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Hydrothermal synthesis, crystal structure, thermal behaviour and magnetic properties of a new ammonium-chromium-iron(III) bis(hydrogenphosphate)

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ABSTRACT

The hydrothermal synthesis and the chemical-physical characterization of an ammonium-chromium(III)-iron(III) bis(hydrogenphosphate), $Cr_{0.34}Fe_{0.66}NH_4(HPO_4)_2$ [CrFeNP] is reported. It was obtained in aqueous media by reaction between chromium(III) chloride, iron(III) chloride, urea, and orthophosphoric acid. The crystal structure of CrFeNP was determined from single-crystal X-ray diffraction data. It crystallizes in the triclinic system, space group *P*-1, and exhibits two types of different infinite tunnels along [0 1 0] and [1 0 0] directions, where the ammonium cations are located. Thermal analysis shows that the solid is stable up to ca. 600 K. The activation energy of the thermal decomposition up to 1273 K was computed by isoconversional methods. In addition, the magnetic behaviour of the material was investigated from magnetic susceptibility and magnetization measurements. CrFeNP undergoes two successive magnetic transitions at temperatures $T_C = 17.9$ K and $T_t = 3.1$ K, which could be related to a ferri- and an antiferromagnetic magnetic phase transitions, respectively.

1. Introduction

In previous works, we have investigated on the crystal and magnetic structures, and the structural and magnetic phase transitions of some iron phosphates such as $Fe(NH_3)_2PO_4$ [1,2] and $NH_4Fe(HPO_4)_2$ [3–7] finding that both phosphates show unusual magnetic behaviour. On the other hand, the sequential formation of $NH_4Fe_2(OH)(PO_4)_2{\cdot}2H_2O$, $NH_4Fe_2(PO_4)_2$ and, finally, $NH_4FePO_4{\cdot}H_2O$ were achieved in solvothermal conditions starting from $FePO_4{\cdot}2H_2O$, $(NH_2)_2CO$ and $(CH_3)_2CO$. In the dissolution-precipitation process, a certain structural memory is conserved in iron(III) cation environments, that disappears in the reduction to iron(II) [8]. We have carried out research on the crystal and magnetic structures of polycrystalline ammonium-iron(III) bis(hydrogenphosphate) [FeNP] from neutron powder diffraction, as well as its thermal decomposition and physical properties [3,4]. The body-centred unit cell (described with no conventional space group with a triclinic crystal structure *I*-1 reported by Yakubovich from single crystal X-ray diffraction data [9]) was transformed into a reduced primitive cell (*P*-1 space group). Combining powder neutron diffraction, magnetization measurements, and specific-heat data, we have studied in detail both the crystal and magnetic structures of $FeND_4(DPO_4)_2$ and $FeNH_4(HPO_4)_2$ compounds [5–7]. The low symmetry of this structure gives rise to a complex pattern of competing super-exchange interactions between the magnetic moments of two types of Fe^{3+} sites that are responsible for the existence of two magnetic phase transitions. The magnetic moments of the Fe^{3+} ions are arranged ferrimagnetically below $T_C = 17.82 \pm 0.05$ K with magnetic moments $\mu_{FI} = 4.19 \pm 0.02\ \mu_B$ at 4 K. They undergo a magnetic phase transition below $T_t = 3.52 \pm 0.05$ K in order to adopt an antiferromagnetic arrangement with equal moment antiphase structure. This is characterized by a long–period propagation vector close to $k_{AF} \approx (1/16, 0, 1/16)$ rlus and a magnetic moment for the Fe^{3+} ions of $\mu_{AF} = 4.41 \pm 0.03\ \mu_B$ at 1.5 K, as was clearly evidenced from the temperature dependence of the magnetization under a low applied magnetic field.

This paper reports the hydrothermal synthesis, structural charac-

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terization and magnetic properties of a new ammonium-chromium(III)-iron(III) bis(hydrogenphosphate). The activation energy of thermal decomposition was obtained using isoconversional methods. Magnetic susceptibility measurements revealed that the sample has ferrimagnetic properties.

2. Materials and methods

2.1. Sample preparation and analytical procedures

$NH_4Cr_xFe_{1-x}(HPO_4)_2$ ($0 \le x \le 1$) solids were hydrothermally synthesised in a stainless steel Teflon-lined vessel under autogenous pressure from a mixture of $MCl_3{\cdot}6H_2O$ (M = Cr, Fe) (1 M, 99%, Merck), H_3PO_4 (85%, Merck), and $(NH_2)_2CO$ (solid, 99%, Merck). The total volume of the reaction mixture was 40 mL, and the autoclave was sealed and heated at 453 K during 10 days. The reaction product was filtered off, thoroughly washed with an excess of ionized water until neutral pH, and dried in air at room temperature. When the molar ratio was C/P = 0.25 and P/M = 15 (M = Cr, Fe) for metal ratio Cr:Fe of 0:10 light violet crystals of $NH_4Fe(HPO_4)_2$ [FeNP] were obtained, for Cr:Fe of 1:9 brilliant green crystals of $NH_4Cr_{0.34}Fe_{0.66}(HPO_4)_2$ [CrFeNP] were achieved and for Cr:Fe of 10:0 no precipitated was obtained. The phosphorus, chromium and iron contents of the solids were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis (Finnigan, Element model) after dissolving a weighed amount in HF (aq). Microanalytical data for nitrogen was obtained with a Perkin Elmer 2400B elemental analyzer.

