



## Research articles

## Tunable critical temperature and magnetocaloric effect in ternary Prussian blue analogue

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## ABSTRACT

A comprehensive study of structural, magnetic and magnetocaloric properties in the ternary Prussian blue analogue (PBA)  $\text{Ni}_{1.5}[\text{Fe}(\text{CN})_6]_x[\text{Cr}(\text{CN})_6]_{1-x}\cdot n\text{H}_2\text{O}$  ( $x = 0, 0.25, 0.5, 0.75$  and  $1$ ) is presented. For all compounds the second-order magnetic phase transition from high temperature paramagnetic to the low temperature ferromagnetic state at the Curie temperature ( $T_c$ ) is observed. We show the possibility of tuning the magnetic and magneto-caloric properties of PBA materials by changing the compositional factor of the metal centres involved in the cyano-bridging. An increase in Fe content leads to increase in the coercive field, whereas the critical temperature decreases from 60 to 22 K. The magnetic entropy change  $\Delta S$ , as well as the related Relative Cooling Power (RCP), vary with  $x$  parameter in the regular way. The highest value of  $\Delta S$  was observed for sample with  $x = 1$  and was equal to  $3.49 \text{ J mol}^{-1}\text{K}^{-1}$  under a magnetic field of 50 kOe, whereas the RCP varied from  $62 \text{ J mol}^{-1}$  ( $145.35 \text{ J kg}^{-1}$ ) to  $118 \text{ J mol}^{-1}$  ( $273.33 \text{ J kg}^{-1}$ ), when  $x$  decreased from 1 to 0.

## 1. Introduction

Magnetocaloric effect (MCE) means an adiabatic temperature change  $\Delta T_{\text{ad}}$  or/and an isothermal entropy change  $\Delta S$  of a magnetic material caused by a change  $\Delta H$  in magnetic field strength. The effect may be employed for cooling in the adiabatic demagnetization process. Previously it was used for reaching temperatures lower than that of liquid helium. At present, research on MCE is focused on quest for materials showing large  $\Delta S$  and  $\Delta T_{\text{ad}}$  in the room temperature range, as well as those relevant for the ultra-low temperature range [1–5].

MCE occurs in all magnetic materials and its value depends on the temperature derivative of magnetization in the given field. In systems with long-range magnetic order it achieves maximum at the ordering temperature  $T_c$ , while in paramagnets or molecular nanomagnets, it is substantial at the lowest temperatures. As the upper limit of magnetic contribution to the entropy is  $\Delta S^{\text{max}} = R \cdot \ln(2J + 1)$ , where  $J$  is the total angular momentum of the magnetic centre, materials with large magnetic moments will show sizeable MCE. The other microscopic parameter important for MCE is the Curie temperature. It was predicted by Oesterreicher and Parker [6] and experimentally checked in Refs. [7,8] that the maximum entropy change  $|\Delta S|^{\text{max}}$  depends on  $T_c^{-2/3}$ . Favourable for the effect is a negligible magnetic anisotropy and a small specific heat of a solid [9]. The dependence of  $\Delta S$  on magnetic field

change  $\Delta H$  is expressed as  $\Delta S \propto \Delta H^n$ , where the exponent  $n$  varies with temperature. Value of  $n$  at  $T_c$  is directly related to the critical exponents, hence study of MCE may provide information important also from the fundamental point of view [6,9].

Besides investigations on MCE refrigerants based on intermetallic alloys, over the last decade a big attention was paid to magnetic molecular materials in view of their application as low-temperature magnetic coolants. MCE in molecular magnets has been investigated most of all for high-spin molecular clusters [10–14] and metal–organic frameworks (MOFs) [15,16]. Investigations of the MCE driven by magnetic order in molecule-based materials have been relatively rare and are limited to cyanido-bridged coordination networks [17–19]. A well-known example of that kind of compounds are Prussian blue analogues (PBA) – a large family of cubic systems with face-centred crystal structure containing hexacyanometalates  $[\text{M}(\text{CN})_6]^{n-}$  and transition metal ions  $\text{M}^{n+}$ . PBAs possess a reach palette of properties such as photomagnetism, room temperature ferromagnetism or zero thermal expansion [20–22]. Due to the cubic structure, the properties of PBAs can be tuned by changing the metal centres involved in the cyano-bridging. In the literature one can find many examples of PBAs incorporating three types of metal ions. One of the first examples of ternary PBA was the mixed ferro-ferrimagnet  $(\text{Ni}_x\text{Mn}_{1-x})_{1.5}[\text{Cr}(\text{CN})_6] \cdot 7.5\text{H}_2\text{O}$ , which accommodated both ferromagnetic ( $J > 0$ ) and

