IMPROVING THERMOELECTRIC TECHNOLOGY PERFORMANCE AND DURABILITY WITH AEROGEL

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ABSTRACT
        The recent interest in thermoelectric technology has spurred the development of advanced materials and device technology. In particular, current work at the Jet Propulsion Laboratory has identified aerogel as an effective sublimation barrier for a wide range of thermoelectric technologies based on SiGe, novel Skutterudites, TAGS, and PbTe. Aerogel is typically known as an extremely porous (>99% porous) silicon dioxide, which has very low thermal and electrical conductivity. Aerogel has interconnected pores, which are generally in the range of angstroms to tens of nanometers. As such, the path required for metal vapor to permeate aerogel is extremely tortuous, thus significantly decreasing sublimation rates. Another added benefit to using aerogel as a coating is that it can also serve as thermal insulation. Since aerogel is made through liquid synthesis it can be cast in or around thermoelectric devices, thus providing intimate contact between the device and the insulation to assist in channeling heat through the thermoelectric legs and eliminated lateral heat loss. Altogether, aerogel coatings could significantly improve a variety of thermoelectric technologies by enhancing durability and performance by acting as an effective sublimation barrier as well as effective thermal insulation, respectively. In this work, a comprehensive assessment of aerogel sublimation barriers for Skutterudite-based power generators is reported.

INTRODUCTION
        The recent interest in thermoelectric technology has spurred the development of advanced materials and device technology. In particular, current work at the Jet Propulsion Laboratory (JPL) involves the integration of aerogel into thermoelectric technology, to improve both performance and durability. The basic concept involves casting aerogel into or around a thermoelectric device such that intimate contact is made between the thermoelectric elements and the aerogel (**Figure 1**). Since aerogel is synthesized using sol-gel chemistry it can be cast in place, thus filling all free void space in a device. Once in place, the inherently low thermal conductivity of aerogel (a few mW/m-K) channels heat through the thermoelectric elements, thus minimizing parasitic heat loss. A more intriguing effect was recently discovered, however, and involves the use of aerogel as a sublimation suppression barrier (**Figure 2**). The inherently micro-meso porous structure of aerogel combined with the cm-scale mean free path of heavy metal vapors significantly slows the sublimation rates of practically all thermoelectric materials relevant to thermoelectric power generation (Skutterudite, PbTe, TAGS and SiGe). Altogether, the integration of aerogel into thermoelectric technology could

have a significant impact on how thermoelectric generators, and to a lesser extent coolers, are designed and fabricated. Intense efforts supported by NASA's Science and Mission Directorate, Project Prometheus and a DOE sponsored project to improve fuel efficiency of vehicles using thermoelectrics are considering aerogel for use in the next generation thermoelectric generator technology.

Efficient thermal-to-electric conversion efficiency using thermoelectric materials is primarily determined by the ZT of the thermoelectric materials and the maximum hot-side (T_{hot}) operating temperature. The latter parameter, T_{hot}, is often limited by the sublimation of volatile metal species, which is considered one of the primary modes of degradation in thermoelectric generators. Current efforts at JPL are focusing on Skutterudite-based thermoelectric technology, thus Antimony (Sb) is the volatile, subliming species. Essentially, sublimation reduces the effective cross-section of the thermoelectric elements, thus resulting in increased electrical resistance and thermal impedance **(Figure 3).** As Sb leaves n-type Skutterudite, the reaction is as follow: $CoSb_3 \longrightarrow CoSb_2 + CoSb$ + Sb (vapor). Simultaneous decomposition into lower cobalt antimonides occurs such that CoSb forms on the outer most regions followed by $CoSb_2$ as shown in an n-type Skutterudite coupon heated in vacuum (10^{-6} torr for) 72 hours at 700C **(Figure 3).** The p-type Skutterudite ($CeFe_3Ru_1Sb_{12}$) decomposes into Ce, Fe and Ru diantimonides as Sb sublimes and a similar depletion band forms along the perimeter of coupons or legs.

