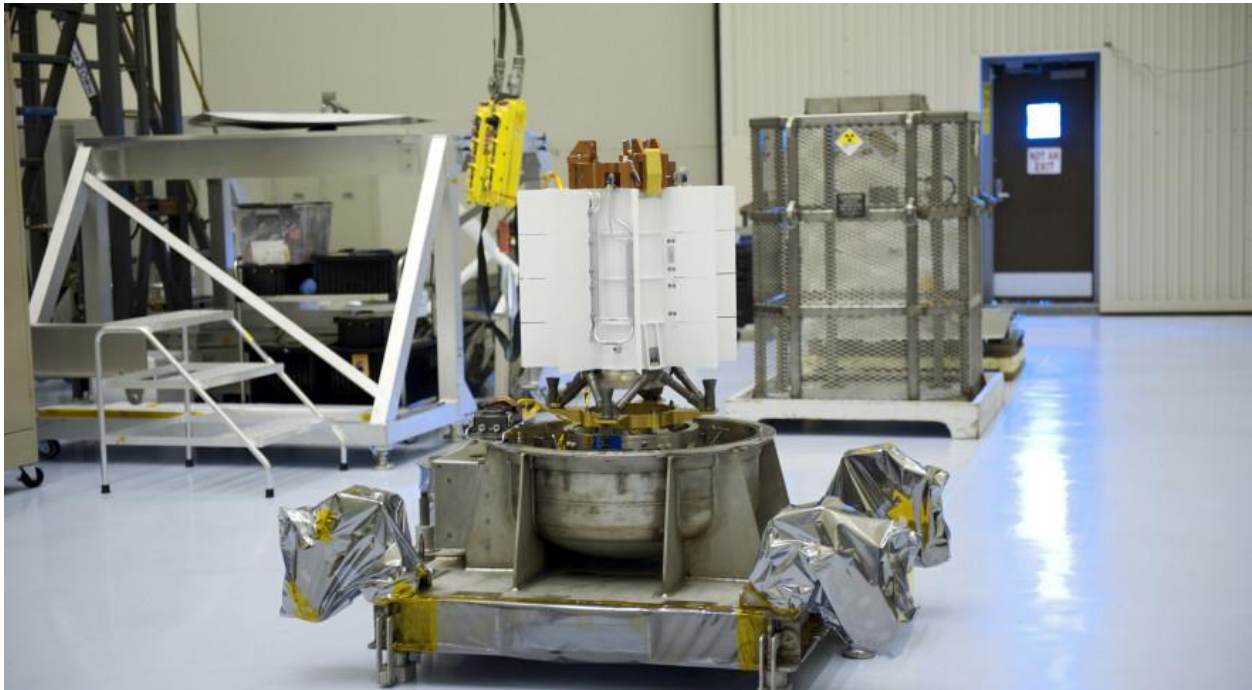


Enhancing NASA's Multi-Mission Radioisotope Thermoelectric Generator Using Highly Efficient Thermoelectric Materials

Jeff Houtmann



A pre-installation image of the MMRTG used on the Curiosity Rover

Source: <http://wordpress.mrreid.org/2011/12/14/curiosity-rover-nuclear-batter/>

Abstract

This project proposal aims to enhance NASA's Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) by identifying and analyzing new material technologies that have been researched for their excellent thermoelectric properties at higher temperatures. By choosing the most efficient thermoelectric material available, the MMRTG's energy conversion efficiency will be greatly improved as thermoelectric generator efficiencies are largely determined by the properties of the materials within the thermocouple devices used to convert the heat into energy. A project that focuses on enhancing the MMRTG is imperative for the future of space exploration as there is global shortage of plutonium fuel production, limiting future missions to available supplies. A more efficient generator will minimize the use of this fuel while maximizing power output, allowing for increased mission capabilities and better conservation of the scarce plutonium fuel. In this report, lanthanum telluride, $\text{Yb}_{14}\text{MnSb}_{14}$, and a multiple-filled skutterudite (SKD) compound are analyzed for their excellent thermoelectric performance. The multiple filled SKD compound is chosen as the ideal material to enhance the MMRTG based on the low cost and low risks associated with the material while producing a nearly identical efficiency relative to the other candidates.

Keywords: eMMRTG, MMRTG, thermoelectric materials, thermoelectric generator, efficiency

Document Scenario

This paper presents a project proposal to enhance NASA's MMRTG. This document may be written for NASA's Radioisotope Power Systems Program and associated developers like the U.S. Department of Energy in hopes to receive funding and approval for developing an enhanced model of the MMRTG. The executive summary is prepared for NASA officials responsible for assigning funding to important technology development projects.

Executive Summary

When NASA missions require spacecraft to operate in the cold and dark environments of deep space, or the dusty atmospheres of planetary bodies like Mars, scientists and engineers depend on reliable plutonium-powered generators to supply spacecraft with heat and electricity where solar power is no longer a feasible option. While NASA has had a successful history with these so-called radioisotope thermoelectric generators (RTGs), their studies have shown that global supplies in the plutonium fuel are diminishing. With NASA's interests set on the exploration of Mars and the moons of outer planets, the demand for the plutonium fuel source that powers these generators is expected to outpace production rates within the next decade. This is highly problematic as future space exploration will be limited to the little fuel that is available, inherently preventing advances in science and our understanding of the solar system. This project seeks to mitigate the current plutonium shortage by enhancing the current model Multi-Mission RTG (MMRTG) with the most ideal advanced thermoelectric material that would directly increase energy conversion efficiencies, resulting in a generator that can produce more power per unit using significantly less fuel.

The efficiencies of thermoelectric generators are mainly determined by the temperature range in which it operates in and the properties of the thermoelectric materials used to acquire a voltage from a temperature difference. The temperature range for the MMRTG is limited by factors like the exterior environment, material properties, and specific design constraints. Depending on the environment, the cold side of the enhanced MMRTG (eMMRTG) could range from 100 – 200 °C. Hot side temperatures ideally should be maximized but are limited to factors that cause material properties to deteriorate at very high temperatures and a restriction that the exterior radiator fins cannot get hotter than 200 °C due to the risk of damaging the system.

After thorough research and thoughtful considerations of design constraints, the best material to enhance the MMRTG's efficiency is proposed to be a compound called a multiple-filled skutterudite (SKD) of the formula $\text{Ba}_{0.08}\text{La}_{0.05}\text{Yb}_{0.04}\text{Co}_4\text{Sb}_{12}$. This material has shown to have excellent thermoelectric properties that allow for a nearly identical efficiency at much safer temperatures and a lower cost compared to the scope of solutions considered. Its lower operating temperature would provide much less of a risk of overheating while still being able to supply an efficiency increase on the same scale as high temperature material solutions.

