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# X-ray Diffraction and $^{57}\text{Fe}$ Mössbauer Spectroscopy Studies of Co-Doped $\text{AgFeO}_2$

K. SIEDLIKA<sup>a,\*</sup>, T. PIKULA<sup>a</sup>, W. FRANUS<sup>b</sup> AND E. JARTYCH<sup>a</sup>

<sup>a</sup>Lublin University of Technology, Institute of Electronics and Information Technology, Nadbystrzycka 38A, 20-618 Lublin, Poland

<sup>b</sup>Lublin University of Technology, Department of Geotechnics, 20-618 Lublin, Nadbystrzycka 40, Poland

Delafossite  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_2$  ( $x = 0, 0.05, 0.1, 0.2$ ) powders were synthesized by co-precipitation method. The structural analysis and hyperfine interactions investigations were performed by X-ray diffraction and the Mössbauer spectroscopy. It was found that the Co-doped delafossite phase with traces of metallic silver was obtained. The investigated samples were fine powders which are typical of the materials synthesized by co-precipitation. The Mössbauer spectroscopy studies revealed random incorporation of cobalt ions into the crystalline lattice of delafossite. Doping of cobalt ions caused the distortion of the oxygen octahedra in  $\text{AgFeO}_2$  which was observed in the increase of the quadrupole splitting value.

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## 1. Introduction

Delafossites are an interesting class of materials attracting considerable scientific attention due to their unique physical properties. They are described by a general formula of  $\text{ABO}_2$ , where A denotes monovalent cation (Ag, Cu, Pd, Pt), and B means trivalent cation (Fe, Al, Cr, Ga, etc.). Delafossite structure is depicted as a stacking of  $\text{BO}_6$  edge-shared octahedral slabs linked together by linearly coordinated A atoms [1]. Depends on the stacking of octahedral layers, crystal structure forms two polytypes, i.e.,  $2H$  (space group  $P6_3/mmc$ ) and  $3R$  (space group  $R-3m$ ).

Recently, much attention has been focused on developing new magnetic materials, e.g., diluted magnetic semiconductors (DMSs) [2] or multiferroics [3]. Also delafossites seem to be a promising candidate for this purpose. Compounds based on  $\text{AFeO}_2$  (where A is Ag or Cu) have complicated magnetic structure due to frustrated exchange interactions caused by the triangular lattice system of Fe ions [4, 5]. These spin arrangements induce ferroelectric polarization, which can be described by the inverse Dzyaloshinskii–Moriya (DM) effect [3]. Recently,  $\text{AgFeO}_2$  was identified as multiferroic delafossite which is paramagnetic at room temperature and shows non-collinear magnetic structure below the Néel temperature [6, 7]. Nevertheless, due to difficulties with the preparation of high-quality silver delafossite samples, the explaining of their magnetic properties is still the open question.

Modification of delafossite magnetic properties is realized by ion substitution of trivalent  $\text{B}^{3+}$  cation [8, 9]. Recently, it was reported that the cobalt doping in copper delafossites induces interesting phenomena. Dong et al.

synthesized thin films of Co-doped transparent  $\text{CuAlO}_2$  semiconductors which exhibited weak ferromagnetism at room temperature [10]. Likewise, Elkhouni et al. presented several papers on cobalt substituted  $\text{CuCrO}_2$  and proved that the incorporation of magnetic ions into delafossite structure induce new spin ordering and enhance magnetization [11, 12].

To our knowledge, studies of  $\text{AgFeO}_2$  delafossite doped with different ions at Fe site have been carried out only by several researchers (e.g., doping Cr to  $\text{AgFeO}_2$  reported in [13]). Therefore, the lack of experimental data motivates further studies on cobalt incorporation into the delafossite structure. Recognizing the structural properties of the Co-doped  $\text{AgFeO}_2$  will enrich knowledge about new delafossite family members and give information over possibilities of modifications of their physical properties to obtain advanced materials. In this work, we synthesized the Co-doped  $\text{AgFeO}_2$  by co-precipitation method. The main goal of the studies was to determine the influence of Co concentration on the structure and hyperfine interactions of  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_2$  with varying  $x$ .

