Experimental Report

Proposal: **5-23-658** **Council:** 10/2012

Title: Cation-exchanged perovskite and tetragonal tungsten bronze phases - anovel route to multiferroic materials

This proposal is a new proposal

Researh Area: Chemistry

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Samples: Cu0.5Ba2Ta5O15
Ni0.5Ba2Ta5O15
Ni0.5TaO3
Cu0.5NbO3
Cu2.5Nb5O15

Instrument	Req. Days	All. Days	From	To
D2B	2	2	11/06/2013	13/06/2013

Abstract:

There has been much interest recently in the study of magnetoelectric and multiferroic phases, which exhibit both ferroelectric and magnetic behaviour, with a particular interest in materials which exhibit coupling between the two behaviours.
We have performed topochemical cation exchange reactions, on known ferroelectric materials of composition NaMO3 (perovskite) and NaBa2M5O15 (tetragonal tungsten bronze) (M = Nb, Ta) to replace the A-site Na+ cations with paramagnetic ions, whilst maintaining the acentric crystal structure of the original phase. As a result we have prepared a number of new phases with magnetic A-cations residing in an acentric MO6 perovskite lattice

Specifically we have prepared Ni0.5Ba2Ta5O15, Cu0.5Ba2Ta5O15, Ni0.5TaO3, Cu0.5NbO3, Cu2.5Nb5O15. These phases containing corner shared arrays of MO6 (M = Nb, Ta) octahedra which adopt an acentric arrangement due to the second-order Jahn teller effect. As a result these phases are acentric magnetic materials, and are thus good candidates to exhibit multiferroic behaviour.

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Neutron powder diffraction data were collected from:

$NaBa_2Nb_5O_{15,}$ $NaBa_2Ta_5O_{15}$, $Na_{1-2x}Ni_xBa_2Ta_5O_{15}$, $Na_{1-2x}Ni_xBa_2Nb_5O_{15}$

These data have allowed us to determine the expanded unit cell of the $NaBa_2M_5O_{15}$ phases, which occurs due to a cooperative rotation of the MO_6 octahedra (Figure 1).

Measurements on the partially nickel substituted phases have allowed us to locate the inserted nickel and we are currently working on understanding how the insertion of nickel changes the dielectric behaviour of these phases.

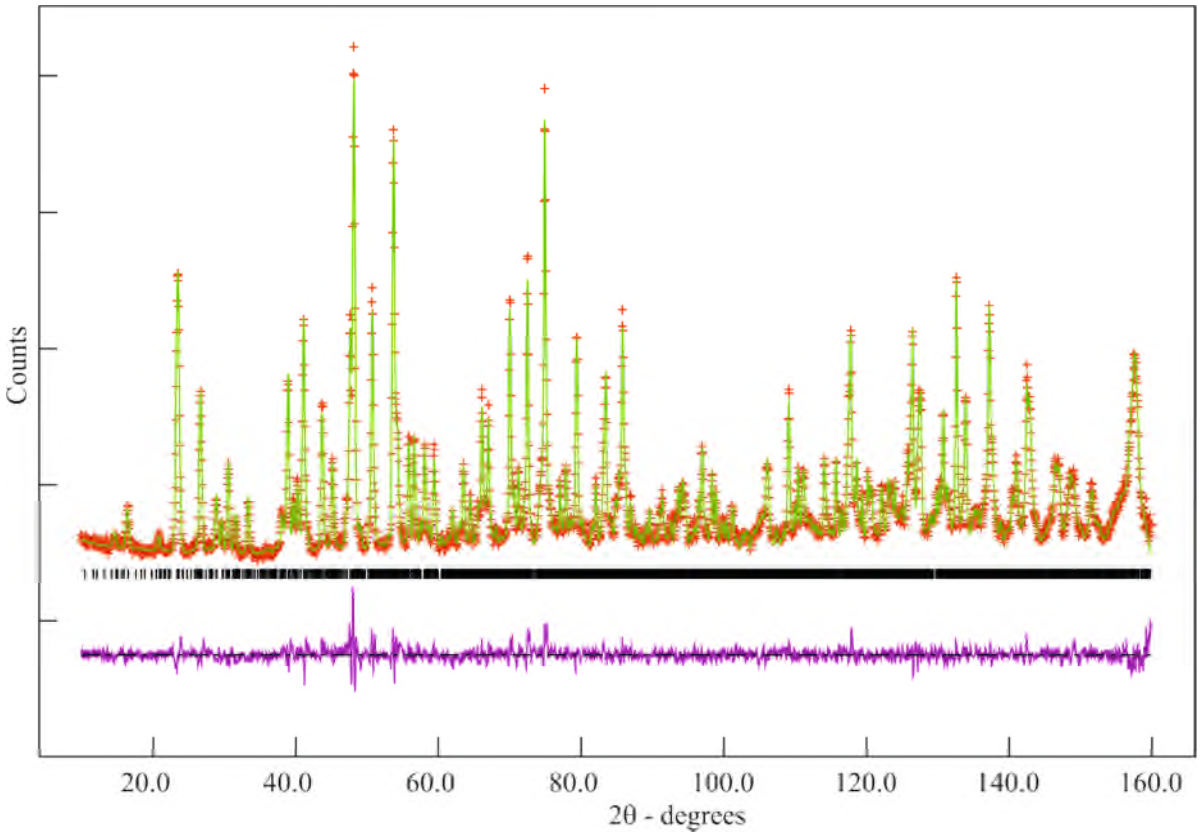

Figure 1: Fit to neutron powder diffraction data collected from $NaBa_2Ta_5O_{15}$.

