Experimental Report

29/07/2014

Proposal: **5-23-655** **Council:** 10/2012

Title: Negative thermal expansion in rareearth tritungstates and trimolybdates. Study on Ho2(MO4)3 and Tm2(MO4)3 (M=Mo and W)

This proposal is a new proposal

Researh Area: Materials

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Samples:
$Ho_2(MoO_4)_3$
$Ho_2(WO_4)_3$
$Tm_2(MoO_4)_3$
$Tm_2(WO_4)_3$

Instrument	Req. Days	All. Days	From	To
D2B	6	4	28/03/2013	01/04/2013

Abstract:

Negative thermal expansion in crystals with gamma-$Sc_2(WO_4)_3$-type structure (Pbcn space group) has resulted in increased interest. Moreover, some of rare-earth trimolybdates and tritungstates show a phase transition at low and/or high temperature. Up to now, the mechanisms of this anomalous behavior and the origin of the structural instability are not well established. Recently, it has been found that Ho and Tm trimolybdates and Tm tritungstate adopt an orthorhombic structure and show NTE, whereas Ho tritungstate adopts a monoclinic structure and shows positive expansion. We want to complete our study of these materials by comparing tungstates and molybdates with more symmetric related materials (NASICON or garnet structures), by analyzing the symmetry adapted modes. We have selected four compounds: $Ho_2(MoO_4)_3$, $Tm_2(MoO_4)_3$, $Ho_2(WO_4)_3$ and $Tm_2(WO_4)_3$ to measure in the beamline D2B, where we have previously obtained successful results.

Negative thermal expansion in rareearth tritungstates and trimolybdates. Study on $Ho_2(MO_4)_3$ and $Tm_2(MO_4)_3$ (M=Mo and W)

(see also the proposal "Structural and electric conductivity anomalies in α-phases with distorted scheelite structure. Study on $Tb_2(MoO_4)_3$ and $Nd_2(MoO_4)_3$" number 7-03-121).

INTRODUCTION.

The discovery that tungstates and molybdates belonging to the $A_2(MO_4)_3$ family (A is a trivalent ion ranging from Al to Dy and M is W or Mo) display negative thermal expansion (NTE) has resulted in increased interest [1]. These materials crystallize in an orthorhombic phase (with γ-$Sc_2(WO_4)_3$-type structure, Pbcn) [2] Neutron and X-ray powder diffraction data of dehydrated $A_2(MoO_4)_3$ (A=Y, Ho, Er, Tm, Yb and Lu) has been measured in D2B at ILL (proposals: 5-24-360 and 5-24-397) and at PANalytical X'Pert Pro diffractometer from 150 to 400K. Crystal structures of yttrium, erbium, and lutetium were obtained by multipattern refinements using amplitude symmetry modes 'AMPLIMODES', implemented in FullProf software [3, 4]. It has been found these compounds undergo NTE when they are dehydrated too. Polyhedral distortion, transverse vibration of A…O-Mo binding oxygen atoms and non-bonded distances A…Mo have been evaluated as functions of temperature and ionic radii, in order to explain the NTE behavior [5]. Several issues (tunability in the coefficient of thermal expansion [6], detection of new phase transitions [7], properties as ion conductivity [8]) have contributed to decide revising and expanding this study to these four compounds and they will be the subject of our future studies, thanks to the data collected in this experiment.

EXPERIMENTAL. The experiments corresponding to the proposals 5-23-655 and 7-03-121 were divided in two parts which were performed in different dates:

- From 28/03/13 to 01/04/13 (which corresponds to the proposal 7-03-121) for measures at high temperature using a furnace heating from 473K to 1273K.
- From 17/05/13 to 21/05/13 (which corresponds to the proposal 5-23-655) using the orange cryostat cooling from 350K to 4K.

In this report we present the preliminary results from the original proposal, although the experiment was divided in two parts on the given dates. We have measured polycrystalline samples of γ-phases of $Ho_2(MoO4)_3$, $Ho_2(WO4)_3$, $Tm_2(MoO_4)_3$ and $Tm_2(WO_4)_3$. The powder neutron diffractometer D2B (Debye-Scherrer geometry) of the Institut Laue-Langevin (Grenoble, France) was used for data collection with an incident wavelength λ=1.5943(1) Å, Ge[335] monochromator, take-off-angle 135º, angular range 5º < 2θ< 165º, without primary collimator and 128 3He tubes 300 mm in height as detection system. The diffraction patterns were obtained with 100 steps of 0.025º in 2θ. Each pattern was collected over 2.5 hours. Two kinds of patterns were extracted from the raw data, one corresponding to a binning of the central equatorial zone of the detector for which the resolution is higher, and another integrating the whole detector for which the counting statistics are better despite a worse resolution. To ensure their total dehydration, because all these samples are highly hygroscopic, all samples were placed in a furnace at 423 K for about 8 hours inside the vanadium container and closed before introducing it into the cryofurnace installed on the D2B diffractometer.

