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Structural, magnetic and optical properties of mulitiferroic $(BiFeO_3)_{1-x}(BaTiO_3)_x$ solid solutions

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ABSTRACT

Binary multiferroic $(BiFeO_3)_{1-x}(BaTiO_3)_x$ [$x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5] solid solutions were synthesized by conventional solid-state reaction method. A good crystalline phase has been optimized at the sintering temperature of 960 °C for 2 h. A single rhombohedral phase was found up to 70 mol% of $BiFeO_3$. The morphotropic phase boundary was found just above $x = 0.3$, and finally it transformed into a cubic structure. The M–H curve revealed $BiFeO_3$ (BFO) as an antiferromanetic material, whereas; induced weak ferromagnetism was observed for $(BiFeO_3)_{1-x}(BaTiO_3)_x$ ceramic with different compositions at room temperature. The results are evidence for destruction of a space-modulated spin structure in bulk materials, via substituent effects, releasing a latent magnetization locked within the cycloid. The calculated values of the direct band gap of the $(BiFeO_3)_{1-x}(BaTiO_3)_x$ ceramics were found to be 2.72, 2.75, 2.80 and 2.85 eV for $x = 0$, 0.1, 0.2 and 0.3, respectively.

1. Introduction

Multiferroic materials, in which some kind of magnetic order and ferroelectricity occur in the same phase, can offer a magnetoelectric effect, showing the potential of controlling charge via an applied magnetic field, or conversely, controlling spin via an applied voltage [1]. Multiferroic materials are more appropriate for the construction of multifunctional devices, such as electric field controlled magnetic data storage devices, sensors, transducers and spintronics devices [1,2]. The low Neel temperature or Curie temperature of almost all the single phase multiferroic materials restricted their applications at room temperature, except for some materials such as $BiFeO_3$. $BiFeO_3$ and its solid solutions have a high Neel temperature and a high Curie temperature. BFO is among the very few such systems actually existing, since these two order parameters are normally mutually exclusive [1]. The single crystal of $BiFeO_3$ is ferroelectric with a Curie temperature of 1043 K [3] and antiferromagnetic ($T_N \sim 643$ K) [4] with a G-type spin structure. The spin is provided by the transition metal cation Fe^{3+}. In this arrangement, the Fe^{3+} cations are surrounded by six nearest Fe^{3+} neighbours; with opposite spin directions. Microscopically, the antiferromagnetic spin order is not homogenous for $BiFeO_3$ single crystals. Neutron diffraction studies have revealed an incommensurately modulated spin structure of $BiFeO_3$ [5,6]. The incommensurately modulated spin structure of BFO has also been confirmed by a line shape analysis of the nuclear magnetic resonance (NMR) spectra [7,8].

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Synthesis of pure BFO is not an easy task because, first of all, evaporation of Bi_2O_3 during the synthesis process makes it difficult to keep the Bi_2O_3 and Fe_2O_3 in stoichiometry, which gives rise to the impurity $Bi_2Fe_4O_9$ phase. The formation of $Bi_2Fe_4O_9$ can be avoided by adding excess Bi_2O_3 but this could also lead to the formation of a Bi-rich $Bi_{25}FeO_{40}$ secondary phase. Secondly, like an incongruent-melting compound; the kinetic cooling process always leads to local deviations from stoichiometry according to the phase diagram of the Bi_2O_3–Fe_2O_3 system [9]. In order to overcome these problems, a rapid thermal process (RTP) with a high heating rate around 50 °C/s was introduced to reduce the evaporation of the volatile component during the synthesis of the $BiFeO_3$ ceramics, [10] and a quenching process following conventional sintering was performed to freeze the metastable $BiFeO_3$ down to room temperature [11].

With excellent multiferroic properties, $BiFeO_3$ has some drawbacks especially in its bulk form. Synthesis of polycrystalline $BiFeO_3$ always results in impurity phases due to the kinetics of its formation. Few researchers have reported the synthesis of single-phase polycrystalline materials. The second problem in studying the physical properties of this material is the high leakage currents and low resistivity of samples at room temperature, making the observation of the ferroelectric loop particularly difficult, and in limiting cases, impeding practical applications. The third problem is due to the presence of a spiral spin arrangement that cancels the macroscopic magnetization arising from the Dzyaloshinskii–Moriya (D–M) interaction and inhibits the linear magnetoelectric effect [12]. In order to improve the multiferroic properties, other materials of perovskite structure were commonly introduced to form solid solutions with $BiFeO_3$. Processing $BiFeO_3$ with other perovskite structured materials, such as $BaTiO_3$ and $PbTiO_3$, would prevent the formation of secondary phases and enhance the electrical resistivity [13,14]. In addition, Ti substitution at the Fe sites can increase the magnetization of the novel compounds [15,16]. As the multiferroic properties of $BiFeO_3$ are attracting renewed interest, and the "$(BiFeO_3)_{1-x}(BaTiO_3)_x$" solid solution appears to be promising for practical multiferroic applications, we have systematically investigated the structure, magnetic and optical properties of this composite.