## 2. Experimental method

The  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_2$  samples with varying  $x$  ( $x = 0, 0.05, 0.1, 0.2$ ) were prepared by co-precipitation method adopted from [14]. The starting reagents were high purity grade:  $\text{AgNO}_3$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NaOH}$ . The appropriate molar ratio of nitrate salts were dissolved in distilled water, and then the  $\text{NaOH}$  solution was added drop by drop until the  $\text{pH} \sim 12$  was reached. Afterward, obtaining solutions were stirred 1 h at room temperature. Products of precipitation were collected by sedimentation, washed several times with distilled water and dried at 373 K overnight. After drying, the samples had a form of flakes which were powdered in an agate mortar and measured using X-ray diffraction (XRD) and the Mössbauer spectroscopy (MS).

\*corresponding author; e-mail: [k.siedliska@pollub.pl](mailto:k.siedliska@pollub.pl)

XRD studies were performed using a PanAnalytical X-Pert Pro diffractometer with Cu lamp. The X'Pert HighScore Plus software equipped with the ICDD PDF2 database was used for the phase analysis.

$^{57}\text{Fe}$  Mössbauer spectra were recorded using Polon spectrometer working in transmission geometry and constant acceleration mode. A  $^{57}\text{Co}$  source in a rhodium matrix was used as a source of 14.4 keV gamma radiation. All values of the isomer shift shown later are related to the  $\alpha\text{-Fe}$ .

### 3. Result and discussion

Figure 1 shows the XRD patterns of  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_2$  powders registered at room temperature. In the case of an un-doped sample ( $x = 0$ ), it was confirmed the purity of delafossite phase (3R: PDF2 Card No. 01-075-2147; 2H: PDF2 Card No. 00-029-1141). Comparison of this pattern with database standards corresponding to the hexagonal polytype 2H- $\text{AgFeO}_2$  and rhombohedral 3R- $\text{AgFeO}_2$  proved that the mixture of both phases was obtained. For the  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_2$  samples ( $x = 0.05, 0.1, 0.2$ ) all XRD patterns are similar to each other. There may be observed only changes in the intensity and broadening of diffraction peaks. We found that lattice parameters  $a = 3.04(1)$  Å and  $c = 12.44(1)$  Å for 2H polytype as well as  $a = 3.04(1)$  Å and  $c = 18.69(5)$  Å for 3R polytype are nearly constant for all powders, and the differences do not exceed uncertainty. Significant anisotropic broadening of diffraction lines was observed. It may be seen that peaks belonging to (00l) family are sharp and well separated. The Scherrer formula applied to them allowed us to estimate the average crystallite size on 35 nm. In contrast, the lines connected with the (10l) family are much more broadened, suggesting crystallite sizes ranged of a few nm.

Despite the appearance of additional peaks indicated as derived from metallic silver (green markers in Fig. 1), in the XRD spectra registered for doped samples there are no peaks indicated impurity phases such  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ , metallic cobalt, and spinel —  $\text{CoFe}_2\text{O}_4$ , which readily form in the conditions similar to the synthesis of  $\text{AgFeO}_2$ . Lack of phases connected with cobalt may indicate that the cobalt ions replace iron ions in the delafossite crystal structure. However, bringing the assumption that  $\text{Co}^{3+}$  should replace  $\text{Fe}^{3+}$  ions during substitution, the appearance of metallic silver is quite unexpected. Nevertheless, because cobalt(II) nitrate was used as starting material during the synthesis, we postulate that in our case trivalent iron ions were substituted by divalent cobalt ions. This assumption may explain the appearance of metallic silver as a secondary phase. The lower valence of cobalt ions than  $\text{Fe}^{3+}$  ions may be the reason for the oxygen vacancies emergence in the octahedral layer, which at the same time causes the lack of oxygen in some linear bonds  $\text{O-Ag-O}$ . A similar interpretation was reported in [15, 16] where the substitution of B-site trivalent ions in  $\text{CuBO}_2$  delafossites by cations like  $\text{Co}^{2+}$ ,  $\text{Sn}^{4+}$  induced the appearance of  $\text{CuO}$  as the secondary phase during

the synthesis process. Hence, we suggest that the substituting ions were rather  $\text{Co}^{2+}$  than  $\text{Co}^{3+}$  and obtained powders are non-stoichiometric compounds with formula  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ .

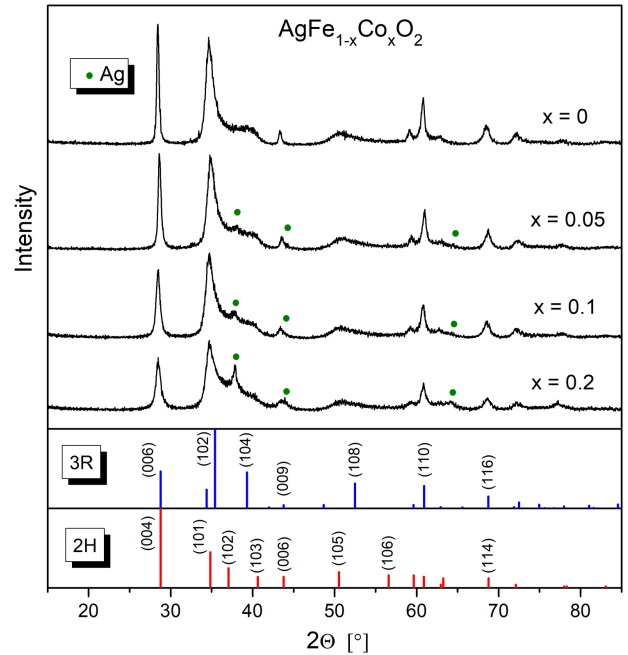


Fig. 1. XRD patterns for various compositions of  $\text{AgFe}_{1-x}\text{Co}_x\text{O}_2$  ( $x = 0, 0.05, 0.1, 0.2$ ) samples.

Results of the Mössbauer spectroscopy studies are presented in Fig. 2 and Table I. Three methods were used in the numerical procedure of fitting of experimental spectra. In the first approximation, all the Mössbauer spectra were fitted by a single quadrupole doublet (method I, Table I) which originates from the paramagnetic delafossite phase. The obtained hyperfine interactions parameters are summarized in Table I. Values of isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta$ ) are similar for all investigated samples and are in good agreement with literature data reported for the  $\text{AgFeO}_2$  compound [13]. The value of isomer shift shows that only high-spin  $\text{Fe}^{3+}$  ions in the octahedral coordination are present in the studied delafossites. Rather high values of the quadrupole splitting mean that strong electric field gradient (EFG) occurs in the  $\text{Fe}^{3+}$  position in the crystalline lattice. Nevertheless, the width of the spectral line  $\Gamma$  (half width at half maximum) for the un-doped sample is significantly higher from the natural width ( $\Gamma = 0.12$  mm/s according to the certificate of the Mössbauer source manufactured by RITVERC GmbH) and slightly decrease with cobalt concentration increasing. This fact and visible asymmetry of all doublets (Fig. 2, left side) suggest that the Mössbauer spectra should be fitted by more than one component.

In the second approach, two quadrupole doublets ( $D1, D2$ ) were fitted as suggested by the presence of two polytypes 2H and 3R in the samples (method II, Table I).

TABLE I

The results from fitting the Mössbauer spectra registered at room temperature:  $\delta$ ,  $\Delta$ , and  $\langle\Delta\rangle$  represent the isomer shift, quadrupole splitting and mean quadrupole splitting values in [mm/s], respectively;  $\Gamma$  is the width of spectral lines [mm/s],  $\delta_{\max}$  and  $\Delta_{\max}$  indicate the most probable values in the quadrupole splitting distribution. The uncertainty of all values is 0.01 mm/s.

Sample	Method I	Method II			Method III	
			$\delta$	$\Delta$		$\Gamma$
AgFeO <sub>2</sub>	$\delta = 0.37$	D1	$\delta = 0.37$	$\Delta = 0.82$	$\Gamma = 0.29$	$\delta_{\max} = 0.38$ $\langle\Delta\rangle = 0.75$ $\Delta_{\max} = 0.69$
	$\Delta = 0.69$	D2	$\delta = 0.35$	$\Delta = 0.56$	$\Gamma = 0.29$	
	$\Gamma = 0.31$					
AgFe <sub>0.95</sub> Co <sub>0.05</sub> O <sub>2</sub>	$\delta = 0.37$	D1	$\delta = 0.37$	$\Delta = 0.82$	$\Gamma = 0.16$	$\delta_{\max} = 0.39$ $\langle\Delta\rangle = 0.69$ $\Delta_{\max} = 0.74$
	$\Delta = 0.69$	D2	$\delta = 0.37$	$\Delta = 0.56$	$\Gamma = 0.15$	
	$\Gamma = 0.18$					
AgFe <sub>0.9</sub> Co <sub>0.1</sub> O <sub>2</sub>	$\delta = 0.36$	D1	$\delta = 0.37$	$\Delta = 0.76$	$\Gamma = 0.21$	$\delta_{\max} = 0.39$ $\langle\Delta\rangle = 0.72$ $\Delta_{\max} = 0.78$
	$\Delta = 0.69$	D2	$\delta = 0.35$	$\Delta = 0.53$	$\Gamma = 0.21$	
	$\Gamma = 0.23$					
AgFe <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	$\delta = 0.36$	D1	$\delta = 0.36$	$\Delta = 0.88$	$\Gamma = 0.16$	$\delta_{\max} = 0.38$ $\langle\Delta\rangle = 0.73$ $\Delta_{\max} = 0.78$
	$\Delta = 0.69$	D2	$\delta = 0.36$	$\Delta = 0.61$	$\Gamma = 0.18$	
	$\Gamma = 0.20$					

