Experimental Report

11/04/2014

Proposal:	**7-03-121**	**Council:**	10/2012

Title: Structural and electric conductivity anomalies in alpha-phases with distorted scheelite structure. Studyon Tb2(MoO4)3 and Nd2(MoO4)3

This proposal is a new proposal

Researh Area: Materials

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Samples: Tb2(MoO4)3
Nd2(MoO4)3

Instrument	Req. Days	All. Days	From	To
D2B	4	4	17/05/2013	21/05/2013

Abstract:

Tungstates and molybdates with scheelite-type structure are technologically important materials with applications as phosphors, detectors, lasers, etc. In recent years, it have been found they exhibit high oxide-ion conduction in intermediate temperature ranges and there has arisen renewed interest in their evolution under pressure, providing valuable insight on structural, electronic and transport properties. The alpha-phases of rare earth molybdates are distorted scheelites and we are interested on its anomalous transport properties (with semiconductor, polaronic and ionic character), which we have correlated to their thermal dependence on the crystal structure. We have structural information from X ray data, but the precise determination of thermal dependence of oxygen displacements would help to explain the correlation with different conductivity mechanisms. We propose to study Tb2(MoO4)3 and Nd2(MoO4)3 compounds in the D2B beamline, at selected temperatures between 10 to 1000K.

Structural and electric conductivity anomalies in alpha-phases with distorted scheelite structure. Study on $Tb_2(MoO4)_3$ and $Nd_2(MoO_4)_3$

INTRODUCTION. Tungstates and molybdates with scheelite-type structure are technologically important materials with applications as phosphors, detectors of ionizing radiation, efficient laser hosts, etc. In recent years, scheelite-type oxides ($PbWO_4$) have been found to exhibit high oxide-ion conduction in intermediate temperature ranges [1]. $RE_2(MO_4)_3$ (with M = W or Mo) adopt different crystalline structures depending on both the rare earth (RE) cation and the method of synthesis. Some of them crystallize in the scheelite-type structure of $CaWO_4$ with one third of the positions occupied by calcium being vacant. Our work provides new results on distorted scheelite molybdates with anomalous behavior in their transport properties. We have studied their electric conductivity and found that it follows the universal dielectric response, which yields three different regimes of conduction (with semiconductor, polaronic and ionic character) [2,3]. Polaronic mechanism, in the intermediate range, was probed using the overlapping large polaron model. At high temperatures, the application of scaling laws suggests an ionic conduction. On the other hand, X-ray diffraction patterns let us calculate the thermal dependence of the lattice parameter: the **a**-parameter showed three distinctly different trends in correspondence with the three conduction regimes observed. In this work we had proposed to study the anomalous thermal dependence of the crystal structure of $Tb_2(MoO_4)_3$ and $Nd_2(MoO_4)_3$ in order to correlate them with the conductivity mechanisms. We have substituted the neodymium molybdate by $Tb_2(WO_4)_3$ because its alpha-phase is difficult to obtain as a pure phase. We chose $Tb_2(WO_4)_3$ as alternative because we want to compare the behavior of tungstates and molybdates with the same structural phase (see also the proposal “Negative thermal expansion in rare earth tritungstates and trimolybdates” number 57431).

EXPERIMENTAL. The experiments corresponding to the proposals 57437 and 57431 were divided in two parts which were each performed at different dates:

- From 28/03/13 to 01/04/13 (which corresponds to this proposal 57437) 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 57431) 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 alpha-$Tb_2(MoO_4)_3$, alpha-$Tb_2(WO_4)_3$ and the standard NACALF. 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 $5º < 2\theta < 165º$, 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 other integrating over the whole detector for which the counting statistics are better despite a worse resolution.

ANALYSIS OF THE DATA. In order to check the data and to obtain the zero parameter and the instrumental function resolution, which is different for measures with either cryostat, furnace or without both of them, we have refined the crystal structure of the standard NACALF with data obtained under 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 [5] of terbium molybdate and terbium tungstate, at different temperatures, we have performed a profile matching (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.