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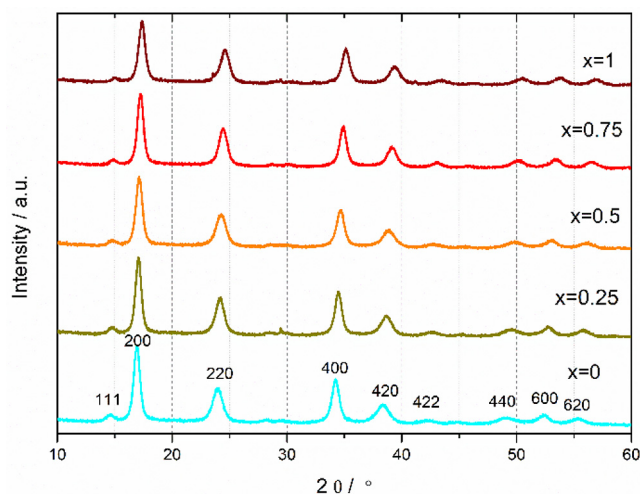


Fig. 1. The XRD patterns of  $\text{Ni}_{1.5}[\text{Fe}(\text{CN})_6]_x[\text{Cr}(\text{CN})_6]_{1-x} \cdot n\text{H}_2\text{O}$  samples with various values of compositional  $x$  factor.

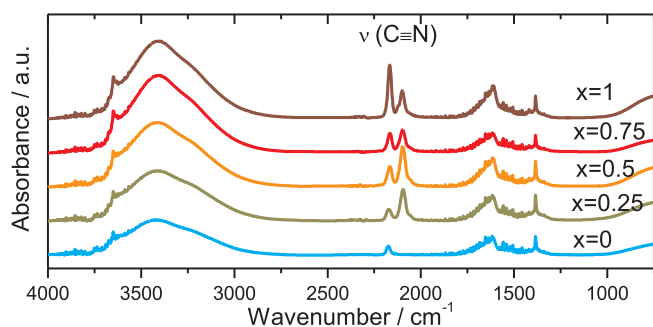


Fig. 2. IR spectra for  $\text{Ni}_{1.5}[\text{Fe}(\text{CN})_6]_x[\text{Cr}(\text{CN})_6]_{1-x} \cdot n\text{H}_2\text{O}$  samples with various values of compositional  $x$  factor.

antiferromagnetic ( $J < 0$ ) exchange interactions [23]. Variation of structural and magnetic properties with composition was also reported for the  $(\text{Co}_x\text{Ni}_{1-x})_{1.5}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  series [24]. The control of physical properties by change of the compositional factor  $x$  was also achieved for thin films of  $(\text{Fe}_x\text{Cr}_{1-x})_{1.5}[\text{Cr}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  [25] and  $(\text{V}_x\text{Cr}_{1-x})_{1.5}[\text{Cr}(\text{CN})_6]_y$  [26] synthesized by the electrochemical deposition as well as for thin films of nickel hexacyanochromate/ferrate obtained with the “layer by layer” deposition technique [27]. Depending on the  $x$  value, the change of colour, critical temperature and coercive field of the films was noted.

The objective of the present work was to obtain in the reproducible process the PBA family compounds, which would show the controlled magnetic and magnetocaloric properties in the possibly wide temperature range. The stoichiometry of the systems under study changed from  $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2$  to  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$  depending on the  $[\text{Cr}(\text{CN})_6]^{3-} : [\text{Fe}(\text{CN})_6]^{3-}$  ratio, while the  $\text{Ni}_3[\text{M}(\text{CN})_6]_2$  core was maintained. The structure of the system reveals the face-centre-cubic packing, thus allowing the formation of cyano linkages between  $\text{Ni}^{2+}$  cations and hexacyanometalate. Here, we report a material with a tunable critical temperature, saturation magnetization, and a coercive field. The series shows the magnetocaloric effect related to  $T_c$  in the 22 K–60 K temperature range and a relative cooling power comparable to those of the intermetallic materials.

