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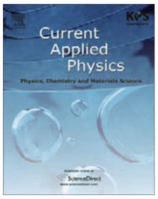

Ferromagnetic order and spin-glass behavior in multi-metallic compound $Ni_{1.125}Co_{0.375}[Fe(CN)_6] \cdot 6.8H_2O$

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ABSTRACT

Multi-metallic Prussian blue compound $Ni_{1.125}Co_{0.375}[Fe(CN)_6] \cdot 6.8H_2O$ has been synthesized. The Mössbauer spectroscopy at room temperature and IR spectra study revealed that the metal ions are bonded through cyanide ligand and the presence of low spin $Fe^{III}(S = 1/2)$ and high spin $Fe^{III}(S = 5/2)$ ions, as showed in these structure: $Fe^{III}(S = 1/2)$-CN-(Co^{II}/Ni^{II})(96%) and $Fe^{III}(S = 5/2)$-NC-(Co^{II}/Ni^{II}) (4%). The Curie constant of $C = 3.00\ cm^3\ K\ mol^{-1}$ and Weiss paramagnetic Curie temperature of $\theta = 16.43$ K were observed in fitting according to Curie–Weiss law. These results indicate that there existed a ferromagnetic exchange interaction in the complexes. The observed value of coercive field (H_c) and remanent magnetization (M_r) at 4 K for the compound are 497 Oe and 1.03 Nβ. The presence of spin-glass behaviours in the compound is ascribed mainly to domain mobility or domain growth under different cooling conditions.

1. Introduction

In the past decade, derived from development of Prussian blue analogue, molecular-based magnets have been object of interest [1–5]. It is well known that Prussian blue family includes multi-metal cyanide [4–7] and the hetero-Prussian blue analogues [8–10], with exhibit various remarkable magnetic properties, such as magneto-optical effect [4,11], thermal magnetic effect [12,13], high T_c [1–3], pressure-induced linkage isomerism acts [14], spin-glass behavior [7,15,16], and so on. Recently, we have synthesized multi-metallic Prussian blue compound $Ni_{1.125}Co_{0.375}[Fe(CN)_6] \cdot 6.8H_2O$. In this paper we report a detailed investigation of the ferromagnetism behavior and spin-glass behavior for the compound by using both dc and ac magnetometry.

2. Experimental section

2.1. Materials and physical measurements

$NiSO_4 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $K_3Fe(CN)_6$ are reagent grade, and without further purification.

For the characterization of the samples we used Perkin Elmer Corporation spectrum one FT-IR spectrometer Fourier transform infrared spectrometer (KBr pellet), with the radiation spectrum of the 4000–400 cm^{-1}; Perkin Elmer Corporation PE2400 II elemental analysis device; Perkin Elmer TGA detector. Magnetization measurements were measured by a Quantum Design MPMS-7S superconducting quantum interference device (SQUID) magnetometer. The powder diffraction data are measured using the Bruker D8 ADVANCE X-ray diffractometer instrument (Cu · Kα).

As the radioactive source for Mössbauer measurements, ^{57}Co (Pd) moving in a constant acceleration mode was used. And the room temperature spectrum was fitted with the MössWin3.0 software. The isomer shifts are reported relative to α-Fe at room temperature.

2.2. Synthesis

Polycrystalline samples of $Ni_{1.125}Co_{0.375}[Fe(CN)_6] \cdot yH_2O$ have been prepared in co-precipitation method following the literature method [7]. A mixture of aqueous solutions of $Co(NO_3)_2$(37.5 ml, 3.75 mmol) and $NiSO_4$ (112.5 ml, 11.25 mmol) was poured in aqueous solution of $K_3[Fe(CN)_6]$ (100 ml, 10 mmol). Then the reaction solution was left to stand at room temperature for an appropriate period of time in order to make reaction completed fully.

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A light brown precipitation was obtained, and precipitation then was filtered, washed many times with demineralized water and finally dried under IR lamp for about 40 min. Elemental analysis to measure C, H, N mass ratio were found: C, 16.33; H, 3.26; N, 19.16%; Calcd.: C, 16.85; H, 3.37; N, 19.66%.

3. Results and discussion

3.1. Characterization

Thermal gravimetric analysis (TG) has given weight ratio of the crystal water in molecular formula weight. In a procedure monitored by TG analysis (see Fig. 1), weight is lost at 37–150 °C, then compound remains thermally stable in the temperature interval of 150–240 °C (weight loss found/calcd.: 29.444%/28.990%), that is situation all the water molecules lose, so the compound contains 6.8 crystal waters by calculation. Finally the compound decomposed at further temperature.

X-ray diffraction experiment of the compound was carried out on Cu Kα. The X-ray diffraction pattern for the compound is shown in Fig. 2 (the numbers beside the peaks are the *d*-values). The lattice parameter in the refinement using FullProf software is 10.200(2) Å, and the space group is Fm3 m.

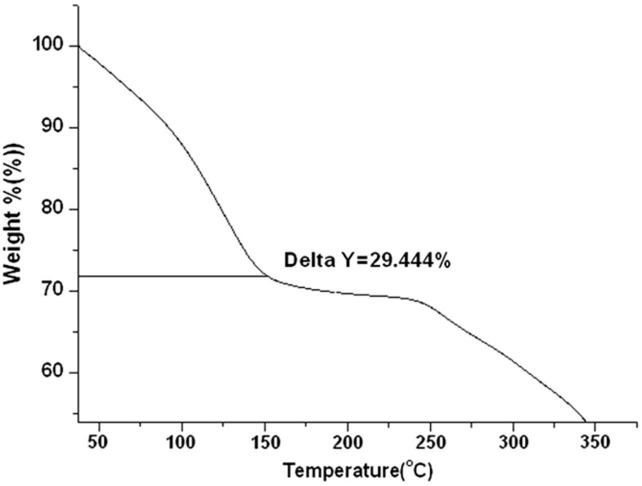

Fig. 1. TG spectrum of the sample.

