

B-Site Disordered New Lead-Free Relaxor Ferroelectric $\text{Gd}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ System

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$\text{Gd}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ solid solutions were synthesized and their structural and physical properties characterized. The X-ray diffraction showed that the average structure of the system at room temperature was orthorhombic ($Pbnm$). The temperature-dependent AC-dielectric constant showed an anomaly (hump) around 500 – 600 K, depending on the frequency. The D-E hysteresis loops were also measured at room temperature and exhibited ferroelectric characteristics. The relaxor ferroelectric behavior of this lead-free centrosymmetric system might be related to the B-site local disorder in the system.

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I. INTRODUCTION

There has been a significant amount of research on non-volatile memory devices, such as magnetic random access memories, ferroelectric random access memories and spin-based electronic devices, for future technologies. Among them, ferroelectric materials, especially perovskite-type complex oxide systems (ABO_3 types, such as $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) [1], $\text{Pb}(\text{Zr}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) [2–4]), have attracted researcher's attention due to, not only their richness in fundamental physics but also their abundance in applications, including piezoelectric devices [5–9]. In the case of lead-zirconate-titanate (PZT) systems, which have been extensively studied, many of their physical properties are well understood. For example, the monoclinic bridging phase at the morphotropic phase boundary between the rhombohedral ($R3m$) and tetragonal ($P4mm$) ferroelec-

tric phases has been well characterized experimentally [10–13] and theoretically through first-principles calculation [14–16]. Ferroelectric relaxor systems, such as PMN and PMN-PT, other aspects of the ferroelectric properties exhibit giant piezoelectric responses, which are useful for ultrasonic, medical and telecommunication applications [17–21]. To now, PZT- and PMN-PT-based ferroelectric devices, such as actuators and sensors, have been used widely and extensively for electronic applications. These are the best candidate materials because of their high dielectric constants and piezoelectric coefficients. However, recent public concerns about lead-containing materials and devices has forced new searches for lead-free ferroelectric materials comparable (or even better than) to the most widely used lead (Pb^{2+} ion)-based ferroelectric material systems. From these efforts, researchers have found various lead-free ferroelectric materials, such as $(\text{Bi}_{1-x}\text{La}_x)(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [22, 23], $(\text{La}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Mn}_{2/5-x}\text{Ni}_x\text{Ti}_{3/5})\text{O}_3$ [24], BiFeO_3 - $\text{Ba}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ [25], $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ [26], $\text{Bi}(\text{Zn}_{3/4}\text{W}_{1/4})\text{O}_3$ [27], $\text{Bi}_{3.25}\text{La}_{0.75}(\text{Ti}_{1-x}\text{V}_x)_3\text{O}_{12}$ [28], etc. However, all the recently-found materials are either

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complicated to synthesize or less promising in their physical properties than current Pb-based systems. Therefore, researcher are still looking for better systems and/or to enhance their understanding of the physical characteristics of ferroelectric systems.

In this paper, we report on newly synthesized $A^{3+}B^{3+}O_3$ -type ferroelectric material, consisting of Gd ions in the A site and Ni and Ti ions in the B-site, *i.e.*, $Gd(Ni_{0.5}Ti_{0.5})O_3$ (GNT-50). The physical and the structural properties of GNT-50 ceramics were determined from X-ray diffraction, temperature-dependence of AC-dielectric constant and DC-conductivity and D-E hysteresis-loop measurements. From those measurements, we found that GNT-50 exhibited relaxor ferroelectric behavior at room temperature even though the structure analysis indicated that the system was in a centrosymmetric phase.

II. EXPERIMENTS

$Gd(Ni_{0.5}Ti_{0.5})O_3$ ceramics (GNT-50) were prepared by using a conventional solid-state reaction method. As starting materials, reagent-grade metal-oxide powders (99.9 % purity of Gd_2O_3 , NiO and TiO_2 powders from Aldrich Chemical Corp.) were weighed properly, mixed with acetone and dried in an oven overnight. Then, the mixed powders were calcined at 1523 K for 4 hours and at 1653 K for 10 hours. After calcination, the powders were ground, mixed with 1 % polyvinyl alcohol and pressed at a 50-kg weight/cm² to make 0.12-cm-thick cylindrical pellets ($\phi = 1.2$ cm). The pellets were sintered at 1753 K for 10 hours.

