$K_xNi_y[Fe(CN)_6].xH_2O$ PRUSSIAN BLUE ANALOGUE: A STUDY OF SIZE EFFECT ON THE STRUCTURAL, OPTICAL AND MAGNETIC PROPERTIECS

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Abstract. *Recently, striking effects of light irradiation on the magnetic state were reported for Prussian blue (PB) analogues $A_xCo_y[Fe(CN)_6]$ (A = Na, K, Rb, Cs). The physical and optical properties of these compounds are dependent on the size of the particles of the measured samples. However, there have been few reports on the formation of nano-sized particles of the material and the effect of size of the particles on the properties of the compounds. In this report, we present a novel synthesis method of the $K_xNi_y[Fe(CN)_6]$ PB nano-particles and investigate the effect of particle size on the properties of the Prussian blue analog $K_xNi_y[Fe(CN)_6]$ by analyzing the results of the X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis absorption and magnetization measurements of the compounds.*
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I. INTRODUCTION

In the field of modern material sciences, molecule-based magnetic materials have been extensively studied, because the design of their properties is easier compared to that of classical magnetic materials such as metal alloys and metal oxides [1, 2]. In particular, Prussian Blue analogues show various characteristic magnetic properties depending on their transition metal ions [3, 4, 5]. A phenomenon of special interest is photo-induced spin transision [6]. This was discovered in Co–Fe Prussian blue analogues. This material has bistable spin state in a certain temperature region depending on the composition and the valence state of metal ions. In a characterstic temperature region, this material exhibits spin transition by photo irradiation, thus the magnetic susceptibility is changable by light.

The PB in nanoparticles shows different properties from their bulk form. For example, Mallah et al. reported a superparamagnetic property with nickel hexacyanochromate nanoparticles [3] and observed the nanosize effect in magnetic phase transition temperature with Prussian blue nanoparticles [7, 8, 9].

Here, we report a new approach for the growth of nanoparticles of cyano-bridged molecule-based magnets in an organic solvent, formamide. This method is to obtain a nano-sized Prussian blue analogue without template in resulting material. Nanoparticles

of $K_xNi_y[Fe(CN)_6]$ (denoted Ni-Fe) were synthesized in formamide solvent and their size was fined by adding water into formamide. We also investigate the effect of particle size on the structural, optical and magnetic properties of Ni-Fe.

II. EXPERIMENT

In a typical synthesis, 0.07 g of $K_4[Fe(CN)_6]\cdot3H_2O$ were diluted in 3 ml of formamide (solution A). Solution B was prepared from 0.07 g of $NiSO_4\cdot6H_2O$ and 2 ml of formamide in a separate flask. B was then added to A at room temperature with vigorous stirring. The mixture was stirred further for 2 hours. The solid was isolated by centrifugation and washed three times by aceton and dried in air. To investigate effect of formamide on the synthesis, three samples were synthesized according to the above procedure except reaction media with various volume ratios of water and formamide.

Structural characterization was performed by means of X-ray diffraction using a Siemens-D5005 diffractometer with Cu Kα radiation. Scanning electron microscopy (FE-SEM) was operated by using a S4800 (Hitachi) microscope. Optical absorption spectra, neglecting reflection losses, were measured with a V-670 spectrophotometer (Jasco) in the range of 190 to 2500 nm at room temperature. The magnetic properties of the resulted nanoparticles were investigated by a magnetic property measurement system PPMS 6000 (Quantum Design).

III. RESULT AND DISCUSSION

The phase of the prepared products was characterized by powder X-ray diffraction (Fig.1). From Fig. 1 we can see that all of the reflection peaks could be readily indexed to a pure facet centered cubic (fcc) phase [space group: Fm3m (no.225) [10] with a lattice constant of a = 10.09 Å (JCPDS 14-291)], and no other impurities were found. For nanosamples, the broadening of the X-ray diffraction peaks can be related not only to the degree of crystallinity, but also to the crystallite size. The broadening of the X-ray diffraction peaks is, therefore, attributed to a significant contribution from lattice disorder and a less dramatic reduction in particle size. Fig. 2 shows the typical field-emission scanning electron microscopy (FE-SEM) images of the obtained products. From these images we can clearly see that the particle size of $K_xNi_y[Fe(CN)_6]$ decreases as increasing formamide content. The average size of sample is about micrometer to 10 nm depending on the ratio of water and formamide (see Fig. 2).

