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Re-entrant spin glass and stepped magnetization in mixed-valence $SrFe_3(PO_4)_3$

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ABSTRACT

The 2 D channel mixed-valent iron (II/III) monophosphate $SrFe_3(PO_4)_3$ was synthesized via one step mild hydrothermal method at 210 °C and characterized by X-ray diffraction techniques and magnetization measurements. Coexistence of antiferromagnetic superexchange and ferromagnetic superexchange interactions was supposed to be in the lattice according to the Goodenough–Kanamori–Anderson rules. Temperature dependent DC magnetization measurement shows that $SrFe_3(PO_4)_3$ is ferrimagnet with three magnetic transitions between 2 and 350 K. Through AC magnetization measurement, re-entrant spin glass was observed due to the competition between ferromagnetic and antiferromagnetic interactions. Furthermore, an interesting field induced stepped magnetization was observed in $SrFe_3(PO_4)_3$ at 2 K with the saturation magnetization $Ms = 2.4\ \mu_B$/f.u. at 5 T.

1. Introduction

In mixed-valent transition metal systems the electrons have different spin states and occupy two degenerate orbitals, e_g and/or t_{2g}, depending on the different valences and different coordinations of the transition metal elements. These compounds feature large spin ground states and significant magnetic anisotropy, which have attracted considerable interest in recent years owing to the important contributions not only in magnetism but also in general fields of physics as thermodynamics, critical phenomena, phase transitions, etc. [1–3]. Besides the magnetic anisotropy, spin glass (SG) is another interesting magnetic phenomenon that raises many questions on physics, which has received significant attention in magnetic materials [4,5]. Classic SG is a magnetic state that the spins were frozen into a disordered magnetic state below the distinct freezing temperature T_f [6]. Two conditions are necessary for the SG: geometry frustration and partial randomness of the interactions between the disorderly occupied magnetic ions in the lattice [7]. In experiment, SG was normally observed in the short range magnetic order system (random magnet) but was rarely observed in stoichiometric ordered compounds with long range magnetic order [8]. Some stoichiometric ordered compounds can show SG-like magnetic relaxation at low temperature due to the competition between ferromagnetic and antiferromagnetic interactions, which are named as re-entrant spin glasses or cluster spin glasses [9].

Iron phosphates have been widely investigated because of the rich structural chemistry and a variety of possible applications, cathodes for Li batteries, heterogeneous catalysis and ion exchange property [10–12]. More than one iron oxidation states and variation of iron sublattices offer the complex network structures, which can give rise to novel magnetic properties. For example, the $Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO_3)_6] \cdot 1.5\,H_2O$ shows unusual spin-glass-like magnetic property and reversible lithium insertion/extraction [13]. Single crystal $RbNa_3Fe_7(PO_4)_6$ shows field-dependent magnetization jumps, where the metamagnetism could be attribute to the combinations of the geometry frustration of magnetic lattice, short Fe(II)…Fe(II) distance and uniaxial magnetic properties of trigonal bipyramidal Fe(II) [14]. Similar field-dependent magnetization step reported so far can be attributed to quantum tunneling magnetization, avalanches, spin rearrangements, or domain-wall depinning [15]. The presence of PO_4 groups is also important since their corners are generally shared by several metallic cations. The PO_4 anion groups can mediate a competition between Fe–O–Fe superexchange (SE) and Fe–O–O–Fe super-superexchange (SSE) interactions. The SSE interaction is often underestimated but strong in some $S = 1/2$ systems [16,17]. The sign and magnitude of SE interaction can be predicated by semi-empirical Goodenough–Kanamori–Anderson rules, which is useful to determine the sign of superexchange interactions by both occupied orbitals of adjacent Fe atoms and geometrical information (bond angles and lengths) of Fe–O–Fe [18]. Ferromagnetic (FM) and

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antiferromagnetic (AFM) interactions for Fe–O–Fe fragments can coexist in iron phosphates [19]. Furthermore, the coexistence of and competition between the FM and AFM couplings in the system will lead to interesting magnetic behaviors.

The structural variety of strontium iron phosphates is rich, which can give rise to original magnetic properties.