The temperature-dependent crystal phase of the GNT-50 was determined from the X-ray diffraction (X'pert PRO MPD; KBSI-SU05) patterns. The flat surfaces of the pellets were Au coated by using DC magnetron sputtering to obtain dielectric and electrical property measurements. The temperature dependence of the dielectric constants (ϵ' : real part) and loss tangent ($\tan\delta = \epsilon''/\epsilon'$, where ϵ'' is the imaginary part of the dielectric constant) of unpoled samples were measured by using an impedance analyzer (HP4194A) over a frequency range from 100 Hz to 10 MHz at a heating rate of 2 K/min. A standard Sawyer-Tower circuit with a high-voltage amplifier (Trek 609D-6), an oscilloscope (LeCroy 9314 AM) and a functional generator (HAMGE, HM8131-2) were used to measure the D-E hysteresis loops of the samples. The I-V characteristics of the samples were also measured by using a current source meter (Keithley 237, U.S.A.).

III. RESULTS AND DISCUSSION

The room-temperature X-ray diffraction pattern of the GNT-50 sample, sintered at 1753 K/10 hrs., is shown in

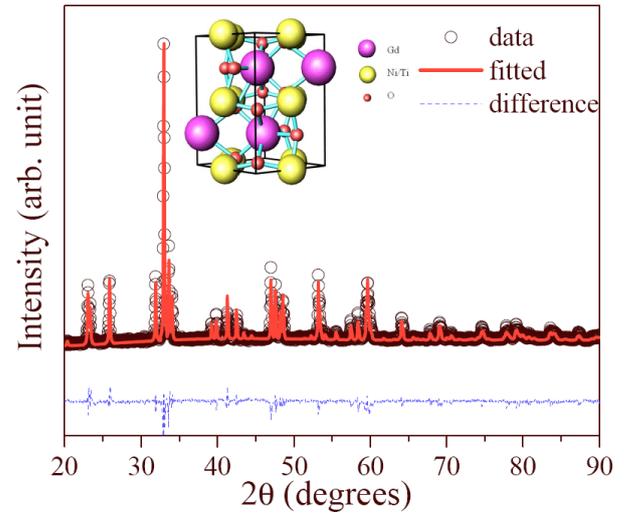


Fig. 1. (Color online) The measured X-ray diffraction pattern (o), the fitted pattern (—) and the difference (---) of the $Gd(Ni_{0.5}Ti_{0.5})O_3$ powder sintered for 10 hours at 1753 K. The inset shows the reconstructed crystal structure of a $Gd(Ni_{0.5}Ti_{0.5})O_3$ system from structure refinement.

Figure 1. The measured (o) and fitted (—) diffraction patterns show good agreement. From an average Rietveld structure analysis [29] using a PowderCell ($R_{wp} = 3.53$) [30], we found that the synthesized sample had a single-phase orthorhombic structure ($Pbmn$) with $a = 5.337(3)$ Å, $b = 5.620(5)$ Å and $c = 7.650(4)$ Å. We found that it had an isostructure with known $GdNiO_3$ and $GdTiO_3$ phases. The obtained lattice constants of GNT-50 were larger than those of $GdNiO_3$ ($a = 5.26063$ Å, $b = 5.48544$ Å, $c = 7.51116$ Å; ICSD #88040) and smaller than those of $GdTiO_3$ ($a = 5.393$ Å, $b = 5.691$ Å, $c = 7.664$ Å; ICSD #8149) systems. The slight difference in ionic radii of the B-site ions, the ionic radii of Ni^{2+} and Ti^{4+} are 69 pm and 61 pm, respectively [25], might not have been large enough to cause a noticeable average structure distortion detectable with our X-ray measurements. Furthermore, we expected that the $Pbmn$ structure would not allow piezoelectricity due to its centrosymmetric nature and should not have ferroelectricity [31].

