Magnetic Domain-Wall Induced Electric Polarization in NdCrO$_3$ Polycrystalline Ceramic

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Abstract: We reported the magnetic, dielectric and magnetoelectric properties of NdCrO$_3$ polycrystalline ceramics. Magnetization curves revealed two magnetic transitions at 227 K and 38 K, which corresponded to Cr$^{3+}$ canted antiferromagnetic ordering and Cr$^{3+}$ spin reorientation phase transition, respectively. At 11.5 K, a Schottky-type anomaly was observed, caused by Nd$^{3+}$ ground doublet Zeeman splitting. High-temperature dielectric relaxation exhibited a type of thermally activated relaxation process, which mainly resulted from the Maxwell–Wagner effect. The spin-reorientation of Cr$^{3+}$ ions and the Nd$^{3+}$ ground doublet splitting were observed to be accompanied by an electric polarization. The polarization could be induced by the presence of the antiferromagnetic-type domain walls, which led to spatial inversion symmetry breaking.

Keywords: NdCrO$_3$ ceramics; magnetic property; magnetoelectric properties

1. Introduction

Multiferroic materials, defined as those with multiple order parameters coexisting and coupling with each other, have received great attention in recent years due to their potential applications in multiple-state memory elements and spintronic devices [1,2]. However, single-phase multiferroics are rare because ferroelectricity and magnetism are often mutually exclusive [3]. Therefore, an exploring of multiferroics based on the emerging physical mechanism is an important and challenging issue. Until now, several mechanisms have been established for magnetically induced ferroelectricity, such as metal–ligand $p$–$d$ hybridization, symmetric-exchange striction, and antisymmetric inverse Dzyaloshinskii–Moriya interaction [4–6]. In recent years, the polarization induced by the magnetic domain wall has been demonstrated theoretically, such as those occurring in Lu$_2$CoMno$_6$ [7], R$_2$NiMno$_6$ [8] and AFeO$_3$ ($A =$ Lu, Y, Gd, Sm) [9,10].

Rare-earth orthochromites (RCrO$_3$) represent an attractive class of compounds due to the cross coupling between the 3d spins of transition metal ions and 4f moments of rare-earth ions, similar to RMnO$_3$. The Néel temperature can be improved without affecting the saturation magnetization when Mn is substituted with Cr [11,12]. RCrO$_3$ ($R =$ La, Pr, Sm, Nd, Gd, Tb, Ho, Dy, Er, Tm, Lu) compounds have shown potential multiferroic properties mostly due to the exchange striction between the R and Cr moments [13–21]. The NdCrO$_3$ magnetization curve differs significantly from those typically found in the rare-earth orthochromites [22]. Below the Néel temperature (227 K), two peaks were observed at about 200 K and 35 K, respectively. In addition, NdCrO$_3$ is with rich ferroelectric property. Indra et al. [19] reported ferroelectricity around $\sim$88 K in NdCrO$_3$, and the synchrotron diffraction study suggested that the ferroelectricity arose from the structural transformation from the...
NdCrO$_3$ polycrystalline ceramics were synthesized by conventional solid-state reaction. The detailed preparation process was similar to our previous work [23]. X-ray diffraction (XRD) patterns of the samples were recorded using a PANalytical Xpert Pro PW 3040 diffractometer with Cu K$_\alpha$ radiation. The morphology of the samples was measured by a field emission scanning electron microscope (FESEM). The dielectric property of the samples was measured by a Precision Impedance Analyzer (Wayne Kerr Electronics, 6500B, Cavendish Square, London, England). A physical properties measurement system (PPMS 9T, Quantum Design) was used for measuring the temperature dependence of the magnetization and dielectric constants of the samples.

3. Results and Discussion

Figure 1a shows the Rietveld refinement result of the XRD data of the NdCrO$_3$ polycrystalline ceramics. The Rietveld refinement with space group $Pbnm$ delivers the lattice parameters of $a =$ 5.420(9) Å, $b =$ 5.483(3) Å, and $c =$ 7.693(3) Å for the compound with a goodness-of-fitting value of $\chi^2 =$ 1.53 and $R_{wp} = 14.6\%$. The FESEM image of the NdCrO$_3$ bulk is shown in Figure 1b. The morphology of the sample consisted of irregular grains of different sizes, in which large grains were formed by stacking the thin plate layer by layer.

