Neutron Diffraction Results for Three-layer Aurivillius Phases Containing Magnetic Transition Metal Cations: Ru (IV), Ir (IV) and Mn (IV)

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The synthesis and characterisation of three-layer Aurivillius-type phases containing magnetic cations M^{4+} (M = Ru, Ir, Mn), based on the substitution M^{4+} for Ti^{4+} in $Bi_2Sr_2(Nb,Ta)_2TiO_{12}$ has recently been reported [1]. These structures show the partial substitution of Sr^{2+} for Bi^{3+} in the $[Bi_2O_2]^{2+}$ layers that results in the decrease of M^{4+} content; the compositions prepared were $Bi_{2-x}Sr_{2+x}(Nb,Ta)_{2+x}M_{1-x}O_{12}$, $x \approx 0.5$. This work looks at the neutron diffraction of these samples and shows the existence of a symmetry-lowering mode.

1. Introduction

Aurivillius phases $[Bi_2O_2]\cdot[A_{n-1}B_nO_{3n+1}]$ are layered oxides composed of α-PbO-type layers $[Bi_2O_2]^{2+}$ alternating with n perovskite-type layers [2, 3]. Interest in Aurivillius phases has focused on their catalytic properties and oxygen ion conductivity, as well as their strong ferroelectricity [4, 5] which arises due to the rotation of BO_6 octahedra, lowering the symmetry from tetragonal to monoclinic, and allowing the perovskite *A*- and *B*-site cations to be displaced relative to the oxygen anion array.

Substituting magnetic transition metal cations into the central octahedral layer of the perovskite-type block, while maintaining ferroelectric displacements in the outer octahedral layers, presents a possible route to multiferroic (magnetoelectric) materials. The crystallographically ordered layering of magnetic and non-magnetic transition metal MO_6 octahedra is shown to be the case in $Bi_{2-x}Sr_{2+x}(Nb,Ta)_{2+x}(Ru/Ir/Mn)_{1-x}O_{12}$, $x \approx 0.5$ [1]. The ordering is likely to be due to the contrast between the coordination environments of the *B*-site cations in the central and outer octahedral layers of the perovskite-type block. However, considerable *B*-site disorder is still observed in some cases, *e.g.* between Nb and Ti in $Bi_2Sr_2Nb_2TiO_{12}$ [6]. Previous reports of magnetic $n = 3$ Aurivillius phases are contradictory. Yu *et al.*[7] reported the synthesis of $Bi_2Sr_2Nb_2MnO_{12}$, *i.e.*, the complete substitution of Mn^{4+} for Ti^{4+} in $Bi_2Sr_2Nb_2TiO_{12}$, presenting (but not refining) X-ray powder diffraction (XRD) data. McCabe and Greaves [8] could not reproduce this phase in the manner reported, observing an impurity phase in neutron powder diffraction (NPD) data, and proposing a single-phase sample of composition $Bi_2La_{0.6}Sr_{1.4}Nb_2MnO_{12}$.. Recently we reported the synthesis and structural properties of a series of phases $Bi_{2-x}Sr_{2+x}(Nb,Ta)_{2+x}(Ru,Ir,Mn)_{1-x}O_{12}$. In order to determine the *B* site ordering variable wavelength synchrotron X-ray diffraction data was used. Here we report the existence of a symmetry-lowering mode in the same system as observed by neutron diffraction data.

2. Experimental

Polycrystalline samples of $Bi_{2-x}Sr_{2+x}B_{2+x}M_{1-x}O_{12}$, where B = Nb, Ta and M = Ru, Ir, Mn were prepared over a range of x by conventional solid state synthesis using stoichiometric quantities of Bi_2O_3 (Aithaca, 99.999%), RuO_2 (Aithaca, 99.99%), IrO_2 (Aithaca, 99.99%), $SrCO_3$ (Aithaca, 99.995%), Mn_2O_3 (Aldrich, 99.999%), Nb_2O_5 (Aldrich, 99.99%), and Ta_2O_5 (Aldrich, 99.99%). Reagents were mixed, ground and pre-heated for 1 hour at 850°C. For each composition, approximately half of the sample volume was then pressed into a pellet and heated in cycles of 950°C for 100 hours, 1000°C for 50 hours, and 1050°C for 50 hours, with intermediate regrinding, until a single phase was produced. The remaining half of the sample used as a 'sacrificial' powder to bury the pellets, in order to minimize the loss of Bi_2O_3 through volatilization.

Neutron powder diffraction data (NPD) were collected at 5K and 293K on the High Resolution Powder Diffractometer at the High-Flux Australian Reactor (HIFAR) facility, Australian Nuclear Science and Technology Organisation (ANSTO). Rietveld-refinements were carried out using the GSAS [9] suite of programs with EXPGUI [10] front-end.

3. Results and Discussion

Low temperature NPD data shows no signs of new peaks from magnetic origin in all the samples (Fig.1). However, the refinement of anisotropic displacement parameters shows displacements of the oxygens on the central layer of the perovskite block (O1, Fig. 2). The central layer of the three-layer Aurivillius phase contains the majority (>99%) of the magnetic cations [1]. In the $Bi_{2-x}Sr_{2+x}Nb_{2+x}Ru_{1-x}O_{12}$, $x = 0.5$ sample this cationic site would have mixed charge ($4^+/5^+$) as only 50% of the site is occupied by Ru^{4+} and the reminder by Nb^{5+}. The nearby O1 site may be expected to show signs of this charge difference. However, a larger effect is visible on these O1 sites. The O1 sites have the largest displacement perpendicular to the direction of the central cation. The largest displacement is in the *ab* plane, suggesting a rotation of the octahedra around the mixed cationic site. If these displacements corresponding to the O1 site were due to thermal motions then they would increase with temperature. However, the displacements increase with decreasing temperature. Thus the displacements are probably related to a symmetry-lowering mode. Symmetry-lowering modes have recently been investigated in three-layer Aurivillius phases by Zhou et al [11].

