Structural, Magnetic and Dielectric Properties of $[(\text{CH}_3)_2\text{NH}_2]\text{Fe}_x\text{Mn}_{1-x}(\text{HCOO})_3$

HONGYANG ZHAO,^{1,3} ZHIDENG HUANG,¹ ZHIBIN MA,^{1,4}
TINGTING JIA,² HIDEO KIMURA,² QIUMING FU,¹ GEMING WANG,¹
HONG TAO,¹ KANG CAI,¹ and ZIRAN FAN¹

1.—Hubei Key Laboratory of Plasma Chemistry and Advanced Materials, Department of Materials Science and Engineering, Wuhan Institute of Technology, 693 Xiongchu Road, Wuhan 430073, China. 2.—National Institute for Materials Science, Sengen 1-2-1, Tsukuba 305-0047, Japan. 3.—e-mail: zhaohy@wit.edu.cn. 4.—e-mail: mazb@wit.edu.cn

The multiferroic phenomenon has interdisciplinary applications in the fields of chemistry, physics, electronics, materials, crystallography, and mechanics. Compared to traditional limited pure inorganic multiferroics, hybrid metal–organic frameworks are numerous and more flexible, and can be tailored to become different types of multiferroic materials. We synthesized $[(\text{CH}_3)_2\text{NH}_2]\text{Fe}_x\text{Mn}_{1-x}(\text{HCOO})_3$ and four crystals were obtained, with $x = 0$ (Mn), 0.1 ($\text{Fe}_{0.1}\text{Mn}_{0.9}$), 0.2 ($\text{Fe}_{0.2}\text{Mn}_{0.8}$), and 0.3 ($\text{Fe}_{0.3}\text{Mn}_{0.7}$). At the maximum Fe doping of $\text{Fe}_{0.3}\text{Mn}_{0.7}$, we observed magnetic properties different from lower-level-doped crystals. The magnetizations at 3 K were 3.50 emu/g, 3.87 emu/g, 3.89 emu/g and 7.38 emu/g corresponding to Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$, $\text{Fe}_{0.2}\text{Mn}_{0.8}$ and $\text{Fe}_{0.3}\text{Mn}_{0.7}$, respectively. $\text{Fe}_{0.3}\text{Mn}_{0.7}$ has three magnetic transitions, at 118.3 K, 40.3 K, and 8.3 K.

Key words: Magnetic properties, dielectric properties, MOFs

INTRODUCTION

In recent years, hybrid organic–inorganic materials have attracted particular interest because of their wide potential applications such as in storage and separation, catalysis, enantioselective separation, and photoluminescence, and as nonlinear optics, solar cells and magnetoelectric multifunctional materials.^{1–4} These applications can be combined and integrated into multifunctional metal–organic frameworks (MOFs). Despite impressive progress so far, tuning MOFs properties in a rational and systematic way remains a considerable challenge that requires careful consideration of chemical substitution.^{2,5} However, MOFs can be tailored as multiferroics more discretely than traditional inorganic materials, and exploration of more MOFs with multiferroic properties could be achieved in the near future.⁶

In MOFs, multiferroic behavior has been demonstrated in $[(\text{CH}_3)_2\text{NH}_2]\text{M}(\text{HCOO})_3$ with $\text{M} = \text{Ni}$, Mn , Co , and Fe .^{7–9} This class of materials combines magnetism of metal ions with organic ferroelectricity. Their antiferroelectric and magnetic transitions are well separated, suggesting weak coupling between these effects.² The effects of the replacement of Mn by various transition elements have been studied in Cu,¹⁰ Co,¹¹ Cr,¹² Fe,^{13,14} etc. We studied several -Fe---Mn-MOFs,^{15,16} where both magnetic and dielectric properties are expected to be different.

In this work, MOFs with a general formula $[(\text{CH}_3)_2\text{NH}_2]\text{X}(\text{HCOO})_3$ are studied, where X represents $\text{Fe}_x\text{Mn}_{1-x}$ ($x = 0, 0.1, 0.2$ and 0.3) for different ion doping concentrations. It has been found that single crystals become more difficult to grow with an increase of Fe doping level. The present paper reports four different dopings, named Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$, $\text{Fe}_{0.2}\text{Mn}_{0.8}$ and $\text{Fe}_{0.3}\text{Mn}_{0.7}$, based on their Fe:Mn ratio. The samples are grown by the hydrothermal method, and their magnetic and dielectric properties are investigated.