A series of new compounds have been synthesized in the last decades: $SrFe_3(PO_4)_3(HPO_4)$ [20], $SrFe_3(P_2O_7)_2$ [21], $SrFe_5(PO_4)(OH)H_2O$ [22], $SrFe_2(PO_4)_2$ [23], $Sr_9Fe_{1.5}(PO_4)_7$ [23] and $SrFe_3(PO_4)_3O$ [24], etc. Among these compounds, divalent iron phosphate $SrFe_2(PO_4)_2$ has a complex two-dimensional network structure. The magnetization measurement shows a canted antiferromagnetic property and several field-induced phase transitions below 7 k [23]. $SrFe_3(PO_4)_3O$ containing Fe(III) ions represents a chain structural type and shows re-entrant spin glass property due to the competition between FM and AFM interactions [9,24].

The 2 D channel mixed valence phosphate $SrFe_3(PO_4)_3$ was first prepared by a rather high temperature hydrothermal treatment at 375 °C and had been fine characterized, which is referred as 375-$SrFe_3(PO_4)_3$ in this paper. $SrFe_3(PO_4)_3$ is a mixed valent iron (II/III) monophosphate and the structure consists of a low-dimensional open-framework that form a 2 D channel in the *ab* plane, where the Sr ions are located. Magnetization measurements show 375-$SrFe_3(PO_4)_3$ exhibits typical ferromagnetic property with $T_C = 55$ K and $\Theta = 10.2$ K as reported [25].

Physical properties of a compound sometimes depend on the different synthesis strategies. Here we are going to focus on the magnetic property of $SrFe_3(PO_4)_3$ synthesized via mild hydrothermal method at 210 °C, which is referred to as 210-$SrFe_3(PO_4)_3$ throughout the paper. The crystal structure of 210-$SrFe_3(PO_4)_3$ was checked by single crystal X-ray diffraction. The structural parameters are consistent well with the previous reported parameters of 375-$SrFe_3(PO_4)_3$. However, the magnetization measurements show 210-$SrFe_3(PO_4)_3$ is ferrimagnet, where the novel re-entrant spin glass and field-induced stepped magnetization are observed owing to the competition between FM and AFM interactions in the ferrimagnet 210-$SrFe_3(PO_4)_3$.

2. Experimental

Black rhombus-shape crystals of $SrFe_3(PO_4)_3$ were synthesized by a mild hydrothermal method, which was reported in a paper focusing on the synthesis and structure of $AMg_xFe_{3-x}(PO_4)_3$ (A=Sr, Ba, Pb) [26]. 0.5 g P_2O_5, 0.1 g $FeCl_2 \cdot 4H_2O$ and 0.1 g $SrCO_3$ as starting materials were mixed in 10 mL distilled water and sealed in an autoclave with a Teflon liner (25 mL), before being heated to 210 °C and kept at that temperature for 72 h, after which they were cooled to room temperature by switching off the furnace. Black rhombus-shaped crystals of $SrFe_3(PO_4)_3$ were obtained as a single phase after washing with distilled water for several times and drying in air.

Single crystal X-ray diffraction data were collected by a Bruker-Smart APEXII CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation ($\alpha = 0.71073$ Å). Data of the compound were processed through the SAINT reduction [27]. The structure of $SrFe_3(PO_4)_3$ were solved by the Patterson methods and subsequently completed by Fourier recycling using the WinGX software package [28]. The crystals were ground up into a fine powder for the powder X-ray diffraction and magnetic measurements.

Fine powder of the crystals (14 mg) was sealed in a gelatine capsule (Quantum Design) and used for the magnetic measurements. DC magnetization measurements were performed on a Quantum Design SQUID magnetometer (MPMS-XL) between 2 and 350 K in applied field of 100 Oe under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. DC magnetization were measured between 4 and 350 K in applied fields of 500 Oe, 1000 Oe and 10,000 Oe (1 T) separately under ZFC condition using a Quantum Design SQUID-VSM magnetometer. Isothermal magnetization was recorded between −5 T and +5 T at 2 K using a Quantum Design MPMS-XL magnetometer. Frequency-dependent AC susceptibility measurements (10.6 mg) at a zero static magnetic field and an applied oscillating magnetic field (H_{AC}) of 3.5 Oe were performed between 4 and 45 K (on heating) at frequencies (*f*) of 10, 100, 200, 500 and 900 Hz using a Quantum Design MPMS-XL magnetometer.