Due to the low risk, low cost, and high efficiency of the SKD compound, a project that utilizes this material to enhance the MMRTG is highly feasible. The result of replacing existing technology with SKD technology would immediately have impacts on the plutonium shortage. eMMRTG models utilizing the SKD material would require less fuel per unit to supply the energy requirements of future space missions, which in effect would lower the projected demands to better compliment production rates. Having less of a demand for fuel will allow for more plutonium to be available for future missions and reduce mission limitations due to the lack of available supply.

Table of Contents

Problem Analysis 7

Overview of Problem and its Significance 7

Engineering Fundamentals of the Problem 9

Lessons from Prior Responses to the Problem 11

Project Objectives and Constraints 12

Candidate Solutions 14

Scope of Solutions Considered..... 14

Explanation of Candidate Solutions 14

 Solution 1: Lanthanum Telluride TECs 15

 Solution 2: $\text{Yb}_{14}\text{MnSb}_{11}$ TECs..... 17

 Solution 3: Multiple-Filled Skutterudite TECs..... 18

Comparative Assessment of Candidate Solutions..... 20

Recommended Solution..... 23

Design and Implementation Challenges 23

Conclusion 24

Glossary 26

Bibliography 27

List of Figures

Figure 1: NASA projections of Pu balance..... 8

Figure 2: Cutaway view of the MMRTG and its components..... 9

Figure 3: Hall concentrations vs. $\text{La}_{3-x}\text{Te}_4$ compositions with a trendline of $n = n_{max}(1 - 3x)$
..... 16

Figure 4: ZT values vs. temperature for different Hall concentrations..... 16

Figure 5: ZT values of the different Mn concentrations 18

Figure 6: Thermal conductivities and ZT values of multiple filled SKDs vs. temperature..... 19

Figure 7: Cost of the different TE materials (Euro/kg)..... 22

Figure 8: NASA's technology readiness levels 24

List of Tables

Table 1: Comparative assessment of candidate materials..... 21

Problem Analysis

This section will provide a synopsis of the engineering problem as well as introduce key information necessary to understand when considering how to confront such a design challenge. The problem analysis will also address what can be learned from similar approaches in the past and identify the main objectives and constraints of this project.

Overview of Problem and its Significance

The United States' National Aviation and Space Agency (NASA) is looking forward to completing a number of future missions to planetary bodies like Mars and the moons of Jupiter and Saturn ("NASA and ESA," 2009). When considering the design challenges that accompany the cold, dark environment of deep space, NASA scientists and engineers have used radioisotope thermoelectric generators (RTGs) to power and supply heat to the scientific instruments aboard spacecraft where solar power is no longer reliable (Cataldo & Bennett, 2011). RTGs of the past have only been able to operate in vacuum environments, but the endeavor to explore planets and moons with atmospheres required for the creation of a more versatile Multi-Mission RTG (MMRTG) that could function in both vacuum and atmospheric environments (Cataldo & Bennett, 2011).

RTGs convert the heat generated by a decaying radioisotope into electricity via an assembly of thermoelectric (TE) materials that are referred to as thermoelectric couples (TECs) ("Radioisotope Power Systems." n.d.). According to NASA, the only known radioisotope that meets the necessary criteria for space missions is plutonium-238 ("About Plutonium-238," n.d.). This isotope has a variety of desirable properties including its ability to produce large amounts of heat while having a long half-life and being safe enough for its applications ("About Plutonium-238," n.d.). While Plutonium-238 (Pu-238) has shown to be the most effective isotope for RTG applications, there lies a major problem in the fact that it is severely limited in global supply.

To address this issue, the US government has provided NASA a means to start domestic production of mission grade Pu-238 in collaboration with DOE National Laboratories at an estimated rate of about 1.5 kg per year (Howe, Crawford, Navarro, & Ring, n.d.). A feasibility study on the reproduction of Pu-238 completed by NASA shows that even with new production of plutonium, demands will still outweigh supplies (Howe, et al., n.d.). This trend can be seen in the following figure relating the projected supply and demand of Pu-238 provided in a presentation about the study.

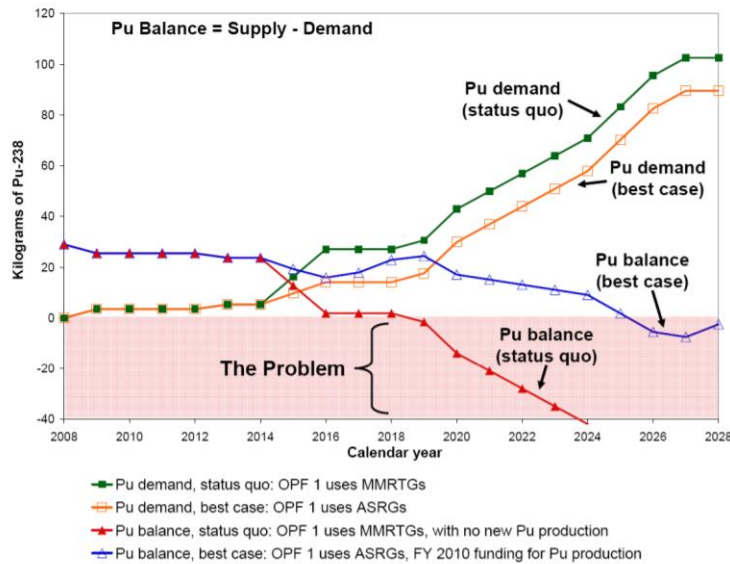


Figure 1: NASA projections of Pu balance

Source: https://www.nasa.gov/pdf/636900main_Howe_Presentation.pdf

The green trendline shows that the predicted demand of pu-238 when using MMRTGs will reach nearly 100 kg by the late 2020s. The blue and orange trendlines describe the supply and demand when utilizing the developing Advanced Sterling Radioisotope Generator (ASRG) technology, but the ASRG program was later canceled due to budget constraints, leaving the MMRTG as the currently available option (Wilson & Wong, 2014). Considering the US is planned to only produce an estimated 1.5 kg of Pu-238 per year, there would not be enough plutonium to meet the projected demands for the next decade unless production is increased significantly.

Due to the MMRTG’s fuel source being in such limited supply, future enhanced MMRTGs (eMMRTGs) will need to be improved to minimize the usage of plutonium. By

upgrading the TECs that take advantage of highly efficient TE materials, the next generation of eMMRTGs will not only increase power outputs for more capable systems, but more importantly require less of the scarce plutonium fuel to produce the necessary power. As future missions will be limited to available fuel supplies, a project that focuses on optimizing the eMMRTG is paramount for the future of space exploration and the advancement of our understanding of the solar system.

