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Room-temperature coexistence of electric and magnetic orders in $NiTiO_3$ and effect of ethylene glycol

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ABSTRACT

In this paper, $NiTiO_3$ powder was synthesized by the sol-gel method. Additionally, $NiTiO_3$ nanoparticles embedded in ethylene glycol (EG) mixtures ratios of Ni + Ti:EG = 1:0, Ni + Ti:EG = 1:1, and Ni + Ti:EG = 1:3 were considered. The phase structure, microstructure, electrical and magnetic properties of these compounds were investigated to reveal the effect of EG addition on these properties. Results indicate that all samples showed coexistence of ferroelectric and antiferromagnetic properties at room temperature, in agreement with predictions made by earlier theoretical calculations. EG addition was found to enhance the ferroelectric performance but reduce the antiferromagnetic properties. Addition of EG resulted in phase transition from R-3 to R3c due to various arrangements of cations in the structures and structural distortion which may be responsible for the differences observed in $NiTiO_3$ powder magnetic and ferroelectric performances.

1. Introduction

Multiferroic materials are a class of materials that yield simultaneous ferroelectricity and ferromagnetism. The ferroelectric and magnetoelectric coupling is related to many fields of condensed matter physics including charge, spin, orbit and lattice [1,2]. Such materials have potential applications in information storage, spintronic devices and sensors, and have become a leading research field in the world [3–6].

For single-phase multiferroic compounds, the coexistence of ferroelectricity and magnetism can be attributed to many different phenomena, including paramagnetic ion doping, structural anisotropy, symmetric lone pair electrons, ferroelectricity driven by geometric and electrostatic forces, and microscopic interaction [7–10]. To date, more than ten kinds of compounds have the intrinsic electromagnetic effect, including the widely studied $BiFeO_3$ and rare earth manganites [11–16]. However, seeking for a single phase multiferroic compounds with strong magnetoelectric effect at room temperature and exploring thier physical mechanisms still remain an important direction in the multiferroic research field.

There has been a recent surge of interest in the $MTiO_3$ (M = Mn, Fe, Ni) compounds as a result of theoretical predictions that such compounds could exhibit multiferroic properties, which could potentially enable switching of the direction of magnetization by the application of an electric field, and advance the development of multiferroic memories with high density and low-power-consumption [17–20].

$NiTiO_3$ belongs to the ilmenite family in structure, in which both Ni^{2+} and Ti^{4+} possess an octahedral coordination on each alternating cation layer of the compound, which is occupied by either Ni^{2+} or Ti^{4+} metals solely. Transition metal titanates in this ilmenite phase are known to show interesting magnetic and electric properties [21–23]. Previous studies of $NiTiO_3$ have reported that these materials possess dielectric [24], semiconducting [25], photocatalytic [26–28], ferroelectric and magnetic [29] behaviors. Specifically, Yuvaraj et al. [30] investigated the conducting and magnetic properties of $NiTiO_3$ by molten salt synthesis. In their study, they reported that $NiTiO_3$ shows antiferromagnetic behavior with a Neel temperature (TN) of 14.9 K and its coercivity was observed to increase below the TN, revealing the coexistence of antiferromagnetic with superparamagnetic behaviors of this compound. Furthermore, Acharya et al. [31] studied the ferroelectric and magnetic properties of $NiTiO_3$ and found that $NiTiO_3$ materials exhibit antiferromagnetic behavior at low temperature and ferromagnetic behavior at room temperature. Xin et al. [32] studied the structural, electrical, magnetic, and ferroelectric properties of $NiTiO_3$ in the IL phase (R-3) and the LN phase (R3c) through abinitio calculation. These studies reported that the IL phase was the ground state and that the Ti ion in its $3d^0$ state dominates ferroelectric polarization, whereas the filled d orbitals of the Ni cation contribute to the antiferromagnetic properties of $NiTiO_3$.

