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Magnetic anisotropy and magnetodielectric coefficients in Cr_2O_3 and $Fe_{0.4}Cr_{1.6}O_3$

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ABSTRACT

The temperature dependence of magnetization, magnetic anisotropy, coercive field and the magnetodielectric coefficient of Cr_2O_3 (undoped) and $Fe_{0.4}Cr_{1.6}O_3$ (doped) was experimentally investigated. Test data shows that the presence of Fe ions at the interstitial spaces of the Cr_2O_3 crystal lattice decreases the Neel Temperature by ~80 K when compared to the undoped Cr_2O_3. Also both the doped and undoped samples display maxima in magnetic anisotropy and magnetodielectric coefficient as a function of temperature. The maxima for the Fe doped samples occurs at a temperature approximately 80 K below the temperature measured for the Cr_2O_3 samples, i.e. similar to the shift observed in the Neel Temperature. These results suggest that Neel Temperature, magnetic anisotropy, and the magnetodielectric coefficients are physically interrelated through competing principal exchange interactions and may provide a useful approach to search for new multiferroic materials.

1. Introduction

Discovering a new single phase multiferroic material with the co-existence of large magnetization and polarization coupling has been a scientific endeavor since the early efforts of Curie in 1894. Multiferroicity is generally defined as the coupling between different ferroic orders (electric, magnetic, or elastic) with one subset producing the magnetoelectric effects (ME) and/or the other magnetodielectric effect (MD) [1,2]. While a few single phase materials exhibit ME/MD behavior [3–6], a fundamental understanding of the intrinsic coupling mechanisms is insufficient to adequately search for new materials with large coupling at room temperature. Therefore, understanding ME or MD coefficients and their relationships to other intrinsic material properties is important. Researchers previously believed that ME/MD is maximized at magnetic transition temperatures; however, recent experimental reports and first principle calculations indicated maximum values at temperatures below magnetic transition temperatures [7–12]. While interesting, a clear explanation for this maximum has not been provided and if a correlation could be found with other intrinsic material properties this information may be useful in searching for new MD/ME materials. In this paper we correlate experimentally measured maxima in MD coefficients with maxima in magnetic anisotropy (K_{eff}) coefficients for both Cr_2O_3 and $Fe_{0.4}Cr_{1.6}O_3$.

Both α-Fe_2O_3 and Cr_2O_3 are crystallographic isomorphs stabilized into a rhombohedral corundum structure with space group R3c but with different magnetic ordering [13]. Cr_2O_3 is a well understood ME material system first predicted by Dzyaloshnskii and measured by Astrov in 1961 [14,15]. Cr_2O_3 is a symmetric insulator with low magnetic moment and low antiferromagnetic ordering temperature i.e. Neel Temperature ($T_N = 310$ K). Researchers have suggested that the magneto electric/magnetoelastic effect in Cr_2O_3 is attributed to changes in magnetic space group symmetry [16]. The magnetic space group symmetry is altered by diffusion/substitution of atoms with similar radius but different magnetic properties such as combining Fe_2O_3 ($T_N = 950$ K) with Cr_2O_3 yielding $Fe_{2-x}Cr_xO_3$ [17–20]. Such substitution is believed to alter the compressive and tensile stress in the material [18] which influences magnetoelastic coupling. Recent neutron diffraction studies on $Fe_{2-x}Cr_xO_3$ series report a reduction in the Neel temperature T_N, with values ranging from 230 K to 250 K as compared to both Cr_2O_3 ($T_N \sim 310$ K) and Fe_2O_3 with $T_N \sim 950$ K [13,20,21]. While the magnetic structure of the solid solution at $0 < x < 0.6$, where $x = Cr/(Cr + Fe)$, is similar to that of hematite, a different unidentified magnetic ordering involving Fe(III) ions is present in the solid solution $x = 0.8$ below its Néel Temperature

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(about 150 K) [22]. This is rather interesting since such magnetic ordering at much lower temperatures than T_N influences the material's magnetic and electrical response. While previous studies evaluated $Fe_{2-x}Cr_xO_3$ alloys magnetic properties [17,18,20,21], reports on the relationship between the MD coefficients with their magnetic properties and/or temperature dependence is unavailable. The present paper attempts to establish a correlation between measured maxima of the effective magnetic anisotropy and magnetodielectric coefficient as a function of temperature for Cr_2O_3 and $Fe_{0.4}Cr_{1.6}O_3$ solid solution.

