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Structural, magnetic and dielectric properties of $Bi_4Nd_{0.5}Gd_{0.5}Ti_3FeO_{15}$ ceramics

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Abstract

Single-phase Aurivillius $Bi_4Nd_{0.5}Gd_{0.5}Ti_3FeO_{15}$ ceramics was synthesized via the solid-state reaction technique. Rietveld refinement of the full XRD pattern was carried out to obtain the detailed structure of the compound. Dielectric response and electrical properties of the ceramics were investigated in a wide range of frequency and temperature by dielectric/impedance spectroscopies. Two dielectric relaxations were distinguished, which were attributed to grains and grain boundaries respectively, by the combination of impedance and modulus analysis. Resistance of grain boundaries was determined much larger than that of grains. The kinetic analysis of temperature dependent dielectric data was performed to study the corresponding relaxation-conduction behaviors in the material. The thermal magnetization measurement evidenced the paramagnetic characteristic of the material, but localized antiferromagentic coupling would exist below 200 K. In addition, a phase transition was observed at ~240 °C.
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Keywords: Aurivillius compound; Dielectric; Impedance analysis; Magnetic; Structure

1. Introduction

Bismuth-based layer-structure compounds, generally known as Aurivillius phases can be described as $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$,where n indicates the number of perovskite-like units. Its crystal structure consists of pseudo-perovskite blocks $(A_{n-1}B_nO_{3n+1})^{2-}$ alternating with $(Bi_2O_2)^{2+}$ layer along the c-axis [1,2]. A high curie temperature, large spontaneous polarization and fatigue-free behaviors, give it a wide applicability in electronic elements, such as piezoelectric, transducers and memory devices [3,4]. Recently, multiferroic single-phase Aurivilius compounds have received considerable attention due to their fantastic physical essence and potential application in multi-field coupling devices [5–7]. For these functional ceramics, different microstructural components such as grains, grain boundaries and electrodes can provide different contribution to the electrical properties of the ceramics [8–11]. The defects such as oxygen vacancy, valence fluctuation of ions and other electrical heterogeneities seriously hinder the performance of these materials [12–15]. Therefore, a properly understanding of the microstructures–defects–electrical is essential. The dielectric and impedance analysis is an effective technique to distinguish the electrical contribution of different microstructural components and provide elementary information about defect behaviors.

In this work, the Aurivillius $Bi_4Nd_{0.5}Gd_{0.5}Ti_3FeO_{15}$ ceramics is synthesized for the first time. The crystal structure of the compound is obtained by XRD Rietveld refinement. Thermal magnetic investigation indicates that the material is a paramagnet. A phase transition is observed at ~240 °C in the material. The dielectric relaxations and electrical properties are studied by dielectric/impedance spectroscopies. Kinetic

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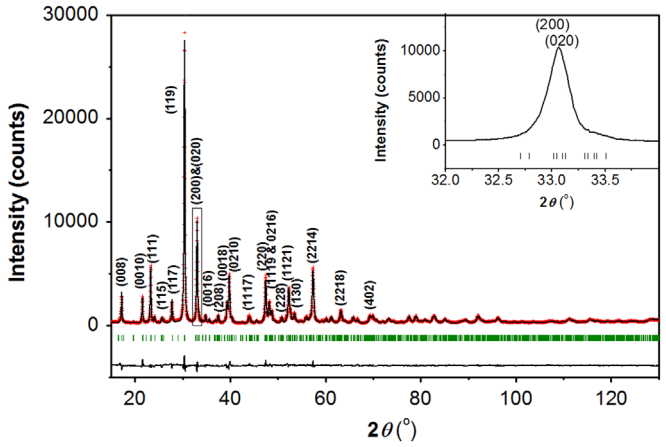

Fig. 1. Rietveld refinement plots of XRD pattern of BNGTF ceramics. The symbol "+" represents the observed value, solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions, and the difference curve is shown at the bottom of the figure. The inset shows the enlarged diffraction profile around $2\theta = 33.1^\circ$, corresponding to (200) and (020) diffractions.

analysis of dielectric and impedance data is performed to discuss the defect-related relaxation and conduction behaviors.

2. Experimental

$Bi_4Nd_{0.5}Gd_{0.5}Ti_3FeO_{15}$ (BNGTF) ceramics were prepared by the high temperature solid state reaction. Stoichiometric amounts of Bi_2O_3, Nd_2O_3, Gd_2O_3, TiO_2, and Fe_2O_3 (purity > 99.9%) dried reagents were mixed thoroughly in ethanol medium. The mixed raw material was initially pre-calcined at 780 °C for 2 h in air. A small amount of polyvinyl alcohol (PVA) was mixed as a binder in the calcined powders and pressed into pellets. The pressed pellets were sintered at 1100 °C for 2 h in air. X-ray diffraction (XRD, Cu-$K\alpha$, X'pert Pro, PANalytical B. V., Almelo, Netherlands) measurements were performed to identify the phase constituent of the sintered samples. The sintering process was repeated until the XRD patterns did not change between two sequential sintering cycles. The XRD data for Rietveld refinement were collected in a 2θ range from 15° to 130°. The pellet faces were polished to make parallel and smooth. Silver past was painted on both sides of the pellets and heated at 600 °C for 15 minutes in order to carry out the electrical measurements. Dielectric and impedance spectra were measured by an impedance analyzer (Agilent 4294A, 40 Hz–10 MHz) in a temperature range from 30 °C to 600 °C, equipped with a variable-temperature thermostat. Magnetic properties were measured using a physical property measurement system (PPMS, Quantum Design, U.S.).