The temperature-dependent dielectric constants (ϵ' ; real part) of the GNT-50 ceramic, shown in Figure 2, have an anomaly (hump) at 580 K (for 300 kHz) and reach zero values around 850 K. The existence of an anomaly and the shift of the anomaly towards higher temperatures when increasing the external frequency suggest that the GNT-50 system exhibited a relaxor behavior even though the system had a very small dielectric constant (~ 10 at room temperature), $\sim 10^3$ times smaller than that of typical relaxor ferroelectric materials. For example, the dielectric constant of the $PbMg_{1/3}Nb_{2/3}O_3$ system is about 18,000 at room temperature [32]. The temperature where the dielectric constant (for example, ~ 580 K for the GNT-50 ceramic) of the $Gd(Ni_xTi_{1-x})O_3$

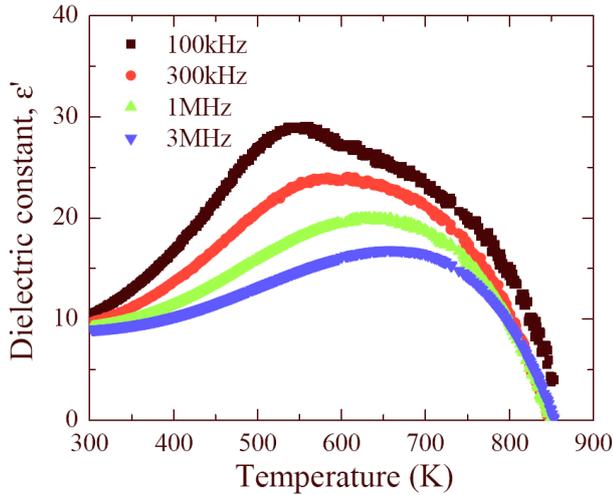


Fig. 2. (Color online) Temperature dependence of the dielectric constants (ϵ') of a $\text{Gd}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramic for various frequencies.

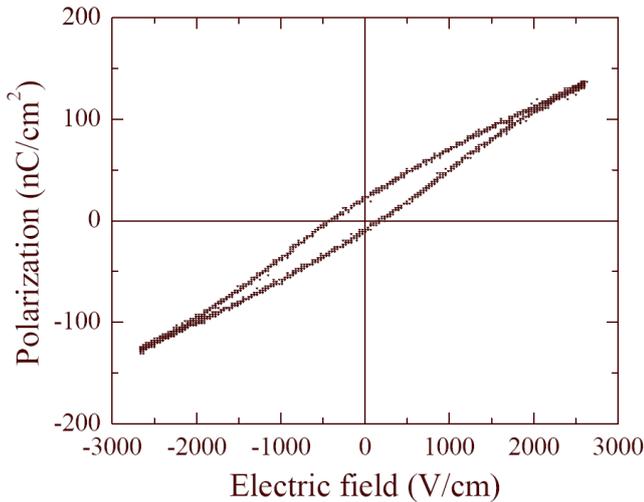


Fig. 3. D-E hysteresis loop of the $\text{Gd}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramic at room temperature measured at 100 Hz.

ceramic is maximum, is not a conventional paraelectric-ferroelectric phase transition temperature. Furthermore, $\text{Gd}(\text{Ni}_x\text{Ti}_{1-x})\text{O}_3$ ceramics do not follow the Curie-Weiss law [33]. The temperature-dependent (373 K to 1473 K) structural phase change, observed through an X-ray diffraction measurement (not shown here), of the GNT-50 sample, provided no evidence of an average structure change. However, we did notice that the peak position shifted to lower angles, which may be due to a thermal effect.

Figure 3 shows the D-E hysteresis loop of the GNT-50 ceramic measured at room temperature. The remnant polarization ($2P_r$) and the coercive field (E_c) from the measured hysteresis loop are 33 nC/cm^2 and 10 V/cm , respectively. It is remarkable that GNT-50 exhibits ferroelectricity at room temperature even though the mea-

