Spin reorientation and giant dielectric response in multiferroic La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$

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Received 8 October 2012
Accepted for publication 4 April 2013
Published 19 April 2013
Online at stacks.iop.org/ANSN/4/025010

Abstract

A multiferroic sample of La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ was prepared by conventional solid-state reaction. X-ray diffraction study revealed La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ exhibiting a single phase with a tetragonal structure (F$_4$K$_2$Ni-perovskite-type structure, and space group of $I\bar{4}mm$). An iodometric titration method was used to determine non-stoichiometric oxygen concentrations ($\delta$) in the La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ ceramic. We found $\delta = -0.017$, which corresponds to a doping level of $n_b = x + 2\delta = 0.466$ (with $x$ being Sr$^{2+}$ content). The field-cooled (FC) magnetization curve indicated that there was a strong increase in spin ordering (SO) at temperature $T_{SO} \sim 100$ K. Below $T_{SR} \sim 50$ K, spins undergo a spin reorientation (SR) turning away from the stripe direction on cooling. Its dielectric constant $\varepsilon(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T)$ was estimated by basing on capacitance and conductance curves measured at different temperatures and frequencies. Dielectric relaxations of charge-ordered La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ ceramic were investigated in a broad temperature range. The giant dielectric constant ($10^4$–$10^5$) with a low dielectric loss of $10^{-2}$–$10^{-1}$ was also found.

Keywords: multiferroic La$_{1.5}$Sr$_{0.5}$NiO$_4$, giant dielectric, spin ordering

Classification numbers: 4.11, 5.02

1. Introduction

Capacitors with large capacitance per unit volume have been widely used in electronic devices, such as memories, energy storage, microwave filters, etc. An important issue of the modern electronics industry is the fabrication of capacitors from materials with a high dielectric constant (which basically depends on temperature and frequency), $\varepsilon(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T)$, where $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ are the real and imaginary parts, respectively). It has been expected that such the materials have high $\varepsilon$ values and low dielectric loss, independent of temperature and frequency. Recently, increasing scientific interest has focused on giant dielectric constant materials, such as CaCu$_3$Ti$_4$O$_{12}$ (CCTO) [1, 2], A(Fe$_{0.5}$B$_{0.5}$)O$_3$ (A = Ba, Sr; B = Nb, Ta) [3–5] La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ [6, 7]. Such materials have giant dielectric constant (up to $10^5$), with weak temperature dependence in a wide range of temperatures (around room temperature). Among these materials, La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ has attracted much interest because its structure is similar to that of high-temperature superconductivity compound La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ [8]. Studies of charge stripe ordered La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ are generally motivated by the desire to understand the charge order and its role in cuprate superconductors [9]. Reports on La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ and isostructural nickelates, however, reveal colossal dielectric constants (CDC), and point to the potential importance of charge ordering (CO) for the dielectric properties [6, 7]. The temperature stability of the checkerboard charge ordered state at half doping [8, 10] has thus attracted attention for dielectric studies [7]. Zhu et al [11] found that the significant dielectric response of CCTO was related to the electronic contribution, 

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and this was very attractive because of its potential practical application. According to this work, the role of the electronic mechanism in CDC materials should be emphasized. CO is a typical electronic mechanism that results from the strong electron interactions, and it has attracted much attention because of its unique physical properties such as electronic ferroelectricity [12].

Investigations of the charge and spin order for $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4+\delta}$ by neutron diffraction have revealed an unusual ground state [8]. The charge order is observed to have both checkerboard and stripe order Bragg reflections, but only spin stripe Bragg reflections are observed. While measurements of the spin excitation spectrum reveal a more complicated excitation spectrum than lower doping levels of $\text{La}_{2-x}\text{Sr}_{x}\text{NiO}_{4+\delta}$, all observed modes are associated with the spin stripe order, and no excitation modes from a checkerboard spin state [13, 14]. Furthermore, the change in dimensionality of the charge order from one dimensional stripe to two dimensional checkerboard orders was observed too [8]. The dielectric responses of these materials have been reported in previous works [6, 7]. However, the relationship between the dielectric response and spin ordering (SO), especially in the vicinity of spin reorientation temperature, was not discussed.

This paper presents the experimental results related to spin reorientation, spin ordered temperature and the dielectric constant dependence on temperature and frequency of polycrystalline $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4+\delta}$. The variation of the dielectric constant with temperature shows a dielectric response in the region of the spin order and spin reorientation, which constitutes evidence that the link between both phenomena is also present.