2.2. Scanning and transmission electron microscopy

SEM micrographs and X-ray microanalysis (SEM/EDX) were recorded using a JEOL-6610LV scanning electron microscope operating at 30 kV and coupled with an Oxford X-Max microanalysis system (EDX). STEM(DF)-EDX and EFTEM studies were performed on a JEOL JEM-2100F field emission transmission electron microscope operated at an accelerating voltage of 200 kV using Gatan 636 Liquid N2 Cooling holder. Fine powder of the sample was dispersed in ethanol, sonified and sprayed on a carbon-coated copper grid, and then allowed to air-dry. Finally, SOLARUS 950 Advanced Plasma Cleaning System was used to clean samples before observation.

2.3. X-ray diffraction studies

Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical X′pert PRO MPD X-ray diffractometer with PIXcel detector, operating in the Bragg-Brentano (θ/2θ) geometry, using CuKα radiation (λ = 1.5418 Å). Data were collected at room temperature between 5° and 80° in 2θ with a step size of 0.02° and count time of 10 s per step. The samples were gently ground in an agate mortar in order to minimize the preferred orientation.

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Xcalibur Gemini R CCD single crystal diffractometer. The measurements were collected at 293 K, using also CuKα radiation. The intensities were measured using the ω scan method. The crystal structures were solved by direct methods. A refined absorption correction was applied. Structures were refined by using full-matrix least squares on F2. Crystallographic calculations were made by using data collection, cell refinement, and data reduction: CrysAlisPRO [10]; program used to solve structure: SUPERFLIP [11] program used to refine structure: SHELXL97 [12], molecular graphics: Mercury [13], software used to prepare material for publication: WinGX publication routines [14].

2.4. Thermal analysis and kinetic data

For the thermal analysis, approximately 15 mg of powder sample was used in a Mettler-Toledo TGA/SDTA851e, in a dynamic nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10 K min^{-1}. Blank runs were performed previously. The evacuated vaporous were also determined with a Pfeiffer Vacuum Thermo Estar TM GSD301T mass spectrometer. The masses 15 (NH_3) and 18 (H_2O) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

The kinetics of a solid-state reaction, in conditions far from equilibrium and assuming the temperature dependence is given by the Arrhenius equation [15,16], can be described by the general equation

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where $f(\alpha)$ is the reaction model, α the extent of conversion, that is determined experimentally as a fraction of the total mass loss in the process, T (K) the temperature, t (s) the time, A (s^{-1}) the pre-exponential factor, E (J mol^{-1}) the activation energy, and R (J mol^{-1} K^{-1}) the gas constant. For a non-isothermal process with a constant heating rate β, $T = T_0+\beta t$, the Eq. (1) can be written as

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

Isoconversional methods were used to carry out the kinetic analysis because they allow estimating the activation energy as a function of the extent of conversion without the need to know either the reaction model or the pre-exponential factor. The basic assumption of these methods is that the reaction rate, for a constant extent of conversion, depends only on temperature [17,18]. A large number of mathematical methods, differential and integral, have been developed to evaluate solid-state kinetics and to get the kinetic parameters from thermal experiment data. The differential methods are very sensitive to the experimental noise and tend to be numerically unstable, especially when the reaction rate is estimated by numerical differentiation of experimental data [19]. The popular differential Friedman method [20] is derived by taking logarithms on the general kinetic Eq. (2)

$$\beta\ln\frac{d\alpha}{dT} = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{3}$$

For different constant heating rates, by linear fitting Eq. (3) to the experimental data, the activation energy is determined. A modified version of the Friedman method has been proposed by Huidobro et al. [21] in order to reduce noise effects.

Integral methods are widely used in the kinetic analysis in spite of the fact they may lead to important errors in the activation energy values. On the one hand, some approximations are used for estimation of the temperature integral and, on the other hand, their intrinsic inconsistency when the activation energy changes with α [16,22]. In order to avoid these drawbacks, incremental integral methods were developed assuming that activation energy is constant in a small interval. Vyazovkin proposed an advanced non-linear method [23,24] where the activation energy is obtained by minimization of the function

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J_i(E_\alpha)}{J_j(E_\alpha)} \tag{4}$$

where

$$J_i(E_\alpha) = \int_{t_{\alpha_i-\Delta\alpha}}^{t_{\alpha_i}}\exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right)dt \tag{5}$$

In this study, the modified Friedman (MFR) and the Vyazovkin (Vyaz) procedures were applied. In any case, the physical meaning of the obtained results should be treated with care [25].

In order to check the values obtained for the apparent activation energy, the factor $c_\alpha = Af(\alpha)$ has been computed directly from Eq. (1). After computing the activation energy by each method mentioned above, for a fixed value of α, the product $Af(\alpha)$ can be obtained by fitting Eq. (6) to the experimental data