To date, solid-state [33], polymer-pyrolysis [34], sol-gel [35], coprecipitation [36], and stearic acid [37] methods have been used to synthesize $NiTiO_3$ powder. The sol-gel method is a relatively new

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technology for preparing inorganic nano materials, and offers the benefits of requiring simple equipment and easy operation, as well as allowing for high purity and high yields in the preparation of ultrafine powders [38]. There have been reports that metastable phases could be stabilized by this synthesis method [39].

In this study, $NiTiO_3$ nanopowders containing various ratios of ethylene glycol (EG) were synthesized by the sol-gel method. Synthesized samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy (RAMAN), fourier transform infrared spectrometer (FT-IR), vibrating sample magnetometry (VSM), and TF analysis methods. Herein, the influence of EG addition on crystal size, morphology, microstructure, ferroelectric, and magnetic properties of the nanocomposites is reported.

2. Experimental details

2.1. Material preparation

Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), tetra-butyl ortho-titanate ($C_{16}H_{36}O_4Ti$, TBOT), ethanol (C_2H_5O, EA), citric acid ($C_6H_8O_7$, CA), and ethylene glycol ($(CH_2OH)_2$, EG) were purchased from Xilong chemical company and were used without further purification.

At first, stoichiometric amounts of nickel nitrate and different portions of EG ratios of Ni + Ti:EG = 1:0, Ni + Ti:EG = 1:1, and Ni + Ti:EG = 1:3 were dissolved in EA by magnetic stirring for 30 min to form green transparent solution. Then CA and TBOT were added to the mixed solution. The solution was stirred for 3 h, allowed to stand at room temperature for 24 h and dried in air dry oven at 100 °C. Finally, pure yellow $NiTiO_3$ nanoparticles were obtained by heating the samples in a sintering muffle furnace at 700 °C for 3 h.

2.2. Material characterization methods

The prepared sample was subjected to various characterizations including XRD, SEM, RAMAN, FT-IR, electrical and magnetization measurements. To characterize the $NiTiO_3$, The crystalline phase of the powders was characterized by X-ray diffraction (XRD) at room temperature using a Rigaku D/Max 2500 powder diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) at a scanning rate of 4 deg/min in the 2θ range of 10–90°. SEM (FEI SIRION 200) was used to observe the micro morphology of the $NiTiO_3$ powders. Sample structure bonding was characterized by laser Raman spectroscopy (RAMAN, HR LabRa800) over a measurement range of 50–1000 nm. FT-IR spectrum of the sample in KBr pellet was recorded in the range of 400–4000 cm^{-1}. Polarization-Electric field (P-E) hysteresis loop measurement was carried out using a TF analyzer 2000 (aix ACCT). The electric measurement was carried out after making electrodes by sliver paint on the parallel sides of the pellet. The magnetic properties of the pure $NiTiO_3$ samples were characterized using VSM modle (Lake Shore 7410) with 2 T magnet in the room temperature. All the magnetic measurements were corrected by subtracting the back ground signal, which mostly came from the sample holder.

3. Results and discussion

3.1. Structural and morphological analysis

We employed XRD to determine the phase purity of $NiTiO_3$ synthesized in 700 °C for 3 h (Fig. 1). The XRD pattern of the sample not containing any added EG (1:0) agrees with that of $NiTiO_3$ with JCPDS file cards No. 83-0198 and has the space group R-3 (148). The lattice parameters refinement from XRD data are $a = b = 5.0325$ (Å), $c = 13.80$ (Å) and $V = 302.74$ ($Å^3$).

