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Role of Water of Hydration In Thermal Expansion Behavior of Prussian Blue Analog $Fe_3[Co(CN)_6]_2.Xh_2o$

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Abstract

Role of water of hydration in thermal expansion of cubic Prussian Blue analog $Fe_3[Co(CN)_6]_2.xH_2O$ has been been investigated below room temperature. Powder X-ray diffraction was used for the study. The hydration-water in the material was found to play an important role on the material's thermal expansion behavior. While the average crystal structure remains unchanged (cubic), thermal expansion behavior of the material is found to switch between positive and negative thermal expansion as water content is varied.

1 Introduction

The physics of positive thermal expansion (PTE) behavior exhibited by most crystalline solids is relatively well known [1, 2]. When temperature increases, lattice constants of a material increase due to the increase in average bond lengths between atoms because of the anharmonic nature of bond vibrations. The expansion of lattice constants upon heating in turn leads to the macroscopic expansion of the solid in general. The thermal expansion coefficient, α, of the PTE materials are usually in the range $0 < \alpha < 20 \times 10^{-6}\ K^{-1}$ [3].

However, occurrence of the opposite behavior, negative thermal expansion (NTE), is not uncommon or rare anymore. Besides being fundamentally important, NTE materials are of huge importance because of their potential for industrial and technological applications [4]. The more usual PTE behavior can be compensated by NTE materials and it is possible to get composite materials having zero thermal expansion (ZTE). In addition, the CTE in a PTE/NTE composite can be tuned or tailored to get a material with preferred intermediate CTE. NTE has been found and reported in selected compounds from various classes of materials such as zeolites [5],

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framework structures such as ZrW_2O_8 [6], oxides having ZrW_2O_8-like structures [7], silicates [8], ZrV_2O_7 [10], quartz [9], Prussian Blue analogs [11-14] and indeed in many other materials. To date, physical mechanism(s) underlying this phenomenon have often remained elusive, although different models involving molecular dynamics, rigid unit modes, phonon softening, electronic valence transitions, and thermal vibrations have had some occasional success. However, the role of water of hydration on thermal expansion behavior in the framework materials has not been studied in detail and thus remains unclear. Indeed, various zeolites [15] have been found to show contraction/expansion upon sorption of guests and few hexacyanoplatinates have been reported to show guest water molecules dependent NTE behavior [16]. However, the effect of water of hydration on the lattice dynamics or vibrational modes of an NTE material and their correlation with the thermal expansion is not yet explored in much details for the framework PB analogs. Therefore, understanding the role of water of hydration on the NTE behavior in such systems is of interest for basic fundamental research as well.

In this study, we explore the effect of water of hydration on the NTE behavior of a PB analog, $Fe_3[Co(CN)_6]_2.xH_2O$, by studying thermal expansion behavior of the hydrated, partially dehydrated, and fully dehydrated compounds using *in-situ* variable temperature powder X-ray diffraction (300-123 K). The correlation between the degree of hydration in the compound and its NTE behavior has been investigated. In addition, we studied the effect of deuteration on the NTE behavior by using deuterated samples in the hydrated and dehydrated form.

2 Experimental Methods

2.1 Synthesis and Characterization

To study the role of water content in the material, protonated polycrystalline samples of PB analog $Fe_3[Co(CN)_6]_2$ were prepared at different degrees of hydration while deuterated samples were prepared in deuterated and dehydrated form to study the effect of deuteration. Powdered sample of $Fe_3[Co(CN)_6]_2.xH_2O$ (Fully hydrated) was obtained using chemical precipitation technique. All the reagents were as-received ACS quality reagents. Aqueous solution of Iron chloride, $FeCl_2.4H_2O$, was mixed with Potassium hexacyanocobaltate, $K_3[Co(CN)_6]$, dissolved in DI water and kept overnight for precipitation while stirring. A mortar and a pestle were used to grind the filtered and dried precipitation. This produced a fine powder suitable for X-ray diffraction. Leftover reagents were removed carefully by repeated washing with water. In order

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to prepare the partially dehydrated compound, we heated the fully hydrated compound at 100º C in a vacuum oven for three hours while heating the fully hydrated compound in a vacuum oven at 150º C for ten hours produced dehydrated compound. To prepare the deuterated compound, we dissolved the $Fe_3[Co(CN)_6]_2.xH_2O$ (Fully hydrated) powder sample in D_2O and kept for few hours while stirring and again filtered, dried and grinded to get the powder deuterated and hydrated sample. Heating the deuterated and hydrated compound for several hours in the vacuum oven at 150º C produced the deuterated and dehydrated phase of the compound.