Engineering Fundamentals of the Problem

The MMRTG functions by converting the heat released by decaying Pu-238 into electricity via the Seebeck effect, a phenomenon where contact between different conductive materials kept at a temperature difference can produce a voltage (Lee & Bairstow, 2015). The voltage is acquired via thermocouple devices (TECs), or assemblies of TE materials (Lee & Bairstow, 2015). The plutonium is nested inside of several general-purpose heat source (GPHS) modules that deliver heat to the hot junctions of the TECs, while their cold junctions are maintained by the exterior environment (Lee & Bairstow, 2015). The figure below provides a cut-away view of the MMRTG model labeling its main components.

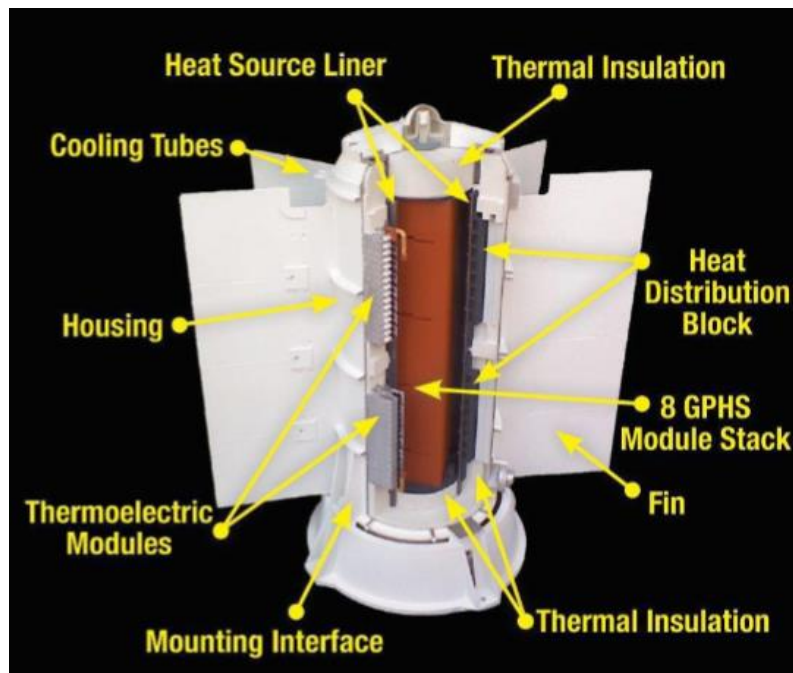


Figure 2: Cutaway view of the MMRTG and its components

Source: <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160010064.pdf>

The efficiencies of all thermoelectric generators (TEGs) largely relate to specific properties of the materials used in their designs. (Zhang & Zhao, 2015). The general equation for determining the energy conversion efficiency of a TEG is given by the constant property model that describes the maximum efficiency as:

$$1) \eta_{max} = \eta_c \cdot \frac{\sqrt{1+ZT_{avg}}-1}{\sqrt{1+ZT_{avg}}+\frac{T_C}{T_H}}$$

where η_c , T_H , and T_C are the Carnot efficiency ($\frac{T_H-T_C}{T_H}$), hot junction temperature, and cold junction temperature values, respectively. (Armstrong et al., 2017). The quantity Z is a dimensionless TE figure of merit used to evaluate the performance of a TE material, where ZT_{avg} is the Z value (often written as ZT) at the average temperature of a projected operating range (Armstrong et al., 2017). The TE figure of merit can be described by:

$$2) Z = \frac{S^2}{\rho\kappa}$$

Where S is the material's Seebeck coefficient, a constant relating the produced voltage of a material in response to a temperature difference, ρ is its electrical resistivity (sometimes described as electrical conductivity, which is the inverse of resistivity), and κ is the material's thermal conductivity (Armstrong et al., 2017).

Equations 1 and 2 are part of the constant property model for determining the efficiencies of TEGs, which assumes that the material properties remain constant over a given temperature range (Armstrong et al., 2017). There does exist accurate ways to calculate the maximum efficiency of a TEG that account for temperature dependencies, however, these methods of calculation require complex number simulations or advanced mathematics. (Armstrong et al., 2017). The constant property model tends to overestimate efficiency values and is not applicable in materials that have properties with high temperature dependence, but it is otherwise useful for an evaluation of TE materials so long as the ZT value at the average temperature is used (Armstrong et al., 2017).

Since the goal is to identify the most desirable TE material, equation 1 will be used in this paper as a comparison tool, using average ZT values over a temperature range to compare candidate materials based on available data rather than precisely compute efficiencies for the

selected materials. The justification behind this is that in general, materials with the highest ZT values over the largest temperature ranges will produce the most efficient TEGs (Zhang & Zhao, 2015).

Lessons from Prior Responses to the Problem

NASA has had much success in flagship missions relying on RTG technology, with many of them still currently active. Voyagers 1 and 2 have been in operation since the late 1970s using Multi-Hundred-Watt RTGs, and Voyager 2 exceeded mission requirements was able to be retargeted after its primary mission to send the first pictures of Uranus and Neptune back to Earth (Cataldo & Bennett, 2011). NASA's Galileo orbiter equipped with General-Purpose Heat Source RTGs also surpassed requirements and the Galileo mission was extended multiple times (Cataldo & Bennett, 2011). The most recent RTG, the MMRTG, has been successfully powering the Mars Science Laboratory Curiosity rover since it landed in 2012, and another MMRTG has been announced to be used for the Mars 2020 rover (Cataldo & Bennett, 2011).

While RTGs of the past have been largely successful, attempts at increasing conversion efficiencies within radioisotope generator systems have not. Lee and Bairstow (2015) have shown that even the latest RTG models have not been able to achieve conversion efficiencies much above six percent (p. 8), but NASA has been working on creating an Advanced Stirling Radioisotope Generator (ASRG) with The U.S. Department of Energy and Lockheed Martin in hopes to achieve efficiencies on the order of four times that (Wilson & Wong, 2014). The ASRG was designed to utilize the higher efficiency Stirling cycle by obtaining work from heat-driven pistons rather than TECs, but the program had to be terminated in 2013 for budget reasons (Wilson & Wong, 2014). Despite termination, NASA has still continued research but as of 2015 a flight ready model may not be ready until as late as 2030 due to long-term testing that needs to be completed, whereas an eMMRTG flight system is estimated to be ready by 2022 (Lee & Bairstow, 2015).

