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Crystal structure refinement of the electron-transfer-active potassium manganese hexacyanoferrates and isomorphous potassium manganese hexacyanocobaltates

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A B S T R A C T

We report on the crystal structure refinements in the novel electron-transfer-active Prussian Blue analogs (PBA) $KMn^{II}_4[Co^{III}_{1-x}Fe^{III}_x(CN)_6]_3 \cdot nH_2O$ ($n \simeq 12$). The series of novel PBA with the end members of $KMn_4[Co(CN)_6]_3 \cdot 11.8\ H_2O$ and $KMn_4[Fe(CN)_6]_3 \cdot 10.5\ H_2O$ have been synthesized for the first time, all showing a number of extra-reflections incompatible with ordinary face-centered cell of the Fm-3m symmetry group. We have analyzed the Rietveld patterns for $x = 0, 0.53, 1$ and found that the extra-reflections could be well fitted using several primitive (P) cell symmetries. The best fitting quality was obtained using the noncentrosymmetric space group (S.G.) $P\bar{4}3m$ ($Z=1$) with the origin of coordinate system shifted into a zeolitic site. In this structure model, the Co–CN–Mn entities are bent owing to the charge introduced by the K^+ insertion that induces also the electron transfer between Mn and Fe. Using Mössbauer spectroscopy the electron transfer activity is identified with the appearance of unsplit resonance at the isomer shift of typically −0.15 mm/s evidencing the low-spin state for Fe^{3+} and Fe^{2+} species. In the same $P\bar{4}3m$ phases doped with $^{57}Fe^{2+}$ into the Mn site, a sequence of discrete values of quadrupole splitting (0 mm/s, 0.9 mm/s, 1.8 mm/s) is observed and attributed to different conformations of the polyhedra, in which the ground states are orbital triplet, doublet and singlet, respectively.

1. Introduction

Prussian Blue (PB) analogs $Rb_xMn^{II}[Fe^{III}(CN)_6]_{(x+2)/3} \cdot zH_2O$ ($x \le 1$) [1–4] and $Cs_xMn^{II}[Fe^{II,III}(CN)_6]_y \cdot zH_2O$ ($x \le 2$) [5–7] have excited a great interest recently owing to the electron transfer occurring within the pairs $Mn^{II}Fe^{III}$ and $Mn^{III}Fe^{II}$. In these and related compounds, the charge transfer manifests itself through a hysteretic 1st order phase transition observed via magnetization [8–11], crystallographic symmetry change [1–4], calorimetry [9,12], X-ray spectroscopy [6,13], Raman shifts [9,14], etc. On the other hand, the cubic-to-rhombohedral phase transition in $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.6H_2O$ was reported to be unrelated to the charge transfer between Fe and Mn and interpreted in terms of order-disorder transformation in the system of displacements of Na^+ ions located in sort of zeolitic cages [15]. Thus, the number of systems susceptible to charge transfer within the family of Prussian Blues remains very limited.

The practical significance of the charge-transfer materials is very important because a functional material property can be induced by external stimuli paving the ways to inventions of new stimuli-switchable devices [16].

It is tempting to search for more electron-transfer-active compounds replacing Rb or Cs with lighter alkali ions. We are not aware of the cyanide-bridged Mn–Fe bimetallic assembly containing K, except only one compound, in which the synthesized mixed-valence manganese hexacyanoferrate was reported to contain the acetate moiety [12,17]. Such a bulky moiety $[O(C_2H_3O_2)_2]$ can be hardly accommodated within the original PBA structure. Therefore, this acetate-based compound [12,17] might have only indirect relation to the Prussian Blue family, whereas the true partially K-filled PB analog remained uninvestigated.

In this work, we have synthesized such a partially K-filled PBA framework compound $KMn^{II}_4[Fe^{III}_{1-x}Co^{III}_x(CN)_6]_3 \cdot 12\ H_2O$ ($0 \le x \le 1$). In Mössbauer spectra, the iron species susceptible to electron transfer are identified with the low-spin (LS) states lacking the quadrupole spitting. The quadrupole-splitting-free (QSF) subspectrum is associated partly with LS Fe^{2+} and partly with LS Fe^{3+} [9]. We found that partial substitution of the complex $[Fe(CN)_6]$ with $[Co(CN)_6]$ does not extinguish the electron-transfer activity.