2. Experimental details

In this paper a solid solution of $Fe_{0.4}Cr_{1.6}O_3$ was fabricated by mechanical alloying of high purity (99.99%) nano crystals of Fe_2O_3 (~15 nm) with Cr_2O_3 (~ 60 nm). Stoichiometric amounts of both materials (Alpha Aesar, USA and Aldrich chemicals) were mechanically ground for 2 h in atmosphere followed by ball milling for ~72 h. Sample dry milling was conducted in air with a 1:7 mass ratio of the materials to zirconia balls. Composite samples were fabricated and the magnetodielectric properties were measured. The composites were prepared by mixing nano powders of either Cr_2O_3 (undoped) or $Fe_{2-x}Cr_xO_3$ (doped) with an epoxy resin (Spurr resin, Polysciences Inc.) at a volume ratio of 50:50. The liquid resin with particles was ultrasonically mixed followed by curing at 70 °C for 12 h. The nanocomposites consisted of densely packed particles producing magnetic coupling between adjacent particles, i.e. dipole–dipole interaction was present. Samples were cut into 3.3 mm × 3.3 mm × 1 mm blocks with silver epoxy electrodes applied along both 3.3 × 3.3 mm^2 areas.

Fourier Transform Infra Ray Spectroscopy (FTIR) was conducted to evaluate the chemical bond formation in both Cr_2O_3 and Fe substituted Cr_2O_3 systems. Micro Raman spectroscopy tests provided information on the magnetic ordering present at room temperature in Cr_2O_3 after Fe substitution. Composites' magnetization measurements at different temperatures along with Zero Field Cooling curves at 50 Oe were also measured using a Superconducting Quantum Interference Device (SQUID, Quantum Design, MPMS XL-5). Dielectric constants were measured using an HP 4274A multi frequency (0–100 kHz) LCR meter with excitation of 1 V and temperature varied from 100 to 300 K at DC magnetic field bias of 1T monitored by a Gauss meter (FW Bell 6010) to evaluate MD as a function of temperature. In the following paragraphs a brief review of the test data generated is provided.

3. Results and discussion

A Scanning Electron Microscope (SEM) image of the $Fe_{0.4}Cr_{1.6}O_3$ powder is shown in Fig. 1. Tests were conducted on both doped and undoped particles as well as composite samples. X-ray diffraction tests were conducted for both doped and undoped composites samples (see Fig. 2). Fig. 2 shows the XRD spectra for Fe_2O_3, Cr_2O_3 and the solid solution powder of $Fe_{0.6}Cr_{1.4}O_3$. The peaks match well the reported spectra [18,23]. The peaks of Fe_2O_3 and Cr_2O_3 phases are well separated before mechanical alloying. However, in the $Fe_{0.6}Cr_{1.4}O_3$ solid solution powder the individual peaks of Fe_2O_3 sample disappear and the broader peaks resemble the peaks corresponding to Cr_2O_3. This suggests Fe atoms diffuse into the Cr lattice sites to form a solid solution of $Fe_{0.6}Cr_{1.4}O_3$. The alloy formation involves the kinetic diffusion of Fe^{3+} ions into the boundary of Cr^{3+} ions due to thermal heating during the milling process [2,4,18]. The overall lattice structure of the $Fe_{0.6}Cr_{1.4}O_3$ solid solution consists of Cr_2O_3 having a fraction of Fe^{3+} ions occupying interstitial spaces.

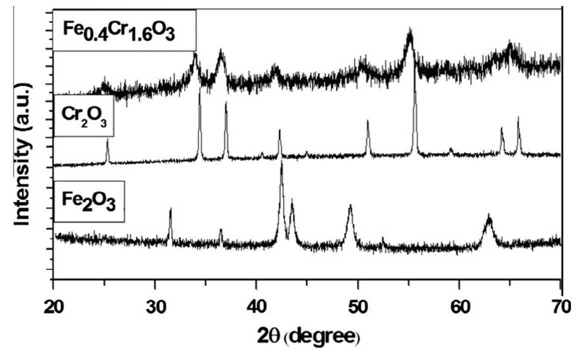

Fig. 2. XRD spectrum for Fe_2O_3, Cr_2O_3 and $Fe_{0.4}Cr_{1.6}O_3$ samples.