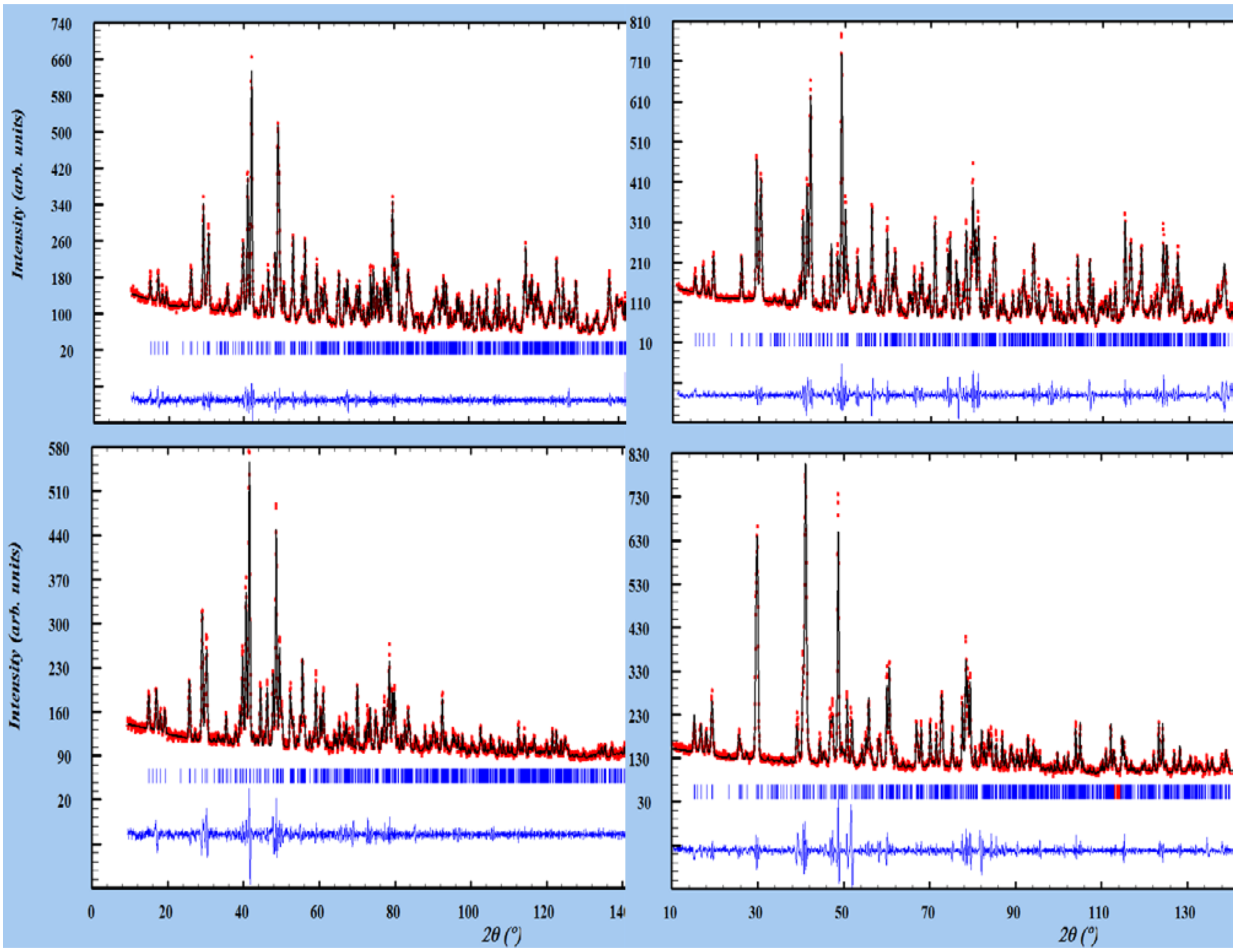

Figure 1. Powder diffraction patterns collected (red) and calculated (black) profile matching for: $Tb_2(WO_4)_3$ at 4 K (top left) and at 1273K (top right); $Tb_2(MoO_4)_3$ at 4 K (bottom left) and at 973K (bottom right) as examples of our results.

RESULTS. In figure 2 we show the temperature dependence of the lattice parameters for both compounds. There is a small discontinuity between lower and higher temperature data and the room temperature results. We expect to obtain a better zero parameter and smoother curves for lattice parameter thermal dependence when we perform the Rietveld refinement in order to calculate the crystal structure for all temperatures. The evolution of the lattice parameters is similar to that obtained by X-ray diffraction. The behaviors of such parameters are quite different in tungstates and molybdates. For both compounds, the volume increases monotonously when the temperature increases, although for terbium molybdate, it is not linear; its slope is greater, at higher temperatures. At high temperature the **a** parameter decreases for $Tb_2(MoO_4)_3$, when the temperature increases and it remains constant for $Tb_2(WO_4)_3$. While the **a** parameter is greater for tungstates (the ionic radii of W is greater than the one of Mo), the **b** and **c** lattice parameters are smaller. For $Tb_2(WO_4)_3$ the temperature dependence of the cell parameters **c** and **b** are similar at low temperature and diverge at high temperature. However, for $Tb_2(MoO_4)_3$ the **c** parameter has an anomalous behavior correlated with the thermal dependence of the **a** parameter. For $Tb_2(MoO_4)_3$ the beta angle starts to decrease already at low temperatures (around 200K) while for $Tb_2(WO_4)_3$ it remains constant. The beta-angle behavior is correlated with the corresponding **a** parameter.