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the XRD pattern of BNGTF ceramics. All the diffraction peaks match well with the PDF card (PDF no. 38–1257, for $Bi_5Ti_3FeO_{15}$), indicating the formation of single-phase 4-layered Aurivillius ceramics. Rietveld refinement of the full XRD pattern was performed using the FullProf program [16]. The full XRD pattern was well fitted with the orthorhombic $A2_1am$ structure. The observed and calculated XRD patterns, and the difference profiles from Rietveld refinement for BNGTF are displayed in Fig. 1. The refined structural parameters are listed in Table 1. In the refinement, we tested two kinds of occupation of Nd/Gd ions, (1) occupying the Bi sites in the perovskite blocks as shown in Table 1; (2) randomly substituting the Bi ions in both the perovskite blocks and the $(Bi_2O_2)^{2+}$ slabs. The model of random occupation of Nd/Gd ions resulted in larger values of the agreement factors (e.g. $R_{wp} \sim 11.8\%$). It implies that the Nd/Gd ions prefer occupying the Bi sites in the perovskite blocks. As pointed out by Armstrong and Newnham, [17] there should exists considerable strain at the interface between the perovskite blocks and $(Bi_2O_2)^{2+}$ slabs in the structure of Aurivillius, i.e. the perovskite blocks and $(Bi_2O_2)^{2+}$ slabs in the bismuth titanate Aurivillius are under compressive and tensile strain, respectively [18]. Thus, the preferred occupation of Nd/Gd ions on the Bi site in the perovskite blocks is reasonable due to the smaller ionic size of Nd^{3+} (radius = 0.111 nm, CN = 8) and Gd^{3+} (0.105 nm, CN = 8) than Bi^{3+} (0.117 nm, CN = 8) [19]. Consequently the release of stress/strain is expected, which would decrease the structural distortion of the Aurivillius structure. As a result, the reduction of unit-cell volume of BNGTF, especially in the *a-b* plane, is observed compared to that of $Bi_5Ti_3FeO_{15}$. In addition, the substitution of Nd/Gd for Bi in the perovskite blocks would weaken the covalent hybridization of the Bi 6s and O 2s/p orbits which results in the ferroelectric distortion in $BiFeO_3$ [20]. The decrease of the structural distortion is evidenced by the XRD data. The XRD profile at ~33.1° (corresponding to (020) and (200) diffractions) which distinctly splits into two peaks in

Table 1
Refined structural parameters for the $Bi_4Nd_{0.5}Gd_{0.5}Ti_3FeO_{15}$ sample at room temperature.

Space group	$A\ 2_1am$ orthorhombic
Cell	a (Å) = 5.4218(6), b (Å) = 5.4175(6), c (Å) = 41.211(1), V (Å^3) = 1210.5(0.2), Z = 4

Atomic parameters

Atom	Site	x	y	z	B (Å^2)
$Bi_1/Nd_1/Gd_1$	4a	0.25	0.2475(8)	0	0.50(1)
$Bi_2/Nd_2/Gd_2$	8b	0.2593(9)	0.2479(7)	0.1047(1)	0.41(4)
Bi_3	8b	0.2711(6)	0.2689(6)	0.2189(1)	0.59(4)
Ti_1/Fe_1	8b	0.2722(9)	0.2287(8)	0.4506(1)	0.16(6)
Ti_2/Fe_2	8b	0.2710(11)	0.2489(8)	0.3459(1)	0.16(6)
O_1	8b	0.5031(31)	0.4984(29)	0.2539(8)	0.29(23)
O_2	4b	0.3176(28)	0.1842(26)	0.5	0.34(20)
O_3	8b	0.3167(21)	0.3191(22)	0.4087(4)	0.57(19)
O_4	8b	0.3387(16)	0.2216(18)	0.3088(4)	0.57(19)
O_5	8b	0.6182(19)	0.5532(18)	0.0509(6)	0.62(16)
O_6	8b	0.0695(24)	-0.0119(23)	0.0402(5)	0.62(16)
O_7	8b	0.5152(30)	0.5017(31)	0.1381(9)	0.62(16)
O_8	8b	0.0694(20)	-0.0549(18)	0.1441(8)	0.62(16)

Agreement factors $R_p = 8.52\%$ $R_{wp} = 10.5\%$ $S = 1.5$

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