Experimental report

28/08/2015

Proposal:	**5-31-2338**	**Council:**	4/2014
Title:	Structure and magnetic order in oxygen-excess Schafarzikite (AB2O4) phases		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:
Fe-Mg-Sb-O
Co-Fe-Sb-Pb-O
Co-Fe-Sb-O
Mn-Co-Sb-O

Instrument	Requested days	Allocated days	From	To
D2B	3	1	25/09/2014	26/09/2014

Abstract:

We are exploring the potential of the scahfarzikite mineral structure (eg $FeSb_2O_4$) to support functionalization to provide useful properties. This programme has revealed for the first time that the channels in the structure can act as hosts for interstitial oxygen, with associated oxidation of transition metal ions present. Oxidation occurs at low temperatures such that possible applications as energy materials may be possible. It is ckear from mass changes that the oxygen does not simply enter as oxide, O2-, ions but also as catenated species such as peroxide. The proposed experiment aims to explore fully the structural and magnetic properties of a range of oxygen-excess phases. We will establish the nature of the interstitial oxygen species and determine how this may change with oxygen content. We will also explore details of the magnetic order and how this changes as a function of temperature.

Structure and magnetic order in oxygen-excess Schafarzikite (AB_2O_4) phases.

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$FeSb_2O_4$ has a tetragonal structure (Fig.1a) with chains of edge-linked FeO_6 octahedra parallel to [001] which form empty channels with Sb^{3+} ions forming the walls. We have discovered that $FeSb_2O_4$ and related phases containing some Fe^{2+} ions can absorb oxygen with concomitant oxidation of Fe^{2+} to Fe^{3+}. NPD data from one such sample revealed the location of oxygen within the channels (Fig.1b), but the statistical reliability was open to question. Oxygen uptake begins at about 350ºC and the process can be reversed by heating in hydrogen at 500ºC. This experiment was linked to an *in situ* experiment on D20 (5-25-229) and examined the structural and magnetic changes to oxidised samples on cooling to 4 K. Here we report the detailed data for the sample $Co_{0.75}Fe_{0.25}Sb_2O_4$.

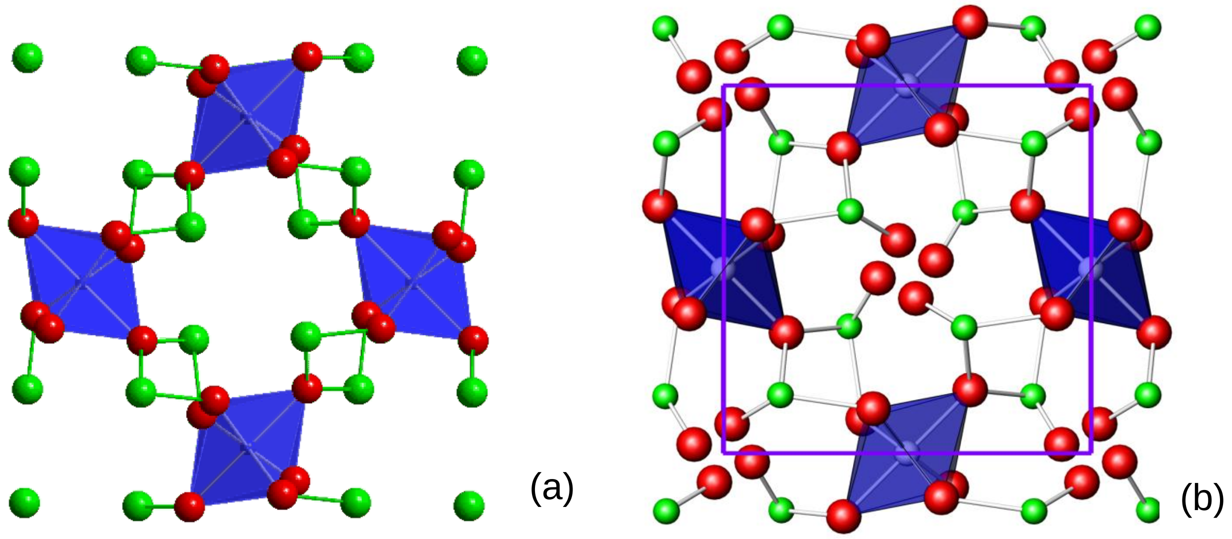

Fig.1. (a) Structure viewed along [001] showing FeO_6 octahedra (blue) and Sb^{3+} (green). (b) The position of interstitial oxygen (red) within the channels (sites partially occupied).