Fig. 3 shows the FTIR spectra for both Cr_2O_3 and $Fe_{0.4}Cr_{1.6}O_3$ nano particles for the wave number 300–2000 cm^{-1}. The merging of the doublet at 581.57 and 635.1 cm^{-1} in the Cr_2O_3 sample into a single broad band in the $Fe_{0.4}Cr_{1.6}O_3$ sample suggests the Fe (III) is being substituted for Cr in the base structure of Cr_2O_3. This indicates a solid solution of $Fe_{0.4}Cr_{1.6}O_3$ nano particles is present rather than a collection of Cr_2O_3 and Fe_2O_3 particles [24].

Fig. 4 shows the Raman spectra recorded at room temperature for both Cr_2O_3 and $Fe_{0.4}Cr_{1.6}O_3$ nano particles. The Raman modes for the Cr_2O_3 sample occur at 338.46 cm^{-1} (E_g), 540.46 cm^{-1} (A_g) and 599.26 cm^{-1} (E_g) [25]. The strongest peak for both samples is observed at 540.46 cm^{-1}. For the $Fe_{0.4}Cr_{1.6}O_3$ sample a broad band extending from 578 to 800 cm^{-1} with a band head at ~675 cm^{-1} is observed. A similar band has also been previously reported in thermally (400 °C) oxidized Cr_2O_3 with $FeCrO_3$ [25,26]. The authors attribute this band to magnon peak representing the energy associated with the collective excitation of the electron spin and anisotropy interactions in the crystal lattice [25]. The presence of this strong magnon peak reduces the spontaneous magnetization and also the temperature dependent magnetic transitions caused due

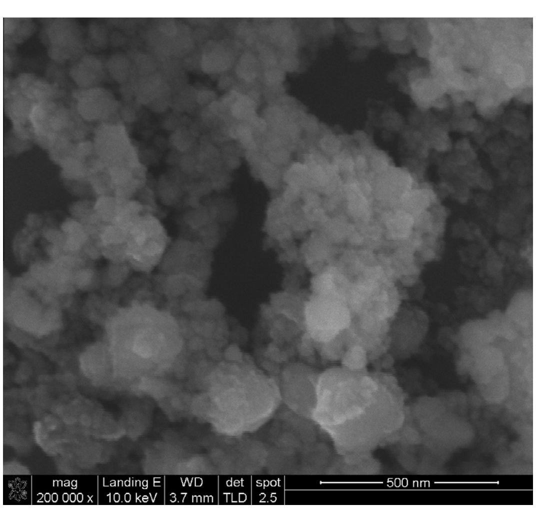

Fig. 1. SEM micrograph of $Fe_{0.4}Cr_{1.6}O_3$ solid solution powder after milling.

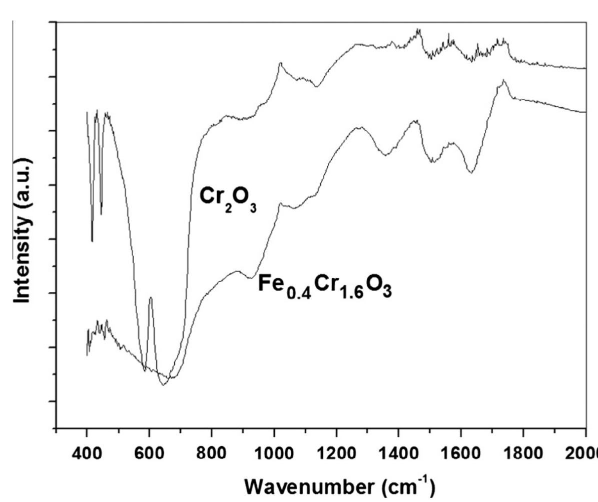

Fig. 3. (a) FTIR spectrum for undoped (Cr_2O_3) and (b) doped ($Fe_{0.4}Cr_{1.6}O_3$) sample.