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

K. Choi<sup>1</sup>, S. Kim<sup>1</sup>, B. Lee<sup>2</sup>, C. Kim<sup>1</sup>

1. Physics, Kookmin Univ., Seoul, South Korea; 2. Hankuk University of Foreign Studies, Yongin, South Korea

### Introduction

Recently, numerous researches have been focused on the magnetic ordering type of multiferroic materials,  $\text{RMn}_2\text{O}_5$ , orthorhombic  $\text{RMnO}_3$  (R=rare earth), delafossite  $\text{CuFeO}_2$ , spinel  $\text{CoCr}_2\text{O}_4$ ,  $\text{MnWO}_4$ , and hexagonal ferrite  $(\text{Ba,Sr})_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  [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,  $\text{CoCr}_2\text{O}_4$  materials have been investigated for multiferroic property and dielectric anomalies have been explained by spin current model. But  $\text{CoCr}_2\text{O}_4$  materials have very small polarization ( $\sim 2 \mu\text{C}/\text{m}^2$ ) [2]. Here, we control spin behavior by substituted non-magnetic ions in  $\text{CoCr}_2\text{O}_4$ .

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  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  mean that lattice distortion effects of the substitution may be ignored, and the electronic structure can be studied.

### Experiment and results

The spinel  $\text{CoCr}_{1.98}\text{Fe}_{0.02}\text{O}_4$  (CCO),  $\text{Co}_{0.9}\text{Zn}_{0.1}\text{Cr}_{1.98}\text{Fe}_{0.02}\text{O}_4$  (CZCO),  $\text{CoCr}_{1.88}\text{Al}_{0.10}\text{Fe}_{0.02}\text{O}_4$  (CACO) powders were prepared by wet chemical solution process. Weighted amounts of cobalt acetate, zinc acetate, aluminum acetate, chrome nitrate, and  $^{57}\text{Fe}$  isotope were dissolved in acetic acid, ethanol, nitric acid, and distilled water. For doping  $^{57}\text{Fe}$  to facilitate Mössbauer measurement, iron isotope was dissolved in a diluted  $\text{HNO}_3$  and then the proper amount of  $^{57}\text{Fe}$  added into the solution. The solution was refluxed at 80 °C 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  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Magnetic properties were characterized by the vibrating sample magnetometer (VSM). The Mössbauer spectra were recorded using a conventional spectrometer a electromechanical with a  $^{57}\text{Co}$  source in a rhodium matrix.

The crystal structure was found to be single-phase cubic spinel with space group of  $Fd3m$ . The lattice constants  $a_0$  were determined to be CCO = 8.340, CZCO = 8.328, and CACO = 8.305 Å, respectively. These results are due to that  $\text{Co}^{2+}$  (0.72 Å) and  $\text{Zn}^{2+}$  (0.74 Å) have the similar ionic radius and they occupies A (tetrahedral) sites and  $\text{Cr}^{3+}$  (0.63 Å) and  $\text{Al}^{3+}$  (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 ( $T_S$ ) 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  $T_S$ . The isomer shifts at all temperatures range are about 0.3 mm/s relative to Fe metal, which means that both Fe ions are  $\text{Fe}^{3+}$  states. The electric quadrupole splittings ( $\Delta E_Q$ ) were

found to be nearly zero values below  $T_N$ . The magnetic hyperfine fields of outer and inner sub-spectrum were  $H_{\text{hf}} = 480$  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.

[1] S-W Cheong and Maxim Mostovoy, Nature, **6**, 13 (2007).

[2] Y. Yamasaki, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, and Y. Tokura, Phys. Rev. Lett., **96**, 207204 (2006).

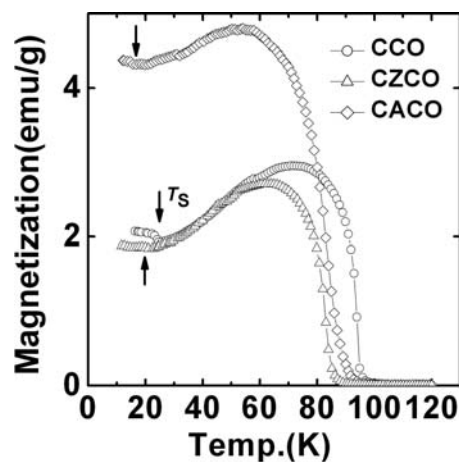


Fig. 1 Magnetization for CCO, CZCO, CACO at various temperatures at 100 Oe.

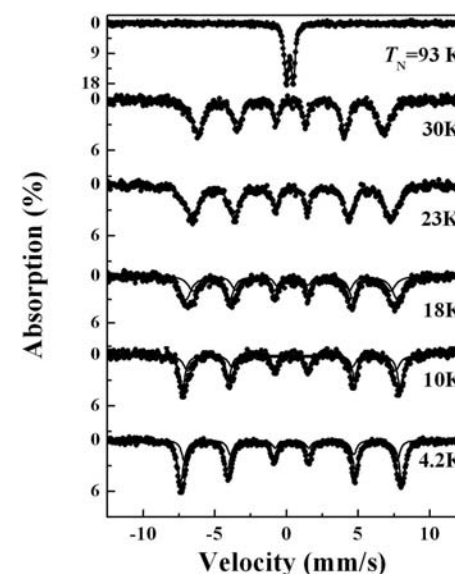


Fig. 2. Mössbauer spectra of CACO at various temperatures.