Thermoelectric technology is known for reliability, which typically results from the simplicity of operation, i.e. no moving parts, static thermal environment, etc. Thus, sublimation must be suppressed to ensure reliable operation over a decade or decades of operation. In the past, Radioisotope Thermoelectric Generators (RTG) employed SiO_2 and Si_3N_4 coatings and or a cover gas of Argon to suppress sublimation for SiGe and TAGS technology, respectively. During the course of the development these schemes were characterized using simple mass loss experiments of coupons and power output of prototypical devices. In the end, a value for acceptable sublimation rate is determined and corresponds to a projected power reduction based on the abovementioned increase in electrical and thermal resistance associated with sublimation. Using the procedures developed under previous programs, several goals have been established for effectively suppressing sublimation in Skutterudite-based technology: 1) Sublimation of Sb must not result in more than a 5% reduction in cross-section over 10 years of operation, which will require a Sb sublimation (flux) rate of ~1 $x10^{-7}$ g/cm^2 hours or ~ 10^{-8} cm/hour, 2) The method for suppressing sublimation should also prevent sublimed species from condensing on the cold-side circuitry, which will likely result in short circuiting and 3) The method for suppressing sublimation should not have a negative impact on the system performance, e.g. if a coating is considered it must have low thermal and electrical conductivity to prevent thermal and electrical shorting.

Recent investigations have determined that Silica-based aerogel could potentially meet all three criteria. Aerogel is a made through Sol-Gel chemistry in which liquid precursors are combined to form a gel, which is then supercritically dried in an autoclave[1] **(Figure 4).** The resulting structure is comprised of an interconnected network of pores ranging from the micro to meso scale and porosity ranging from 90 to 99% (density from 30 to 300 mg/cc). The nanometer scale porosity combined with the homogeneous dispersion of pores creates a highly tortuous path for vapor to permeate. It is for this reason that aerogel is currently being considered as a sublimation barrier **(Figure 2).** The mean free path of most heavy metal vapors, like Sb, are in the range of centimeters, thus it is expected that the permeation rate of Sb vapor through aerogel should be low. Additionally, since aerogel has low thermal and electrical conductivity it should not impose a negative impact on

the device efficiency and it is likely that the device performance can be improved. In SiGe technology, significant parasitic heat loss resulted from gaps between the SiGe unicouples and the multi-foil insulation used to prevent the hot-side components from heating the cold-side components. Since aerogel is cast in place, intimate contact can be made between the thermoelectric elements and the thermal insulation, thus reducing parasitic heat loss. Although the benefits of using aerogel as thermal insulation are clear, the emphasis of this report is on the use of aerogel for sublimation suppression. In this report, detailed analysis of aerogel sublimation suppression coatings for Skutterudite-based technology is presented. Specifically, the sublimation rates of aerogel-coated coupons in various environments, temperatures and time periods along with detailed analysis of aerogel stability at elevated temperature under various atmospheres will be covered.

EXPERIMENTAL

The standard two-step sol-gel process was used to prepare the aerogel in this work. The first step involves combining and refluxing requisite amounts of tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS), ethanol and nitric acid. Water, ammonia hydroxide base, and acetonitrile are then added. This solution or "sol" was then poured into the appropriate molds containing sublimation coupons, and allowed to solidify or "gel". After gelation, the samples were transferred into a critical point dryer pre-filled with acetonitrile. The apparatus was sealed, heated to 295C and pressurized to 5.5 MPa. These are the conditions required to establish supercritical conditions for acetonitrile

The n-type and p-type Skutterudite compositions were $CoSb_3$ and $CeFe_3Ru_1Sb_{12}$, respectively. Both types were prepared by combining the appropriate pure metals, melting in a quartz ampoule, followed by heating to 1200C for 24 hours, cooling to room temperature and re-heated at 700C for 48 hours. The ampoules were then transferred to a glove box where they were broken to extract the ingots. The ingots were then milled in a vibratory mill to produce a fine powder and hot pressed at 120 MPA in a graphite die at 700C under flowing argon. The hot pressed slugs were then diced to the appropriate geometry.

Thermal stability was characterized using linear shrinkage as the metric. Aerogel coupons were heated to various temperatures in high vacuum (10^{-6} torr) and ambient air for various times. The longest dimension was measured before and after heating to determine the percent shrinkage. FTIR analysis was performed to investigate the change of aerogel before and after heating. Aerogels as made, heated at 1000 ^{o}C in vacuum, and heated at 1000°C in air were separately prepared and investigated with FTIR in the range of 400 ~ 4000 cm^{-1}.

RESULTS AND DISCUSSION

Initially, sublimation barrier studies of Skutterudite coupons were conducted in accordance with the protocols established under the SiGe and TAGS RTG development programs in which uncoated coupons and coupons coated with various thin films were heated in their respective projected operating environment and periodically weighed to determine mass loss. SiGe-based, RTG technology employed 25 micron thick, Chemical Vapor Deposited (CVD) composite films of SiO_2 and Si_3N_4 to suppress sublimation. TAGS-based technology employed a cover gas consisting of approximately 1 atm of argon to suppress sublimation. Both approaches were attempted to suppress sublimation in Skutterudite-based technology and neither provided adequate results.

