Experimental report

19/06/2020

Proposal: 5-21-1118 **Council:** 10/2018

Title: Unveiling the origin of extra-low thermal conductivity in thermoelectric R1-xCo4Sb12 skutterudites prepared under high pressures

Research area: Chemistry

This proposal is a new proposal

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Samples: RxCo4Sb12
SrMn0.9Co0.1O3
Sr2CaNb2O9
H3OSbWO6
LaSrGa0.8Mn0.2O4
Sn0.93Ce0.07Se
P(black form)

Instrument	Requested days	Allocated days	From	To
D2B	4	2	24/06/2019	26/06/2019

Abstract:

Recently, we have found that high pressure (HP) synthesis promotes a boost in the filling fraction of filled-skutterudite thermoelectric materials, leading to a glass-like, ultralow thermal conductivity. This is the effect of additional scattering of high-energy phonons on the lattice thermal conductivity of caged crystals. Additionally, a thorough analysis of the temperature-dependent atomic displacement parameters (ADP) based on the Einstein model may permit to establish a direct relationship between the ADPs of the guest atom and the magnitude of the lattice thermal conductivity, as demonstrated for some filled M1-xCo4Sb12 skutterudites. We aim 1) to investigate the structural influence of the extra filling in HP skutterudites of different compositions: La0.5Co4Sb12; Ce0.5Co4Sb12, Yb0.5Co4Sb12, Mm0.5Co4Sb12 (Mm= Mischmetal: cocktail of Ce, Nd and other rare earths), Sr0.5Co4Sb12, K0.5Co4Sb12, all of them prepared at 3.5 GPa, and 2) to study the thermal evolution above RT, up to 800ºC, in order to fit the ADPs to the Einstein model. For this we ask for 4 days at D2B diffractometer.

Thermoelectric materials hold promise for sustainable development by providing a very reliable and clean option for energy conversion from temperature difference. Several approaches and materials have been explored to improve thermoelectric efficiency. Among them, skutterudites ($R_xCo_4Sb_{12}$, where R denotes the filler element) are one of the best materials used for this purpose[1], based on the phonon-glass electron crystal (PGEC) concept proposed by Slack[2], which describes ‘‘rattling’’ atoms in structural cages, disturbing the propagation of phonons, thus reducing the lattice thermal conductivity.

To apply the PGEC approach, different elements have been used[3,4] to significantly reduce the thermal conductivity by filling the empty structural voids at the 2a positions of the skutterudite structure (defined in the *Im-3* space group). Recently, we have found that a **high-pressure synthesis** is a very efficient method that we can use in order to fill these structural voids, therefore reducing the lattice thermal conductivity. Moreover, previous structural results show a **phase segregation** (R-rich and R-poor regions) in these compounds that suggest the existence of a more complex structure. This phase segregation is a relevant feature, since causes an extra reduction of the thermal conductivity[5,6].

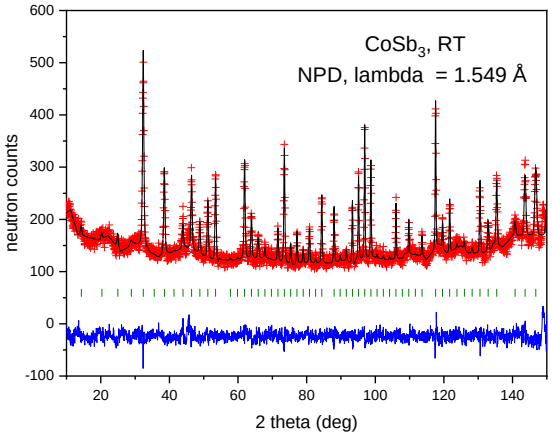

Figure 1. Rietveld refinement NPD profile for $CoSb_3$ skutterudite at room temperature (RT). Observed (red crosses), calculated profile (black line) and difference (blue line).

In order to comprehend the effect of different fillers on the structural properties, we have prepared several skutterudites; the unfilled one, $CoSb_3$, and other ones filled with different elements, such as K, Y and Yb. The limited amount of sample available from the high-pressure synthesis (< 1g) required us to perform long measurements. Neutron powder diffraction (NPD) data were collected in the diffractometer D2B. The high intensity mode ($\Delta d/d \approx 5 \cdot 10\text{-}4$) was selected, with a neutron wavelength $\lambda = 1.594$ Å within the angular 2θ range from 10° to 150°. About 1 g of the sample was contained in a cylindrical vanadium holder (dia. 8 mm), and the counting time was 4 h. The measurements were carried out in air at 298, 473, 673, 873 and 1073 K.