In both Co-rich and Fe-rich ends of the series of the solid solutions, the X-ray diffraction reflections were observed extraneous with respect to the archetypal PB face-centered $Fm\bar{3}m$

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crystal system. These reflections can be generated within a simple cubic crystal system, using either a noncentrosymmetric space group (S.G.) $P\overline{4}3m$, or a centrosymmetric one $Pm\overline{3}m$. In this work, we have compared these two structure models, and made a choice in favor of noncentrosymmetric structure. We argue that the lack of the center of symmetry is related to ordering between the guest species K^+ and H_2O within the sites of zeolitic type.

We have analyzed other possible reasons for the genesis of extraneous reflections. Namely, the ordering between Jahn–Teller (JT) active ions Mn^{3+} and JT-inactive Mn^{2+}, and the ordering in the system of large vacancies of the whole complex $[Co(CN)_6]$. In these two cases, the center of symmetry may not be lost. Therefore, we have also performed the crystal structure refinement in the centrosymmetric $Pm\overline{3}m$ group as suggested previously for the archetypal PB $Fe_4[Fe(CN)_6]\cdot 14\ H_2O$ [18,19]. It turned out, however, that the R-factors achievable with the noncentrosymmetric group $P\overline{4}3m$ are better. More importantly, the refined cationic composition for the proposed $P\overline{4}3m$ structure model is only consistent with the results of elemental analysis. Other refinements, using the $Pm\overline{3}m$ space group converged to unrealistic formulas diverging with the results of chemical analysis.

2. Experimental

2.1. Syntheses

The target materials were synthesized from the potassium cyanometallates $K_3[Fe(CN)_6]$, $K_3[Co(CN)_6]$, manganese nitrate decahydrate $Mn(NO_3)_2\cdot 10H_2O$ and potassium chloride KCl, all purchased from Alfa Aesar. The reagents were better than 99%-pure and used without further purification.

To synthesize the compounds containing the substantial amounts of K we have applied the conditions distinct from those reported previously for alkali-free $Mn_3[Co(CN)_6]_2\cdot 12H_2O$ [20], and $Mn_3[Fe(CN)_6]_2\cdot xH_2O$ [21,22].

Firstly, the excess of $K_3[Fe(CN)_6]$ or $K_3[Co(CN)_6]$, namely, the use of the 1:1 molar ratio Mn:Fe (Mn:Co) already results in the novel phases of the compositions close to $KMn_4[Fe(CN)_6]_3\cdot n\ H_2O$ and $KMn_4[Co(CN)_6]_3\cdot n\ H_2O$, although their crystallinity is not very good. Secondly, KCl was added in large excess, and this condition allows us to obtain the novel phases with the improved crystallinity.

The first condition is most important to avoid the formation of the 3:2 phase. Despite the presence of K ion in starting reagents, adding KCl in large excess helps to narrow the X-ray diffractional (XRD) reflections characteristic of the novel $P\overline{4}3m$ phase. We observed that these reflections appear broadened if the excess of KCl is not added. In this case, two systems of reflections of different widths can be clearly distinguished in the XRD patterns. In perovskites, similar coexistence of two systems of reflections was explained previously by the formation of antiphase domains [23,24].

The robust algorithm of synthesizing the domain-free particles, which we used to obtain the samples for final structure refinements, was the following: (i) the solution of 0.025 M of $Mn(NO_3)_2\cdot 10H_2O$ and 2.5 M of KCl was added to the solution of 0.025 M of $K_3[Co(CN)_6]$ and 2.5 M of KCl at 50 °C; (ii) the suspension was stirred in a beaker for 10 min and then cooled down; (iii) obtained precipitate was washed three times, removing the juice above the deposit on the bottom of the beaker with a syringe.

To verify that the solid solution possesses the same structure the mixed Fe–Co hexacyanometallate was synthesized under similar conditions, starting from the 1:1:2 molar ratio of Fe:Co:Mn. The elemental analysis showed in the product the molar ratio 0.47:0.53 of Fe:Co. In deficiency of Mn, this reaction showed that the cyanide $K_3[Co(CN)_6]$ reacted more quickly than $K_3[Fe(CN)_6]$ and expended itself in a larger proportion.