Figure 2 shows the zero-field-cooled (ZFC) and field-cooled (FC) temperature-dependent dc magnetization from 5 K to 320 K under a measuring field of 100 Oe. Two magnetic transitions, $T_N$ and $T_{SR}$, occurred at about 227 K and 38 K, respectively, which were consistent with previous studies [22,24–26] and their magnetic behavior could be explained by the strong effective field on the Nd$^{3+}$ moments exerted by the ordered Cr$^{3+}$ spin system [27,28]. The first transition temperature $T_N$
(227 K) corresponded to canted AFM transition of the Cr$^{3+}$ magnetic moments and the system showed a weak ferromagnetism. Thus, below $T_N$, the Cr$^{3+}$ moments configuration was from $\Gamma_2 (F_x, G_y, G_z)$ into $\Gamma_1 (A_x, G_y, C_z)$ at 38 K (spin reorientation) due to the magnetic crystal anisotropy. From the ZFC curves in Figure 2, a small hump was observed at $T \approx 11.5$ K (named as $T_{SP}$), which originated from the two-level Schottky effect caused by the split of the ‘Nd’ ground doublet [29]. The inset showed the reciprocal of the dc magnetic susceptibility curve (FC) and obeyed the Curie–Weiss law. Furthermore, the derived effective magnetic moment was $\sim 5.845 \mu_B$/f.u., which was bigger than the theoretical one (5.3 $\mu_B$/f.u.). The difference was either due to the magnetic polarization of the Nd moments by the Cr moments or ascribed to a slight change of the susceptibility due to the crystal field splitting effects of the excited $^7F_j$ levels [23].

**Figure 2.** (Color online) Temperature-dependent magnetization curve of NdCrO$_3$ at the magnetic field of 100 Oe. The inset shows the reciprocal of the dc magnetic susceptibility vs. the temperature.

Frequency dependence of the real part ($\varepsilon'$) of the dielectric constant (Figure 3a) and the loss (tan $\delta$) (Figure 3b) from 100 K to 360 K exhibited a thermal-activated relaxation behavior [23]. In the frequency range probed, dielectric relaxations could arise from two mechanisms: (a) the mobility of oxygen vacancies. The activation energy in various perovskite materials was in the range of 0.9–1.48 eV for the dielectric relaxations related to the mobility of oxygen vacancy [30]. In general, for a thermally activated relaxation process, the variation of peak position ($T_M$) can be described by the Arrhenius law:

$$F = f_0 \exp \left( -\frac{E_a}{k_B T_{M}} \right)$$ (1)

