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Effect of cobalt-doping on the magnetic properties and crystal structure of delafossite $AgFeO_2$ nanoparticles

Takahiro Yamazaki*, Shota Morimoto, Kuminori Hyodo, Tomoya Ishikawa, Yuko Ichiyanagi

Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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A B S T R A C T

Delafossite oxides are expected to be widely used in future applications, such as dilute magnetic semiconductors and multiferroic materials. $AgFe_{1-x}Co_xO_2$ ($0 \leq x \leq 0.2$) nanoparticles were synthesized by co-precipitation from silver nitrate, iron (III) nitrate, cobalt (II) nitrate, and sodium hydroxide. The resulting samples had approximately 10 nm diameter, determined by X-ray powder diffraction and TEM imaging. X-ray absorption fine structure and X-ray absorption near edge structure spectra of the samples indicated that the lattice constant axis decreased with increasing Co ion doping, and Fe and Co ions mainly occurred as trivalent Fe^{3+} and Co^{3+}. Measurement of the magnetic properties by a SQUID magnetometer showed a gradual shift in the magnetic transition temperature (T_{N1}) from 14.4 to 11.2 K with increasing Co ion doping.

1. Introduction

Delafossite oxides ($A^{I}B^{III}O_2$) [1] have attracted considerable theoretical [2] and experimental [3–5] attention recently due to their interesting magnetic and electric properties, which have also seen them employed in a wide range of important applications. These oxides are composed of a hexagonal *A* layer sandwiched by O layers positioned between hexagonal *B* layers along the c axis.

This structure is seen such materials as hole-doped $CuAlO_2$ and $AgAlO_2$, p-type transparent semiconducting oxides that have been shown theoretically to exhibit superconductivity [6] or properties of a dilute magnetic semiconductor (DMS) [7,8].

Furthermore, compounds based on $AFeO_2$ (where *A* is Ag or Cu) have complicated magnetic spin due to frustrated exchange interactions caused by the triangular lattice system of Fe ions in their structure [9,10]. These spin arrangements induce ferroelectric polarization, which can be described by the inverse Dzyaloshinskii-Moriya (DM) effect. Therefore, these materials are expected to be multiferroic, exhibiting both (anti)ferromagnetic and ferroelectric properties [11–13].

Terada et al. [14,15] identified multiferroic delafossite $AgFeO_2$ single crystals with magnetic transition temperatures at $T_{N1} = 15$ and $T_{N2} = 9$ K, and showed they had a cycloid magnetic structure, as shown in Fig. 1 [16,17]. They derived an expression of ferroelectric polarization due to the inverse DM effect originating from a particular non-collinear magnetic structure in the triangular lattice formed by Fe^{3+} ions. In particular, they showed that a magnetic phase transition occurred for $9 \leq T \leq 15$ K, coincident with a large spontaneous electric polarization in the laminated axis (c-axis) direction, and multiferroic characteristics were observed with a non-magnetic field [15]. Antibacterial activity of $AgFeO_2$ nanoparticle modified polyethylene glycols (PEGs) was recently investigated against different pathogenic bacteria for possible water-treatment applications [18]. It is expected that $AgFeO_2$ would exhibit novel magnetic properties and excellent multiferroic characteristics.

However, few previous studies have investigated the effects of doping on Ag-based delafossite oxides, mainly due to the difficulty of preparing high quality samples of these oxides. Characteristic polarized/magnetic phases, such as vortex and spiral phases, develop on nanoparticle surfaces [19–22]. However, the relationship between local crystal structure and magnetic properties remains unclear.

The current study investigates magnetic properties of frustrated magnetic materials, controlling the crystal structure to explore its influence on magnetically frustrated phases using delafossite oxide $AgFe_{1-x}Co_xO_2$ ($0 \leq x \leq 0.2$) nanoparticles prepared by a wet chemical method [14,23–25]. Local structure was measured by XAFS and magnetization was measured by focusing on the magnetic structure transition temperature and its underlying mechanism. Physical

* Corresponding author.
E-mail address: yamazaki-takahiro-rh@ynu.jp (T. Yamazaki).

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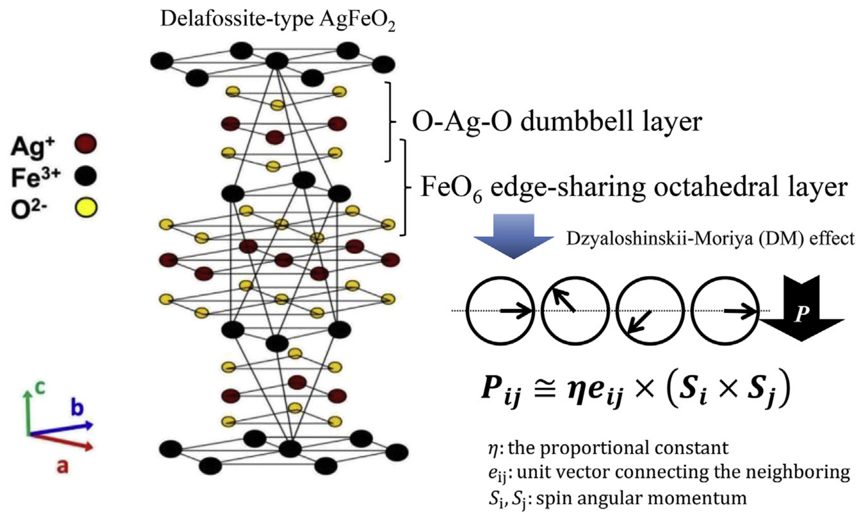

