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Precursor synthesis and magnetic properties of $Cd_{1-x}Fe_xO$ ($0 \le x \le 0.07$)

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The polycrystalline solid solutions $Cd_{1-x}Fe_xO$ ($0 \le x \le 0.07$) possessing ferromagnetic properties at 5 K and room temperature have been synthesized by a precursor method using the formate $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$.

The intensive development of advanced branches of science and engineering (including spintronics) based on the use of spin polarization in semiconductors, requires the creation of new functional materials combining the valuable properties of semiconductors and ferromagnetics.¹ Cadmium oxide belongs to such materials owing to a developed defect structure and unique physical properties, which are responsible for its practical applications.²⁻⁴ The electrical and optical properties of cadmium oxide depend on the degree of its imperfection, the presence of heteroatomic impurities and the morphology, surface microstructure and particle size, which are determined by the synthesis conditions. The thermal treatment of CdO powder in a vacuum or in a hydrogen atmosphere leads to the appearance of roomtemperature magnetization.⁴ In our opinion, this effect is due to an increased structure imperfection of cadmium oxide: annealing in a vacuum gives rise to oxygen vacancies (V₀), and annealing in a hydrogen atmosphere leads to vacancies in the cadmium sublattice (V_{Cd}). Vacancies in the cadmium and oxygen sublattices induce spin-polarized states of O2p and 4d orbitals of Cd in the vicinity of the Fermi level, which determines its ferromagnetic properties. The introduction of transition metal ions into the crystal structure of cadmium oxide considerably affects its electrical, magnetic and optical properties.⁵⁻¹⁰ The doping of CdO with iron (~1-2 at%) results in an abrupt enhancement of electrical conductivity5 and in the appearance of weak ferromagnetic properties^{6,7} intensifying upon heating in a vacuum or in a hydrogen atmosphere. However, upon contact with hydrogen, some cadmium is reduced to the metal and isolated as an impurity phase even at relatively low temperatures:

$$CdO + H_2 = Cd^0 + H_2O.$$
 (1)

This fact decreases the value of results^{6,7} and requires further investigations to synthesize iron-doped ferromagnetic cadmium oxide containing no impurities.

The aim of this work was to develop a precursor method for the synthesis of the phase-homogeneous polycrystalline solid solutions $Cd_{1-x}Fe_xO$ with a maximum possible degree of iron for cadmium substitution and to examine their structural and magnetic properties. Cadmium formate $Cd(HCOO)_2 \cdot 2H_2O$ in whose structure some Cd^{2+} positions are replaced by Fe^{2+} cations was chosen as a precursor. Cadmium formate belongs to a group of isostructural M(HCOO)_2 \cdot 2H_2O compositions (M = Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd) capable of forming numerous solid solutions with each other.¹¹ Cadmium and iron formates form a continuous series of well soluble in hot water solid solutions $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$,¹² and their use as a precursor in the synthesis of $Cd_{1-x}Fe_xO$ gives an unlimited resource of iron.

 $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ ($0 \le x \le 0.2$) was synthesized by the dissolution of $Cd(HCOO)_2 \cdot 2H_2O$ and $Fe(HCOO)_2 \cdot 2H_2O$ formate mixtures in hot distilled water and the subsequent evaporation at 60 °C in air until the formation of a solid residue. Cadmium and iron formates were prepared by the following reactions:

$$CdCO_3 + 2HCOOH + H_2O = Cd(HCOO)_2 \cdot 2H_2O + CO_2, \quad (2)$$

$$Fe + 2HCOOH + 2H_2O = Fe(HCOO)_2 \cdot 2H_2O + H_2.$$
 (3)

To avoid the possible oxidation of Fe^{2+} to Fe^{3+} by atmospheric oxygen,¹³ the crystallization of iron formate was carried out by evaporation in a nitrogen atmosphere. An alternative way of precursor synthesis was to conduct reactions (2) and (3) simultaneously on heating in air:

$$(1-x)CdCO_3 + xFe + 2HCOOH + (2-x)H_2O =$$

= $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O + (1-x)CO_2 + xH_2.$ (4)

To produce $Cd_{1-x}Fe_xO$, the $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ samples, where x = 0.0, 0.01, 0.025, 0.05, 0.07, 0.075, 0.1, 0.15 or 0.2, were heated at 250–300 °C until complete decomposition to form a dark brown mass. Then, the products of thermolysis were thoroughly ground in an agate mortar and annealed at 400 °C for 2 h.

