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Structural refinement of $Nd[Fe(CN)_6] \cdot 4H_2O$ and study of $NdFeO_3$ obtained by its oxidative thermal decomposition at very low temperatures

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Abstract

The crystal structure of $Nd[Fe(CN)_6] \cdot 4H_2O$ has been refined by Rietveld analysis using high resolution synchrotron powder X-ray diffraction data. It belonged to the orthorhombic crystal system, *Cmcm* space group, with cell parameters: $a = 7.473952(1)$ Å, $b = 12.919104(2)$ Å and $c = 13.800549(2)$ Å. The change in space group from $P6_3/m$ which is observed in the pentahydrates ($LnFe(CN)_6 \cdot 5H_2O$) to *Cmcm* in the tetrahydrates has been analyzed to be a consequence of the change in 9-fold coordination of Nd^{3+} in the pentahydrates to 8-fold coordination in the tetrahydrates, which changes the Nd^{3+} environment from tricapped trigonal prism to a distorted tricapped trigonal prism or square antiprism. Its decomposition process in air to produce $NdFeO_3$ has been followed by thermogravimetric and differential thermal analysis, IR spectroscopy and laboratory powder XRD. We found that it is possible to synthesize crystalline $NdFeO_3$ at temperatures as low as 380 °C and refine the structure of single phase crystalline $NdFeO_3$ synthesized by this method at 600 °C.

Keywords: $Nd[Fe(CN)_6] \cdot 4H_2O$; Structure refinement; Synchrotron X-ray diffraction; $NdFeO_3$; Low temperature synthesis

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1. Introduction

Heteronuclear complexes of the type $LnM'L_n \cdot nH_2O$, $LnM'_xM''_{1-x}L_n \cdot zH_2O$ or $(Ln, A)M'L_n \cdot zH_2O$ (where Ln is a lanthanide, A is an alkaline earth metal, M′ and M″ are transition metals and L is a ligand) have been extensively studied as precursors for the low temperature synthesis of high surface area perovskite-type oxides $LnMO_3$, $LnM'_xM''_{1-x}O_3$ and $(Ln, A)M'O_3$, respectively [1–17]. This method was first proposed by Gallagher in 1968 [5]. The mixing of metal cations at the atomic level and with the desired stoichiometry of the metals in the heteronuclear complex allows lowering the synthesis temperature down to the range 600–800 °C, well below the usual temperatures used in the conventional ceramic method, thus avoiding the sintering of the material and producing high surface area and homogeneous materials. Because powders with excellent properties to use in screen-printing are produced, this method is preferred for the preparation of homogeneous thick films for sensor applications [3,9–11,16,17]. Perovskite-type oxides are also extensively used as catalyst for a number of applications, i.e., as tree-way catalysts [18], methane flameless combustion [19], NO reduction by CO [20] and catalytic destruction of VOCs [21] among others. Despite the potentiality of the heteronuclear complexes decomposition method to produce

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homogeneous high surface area materials, few publications reported its use for catalysts preparation [12,13]. Some of us have used alkaline earth nitroprussides ($AFe[(CN)_5NO]\cdot nH_2O$) to prepare high surface area $AFeO_{3-\delta}$ perovskites [14,15] in the temperature range 700–900 °C with a high Fe(IV) content. Moreover, we have prepared a new polytype in the system $BaFeO_{3-\delta}$, $BaFeO_{2.8-\delta}$ [15], and solved its structure ab initio from high resolution synchrotron powder X-ray diffraction.

Lanthanide hexacianometallates are among the most used heteronuclear complexes for perovskite oxide synthesis [1–4,6,7–9,11,16,17], thus, the study of their structures and decomposition processes is very important to understand the synthesis of homogeneous perovskite-type oxides materials at low temperatures.

Among the lanthanide hexacianometallates, the lanthanide hexacyanoferrates (III) *n*-hydrates ($Ln[Fe(CN)_6]\cdot nH_2O$) have been extensively studied [22–33]. The large lanthanide ions (La, Ce and Pr) form the hexagonal pentahydrate ($Ln[Fe(CN)_6]\cdot 5H_2O$), belonging to the space group $P6_3/m$, while the smaller ones (Sm ~Yb) form the tetrahydrate ($Ln[Fe(CN)_6]\cdot 4H_2O$) with the space group *Cmcm*. Masuda and co-workers [31,32] have found that the boundary complex is the neodimium compound ($Nd[Fe(CN)_6]\cdot nH_2O$), where the *n* value can change reversibly from 4 (space group *Cmcm*) to 5 (space group $P6_3/m$). The large value of the equivalent isotropic thermal parameter ($B_{eq} = 12\,Å^2$) for the three O(1) corresponding to coordinated water molecules guide them to the conclusion that these molecules are vigorously moving and one of them seems to easily dissociate. The structure of the pentahydrate has been refined by them [31], however, even if they mention that the tetrahydrate is isostructural with other tetrahydrates of lanthanide hexacianoferrates, its structure has not been refined up to now.