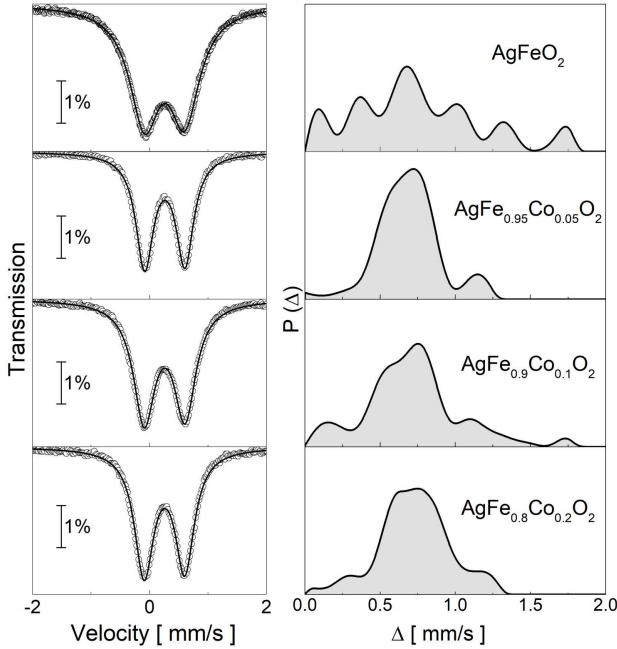


Fig. 2. Room-temperature Mössbauer spectra and corresponding distributions of quadrupole splitting for the AgFe<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> ( $x = 0, 0.05, 0.1, 0.2$ ).

Obtained isomer shift values for both components are equal and do not change with increasing cobalt concentration. This fact suggests that for both polytypes Fe<sup>3+</sup> ions have the same nearest atomic neighborhood [14]. The obtained  $\Delta$  values for D1 and D2 are close to 0.8 and 0.5 mm/s, respectively.

However, the best numerical fitting was achieved by assuming the distribution of quadrupole splitting values. The result of the third method of numerical fitting is shown on the right side of Fig. 2. and the derived hyperfine interactions parameters are listed in Table I. In all

cases, discrete distributions are obtained; this behavior is characteristic of a definite number of iron ion environments in the structure. For the un-doped sample, six well-shaped peaks with different average values are present in the obtained distributions, whereas Co-doped samples exhibit the broad predominating peak and several smaller ones. It may be associated with the change of EFG in the iron neighborhood. The similar effect of dispersion narrowing of quadrupole splitting distribution was observed in [17, 18], where the  $\alpha$ -NaFeO<sub>2</sub> and LiFeO<sub>2</sub> were substituted by Ni<sup>2+</sup> ions. The large diversity in the shape of the quadrupole splitting distributions suggests the random distribution of cobalt ions in the delafossite structure. Moreover, the most probable value of quadrupole splitting ( $\Delta_{\max}$ ) slightly grows with increasing cobalt concentration (see Table I, method III). This fact may be connected with the incorporation of cobalt ions into the delafossite structure which causes the changes of EFG symmetry in the Fe<sup>3+</sup> site.

#### 4. Conclusions

Delafossite AgFe<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> ( $x = 0, 0.05, 0.1, 0.2$ ) fine powders were successfully synthesized by co-precipitation method. The XRD study proved to obtain of Co-doped delafossite phase with traces of metallic silver as the impurity. The lack of cobalt-containing secondary products suggests that Co<sup>2+</sup> substitute Fe<sup>3+</sup> ions in delafossite lattice.

The Mössbauer spectroscopy studies revealed the distribution of quadrupole splitting values which is the result of random incorporation of cobalt ions in the crystalline lattice. In addition, the changes in the values of quadrupole splitting prove that cobalt doping caused the increase of distortion level of the oxygen octahedra. However, the issue of cobalt distribution in the delafossite structure is still unclear and need further investigations.

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