We also collected neutron powder diffraction data from $Na_{1-x}M_xTaO_3$ (M = Ni, Cu) phases prepared by cation exchange from $NaTaO_3$.

The neutron powder diffraction data collected from the copper exchanged sample indicate that it has a composition of $NaCu_{1.5}Ta_4O_{12}$ ($Na_{0.25}Cu_{0.375}TaO_3$) with an ordered arrangement of the sodium, copper and vacancies on the A-site of the resulting perovskite material.

Neutron powder diffraction data collected from the nickel substituted $NaTaO_3$ sample (Figure 2) show that it has a composition of $Ni_{0.5}TaO_3$. Sodium-for-nickel cation exchange leads to a dramatic distortion of the network of corner-linked TaO_6 octahedra which convert the 12-coordinate A-site in $NaTaO_3$ into two 6-coordinate, pseudo octahedral sites in $Ni_{0.5}TaO_3$ (Figure 3). The resulting structure is directly analogous to the paraelectric form of $LiTaO_3$. Close inspection of the data reveal that the structure of $Ni_{0.5}TaO_3$ is in fact triclinic, due to the smaller size of Ni^{2+} compared to Li^+.

Neutron powder diffraction data collected at 5 K show that, unlike isostructural $LiTaO_3$ and $LiNbO_3$, $Ni_{0.5}TaO_3$ does not undergo a symmetry breaking structural transition to a polar phase at low temperature.

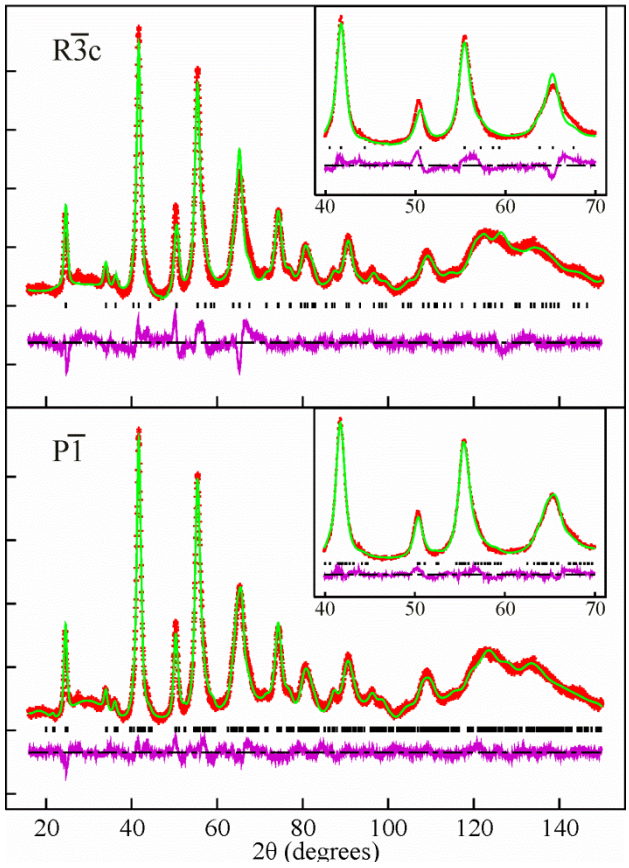

Figure 2: Fits to neutron powder diffraction data collected from $Ni_{0.5}TaO_3$ at 298K.

This work has been submitted for publication and is currently in review.

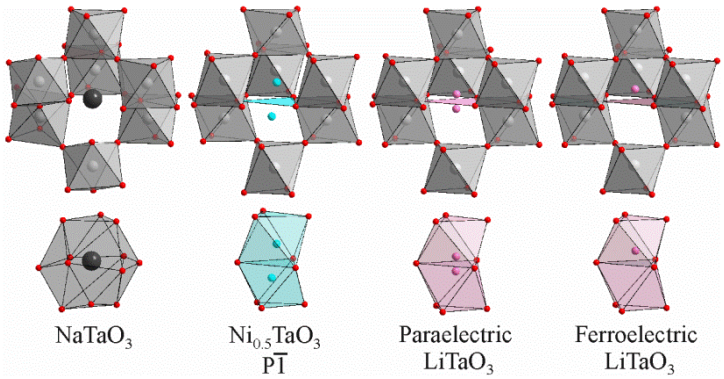

Figure 3: The TaO_3 framework and A-cation site(s) of $NaTaO_3$, $Ni_{0.5}TaO_3$, paraelectric and ferroelectric $LiTaO_3$. Grey, black, blue, pink, and red spheres represent tantalum, sodium, nickel, lithium, and oxygen respectively.