Spin control by doping non-magnetic ions in magnetic ordering type of multiferroic materials.

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Introduction

Recently, numerous researches have been focused on the magnetic ordering type of multiferroic materials, RMn₂O₅, orthorhombic RMnO₃ (R=rare earth), delafossite CuFeO₂, spinel CoCr₂O₄, MnWO₄, and hexagonal ferrite (Ba,Sr)₂Zn₂Fe₁₂O₂₂[1]. These materials are reported showing ‘frustration magnet’ due to canted spiral magnetic spin. These phenomena bring about incommensurate spin behavior and ferroelectricity by spin current model. Especially, CoCr₂O₄ materials have been investigated for multiferroic property and dielectric anomalies have been explained by spin current model. But CoCr₂O₄ materials have very small polarization (~2μC/m²) [2]. Here, we control spin behavior by substituted non-magnetic ions in CoCr₂O₄.

The objective of the present research is to elucidate the role of the Cr ion in the multiferroic effect by replacing the Cr ion in the multiferroic material with a similar transition metal ion Fe. The similar ionic radii of Fe³⁺ and Cr³⁺ mean that lattice distortion effects of the substitution may be ignored, and the electronic structure can be studied.

Experiment and results

The spinel CoCr₁.⁹⁸⁵⁷Fe₀.⁰²O₄ (CCO), Co₀.⁹Zn₀.₁Cr₁.⁹⁸⁵⁷Fe₀.⁰²O₄ (CZCO), CoCr₁.₈₈Al₀.₁⁰⁵⁷Fe₀.⁰₂O₄ (CACO) powders were prepared by wet chemical solution process. Weighted amounts of cobalt acetate, zinc acetate, aluminum acetate, chrome nitrate, and ⁵⁷Fe isotope were dissolved in acetic acid, ethanol, nitric acid, and distilled water. For doping ⁵⁷Fe to facilitate Mössbauer measurement, iron isotope was dissolved in a diluted HNO₃ and then the proper amount of ⁵⁷Fe added into the solution. The solution was refluxed at 80 oC for 12 hours to allow the gel formation and then dried at 120 °C in a dry oven for 24 hours. The dried powder was grounded and annealed at 1000 °C for 3 hours in air. The crystal structures of the samples were examined by x-ray diffraction with Cu Kα radiation ( λ = 1.5406 Å ). Magnetic properties were characterized by the vibrating sample magnetometer (VSM). The Mössbauer spectra were recorded using a conventional spectrometer a electromechanical with a ⁵⁷Co source in a rhodium matrix.

The crystal structure was found to be single-phase cubic spinel with space group of Fd₃m. The lattice constants a₀ were determined to be CCO = 8.340, CZCO = 8.328, and CACO = 8.305 Å, respectively. These results are due to that Co²⁺(0.72 Å) and Zn²⁺(0.74 Å) have the similar ionic radius and they occupies A (tetrahedral) sites and Cr³⁺(0.63 Å) and Al³⁺(0.51 Å) have the different ionic radius and they occupies B (octahedral) sites. The Bragg factor RB and RF were below 5 %, respectively.

The zero field cooled (ZFC) magnetization curves taken at 100 Oe for various temperatures are shown in Fig. 1. The ferrimagnetic transition were observed at around 90 ~ 97 K, which was determined as Néel temperature. ZFC curves showed an abnormal magnetic transition (Tₛ) at 28 K(CCO), 18 K(CZCO), 20K (CACO), which are associated with spiral magnetic order in the systems. With Al ions substituted in B site, the magnetic transition temperature decreases, but the magnetization increase. Mössbauer spectra of CACO were taken at various temperatures ranging from 4.2 to 93 K as shown in Fig. 2. Two magnetic phases were developed and showed two sharp sextets of spectra below Tₛ. The isomer shifts at all temperatures range are about 0.3 mm/s relative to Fe metal, which means that both Fe ions are Fe³⁺ states. The electric quadrupole splittings(ΔE_Q) were found to be nearly zero values below T_N. The magnetic hyperfine fields of outer and inner sub-spectrum were H_m = 480 and 462 kOe, respectively. These effects can be explained by Al substitute specification B site. These results bring forth the decreasing Néel and spin-reorientation temperature and increasing magnetic moments.