Experimental report

18/09/2016

Proposal:	**DIR-138**	**Council:**	4/2015

Title: Structure examination of the firstmixed anion phases related to schafarzikite, FeSb2O4

Research area: Chemistry

This proposal is a new proposal

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Samples: Mg,Co,Fe)(Sb,Pb)2(ONF)4
Mg,Co,Fe)(Sb,Pb)2(ONF)4+x

Instrument	Requested days	Allocated days	From	To
D2B	3	3	16/10/2015	19/10/2015

Abstract:

Structure and magnetic order in fluorinated schafarzikite (AB_2O_4) phases.

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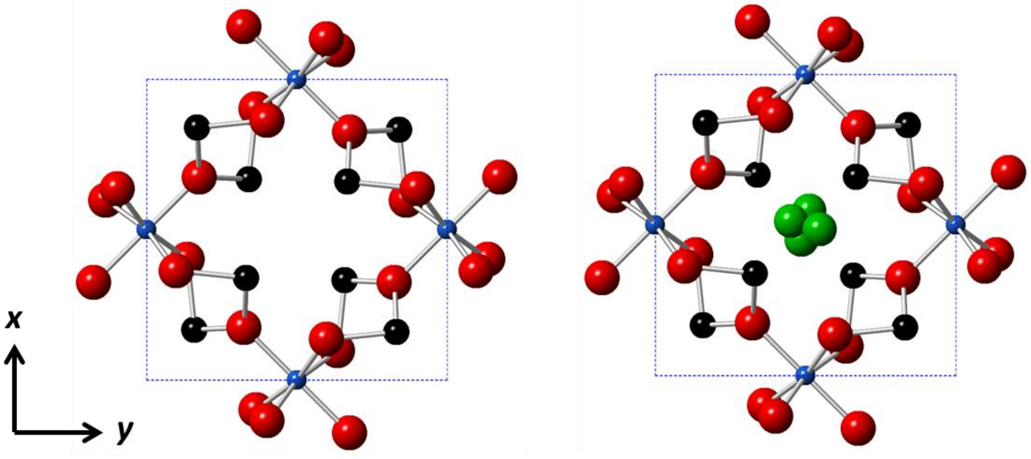
Schafarzikite, FeSb2O4, is a tetragonal crystal system consisting of chains of edge sharing octahedra running parallel to [001]. The chains are arranged such that a channel results which runs parallel to the octahedral chains (Figure 1). This structural feature is heavily dependent on the structural directing effect of the Sb^{3+} lone pair of electrons which line the walls of the channels. It was recently discovered that phases relating to the tetragonal mineral are able to accommodate excess anions within the channels of the structure (exp 5-31-2338). During further investigation of this property, it was discovered that heating phases containing Fe under an atmosphere of fluorine gas at temperatures above 200 ºC resulted in a low temperature absorption of the fluorine. Neutron diffraction was used to identify the location of the excess anions within the host lattice and the structural changes which accompany the fluorination process. Here we discuss some of the findings for the composition $Co_{0.50}Fe_{0.50}Sb_2O_4F_x$.



(a) (b)

Figure 1 a. The structure of $Co_{0.50}Fe_{0.50}Sb_2O_4$ along [001]. Elements are indicated as: O^{2-} (red), Sb^{3+} (black), and Co^{2+}/Fe^{2+} (blue); (b)The fluorinated analogue of $Co_{0.50}Fe_{0.50}Sb_2O_4$, location of the interstitial F^- (green sphere) was obtained from difference Fourier synthesis of neutron powder diffraction data, D2B.

The host lattice was refined using GSAS [1] and difference Fourier synthesis was used to locate the site of the excess fluorine anions. Similar to the oxygen excess phases (5-31-2338) the fluoride was located within the channels of the lattice (Figure 1b). The channel position was refined using data from the central portion of the detector to give a stable fit (Figure 2) and an occupancy of $Co_{0.50}Fe_{0.50}Sb_2O_4F_{0.488}$ was returned. The structure displays the characteristic contraction of *a* and expansion of *c* upon insertion of interstitial anions within the channel when compared with the parent phase. This behaviour is typical of these types of materials and has been linked to the oxidation of Fe^{2+} to Fe^{3+} which creates increased repulsion between adjacent cations in the edge sharing octahedral chains. The F^- stoichiometry, $F_{0.488}$, determined from the NPD refinement indicates near total oxidation of the iron species to Fe^{3+} in conjunction with previous studies (manuscript in preparation). Unlike the oxygen excess phases, the fluoride is located more centrally within the channel where the shortest Sb-F bond is 2.16(7) Å compared with 1.91(5) Å in the equivalent oxygen excess material. This is the subject of ongoing investigation and highlights a different bonding motive between the oxygen excess and fluorinated phases, this likely arising from the difference in preparation temperatures and internal redox mechanism.

