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Bulk oxides: asymmetry between p-and n-type transport properties

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The thermoelectric power (TEP) of transition metal oxides shows large difference depending on the sign of the charge carriers. In electron-doped oxides, the best TEs in terms of the figure of merit are heavily doped transparent conductors (as doped ZnO). The physics is very similar to that of semiconductors, though the defects chemistry differs: the existence of planar defects created by the doping elements, is far from the random distribution in semiconductors. In contrast the best p-types are layered cobaltites (CdI_2 -type layers with edge-shared CoO_6 octahedras). The Co cations adopt a low spin state. Both electronic correlations and spin entropy have to be considered to explain the S(T) curve for T <150K, whereas for T>150K, the spin/orbital configurations and the doping level in the generalized Heikes formula are dominating. This description supported by the results obtained for perovskite ruthenates was recently unvalidated for the quadruple perovskite $ACu_3Ru_4O_{12}$, showing very different S(T) without S saturation up to $\sim$ 900K. Their Pauli paramagnetism enlights the role of the spins upon thermopower. Similarly, searching for other n-types, interesting TE properties have been found in $Ba_{1.2}Mn_8O_{16}$: the S(T) evidences a charge/orbital ordering in this manganite ($v_{Mn} = 3.7$) coupled to an abrupt change in the unit-cell volume. $Ba_{1.2}Mn_8O_{16}$, although of n-type, exhibits a cst. $|S| \approx 92\mu V.K^{-1}$ for T>400K, explained by the generalized Heikes formula rather used for p-type. This difference with other n-type oxides is related to the Mn^{3+}/Mn^{4+} magnetism and the contribution of e_g orbitals for the transport properties. In this presentation, the richness of the TE properties of metal transition oxides will be emphasized focusing on the important role of the spins.