2. Experimental details

A polycrystalline ceramic of $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4+\delta}$ was prepared by the solid-state reaction method. High-purity powders of $\text{La}_2\text{O}_3$, $\text{SrO}$ and $\text{NiO}$ (99.9%) were combined with stoichiometrical quantities, and pre-annealed at 950°C for 10 h. The pre-annealed mixture was then re-ground, and pressed into a pellet. This pellet was finally sintered at 1100°C for 48 h in air. After sintering, it was cooled down to 500°C and kept at this temperature for 10 h before cooling down to room temperature. Its crystal structure was checked by an x-ray diffractometer (SIEMENS-D5000), using Cu-Kα radiation of $\lambda = 1.5406$ Å. The temperature dependence of magnetization for the sample was performed on a physical property measurement system (PPMS) quantum design. To measure the dielectricity, silver electrodes were fabricated by sputtering the silver layers on both sides/surfaces of a flat disc-shaped capacitor in the configuration of Ag/$\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4+\delta}$/Ag. Temperature and frequency dependences of the dielectric constant, $\varepsilon(\omega, T)$, were assessed by means of the capacitance and conductance data measured by using an HP-4192A impedance analyzer. Theoretically, the real part, $\varepsilon'(\omega)$, and the loss coefficient, $\tan \delta(\omega)$, depend on frequency of a flat disc capacitor (an insulating layer is sandwiched by two metallic electrodes) and are defined as

$$\varepsilon'(\omega) = \frac{C(\omega) d}{\varepsilon_0 S},$$

$$\tan \delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)},$$

where $\omega = 2\pi f$ is the angular frequency, $\varepsilon_0 = 8.85 \times 10^{-12}$ F m$^{-1}$ is the dielectric constant of vacuum, $S$ is the area of the electrodes and $d$ is the distance between two electrodes.

3. Results and discussion

Figure 1 shows an x-ray diffraction (XRD) pattern of $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4+\delta}$ recorded at room temperature. The inset shows the unit cell built from powder XRD data.
and O(2). Among these, the O(1) and O(2) positions are in the Ni–O and La–O planes, respectively. Additionally, oxygen O(2) is considered as a bridge/connection between La and Ni ions along the c axis. Ni ions are located at the 2a sites of the space group $I4/mmm$ with the $(0, 0, 0)$-original coordinate. This means that Ni ions are in the center of NiO octahedrons. La(or Sr) and O(2) ions are located at the positions $(0, 0, z)$ in the sites 4e. Meanwhile, the O(1) ions are at $(1/2, 0, 0), (0, 1/2, 0)$ in the sites 4c, see the inset of figure 1. Here, Sr is assumed to substitute randomly for La on the sites 4e. Having used an iodometric titration method to determine non-stoichiometric oxygen concentration ($\delta$) in La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$, we determined $\delta = -0.017$, which corresponds to a doping level of $n_h = x + 25 = 0.466$ (here $x = 0.5$) [15]. Obviously, the obtained values of $\delta$ and $n_h$ are in good agreement with those reported by Freeman et al [16] and Wu and Neumeier [17]. Here, the Sr$^{2+}$ substitution for La$^{3+}$ in La$_{2-x}$Sr$_x$NiO$_4$-based compounds is charge-compensated by the generation of extra holes (due to the transformation of Ni$^{2+}$ to Ni$^{3+}$) and/or non-stoichiometric oxygen. The presence of interactions of Ni$^{2+}$–Ni$^{2+}$ and Ni$^{3+}$–Ni$^{3+}$ leads to the magnetic properties of La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$, as further assessed below.

Having studied neutron diffraction on a La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ single crystal, Freeman et al [15] have found the SO state at temperature $T_{SO} \approx 80$ K, while below the temperature $T_{SR}\approx 57$ K the spins undergo a spin reorientation (SR) turning away from the stripe direction as the sample is cooled down to low temperature. The SR is intrinsic to charge stripe ordered La$_{2-x}$Sr$_x$NiO$_{4+\delta}$, but $T_{SR}$ depends on the doping level ($n_h$). According to Freeman et al [18], in each case the spins rotate in the same way, away from the stripe direction on cooling. The size of the reorientation in $x = 0.37$ ($\Delta \Phi \sim 14.6^\circ$), and more approximately in $x = 0.275$ and 0.4, is similar to that in $x = 1/3$ (,$\Delta \Phi \sim 13^\circ$), but smaller than in $x = 1/2$ (,$\Delta \Phi \sim 26^\circ$). They also indicated that for doping levels of $x = 0.275$, 0.37 and 0.4, the SR occurs around 15 K. At particular compositions of $x = 1/3$ and 1/2, however, $T_{SR}$ is about 50 K [18], close to the value observed in our present work. We can confidently infer the origins of the features in the magnetization from our experience of joint magnetization and neutron diffraction studies of La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ [15, 18, 19].

In figure 2 we show the field-cooled (FC) magnetization curve of La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ under an applied field of 1 kOe. On cooling, the FC curve increases monotonically, and then the gradient increases on cooling as the material undergoes SO at $T_{SO} \approx 100$ K. At $T_{SR} = 50$ K there is a small hump in the FC curve. This hump becomes more visible if performing the variation of (d(1/M)/dT versus $T$, see the inset of figure 2.