The important lesson to be learned from this is that a project focusing on enhancing the MMRTG involves less risk, as much of the technology to be utilized already exists and has proven itself to work in space applications. The only major changes would be made to the thermoelectric couple technology as the eMMRTG is expected to rely on the same design as the

MMRTG, expediting testing processes and reducing the burden on budgets (Lee & Bairstow, 2015). These factors suggest that enhancing the MMRTG allows for a much more practical and immediate response to the current pu-238 shortage before other technologies become more mature.

Project Objectives and Constraints

The main objective of this project is to identify candidate high performance TE materials that pose a high interest for their applications in enhancing NASA's MMRTG and propose the most efficient material in order to achieve this goal. By selecting the most promising TE material available, NASA will be able to create the next generation of eMMRTGs that maximize power output while minimizing the use of Pu-238 fuel. These specific outcomes of creating a more efficient MMRTG are crucial for the future of space exploration for the following reasons:

- More efficient use of scarce pu-238 fuel
 - Hammel, Otting, Bennett, Keyser, and Sievers reported that spacecraft for future missions like Europa requiring 5 MMRTG units would only require 4 eMMRTGs, saving 20% to 33% in fuel (n.d.)
- A more powerful generator will increase mission capabilities by being able to supply more power per unit than currently possible

When attempting to increase the efficiency of the current MMRTG, there are several physical design restrictions that need to be considered. Many of the physical constraints of this project can be observed in the equations previously explored. The first limiting parameter for the maximum efficiency of a TEG is its Carnot efficiency, defined to be the ratio of the temperature difference to the hot junction temperature, which is largely why higher temperature differences are preferred for these applications. Term two of equation 1 limits the Carnot efficiency further depending on the average ZT and the operating temperature range. The temperature ranges and average ZT values are limited mainly by material properties and the environment that the eMMRTG will be exposed to.

While one of the goals in maximizing TEG efficiency is to have a wide temperature range, this comes with its complications. Certain materials can degrade at higher temperatures,

restricting the hot junction temperature and requiring the material to be sealed with a cover gas and additional insulation to protect the TECs, adding size and mass to the unit (Lee & Bairstow, 2015). The root fin temperature of the eMMRTG is to be between 50 °C and 200 °C, which is a stricter design limitation as NASA pointed out that “[e]xcursions outside of [this range] would likely shorten the life of a generator or threaten components in other ways” (Zakrajsek, Cairns-Gallimore, Otting, Johnson, & Woerner, 2016, p. 11). This is especially important to consider when attempting to design a model with extremely high hot junction temperatures as it would be increasingly difficult to maintain root fin temperatures with increases in the hot junction temperature. As for the eMMRTG’s cold junction temperature, this will depend on the environment and is expected to be between 100 and 200 °C (Lee & Bairstow, 2015). The physical limitations, material properties, and the operating environment are the main constraints to consider when attempting to maximize the efficiency for future eMMRTGs.

Candidate Solutions

This section of the report will identify three candidate materials for their potential in enhancing the MMRTG. This section includes explanations on why these materials were selected, an analysis of each material and their desirable properties, and a side-by-side comparison of the materials.

Scope of Solutions Considered

Ideal materials for thermoelectric applications are those that have a large Seebeck coefficient with a low electrical resistivity and thermal conductance. More importantly, these properties must remain consistent and stable over a large temperature range. Equations 1 and 2 defined in the Engineering fundamentals of the problem section of this report show that materials with such properties will result in large average ZT values and a higher Carnot efficiency which will ultimately increase TEG efficiency. The solutions selected are those that have gained interest from NASA for RTG applications and have been studied to have the desirable thermoelectric properties (Lee & Bairstow, 2015). Since the eMMRTG is projected to operate at cold junction temperatures ranging from 100 - 200 °C (373 – 473 K), each material will be analyzed from a standard cold temperature of 150 °C (423 K) taken as the average temperature of the expected range.

The main contributing factors that account for increasing maximum TEG efficiency are high average ZT values over large temperature ranges. However, maximum efficiencies are calculations based on ideal cases that ignore inevitable flaws that will result in heat escaping the system and leaking into the environment. In a realistic case, factors like generator configuration and proper insulation of the TECs and heat source modules will also attribute to its efficiency. This paper will work from the ideal scenario that the design itself is optimized and focus on the TE materials as they are the basis of the energy conversion technology within RTG systems.

Explanation of Candidate Solutions

The candidate materials chosen for this project proposal are lanthanum-telluride, a Zintl compound of the formula $\text{Yb}_{14}\text{MnSb}_{11}$, and filled skutterudites. These materials have been selected based on promising research and NASA's interest for their improved performance at higher temperatures over existing RTG technologies (Lee & Bairstow, 2015). Each material will be described in depth and be presented with relevant research describing their thermoelectric properties. The average ZT values will be estimated based on existing data using the highest recorded stable temperatures and a standard cold temperature of 423 K to later calculate the maximum efficiencies via equation 1 for each material.

Solution 1: Lanthanum Telluride TECs

Over the past few decades, lanthanum telluride has been studied for its desirable thermoelectric properties and impressive thermal stability at higher temperatures (May, Fleurial, & Snyder, 2008). Lanthanum Telluride materials are a type of chalcogenide of the form $\text{La}_{3-x}\text{Te}_4$, where x is a variable describing different concentrations of lanthanum vacancies that can range from $0 \leq x \leq 1/3$ (May et al., 2008). Varying the value of x results in improvements of the material's thermoelectric properties as the introduction of lanthanum vacancies can greatly reduce thermal conductivity (Viennois, Niedziolka, & Jund, 2013). May et al. have studied different compositions of lanthanum telluride and their thermoelectric properties and have been able to plot ZT curves consistent with previous experiments (2008).

The study characterized the different compositions of $\text{La}_{3-x}\text{Te}_4$ by their carrier concentrations to methodize data acquisition of thermoelectric properties and ZT values for the range of compositions studied (May et al., 2008). The relationship between the x value of each $\text{La}_{3-x}\text{Te}_4$ sample and their respective Hall concentrations is shown below.

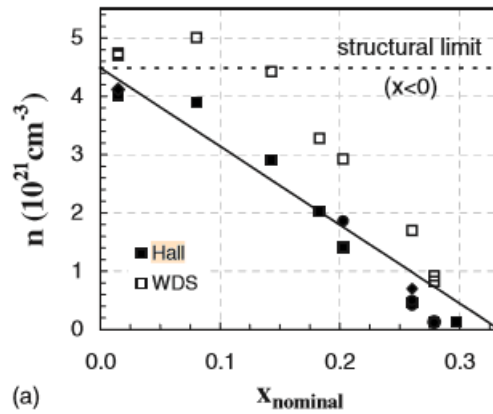


Figure 3: Hall concentrations vs. $La_{3-x}Te_4$ compositions with a trendline of $n = n_{max}(1 - 3x)$

Source: <https://authors.library.caltech.edu/11700/1/MAYprb08.pdf>

Each Hall concentration was converted to a reduced Hall concentration, which is the ratio of the Hall concentration to the maximum allowed concentration shown by the dotted line at a value of $4.5 \times 10^{21} \text{ cm}^{-3}$ (May et al., 2008). The reduced Hall concentrations were then used in conjunction with a highly involved procedure beyond the scope of this proposal to gather data for Seebeck coefficients, electrical conductivities, and thermal conductivities up to 1273 K (May et al., 2008). This data was then used to calculate ZT values for the different reduced Hall concentrations over the temperature range studied (May et al., 2008).