The samples were characterized using XRD to ensure the correct phase of the compound. Elemental analysis on the samples was done using X-ray fluorescence measurements to confirm the right elemental ratios. Characterization using FTIR spectroscopy ensured the presence of cyanide bonds and presence and absence of water of hydration depending on the hydrated and dehydrated materials. Number of water molecules present in the samples per formula unit was determined using DSC/TGA measurements. A two step mass loss was observed in the TGA curve for the hydrated materials. The first step corresponds to the removal of interstitial water molecules. The second step is because of removal of lattice water present in the material.

2.2 Structure

All the phases of the PB analog $Fe_3[Co(CN)_6]_2$ – protonated and fully hydrated, protonated and partially dehydrated, protonated and dehydrated, deuterated and hydrated, and deuterated and dehydrated – were found to crystallize with a face centered cubic structure (space group F-43m) where alternate FeN_6 and CoC_6 octahedra are linked with linear cyanide (C-N) ligand (Fig. 1). We did not observe any structural phase transition in the temperature range we studied. The PB analog framework is relatively open and there exists pores between the octahedra. However, not all the octahedra are complete. Water molecules, which can be tuned, are present at the lattice sites as well as at the interstitial positions. In general, it is possible to systematically vary the charge and ion size in the PB analog frameworks which adds more degrees of freedom and makes the PB analogs a good platform study the thermal expansion behavior and its correlation with the various other parameters. In addition, the presence of tunable lattice and interstitial water molecules makes them even more interesting to study the effect of water of hydration on the thermal expansion behavior.

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3 Results and Discussions

Powder X-ray diffraction (PXRD) on a commercial Rigaku Ultima III X-ray diffractometer with monochromatic CuKα (λ = 1.54 Å) radiation was used to study the thermal expansion behavior of each phase by monitoring the variation of lattice parameter with temperature. The diffractometer was operated in Brag-Brentano geometry. Samples were mounted inside a cold stage and were rapidly cooled under vacuum. The rapid cooling prevented water loss. Structural parameter including lattice parameters were obtained by least-squares fits to the observed diffraction patterns using Rietveld-refinement package GSAS [17]. The refinements were initiated in the space group $F\bar{4}3m$. Available atomic positions were used from ICSD database [18]. Refined parameters were lattice constant, atom positions, thermal parameters, background parameters and peak profiles. Coefficients of thermal expansion are determined from the least squares fit to the lattice parameters vs. temperature data.

Analysis of our XRD data indicates that water of hydration in the studied PB analog $Fe_3[Co(CN)_6]_2$ plays an important role in the thermal expansion behavior. Thermal expansion switches between PTE and NTE with varying water content. The average structure which is cubic remained the same. Figure 2 shows the variation of the optimized lattice parameters as a function of temperature as obtained from the Rietveld refinement of the PXRD data for the studied phases of the PB analog. Structural refinement of the PXRD data collected at 298, 273, 248, 223, 198, 173, 148, 123 K reveals that variation of lattice parameter with temperature – for both the protonated and deuterated hydrated materials – follows a non-monotonic parabolic trend while the dehydrated forms of the protonated and deuterated compounds seem to show linear behavior. However, the lattice parameters are shifted to the lower side for the deuterated material reflecting the size effect of deuterium. In particular, the hydrated materials, both protonated and deuterated, show both PTE and NTE behavior in the studied temperature range. Our study indicates that the hydrated material show non-monotonic thermal expansion behavior showing PTE behavior below 200 K and NTE behavior above 200 K. Such a non-monotonic thermal expansion behavior is very unusual and rare considering the high-symmetric cubic structure of the system. However, the dehydrated materials show negative thermal expansion while the partially dehydrated protonated material shows PTE behavior over the whole temperature-range. Table 1 summarizes determined coefficients of thermal expansion.

