# Experimental report

19/08/2015

**Proposal:** **5-25-229**

**Council:** 4/2014

**Title:** In situ redox studies of schafarzikite related phases.

**Research area:** Chemistry

**This proposal is a new proposal**

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**Local contacts:** Thomas HANSEN

**Samples:** Co-Fe-Sb-Pb-O
Co-Fe-Sb-O

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 0 | 0 | | |
| D20 | 4 | 4 | 26/09/2014 | 30/09/2014 |

## Abstract:

We are exploring the potential of the schafarzikite 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, $O^{2-}$, ions but also as catenated species such as peroxide. The proposed experiment aims to explore, in situ, the structural changes that occur when oxygen is inserted and removed from scahfarzikite phases. Some materials show a two-step insertion reaction and we will examine the thermodynamics associated with this by conducting this real time study.

# In situ redox studies of schafarzikite related 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 enclose channels surrounded by $Sb^{3+}$ ions. 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 studied the structural changes *in situ* in order to provide comprehensive information about the processes occurring during this reaction. In this report we consider the information obtained from the oxidation of a sample with composition $Co_{0.25}Fe_{0.75}Sb_{1.5}Pb_{0.5}O_4$; this composition was chosen to provide significant oxygen uptake since it has $0.5Fe^{2+}$ per formula unit.

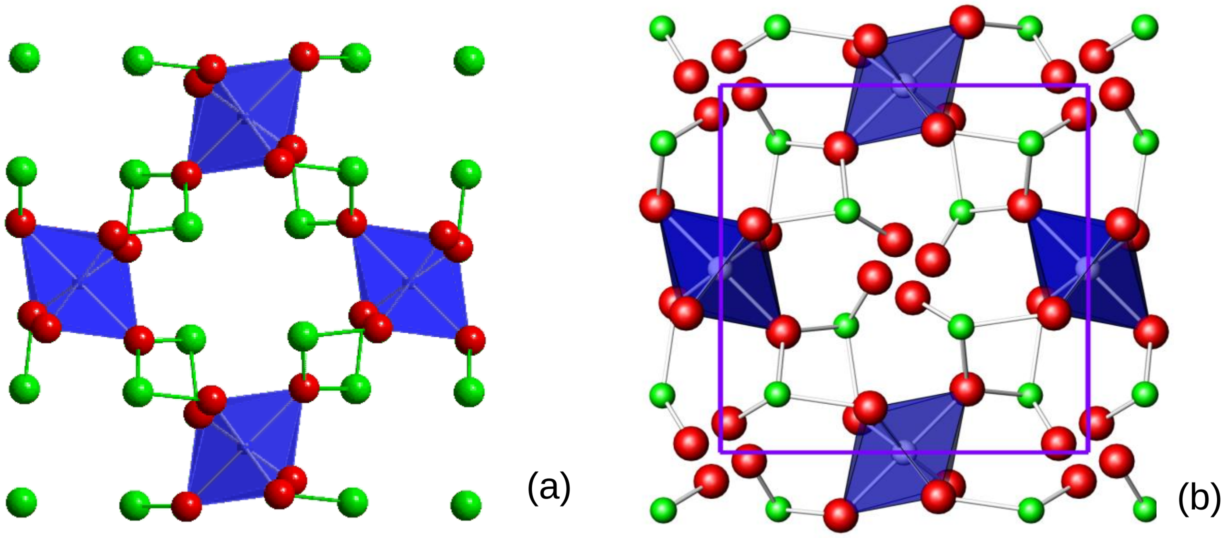

Fig.1. (a) Structure viewed along [001] showing $FeO_6$ octahedra (blue) and $Sb^{3+}$ (green). (b) The position of interstitial oxygen (red) within the channels (sites partially occupied).

The sample was positioned in a quartz tube using silica wool and was heated at 1º $min^{-1}$ to 500ºC in oxygen gas. Data were collected over 5 minute intervals. Data were also collected for an empty quartz tube at 100ºC intervals up to 500ºC. This allowed background subtraction for quartz at temperatures close to each dataset collected. Sequential Rietveld refinement was performed for all datasets using GSAS. [1] Fig.2 shows the change in unit cell parameters on heating. As oxygen incorporation occurs at temperatures above 350ºC, we see that *a* decreases and *c* increases. The increase in *c* is attributed to increased cation repulsions within the chains of octahedra as $Fe^{3+}$ is formed. The site occupancy for the interstitial oxygen ions is shown in Fig.3.