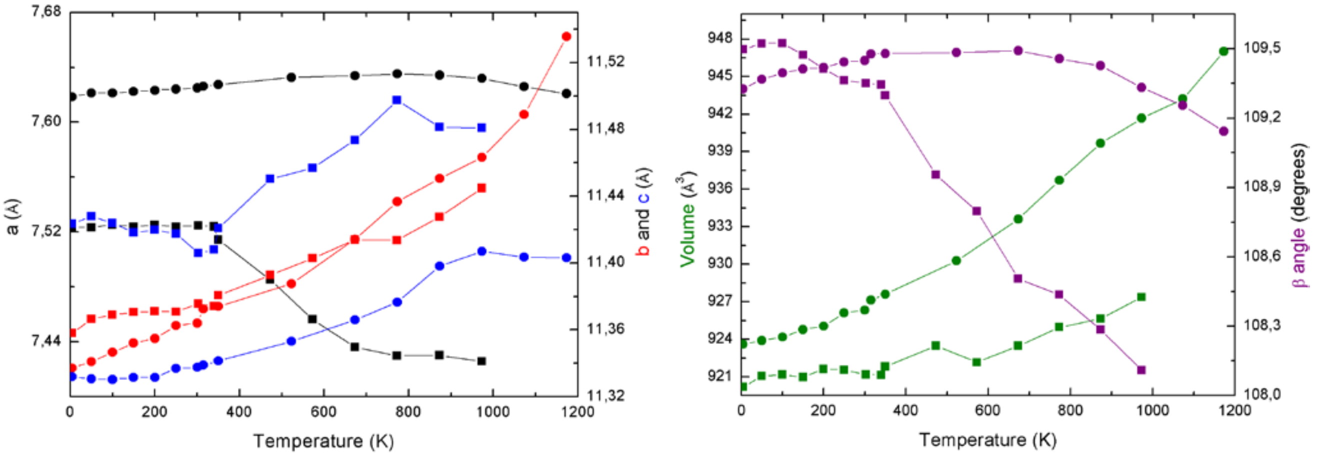

Figure 2. Temperature dependence of the lattice parameters. The curve for $Tb_2(WO_4)_3$ is plotted with circles and curve for $Tb_2(MoO_4)_3$ is plotted with squares. At the left side, the lattice parameters **a**, **b** and **c** are black, red and blue, respectively. At the right side, the beta angle and volume are purple and green, respectively.

FUTURE WORK. We will perform the Rietveld refinement to study the thermal dependence of the oxygen displacements. We suggest that the transversal displacements of oxygen atoms in bridges Tb-O-M (M=Mo or W), joined to the tetrahedral elongation, explain this anomalous behavior. Moreover, from the calculated bond-valence contour maps [6], we can find new sites for the oxygen atoms at high temperatures, which will favor the conduction by oxygen atoms or vacancies. A precise determination of oxygen atoms would help to explain the correlation between the different conductivity mechanisms and the thermal dependence of the crystal structure. Up to now there is only an incomplete description of the band-like transport behavior due to large polaron formation in connection with the crystal structure, in comparison to the more typical case associated to hopping due to small polarons. On the other hand, we are investigating the pressure dependence of both compounds by theoretical *ab initio* calculations (performed with the VASP code [7], within the PAW pseudopotential method and the PBEsol form of the exchange correlation fuctional) and X-ray diffraction. This is a kind of study which is fast becoming an important subject on its own because pressure can provide valuable insight on the structural, electronic, and transport properties of these materials.

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References. [1] H. Huang, X. Feng, W. Zhu, Y. Zhang, T-L. Wen and T.B. Tang, J. Phys. Condens. Matter 15, 5689 (2003) [2] C. Guzmán-Afonso, M. E. Torres, C. González-Silgo, N. Sabalisck, J. González-Platas, E. Matesanz and A. Mujica, Solid State Commun. 151, 1654 (2011) [3] C. Guzmán-Afonso, C. González-Silgo, M. E. Torres, E. Matesanz and A. Mujica, J. Phys.: Condens. Matter. 25, 035902 (2013) [4] J. Rodríguez-Carvajal, Physica B, 192, 55 (1993) [5] R. A. Young, The Rietveld Method (Oxford Science Publications, Oxford, 1993) [6] J. González-Platas, C. González-Silgo and C. Ruiz-Pérez, J. Appl. Crystallogr. 32, 341 (1999) [7] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996)