EXPERIMENTAL

Preparation of $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$ Single Crystal

$[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$ was prepared by the hydrothermal method: 0.99 g manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 30 mL *N,N*-dimethylformamide (DMF) and 30 mL deionized water mixed solution. After complete dissolution, the mixed liquor was heated in a polytetrafluoroethylene-lined autoclave for 3 days at 140°C . After the reaction, the supernatant was transferred into a glass beaker and crystallized at room temperature, with cubic crystals appearing after 3-7 days. The crystals were washed with ethanol.

Preparation of Fe Doped $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$ Crystals

Fe-doped $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$ was synthesized in a similar manner to the undoped sample. Fe/Mn mole ratios were 1:9, 2:8 and 3:7 for $\text{Fe}_{0.1}\text{Mn}_{0.9}$, $\text{Fe}_{0.2}\text{Mn}_{0.8}$ and $\text{Fe}_{0.3}\text{Mn}_{0.7}$, respectively. The starting materials ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were stoichiometry weighed and added into *N,N*-dimethylformamide and deionized water mixed solution as above, and then a similar procedure was followed but with a longer crystallization time (more than 7 days).

Characterization

The synthesized crystal phases were determined by powder x-ray diffraction (XRD; D8 Advance and Davinci Design) using Cu K α radiation. The Raman scattering spectrum was measured on a Laser Co-focal Microscopy Raman Spectrometer (DXR; American Thermo Electron). The dielectric properties were measured using a HP4248 LCR meter and a precision impedance analyzer (Agilent Technologies 4294A). Magnetic properties were measured using the commercial Quantum Design superconducting quantum interference device magnetometer.

RESULTS AND DISCUSSION

The four samples were ground into powder and characterized using XRD, as shown in Fig. 1. In $\text{Fe}_x\text{Mn}_{1-x}$ -MOFs, Fe and Mn with different mole ratios incorporate into a metal-organic framework. The Mn and Fe have similar ionic radius, suggesting a minor lattice distortion caused by the substitution. The XRD measurements indicate the four investigated MOFs are well-crystallized materials, and are mainly grown layer by layer along the [012] direction. However, with increasing Fe concentration, the crystal layer stacking along the [012] direction becomes disordered. Above Fe = 30%, crystallization becomes difficult. The left side of Fig. 2 is drawn through a data file⁹ by the CrystalMaker software, and clearly displays a $[(\text{CH}_3)_2\text{NH}_2]\text{Fe}_x\text{Mn}_{1-x}(\text{HCOO})_3$ crystal structure. On the right side, there are mainly two kinds of chains ($-\text{Mn}/\text{Fe}-\text{O}-\text{C}-\text{O}-\text{Mn}/$

Fig. 1. X-ray diffraction (XRD) of four samples measured at room temperature.

Fe- and $-\text{H}-\text{C}-\text{O}-\text{Mn}/\text{Fe}-\text{O}-\text{C}-\text{H}-$) which show important effects especially for the magnetic properties.

Raman scattering can be used to study the vibrational modes of both crystalline and amorphous materials. We found that the Raman shifts of the four samples are almost the same at room temperature (Fig. 3). The fundamental internal vibrations of HCOO^- ion consists of the C-H stretching mode ν_1 , the symmetric C-O stretching mode ν_2 , the antisymmetric C-O stretching mode ν_4 , the symmetric O-C-O bending (scissor) mode ν_3 , the C-H in-plane bending mode ν_5 , and the C-H out-of-plane bending mode ν_6 .^{17,18} The Raman bands at 2860.06 cm^{-1} , 1369.17 cm^{-1} , 1075.62 cm^{-1} and 795.22 cm^{-1} are assigned to be ν_1 , ν_2 , ν_6 and ν_3 , respectively (Table I). There are nine skeletal modes of H_2NC_2 , but only four of them were observed. Most of the NH_2 -related bands could not be seen or were very weak at room temperature. Therefore, only the very weak band at 1627.33 cm^{-1} was observed and assigned as scissoring $\delta(\text{NH}_2)$. In addition, the antisymmetric stretching ($\nu_{\text{as}}(\text{CNC})$), symmetric stretching ($\nu_{\text{s}}(\text{CNC})$), and bending ($\delta(\text{CNC})$) modes of the CNC group were observed at 1031.75 cm^{-1} , 899.06 cm^{-1} and 413.89 cm^{-1} , respectively. There are 18 degrees of freedom corresponding to the modes of the two methyl groups, which can be subdivided into symmetric stretching ($\nu_{\text{s}}(\text{CH}_3)$), antisymmetric stretching ($\nu_{\text{as}}(\text{CH}_3)$), bending ($\delta(\text{CH}_3)$), rocking ($\rho(\text{CH}_3)$), and torsion ($\tau(\text{CH}_3)$). The bands at 3048.85 cm^{-1} , 2977.15 cm^{-1} , 1464.39 cm^{-1} are assigned to be the modes of $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_3)$ and $\delta(\text{CH}_3)$, respectively. The assignment of modes is straightforward in Table I.

