The structure and magnetic properties of molecule-based magnet nanoparticles 
$K_x V_y [Cr(CN)_6]_z . nH_2O$

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Abstract

We have synthesized $K_x V_y [Cr(CN)_6]_z . nH_2O$ molecule-based magnet nanoparticles belonging to the Prussian blue (PB) family of compounds. The synthesized samples were characterized by infrared spectroscopy (IR), Raman spectroscopy, UV–Vis spectroscopy, differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The crystal structure was refined from the x-ray powder diffraction profile by the Rietveld method. The samples are cubic, Fm3m space group with lattice parameter $a = 1.045 \text{ nm}$. The magnetic properties are determined from thermal variation of the magnetization and hysteresis loop. The most interesting result is the successful preparation of $K_x V_y [Cr(CN)_6]_z . nH_2O$ crystal Prussian blue nanomaterial which had Curie temperature ($T_C$) approaching room temperature.

Keywords: Prussian blue, FTIR, magnetic property, Raman scattering

Classification numbers: 4.02, 5.02

1. Introduction

The synthesis of materials with new and predictable properties is a challenge for chemists and physicists. A few years ago, inorganic molecular chemists were engaged in the synthesis of high-temperature molecule-based magnets, and this area remains very active. Presently, two families of molecule-based materials behave as room-temperature magnets. The first family can be formulated as $V[TCNE]_x . yCH_2Cl_2$ and was obtained by Manriquez et al [1]. However, the compound decomposes before reaching $T_C$, and up to now it has not been fully characterized [2]. The second family of materials that behave as room-temperature magnets, $V[Cr(CN)_6]_x . nH_2O$, was obtained in 1995 by Ferlay et al [3]. This amorphous Prussian blue(PB) analogue has a Curie temperature of 315 K and a low magnetization at saturation (0.15 $\mu_B$). It is an air-sensitive compound that contains $V^{II}$ and $V^{III}$ cations. Other members of the PB family with vanadium and chromium cations have since been obtained by other authors and these have higher Curie temperatures and saturation magnetizations in line with their stoichiometry [2–5]. Two significant improvements of the synthetic procedure have led to better organized samples. Thus, a sol-gel approach and the use of potassium counterions allowed Girolami and Holmes to obtain a crystalline analogue with which a $T_C$ value of 376 K was reached, the highest in the series [6]. On the other hand, the use of catalytic amounts of $V^{III}$ during the synthesis allowed Garde et al to obtain stoichiometric $C_{310}V^{IV}$ compounds presenting the expected magnetization at saturation [7]. In this paper we report on the synthesis, sample characterization and crystal structure of vanadium–chromium PB analogues. The x-ray diffraction (XRD) pattern analysis indicated that these compounds possessed a face-centered cubic (fcc) crystal structure, Fm3m space group with lattice parameter $a = 1.045 \text{ nm}$. The resultant products were characterized by infrared spectroscopy (IR), Raman spectroscopy and UV–Vis spectroscopy. The magnetic properties are determined from thermal variation of the magnetization and hysteresis loop. Results of the study of low temperature magnetic relaxation in the temperature range
with strong irreversibility in zero-field-cooling (ZFC) and field-cooling (FC) magnetization are presented and discussed.

2. Experimental

The synthesis of two vanadium-chromium PB analogues has been carried out by a route similar to that described in [8] but with some modifications. $K_xV_y[Cr(CN)_6]_z\cdot nH_2O$ samples were obtained by mixing saturated aqueous solution $K_3[Cr(CN)_6]$ and aqueous solution $VCl_2$ under anaerobic conditions. A deep blue precipitate occurred immediately; it was left in its mother solution for one day under argon. The blue precipitate was then filtered and washed several times with distilled water. Finally, the sample was dried under a vacuum for 6 h, at 60°C.