The $Cd(HCOO)_2 \cdot 2H_2O$ and $Fe(HCOO)_2 \cdot 2H_2O$ formates isolated by evaporation are white and light green powders,



respectively. Cadmium formate forms crystals of a flattened shape with moderate cleavage in the direction parallel to flattening and bad cleavage in other orientations. The reflective indices of $Cd(HCOO)_2 \cdot 2H_2O$ crystals are $N_g = 1.548$, $N_m = 1.509$, and $N_{\rm p} = 1.497$. Iron formate is characterized by the formation of laminar and hexagonal scaly crystals with the reflective indices $N_{\rm g} = 1.563$, $N_{\rm m} = 1.536$, and $N_{\rm p} = 1.524$. During the evaporation of solutions of cadmium and iron formate mixtures, almost white $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ powders with a weak yellow-green tint are formed at x > 0.1. The shape of $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ crystals is also laminar, and the reflective indices differ insignificantly from those for pure cadmium formate. The reflective indices of $Cd_{0.95}Fe_{0.05}(HCOO)_2 \cdot 2H_2O$ crystals are $N_g = 1.551$, $N_{\rm m} = 1.509$, and $N_{\rm p} = 1.499$. The $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ crystals with iron content of >5 at% feature a wave-like extinction, which impedes their orientation and measurements of reflective indices.

According to the X-ray phase analysis data,[†] the products of thermal decomposition of $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ ($0 < x \le \le 0.075$) at 250–300 °C mainly consist of CdO and small amounts (~0.5 wt%) of a cadmium metal impurity. Upon annealing at 400 °C in a muffle furnace, they represent monophase samples of the solid solutions $Cd_{1-x}Fe_xO$ with assigned iron concentrations. The existence of these solid solutions is confirmed by a regular decrease in the lattice parameter and density when the iron concentration increases up to 7 at% (Table 1). A further increase in the iron concentration leads to the formation of an impurity phase of $CdFe_2O_4$ ferrite. Figure 1 presents X-ray diffraction and microstrain patterns of $Cd_{1-x}Fe_xO$ samples, where x = 0.0, 0.01, 0.025, 0.05 and 0.07. Table 1 gives the lattice parameters,



Figure 1 (*a*) X-ray diffraction patterns and (*b*) peak widths (FWHM) of $Cd_{1-x}Fe_xO$ [x = (1) 0.0, (2) 0.01, (3) 0.025, (4) 0.05, and (5) 0.07] solid solutions synthesized by the heat treatment of $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ in air at the maximal annealing temperature of 400 °C.

[†] The phase analysis of the precursors and their thermolysis products was carried out on a polarization transmission microscope (the refractive indices were determined by the immersion method at room temperature) and a STADI-P X-ray powder automatic diffractometer (STOE) in CuK α_1 radiation using the library of X-ray diffraction data PDF-2 (ICDD Release 2009). The coherent scattering regions (CSRs) and microstrain of particles were determined by X-ray diffraction using the Williamson– Hall method.¹⁴ The density of the Cd_{1-x}Fe_xO powders was determined with the use of an AccuPyc II 1340 automatic helium pycnometer with a 1 cm³ working chamber. The magnetic properties were measured on an MPMS XL7 SQUID magnetometer (Quantum Design) in magnetic fields to 60 kOe.

Table 1 Crystallographic characteristics of cadmium oxide and the solid solutions $Cd_{1-x}Fe_xO$ synthesized by the thermolysis of formates.

Entry	Sample	a/Å	CSR/nm	Microstrain	$ ho/{ m g~cm^{-3}}$
1	CdO	4.6962(5)	104.9	0.000023	8.06(6)
2	Cd _{0.99} Fe _{0.01} O	4.6956(5)	87.4	0.000303	7.96(6)
3	Cd _{0.975} Fe _{0.025} O	4.6946(5)	90.4	0.000425	7.82(3)
4	Cd _{0.95} Fe _{0.05} O	4.6941(5)	80.3	0.000514	7.67(2)
5	Cd _{0.93} Fe _{0.07} O	4.6934(5)	80.5	0.000612	7.66(2)

densities, CSR and microstrain values. The formation of metallic cadmium during the thermal decomposition of precursors can be induced by the thermally stimulated intramolecular interaction of the cationic and anionic formate components:

$$Cd^{2+} + 2HCOO^{-} = Cd^{0} + H_2O + CO + CO_2$$
 (5)

or

$$Cd^{2+} + 2HCOO^{-} = Cd^{0} + H_{2} + 2CO_{2}.$$
 (6)

Indeed, on heating in air at 300–350 °C, $Cd(HCOO)_2 \cdot 2H_2O$ decomposes to afford CdO containing ~1% Cd. When heating occurs in a helium atmosphere, thermal decomposition gives rise to metallic cadmium in the form of a grey powder.

