

# Experimental report

03/08/2017

**Proposal:** 5-25-248

**Council:** 4/2016

**Title:** Disrupting negative thermal expansion in the DO9 structure type: the role of intercalated protonic species and framework vacancies

**Research area:** Chemistry

**This proposal is a new proposal**

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**Samples:** ReO<sub>3</sub>  
ReO<sub>3</sub>-xHy  
ScF<sub>3</sub>.xH<sub>2</sub>O  
ScF<sub>3</sub>  
ReO<sub>3</sub>-x

Instrument	Requested days	Allocated days	From	To
D20	3	3	09/09/2016	12/09/2016

## Abstract:

Members of the DO9 cubic structure type, e.g. ReO<sub>3</sub> and ScF<sub>3</sub>, belong to a small family of undistorted materials that have a completely vacant A-site in the ABO<sub>3</sub> perovskite structure, consists of corner sharing MO<sub>6</sub> (M = Re, Sc) octahedral, with the M at the center, and linear M-O(F)-M links. This structure type allows rigid, cooperative rotation of the octahedral units and both materials exhibit negative thermal expansion (NTE) across an extended temperature range, attributed to an unusually large anharmonicity in the soft M<sub>3</sub> mode, which consists of rigid anti-phase rotations of neighbouring MO<sub>6</sub> octahedra. Intercalation into the vacant A-site is expected to perturb this mode, potentially influencing the NTE properties. Varying ranges of NTE have been reported in ReO<sub>3</sub>, synthesised by different routes, and ScF<sub>3</sub> is known to absorb water into the structure to form ScF<sub>3</sub>.xH<sub>2</sub>O. This proposal aims at understanding the observed NTE properties in ReO<sub>3</sub> and ScF<sub>3</sub> as a function of hydrogenous species content. This work has wider implications in a range of materials in the field of Energy materials that adopt the perovskite structure type, from proton conductors to photovoltaics.

## Introduction

ReO<sub>3</sub> crystallises in the cubic space group Pm-3m with the undistorted DO<sub>9</sub> structure type and a lattice parameter at RT of about 3.74 Å. It exhibits negative thermal expansion (NTE) in the range 2-300 K, although the range and size of the NTE are highly sample dependent. In our previous work (TEST-1433, 5-24-373), leading to publications [1,2], we showed 2 regions of NTE in ReO<sub>3</sub> as a function of temperature and that the structure was also able to accommodate water, leading to a marked incoherent scattering contribution to the background. Careful vacuum drying of the materials close to the decomposition temperature, or vapour growth of single crystals, led to samples that closely followed the predicted NTE predicted by lattice dynamics. [1] Exposure of the vacuum dried material to a humid atmosphere led to uptake of water but simple heat cycling of the materials failed to result in the same NTE range as crushed single crystal materials. We postulated that the differences were caused by hydrogenous species disrupting the cooperative modes that led to NTE. [3] Other published attributed it to the presence of static disorder of the ReO<sub>6</sub> octahedra. [4] In 2010, ScF<sub>3</sub> was also shown to exhibit NTE over a wide temperature range [5], also with the DO<sub>9</sub> structure type and a slightly larger lattice parameter of 4.02 Å. Earlier work [6-8] showed that ReO<sub>3</sub> is able to form a series of bronzes of the type ReO<sub>3</sub>H<sub>x</sub> up to x=1.36 and that x=0.35 was attainable by boiling in water.

## Proposed aims of the experiment when submitted

The proposal aimed to investigate the effects of oxidation state, oxygen vacancies and possible water intercalation on NTE in the simple DO<sub>9</sub> structure type by measuring a series of samples and use this information in the wider field of study of energy materials based on the perovskite structure, such as proton conducting oxides as fuel cell electrolytes and hybrid photovoltaics. In the case of ScF<sub>3</sub>, the material is stoichiometric and there is no possibility of variable oxidation state. This material was to act as the reference for water intercalation into the vacant A-site of the perovskite. Various ReO<sub>3</sub> samples were prepared and treated under saturated water vapour environments. The range of materials was chosen to investigate the effect of oxygen vacancy fulling with water and also the possibility for water to enter the vacant A-site. IR, Raman, DSC, TGA, QENS and INS studies were planned in parallel, with QENS and INS proposals submitted to NIST.