Structural characterization was analyzed by means of XRD using a D5005 diffractometer at room temperature with CuKa radiation ($\lambda = 1.54056\ \text{Å}$). The infrared spectra were recorded under argon on a Nicolet 6700 FTIR spectrophotometer, in the 4000–400 cm$^{-1}$ range with KBr pellets containing 1% of the sample in mass. Raman measurements were performed in a back scattering geometry using a micro-Raman LABRAM-1B and 632.8 nm line of He–Ne ion laser. The magnetic properties of the samples were investigated by a Physical Property Measurement System (PPMS) 6000 (Quantum design).

3. Results and discussion

The powder XRD patterns of the samples are shown in figure 1. Compounds M1 and M2 are crystalline, and their diffraction patterns can be indexed to face-centered cubic (fcc) unit cells with a lattice constant of approximately 1.045 nm. Estimation of the mean size of the PB particles is performed from the width of the (200) Bragg reflection using the Debye–Scherer equation. The average crystallite sizes are about 8 and 10 nm for M1, M2, respectively. Moreover, there are two peaks (symbol * in figure 1) for M1, which were introduced from the starting material and were not completely washed out by water or ethanol.

Figure 1. XRD of $K_xV_y[Cr(CN)_6]_z\cdot nH_2O$. 

Figure 2 shows typical field emission scanning electron microscopy (FE-SEM) images of the obtained products. From these images we can clearly see that $K_xV_y[Cr(CN)_6]_z\cdot nH_2O$ particles are cubic in shape. The particle size of the sample is about 50 to 200 nm.

The composition of the sample is confirmed by energy-dispersive x-ray (EDX) analysis, which reveals the presence of C, N, O, V, Cr and K. Figure 3 shows the EDX spectrum of the sample. The EDX data of the sample are shown in table 1. The result proves that the V:Cr ratio is about 1.64.

The formation of PB was confirmed by the Fourier transform infrared (FTIR) spectroscopy of the $K_xV_y[Cr(CN)_6]_z\cdot nH_2O$ sample. Cyano complexes can be easily identified since they exhibit sharp $\nu$(CN) at

![Figure 2: FE-SEM images of PB $K_xV_y[Cr(CN)_6]_z\cdot nH_2O$.](image)

![Table 1: EDX data of the sample.](table)

| Element | Mass (%) | Atom% |
|---------|----------|-------|
| C       | 15.22    | 30.93 |
| N       | 21.89    | 38.16 |
| Al      | 0.08     | 0.07  |
| K       | 0.38     | 0.23  |
| V       | 35.97    | 17.24 |
| Cr      | 22.34    | 10.49 |

Figure 3. EDX spectrum of the sample.
shows the UV–Vis absorption spectra of PB. Figure 4 shows the IR spectrum of PB. The TGA curve shows an endothermic process at about 180 °C corresponding to water loss and an exothermic process at about 530 °C corresponding to sample decomposition.

The results of TGA and DTA are shown in figure 6. TGA was carried out to determine the number of associated water molecules per formula unit. The TGA curve indicates that the samples lose water from room temperature up to about 180 °C. A plateau is observed between 180 and 240 °C. The total mass loss up to the midpoint of the plateau corresponds to the mass of all water molecules. At about 240 °C, a break corresponding to the decomposition of the compounds occurs. The DTA curve shows an endothermic process at about $T = 141 ^\circ C$ corresponding to water loss and an exothermic process at about $T = 530 ^\circ C$ corresponding to sample decomposition.

In the IR spectrum δ(H=O=H), δ(O−H) and δ(V=O) stretching bands appear. It has been reported that the PB analogues have Crt(CN)6 vacancies and the oxygen of H2O fills the empty nitrogen sites of the vacancy (figure 5). The mean number of Cr neighbors around V is less than six. The less vacancies there are, the higher $T_C$ is [2].

The M2 sample was also studied dynamically using Raman spectroscopy as shown in figure 8. There are two strong vibrational bands at 2094 and 2154 cm$^{-1}$, respectively, which are most likely caused by the stretching vibration of the C≡N group of PB [9, 13]. The cyanide stretching modes are known to be sensitive to the oxidation state of
the coordinating metals. Therefore, changes in the Raman spectra are due to oxidation state changes in V and Cr. Cyanide coordinated to Cr(II) has a single resolvable low-wavenumber peak at 2094 cm$^{-1}$, which could be assigned to $\nu$(Cr$^{II}$–C≡N–V$^{III}$). Cyanide coordinated to Cr(III) has three high-wavenumber peaks at 2154 cm$^{-1}$, which could be assigned to $\nu$(Cr$^{III}$–C≡N–V$^{II}$). This analysis indicates various valence states of both V and Cr exist, resulting in the effect on the exchange interaction, consequently affecting the transition temperature [14].

