PROGRESS STATUS OF THE DEVELOPMENT OF HIGH-EFFICIENCY SEGMENTED THERMOELECTRIC COUPLES

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Introduction: Radioisotope Thermoelectric Generators have been successfully used to power spacecrafts for deep space missions as well as for terrestrial applications where unattended operation in remote locations is required. They have consistently demonstrated their extraordinary reliability and longevity (more than 30 years of life). NASA's Radioisotope Power Systems Technology Advancement Program is pursuing the development of more efficient thermoelectric technologies that can increase performance by a factor of 2 to 4X over state-of-practice systems that are limited to device-level efficiencies of 7.5% or less, and system-level specific power of 2.8 to 5 W/kg. Over the last few years, under the Advanced Thermoelectric Couples (ATEC) task, several advanced high-temperature thermoelectric materials, including n-type $La_{3-x}Te_4$, p-type $Yb_{14}MnSb_{11}$, and n- and p-type filled skutterudites, have been developed for integration into advanced power generation devices at the Jet Propulsion Laboratory (JPL). The stability of their thermoelectric properties has been demonstrated for over 10,000 hours up to 1273K. Stable metallization and sublimation suppression barriers/coatings have been successfully developed. JPL is now focusing on developing segmented couples based on these high-temperature materials to achieve high conversion efficiencies. Recent performance tests have demonstrated 11 to 15% conversion efficiencies with cold and hot-junction temperatures in the 423-473K and 973–1273K range, respectively.

Components development status: Figure 1 illustrates advanced thermoelectric (TE) materials segmentation in the advanced couples under development at the Jet Propulsion Laboratory. The synthesis of these materials, using a ball milling technique, has been reproducibly scaled up to ~100-200g batches. n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$ are used as the high-temperature segments and are capable of operating at temperatures up to 1273K. Both of these materials exhibit ZT values greater than 1 at 1273K. Between 873K and 1273K, the average ZT values for n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$ are ~ 1.0 and ~1.1, respectively. The lower segments are made of skutterudite (SKD) materials: p-$Ce_{0.9}Fe_{3.5}Co_{0.5}Sb_{12}$ and n-$(Ba,Yb)_xCo_4Sb_{12}$. The average ZT values for the skutterudite materials over the 600 C – 200C temperature range are 1.1 and 0.7 for the n-type and p-type materials, respectively. SKD materials are capable of long-term operation at temperatures up to 873K. Figure 2 shows the TE figure of merit values for both these new materials and state-of-the-art TE materials that have been employed in the GPHS and MMRTG RTGs. Extended TE property life tests for these materials have shown that their thermoelectric properties were virtually unchanged after up to 1 year of testing up to 1323K for n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$ and up to 923K for SKD materials. Testing is continuing to further assess and model the variations of the advanced TE materials TE properties over time.

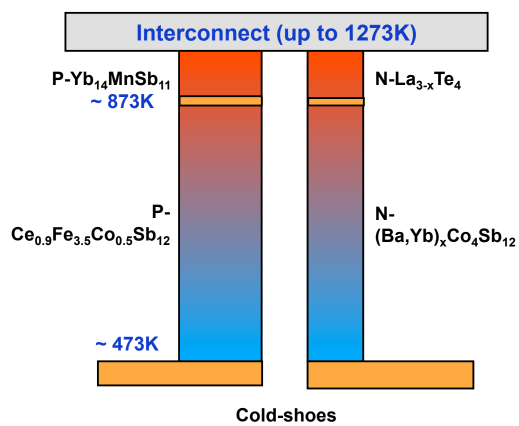

Figure 1. Illustration of the segmented couple under development at the Jet Propulsion Laboratory.

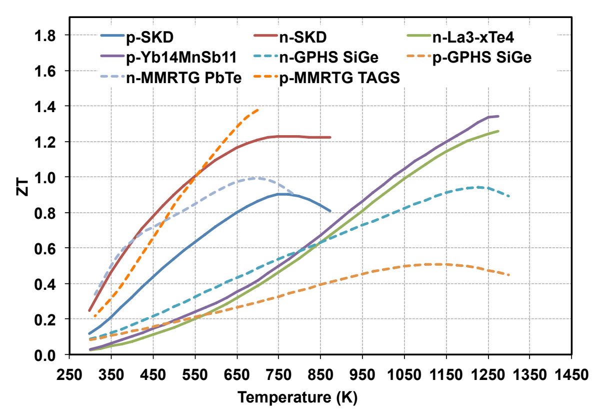

Figure 2. Thermoelectric figure of merit, ZT, as a function of temperature for ATEC TE materials and state-of-the-art GPHS and MMRTG TE materials.