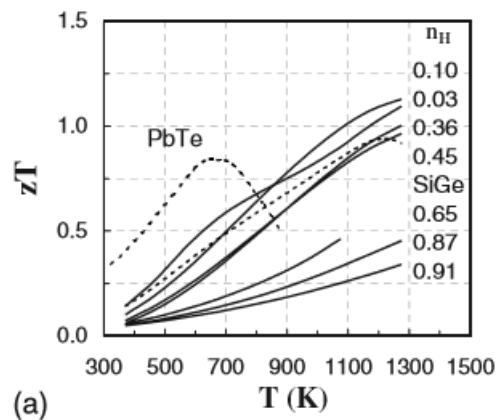


Figure 4: ZT values vs. temperature for different Hall concentrations

Source: <https://authors.library.caltech.edu/11700/1/MAYprb08.pdf>

The highest maximum ZT value observed was found in the $\text{La}_{3-x}\text{Te}_4$ composition corresponding to a reduced Hall concentration of 0.03 (May et al., 2008). This reduced concentration relates to an original concentration value of $1.2 * 10^{21} \text{ cm}^{-3}$ which can then be used with the trendline in figure 3 to calculate its corresponding x value of ≈ 0.24 , providing the formula $\text{La}_{2.76}\text{Te}_4$ (May et al., 2008). The linearity of the ZT curve for this composition allows for a relatively accurate estimation of the ZT_{ave} value. Using the previously defined cold temperature of 423 K and the maximum observed temperature of 1273 K, the average temperature for the possible operating range of an eMMRTG utilizing this material is 848 K. Based on figure 4, the ZT value for $\text{La}_{2.76}\text{Te}_4$ at the average temperature is about 0.7.

Solution 2: $\text{Yb}_{14}\text{MnSb}_{11}$ TECs

$\text{Yb}_{14}\text{MnSb}_{11}$ (YMS) is another high-performance thermoelectric material to receive attention from NASA to possibly replace current state-of-the-art materials for high-temperature TEG applications (Snyder, Gascoin, Brown, & Kauzlarich, 2009). This material is a part of a family of compounds called Zintl phases of the formula $\text{A}_{14}\text{MPn}_{11}$ where A, M, and Pn can be a range of different elements (Grebekemper et al., 2015). YMS has a large unit cell and complex structure, both of which attribute to a low thermal conductivity (Grebekemper et al., 2015). This material has shown to withstand temperatures up to 1273 K with little effect on its thermoelectric performance, showing a thermal stability similar to that of lanthanum telluride materials (Grebekemper et al., 2015). Recent advancements in high purity, large quantity synthesis of YMS shown by Grebekemper et al. have resulted in improved thermoelectric performance by allowing for more precise control over the stoichiometries of YMS compounds (2015).

Using new methods of material synthesis, Grebenkemper et al. created samples of YMS with varying concentrations of manganese and studied their thermoelectric properties from room temperature to 1275 K (2015). Their experiment produced data consistent with research done by NASA's Jet Propulsion Laboratory for their ATEC (Advanced Thermoelectric Couple) project, which had shown the largest maximum ZT for the YMS material (Grebenkemper et al., 2015).

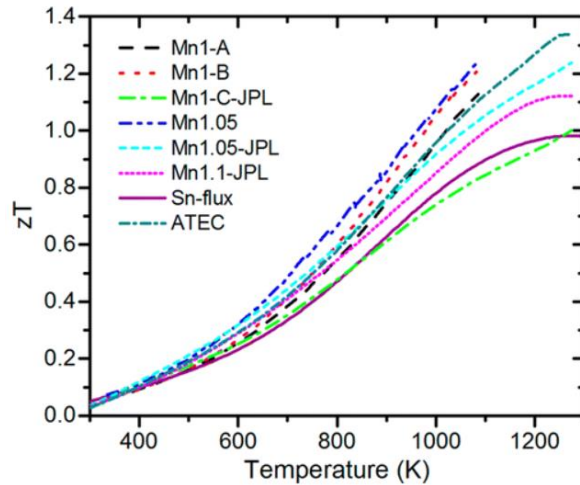


Figure 5: ZT values of the different Mn concentrations

Source: <https://pubs.acs.org/doi/10.1021/acs.chemmater.5b02446>

While the largest ZT values were obtained in NASA's studies with the ATEC project, little of this data is publicly available. The largest maximum ZT value produced by an experiment conducted by Grebenkemper et al. with their Mn1.05 sample tested at the Jet Propulsion Laboratory (2015). With the same operating temperatures as lead telluride, the average temperature of 848 K for the Mn1.05-JPL sample produces a ZT of about 0.7. While the ZT curve is slightly less linear and, therefore, more prone to error when using the constant property model for efficiency calculation, the YMS compound will likely perform similarly to optimized lead telluride samples as they boast similar ZT values over the same operating temperatures.

Solution 3: Multiple-Filled Skutterudite TECs

Another highly promising group of materials for TEG applications are skutterudite (SKD) compounds. These compounds are based on the general formula MX_3 , where the M element is typically cobalt, rhodium, or iridium and the X element is typically phosphorus,

arsenic, or antimony (Shi et al., 2011). The most commonly studied for thermoelectric purposes is the CoSb_3 (cobalt antimonide) variation for having ideal structural properties while being cheaper and less harmful for the environment than other SKDs (Rogl & Rogl, 2017). SKDs can have their thermoelectric performance enhanced further through the introduction of other elements to produce what is called a filled skutterudite (Shi et al., 2011). Research has shown these types of SKDs to achieve average ZT values greater than one for temperature ranges of around 300 – 900 K (Rogl & Rogl, 2017).

Shi et al. were able to achieve record high SKD ZT values by filling the CoSb_3 SKD with multiple filler elements (2011). In their work, CoSb_3 SKDs with different concentrations of barium, lanthanum, and ytterbium fillers were synthesized and their effects on thermoelectric properties were observed (Shi et al., 2011). Optimizing the concentrations of these fillers resulted in the reduction of thermal conductivities which allowed for high figures of merit for temperatures up to 850 K, shown in the figure below (Shi et al., 2011).