## 2. Experimental

### 2.1. Synthesis of the $\text{Ni}_{1.5}[\text{Fe}(\text{CN})_6]_x[\text{Cr}(\text{CN})_6]_{1-x} \cdot n\text{H}_2\text{O}$ series

A solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (18 mmol) in 100 mL of ultrapure

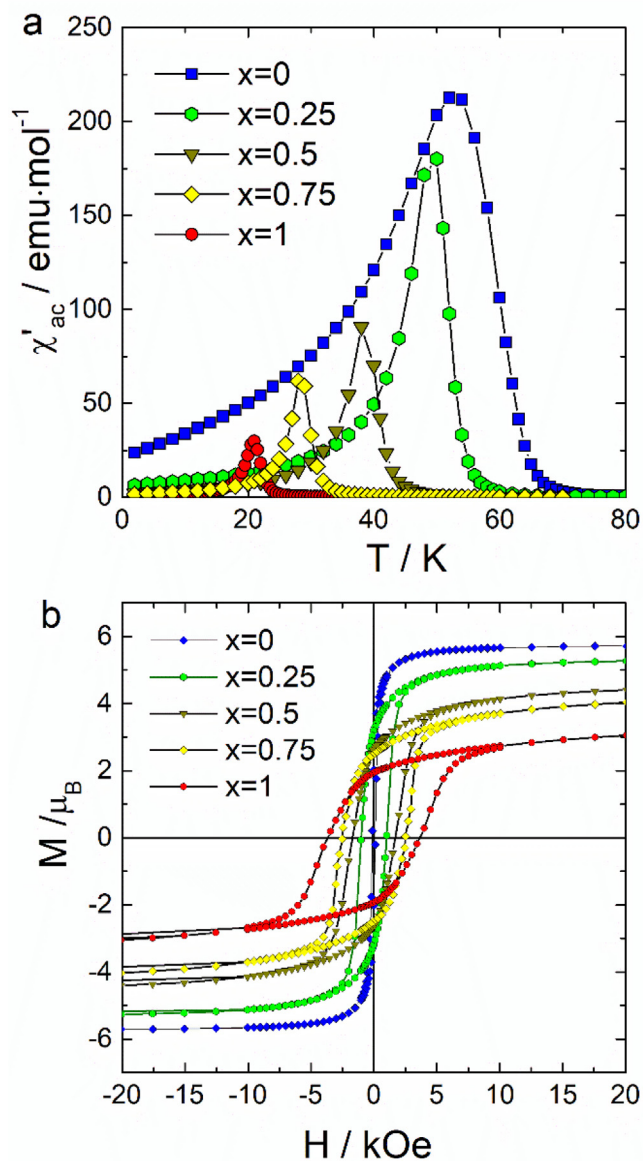


Fig. 3. Temperature dependence of real component of AC susceptibility (a) and magnetization vs field at 2 K (b), measured for  $\text{Ni}_{1.5}[\text{Fe}(\text{CN})_6]_x[\text{Cr}(\text{CN})_6]_{1-x} \cdot n\text{H}_2\text{O}$  samples with various values of compositional  $x$  factor.

Table 1

Magnetic data for the  $\text{Ni}_{1.5}[\text{Fe}(\text{CN})_6]_x[\text{Cr}(\text{CN})_6]_{1-x} \cdot n\text{H}_2\text{O}$  ( $x = 0, 0.25, 0.5, 0.75$  and 1).

Sample	$a$ (Å)	$T_c$ (K)	$H_c$ (kOe)	$M_{\text{sat}}$ ( $\mu_B$ )	$\theta_{\text{CW}}$ (K)	$C$ ( $\text{emuKmol}^{-1}$ )
$x = 0$	10.48	60	0.016	5.7	82	3.91
$x = 0.25$	10.41	52	1	5.3	72	3.65
$x = 0.5$	10.38	41	1.7	4.6	61	3.21
$x = 0.75$	10.30	30	2.5	4.3	46	2.94
$x = 1$	10.22	22	3.6	3.8	26	2.34

water was added dropwise to a solution  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{Cr}(\text{CN})_6]$  (100 mL of ultrapure water). A precipitate was formed immediately and was stirred overnight. The solid was then centrifuged, washed with ultrapure water and dried in the air. The compositional factor  $x$ ,  $x = n_{\text{Fe}} / (n_{\text{Fe}} + n_{\text{Cr}})$ , was varied from 0 to 1, keeping the total potassium hexacyanometalate concentration of 10 mmol. Elemental analysis for C, N, H was carried out by standard microanalytical methods. The

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