Experimental report

27/02/2019

Proposal: 5-24-602 **Council:** 4/2017

Title: Exploring the high-temperature crystallographic features of thermoelectric materials based on SrTiO3 perovskite

Research area: Chemistry

This proposal is a new proposal

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Samples: SrTi1-xMx (M= W, Ta, Nb, Mo)
Sr1-xTi0.9M0.1O3 (M= W, Ta, Nb, Mo)
Sr0.9R0.1TiO3 (R= Ce, Pr, Nd, Eu

Instrument	Requested days	Allocated days	From	To
D2B	4	2	03/04/2018	05/04/2018

Abstract:

Recently, some oxides have been investigated as environment-friendly thermoelectric materials, in particular, some reduced or donor-doped perovskite-type titanates derived from SrTiO3, showing n-type metallic behavior with large Seebeck coefficients. Here we propose to study several series of compounds involving different doping strategies, either at the Sr or Ti positions of the SrTiO3 perovskite, and the incorporation of vacancies at Sr positions and at the oxygen sublattice in order to decrease the thermal conductivity and improve the figure of merit.The goal of this proposal is twofold: i) to analyze the effect of doping on the crystal structure of three series of compounds: Sr0.9R0.1TiO3-d (R= Ce, Pr, Nd, Eu); SrTi1-xMxO3-d (M= Nb, Ta, Mo, W) and the corresponding Sr-defective specimens, in connection with their thermoelectric properties, and ii) to investigate their temperature evolution with emphasis in the anisotropic displacement parameters analyzed in terms of Einstein oscillators yielding the characteristic energies corresponding to each phonon mode. For this task we ask for 4 days at D2B diffractometer provided with a furnace.

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This experiment was carried out in April 2018. In this time the family of compounds with general formula $Sr_{1-x}(Ti_{0.9}Nb_{0.1})O_{3-\delta}$ (x = 0, 0.1 and 0.2) was extensely measured at RT (25ºC) and elevated temperatures up to 800 ºC. In these samples we find that a conspicuous effect on thermal properties is associated with the introduction of Sr^{2+} vacancies, leading to a extremely low thermal conductivity, achieving competitive values of κ for applications of $\approx$ 1.6 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 823 K for $Sr_{1-x}Ti_{0.9}Nb_{0.1}O_{3-\delta}$ (x = 0.1 and 0.2). In order to understand the relationship between the enhancement of thermal properties and the crystalline structures, the temperature-dependent neutron powder diffraction (NPD) studies resulted in a relevant tool.

For x = 0.1 a short neutron wavelength (λ= 1.051 Å) was chosen to access a wide region of the reciprocal space. The RT neutron pattern confirms the cubic symmetry with unit-cell parameter a= 3.91726(4) Å; the structure was therefore defined in the cubic $Pm\bar{3}m$ space group with Sr located at 1b Wyckoff site (½, ½, ½); Ti and Nb distributed at random at 1a (0,0,0) site; and O1 at 3d(1/2,0,0). The Ti *vs* Nb and O1 occupancies were refined, yielding a crystallographic formula at RT $Sr_{0.9}Ti_{0.88(1)}Nb_{0.12(1)}O_{2.85(4)}$, showing a significant oxygen deficiency. The anisotropic displacement factors of O1 were also refined. The Ti/Nb rate is similar to that expected, while the oxygen positions show a conspicuous non-stoichiometry. For the determined occupancy factors, the oxidation state of Ti is 3.75+. The final structural parameters and agreement factors are gathered at Table 1 for this perovskite oxide at RT. The structural refinement from data collected above RT (300, 600, 800ºC) was correctly performed in $Pm\bar{3}m$. The good agreement between observed and calculated profiles is displayed in Figure 1a and Figure 1b for the 25ºC and 800ºC patterns, respectively.

Figure 2 illustrates the cubic crystal structure at 800ºC, displaying a remarkable anisotropy in the disk-shaped (oblate) displacement ellipsoids for oxygen atoms. Figure 3 displays the thermal variation of the unit-cell volume of the perovskite oxide; the inset shows the U_{ij} thermal displacement across the measured temperature range. For the cations (Sr, Ti, Nb) the thermal displacement parameters are constrained, by symmetry, to be spherical. For oxygen atoms at 800ºC, the anisotropic ellipsoids exhibit root mean square (r.m.s.) displacements of 0.18 Å perpendicular to the Ti-Ti distance and 0.11 Å parallel to it. This suggests that the thermal vibrations are mainly

permitted in a perpendicular direction to the covalent Ti(Nb)-O-Ti(Nb) chemical bonds, as usual in many perovskite-like oxides.

A similar analysis was performed for x = 0.2.