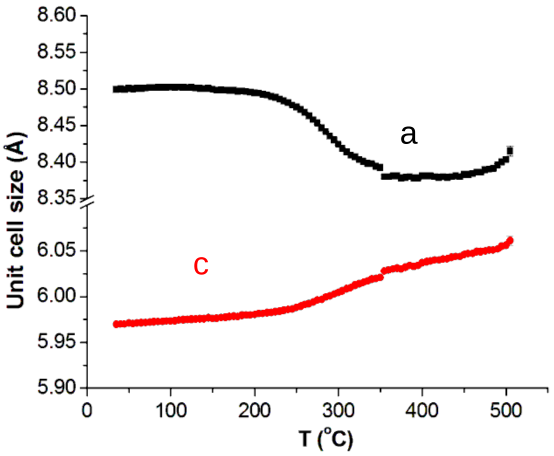

Fig.2 Change in unitcell with temperature

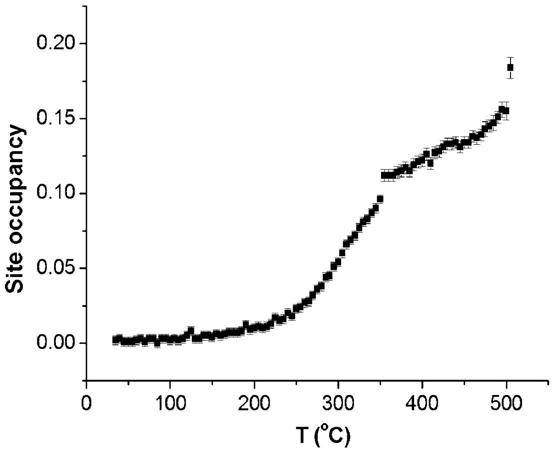

Fig.3 Channel site ocupancy

The position of the oxygen within the channels is confirmed and the overall composition indicated by the site occupancy agrees well with thermal analysis (TG) data. The change in average M-O distance within the chains of octahedra is shown in Fig.4 and the change in Sb(Pb) – Sb(Pb) distance across the channels is shown in Fig.5.

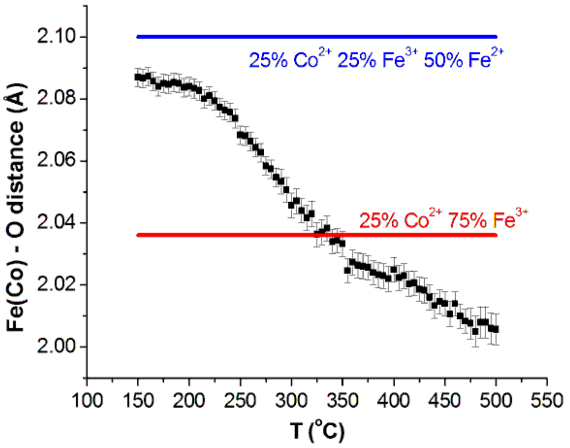

Fig.4 Change in M-O distance in the chains of octahedra.

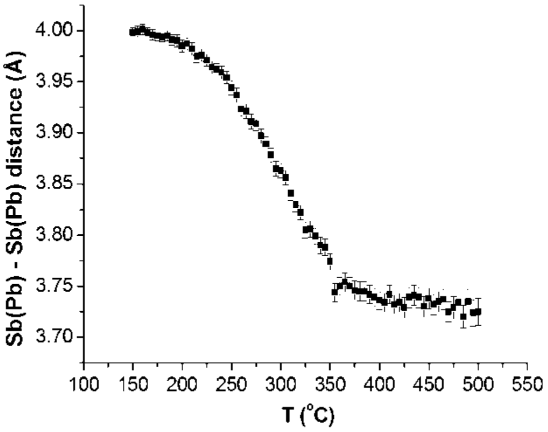

Fig.5 Change in Sb(Pb)-Sb(Pb) distance across the channels.

There is a clear reduction in the M-O distance in the octahedral chains which is consistent with cation oxidation within the chains. The bond distance change is in reasonable agreement with that expected based on bond valence sums assuming oxidation of $Fe^{2+}$ to $Fe^{3+}$. There is also a significant reduction in the Sb(Pb) – Sb(Pb) distance across the channels, which is in accordance with the decrease in the unitcell *a* parameter that occurs on oxidation. This suggests that links occur across the channels caused by the absorption of oxygen. The oxygen uptake derived from both site occupancies in the NPD refinements and the TG data is significantly higher than expected for the simple incorporation of oxide ($O^{2-}$) ions and oxidation of $Fe^{2+}$ to $Fe^{3+}$. We therefore believe that oxygen forms peroxide ($O_2^{2-}$) or even superoxide ($O_2^-$) bridges across the channels and this is consistent with the channel diameter contraction seen in Fig.5. Occupancy of two adjacent interstitial oxygen sites is compatible with the formation of such catenated species as shown in Fig.6 which shows the variation of this O-O distance with oxidation. For small oxygen excess, there is a high uncertainty in the O-O distance because of the low site occupancy, but overall, the distance is as expected for peroxide or superoxide formation, as shown in Fig.6 where typical distance for these species are indicated.

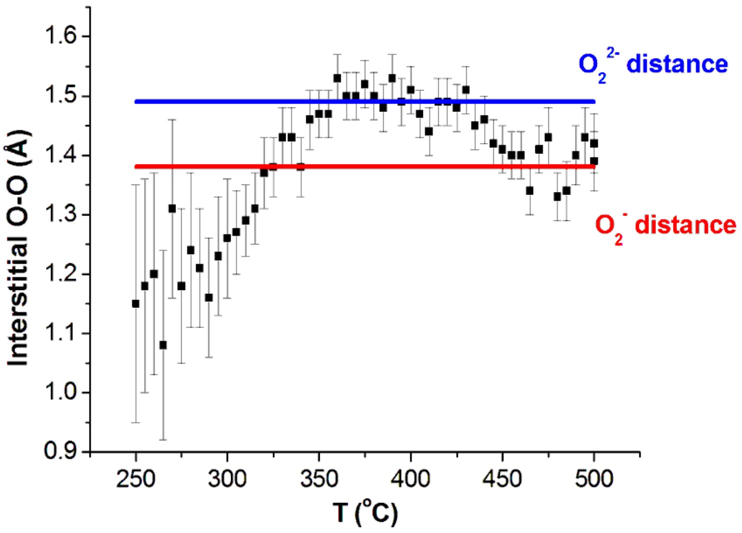

Fig.6 Variation in interstitial O-O distance

## Reference

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