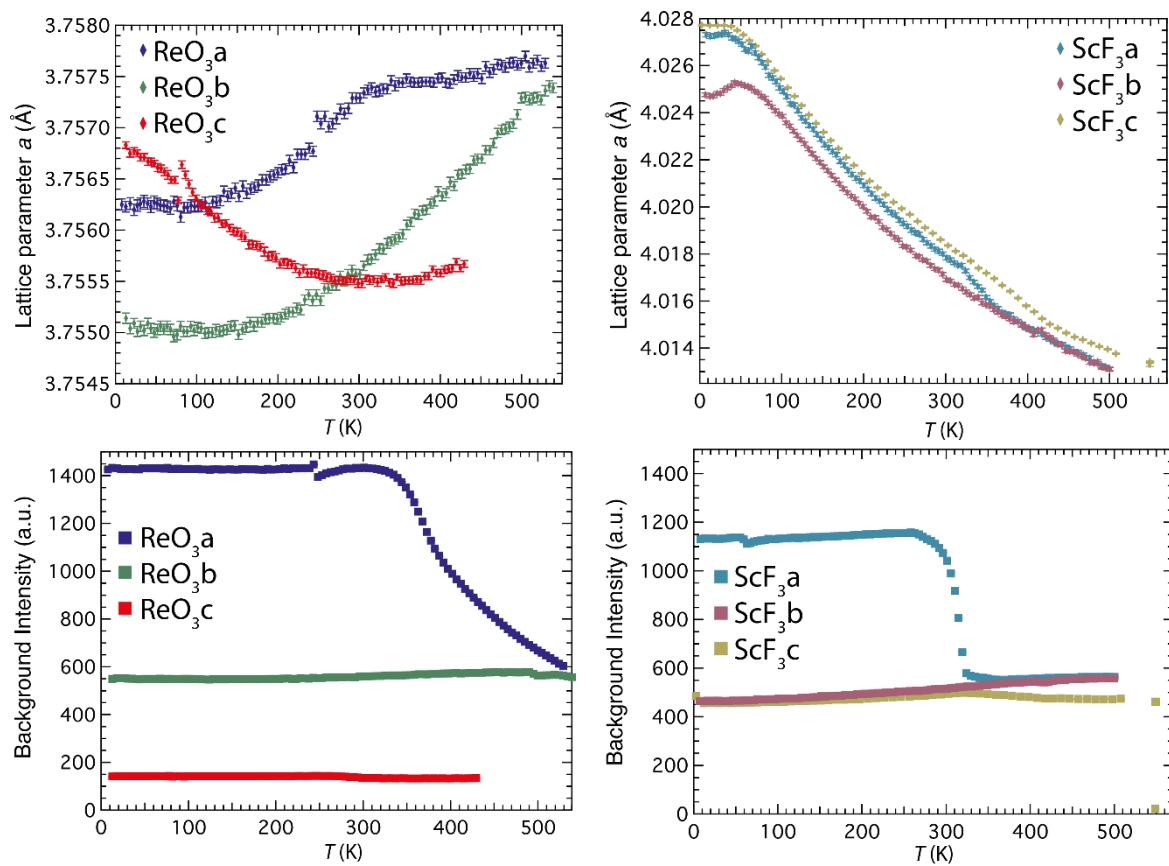
## Experiment

D20 was used in its high resolution set-up and a wavelength of 1.87 Å (Ge115) to measure the following samples:

1. ScF<sub>3</sub> anhydrous from 2-500 K.
2. ScF<sub>3</sub>.xH<sub>2</sub>O from 2-500 K in a non-sealed can followed by a second cycle from 2-500 K.
3. ReO<sub>3</sub>.xH<sub>2</sub>O from 2-500 K in a non-sealed can followed by a second cycle from 2-500 K.
4. Crushed single crystal ReO<sub>3</sub> from 2-500 K.

These samples covered points 1, 2, 5, 6 and 7 in the original plan. There was insufficient beam-time to measure vacuum dried then water treated ReO<sub>3</sub> samples, but similar data was available from previous NPD experiments.

## Initial Results



The above Figure shows the data for  $\text{ReO}_3$  (left) and  $\text{ScF}_3$  (right). Some minor issues with temperature readouts can be seen but the results are clear. Single crystal  $\text{ReO}_3$  (sample c) shows the predicted behaviour whereas samples a and b (heating cycle 1 and 2 respectively) show the effect of water intercalation into the host structure. This can also be seen in the lower left plot, which shows the background intensity as a function of temperature. Of further note is that even after temperature cycling the background from sample b is much higher than for the crushed single crystals, suggesting retention of hydrogenous species in the structure. The NTE range is markedly different than sample c, which follows the lattice dynamics predictions. In the case of  $\text{ScF}_3$  the magnitude of the NTE is very similar between sample a and c (hydrated and anhydrous respectively) and cycling shows that the behaviour of the hydrated sample once dehydrated is identical to the anhydrous sample (b *cf.* c – the absolute offset is caused by sample positioning inaccuracy). Therefore, the results clearly show that water can be intercalated into the vacant A-site in  $\text{ScF}_3$  in small quantities but that it leaves the material below 100 °C and has little to no effect on the NTE. In  $\text{ReO}_3$  the NTE behaviour of a water treated powder sample never regains that of the single crystal material unless the sample is vacuum dried and annealed in a dry, high oxygen environment close to the decomposition temperature (non-neutron based results). This, coupled with the increased NPD data background, shows OH groups remain in the structure and it is very likely that these disrupt the cooperative octahedral tilt modes, suppressing NTE.

## Current Status

NPD data are fully analysed for all samples measured, support work from IR and Raman scattering is continuing and TGA/DSC/MS studies are almost complete, as a result of long term studies on crushed single crystal ReO<sub>3</sub>, commercial ReO<sub>3</sub> and vacuum dried ReO<sub>3</sub> water uptake and release. QENS and INS studies are ongoing, due to sample size issues limiting the number of sample compositions we can effectively measure in a single beam-time (a cost issue for ReO<sub>3</sub>). Complete measurements require recycling/chemical purification of the samples and residual activity (average of 2-3 months) has delayed sample recovery post exposure to neutrons.

The diffraction, QENS, INS and supporting technique results (IR, Raman, TGA, DSC, MS) will form part of the PhD thesis of Carin Österberg at Chalmers University in Gothenburg, expected during late 2018, and the results will be published once we complete the QENS and INS studies.

*The diffraction experiment met all the primary aims and is considered a success.*

## References

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