Fig. 1. Schematic image of crystal structure of delafossite-type $AgFeO_2$ and the cycloid magnetic structure induced Dzyaloshinskii-Moriya (DM) effect.

properties and structure of the frustrated state contributing to the Dzyaloshinskii-Moriya (DM) interaction were investigated by replacing Fe atoms, which are responsible for the magnetism, with different atoms.

2. Experimental

Powder specimens of delafossite $AgFe_{1-x}Co_xO_2$ ($x = 0$, 0.02, 0.05, 0.10, 0.20) nanoparticles were prepared by a co-precipitation method. Aqueous solutions of silver nitrate ($AgNO_3$, >99%), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, > 99.9%), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, > 99.9%) and sodium hydroxide (NaOH, 98%), sourced from Wako Pure Chemical Industries, Ltd., were mixed at molar ratio Ag:Fe:Co:Na = 1:1-x:x:8, and pH was adjusted to approximately 11 using NaOH [23]. The suspensions were stirred at 363 K for 1 h, and the resulting precipitates were washed twice with distilled water, then dried at approximately 350 K for 24 h. Finally, the obtained samples were pulverized in a mortar and used without further refinement.

Precipitate particle size and morphology were determined by transmission electron microscopy (TEM, JEM 2000FX II) and Cu Kα X-ray powder diffraction (XPD, Rigaku, MiniFlex, $\lambda = 0.154$ nm).

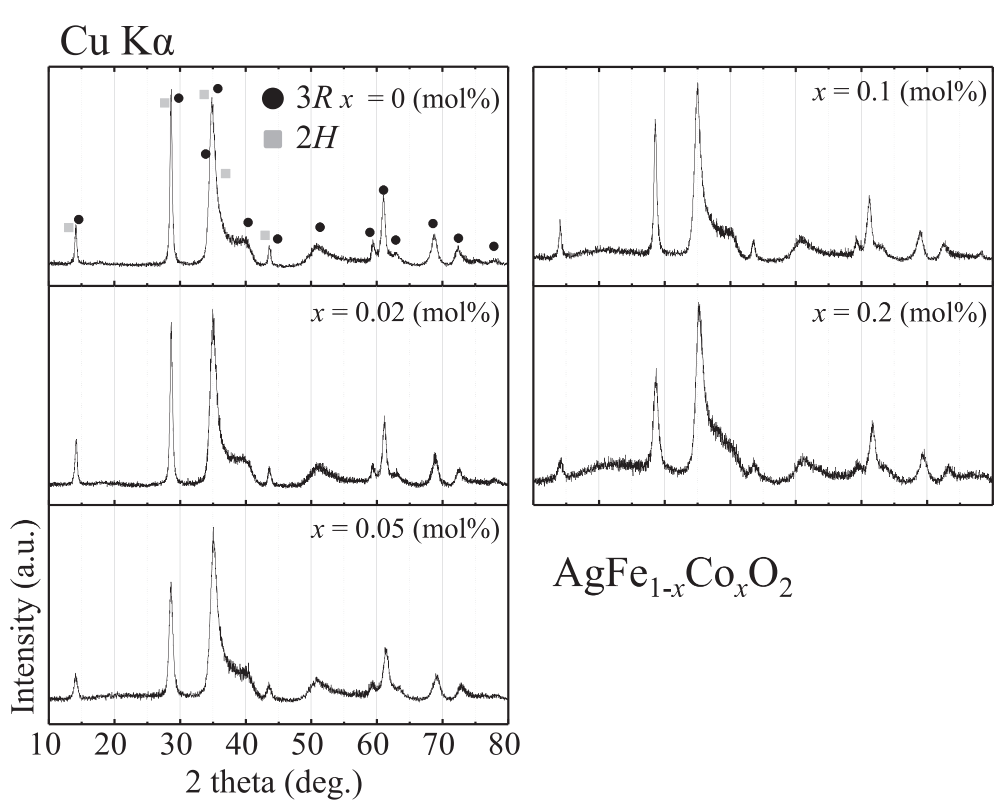

Fig. 2. X-ray powder diffraction patterns for various compositions of $AgFe_{1-x}Co_xO_2$ ($x = 0$, 0.02, 0.05, 0.1, 0.2) nanoparticles, respectively.