Journal of Solid State Chemistry 258 (2018) 163–169

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis, magnetic and vibrational properties of two novel mixed-valence iron(II)-iron(III) formate frameworks

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ARTICLE INFO

Keywords:
Metal organic framework
Magnetization
Infrared
Raman
DFT calculations

ABSTRACT

We report synthesis of two novel mixed-valence iron(II)-iron(III) formate frameworks templated by N-ethylmethylammonium ($EtMeA^+$) and 2-Hydroxyethylammonium (HEA^+) cations. X-ray diffraction shows that these compounds crystallize in the $P\bar{3}1c$ niccolite-type structures. Optical studies confirm mixed-valence character of these compounds. Magnetic investigation reveals that both N-ethylmethylammonium iron formate (EtMeAFeFe) and 2-Hydroxyethylammonium iron formate (HEAFeFe) exhibit magnetic order at 36.5 and 37.0 K, respectively. EtMeAFeFe also exhibits large negative magnetization below 31.0 K indicating that this compound is an N-type ferrimagnet. We also present Raman and IR data for both compounds. In order to help assignment of modes corresponding to the $EtMeA^+$ cation, we also performed quantum chemical calculations to derive the harmonic and anharmonic vibrational wavenumbers. The performed calculations revealed that protonation should affect most strongly modes related to vibrations of the N–H bonds as well as the stretching modes of the CH_2 and CH_3 groups attached to the N atom.

1. Introduction

Dense metal-formate frameworks are compounds composed of metal cations linked by $HCOO^-$ ligands to form extended three-dimensional structures with cavities occupied by ammonium cations or protonated amines. These compounds received great interest in recent years because combination of different metal centers and cations located at cavities of the framework allows obtaining huge number of compounds exhibiting various functionalities. Most extensively studied compounds of general formula $[cat][M^{II}(HCOO)_3]$ (M=Cd, Mg, Zn, Mn, Fe, Co, Ni, Cu) crystallize in perovskite- or chiral-type structures and they have attracted attention mainly due to their magnetic [1–7], ferroelectric [8–10], multiferroic [11–24], negative thermal expansion [25] and negative linear compressibility [26] properties.

Heterometallic and mixed-valence formate frameworks are much less common. One group constitute compounds of general formula $[cat][M^{I}_{0.5}M^{III}_{0.5}(HCOO)_3]$ (M^I=Na, K; M^{III}=Cr, Fe, Al.) that also crystallize in perovskite-type structures [27–32]. Among these compounds, ferroelectric properties were discovered for $[CH_3CH_2NH_3][Na_{0.5}M^{III}_{0.5}(HCOO)_3]$ (M^{III}=Fe, Cr, Al) [29,30] whereas $[CH_3CH_2NH_3][M^{I}_{0.5}Cr_{0.5}(HCOO)_3]$ (M^I=Na, K), $[CH_3CH_2NH_3][Na_{0.5}Al_{0.5}(HCOO)_3]$: Cr^{3+} and $[(CH_3)_2NH_2][M^{I}_{0.5}Cr_{0.5}(HCOO)_3]$ ((M^I=Na, K) were shown to exhibit efficient chromium-based luminescence [28,30,32]. Second group constitute niccolite-type formates of general formula $[cat][M^{II}M^{III}(HCOO)_6]$ (M^{II}= Cd, Mg, Zn, Mn, Fe, Co, Ni, Cu; M^{III}=Fe, Cr, Al) [33–44]. These compounds exhibit interesting magnetic and luminescent properties [33–44]. Especially interesting properties were, however, observed for mixed-valence iron(II)-iron(III) frameworks. Up to now only three such compounds are known, i.e., $[(CH_3)_2NH_2][Fe^{II}Fe^{III}(HCOO)_6]$ (DMAFeFe), $[(C_2H_5)_2NH_2][Fe^{II}Fe^{III}(HCOO)_6]$ (DEtFeFe) and $[CH_3CH_2NH_3][Fe^{II}Fe^{III}(HCOO)_6]$ (EtFeFe) [33,35,36,38,41,43,44]. All of them are extensively colored (dark blue or even black) and they show magnetic order near T_{ord}=39 K as well as negative magnetization below T_{comp} = 22–29 K [34,38]. DMAFeFe and DEtFeFe undergo order-disorder phase transitions at 152–155 and 240 K, respectively, and are regarded as mixed-valence multiferroic materials [35,38,41,43,44]. Very recent studies of DEtFeFe showed that this compound has four different switchable physical properties, i.e., in addition to the known previously reversible phase transition and switchable dielectric constant, it also exhibits magnetic poles reversal and tunable positive and negative exchange bias fields at low temperatures [44]. It is worth adding here that interesting magnetic properties have also been reported for iron and iron oxide nanoparticles, including mixed-valence Fe_3O_4 [45–48].