Table 1. Structural parameters after the Rietveld refinement of $Sr_{0.9}(Ti_{0.9}Nb_{0.1})O_{3-\delta}$ from NPD data at 25ºC in the $Pm\bar{3}m$ space group, a = 3.91726 (4) Å, with λ= 1.051 Å. Discrepancy factors: R_p = 3.14%, R_{wp} = 4.27%, R_{exp} = 2.49%, R_{Bragg} = 3.14%, χ^2 = 3.27

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Sr	0.50000	0.50000	0.50000	0.0065(4)*	0.9
Ti	0.00000	0.00000	0.00000	0.0028(6)*	0.877(5)
Nb	0.00000	0.00000	0.00000	0.0028(6)*	0.123(5)
O1	0.50000	0.00000	0.00000	0.0085(5)	0.95(1)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0035(7)	0.0109(4)	0.0109(4)	0.00000	0.00000	0.00000

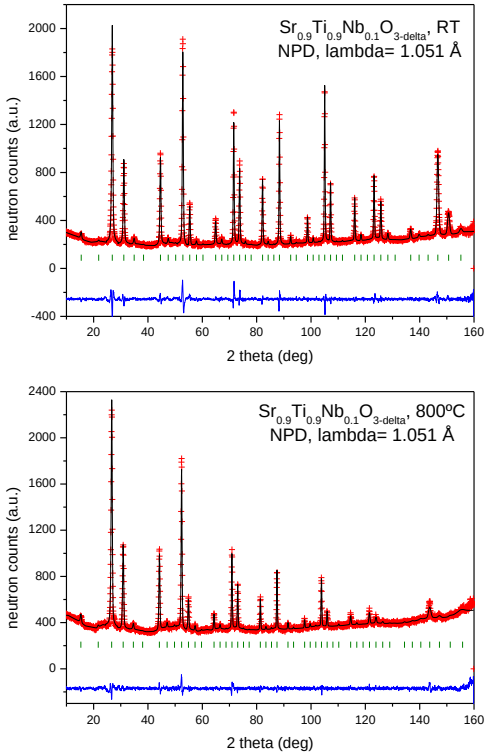

Figure 1. Observed (red crosses), calculated (black line) and difference (lower blue line) NPD profiles for $Sr_{0.9}(Ti_{0.9}Nb_{0.1})O_3$, at 25ºC (upper panel) and 800ºC (lower panel). The allowed Bragg positions are shown as green vertical marks.

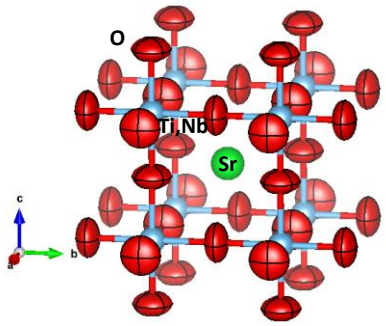

Figure 2. View of the crystal structure of $Sr_{0.9}(Ti_{0.9}Nb_{0.1})O_3$ at 800ºC, highlighting the anisotropic ellipsoids for O atoms (99% probability), shaped as disks perpendicular to the Ti(Nb)-O-Ti(Nb) chemical bonds.

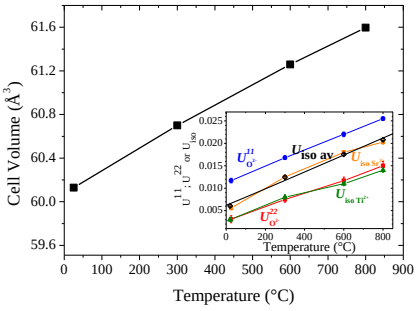

Figure 3. Thermal evolution of the unit-cell volume for $Sr_{0.9}(Ti_{0.9}Nb_{0.1})O_3$ in the 300- 900ºC temperature range. The inset shows the evolution of the ADPs for Sr (orange), Ti (green) and O (red and blue) atoms, and the unit-cell averaged U_{iso} (black) and corresponding Debye-fit (black line) with θ_D=437 K.

Conclusions

Rietveld refinements of the neutron diffraction data show a substantial oxygen deficiency composition in the samples containing Sr-vacancies, giving compositions of $Sr_{0.9}Ti_{0.88(1)}Nb_{0.12(1)}O_{2.85(4)}$ and $Sr_{0.8}Ti_{0.875(3)}Nb_{0.125(3)}O_{2.50(2)}$. The existence of Sr-cation and O-anion defects and the reduction of Ti^{4+} to Ti^{3+} in the samples, affect dramatically to the electronic and thermal properties of the materials.

Finally, a manuscript is being written regarding these crystallographic results and specific properties such as Seebeck effect, electrical and thermal conductivities.