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4 Conclusion

We investigated crystal structural properties and thermal expansion behavior of protonated and deuterated $Fe_3[Co(CN)_6]_2$ with varying degrees of hydration. We found that degree of hydration in $Fe_3[Co(CN)_6]_2$ is a key factor in its thermal expansion behavior. Thermal expansion of $Fe_3[Co(CN)_6]_2$ switches between PTE and NTE as we vary the water content in the material. The focus of this work is to quantify and categorize the TE behavior of the PB analog under investigation. Further investigation is required to understand the exact nature and mechanism of the exhibited thermal expansion behavior.

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Tables with captions

TABLE I

Thermal expansion behavior of PB analog $Fe_3[Co(CN)_6]_2.xH_2O$ as obtained from the X-ray diffraction data for the protonated and deuterated phases of fully hydrated, partially dehydrated, and completely dehydrated compounds.

Compound	Degree of hydration	a (123 K) [Å]	Average α [$x10^{-6}$ K^{-1}]	T [K]
$Fe_3[Co(CN)_6]_2.28H_2O$	Hydrated	10.19439(9)	+19.56	123-198
			-39.06	198-298
$Fe_3[Co(CN)_6]_2.13H_2O$	Partially dehyd.	10.21034(8)	+7.80	123-298
$Fe_3[Co(CN)_6]_2.0H_2O$	Dehydrated	10.17265(8)	-29.49	123-298
$Fe_3[Co(CN)_6]_2.28D_2O$	Hydrated	10.21740(7)	+19.57	123-198
			-68.42	198-298
$Fe_3[Co(CN)_6]_2.0D_2O$	Dehydrated	10.19800(9)	-49.03	123-298

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Figure captions

FIGURE 1

Crystal structure of the PB analog $Fe_3[Co(CN)_6]_2.xH_2O$ showing alternate octahedra. Not all octahedra are occupied by ions, and water molecules are present on lattice or interstitial positions between the octahedra.

FIGURE 2

Variation of Rietveld refined lattice parameter with temperature for different phases of the protonated and deuterated $Fe_3[Co(CN)_6]_2$.

List of figures

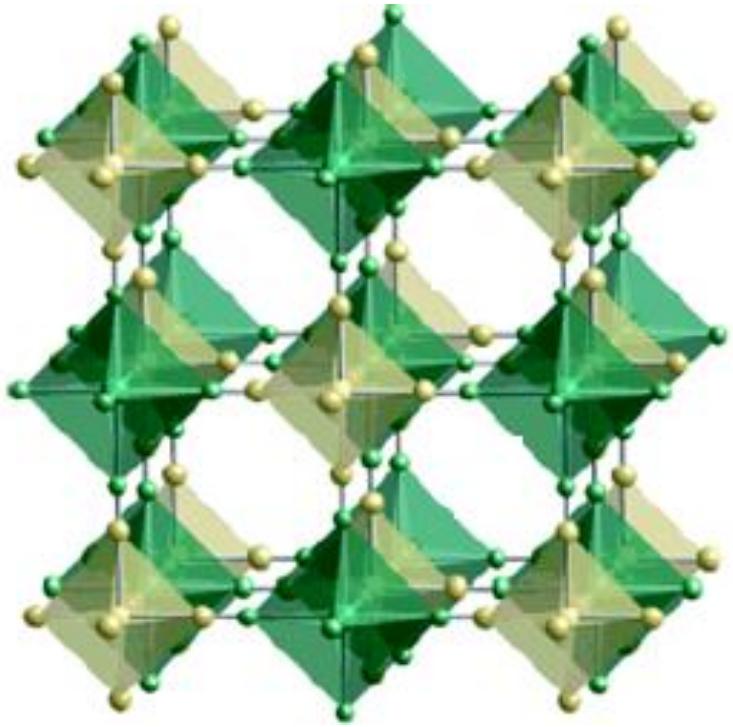

FIG. 1 (Color online).

