Fabrication and properties of thermoelectric modules made of 3d transition-metal oxides

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Abstract

Thermoelectric energy conversion is a technology that attracts renewed interest as a new energy resource. Owing to the pressing needs for reduction of the carbon-dioxide emission, the thermoelectric power generation has received a renewed interest from the viewpoint of waste-heat recovery into electric power. In particular, there appear ever-increasing demands for energy alternative to nuclear power after the disastrous accident in Fukushima since 2011. There is a finite coupling between the electrical and entropy currents, which is known as the thermoelectric phenomena, i.e., the Seebeck or the Peltier effects because electrons / holes in solid carry the electricity together with the entropy. The thermoelectric energy conversion generates energy from the temperature gradient and/or the heat flow. The thermoelectric energy conversion efficiency is defined by the ratio between the output electrical power with the thermal entropy flux. By optimizing the efficiency with respect to a load resistance, the maximum efficiency $\eta_{\max}$ is obtained:

$$\eta_{\max} = \frac{\Delta T}{T_H} \frac{\sqrt{1+Z\langle T\rangle}-1}{\sqrt{1+Z\langle T\rangle}+T_H/T_L} = \eta_{Carnot} \frac{\sqrt{1+Z\langle T\rangle}-1}{\sqrt{1+Z\langle T\rangle}+T_H/T_L},$$

where the dimensionless figure of merit of the thermoelectric material $Z\langle T\rangle$ has been introduced:

$$Z\langle T\rangle = \frac{S^2}{\rho\kappa}\frac{T_H+T_L}{2} = \frac{PowerFactor}{\kappa}\frac{T_H+T_L}{2},$$

where S, ρ, κ are the Seebeck coefficient, the electric resistivity, and the thermal conductivity, respectively. Obviously, $\eta_{\max}$ is limited by the efficiency of the Carnot cycle η_{Carnot}, and accordingly, a higher temperature T_H with a larger temperature difference ΔT gives a larger $\eta_{\max}$. Thus, oxides are quite attractive in this respect because of the chemical stability in air at high temperature, but $\eta_{\max}$ is not satisfactory at present. After the discovery of the thermoelectric oxide: Na_xCoO_2, oxide thermoelectrics using 3d transition-metal oxides have been extensively investigated for the last decade. Compared with other thermoelectric materials, 3d transition-metal oxides are quite unique in the sense that (i) the electron correlation is strong enough to make the Heikes formula:

$$S(T\to\infty) = -\frac{k_B}{e}\ln\frac{2x}{1-x} \cong -86.2\left[\mu V/K\right]\ln\frac{2x}{1-x},$$

where x is the carrier concentration per unit cell, (ii) the resistivity is barely metallic in which the mean free path is of the order of the unit cell length, and (iii) the spin fluctuation significantly affects the properties. By using such oxides, we have fabricated thermoelectric modules made of oxides with large S. Therefore, we have chosen $[(Ca_{1-x}Y_x)_2CoO_3]_{0.62}CoO_2$ and $La_{1-x}Ca_xMnO_3$ for the *p*-type materials and $Ca_{1-x}Yb_xMnO_3$ and $Zn_{1-x}Al_xO$ for the *n*-type materials for this purpose.