The magnetization m(H) curves at 5 and 300 K (Figures 2 and 3) show that the $Cd_{1-x}Fe_xO$ samples are ferromagnetic. This conclusion is confirmed by the presence of a hysteresis and residual magnetization (insets in Figures 2 and 3). The Curie temperature of Cd_{0.95}Fe_{0.05}O is 560 K. The magnetization of $Cd_{1-x}Fe_xO$ increases with the iron concentration in the whole examined interval reaching maximal values for the sample with x = 0.07: $m_{\rm S} = 2.450$ emu g⁻¹ at T = 5 K and $m_{\rm S} = 0.900$ emu g⁻¹ at T = 300 K (Figures 2 and 3, Table 2). Pure CdO behaves as a diamagnetic with a ferromagnetic component at both temperatures (insets in Figures 2 and 3), in agreement with the results reported earlier.⁴ The magnetic characteristics of Cd_{1-x}Fe_xO samples were compared with the available literature data using Cd_{0.99}Fe_{0.01}O as an example, since powders of the same composition were studied^{6,7} at room temperature. The saturation magnetization of the synthesized Cd_{0.99}Fe_{0.01}O sample is 0.018 emu g⁻¹ at T = 300 K, which is much higher than $m_{\rm S}$ = = 0.00293 and $m_{\rm S}$ = 0.0055 emu g⁻¹ (see refs. 6 and 7, respectively). As noted above, the annealing of the Cd_{0.99}Fe_{0.01}O powder in helium results in a stepwise growth of the saturation magnetization of $Cd_{1-x}Fe_xO$ powders to $m_S = 0.00837$ and $m_S =$ = 0.00594 emu g^{-1} (see ref. 6 and 7, respectively). This effect is connected with the partial reduction of cadmium and its isolation



Figure 2 Magnetization curves of the $Cd_{1-x}Fe_xO$ [x = (1) 0.0, (2) 0.01, (3) 0.025, (4) 0.05, and (5) 0.07] samples at 5 K. Insets: (*a*) magnetization curves for pure CdO (1–1) before and (1–2) after subtraction of the diamagnetic contribution; (*b*) hysteresis loops for the $Cd_{1-x}Fe_xO$ samples.

Table 2 Coercive force $H_{\rm C}$ and saturation magnetization $m_{\rm S}$ for CdO and Cd_{1-x}Fe_xO samples at T = 5 and 300 K.

Entry	Sample	$H_{\rm C}/{\rm Oe}$	$m_{\rm S}$ /emu g ⁻¹	T/K
1	CdO	230 50	0.0075 0.0012	5 300
2	Cd _{0.99} Fe _{0.01} O	800 10	0.480 0.018	5 300
3	Cd _{0.975} Fe _{0.025} O	580 10	0.810 0.140	5 300
4	Cd _{0.95} Fe _{0.05} O	460 12	1.520 0.500	5 300
5	Cd _{0.93} Fe _{0.07} O	450 22	2.450 0.900	5 300



Figure 3 Magnetization curves of the $Cd_{1-x}Fe_xO$ [x = (1) 0.0, (2) 0.01, (3) 0.025, (4) 0.05, and (5) 0.07] samples at 300 K. Insets: (*a*) magnetization curves for pure CdO (1–1) before and (1–2) after subtraction of the diamagnetic contribution; (*b*) hysteresis loops for the $Cd_{1-x}Fe_xO$ samples.

from the oxide structure in the form of metal. Consequently, the growth of magnetization of $Cd_{1-x}Fe_xO$ upon exposure in a reducing hydrogen atmosphere^{6,7} can be explained not only by an increased concentration of V_{Cd} vacancies caused by the removal of metal from the oxide but also by the enhancement of the iron content related to this process, which agrees with the results of our studies (Figures 2 and 3).

Thus, the use of the $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ formate as a precursor makes it possible to obtain ferromagnetic solid solutions $Cd_{1-x}Fe_xO$ stable in time, whose saturation magnetization at low and room temperatures increases with the concentration

of iron. The advantage of the developed synthesis method is that it allows one to accurately assign the elemental composition of both a precursor and its thermolysis product. Moreover, for the preparation of samples with high magnetization values, there is no need to use annealing in a hydrogen atmosphere. The thermal decomposition of the $Cd_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O$ precursor in air provides conditions sufficient for the production of impurity-free oxide $Cd_{1-x}Fe_xO$ with a rock salt structure and for the formation of its magnetic properties. The saturation magnetization of the solid solutions $Cd_{1-x}Fe_xO$ (Table 2) are comparable with those of $Zn_{1-x}Fe_xO$ synthesized earlier by the precursor method using the $Zn_{1-x}Fe_x(HCOO)_2 \cdot 2H_2O^{15}$ formate.

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