Fig. 1 illustrates the pattern of the unfilled skutterudite, $CoSb_3$, at room temperature. It can be Rietveld-refined appropriately in the cubic *Im-3* space group.

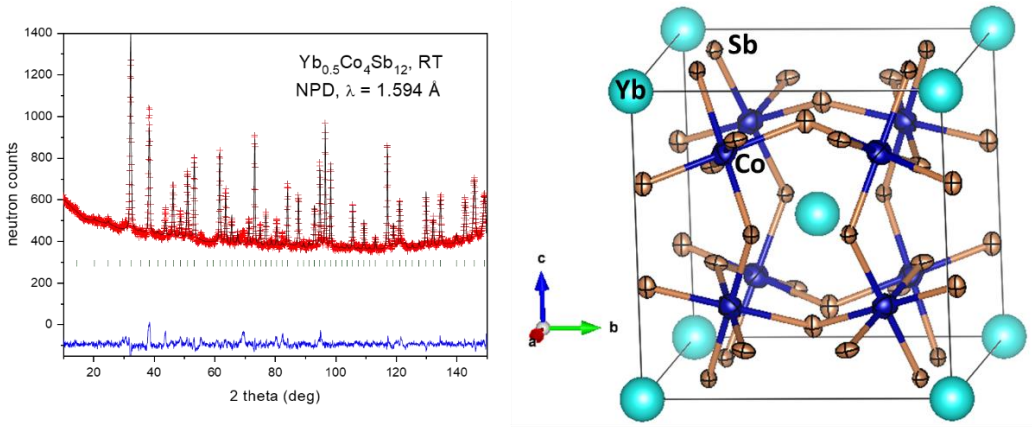

Figure 2. Rietveld-refined NPD profile for $Yb_{0.5}Co_4Sb_{12}$ skutterudite and the corresponding crystal structure for this composition.

Fig. 2 illustrates the refinement of one of the selected compositions. It can be seen that the filler Yb atoms are located at the 2a positions. The filling fraction for the ytterbium is about 0.3, according to the refinement data, which means that not all the voids are filled.

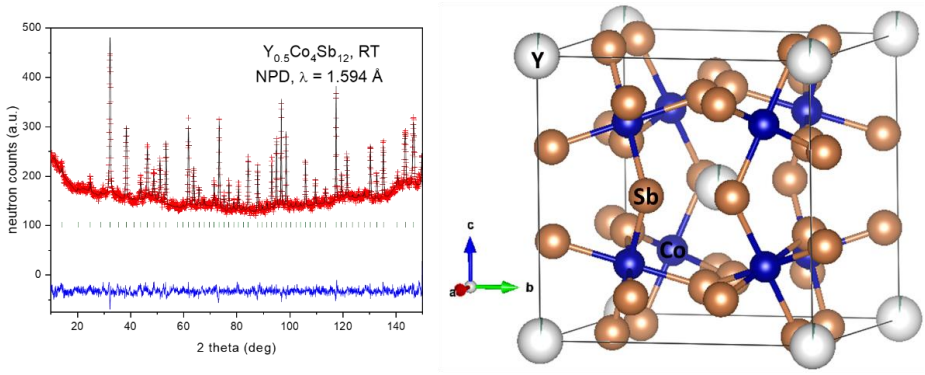

Figure 3. Rietveld-refined NPD profile for $Y_{0.5}Co_4Sb_{12}$ skutterudite and the corresponding crystal structure for this composition.

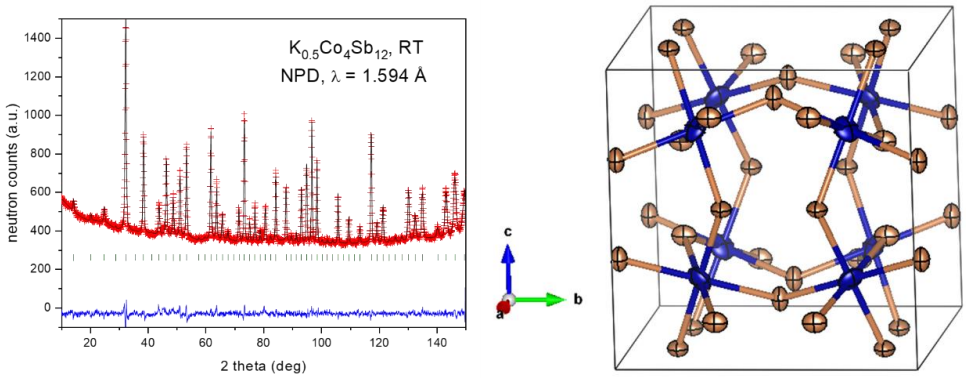

Figure 4. Rietveld-refined NPD profile for $K_{0.5}Co_4Sb_{12}$ skutterudite and the crystal structure for this composition.