For the prepared samples with EG (1:1 and 1:3), the sample patterns agree well with $NiTi_{0.99}O_3$, JCPDS file cards No. 79-1213, and have the space group R-3 (148). The lattice parameters of sample (1:1) are $a = b = 5.0331$ (Å), $c = 13.7994$ (Å) and $V = 302.73$ ($Å^3$), for the sample (1:3), $a = b = 5.0329$ (Å), $c = 13.7993$ (Å) and $V = 302.71$ ($Å^3$). These samples can be well indexed as an ilmenite structure with planes (0 1 2), (1 0 4), (1 1 0), (0 2 1), (0 2 4) and (1 1 −6) [40,41]. The XRD results revealed that the addition of EG resulted in small difference in the lattice parameter and volume reduction. These samples were single phase within the resolution of the equipment, as no other diffraction peaks indicating any impurities were observed.

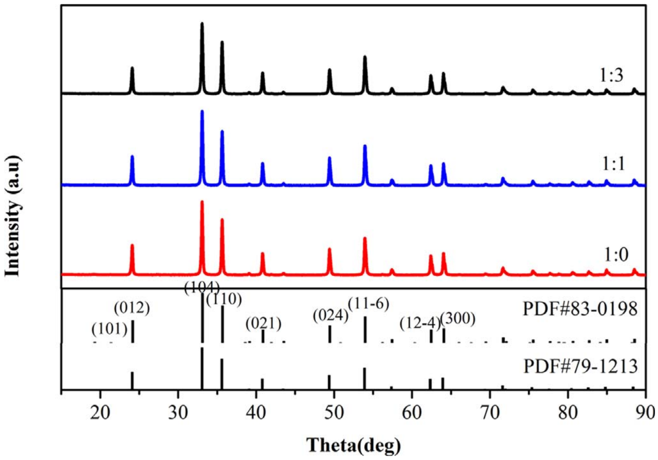

Fig. 1. XRD pattern of as-prepared $NiTiO_3$ samples, 1:0 → n (Ni + Ti): n (EG) = 1:0, 1:1 → n (Ni + Ti): n (EG) = 1:1, 1:3 → n (Ni + Ti): n (EG) = 1:3.

The mean crystal sizes of samples obtained from the Debye- Sherr's formula:

$$D = \frac{0.89\lambda}{\beta\cos\theta} \tag{1}$$

where D is the size of the crystal, 0.89 is the Sherr's constant, λ of 1.5406 Å is the wavelength of the X-ray Cu Ka source, β is the width at half maximum of the diffraction peaks, and θ is the diffraction angle.

The average crystal sizes of the samples were 51.6 ± 0.3 nm (1:0), 46.8 ± 0.4 nm (1:1), and 43.8 ± 0.4 nm (1:3), respectively. The observed crystal size decreased as the amount of added EG increased. This effect may be due to the reduction of acidity as more EG is added, which decreased the crystallinity of $NiTiO_3$. The particle size reduction may largely be attributed to the modified viscosities of the solvent blends [42].

The morphology of the as-synthesized $NiTiO_3$ nanoparticles with various ratios of EG (0/1/3) formed at 700 °C for 3 h was studied by FE-SEM (Fig. 2). Fig. 2(a) suggests that the sample particle containing no added EG (1:0) underwent slight agglomeration, as the powder exhibited hexagonal particles with nonuniform morphology in size and shape. The images for the samples containing EG (1:1) and (1:3), are shown in Fig. 2(b) and (c) respectively, showing that these powders were dispersed uniformly with low degree of crystallization. The micrographs from this SEM study confirmed that the crystalline degree of $NiTiO_3$ powder decreased with a larger amount of added EG. Many pores observed in microstructure, which may be related to the fusion and growth of nanoparticles.

3.2. Raman and FT-IR analysis

Raman scattering spectra can offer additional evidence of phase transition and structural changes, providing more information about crystallite vibrations and distortions of the crystal lattice besides XRD analysis. To further explore the effect of EG addition on microstructural characteristics, Raman spectra were recorded at room temperature, and are shown in Fig. 3. Ten Raman active modes around 191, 229, 246, 290, 345, 394, 465, 483, 612, and 708 cm^{-1} were observed with the