An attempt was made to implement the same structure in $NaMn_4[Fe(CN)_6]_3\cdot n\ H_2O$ synthesized under similar conditions. We found via elemental analysis that Na enters the PBA in a larger proportion, and no characteristic reflections were observed specific for the novel structure of the $P\overline{4}3m$ symmetry. The standard $Fm\overline{3}m$ structure was observed and the analyzed composition was $Na_{0.7}Mn[Fe(CN)_6]_{0.9}\cdot 2\ H_2O$.

As the reference compound with the standard $Fm\overline{3}m$ structure the K-free $Mn_3[Co(CN)_6]_2\cdot 12\ H_2O$ was also synthesized, as well as its Fe- and $Fe_{0.5}Co_{0.5}$ analogs. Conditions of these syntheses were used as described previously [20].

2.2. Characterization

Elemental analyses of the synthesized samples were performed by inductively coupled plasma mass spectrometry for Co, Fe, Mn, and K. The atomic emission spectrometer (ICP-AES) on an IRIS Interpid II XSP Instrument (Thermo Electron Corporation) was employed.

X-ray Diffraction (XRD) patterns were measured on a PW3040/60 X'pert PRO (PANalytical) diffractometer using Cu Ka source ($\lambda \simeq 1.54$ A). Rietveld structure refinements were performed using the FULLPROF program [25]

Magnetic measurements were performed with a SQUID (Quantum Design) magnetometer in the temperature range between 5 K and 300 K for the applied field of 0.5 T

Mössbauer spectra were measured with a Topologic 500 A spectrometer at the temperatures between 78 K and room temperature. Mössbauer source $^{57}Co(Rh)$ of approximately 20 mCi was employed. The measurements at heating the sample above room temperature were performed in a Wissel GMBH furnace. Isomer shifts are reported relative to α-Fe at room temperature.

The water content in the samples was estimated by thermogravimetric analysis carried out using a Setaram Setsys 16/18 analyzer measuring the weight loss in an air flow of 25 mL/min with a heating rate of 10 K/min.

3. Results and discussion

3.1. Materials

The precipitates $KMn_4[Co_{1-x}Fe_x(CN)_6]_3\cdot n\ H_2O$ were white powders for the iron-free compound (x=0), dark brown powders

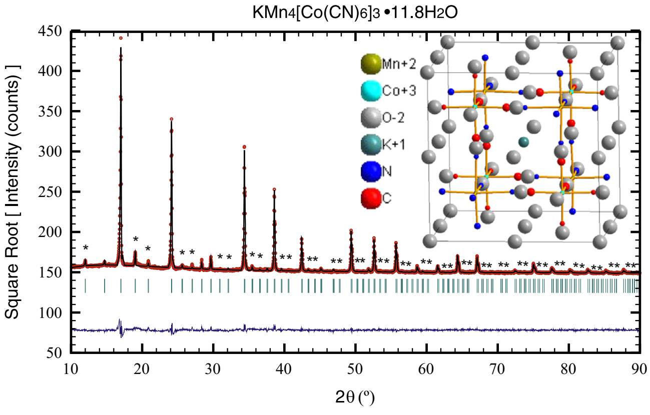

Fig. 1. Rietveld refinement of the novel noncentrosymmetric structure of the hexacyanocobaltate $KMn_4[Co(CN)_6]\cdot 11.8H_2O$, with Rp=17.2%, Rwp=9.24%, Re=4.19%, $\chi^2=4.86\%$, $R_{Bragg}=6.62\%$. The inset shows the structure refined in S.G. $P\overline{4}3m$ with the origin at a zeolitic (O3) site. Displacement ellipsoids are shown for the 25%-level of probability. Note, for the sake of magnification of minor reflections, the representation of the XRD patterns in form of $\sqrt{I}$ vs Θ is used in theoretical, experimental and differential patterns. The reflections which could not be indexed in the face-centered cubic system are marked with asterisks.