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Unconventional Reduction of Thermal Conductivity in Thermoelectric Oxides

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Abstract – High thermal conductivity values generally observed for oxide thermoelectric materials are shown to be reduced efficiently by some unconventional ways, in which a slight change in crystal structure or a small amount of additives only slightly changes the mean free path of phonons, but greatly reduces the sound velocity, leading to a marked reduction of the thermal conductivity. Examples are shown for $SrCoO_3$-based perovskite with structural phase transition, and co-doped ZnO. In particular, the lattice thermal conductivity of ZnO is selectively suppressed with maintaining the carrier mobility, demonstrating that such an unconventional thermal conductivity reduction is promising to develop thermoelectric oxides with higher *ZT* values.

The lattice thermal conductivity, κ_{ph}, of metal oxides is known to be generally high, mainly because of the small atomic mass of oxygen, the major constituent element of oxides. This fact has been claimed as an inherent disadvantage of oxide materials for thermoelectric applications. In fact, the thermal conductivity, κ, of ZnO is as high as *ca.* 50 W/m K at room temperature, resulting in a rather low thermoelectric figure-of-merit, $Z = S^2\sigma/\kappa$, of ZnO-based materials despite their quite high $S^2\sigma$ values, where S is the Seebeck coefficient and σ is electrical conductivity. These facts, on the other hand, imply that if the high κ_{ph} values of ZnO can be reduced effectively with maintaining the σ values, high Z values should be expected. However, conventional methodology for κ reduction such as alloying effect (solid solution formation) and inclusion effect has been revealed to be ineffective for ZnO, because such a way indeed reduces κ, but σ decreases more. These results suggest that ordinary phonon scattering centers might scatter electrons more effectively.

$SrCoO_3$-based perovskite-type oxides are generally oxygen-deficient, and are known to undergo a structural phase transition between the orthorhombic brownmillerite (BM) structure and the cubic perovskite (P) structure. Whereas oxygen vacancies in the BM phase align along the [110] direction, those in the P phase randomly distribute. The structural phase transition between the BM and P phases is therefore an order-disorder transition of the oxygen ion sublattice in the oxide, and we expected that the disordered oxygen vacancies might act as selective scattering centers for phonons, because the conduction band of the oxide predominantly consists of the Co3d orbitals. A sample piece of the oxide was held at a given temperature, T_q, for 24 h in air, and then quenched into liquid N_2 in order to freeze instantly the crystal structure at T_q, quenched temperature. The thermal diffusivity, α, being proportional to $\kappa = \alpha \cdot C_p \cdot \rho$ in this case ($C_p \cdot \rho$ is the specific heat per unit volume and was confirmed to be virtually constant), was measured at room temperature. The sample piece was subsequently held at 1200 °C for 24 h in air and cooled down slowly, followed by the α measurement at room temperature in order to confirm that the changes in α against T_q are completely reversible. This sequence was repeated over various T_q from 300 °C to 1200 °C on a single sample piece. As shown in Fig. 1, the α value of the oxide greatly reduced to almost a half of the original value when the sample was quenched at around 800 °C. Surprisingly, the sound velocity also decreased in a manner virtually the same as that of α, indicating that the reduction in α is predominantly due to the decrease in the phonon velocity but not the phonon mean free path. The Rietveld refinement of the XRD patterns of the oxide revealed that the oxide mainly consists of the P phase at room temperature, and transforms to the BM phase at high temperature via a 2-phase coexisting region at 600 - 900 °C. These results strongly suggest that the reduction of α, and hence κ, at around 800 °C cannot be rationalized by an enhanced scattering of phonons by randomly distributed oxygen vacancies. Since the 2-phase region coincides with the suppression of the sound velocity, a wider distribution of the M-O bond lengths and bond angles at the P-to-BM phase transition might cause a decrease in the phonon group velocity.

A similar decrease in the sound velocity was also observed for ZnO co-doped with Al and Ga. Consequently, a marked suppression in κ of the oxide resulted in a substantial increase in ZT up to 0.65 [1] from 0.3 for Al-doped ZnO. Moreover, selective suppression of κ_{ph} was confirmed for co-doped ZnO by an increase in the mobility-to-κ_{ph} ratio, μ/κ_{ph}.

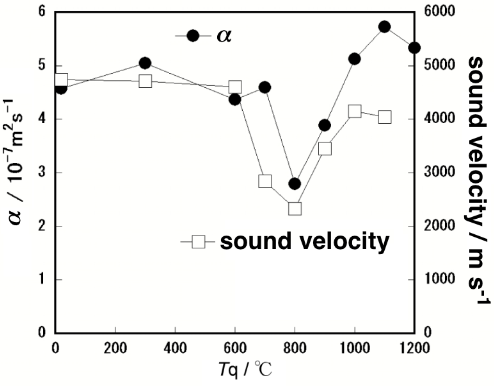

Figure 1: Thermal diffusivity, α, and sound velocity measured at room temperature for a single sample piece of $SrCoO_3$-based oxide quenched at various T_q.

Reference

[1] M. Ohtaki, K. Araki, Y. Yamamoto, *J. Electron. Mater.*, **38** (2009) in press, DOI:10.1007/s11664-009-0816-1.