Motivated by recent discovery of interesting properties of mixed-valence formate frameworks, we have attempted to synthesize novel

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http://dx.doi.org/10.1016/j.jssc.2017.10.016
Received 31 July 2017; Received in revised form 18 September 2017; Accepted 12 October 2017

mixed-valence compounds of general formula [cat][$Fe^{II}Fe^{III}(HCOO)_6$] by using not yet employed protonated amines. In family of metal formate frameworks, shape and size of the protonated amine play a crucial role in stability of the structure, electric and even magnetic properties [1,35,38]. We have expected, therefore, that employment of new protonated amines will lead to discovery of new compounds exhibiting interesting physicochemical properties. An important limitation in the synthesis of metal formate frameworks is size of the protonated amine since it cannot be larger than size of the available cavities of the metal formate frameworks. In case of niccolite-type structures, characteristic for majority of heterometallic and mixed-valence formates, the crystal cavities form channels expanding along the *c* axis that may accommodate even large cations such as $(C_2H_5)_2NH_2^+$ [38]. In this article, we will show that successful synthesis of two novel mixed-valence formate frameworks could be performed using N-ethylmethylamine, which was not yet employed in synthesis of any formate frameworks, and 2-aminoethanol (ethanolamine, 2-hydroxyethylamine), which was previously employed in synthesis of divalent metal formate frameworks but with different chemical composition ($[NH_3C_2H_4OH]_2[M^{II}(HCOO)_4]$ instead of $[NH_3C_2H_4OH][M^{II}(HCOO)_3]$) and structure (layered, not perovskite) [49]. The obtained compounds were characterized for structural, optical and magnetic properties by x-ray diffraction, diffuse reflectance and SQUID, respectively. Our aim was also to understand phonon properties of the studied compounds by Raman and IR spectroscopy as well as DFT calculations.

2. Experimental

2.1. Materials and instrumentation

All reagents (analytically grade) used for synthesis are commercially available and used without further purification. Elemental analysis (C, H, N) was performed on a Elementar Vario EL CHNS analyzer. Magnetization of a large number of freely oriented single crystals of HEAFeFe and EtMeAFeFe (about 30 and 20 mg in total) were measured using a commercial Quantum Design SQUID (superconducting quantum interference device) magnetometer at temperatures ranging from room temperature down to 2 K and in applied external magnetic fields up to 50 kOe. The background coming from a weakly diamagnetic sample holder was found to be negligible in comparison to the total signal measured, so its subtraction was omitted. No demagnetization corrections were made to the data reported here either.

The powder diffraction data were collected using X'Pert PRO X-ray diffraction system equipped with PIXcel ultra-fast line detector and Soller slits for *Cu* K_α radiation. The samples were measured in a reflection mode using the Bragg-Brentano geometry. IR spectra have been measured with Nicolet iS50 FTIR spectrometer using standard KBr pellet method in the mid-IR (4000–400 cm^{-1}) and suspension in Nujol in far-IR (400–50 cm^{-1}) region. Raman spectra were measured using a Renishaw InVia Raman spectrometer equipped with confocal DM 2500 Leica optical microscope, a thermoelectrically cooled CCD as a detector and an argon laser operating at 488 nm. The spectral resolution of IR and Raman spectra was 2 cm^{-1}. Diffuse reflectance spectra were measured using a Cary 5E spectrophotometer with the Praying Mantis diffuse reflectance accessory.