Commensurate (checkerboard) CO should be observed when the doping concentration of holes (Ni$^{3+}$) is 50%, such as for La$_{1.5}$Sr$_{0.5}$NiO$_4$. The commensurate CO of La$_{1.5}$Sr$_{0.5}$NiO$_4$ will appear at a higher temperature ($T_{CO} = 480$ K), and it will change to incommensurate charge ordering (ICO) (charge stripe) partially when the temperature decreases to 180 K($T_{ICO}$) [10], where the giant dielectric constant has been concluded to be closely related to CO. Taking into account for giant dielectric constants as investigated on La$_{1.5}$Sr$_{0.5}$NiO$_4$ [6, 20], we have also considered the temperature dependences of $\epsilon'\omega, T$ and $\tan\delta\omega, T$ at various frequencies for La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$. The data obtained are shown in figure 3. The real part $\epsilon'\omega, T$ reveals a pronounced step-like increase from order 10$^2$ to 10$^4$ at freezing temperature ($T_f$) and almost no change in a wide temperature range of 150–300 K. Its value at a given frequency is 10$^5$ or higher, revealing CDC existing in La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$, see figure 3(a). This is the common feature of CDC materials, such as CCTO [1, 2] and LaFeO$_3$ (A = Ba, Sr, B = Nb, Ta) [3–5]. When the temperature decreases to about 100 K, the dielectric constant gradually decreases and reaches a low platform value of about 10$^2$. At temperatures below 50 K, no CDC state is observed. Concurrently, $\epsilon''\omega, T$ shows well pronounced peaks. Low-temperature relaxations are observed in this sample, where typical relaxation steps (figure 3(a)) and peaks (see inset in figure 3(b)) are quite similar to the results reported early on a CCTO single crystal [1] and thin films [2]. The type of the Maxwell–Wagner relaxation step found in all investigated materials with CDC values is the so-called low-temperature relaxation. Notably, as shown in figure 3(a), with increasing frequency, the relaxation step is shifted toward higher temperatures. The coincidence of the onset temperature of the giant dielectric constant step with the incommensurate CO temperature ($T_{ICO}$) is found as shown in [6], where the CDC has been assigned to the CO. Localized small polarons are formed through holes (Ni$^{3+}$), and
the polarization due to strong electron–phonon interactions is found in nickelates [21], and thermal activated hopping of these localized small polarons should contribute to the CDC in CCTO between commensurate and incommensurate CO temperatures [22]. Therefore, we believe that the CDC effect in La$_{1.5}$Sr$_{0.5}$NiO$_{4+δ}$ is correlated with a spontaneous rearrangement of the CO from a checkerboard pattern to a stripe-type charge order and incommensurate CO. The rearrangement affects not only thermal activation energies, as mentioned above, but also the dielectric constant itself.

Below 100 K, the dielectric constant decreases very quickly while magnetization increases. Then there seems to be a link between the spin ordered state of material and its dielectric constant in this low-temperature region. We determined frequencies dependence of freezing temperature ($T_f$) from the peaks of the $\varepsilon''(f)/f$ at various frequencies. $T_f$ increases with frequency, which is reminiscent of relaxor-like behavior. The imaginary part $\varepsilon''(T)$ also shows a corresponding peak at $T_f$. Figure 4 shows the frequency change as a function of $T_f$. Interestingly, the frequency dependence of $T_f$ behavior is similar to Vogel–Fulcher law, which describes energy scale of the dipolar interactions and is expressed as

$$\tau(T) = \tau_0 \exp \left(\frac{E_a}{k_B(T - T_0)}\right),$$

(3)

where $\tau$ is relaxation time, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant and $T_0$ is an effective temperature which describes the energy scale of the dipolar interactions. Further, $f = 1/\tau$ is relaxation frequency, so another form of equation (3) is given as

$$\ln(f) = \ln(f_0) - \frac{E_a}{k_B(T - T_0)}.$$  

(4)

A solid line in figure 4 shows the best fit of ln($f$) dependence on freezing temperature $T_f$ to equation (4). The best results were obtained with $E_a/k_B = 161.5$ K, $T_0 = 41.8$ K and $\tau_0 = 1.1 \times 10^{-6}$ s. This result reconfirms that there is a weak magnetic interaction in La$_{1.5}$Sr$_{0.5}$NiO$_{4+δ}$.

4. Conclusion

We have synthesized the La$_{1.5}$Sr$_{0.5}$NiO$_{4+δ}$ ceramic single phase with a tetragonal structure, and then investigated its magnetic and dielectric properties. Our results showed that 100 K is the SO temperature, while at $T_{SR} = 50$ K spins undergo a SR. Furthermore, this material exhibited a giant dielectric constant of $\sim 10^5$, and low dielectric loss of $10^{-2}$–$10^{-1}$ in the low-frequency range. This giant dielectric constant effect is explained by the correlation with the charge order pattern of the material. The low-frequency dielectric response of La$_{1.5}$Sr$_{0.5}$NiO$_{4+δ}$ was also observed. This behavior with typical relaxation steps and peaks at $T_f$, $T_i$ increases with frequency and obeys the Vogel–Fulcher law.

Acknowledgments

Some experiments were performed on facilities belonging to the National Key Laboratory for Electronic and Devices, Institute of Materials Science. This work in Vietnam was supported by the National Foundation for Science and Technology under grant no. 103.02-2010.29. In Korea, it was also supported by the Converging Research Center Program funded by the Ministry of Education, Science and Technology (2012K001431).

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