The UV-vis spectra of some typical samples were shown in Fig. 3. The compound of Ni-Fe has broad absorption peaks at around 320 nm and 440 nm. These bands correspond to the CT from Ni^{II} to Fe^{III} as suggested in Ref. [10]. It is also important to note that several dinuclear compounds with the CT bands in the 385-565 nm range [11]. The spectrum of the Co-Fe sample has a broad intervalence charge-transfer (CT) band from Fe^{II} to Co^{III} in the visible region between 450 and 650 nm and a sharp, higher energy peak around 380 nm, which has been previously identified as an Fe^{2+} to Co^{3+} electronic transition [6].

Magnetic measurements confirmed the formation of the nanoparticles. Fig. 4 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves in the range of
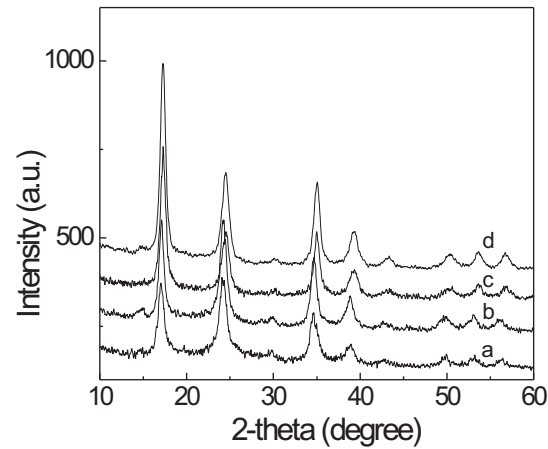
Fig. 1. XRD patterns of Ni-Fe Prussian Blue analogues: For clarify we show only spectra of sample with (a) 100% water (b) 60 % water (c) 30% water and (d) only formamide
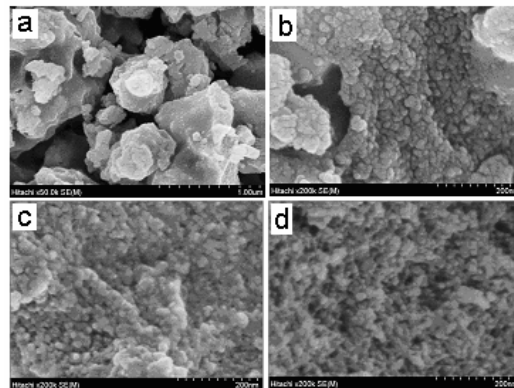

Fig. 2. FE-SEM images of of Ni-Fe coumpounds/nanoparticles with various water contents: (a) 100% water (b) 60 % water (c) 30% water and (d) only formamide. The labels (a, b, c, d) in this figure correspond to those in Fig. 1

2–20 K obtained for the micro- and nanosamples. For the ZFC experiment, the sample was cooled in zero field and then heated in a field of 10 Oe, while the net magnetization of the sample was recorded. The FC data were obtained by cooling the sample under a magnetic field of 10 Oe after the ZFC experiments and recording the change in net sample magnetization with temperature. The ZFC curves show a narrow peak at 4.9 K for Ni-Fe nanosample, which indicates the blocking temperature (T_B) of the nanoparticles with a mean volume. The FC curve increases with decreasing temperature and never reaches saturation, indicating that, even at the lowest investigated temperature, a fraction of the
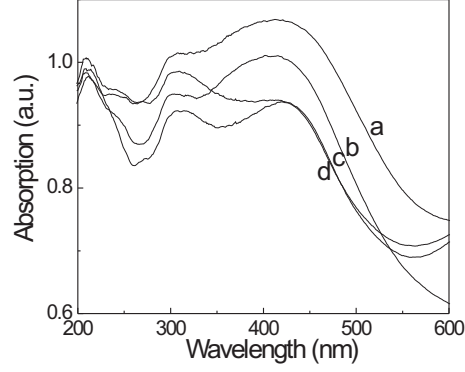
Fig. 3. Absorption of Ni-Fe coumpounds/nanoparticles: (a) 100% water (b) 60 % water (c) 30% water and (d) only formamide. The labels in this figure also correspond to those in Fig. 1 and Fig. 2.