In the case of Fig. 3, the yttrium filling fraction is lower than the previous one (Yb), being only 0.16.

According to the pattern of Fig. 4, and differently from the previous compositions, no filler element seems to be located at the 2a positions. Therefore, the potassium it is not an adequate element to fill the voids in the skutterudite structure.

Fig. 5 illustrates the patterns of the $Y_{0.5}Co_4Sb_{12}$ sample, showing the temperature evolution of the compound. There are no signs of degradation up to 1073 K, although some anomalies appear around 35º.

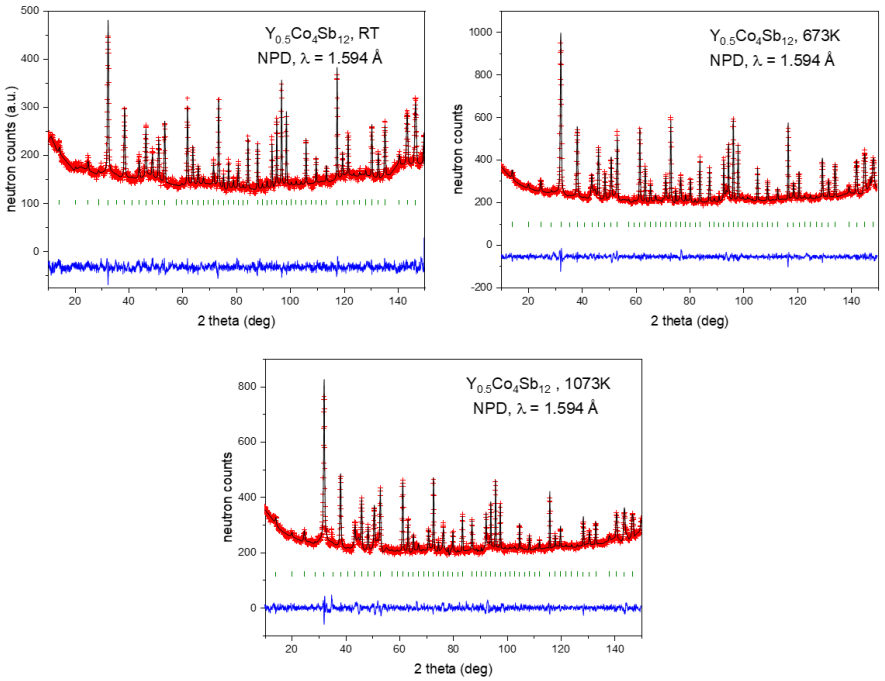

Figure 5. Rietveld-refined NPD profile for $Y_{0.5}Co_4Sb_{12}$ at different temperatures, 298K, 673K and 1073K.

References

1. Rull-Bravo, M., Moure, A., Fernández, J.F., and Martín-González, M. (2015). Skutterudites as thermoelectric materials: Revisited. RSC Adv. *5*, 41653–41667.

2. Slack, G.A. (1995). CRC Handbook of Thermoelectrics D. M. Rowe, ed. (CRC Press).

3. Qiu, P.F., Yang, J., Liu, R.H., Shi, X., Huang, X.Y., Snyder, G.J., Zhang, W., and Chen, L.D. (2011). High-temperature electrical and thermal transport properties of fully filled skutterudites RFe 4 Sb 12 (R = Ca, Sr, Ba, La, Ce, Pr, Nd, Eu, and Yb). J. Appl. Phys. *109*, 063713.

4. Tang, Y., Hanus, R., Chen, S.W., and Snyder, G.J. (2015). Solubility design leading to high figure of merit in low-cost Ce-CoSb3 skutterudites. Nat. Commun. *6*, 1–7.

5. Gainza, J., Serrano-Sánchez, F., Prado-Gonjal, J., Nemes, N.M., Biskup, N., Dura, O.J., Martínez, J.L., Fauth, F., and Alonso, J.A. (2019). Substantial thermal conductivity reduction in mischmetal skutterudites Mm x Co 4 Sb 12 prepared under high-pressure conditions, due to uneven distribution of the rare-earth elements. J. Mater. Chem. C *7*, 4124–4131.

6. Serrano-Sánchez, F., Prado-Gonjal, J., Nemes, N.M., Biskup, N., Varela, M., Dura, O.J., Martínez, J.L., Fernández-Díaz, M.T., Fauth, F., and Alonso, J.A. (2017). Low thermal cond. in La-filled cobalt antimonide with an inhomogeneous filling factor prepared under HP conditions. J. Mater. Chem. A *6*, 118–126.