ANALYSIS OF THE DATA. In order to check the data and to obtain the zero parameter and the instrumental function resolution, which it is different for measures with cryostat, furnace or without both of them; we have refined the crystal structure of the standard NACALF with data obtained in different conditions using the FullProf software [4]. However, some changes in the experimental conditions were not measured with the standard, then, before an exhaustive Rietveld refinement of the four compounds, at different temperatures, we have performed a Le Bail fitting [9] (without crystal structure) using the FullProf software, in order to see the thermal dependence of the cell parameters and to compare them with those obtained by X-ray diffraction. In figure 1, these preliminary refinements are shown.

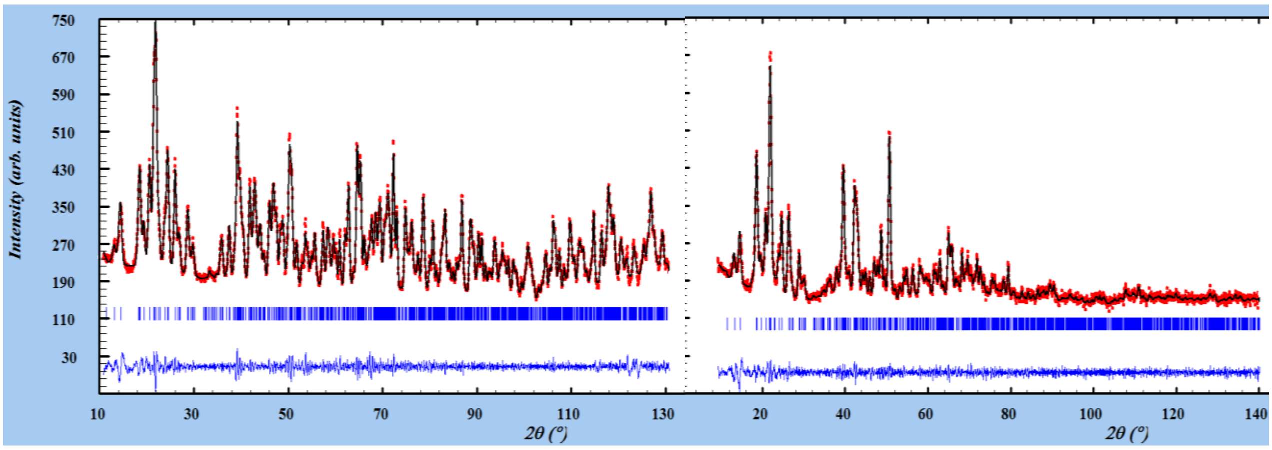
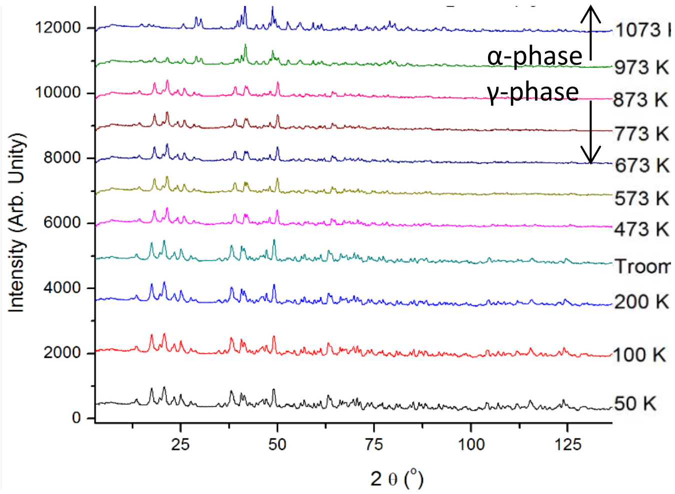


Figure 1. Powder diffraction patterns collected (red) and calculated (black) profile matching for: $Tm_2(MoO_4)_3$ at 4 K (left) and at 1073K (right) for $Tm_2(WO_4)_3$ as examples of our results.



In Figure 2 shows the irreversible phase transition of the $Ho_2(WO_4)_3$ towards the α-phase, as we expected above 900K. This explains the result found by Xiao *et al* [10] about the positive expansion of this compound with a monoclinic structure. This transition is an irreversible process.