Various sputtered films were rapidly consumed by the highly corrosive Sb vapor and 1 atm of argon reduced sublimation, but only by a factor of 10 where a factor 10^5 is required. One somewhat promising approach involved the hot pressing of 12 micron Ti foil to the surface of Skutterudite elements. Significant reduction in Sb sublimation rates was achieved, but with time the Ti was consumed by Sb to form $TiSb_2$, which resulted in coating embrittlement.

To achieve significant reductions in sublimation rates an alternative approach using aerogel was pursued. To date, three iterations of coupon design have been investigated in which Skutterudite n and p-type coupons were encapsulated by various forms of aerogel **(Table I).** The first type consisted of cube-shaped Skutterudite coupons **(Figure 5),** which were placed in an alumina crucible and then filled with a silica sol. The silica sol is composed of Tetrethylorthosilicate TEOS, acetonitrile, water, ammonia hydroxide and an approximately 20 wt% alumina powder to serve as an opacifying agent. The amount of each component varied depending on the density of aerogel. The sol gelled around the coupon and the gel was allowed to age for 1~2 days and was then supercritically dried in acetonitrile at 800psi and 295C. The sublimation rates of most coupons were measured using a custom designed ThermoGravimetric Analyzer (TGA) purchased from Netzsch Instruments. The TGA (STA 449 C Jupiter ®) was outfitted with all alumina components and as such could with stand exposure to the corrosive metal vapors such as Sb. A turbomolecular pump was integrated into the apparatus to allow testing under high vacuum (10^{-6} torr). The TGA profile was increased at a rate of 10^oC/minute up to predetermined temperatures for isotherms at 400, 500, 600 and 700C. Each isotherm was held for one hour to achieve a linear weight loss profile used to measure the sublimation rate. The slope of the weight versus time plot provides the weight loss in terms of a flux normalized by surface area. The units used are grams/cm^2·hours and are consistent with units used in the past for SiGe sublimation evaluation. In some cases the isothermal time interval of one hour was not sufficient and the interval was extended to 10 hours to obtain a greater degree of accuracy. As a rough approximation a flux rate of ~10^{-5} grams/cm^2·hours over a one hour interval for a 2 gram sample is within the detection limit of the apparatus.

Table I. Coupon Configurations

Generation	Coupon Configuration	Sol	Supercritically Drying
1st	Square-cube	TEOS/Acetonitrile/Water/NH OH/Alumina powder	Acetonitrile, 800psi 29!
2nd	Press fit in graphite cup	TEOS/Acetonitrile/Granular oxide/Water/NH$_4$OH	Acetonitrile, 800psi 29!
3rd	Sphere suspended by wi	TMOS/Acetonitrile/Fumed silica/Granular oxide/Water/NH$_4$OH	Acetonitrile, 800psi 29!

First Generation Coupon Testing

The first generation coupon experiments were conducted for uncoated Skutterudite coupons and coupons encapsulated with 50 and 100 mg/cc aerogel **(Figures 6a, b,c).** The uncoated sample is an n-type Skutterudite coupon in which the sublimation rates were 5.3 x 10^{-3}, 5.16 x 10^{-3}, and 2.15 x 10^{-2} grams/cm^2-hours for the isothermal plateaus at 500, 600 and 700C, respectively. At 400C the

weight loss response was too low to accurately measure a loss rate. Incidentally, the p-type sublimation rates (not shown) are similar and not shown for simplicity. When the Skutterudite cubes are encapsulated in the 50 mg/cc and 100 g/cc aerogel the weight loss is slowed at 700C, the most critical temperature, but only by a factor of 7 and 20, respectively. Although this was the first attempt at suppressing sublimation with aerogel the results do not meet NASA requirements for performance duration, but the results clearly indicate that the aerogel did indeed slow sublimation, especially as the density of the aerogel increases. Interestingly, all post-test analyses indicated that cracks propagated through the aerogel coatings and appeared to originate from the tops of the Skutterudite cubes **(Figure 7).** It is believed that these cracks as well as leakage from the bottom of the cubes were the primary paths for Sb vapor to escape. Likewise, the aerogel processing and coupon design were re-engineered to assure that the only Sb loss occurred as a result of permeation through the aerogel. The second generation coupon testing addressed these issues.