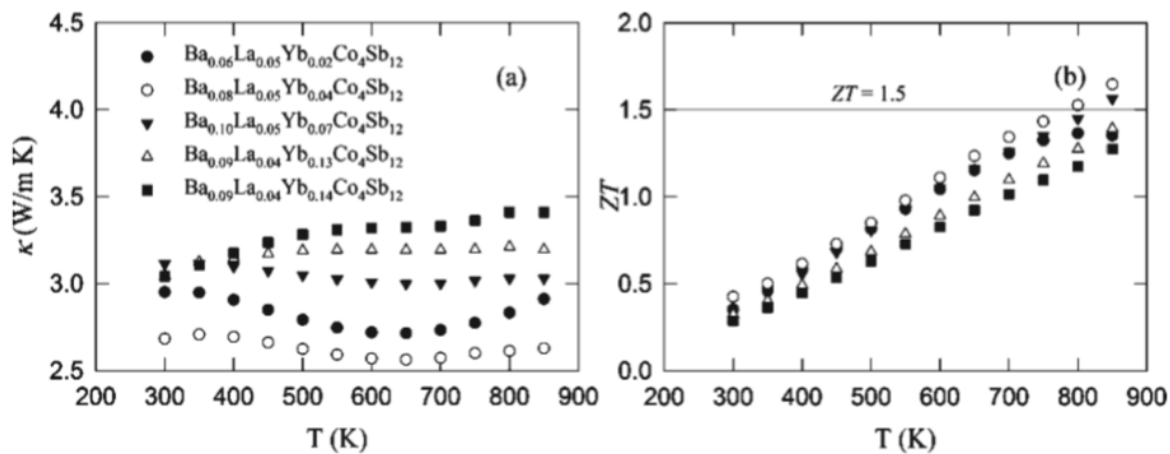


Figure 6: Thermal conductivities and ZT values of multiple filled SKDs vs. temperature

Source: <https://pubs.acs.org/doi/abs/10.1021/ja111199y>

A maximum ZT of 1.7 was recorded in the $\text{Ba}_{0.08}\text{La}_{0.05}\text{Yb}_{0.04}\text{Co}_4\text{Sb}_{12}$ compound, which was the highest ever recorded at the time (Shi et al., 2011). The data in this experiment shows a linear trend of ZT values with respect to changes in temperature allowing for a more accurate estimation of the average ZT value for the purpose of this project proposal. With a predicted cold

temperature of 423 K and the maximum studied temperature of 850 K, the ZT value at the average temperature of 637 K appears to be around 1.2.

Comparative Assessment of Candidate Solutions

Using the data previously presented, each material will be analyzed based on efficiency calculations and important parameters like cost and safety. With the approximated ZT values based on experimentally produced ZT curves and the operating temperatures observed, maximum efficiencies were able to be calculated and converted into a percentage using equation 1 defined in the engineering fundamentals of the problem section of this report. A comparison of each material’s respective efficiency provides an idea of how these materials could perform when implemented into the eMMRTG.

Comparative Assessment of Candidate Materials			
	YMS (Yb₁₄Mn_{1.05}Sb₁₁)	Lanthanum Telluride (La_{2.76}Te₄)	Multiple-Filled SKD (Ba_{0.08}La_{0.05}Yb_{0.04}Co₄Sb₁₂)
Cold Temperature (K)	423	423	423
Hot Temperature (K)	1273	1273	850
Carnot Efficiency Coefficient	0.6677	0.6677	0.5024
Dimensionless ZT_{ave}	0.7	0.7	1.2

Comparative Assessment of Candidate Materials			
Maximum Efficiency * 100 (%)	12.40	12.40	12.25

Table 1: Comparative assessment of candidate materials

The efficiency calculations show each of the materials to produce nearly identical efficiencies. The exceptional performance and high ZT values of the SKD material compensate for its lower hot junction temperature compared to $\text{La}_{2.76}\text{Te}_4$ and YMS materials. The similar efficiencies suggest that each of these materials might provide nearly the same performance in terms of energy conversion. This makes other factors like cost and risk of overheating especially important when selecting the ideal material.

In a review of literature, Rogl and Rogl (2017) provide a figure comparing costs of the popular thermoelectric materials shown below.

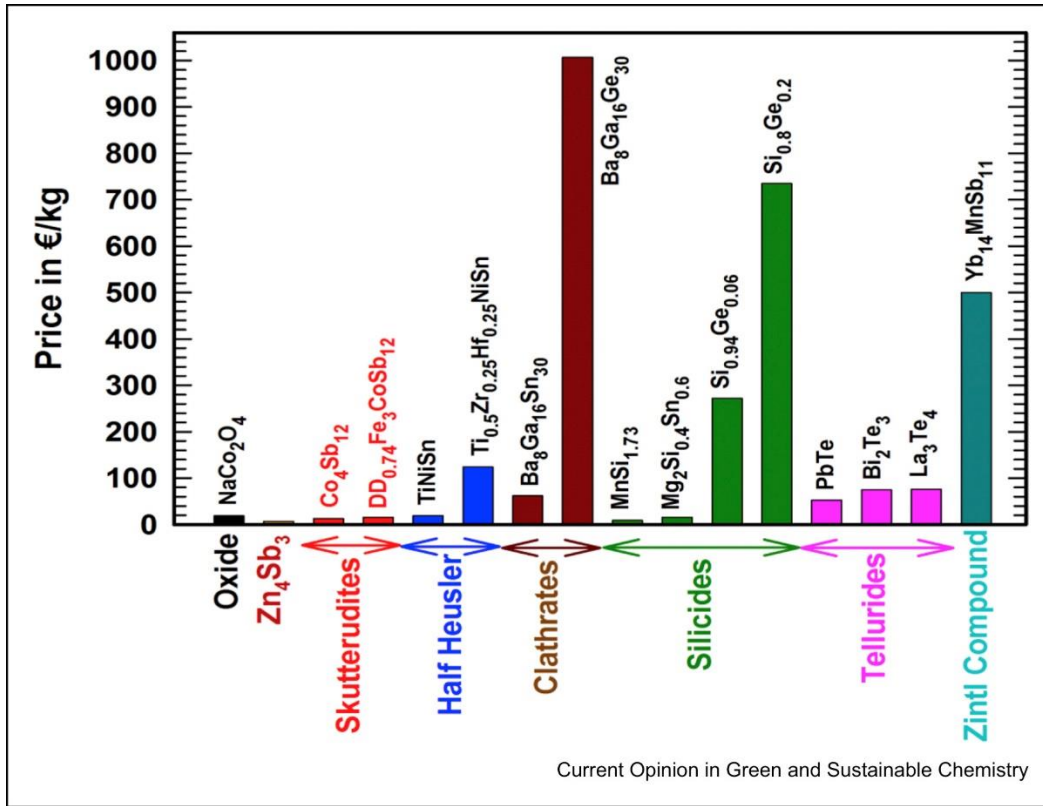


Figure 7: Cost of the different TE materials (Euro/kg)

Source: <https://www.sciencedirect.com/science/article/pii/S2452223617300068#!>

The figure shows the Co₄Sb₁₂ and similar double filled SKDs to be considerably less expensive than lanthanum telluride and much cheaper than the costly YMS Zintl compound. The ability for SKDs to operate at much lower temperatures yet produce nearly the same maximum efficiency as YMS and La_{2.76}Te₄ is another crucial property as the lower operating temperature will involve less risk for the system to overheat and will not require additional measures to control exterior temperatures of the system that may come with using higher temperature materials.

