Experimental report

30/05/2025

Proposal: CRG-3121 **Council:** 4/2024

Title: Study of the impact of Sb vacancieson skutterudite structure for thermoelectric applications through neutron thermodiffraction

Research area:

This proposal is a new proposal

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Samples: Fe0.5Ni0.5Sb3-d

Instrument	Requested days	Allocated days	From	To
D1B	2	2	05/04/2024	07/04/2024

Abstract:

Skutterudites with the general chemical formula $Fe_{0.5}Ni_{0.5}Sb_{3-\delta}$ have been investigated, both experimentally and theoretically, for thermoelectric applications. These compositions have been selected due to their potential to achieve elevated ZT values (greater than 1) demonstrated by $CoSb_3$ skutterudite materials, which is isoelectronic and isostructural.[1]

We aimed to determine precisely the structural parameters of 3 skutterudite samples with nominal composition $Fe_{0.5}Ni_{0.5}Sb_3$, $Fe_{0.5}Ni_{0.5}Sb_{2.97}$ and $Fe_{0.5}Ni_{0.5}Sb_{2.9}$, in order to associate them with potential variations in thermoelectric properties. The scattering factors of the transition metals cannot be easily distinguished using X-ray diffraction (Z_{Fe} = 26, Z_{Ni} = 28), while neutron diffraction offers a much larger contrast in the scattering lengths of all elements in our samples (9.45, 10.3, 5.57 fm for Fe, Ni and Sb, respectively).[2]

Neutron powder diffraction (NPD) data were collected in D1B using λ = 1.28Å, within the angular 2θ range from 5° to 120°. Long scans of 1 - 3 h were measured in vacuum at room temperature, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C using a standard cryofurnace and 8mm V sample holders for all samples.

Preliminary Rietveld fits of their crystal structures against RT data confirm all three samples crystallise with skutterudite structure in the cubic *Im-3* space group, which is represented on the Figure 1. Figure 2 shows the refined RT scan for $Fe_{0.5}Ni_{0.5}Sb_3$ as a reference, with cell parameter *a* = 9.019(1) Å. Bragg tick marks identify (top to bottom) the main phase, along with minor amounts of secondary Sb (3.2(2)%) and Fe_3O_4 (1.1(1)%, not visible from laboratory XRD) as well as the magnetic structure of Fe_3O_4 (R_{mag} = 6.4%). To determine the occupancy of the constituent elements in the samples and the possible order-disorder of the transition metal elements, in order to relate this results with the thermoelectric behaviour of the prepared samples. No cationic order has been found. Cell parameters, atomic positions and atomic displacement parameters are included in Table 1.

Table 1. Structural parameters for $Fe_{0.5}Ni_{0.5}Sb_3$.

Structural parameters	**$Fe_{0.5}Ni_{0.5}Sb_3$**
a (Å)	9.019(1)
b (Å)	9.019(1)
c (Å)	9.019(1)
Fe/Ni	
x	0.25
y	0.25
z	0.25
Occ.	0.083
B_{iso} (Å^2)	0.352(2)
Sb	
x	0
y	0.33586
z	0.15791
Occ.	0.500(1)
B_{iso} (Å^2)	0.464(2)

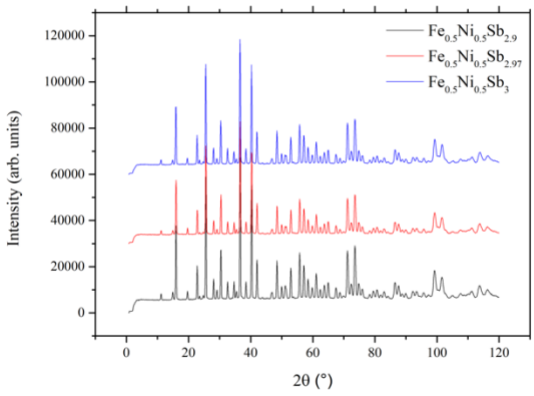

Figure 1. Rietveld fits of the three samples at RT.

