Coating Thermoelectric Devices To Suppress Sublimation
Thermoelectric materials are covered with adherent, chemically stable metal outer layers.

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A technique for suppressing sublimation of key elements from skutterudite compounds in advanced thermoelectric devices has been demonstrated. The essence of the technique is to cover what would otherwise be the exposed skutterudite surface of such a device with a thin, continuous film of a chemically and physically compatible metal. Although similar to other sublimation-suppression techniques, this technique has been specifically tailored for application to skutterudite antimonides.

The primary cause of deterioration of most thermoelectric materials is thermal decomposition or sublimation—one or more elements sublime from the hot side of a thermoelectric couple, changing the stoichiometry of the device. Examples of elements that sublime from their respective thermoelectric materials are Ge from SiGe, Te from Pb/Te, and now Sb from skutterudite antimonides. The skutterudite antimonides of primary interest are CoSb₃ [electron-donor (n) type] and CeFe₃–CoSb₃ [electron-acceptor (p) type]. When these compounds are subjected to typical operating conditions [temperature of 700 °C and pressure <10⁻³ torr (0.0013 Pa)], Sb sublimes from their surfaces, with the result that Sb depletion layers form and advance toward their interiors. As the depletion layer advances in a given device, the change in stoichiometry diminishes the thermal-to-electric conversion efficiency of the device.

The problem, then, is to prevent sublimation, or at least reduce it to an acceptably low level. In preparation for an experiment on suppression of sublimation, a specimen of CoSb₃ was tightly wrapped in a foil of niobium, which was selected for its chemical stability. In the experiment, the wrapped specimen was heated to a temperature of 700 °C in a vacuum of residual pressure <10⁻³ torr (0.0013 Pa), then cooled and sectioned. Examination of the sectioned specimen revealed that no depletion layer had formed, indicating the niobium foil prevented sublimation of antimony at 700 °C. This was a considerable improvement, considering that uncoated CoSb₃ had been found to decompose to form the lowest antimonide at the surface at only 600 °C. Evidently, because the mean free path of Sb at the given temperature and pressure was of the order of tens of centimeters, any barrier closer than tens of centimeters (as was the niobium foil) would have suppressed transport of Sb vapor, thereby suppressing sublimation of Sb.

Coatings of thermoelectric devices with adherent, chemically stable metal outer layers are of particular interest for devices that must operate at high temperatures in an environment where sublimation of Sb is a problem.