IMPROVING VERY HIGH TEMPERATURE THERMOELECTRIC PERFORMANCE OF Yb_4Sb_3 THROUGH DUAL SUBSTITUTIONS : A THEORETICAL STUDY

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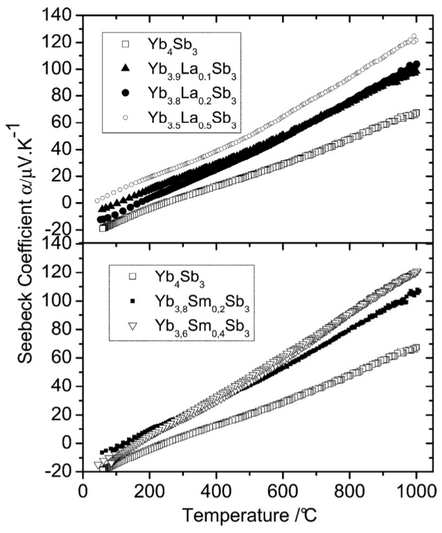
Context

Rare-earth antimonides with the anti-Th_3P_4 crystal structure were reported as potential candidates for high-temperature applications. Out of the four compositions reported in 2009 [1], the binary compound Yb_4Sb_3 stood out as the most promising composition : its Seebeck coefficient was the highest and reached 70 µV/K at 1300 K, and it was the only p-type thermoelectric conductor of the family.

Improvement attempts were conducted by substituting Yb atoms with another rare-earth, for instance with La or Sm, or by substituting Sb atoms with another pnictogen, such as Bi. Reported results show that lanthanum substitution improves thermoelectric properties, whereas bismuth substitution makes little to no change, as shown on the figure on the right.

In order to understand these differences in behaviour, the electronic structure of the La- and Bi-substituted compounds and their transport properties will be simulated.



Thermoelectricity ?

A thermoelectric material directly transforms a temperature gradient into an electrical current (Seebeck effect), or transfers heat when an electrical current is applied (Peltier effect).

For a given material, the higher the thermoelectric figure of merit ZT, the better the thermoelectric performances

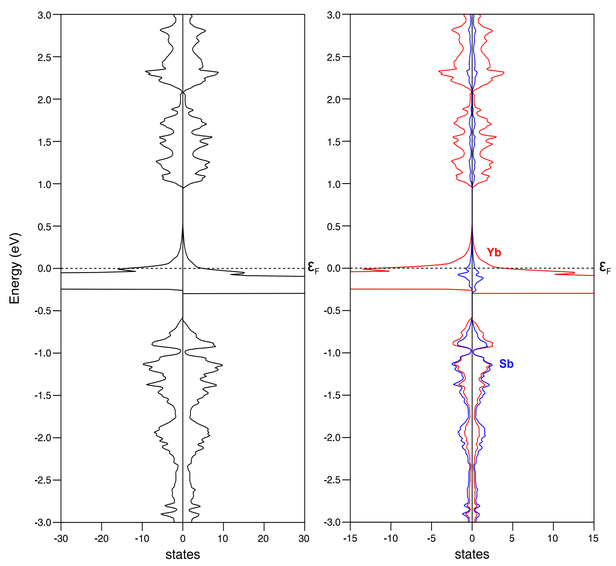
Seebeck coefficient — Electric conductivity — Electronic thermal conductivity — Lattice thermal conductivity

$$ZT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{lat}} T$$

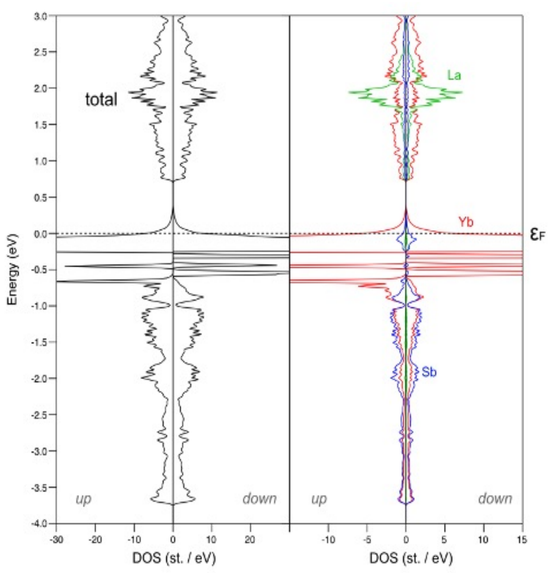
Computational details

- DOS calculated with **VASP** [2] code (v. 6.2.0) on optimized structures, PBE functional, 7x7x7 k-points
- Band-structure computed with **VASP**, PBE functional, 50 k-points per line
- Transport properties simulated with **BoltzTraP2** [3] (v. 24.1.1) on a **VASP** DOS calculation with 11x11x11 k-points