The analysis of high temperature data confirms the coherent evolution of the cell parameter (Fig. 2b and 3a) and thermal factors (B_{iso}, Fig. 3b), reflecting the expected increased thermal motion of atoms within the crystal lattice.[3]

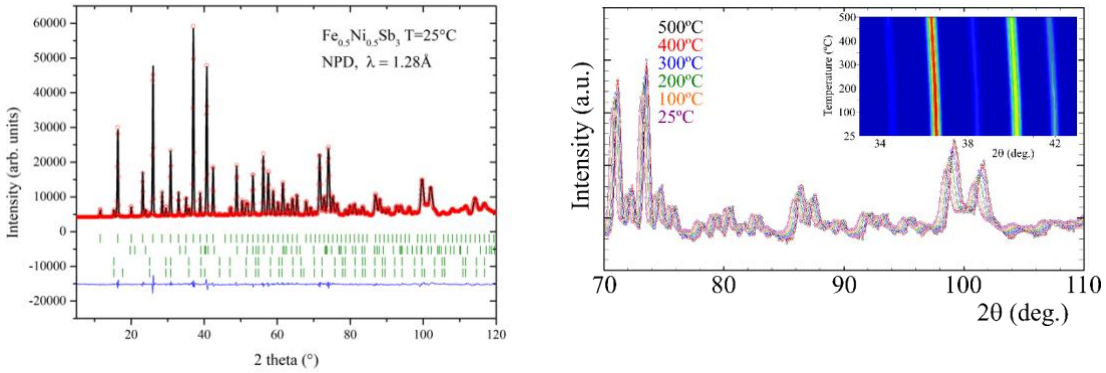

Figure 2. a) Rietveld fit of neutron powder diffraction profile for $Fe_{0.5}Ni_{0.5}Sb_3$. 2nd and 3rd rows of Bragg ticks (green) stand for secondary Sb and Fe_3O_4, which magnetic structure is included in the 4th phase. b) Temperature evolution of the NPD patterns of the same sample on selected angular regions.

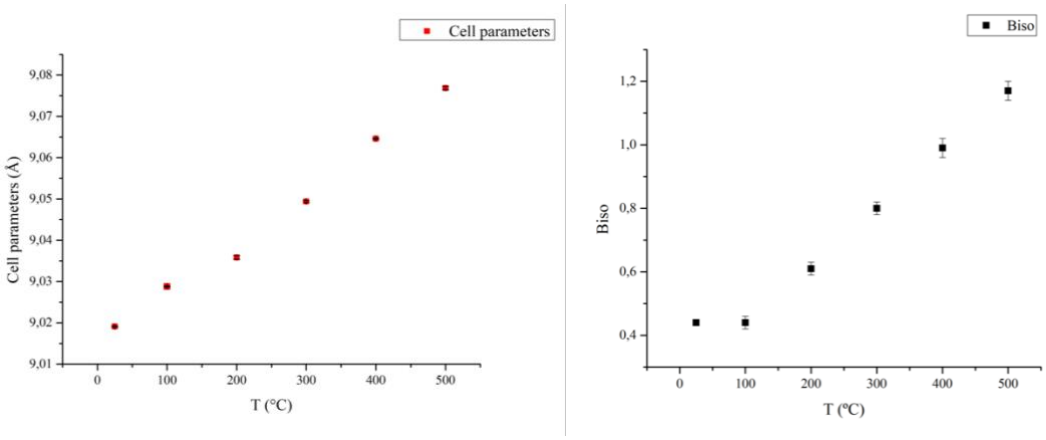

Figure 3. a) The temperature dependence of the B_{iso} factor for the sample $Fe_{0.5}Ni_{0.5}Sb_3$ b) The increase of cell parameters depending on the temperature for the sample $Fe_{0.5}Ni_{0.5}Sb_3$.

ADPs (atomic displacement parameters) will be calculated and analyzed. These values are related to the vibration of the atom or to static disorder and can be correlated with the thermal conductivity of the material, using Einstein analysis.

References

[1] Rogl, G., & Rogl, P. (2017). Current opinion in green and sustainable chemistry, 4, 50-57

[2] SEARS, Varley F. Neutron news, 3(3) (1992) 26-37

[3] Serrano-Sánchez, F., Prado-Gonjal, J., Nemes, N. M., Biskup, N., Dura, O. J., Martínez, J. L., Alonso, J. A. (2018). ACS Applied Energy Materials, 1(11), 6181-6189.