Project Recommendations

This section of the report will identify the multiple filled SKD compound as the ideal TE material out of the candidate solutions to enhance the MMRTG. The challenges associated with designing and implementing TECs with this material into an eMMRTG model are discussed, ending with a conclusion to the project proposal.

Recommended Solution

The multiple filled SKD is selected as the recommended TE material to be used in the TECs for NASA's eMMRTG. Based on maximum efficiency calculations, the materials analyzed would perform very similarly to each other with estimated conversion efficiencies of 12.40, 12.40, and 12.25 percent for the $\text{La}_{2.76}\text{Te}_4$, YMS, and multiple filled SKD materials, respectively. While the lanthanum telluride and YMS technically do have higher estimated efficiencies, sacrificing the negligible 0.15 percent in efficiency is certainly worth the additional benefits that the SKD material has over the other candidate materials.

Namely, filled SKDs are the most inexpensive option and its ultra-high figure of merit allows for nearly identical performance to the other candidate materials a much lower hot junction temperature of 850 K compared to 1273 K. This significantly lower temperature will be a safer option in the long run as it mitigates the risk of exceeding the maximum allowable root fin temperature of 200 °C and damaging the system. While each of the candidate materials are highly competitive in terms of their efficiency calculations, it is additional factors like lower cost and increased safety that the SKD materials possess over the other materials reviewed that make it the most ideal material to use for the enhancement of the MMRTG.

Design and Implementation Challenges

Much of the challenges associated with design and implementation of the eMMRTG will largely concern the new SKD thermocouples as the much of the original MMRTG design will remain unchanged (see Lessons from prior responses). Since the main design and structure of the MMRTG is to be maintained with the eMMRTG model, the design challenges would only come with replacing the existing TECs with those that utilize the SKD material and ensuring that they work with the rest of the system. The main challenge comes with the implementation of this project as the SKD technology would need to complete a standard technology maturation process before a flight ready eMMRTG model can be made. The maturation of technology is typically described by NASA using a technology readiness level (TRL), which is a scale from one to nine describing the specific stages of technological development (Mai, 2017). These stages are described in detail in figure 8.

As there is already a functioning MMRTG as a proof of concept, NASA has determined that an eMMRTG utilizing new TEC technology has a TRL of four (Lee & Bairstow, 2015). NASA’s Radioisotope Power Systems (RPS) program would be responsible for funding projects that develop this technology to higher levels (Zakrajsek, Woerner, Cairns-Gallimore, Johnson, & Qualls, 2016). A project involving the maturation of SKD technology to TRLs five and six will

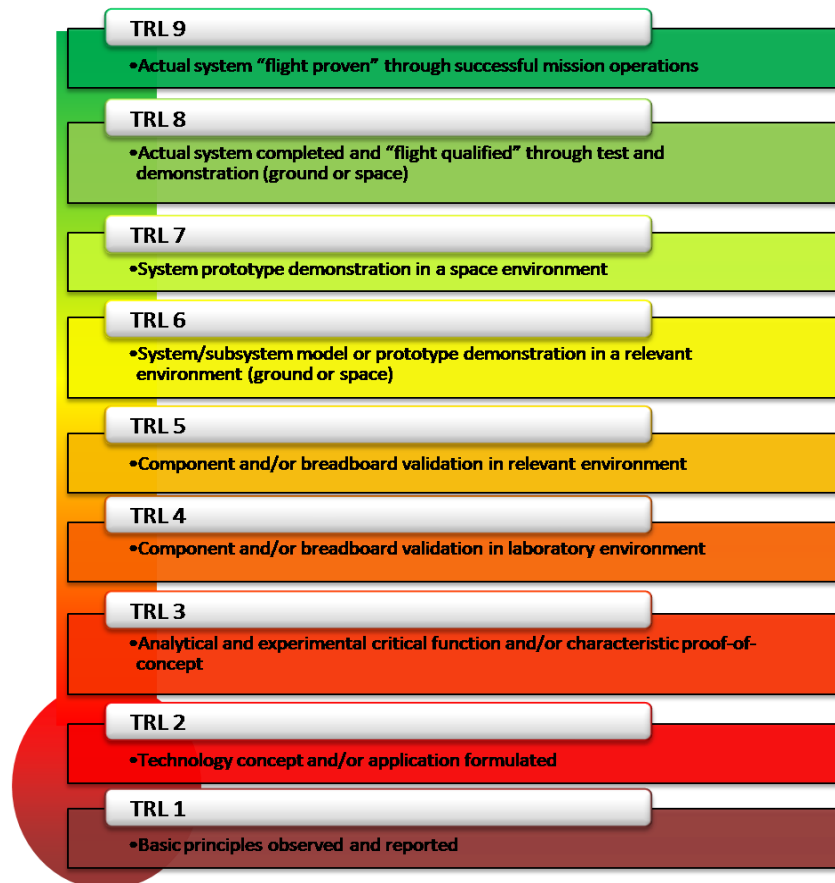


Figure 8: NASA's technology readiness levels

Source: <https://www.nasa.gov/sites/default/files/trl.png>

involve specific requirements and technology maturation plans to be worked out with the Department of Energy (Zakrajsek et al., 2016). Successful completion of a technology maturation plan would lead to full-scale development of flight systems via a third party developer known as Teledyne Energy Systems managed by the Department of Energy (Lee & Bairstow, 2015).