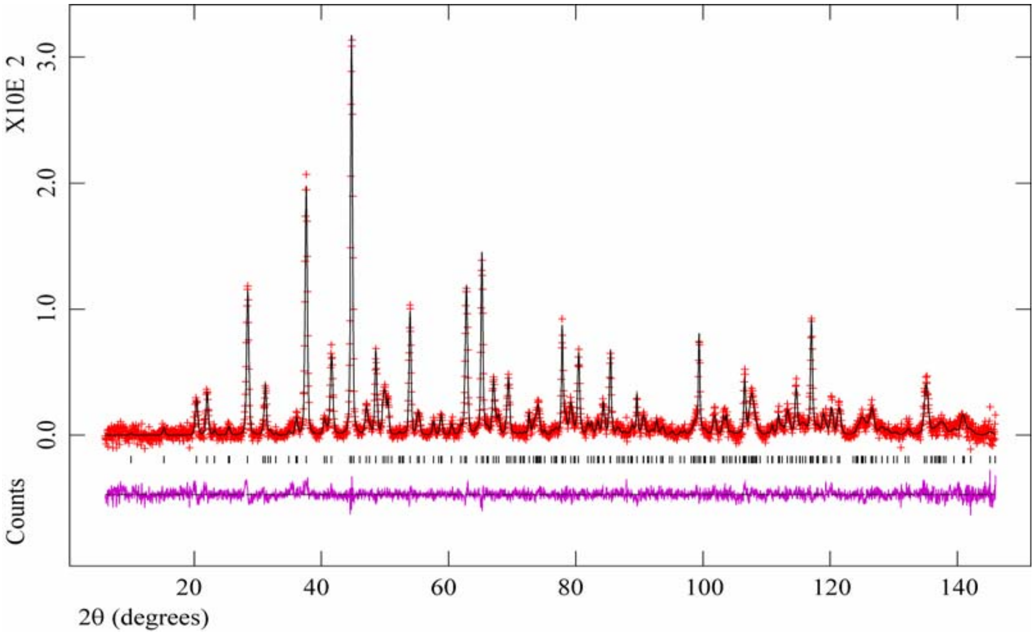

Fig. 1. Final fit to Rietveld-refined λ = 1.49 Å NPD data for $Bi_{2-x}Sr_{2+x}Nb_{2+x}Ru_{1-x}O_{12}$, $x = 0.5$. Observed data are shown as crosses (+), calculated data as a solid line, and the differences as a solid line below. Goodness-of-fit = 4.301 for 54 refined parameters. Overall powder *R*-factors: $R_p = 0.0850$ $wR_p = 0.0574$.

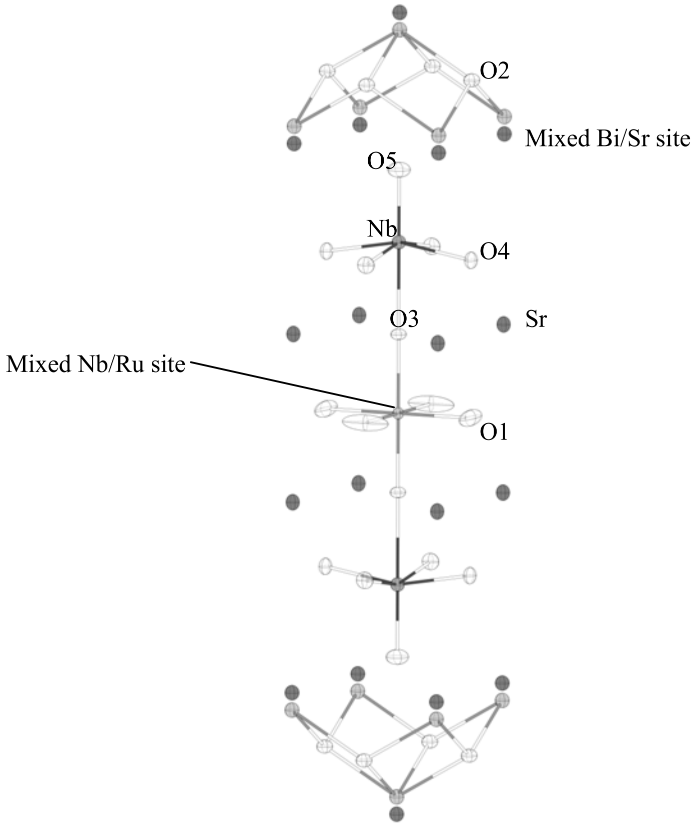

Fig. 2. ORTEP diagram of the structure of $_{-x}Sr_{2+x}Nb_{2+x}Ru_{1-x}O_{12}$, $x = 0.5$ obtained from Rietveld refinement against low temperature NPD.

The symmetry-lowering mode and substitution of the central perovskite layer with ~50% magnetic cations highlights the potential for multiferroic behaviour in these systems.

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