The magnetic moment versus magnetic field loops (M-H loops) of the MOFs crystals measured are shown in Fig. 4 for Mn (a), $\text{Fe}_{0.1}\text{Mn}_{0.9}$ (b), $\text{Fe}_{0.2}\text{Mn}_{0.8}$ (c) and Fig. 5 for $\text{Fe}_{0.3}\text{Mn}_{0.7}$. The M-H loops show little hysteresis with small magnetization values which increase almost linearly with the magnetic field. This is a strong indication that our samples are antiferromagnetic or weakly ferrimagnetic. In addition, the value of the magnetic moment

Fig. 2. The crystal structure and molecular chains for $\text{Fe}_x\text{Mn}_{1-x}$ -MOFs.

Fig. 3. Room-temperature Raman spectra of Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$, $\text{Fe}_{0.2}\text{Mn}_{0.8}$, $\text{Fe}_{0.3}\text{Mn}_{0.7}$.

increases gradually from Mn to $\text{Fe}_{0.3}\text{Mn}_{0.7}$. The magnetizations at 3 K with an applied magnetic field of 0.5 T are 3.50 emu/g, 3.87 emu/g, 3.89 emu/g and 7.38 emu/g for Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$, $\text{Fe}_{0.2}\text{Mn}_{0.8}$ and $\text{Fe}_{0.3}\text{Mn}_{0.7}$, respectively. Similar results of weak ferromagnetic properties have been previously reported in $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$, which shows a similar magnetization of 3.51 emu/g at 2 K and 0.5 T.¹⁹ It is clear that the magnetization increased with the increase of the doping of Fe.

The top insets in Fig. 4 show the zero-field-cooled and field-cooled (ZFC–FC) curves measured from 2 K to 20 K with an applied magnetic field of 500 Oe. The divergence of the ZFC–FC curves implies the onset of magnetic ordering or freezing of the magnetic

Table I. Raman wavenumbers (in cm^{-1}) of DMFeMn and suggested assignments

Raman wavenumbers (in cm^{-1})	Assignments
3048.85 m	$\nu_{\text{as}}(\text{CH}_3)$
2977.15 s	$\nu_{\text{s}}(\text{CH}_3)$
2860.06 m	$\nu_1(\text{HCOO}^-)$
1464.39 w	$\tilde{\nu}_{\text{as}}(\text{CH}_3)$
1369.17 s	$\nu_2(\text{HCOO}^-)$
1075.62 w	$\nu_6(\text{HCOO}^-)$
1031.75 w	$\nu_{\text{as}}(\text{CNC})$
899.06 m	$\nu_{\text{s}}(\text{CNC})$
795.22 m	$\nu_3(\text{HCOO}^-)$
413.89 w	$\tilde{\nu}(\text{CNC})$
186.11 s	L (HCOO^-)

s strong, m medium, w weak, vw very weak, sh shoulder.

domains. The magnetic transition point (T_N) is observed at 9.1 K, 8.8 K and 8.6 K for the Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$ and $\text{Fe}_{0.2}\text{Mn}_{0.8}$, respectively (Table II). It is obvious that the Curie temperature decreases with increasing Fe doping level. This is consistent with previous studies²⁰ which found that Fe-doped samples showed an obvious decrease in Curie temperature, because of the average Fe–Fe separation approaching the size of the charge carriers (polarons).²¹