The thermal variation of the magnetization for the compound is shown in figure 9. The field-cooled magnetization versus $T$ curve, in an applied field of 1000 Oe, presents a break at 276 K, confirming the presence of a magnetic order below this temperature. The highest Curie temperature, achieved in a chromium vanadium ferrimagnet, containing vanadium (II) and chromium (III), is about 315 K [3, 15]. A simple model, based on the magnetic orbital symmetry and energy, can rationalize this high value of $T_C$. The molecular field theory developed by Neel for ferrimagnets with cubic structure is a valuable tool to analyze the relationship between the critical temperature, $T_C$, the mean number of magnetic nearest neighbors, $z$, the exchange parameter between two metal ions (through the bridging ligand), $J(H = -JS_1S_2)$, and the metal ion spin values, $S_1$ and $S_2$ [2, 4, 16]. The exchange parameter $J$ is related to the molecular mean field parameter $W$ that expresses the interaction between the magnetic moments supported by two independent sublattices forming the 3D material:

$$W = \frac{z|J|}{N_A g^2 \beta^2},$$

where $N_A$ is Avogadro’s constant, $\beta$ is the Bohr magneton, and $g$ is the mean $g$ factor. For PB analogues $M'[M(CN)\beta]y$, the critical temperature $T_C$ is given by

$$T_C = W \sqrt{C_M C_M} = \frac{z|J| \sqrt{C_M C_M}}{N_A g^2 \beta^2}.$$

The Curie constants

$$C_M = (N_A \beta^2 / 3k) g_M^2 S_M (S_M + 1),$$

$$C_M = \gamma(N_A \beta^2 / 3k) g_M^2 S_M (S_M + 1)$$

correspond to one $M'$ and $\gamma M$, respectively. The number of nearest neighbors of $M'$ is $z$. Its mean value is equal to 6y in PB analogues. The expression is valid for ferro- or ferrimagnets when the interaction with the second nearest neighbors can be neglected [4]. This is a reasonable assumption for the compound, where the next neighbors are at 10.45 Å.

The hysteresis loops at different temperatures for M1 are given in figure 10. The results indicate that at 10 and 100 K, the compound is ferrimagnetic material. At 300 K, the compound is paramagnetic material. This analysis is a reasonable result of the thermal variation of the magnetization as shown in figure 9.

4. Conclusion

We have presented the structural and magnetic properties of vanadium–chromium PB analogue K$_4$V$_4$[Cr(CN)$_6$]$_2$. It is a member of hexacyanometallate-based molecular magnetic nanomaterials. It crystallizes in the face-centered cubic structure, and the relationship between the critical temperature, $T_C$, the mean number of magnetic nearest neighbors, $z$, the exchange parameter between two metal ions (through the bridging ligand), $J(H = -JS_1S_2)$, and the metal ion spin values, $S_1$ and $S_2$ [2, 4, 16]. The exchange parameter $J$ is related to the molecular mean field parameter $W$ that expresses the interaction between the magnetic moments supported by two independent sublattices forming the 3D material:

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$$T_C = W \sqrt{C_M C_M} = \frac{z|J| \sqrt{C_M C_M}}{N_A g^2 \beta^2}.$$
structure with space group Fm3m and lattice parameter a = 1.045 nm. The compound is a ferrimagnetic material with Curie temperature of about 276 K. The V : Cr ratio \textit{priori} is the most important parameter for the magnetic properties of the compound. The less vacancies there are, the higher \( z \) and \( |J| \) are, and therefore \( T_C \) reaches a higher temperature. This study has shown that a strong relationship exists between structure, disorder and magnetic behavior in Prussian blue analogues.

Acknowledgments

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