2.2. Synthesis of the samples

In order to synthesize the compounds, 3 mmol of $FeCl_2$ (98%, Sigma-Aldrich) and 3 mmol of $FeCl_3$ (97%, Sigma-Aldrich) were dissolved in a mixture containing 3 mL of HCOOH (98%, Fluka), 1.5 mL of methanol (99.8%, Sigma-Aldrich) and 1.5 mL of 1-methyl-2-pyrrolidinone (99.5%, Sigma-Aldrich). To this solution, a mixture containing 3 mL of HCOOH, 1.5 mL of methanol, 1.5 mL of 1-methyl-2-pyrrolidinone and 1 mL of N-ethymethylamine (97%, Sigma-Aldrich) (or 1 mL of 2-aminoethanol, 99.5%, Sigma-Aldrich) was added and mixed. The solution was transferred into a glass tube and left undisturbed. Black (dark blue after grinding) crystallites of EtMeAFeFe and HEAFeFe, collected after 2 and 14 days, respectively, were filtered from the liquids, washed 5 times by methanol and dried at room temperature. Anal. Calculated for EtMeAFeFe (%): C, 24.33; H, 4.05; N, 3.16; found (%): C, 24.25; H, 4.16; N, 3.18. Anal. Calculated for HEAFeFe (%): C, 21.63; H, 3.15; N, 3.15; found (%): C, 21.65; H, 3.22; N, 3.17.

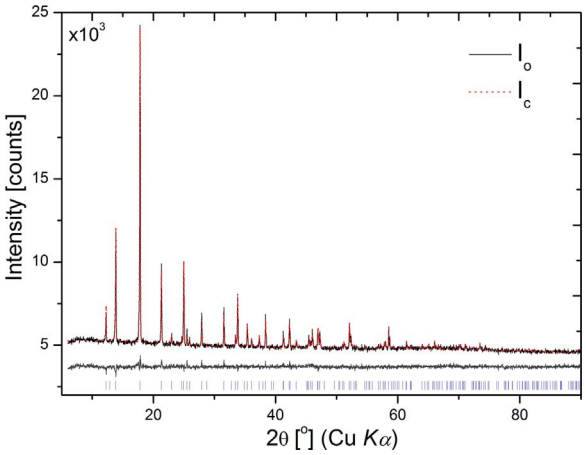

Fig. 1. The results of the Rietveld refinement for EtMeAFeFe powders. The model of the crystal structure was taken from [$(C_2H_5)_2NH_2$][$Fe^{II}Fe^{III}(HCOO)_6$], crystal system trigonal, space group $P\bar{3}1c$ [38]. The final agreement R factors for the profile: R_p:0.013; wR_p = 0.017; GooF = 1.2; and for the structure: R_F = 0.067; wR_F=0.052. The refined lattice parameters: a = 8.3389(2) Å, c = 13.7419(5) Å. I_o and I_c denote observed and calculated intensities, respectively. The residuals and peak positions are given at the bottom.

2.3. Crystallographic structure determination

The Rietveld method [50] was applied to refine collected patterns using Jana2006 [51] software. The results of the refinement are presented in Fig. 1 and S1 as well as in Table S1.

2.4. Computational methods

The geometry optimization of a single EtMeA molecule and $EtMeA^+$ cation was performed with the use of Gaussian 03 program package [52]. All calculations were performed using density functional three-parameters hybrid (B3LYP) methods [53–55] with the 6–311 G(d,p) [56,57] basis set starting from the X-ray geometry. The IR and Raman wavenumbers (harmonic and anharmonic) have been calculated for optimized geometries of the EtMeA molecule and $EtMeA^+$ cation. The Potential Energy Distribution (PED) of the normal modes among the respective internal coordinates was calculated using the BALGA program [58]. The theoretical Raman intensities were calculated using the Chemcraft computer program [59].

3. Results and discussion

3.1. Formation of EtMeAFeFe and HEAFeFe

Formation of the studied compounds involves a few steps. In the first step, $HCOO^-$ anions react with Fe^{II} and Fe^{III} cations to form extended framework composed of the iron ions bridged by formate linkers. Such anionic framework contains cavities that are templated in the second step by protonated amines to maintain electrical neutrality. It is important to use a non-coordinating solvent to avoid its incorporation into the structure. It is also important to use protonated amines with the appropriate size to fit in the cavities of the frameworks.