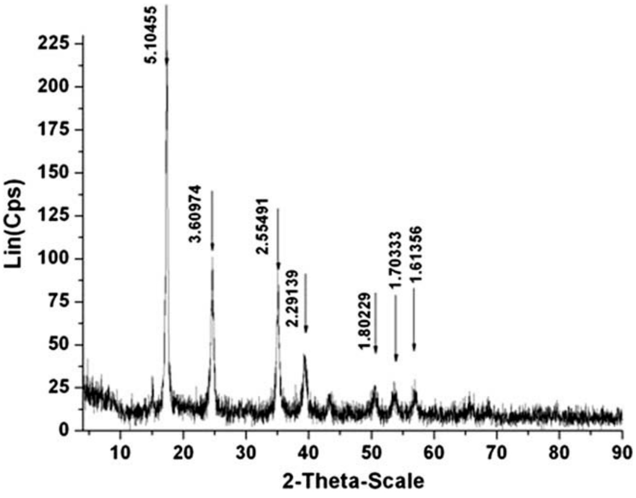

Fig. 2. The X-ray diffraction pattern.

The FT-IR spectrum of the compound is shown in Fig. 3. It shows two CN stretching bands at 2163.73 and 2105.66 cm^{-1} in the regions 2200–2000 cm^{-1} indicating the existence of two types of bridging cyanide group in this compound [7]. Meantime, the broad peak at 3403.72 cm^{-1} and peak at 1612 cm^{-1} correspond to the ν(O–H) of the crystal water.

3.2. Mössbauer spectroscopy

The room temperature Mössbauer spectroscopy of the compound recorded is shown in Fig. 4. The observed spectra can be fitted two components having chemical shifts (CS) of −0.176 mm/s and 0.187 mm/s and quadrupole splitting (QS) of 0.432 mm/s and 0.491 mm/s, respectively. The component (the bigger green lines) with CS = −0.176 mm/s and QS = 0.432 mm/s which relatives intensities is 96% may be identified as low spin Fe^{3+} ($S = 1/2$)[7,17]. The second doublet (the smaller blue lines) with CS = 0.187 mm/s and QS = 0.491 mm/s which relative intensities is 4% may be identified as high spin Fe^{3+} ($S = 5/2$) [7]. Therefore there are two structures in the compound: Fe^{III}($S = 1/2$)-CN-(Co^{II}/Ni^{II}) (96%) and Fe^{III}($S = 5/2$)-NC-(Co^{II}/Ni^{II}) (4%). That is similar to a

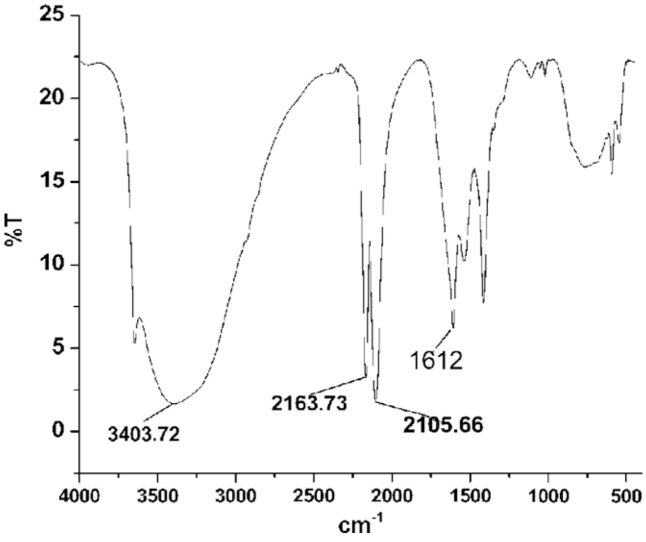

Fig. 3. FT-IR spectrum of the sample.

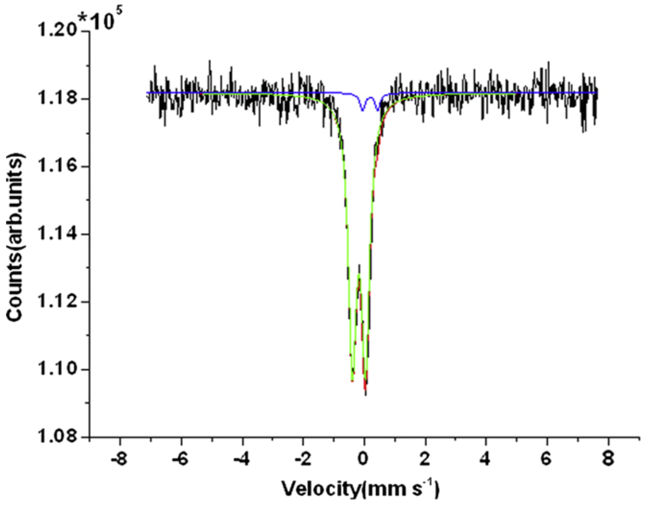

Fig. 4. Mössbauer spectrum of the sample of the sample.