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A study on thermoelectric properties of perovskite-type oxides

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Thermoelectric energy conversion technology attracts renewed interest as a new energy resource. Thermoelectric materials can directly convert waste heat from automobiles, facilities, and power plants into electrical energy. Since electrons in solids carry electricity together with thermal entropy, there is a finite coupling between the electrical and heat currents, which is known as the thermoelectric phenomena. The potentiality of the thermoelectric materials is indicated in terms of the dimensionless figure of merit, i.e., $ZT=S^2\sigma T/\kappa$, where S, σ, κ, and T are the Seebeck coefficient, the electric conductivity, the thermal conductivity, and the absolute temperature, respectively. The thermoelectric energy conversion generates energy from the temperature gradient and the heat flow. The thermoelectric energy conversion efficiency η is defined by the ratio between the output electrical power *P* with the heat flux *Q*, i.e., $\eta=P/Q$. By optimizing the efficiency with respect to a load resistance, the maximum efficiency η_{max} is obtained as a monotonically increasing function of ZT. Obviously, a higher temperature with a larger temperature difference and to be a larger ZT gives a larger η_{max}. In this respect, oxides are quite attractive because they are thermally and chemically stable for long time use at high temperatures in air for thermoelectric conversion. Recently, oxides have been studied extensively as a possible candidate for thermoelectric materials at high-temperatures since the discovery of large Seebeck coefficient (S=100μV/K) and low electric resistivity (ρ=0.2*m*Ωcm) at room temperature in the layered cobalt oxide Na_xCoO_2.[1] The misfit-layered cobalt oxide $Ca_3Co_4O_9$ has also been studied as a candidate for p-type thermoelectric materials and typically exhibits S=130μV/K, ρ=15*m*Ωcm, and κ=1.0W/mK at room temperature.[2] For instance, fabrication and power generation of oxide thermoelectric modules consisting of p-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ and n-type $La_{0.9}Bi_{0.1}NiO_3$ bulks have been reported.[3] In face, power charging a portable phone has been successful using this oxide thermoelectric module, however, the maximum efficiency η_{max} was as low as 1.4%.[4] To enhance η_{max}, Urata *et al*.[5] have built thermoelectric modules consisting of p-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ and n-type $CaMn_{0.98}Mo_{0.02}O_3$ bulks and calculated η_{max} to be 2.0% from ZT values. However, the n-type legs were damaged by thermal stress between the alumina substrate. [5] To overcome the lack of oxide thermoelectric materials, we have paid attention to perovskite-type oxides which form both n-type and p-type conductors, since many kinds of metal elements can fit into the perovskite structure with the general formula ABO_3. Perovskite-type oxides such as titanate, manganate, ferrate, and cobaltate phases reveal a large Seebeck coefficient, S, which is one of the essential prerequisites for potential thermoelectric materials. The large S values are caused by a strong interplay between charge, orbital states, electron spin states, and crystal structure. Koshibae *et al*.[6] proposed that the high-temperature limit of S values in 3d transition metal oxides is given by Heikes formula from a localized picture. When both a degeneracy of spin and orbital degrees of freedom of 3d transition metal and the Heikes formula give large values, the large S at room temperature can be expected. Therefore, control of spin and orbital states of 3d transition metal ions would improve the ZT values of thermoelectric oxides. In this paper, the thermoelectric properties S, ρ, and κ, of the perovskite-type oxides, $Pr_{1-x}Sr_xMnO_3$, $Pr_{1-x}Ca_xMnO_3$, and $La_{1-x}Sr_xFeO_3$ will be investigated in order to clarify the possibility of the thermoelectric modules consisting of perovskite-type oxides.

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