Figure 2. Powder diffraction patterns collected for $Ho_2(WO_4)_3$ from 50K to 1073K.

RESULTS. The temperature dependence of the lattice parameters for the four compounds is shown. The evolution of the lattice parameters is close to that obtained by X-ray diffraction. The behaviors of such parameters are very similar in tungstates and molybdates and the volume decreases monotonously (with similar slope) when the temperature increases. Then, the coefficients of thermal expansion are not affected by the choice of the transition metal (Mo^{6+} or W^{6+}) nor the rare earth (Tm^{3+}, Ho^{3+}), contrary to the arguments of the majority of authors [6], they found that the cation larger size lead to stronger NTE while a smaller cation size always brings about less pronounced NTE. Moreover, the results from this experiment, together with those observed by X-ray diffraction confirm the phase transitions γ-β [7] and γ-α (never described) for $Ho_2(MoO_4)_3$ and $Ho_2(WO_4)_3$, respectively. The uniformity and monotonous dependence with temperature of the lattice parameters, in addition the collection of high temperature data of the different phases α, β and γ, will allow us a complete structural determination, by Rietveld refinement [11], to understand the negative thermal expansion and phase transitions in this family of compounds.

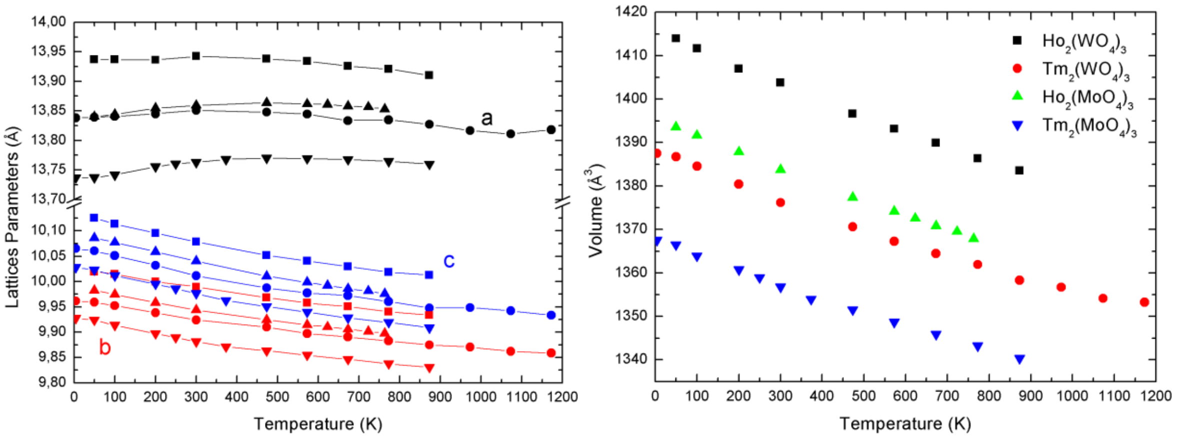


Figure 3. Temperature dependence of the lattice parameters (left) and volume (right) for $Ho_2(WO_4)_3$ (squares), $Tm_2(WO_4)_3$ (circles), $Ho_2(MoO_4)_3$ (up-triangles) and $Tm_2(MoO_4)_3$ (down-triangles). At the left side, lattice parameters **a**, **b** and **c** are black, red and blue, respectively.

FUTURE WORK. We will perform the Rietveld refinements [11] to determinate the thermal dependence of the crystal structure, particularly, for the transversal displacements of the oxygen atoms in bridges A-O-M (A=Tm or Ho and M=Mo or W) and the polyhedral distortion. This evolution can be expressed in terms of a distortion of a more symmetric structure (*Im-3m*) given by a symmetry modes analysis [3], in order to understand why other related structure as garnet, nasicon, low temperature phase of $Al_2(WO_4)_3$ do not exhibit NTE and to relate to other polymorphic phases (named α and β). To aid on this study, theoretical *ab initio* calculations are being performed with the VASP code [11], within the PAW pseudopotential method and the PBEsol form of the exchange. This kind of study can provide a valuable insight on the structural stability of the five possible different phases with space groups: *Pbcn* (γ-phase with NTE), $P2_1/c$ (lower temperature phase without NTE), *Pba2* (β'-phase, ferroelectric), $P\text{-}42_1m$ (β-phase, paraelectric), *C2/c* (scheelite modulated α-phase). Finally, the knowledge of the crystal structure dependence at high temperature will allow us to delve into the mechanisms of ionic conduction in these compounds, whose explanation is currently controversial [8].

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