The bottom insets in Fig. 4 are the fittings of inverse magnetic susceptibility $1/\chi$ versus temperature for pure Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$ and $\text{Fe}_{0.2}\text{Mn}_{0.8}$ by the Curie–Weiss law. The temperature ranges from 10 K to 20 K and the magnetic field is 500 Oe. C is the Curie–Weiss constant, which is calculated by the inverse slope of the Curie–Weiss fitting line. The effective paramagnetic moment (μ_{eff}) on the B-site

Fig. 4. Magnetic hysteresis loops measured at 3 K for (a) Mn; (b) $\text{Fe}_{0.1}\text{Mn}_{0.9}$ and (c) $\text{Fe}_{0.2}\text{Mn}_{0.8}$. The top inset in every figure shows the zero-field-cooled (ZFC) and field-cooled (FC) curves measured from 2 K to 20 K with a magnetic field of 500 Oe. The bottom insets show the plot of $1/\chi$ versus temperature from 10 K to 20 K, and the solid red line is the Curie-Weiss fitting.

was calculated to be $\mu_{\text{eff}} = 2.828 \sqrt{C} \mu_B$, where μ_B is the Bohr magneton. The Curie-Weiss temperature (θ) is the intercept of the temperature, and is found to be -19.36 K, -20.17 K and -20.18 K for Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$ and $\text{Fe}_{0.2}\text{Mn}_{0.8}$, respectively (Table II). The negative values indicate that the samples are exhibiting an antiferromagnetic exchange interaction. Notably, with an increase of the doping level of Fe, the values of C and μ_{eff} increased, while the values of θ and T_N decreased.

Magnetization as a function of magnetic field for $\text{Fe}_{0.3}\text{Mn}_{0.7}$ was measured at temperatures of 3 K, 50 K and 300 K. As shown in Fig. 5, a moment-unsaturated hysteresis loop with a coercive field of 212 Oe at 3 K is observed with antiferromagnetic and ferromagnetic components in a magnetic field of 1 kOe. The magnetization is estimated to be 0.58

Fig. 5. Magnetic hysteresis loops measured at different temperatures of 3 K, 50 K and 300 K for the crystal of $\text{Fe}_{0.3}\text{Mn}_{0.7}$; inset the magnifications of 50 K and 300 K.

$\mu_B/\text{f.u.}$ at 1 kOe, which is smaller than the theoretical value of $9 \mu_B/\text{f.u.}$ if all Fe and Mn ions are ordered ferromagnetically. At 50 K and 300 K, hysteresis behavior still remains in the M - H curve, with a coercive field of 201 Oe and 170 Oe, respectively. The magnetic moment is $0.089 \mu_B/\text{f.u.}$ at 50 K and $0.033 \mu_B/\text{f.u.}$ at 300 K in a magnetic field of 5 kOe. Therefore, the total behavior of M - H at 3 K and 50 K is dominated by the antiferromagnetic contribution.

Figure 6 displays the temperature dependence of the ZFC-FC magnetization curve for $\text{Fe}_{0.3}\text{Mn}_{0.7}$ from 2 K to 150 K in a magnetic field of 500 Oe. From high temperature to low temperature, three magnetic peaks were observed at 118.3 K, 40.3 K and 8.3 K. Curie-Weiss fitting of the $1/\chi - T$ curve was carried out from 125 K to 150 K, when the sample is in a paramagnetic state, as shown in the inset. The Curie-Weiss temperature $\theta = -301.85$ K indicates that $\text{Fe}_{0.3}\text{Mn}_{0.7}$ undergoes a strong antiferromagnetic transition at 118.3 K. From the color of the samples, we believe the distributions of Fe and Mn ions is not homogeneous, and as a result Fe-rich and Mn-rich clusters will form in $\text{Fe}_x\text{Mn}_{1-x}$. Consequently, MnO_6 octahedra do not directly share apical oxygens. The Goodenough-Kanamori rules may not be used in this system. However, there are -Mn-O-C-O-Mn- chains, which are antiferromagnetically ordered. If Fe-O-Fe and Mn-O-Mn mechanisms exist in the structure, the strong antiferromagnetic $e_g^2\text{-O-}e_g^2$ (Fe-O-Fe) interaction is favored by virtual charge transfer due to the two half-filled e_g of HS Fe ions. For Mn-O-Mn, it can order both antiferromagnetically and ferromagnetically through superexchange mechanism, as does LaMnO_3 .²² However, no evidence of orbital ordering can be found in the present compound. Furthermore, based on the small magnetic moment observed in the M - H loop at 3 K, it can be concluded that -Mn-O-C-O-Mn- or -H-C-O-Mn-O-C-H- is antiferromagnetically ordered in $\text{Fe}_{0.3}\text{Mn}_{0.7}$. Because only one unpaired electron occupies the e_g orbital, Mn-ordering is much weaker than Fe-ordering. Hence, the temperature of -Fe-O-C-O-Fe- ordering will be higher than that of -Mn-O-C-O-