2. Experimental details

A traditional mixed oxide ceramics process was utilized for the production of the $(BiFeO_3)_{1-x}(BaTiO_3)_x$ solid solutions. Taking $BiFeO_3$ and $BaTiO_3$ individually in proper stoichiometric proportions, a series of samples of the BF–BT system were prepared by solid state reaction. First of all, $BaTiO_3$ was prepared by the solid state method using materials of commercial reagent-grades of TiO_2 and $BaCO_3$ with purity ~99.8%. These reactants were carefully weighed in stoichiometric proportions (1:1 mol ratio) and mixed thoroughly by grinding in an agate mortar. The Mixed powder was calcinated in a furnace for 2 h at the temperature of 800 °C; this was followed by the sintering at a temperature of 950 °C to achieve the perovskite phase formation of $BaTiO_3$. Similarly, $BiFeO_3$ ceramic was prepared from Bi_2O_3 and Fe_2O_3 reactants followed by calcination at 600 °C for 2 h and sintering at 870 °C for 5 min.

We have synthesized the $(BiFeO_3)_{1-x}(BaTiO_3)_x$ solid solution with the content of $BaTiO_3$ as 0.1, 0.2, 0.3, 0.4 and 0.5, respectively. The $BiFeO_3$ and $BaTiO_3$ in stoichiometric proportion were mixed and ground in an agate mortar for 5 h. The raw powders were calcinated at 800 °C for 4 h in an open crucible to achieve perovskite phase formation. Powders of different compositions were mixed with a few drops of 6% concentrated aqueous polyvinyl alcohol (PVA) binder and again ground in the agate mortar for 2 h. The mixed powders with different composition were pressed into pellets with a pressure of 1.47×10^8 Pa. In order to evaporate the aqueous polyvinyl alcohol (PVA) binder, these pellets of different compositions were heated at a temperature of 250 °C for one hour. Next, these pellets of the $(BiFeO_3)_{1-x}(BaTiO_3)_x$ solid solutions with different composition were sintered at temperature of 960 °C for 2 h. Then the samples are named after their compositions, e.g., 90BF-10BT stands for $(BiFeO_3)_{0.9}(BaTiO_3)_{0.1}$.

Samples of the BFO and $(BiFeO_3)_{1-x}(BaTiO_3)_x$ solid solutions of different compositions were characterized by X-ray diffraction to confirm their proper phase formation. The microstructure of these samples was characterized by a Bruker AXS D-8 advanced diffractometer with Cu Kα radiation (1.54 Å) and step size of 0.02°/s. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 1 T. A UV-VIS-NIR spectrometer (Varian Cary 5000 model) was used for the optical characterization of different samples of the BF–BT system. A field emission scanning electron microscope (FEI Quanta 200F model) was used to study the surface morphology of the different samples. Energy dispersive X-ray spectroscopy (EDXS) was carried out to confirm the concentration and ratio of the elements Bi, Fe, O, Ba and Ti in the $(BiFeO_3)_{1-x}(BaTiO_3)_x$ composite.

3. Results and discussion

The XRD diffraction patterns of different samples of $(BiFeO_3)_{1-x}(BaTiO_3)_x$ with various compositions, such as $x = 0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$, and $x = 0.5$ are shown in Fig. 1. Samples with $BaTiO_3$ content were found to crystallize in the perovskite single phase. On the other hand, the $BiFeO_3$ ($x = 0$) ceramic crystallized in the perovskite $BiFeO_3$ with a small amount of $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ impurity phases [17]. It is a difficult task to prepare single phase $BiFeO_3$ because of the low structural stability of the perovskite $BiFeO_3$ and the volatile nature of Bi_2O_3. Crystallization in the $(BiFeO_3)_{1-x}(BaTiO_3)_x$ ceramics is attributed to the stabilization of the perovskite phase. The XRD patterns of $(BiFeO_3)_{1-x}(BaTiO_3)_x$ have been analyzed and the single rhombohedral phase was found up to 70 mol% of $BiFeO_3$. The morphotropic phase boundary was found just above $x = 0.3$, and finally it transforms into a cubic structure, confirming the earlier reports [17]. This result agreed with the phase diagram of $(BiFeO_3)_{1-x}(BaTiO_3)_x$ proposed by Kumar et al. , in which the composition around $x = 0.3$ should be in the range