Unveiling the Structural Behavior under Pressure of Filled $M_{0.5}Co_4Sb_{12}$ (M = K, Sr, La, Ce, and Yb) Thermoelectric Skutterudites

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Skutterudite-type compounds based on $\square Co_4Sb_{12}$ pnictide are promising for thermoelectric application due to their good Seebeck values and high carrier mobility. Filling the 8*a* voids (in the cubic space group $Im\bar{3}$) with different elements (alkali, alkali earth, and rare earth) helps to reduce the thermal conductivity and thus increases the thermoelectric performance. A systematic characterization by synchrotron X-ray powder diffraction of different *M*-filled Co_4Sb_{12} (*M* = K, Sr, La, Ce, and Yb) skutterudites was carried out under high pressure in the range ∼0–12 GPa. The isothermal equations of state (EOS) were obtained in this pressure range and the Bulk moduli (B_0) were calculated for all the filled skutterudites, yielding unexpected results. A lattice expansion due to the filler elements fails in the description of the Bulk moduli. Topochemical studies of the filler site environment exhibited a slight disturbance and an increased ionic character when the filler is incorporated. The mechanical properties by means of Bulk moduli resulted in being sensitive to the presence of filler atoms inside the skutterudite voids, being affected by the covalent/ionic exchange of the Co–Sb and Sb–Sb bonds.

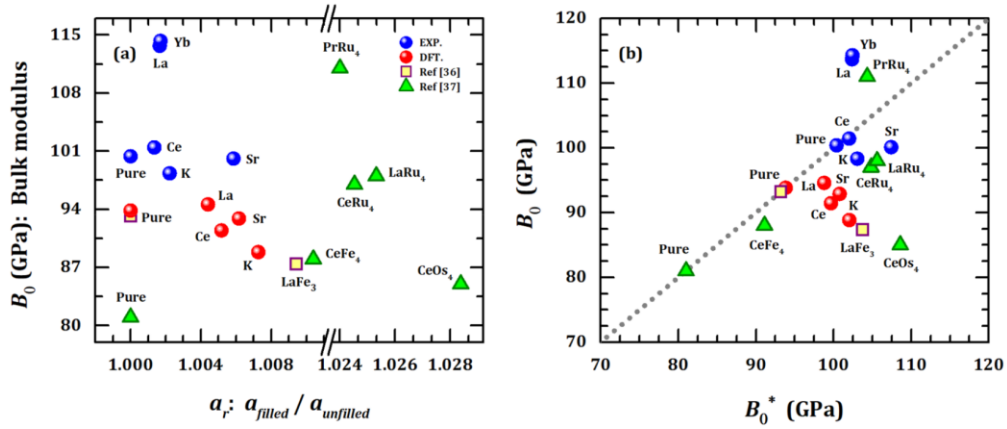

Fig. 1: (a) Bulk modulus (B_0) against the relative lattice constant a_r ($a = a_{filled}/a_{unfilled}$) for the unfilled Co_4Sb_{12} (denoted as "pure") and $M_{0.5}Co_4Sb_{12}$ skutterudites (*M* = K, Sr, La, Ce, and Yb) investigated. It also includes the B_0 values for filled skutterudites MRu_4Sb_{12} (*M* = La and Pr), CeT_4Sb_{12} (*T* = Fe, Ru, and Os) and $LaFe_3CoSb_{12}$. (b) Comparison between Bulk modulus estimated considering a simple expansion of the unit cell volume and theoretically/experimentally obtained (B_0). The grey dotted line stands for $B_0 = B_0^*$.

Keywords: Elements, Thermal conductivity, Lattices, Diffraction, Phase transitions.