where $f_0$ is the pre-exponential, $E_a$ is the activation energy. Figure 3c shows the Arrhenius plots of tan $\delta$ for the relaxation. The solid line shows the fitting to the experiment data by Equation (1). The activation energy was derived to be about 0.313 eV. Therefore, the type of dielectric relaxation was not attributed to the mobility of oxygen vacancies. (b) Maxwell–Wagner relaxation originating from different conductivities between regions in the sample [31]. The characteristic of the Maxwell–Wagner relaxation mechanism is the $f^{-1}$ dependence of the imaginary part of dielectric constant data ($\varepsilon''$) at lower frequencies [23,31]. The slope of log($\varepsilon''$) vs. log($f$) is about $-1$ in the frequency range of $10^2$–$10^6$ Hz, as shown in the inset of Figure 3b at 110 K, clearly suggesting the presence of the Maxwell–Wagner relaxation. Since the contributions arising from grain (g), grain boundary (gb), and specimen-electrode interface can be separated by Nyquist plots [32], the Nyquist plot ($Z''$ vs. $Z'$) was studied (shown in Figure 3d). The Nyquist plot was well fitted with an equivalent circuit. The circuit made up of two sub-circuits in the series indicated that there were two relaxations corresponding to the grain boundaries and grains [32,33].
with an orthorhombic structure [9]. Moreover, additional calculations ratified that the mechanism was AFM domain boundaries, i.e., it does not require non-collinear magnetism or spin-orbit coupling. In addition, Yang reported that an improper polarization originates from an exchange striction mechanism that drives a polar displacement of the oxygen ions located at the magnetic domain walls in SmFeO3 with an orthorhombic structure [9]. The results indicated that there are native magnetoelectric coupling. As mentioned before, the magnetic configuration was changed from $\Gamma_2(F_x, C_y, C_z)$ to $\Gamma_1(A_x, G_y, C_z)$ at 38 K. $\Gamma_1(A_x, G_y, C_z)$ configuration is an AFM-type magnetic structure. Therefore, the electric polarization does not arise from the non-collinear magnetism. Yanez-Vilar [7] reported that a polarization may arise as a result of anti-phase AFM domain boundaries, i.e., it does not require non-collinear magnetism or spin-orbit coupling. In addition, Yang reported that an improper polarization originates from an exchange striction mechanism that drives a polar displacement of the oxygen ions located at the magnetic domain walls in SmFeO3 with an orthorhombic structure [9]. Moreover, additional calculations ratified that the mechanism was general among magnetic perovskites with an orthorhombic SmFeO3-like structure. Therefore, we may elucidate the dielectric anomaly by an AFM-type spin arrangement at domain walls that break the spatial inversion symmetry and cause polarization along a specific direction. Such an explanation agrees well with the theoretical calculations for the NdCrO3 material [9].

Figure 4a shows the dielectric behavior at a high frequency ($10^6$ Hz) in 5 K–65 K at zero and 2 T fields. At a zero magnetic field, there were dielectric anomalies around $T_{SR}$ and $T_{SP}$ marked in Figure 4b and the behaviors were more significant when an external magnetic field was applied. The results indicated that there are native magnetoelectric coupling. As mentioned before, the magnetic configuration was changed from $\Gamma_2(F_x, C_y, G_z)$ to $\Gamma_1(A_x, G_y, C_z)$ at 38 K. $\Gamma_1(A_x, G_y, C_z)$ configuration is an AFM-type magnetic structure. Therefore, the electric polarization does not arise from the non-collinear magnetism. Yanez-Vilar [7] reported that a polarization may arise as a result of anti-phase AFM domain boundaries, i.e., it does not require non-collinear magnetism or spin-orbit coupling. In addition, Yang reported that an improper polarization originates from an exchange striction mechanism that drives a polar displacement of the oxygen ions located at the magnetic domain walls in SmFeO3 with an orthorhombic structure [9]. Moreover, additional calculations ratified that the mechanism was general among magnetic perovskites with an orthorhombic SmFeO3-like structure. Therefore, we may elucidate the dielectric anomaly by an AFM-type spin arrangement at domain walls that break the spatial inversion symmetry and cause polarization along a specific direction. Such an explanation agrees well with the theoretical calculations for the NdCrO3 material [9].

Figure 3. (Color online) (a) The real part ($\varepsilon'$) of the dielectric constant vs. temperature at various frequencies. (b) Corresponding dielectric loss (tan $\delta$). The inset is log ($\varepsilon'$) vs. log (f) at 110 K in the low frequency region and the solid line is the one with slope −1. (c) The ln$f$ vs. 1000/T derived from tan $\delta$. (d) Nyquist plots at 300 K for the circuit shown.
AFM-type spin arrangement domain walls, which leads to spatial inversion symmetry breaking.

4. Conclusions

In summary, the magnetic, dielectric and magnetoelectric properties of polycrystalline NdCrO$_3$ ceramics were studied. Magnetization measurements showed that there were three magnetic transitions at 227 K, 38 K and 11.5 K, respectively. The dielectric constant measurements showed that the high temperature relaxation results from the Maxwell–Wagner effect. The abnormal dielectric phenomena at $10^6$ Hz at a low temperature indicated that there was native magnetoelectric coupling. Further analysis showed that the magnetic field-dependent polarization can be induced by the presence of the AFM-type spin arrangement domain walls, which leads to spatial inversion symmetry breaking.

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