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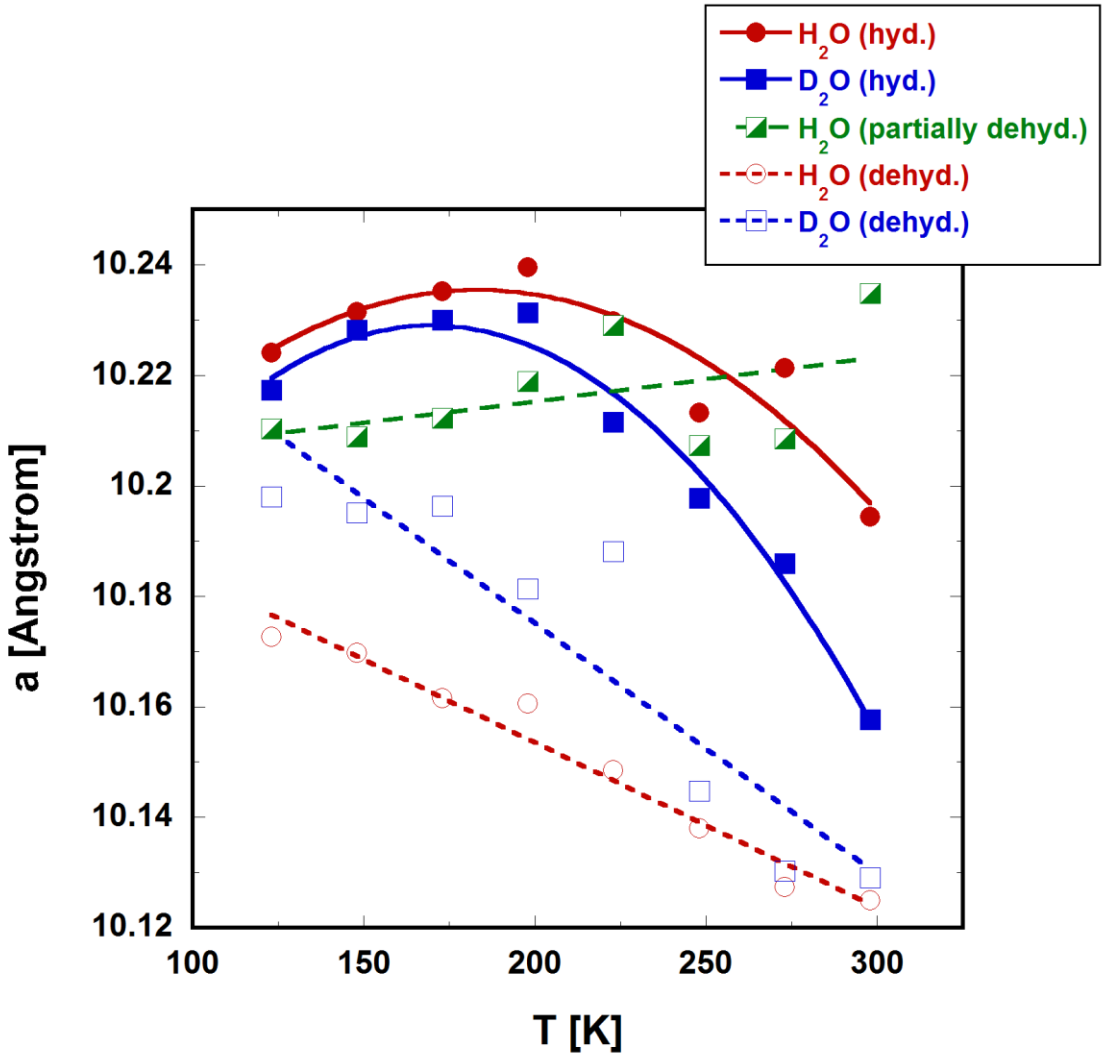

FIG. 2 (Color online).