Conclusion

Upon the successful implementation of this project, newly enhanced MMRTG models would immediately impact future mission capabilities. Increased energy conversion efficiencies will allow for an increased power output per unit that would be able to supplement more advanced spacecraft. Conversion efficiencies in the future eMMRTG systems will see direct improvement from their predecessors after replacing their existing thermocouple technologies with those based on multiple filled SKDs. Future missions requiring multiple RTG units may require less generators when using more efficient eMMRTGs over MMRTGs, greatly reducing fuel needs and lowering mission costs. The fuel saved with higher efficiency eMMRTGs will allow for current plutonium production rates to better meet projected demands and decrease future mission limitations due to the lack in availability of Pu-238 fuel.

Another appealing element of this project is the low risks presented with enhancing the MMRTG with the proposed SKD material. The eMMRTG will utilize the same technologies as the current MMRTG model with exceptions to substituting SKD thermocouples. The SKD material would operate at a much lower temperature and would be less expensive than the other materials analyzed while producing a nearly identical maximum efficiency. Making a simple change to the thermocouple technology in the MMRTG using the highly efficient, safe, and lower cost SKD, contribute to this project being of low risk and high reward. The clear benefits and low risk of enhancing the MMRTG by method of upgrading existing TECs with SKD technology suggest that this project is highly worth pursuing.

Glossary

eMMRTG – Enhanced Multi-Mission Radioisotope Thermoelectric Generator

Equation 1 –
$$\eta_{max} = \eta_c \cdot \frac{\sqrt{1+ZT_{avg}}-1}{\sqrt{1+ZT_{avg}}+\frac{T_C}{T_H}}$$

MMRTG – Multi-Mission Radioisotope Thermoelectric Generator

RTG – Radioisotope Thermoelectric Generator

SKD – Skutterudite

TE – thermoelectric

TEC – Thermoelectric Couple

TEG – Thermoelectric Generator

YMS – Yb₁₄MnSb₁₁

Zintl Phase – “[T]he product of a reaction between a group 1 (alkali metal) or group 2 (alkaline earth) and any post-transition metal or metalloid (i.e. from group 13, 14, 15 or 16). It is named after the German chemist Eduard Zintl who investigated them in the 1930s.”¹

ZT – Thermoelectric figure of merit

¹ https://en.wikipedia.org/wiki/Zintl_phase

Bibliography

- About plutonium-238. (n.d.). Retrieved from <https://rps.nasa.gov/about-rps/about-plutonium-238/>
- Armstrong, A., Boese, M., Carmichael, C., Dimich, H., Seay, D., Sheppard, N., & Beekman, M. (2017, January). Estimating energy conversion efficiency of thermoelectric materials: Constant property versus average property models. *Journal of Electronic Materials*, *46*(1), 6-13. Retrieved from 10.1007/s11664-016-4890-x
- Cataldo, R. L., & Bennett, G. L. (2011, October 21). U.S. space radioisotope power systems and applications: Past, present and future, *Radioisotopes*, Nirmal Singh, IntechOpen, DOI: 10.5772/23914.
- Grebenkemper, J. H., Hu, Y., Barrett, D., Gogna, P., Huang, C., Bux, S. K., & Kauzlarich, S. M. (2015). High temperature thermoelectric properties of Yb₁₄MnSb₁₁ prepared from reaction of MnSb with the elements. *Chemistry of Materials*, *27*(16), 5791-98. DOI: 10.1021/acs.chemmater.5b02446
- Hammel, T., Otting, B., Bennet, R., Keyser, S., & Sievers, B. (n.d.). The enhanced MMRTG – eMMRTG – Boosting MMRTG power output. Retrieved from <http://anstd.ans.org/wp-content/uploads/2015/07/1015.pdf>
- Howe, S. D., Crawford, D., Navarro, J., & Ring, T. (n.d.). Economical production of pu-238: Feasibility study. Retrieved from https://www.nasa.gov/pdf/636900main_Howe_Presentation.pdf
- Lee, Y., & Bairstow, B. (2015, September 1). Radioisotope power systems reference book for mission designers and planners. Retrieved from <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160001769.pdf>
- Mai, T. (2017, August 7). Technology readiness level. Retrieved from https://www.nasa.gov/directorates/heo/scan/engineering/technology/txt_accordion1.html
- May, A. F., Fleurial, J., & Snyder, J. G. (2008, September 19). Thermoelectric performance of lanthanum telluride produced via mechanical alloying. *Physical Review B*, *78*(12). DOI: 10.1103/PhysRevB.78.125205

- NASA and ESA prioritize outer space missions. (2009, February 18). Retrieved from <https://www.jpl.nasa.gov/news/news.php?feature=2035>
- Radioisotope power systems for space exploration. (n.d.). Retrieved from https://www.jpl.nasa.gov/news/fact_sheets/radioisotope-power-systems.pdf
- Rogl, G., & Rogl, P. (2017, April). Skutterudites, a most promising group of thermoelectric materials. *Current Opinion in Green and Sustainable Chemistry*, 4, 50-57. Retrieved from <https://doi.org/10.1016/j.cogsc.2017.02.006>
- Shi, X., Yang, J., Salvador, J. R., Chi, M., Cho, J. Y., Wang, H., ... Chen L. (2011). Multiple-filled skutterudites: High thermoelectric figure of merit through separately optimizing electrical and thermal transports. *Journal of the American Chemical Society*, 133, 7837-46. DOI: [dx.doi.org/10.1021/ja111199y](https://doi.org/10.1021/ja111199y)
- Snyder, J. G., Gascoin, F., Brown, S., & Kauzlarich, S. Yb₁₄MnSb₁₁ as a High-Efficiency Thermoelectric Material. Retrieved from <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20090022350.pdf>
- Viennois, R., Niedziolka, K., & Jund, P. (2013, November 18). Physical properties of the thermoelectric cubic lanthanum chalcogenides La_{3-y}X₄ (X = S, Se, Te) from first principles. *Physical Review B*, 88(17). DOI: <https://doi.org/10.1103/PhysRevB.88.174302>
- Wilson, S. D., & Wong, W. A. (2014, July 28). NASA Glenn Research Center support of the ASRG project. Retrieved from <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20140017751.pdf>
- Xhang, X., & Zhao, L., (2015). Thermoelectric materials: Energy conversion between heat and electricity. *Journal of Materiomics*, 1(2), 92-105. Retrieved from <https://doi.org/10.1016/j.jmat.2015.01.001>
- Zakrajsek, J. F., Cairns-Gallimore, D., Otting, B., Johnson, S., & Woerner, D. (2016, March 23). Usage of multi-mission radioisotope thermoelectric generators (MMRTGs) for future potential missions. Retrieved from <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20170000017.pdf>

Zakrajsek, J. F., Woerner, D. F., Cairns-Gallimore, D., Johnson, S. G., & Qualls, L. (2016, March 5). NASA's Radioisotope Power Systems Planning and Potential Future Systems Overview. Retrieved from

<https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160010064.pdf>