A sublimation suppression coating has been developed for $Yb_{14}MnSb_{11}$ and sublimation rates on the order of 4 x 10^{-6} g/cm^{2}hr have been achieved and maintained over up to 8,000 hrs. The sublimation rate for uncoated $La_{3-x}Te_4$ is on the order of 10^{-6} g/cm^{2}hr at 1173K and a sublimation coating, only required for long-term operation at temperatures above 1173K, is under development. Sublimation suppression has been demonstrated for up to 6,000 hrs at 873K for SKD coupons encapsulated in aerogel.

Advanced thermoelectric couples development status: A metallization for skutterudite materials was developed and was demonstrated to be stable for more than 5,000 hrs up to 873K. An initial metallization has also been developed for n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$. Optimization of the high-temperature segments metallization is in progress. A first iteration spring-loaded couples composed of n-type $La_{3-x}Te_4$, p-type $Yb_{14}MnSb_{11}$ upper segments and skutterudite lower segments (as illustrated in Figure 1) have been fabricated and tested in a vacuum environment. Figure 3 shows a n-$La_{3-x}Te_4$/n-$(Ba,Yb)Co_4Sb_{12}$ and p-$Yb_{14}MnSb_{11}$/p-$Ce_{0.9}Fe_{3.5}Co_{0.5}Sb_{12}$ spring-loaded couple in a test fixture.

Figure 4 shows the calculated and demonstrated efficiency values for n-$La_{3-x}Te_4$/n-$(Ba,Yb)Co_4Sb_{12}$ and p-$Yb_{14}MnSb_{11}$/p-$Ce_{0.9}Fe_{3.5}Co_{0.5}Sb_{12}$ couples as a function of hot- and cold-junction temperatures. Test performance results have demonstrated 10 to 15% conversion efficienciy values at beginning of life with couple cold- and hot-junction temperatures in the 425–475K and 973-1273K, respectively. When operating at a hot-junction of 973K (typical MMRTG couples hot-junction temperature), the advanced couples operate at an efficiency of about 10%, about a 40% improvement over MMRTG couples for the same temperature gradient. Life testing is in progress to assess the degradation mechanisms for these first iteration couples and to provide input for the development of improved couple interfaces that will be incorporated into a second iteration couple build.

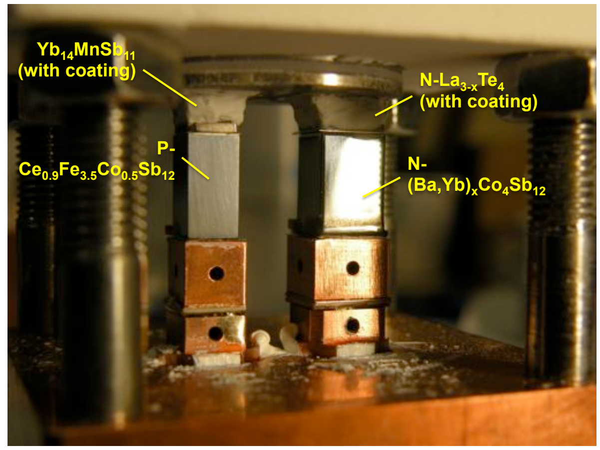

Figure 3. Photograph of n-$La_{3-x}Te_4$/n-$(Ba, Yb)Co_4Sb_{12}$ and p-$Yb_{14}MnSb_{11}$/p-$Ce_{0.9}Fe_{3.5}Co_{0.5}Sb_{12}$ advanced spring-loaded couple in a test fixture.

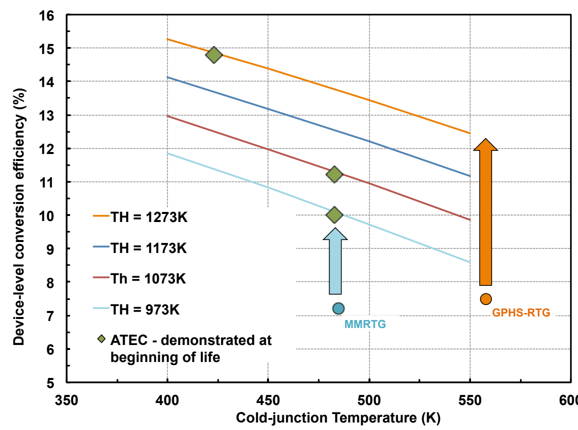

Figure 4. Calculated and demonstrated n-$La_{3-x}Te_4$/n-$(Ba,Yb)Co_4Sb_{12}$ and p-$Yb_{14}MnSb_{11}$/p-$Ce_{0.9}Fe_{3.5}Co_{0.5}Sb_{12}$ couple efficiency values. The efficiency values for MMRTG and GPHS RTG couples are also plotted for comparison.