Fig.2 shows NPD data at 300 K and 4 K obtained from the central region of the detectors. The additional peaks arising from magnetic order indicate a C-type magnetic order with moments on Co/Fe ions directed along z. The unoxidised sample shows a similar magnetic order. The structural date derived from the refinements (GSAS [1]) are reported in Table I. Except for the expected decrease in *a* and *c* unit cell parameters and the isotropic displacement parameters (U_{iso}), cooling from 300 K to 4 K causes no significant changes to the nuclear crystallographic structure. Indeed the positional parameters and

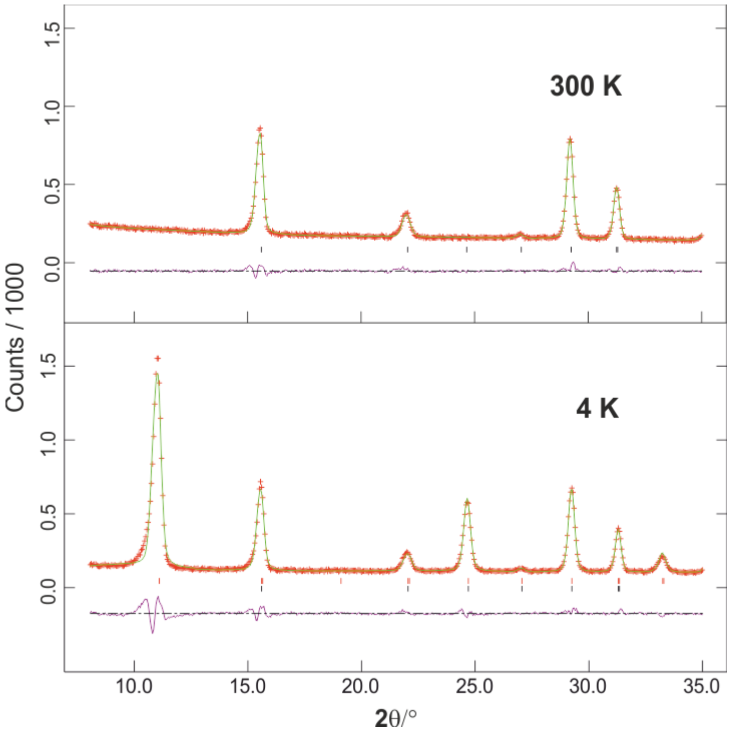

Fig.2 NPD refinements at 300 K and 4 K

the interstitial site occupancy agree within 1-2 standard deviations. Importantly, the interstitial site (O3) occupancy for both datasets is 0.038(3) which provides an overall composition of $Co_{0.75}Fe_{0.25}Sb_2O_{4.15}$ and the presence of intrachannel oxygen insertion is confirmed in this material. In the magnetic structure, each chain of Co/FeO$_6$ octahedra displays ferromagnetic order and is antiferromagneticlly coupled to adjacent chains along [001]. The refined magnetic moment was obtained using a Co^{2+} form factor – oxidation of Fe to Fe^{3+} is known to occur from Mossbauer spectroscopy. The moment of 4.11(3) μ_B is typical for both Fe^{3+} (d^5)and Co^{2+} (d^7) ions; the latter always show a large orbital contribution to the moment.

Table I. Refined structural parameters; data at 4 K in italics.

Atom	**x**	**y**	**z**	**multiplicity**	**occ**	**$100u_{iso}$/Å^2**
Co/Fe	0	0.5	0.25	4	0.75/0.25	1.6(1) *1.3(1)*
Sb	0.1692(3) *0.1689(4)*	0.1608(3) *0.1605(4)*	0	8	1	2.19(5) *1.62(5)*
O1	0.6777(2) *0.6770(2)*	0.1777(2) *0.1770(2)*	0.25	8	1	2.41(4) *1.83(4)*
O2	0.0987(3) *0.0987(3)*	0.6341(3) *0.63444(3)*	0	8	1	2.41(4) *1.83(4)*
O3	0.531(6) *0.532(6)*	0.407(4) *0.405(5)*	0.235(8) *0.234(9)*	16	0.038(3) *0.038(3)*	2.41(4) *1.83(4)*
a=8.4222(3) Å [*8.4123(3)* Å]; c=5.9519(2) Å [*5.9432(1)* Å]. μ(Co/Fe) = *4.11(3)* μ_B						

1. A. C. Larson, R. B. V. Dreele, *General Structural Analysis System (GSAS)*, Los Alamos National Laboratory LAUR 86-748, 1994.