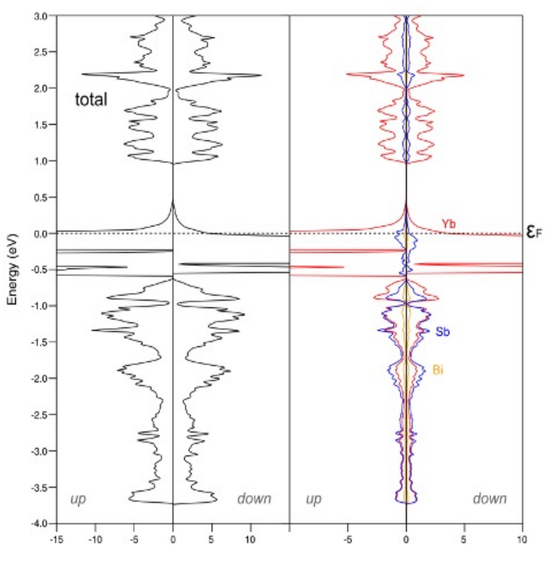
Density of states



Yb_4Sb_3



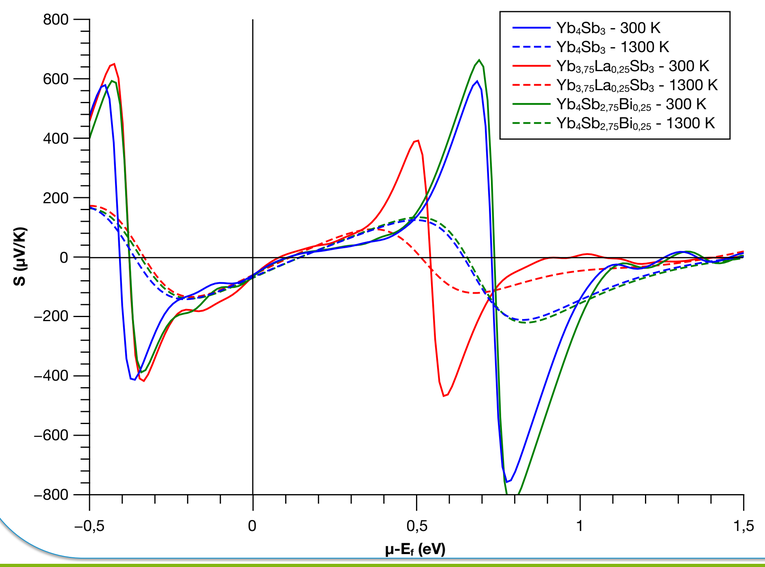
$Yb_{3.75}La_{0.25}Sb_3$



$Yb_4Sb_{2.75}Bi_{0.25}$

- **Around the Fermi level in Yb_4Sb_3 :** heavy band of f states belonging to Yb playing an important role in conduction
- **In $Yb_4Sb_{2.75}Bi_{0.25}$:** no big changes in the electronic structure. Sb states in the valence band are replaced by Bi states at the same place → no real effect on transport properties
- **In $Yb_{3.75}La_{0.25}Sb_3$:** states of the heavy band shifted towards the conduction band → will affect the transport properties

Effect of substitution on thermoelectric properties



- Around the Fermi level : better Seebeck coefficients to be achieved without tweaking too much the carrier concentration
- No noticeable difference between Yb_4Sb_3 and $Yb_4Sb_{2.75}Bi_{0.25}$ as expected
- Interest in pushing the rare-earth substitution to achieve event better Seebeck coefficients

Conclusion

- Bi substitution has no effect neither on electronic properties nor on transport properties
- La substitution shifts some rare-earth states from the valence to the conduction band, which modifies the transport properties
- Better Seebeck coefficients seem to be easily reachable without tuning too much the carrier concentration
- Interest in substituting the compounds further but not too much, as the compound is not monophasic anymore after $Yb_{3.5}La_{0.5}Sb_3$

[1] Chamoire *et al.*, Dalton Trans. **2010**, *39*, 1118-1123
[2] Kresse *et al.*, J. Phys. Rev. B. **1993**, *47*, 558-561
[3] Madsen *et al.*, J. Comput. Phys. Commun., **2018**, *175*, 67-71
[4] Bouteiller *et al.*, Mater. Adv., **2024**, *5*, 1217-1225