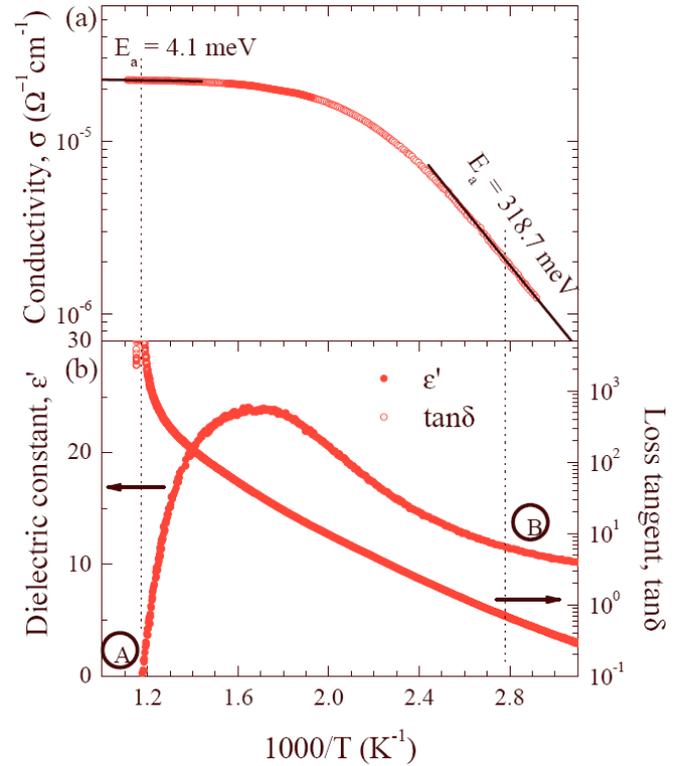


Fig. 4. (Color online) Temperature dependence of (a) the DC electrical conductivity of a $\text{Gd}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramic (dots) and the fitted activation energy (solid line) obtained from the variation of the conductivity, (b) the dielectric constant (ϵ') and the loss tangent ($\tan\delta$), at 300 kHz.

sured P_r value is three orders of magnitude smaller than that of the known Pb-based relaxor ferroelectric system, prohibiting replacement of Pb-based ferroelectric devices. (For example, the room temperature P_r value of a $(\text{PbMn}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{0.75}(\text{PbTiO}_3)_{0.25}$ single crystal is $30 \mu\text{C/cm}^2$ [34].) The physical origin of the small ferroelectricity of GNT-50 might be attributed to the electrical response of the local disordering due to the B-site's (Ni^{2+} and Ti^{4+}) ionic size mismatch. Since the ionic size difference between Ni^{2+} and Ti^{4+} is very small, we expect the amount of polarization due to the inhomogeneous local distribution of the B-site ions to also be small.

Figure 4(a) shows the temperature-dependent I-V characteristic of the GNT-50 ceramic for various temperatures. The corresponding dielectric constant and loss tangent of the GNT-50 ceramic measured at 300 kHz are also shown in Figure 4(b) for comparison. The increase in the electrical conductivity with temperature is attributed to the increasing dielectric loss (leakage current) in the system (see Figure 4(b)). Furthermore, the increasing dielectric loss with temperature forces a reduction of the permanent dipole moments' alignments in the system, causing the loss of ferroelectricity in the system. The nonlinear variation of the conductivity, as a

function of the temperature (see Figure 4(a)), suggests that the activation energy (E_a) of the system is different in the given temperature regions. By fitting the expression $\sigma(T) = \sigma_o \exp(-E_a/k_B T)$ to the measured data we obtained the activation energy as a function of temperature. For higher temperatures (region **A**), E_a was ~ 4.1 meV and for the lower temperatures (region **B**), E_a was ~ 318.7 meV. The discrepancy in activation energy at the two different temperature regions and the variation of the activation energy with temperature might be related to an increase in the hopping channel at higher temperature (lower activation energy). From this observation, we speculate that the system was no longer dielectric.

IV. SUMMARY

In summary, we found a new room-temperature relaxor ferroelectric material, a $\text{Gd}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramic, having a single orthorhombic phase ($Pbnm$). The temperature- and frequency-dependent dielectric constant of the GNT-50 ceramic showed the existence of an anomaly (hump) in the dielectric constant and a relaxor behavior. The measured D-E hysteresis loop at room temperature suggested the existence of ferroelectricity in this new compound, even though the system showed smaller $2P_r$ and E_c and a centrosymmetric phase. The physical origin of the ferroelectricity in the GNT-50 system (considering that GdTiO_3 and GdNiO_3 are not ferroelectric systems) might be due to the existence of a B-site local disorder caused by the slight differences in the B-sites' ionic radii in the system.

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