Thermoelectric Properties of Transition-Metal Pnictides with Marcasite and Pyrite Structures*

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The chief ingredients in the making of a thermoelectric material are large thermoelectric power, metallic resistivity, and low thermal conductivity. Here, I will demonstrate that the transition-metal pnictides $FeAs_2$ and $PtSb_2$ exhibit a semiconductor-to-metal transition upon chemical substitution and enhanced thermoelectric properties in the metallic state.

$FeAs_2$ crystallizes in an orthorhombic marcasite structure, while $PtSb_2$ in a cubic pyrite structure. The structures consist of $FeAs_6$ or $PtSb_6$ octahedra. The $FeAs_6$ are linked on the edge, while the $PtSb_6$ at the corner. The octahedra are tilted to form diatomic molecule, namely As_2 or Sb_2, which favors an electron count of $[As_2]^{-4}$ and $[Sb_2]^{-4}$ in order to fill up the π^* molecular orbital. Thus an electron count of Fe^{4+} ($3d^4$) and Pt^{4+} ($5d^6$), together with the crystalline-electric-field splitting of the d orbital in orthorhombic or cubic symmetry, accounts for the semiconducting natures of $FeAs_2$ and $PtSb_2$.

Both compounds exhibits a transition from semiconducting to metallic state upon chemical substitution, namely $Fe(As_{1-x}Se_x)_2$ and $Pt_{1-x}Ir_xSb_2$. The former exhibits n-type transport, while the latter p-type. For $Fe(As_{1-x}Se_x)_2$ with $x = 0.05$, a resistivity of 2 mΩcm and thermoelectric power of 120 μV/K at room temperature results in a power factor of approximately 10 $\mu W/cmK^2$. For $Pt_{1-x}Ir_xSb_2$ with $x = 0.01$, we estimate a power factor of approximately 35 $\mu W/cmK^2$ using a room-temperature resistivity of 0.5 mΩcm and thermoelectric power of approximately 100 μV/K. Together with the reduced thermal conductivity, dimensionless figure of merit ZT exceeds 0.1 for $Pt_{1-x}Ir_xSb_2$ at room temperature.

Thus, transition-metal pnictides provide an appealing playground for the development of good thermoelectric materials.

*This work was done in collaboration with K. Kudo, S. Nakano, Y. Nishikubo at Okayama University.