by the space charge and ionic motion.

#### 4 Conclusions

The effect of Nd doping on dielectric dispersion and ferroelectric properties of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  ceramics (BNdT,  $x = 0, 0.25, 0.50, 0.75$  and  $1.00$ ) were investigated. With the increase of the Nd content from  $x = 0$  to  $1.0$ , the Curie temperature decreased from  $645^{\circ}$  to  $220^{\circ}$  and the dielectric constant peak broadened. The remanent polarization of the BNdT ceramics ( $P_r \approx 8.2 \mu\text{C}/\text{cm}^2$ ) was higher than that of BIT ceramics ( $P_r = 4.2 \mu\text{C}/\text{cm}^2$ ). The conductivity was decreased by Nd doping, and corresponding conductivity exhibited the minimum value at  $x = 0.75$ . As the temperature increased, the strong dielectric dispersion and the increased polarization were exhibited. In spite of Nd doping, defects such as bismuth and oxygen vacancies still affected the dielectric dispersion and ferroelectric properties.

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