Detailed studies of the decomposition process for $Ln[Fe(CN)_6]\cdot nH_2O$ have been made by Sadaoka and co-workers [2,4,6]. They found that after calcinations for 30 min [4] or 1 h [2] they could obtain a single perovskite phase at temperatures between 620 and 830 °C, depending on the lanthanide, increasing the minimum temperature as the ionic radii of the lanthanide decreases. They also found that it was possible to obtain single phase $LaFeO_3$ by increasing the time up to 100 h at a temperature of 350 °C, but did not make the same study for $NdFeO_3$.

In the present paper we refine the structure of $Nd[Fe(CN)_6]\cdot 4H_2O$ using high resolution synchrotron X-ray powder diffraction (SXRPD). We also study the decomposition process to produce $NdFeO_3$ using IR, thermogravimetric and differential thermal analysis (TGA and DTA) and laboratory powder XRD and refine the structure of $NdFeO_3$ obtained at temperatures between 380 and 600 °C.

2. Experimental

$Nd[Fe(CN)_6]\cdot 4H_2O$ was prepared by mixing equal volumes of 1 M $K_3[Fe(CN)_6]$ and 1 M $Nd(NO_3)_3\cdot 6H_2O$, stirred during two hours, filtered and thoroughly washed with water, ethanol and ethyl ether and finally stored in a dry box with silica gel.

IR spectroscopy, thermogravimmetric analysis (TGA), and powder XRD were used to follow the decomposition process. IR spectra were recorded with an FTIR Perkin Elmer 1600 in the transmission mode using KBr pellets. Thermogravimetric and DTA measurements were performed in a Shimadzu TGA/DTA 50 at 5 °C/min under flowing air. Laboratory powder XRD experiments for samples prepared at 320, 380 and 400 °C were performed with a Rigaku Miniflex diffractometer with Cu*K*α radiation ($\lambda = 1.5418\,Å$) between 20° and 90° in 2θ, steps of 0.02° and counting time of 4 s. Laboratory powder XRD pattern for the sample prepared at 600 °C was taken in a Philips PW1710 diffractometer, with Cu*K*α radiation ($\lambda = 1.5418\,Å$) between 20° and 90° in 2θ, steps of 0.02° and counting time of 5 s. Rietveld structure refinements of $NdFeO_3$ samples were performed using the FULLPROF program [34], with laboratory powder XRD data, in the space group *Pnma*, with the initial structural model informed in Ref. [35]. For the samples prepared at 380 and 400 °C, only profile parameters, overall isotropic temperature factor, cell parameters and scale factor were refined. Atomic positions were fixed to the values obtained from the initial model because the diffraction patterns were not of enough quality. For the sample prepared at 600 °C, atomic positions and isotropic temperature factors were also refined.

The high resolution SXRPD data for the structural refinement of $Nd[Fe(CN)_6]\cdot 4H_2O$ were collected at room temperature at the SUNY X3B1 powder diffraction beamline of NSLS, Brookhaven National Laboratory. The wavelength (0.700016 Å) was selected by a monochromator consisting of two parallel Si(111) crystals. The incident beam was monitored by an ion chamber. The out-of-plane resolution in the diffracted beam was given by slits whereas the in-plane resolution was determined by a Ge(111) analyzer crystal. The diffracted beam was measured with an NaI(Tl) scintillation detector. The sample was rocked about the diving portion in a zero-background quartz sample holder. Data were collected between 2.000° and 40.016° in 2θ with a step size of 0.003° and a counting time of 1 s per step. Rietveld structure refinement was also performed using the FULLPROF program, in the space group *Cmcm* using as initial model the structure of $Gd[Fe(CN)_6]\cdot 4H_2O$ [33]. A pseudo-Voigt function convoluted with an axial divergence asymmetry function [36] was chosen to generate the peak shapes. The background intensities were subtracted as the linear