Experimental Report

Proposal: **5-21-1078** **Council:** 10/2012

Title: Neutron diffraction studies on ND4[Co1-xNixPO4]•D2O

This proposal is a new proposal

Researh Area: Materials

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Samples: ND4[Co1-xNixPO4]•D2O (x = 0.00, 0.34, 0.55, 0.59, 0.71)

Instrument	Req. Days	All. Days	From	To
D2B	2	2	01/03/2013	03/03/2013

Abstract:

NH4M(II)PO4•H2O have been studied,by several research groups, since they were first described in 1864 by Debray. These compounds have been used as pigments for protective paint finishes on metal and as fire retardants in paints and plastics,and they can be also applied as catalyst and fertilizers.

Our research group has synthetized by hydrothermal synthesis and characterized by X-Ray diffraction and thermogravimetry measurements,a family of ammonium-cobalt nickel phosphates,NH4[Co1-xNixPO4]•H2O(x=0.00,0.34,0.55,0.59,0.71,1.00) which crystallize in the Pnma and Pnm21 space group depending on the ratio between Co(II) and Ni(II) ions in the structure. With X-Ray data we are not able to differentiate between cobalt and nickel atoms because of occupational disorder,therefore neutron measurements were done in D1B to obtain a full characterization of this family. During this experiment magnetic order were observed at low angle and temperature in some compounds of the family,but we need high resolution to study more in detail these magnetic order.

In order to perform this experiment 2 days on the D2B powder diffractometer operating at low temperature conditions,will be necessary.

Neutron diffraction studies on $ND_4[Co_{1-x}Ni_xPO_4]\cdot D_2O$

We have collected neutron diffraction data in the ammonium-cobalt-nickel phosphates, $ND_4[Co_{1-x}Ni_xPO_4]\bullet D_2O$ systems using the beam time allocated in the date 01/03/2013 (5-21-1078). The aim of these experiments was to have a better statistics for determining the crystal structure of these materials. Experiments were performed at room temperature with a wavelength of λ = 1.59418 Å. Data were collected during approximately 3 hours.

Ammonium-cobalt-nickel phosphates, $NH_4[Co_{1-x}Ni_xPO_4]\bullet H_2O$ (x = 0.00, 0.34, 0.55, 0.59, 0.71, 1.00) were characterized by chemical and thermal analyses (TG-MS and DSC) and powder X-ray diffraction. The crystal structures for all members of this family have been determined by single-crystal X-ray diffraction. Although these layered compounds have an orthorhombic crystal structure, the space group appears as a function of the composition. The single crystal X-ray data show us that solids with x = 0.00 and x = 0.34 crystallize in the *Pnma* space group. This form is different from the deuterated form described by Carling et al. (1) and it is also different from the form described by Yakubovich et al. (2). However the solids with x = 0.71 and x = 1.00 crystallize in $Pmn2_1$ space group, which are isostructural with the deuterated compounds described by Carling. For intermediate values of x, 0.55 and 0.59, the systems crystallize in both space groups, probably because of occupational disorder. In order to explain this situation and to be able to differentiate between the positions of Co and Ni (bc of 10.3 and 2.49 for Ni and Co, respectively), we have synthesized the deuterated compounds and performed the neutron diffraction experiments.

Previous neutron diffraction measurements (CRG-1900) of the deuterated compounds, $ND_4[Co_{1-x}Ni_xPO_4]\bullet D_2O$ (x = 0.00, 0.38, 0.49, 0.68, 0.85), showed that the Ni and Co are in the same positions and some compounds show magnetic order (3).

D2B neutron diffraction experiments of the deuterated compounds at room temperature confirm the crystal structure obtained on D1B and show clearly the hydrogen bonds and positions. Figure 1 shows the results for the compound with x= 0.85.

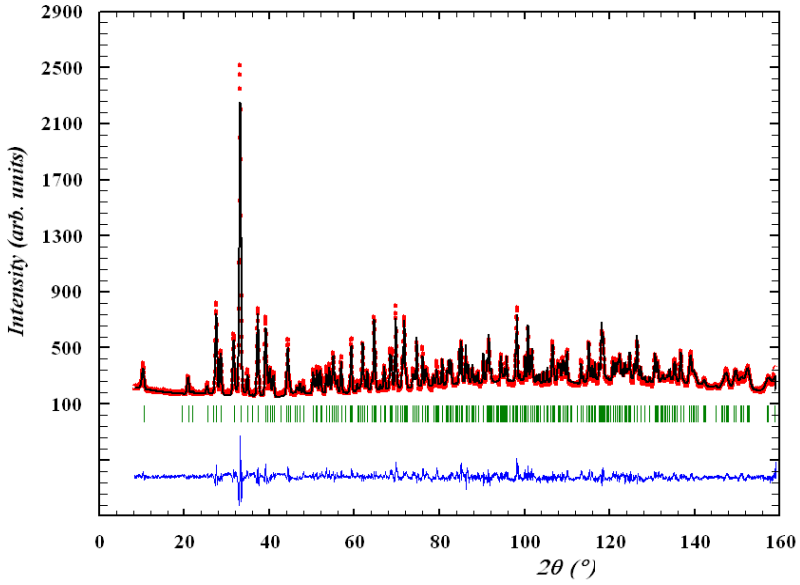

Fig. 1.- D2B-powder neutron-diffraction pattern of $Co_{0.15}Ni_{0.85}ND_4PO_4 \cdot D_2O$ measured at room temperature

We are now working and making progress in the interpretation of the rest of neutron diffraction data.

References

1. Carling, S. G.; Day, P.; Visser, D. Inorg. Chem. 1995, 3917.
2. Yakubovich, O. V.; Karimova, O. V.; Dimitrova, O. V.; Massa, W. Acta Cryst. 1999, C55, 151.
3. Torre-Fernández, L.; Trobajo, C.; de Pedro, I.; Alfonso, B.F.; Fabelo, O.; Blanco, J.A.; García, J.R.; García-Granda, S. J. Solid State Chem. 2013, 206, 75.