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Magneto-thermal conduction and phonon anomalies across magnetic transitions in multiferroic (poly and nanocrystalline) bismuth ferrite

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ABSTRACT

Bismuth ferric oxide (BFO) or bismuth ferrite is a multiferroic material with perovskite structure in which ferroelectric and antiferromagnetic orderings coexist. The magneto-electric coupling in this material makes it interesting from fundamental physics and applications points of view. As a result of complex magneto-elastic coupling and spin-glass behavior at low temperatures, the material exhibits a number of phase transitions driven by magnetic ordering. Earlier reports indicate that the primary order parameter in these transitions is not polarization but are related to magnon mode softening. In order to throw more light on the magneto-elastic and phonon related properties of this material, we measured the thermal transport properties, thermal conductivity and specific heat capacity, in the presence of an external magnetic field and compared the results with the zero field case. Results are reported for polycrystalline as well as nanocrystalline samples of BFO between 140 K and 250 K. A photopyroelectric thermal wave technique has been employed for the measurements. Anomalies in thermal properties observed at 140 K, 200 K and 240 K in polycrystalline samples as well as their changes with applied field are explained in terms of magneto-elastic and spin–phonon couplings. It is found that the transitions get less well defined and one of the transition temperatures get shifted upwards considerably as the particle sizes are reduced to nanometer scales. Particle size dependences of phonon and magnon–phonon scattering are invoked to explain these results.

1. Introduction

Magneto-electric materials that are multiferroic exhibit ferroelectric (or anti-ferroelectric) properties coupled to ferromagnetic (or anti-ferromagnetic) ones [1–3]. Multiferroic materials exhibit novel properties, such as variation in the remnant electric polarization with applied magnetic fields or variations in magnetization with applied electric fields. Bismuth ferric oxide, $BiFeO_3$ (or BFO), is a material known to be one of the very few materials that exhibits multiferroism at room temperature. The co-existence of ferroelectric (FE) and antiferromagnetic (AFM) orderings at room temperature makes this material one of the most promising candidates for room temperature magneto-electric applications such as magnetic field sensors.

Bulk BFO is a material with rhombohedrally distorted ferroelectric perovskite structure, with R_3C space group, exhibiting a Curie temperature $T_c = 1100$ K [4]. The rhombohedral unit cell parameters are $a = 5.63$ Å and $\alpha = 89.35°$. BFO shows G-type ferromagnetism up to Neel temperature $T_N = 643$ K [5], where all the neighboring magnetic moments are oriented anti-parallel to each other. Magnetic ordering in BFO is rather complex due to the Dzyloshinsky–Moriya (DM) interaction, which results in a canted AFM ordering of the Fe^{3+} spins in the system. These canted Fe^{3+} moments induce a lattice strain which increases the free energy of the lattice. In order to minimize the free energy a spiral spin structure is superimposed on the AFM ordering, resulting in a rotation of the spins. The axis along which the spins are aligned rotates throughout the crystal, resulting in a spiral spin structure with a large period, with periodicity approximately 62 nm, which is incommensurate with the lattice parameter of the material [4,5]. For bulk BFO, the magnetic hysteresis loop exhibits AFM characteristics with zero coercivity. The existence of the modulated magnetic structure in BFO has been experimentally confirmed by neutron diffraction, Mossbauer spectroscopy, NMR and EPR measurements, but several questions related to magnetic orderings still remain unresolved [5–8].

In a complex system like BFO exhibiting multiferroic properties, scattering between different types of quasiparticles play a significant role in determining their microscopic properties. An effective method to detect coupling between lattice phonons and other quasiparticles such as magnons and spinons is to measure the thermal conductivity of the material and its magnetic field dependence. Spin–phonon or magnon–phonon couplings are, in favorable situations, revealed by a measurement of the magnetic field dependence of thermal conductivity. In systems exhibiting

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magnetic phase transitions or changes of either ground state or spin structure, magnetic excitations strongly scatter phonons, which get reflected in thermal conductivity measurements. Measurement of heat capacity (C_p) helps to gather information about entropy changes during phase transitions. In multiferroic systems one can expect abnormal variations of C_p near temperatures where magnetic transitions occur. So variation of C_p as a function of temperature and magnetic field would be an effective tool to examine the nature of such transitions. In favorable situations C_p (H, T) data allows one to estimate magneto-caloric effect in the material.

Recent measurements of dielectric constant and mechanical response of multiferroic BFO in the polycrystalline ceramic phase indicate four phase transitions at temperatures below room temperature, reported at $T_1=50$ K, $T_2=140$ K, $T_3=200$ K and $T_4=240$ K [9]. It has been reported that these transition temperatures show significant shift from bulk ceramic phase when the BFO particle sizes are scaled down to nanometer range. Temperature dependent Raman and dielectric spectroscopy measurements on BFO nanoparticles reveal that these transition temperatures get shifted respectively to 113, 148, 203 and 253 K (with an uncertainty ± 5 K), and to 85, 168, 205 and 230 K respectively [10]. Such deviations are obvious in nanoparticles of BFO because size reduction to nanometer scales induces extra strain, co-ordination distortion and lattice disorder on the surface compared to bulk particles, which result in a different frustrated spin structure and high magnitude for magnetic spin–strain interaction [11]. Park et al. [12] inferred that the anomalous magnetization behavior of BFO nanoparticles arise from a complex interplay between the finite size effects, inter-particle interactions and random distribution of anisotropy axes in nanoparticle assemblies.