3. Results and discussion

The structure parameters were refined with single crystal X-ray diffraction data [24]. There was no significant difference between the structure parameters of 210-$SrFe_3(PO_4)_3$ and of 375-$SrFe_3(PO_4)_3$. $SrFe_3(PO_4)_3$ crystallizes in the orthorhombic space group *Imma* (No. 74), $a = 10.438(2)$ Å, $b = 13.421(3)$ Å, $c = 6.556(1)$ Å, $V = 918.4(3)$ Å^3 and $Z = 4$ with $R/Rw = 0.031/0.068$ [26]. Two crystallographically different Fe sites, Fe (1) and Fe (2), exist in the crystal structure as shown in Fig. 2A. All the Fe atoms are coordinated by six oxygens and form distorted octahedra. The degree of distortion in the FeO_6 octahedron was calculated: $\Delta = (1/6)\Sigma((R_i - R_a)/R_a)^2$, where R_i is an individual bond length and R_a is the average bond length. The calculation yields degree of distortion of 3.1×10^{-4} for $Fe^{2+}O_6$ and 1.3×10^{-3} for $Fe^{3+}O_6$. Two slight distorted Fe^{2+} octahedra were connected with other to form a dimer by edge sharing, where the $Fe^{2+} \ldots Fe^{2+}$ distance is 3.157(1) Å and Fe^{2+}–O–Fe^{2+} angel is 97.363(7)°. The Fe^{3+} octahedron was connected with the dimer of Fe^{2+} octahedra by corner sharing with $Fe^{2+} \ldots Fe^{3+}$ distance of 3.5572(6) Å and Fe^{3+}–O–Fe^{2+} angel of 120.2(1)°. According to the semi-empirical Goodenough–Kanamori–Anderson rules, a 180° superexchange interaction (the magnetic ion–ligand–magnetic ion angle is 180°) of two magnetic ions with partially filled *d* shells is strongly antiferromagnetic, whereas a 90° superexchange interaction is ferromagnetic but weaker. As shown in Fig. 2B, it could satisfy coexistence of J_1 ferromagnetic superexchange interaction between two Fe^{2+} ($Fe^{2+}-O-Fe^{2+}$ angel is 97.363(7)°) and J_2 antiferromagnetic superexchange interaction between Fe^{2+} and Fe^{3+} (Fe^{3+}-O-Fe^{2+} angel is 120.2(1)°) in the lattice without frustration. The superexchange interactions formed a complex 3D magnetic

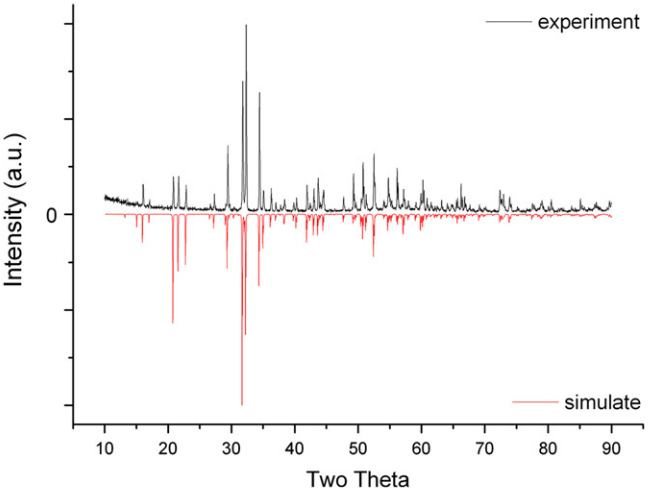

Fig. 1. Powder XRD pattern of 210-$SrFe_3(PO_4)_3$. Red one stands for simulated pattern based on single crystal structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)