Table II. The parameters of Curie-Weiss fitting for FC at 500 Oe

Samples	pure Mn	$\text{Fe}_{0.1}\text{Mn}_{0.9}$	$\text{Fe}_{0.2}\text{Mn}_{0.8}$
C	4.93	5.51	5.54
μ_{eff}	6.28	6.64	6.66
θ	-19.36	-20.17	-20.18
T_N	9.1	8.8	8.6

Fig. 6. $\text{Fe}_{0.3}\text{Mn}_{0.7}$ zero-field-cooled and field-cooled (ZFC-FC) curves measured from 2 K to 20 K with a magnetic field of 500 Oe. The left inset shows magnification from 2 K to 20 K. The right inset is the plot of $1/\chi$ versus temperature from 110 K to 150 K and the solid red line is the Curie-Weiss fitting.

Mn-ordering. Based on the above reasons, the origins for the magnetic transitions at temperatures of 118.3 K, 40.3 K and 8.3 K are attributed to -Fe-O-C-O-Fe-, -Fe-O-C-O-Mn- and -Mn-O-C-O-Mn- orderings, respectively.

Figure 7 gives the dielectric constant as a function of temperature of pure Mn and $\text{Fe}_{0.1}\text{Mn}_{0.9}$. The samples of $\text{Fe}_{0.2}\text{Mn}_{0.8}$ and $\text{Fe}_{0.3}\text{Mn}_{0.7}$ are not large enough for the measurement of dielectric properties due to the aforementioned difficulties in crystal growth as a function of Fe doping. Their dielectric constant ϵ versus temperature measurement was measured with a frequency range from 100 kHz to 1000 kHz. Both Mn and $\text{Fe}_{0.1}\text{Mn}_{0.9}$ show a dielectric peak or dielectric step, which gradually shifts to a higher temperature with increasing frequency. As shown in Fig. 7, the abnormal dielectric temperatures shift lower with increasing measurement frequency, indicating relaxor-like behavior in Mn and $\text{Fe}_{0.1}\text{Mn}_{0.9}$. The temperature-dependent transformation of the dielectric constant in ferroelectric materials reveals that the symmetry of the crystal structure changes with the dipole distance of positive and negative charges.²³ The shift of the maximum toward a lower temperature indicates a phase transition temperature which may be associated with improper ferroelectric characteristics.²⁴ A small spontaneous polarization appears only as a secondary effect owing to a coupling with a primary order parameter at improper ferroelectric transition.¹⁷ This transition is only connected with a small

Fig. 7. Dielectric constants with temperature at different frequencies (100 kHz-1000 kHz) for (a) Mn and (b) $\text{Fe}_{0.1}\text{Mn}_{0.9}$.

dielectric anomaly, and no Curie-Weiss Law is expected to hold.²⁵ After Fe doping, the transition becomes more obvious because of the microstructure modulation. Dielectric measurements at lower temperatures were not possible due to facility limitations.

CONCLUSIONS

We used Fe to replace Mn in $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$ and four crystals of Mn, $\text{Fe}_{0.1}\text{Mn}_{0.9}$, $\text{Fe}_{0.2}\text{Mn}_{0.8}$ and $\text{Fe}_{0.3}\text{Mn}_{0.7}$ were obtained. The magnetic properties of these samples are investigated. We found at the maximum Fe doping level of $\text{Fe}_{0.3}\text{Mn}_{0.7}$, magnetic properties are different from low-level-doped samples. Three magnetic transitions are observed in $\text{Fe}_{0.3}\text{Mn}_{0.7}$ at temperatures of

118.3 K, 40.3 K, and 8.3 K, believed to correspond to Fe–O–C–O–Fe-, -Fe–O–C–O–Mn-, and -Mn–O–C–O–Mn- orderings, respectively. Future work will concentrate on research on the coexistence of magnetic and ferroelectric domains to make multiferroic MOFs into usable devices.

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