The physical properties of single crystal materials do change significantly as they are scaled down to nanometer sizes, and it is important to understand the size dependent changes in material properties to find potential applications such as nanoscale sensors and devices [13–15]. Though good amount of work related to magnetic and dielectric properties of BFO in the bulk and nanoforms have been reported, several questions related to the nature of the spin reorientations and their interactions with lattice phonons still remain unanswered. In an attempt to address issues related to the occurrence of multiple spin–reorientation phase transitions in BFO at low temperatures, we have carried out measurement of the variations in thermal transport properties at low temperatures in the presence and absence of external magnetic field. Though limited work on the variations of specific heat capacity across these multiple transitions have appeared in literature, no results on the variations of thermal conductivity are available. The present work aims at reporting the low temperature thermal properties of BFO in its polycrystalline and nanocrystalline phases, and their variations with an external magnetic field. The work also aims at gathering information about magneto-caloric effect (MCE), induced by the coupling of magnetic sub-lattices with external magnetic field, which alters the magnetic part of entropy due to change in field [16]. One of the main goals of recent studies on MCE has been to find useful magnetic materials, which have large entropy changes at low applied magnetic fields, for possible applications in magnetic refrigeration [17].

Any dynamic measurement of the thermal conductivity across a transition temperature is difficult as the sample cannot be kept in a steady state during measurements. Thermal wave measurements based on the photothermal effect, such as thermal wave interferometry, photothermal deflection technique, photoacoustic method and photopyroelectric measurement, help to get over this difficulty. In these techniques one measures the thermal diffusivity rather than thermal conductivity. Thermal diffusivity measurements do not suffer from heat losses from the sample during measurements and hence are more accurate than a direct measurement of thermal conductivity by any steady state method. With a proper choice of boundary conditions, a photothermal technique, such as photopyroelectric (PPE) method, enables a simultaneous measurement of thermal diffusivity and effusivity, from which the thermal conductivity and specific heat capacity can be extracted. The photopyroelectric technique has been used earlier to measure the variations of thermal conductivity and heat capacity of a few crystalline solids as they undergo phase transition with variations in temperature [18,19].

In this work we report the thermal diffusivity, thermal conductivity and specific heat capacity of polycrystalline as well as compacted nanocrystalline forms of BFO in the presence of an external magnetic field as the material undergoes three of the four successive phase transitions cited above. Measurements have been limited to the upper three transition temperatures, all below room temperature, as these are the prominent ones in which spin couplings are known to play significant roles.

2. Experimental methods

2.1. Sample preparation and characterization

The hydrothermal method was followed to synthesize polycrystalline as well as nanocrystalline samples of BFO. Polycrystalline samples were synthesized from an equimolar mixture of $Bi(NO_3)_3\cdot 5H_2O$ and $Fe(NO_3)_3\cdot 9H_2O$ in 40 ml with KOH used as mineralizer. The mixture was ultrasonically dispersed in KOH for 15 min and then transferred into a Teflon-lined autoclave for hydrothermal treatment. The hydrothermal treatment was performed for 6 h at 200 °C, with concentration of KOH maintained at 4 M [20]. The solution was then filtered and washed, first with 10% acetic acid followed by de-ionized water. In order to scale down BFO to nanometer sizes, an additional chemical reagent, potassium nitrate, was added. The hydrothermal conditions for this included maintenance of temperature at 200 °C for 24 h, keeping KOH concentration at 12 M [21]. The same procedure was followed for filtration and washing, but with distilled water and absolute ethanol. The samples were then dried. Compressed circular pellets of polycrystalline samples with diameter 12 mm were obtained by applying pressure in the range 8–9 t followed by sintering at 820–850 °C. For nanocrystalline sample a much reduced palletizing pressure (4–5 t) and sintering temperature (450–500 °C) were used. The samples were carefully lapped down in thickness to about 0.5 mm for photopyroelectric measurements. For both samples, densities close to 90% of the theoretical density were achieved.

The X-ray powder diffraction patterns of the samples were recorded with a diffractometer working in the angular range 5–360° (Bruker, Model: AXS D8 Advance). The grain morphology and particle sizes of the samples were examined with a scanning electron microscope (Jeol, Model: 6390 LV) and a transmission electron microscope (Jeol, Model: JEM 2100F) respectively.

The temperature dependence of the dielectric constant (ε_r) and tan δ loss of the samples, keeping the frequency at 500 kHz, were measured for comparison with earlier measurements. An Impedance analyzer (Hewlett Packard, Model: 4194A) along with a home built sample holder, whose temperature could be varied with a cold finger, was used for these measurements. The DSC thermograms for the samples were recorded in the temperature range 140–300 K with a differential scanning calorimeter (Metler Toledo, Model 822^e).

2.2. Photopyroelectric thermal wave measurements

A photopyroelectric (PPE) technique was employed to determine the thermal properties of compressed samples [18,19]. For