particles is still in the superparamagnetic state. For the microsample The FC and ZFC diverges at the temperature of 6 K.
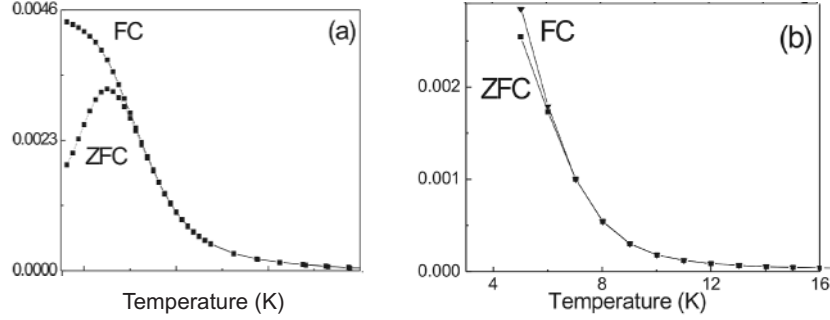

Fig. 4. Zero-filed-cooled (ZFC) and field-cooled (FC) magnetization vs. temperature plots for samples of Ni-Fe with (a) 100% formamide and (b) 100% water solvent at an external magnetic field of 10 Oe.

The increase in the FC values with decreasing temperature and the maximum peak in the ZFC magnetization are indications of cluster spin-glass behavior in nanoparticles [12, 13]. In a simple description specific to our samples, the cluster spin-glass state contains disordered interacting clusters, and each cluster consists of ferrimagnetically ordered Fe^{3+} and Ni^{2+} regions. For PB analogs, Curie temperature T_c is expressed as [5]

$$T_c = [2(Z_{ij}Z_{ji})^{1/2}|J_{ij}|/3k_B][S_i(S_i+1)S_j(S_j+1)]^{1/2} \tag{1}$$

where $i = j =Fe^{3+}$, $S_i=S_j= 5/2$, Z_{ij} or Z_{ji} is the number of the nearest-neighbor i(j)-site ions surrounding a j(i)-site ion. k_B is the Boltzmann constant, and J is the magnetic interaction constant. As the lattice parameter of nanocrystals does not change, we suppose that the magnetic interaction constant J_{ij} between the Fe^{3+} ions of PB nanoparticle is

almost the same as that of bulk. Therefore, the decrease in the Curie temperature T_c of the PB nanoparticle is perhaps due to the diminution of the average number of nearest magnetic interaction neighbors in PB particle with perfect crystal structure. Besides, defects could be present on the surface or internal of the Prussian blue particle, which may affect the T_c.

In this work, we have developed a new approach for the growth and organization of cyano-bridged molecule-based magnetic nanoparticles using formamide solvent. We have shown that the volume ratios of water and formamide controlled growth of molecule-based nanoparticles. This approach opens a new perspective for the preparation of a large range of nano-sized molecule-based magnets.

IV. CONCLUSION

In summary, Prussian blue analogue $K_xNi_y[Fe(CN)_6]$ nanoparticles in different size and morphology were prepared using a new solvent, formamide. The size of particles was controlled by ratio of formamide and water. The size and morphology of the nanoparticles strongly depend on the reactant concentration. We have presented the structural, absorption and magnetic properties of Ni-Fe samples. They are the member of hexacyanometallate based molecular magnetic materials. It crystallizes in the FCC structure with space group Fm3m. The branching between FC and ZFC magnetization curves indicate some signature of spin glass type of behavior in these "ferromagnetic" compounds.

V. ACKNOWLEDGMENT

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