A change in the magnetic order of the system has been observed upon cooling between the parent and fluorinated systems. A change from a mixture of A- and C-type ordering ($Co_{0.50}Fe_{0.50}Sb_2O_4$) to purely C-type, ferromagnetic ordering in a chain and antiferromagnetic ordering between chains ($Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.488}$) and a magnetic moment of 3.55(5) μ_B upon fluorination is observed. This is consistent with changes in the intrachain Co/Fe separation distance, expansion of c, afforded by oxidation of the iron sites. This increases the dominance of the 90 superexchange mechanisms removing all A- type character.

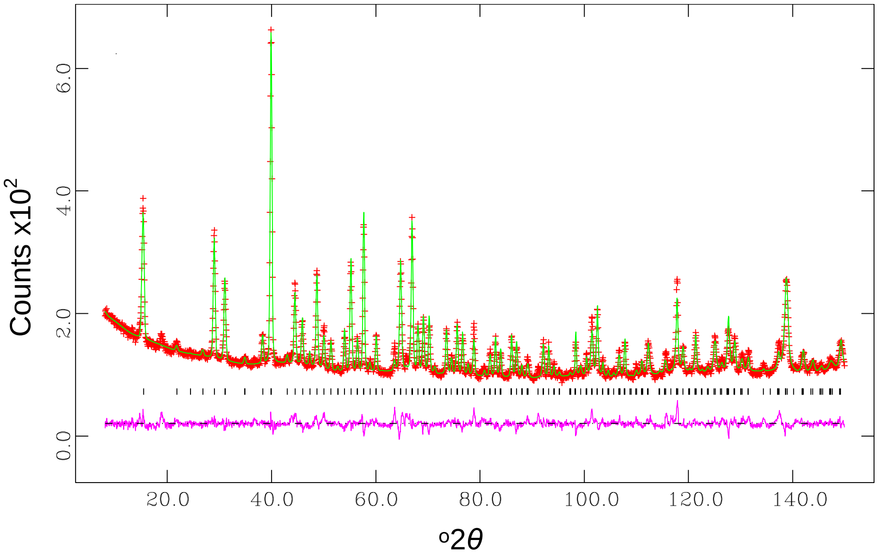


Figure 2 The refined NPD fit of $Co_{0.50}Fe_{0.50}Sb_2O_4F_x$, 300K. The structure (green) compared with the raw data (red points), is shown to be in excellent agreement by the difference profile (purple line). Reflection positions of the main phase are shown by the black tick marks.

Table 1 Structural parameters obtained from the final Rietveld refinement of $Co_{0.50}Fe_{0.50}Sb_2O_4F_{0.23}$ NPD data at 300 K (χ^2 = 4.525, R_{wp} = 0.0392) and 4 K (data in italics, χ^2 = 6.103, R_{wp} = 0.0440). *Uiso values were constrained for O1, O2 and F positions as a means of obtaining a best estimate of isotropic displacement and occupancy due to the partial occupancy of the F site.

Atom	*x*	*y*	*z*	Occupancy	Multiplicity	U_{iso}/Å^2
Co/Fe	0	0.5	0.25	0.50/0.50	1	1.19(8) *0.97(7)*
Sb	0.1663(5) *0.1663(5)*	0.1632(5) *0.1625(5)*	0 0	1	8	2.06(7) *1.81(6)*
O	0.0998(4) *0.1000(4)*	0.6341(4) *0.6356(4)*	0 *0*	1	8	2.15(6)* *1.75(5)**
O	0.6744(3) *0.6737(3)*	0.1744(3) *0.1737(3)*	0.25 *0.25*	1	8	2.15(6)* *1.75(5)**
F	0.553(3) *0.560(2)*	0.465(4) *0.474(3)*	0.168(4) *0.265(4)*	0.122(4) *0.127(4)*	16	2.15(6)* *1.75(5)**
a = 8.4270(3) Å [*8.4123(2)* Å]; *c* = 5.9501(2) Å [*5.9385(2)* Å]						

[1] A. C. Larson, R. B. Von Dreele, *General Structural Analysis System (GSAS)*, Los Alamos National Laboratory LAUR 86-748 (2000).