Second Generation Coupon Testing

It was believed that the cracks in the aerogel were caused by two factors.   First, it is common for the aerogel to shrink between 1 and 5 % when heated to 700C. Secondly, the orthogonal edges of the Skutterudite cubes acted as stress intensifiers. Thus, as the aerogel shrinks around the cube, the edges of the cube likely initiated cracks, which propagated through the thickness of the aerogel coating. To mitigate the cracking and simultaneously eliminate Sb vapor from escaping from the bottom of the coupon a second generation coupon was designed and implemented. Basically, a graphite cup was precision machined so that a 6.4mm diameter cylindrical coupon could be pressed into it. All the edges of the graphite cup were chamfered to eliminate orthogonal edges and the entire cup/coupon assembly was fully encapsulated in aerogel.   Another improvement was to further increase the density of the aerogel since the first generation experiments indicated that the higher the density the lower the sublimation rate.   However, the particular Sol-Gel process used typically results in greater aerogel shrinkage, associated with supercritical drying, as the density of the gel increases. The primary modification to the previous Sol-Gel procedure was the addition of oxide powders (Titania or Silica) into the silica sol before casting. The oxide powder was added, because it is known to opacify against infrared radiation[2]. With these modifications, the aerogel was considered a composite with overall density of over >120 mg/cc comprised of a 40 mg/cc silica aerogel network "gluing" together a homogeneous distribution of >80 mg/cc titania. Finally, to further eliminate the effects of shrinkage associated with high temperate exposure, pure antimony pellets were also tested, which only required heating to 500C to achieve substantial sublimation rates.

Since Sb was known to be the primary element lost from sublimation, a fundamental study was conducted on pure Sb pellets encapsulated with second generation coupon design **(Figure 8a).** Uncoated Sb pellets, 40 mg/cc pure silica aerogel coatings and the improved composite aerogel coatings were compared using the TGA apparatus**.** The pure antimony sublimation rate was approximately 1 g/cm^2-hours at 500C, while the 40 mg/cc and composite aerogel coatings were 1.5 x 10^{-3} and non-detectable for the aerogel composite over the 1 hour isotherm (**Figure 8c**). To increase signal sensitivity, the aerogel composite encapsulated Sb sample was held for 10 hours at 500C and a sublimation rate of 7 x 10^{-5} g/cm^2-hours was measured (**Figure 8d**). Essentially, combining the second generation coupon testing with the composite aerogel resulted in a factor of 14000 decrease in sublimation rate of pure Sb. After testing, discolored regions in the aerogel appeared to indicate where the Sb vapor permeated and condensed upon cooling (**Figure 8b**). A noticeable "cloud" of Sb appeared to condense directly above the Sb pellet, but did not permeate entirely through the aerogel.

More interesting was the barely noticeable condensation that appeared to condense along the vertical, graphite cup-to-aerogel interface. It is believed that negligible condensation along this interface indicates that a good seal is made and significantly reduced Sb vapor loss associated with leakage as was suggested was the primary mode of Sb vapor loss in the first generation coupon design. Although these results were encouraging for pure Sb coupons, more meaningful results could only be achieved testing Skutterudite coupons. This would require testing at 700C, which would require further modifications to the Sol-Gel chemistry to decrease shrinkage associated with heating to higher temperatures. Hence a third generation coupon test group was conducted in which the second generation coupon design was used and a new aerogel formulation was developed.

Third Generation Coupon Testing

The promising results achieved using pure Sb coupons prompted characterization of n and p-type Skutterudite coupons using the second generation coupon design. Essentially, the same tests were conducted for the Skutterudite coupons as was for done for the Sb coupons except that the temperature range was increased to 700C, which would require greater thermal stability to reduce shrinkage at these elevated temperature. As previously mentioned, severe cracking resulted when the aerogel coatings shrank greater than 5% around the coupons. It is important to note that there are several steps in aerogel processing that can cause aerogel to shrink and likely crack when used as an encapsulant. First, shortly after the liquid sol transforms into free standing gel, the gel is often aged for > 24 hours. Ageing can cause some shrinkage although typically only a few %. Secondly, as supercritical fluid leaves the gel the gels often expand ~ 10% the original volume and contract or shrink as the autoclave is cooled and all the supercritical fluid is expelled. Significant shrinkage can be caused by this step especially as the density of the aerogel network is increased above ~75 mg/cc using the TEOS-based sols. Controlling this shrinkage is extremely important if aerogel is to be used as a cast-in-place encapsulant. The third mechanism for causing shrinkage, as previously mentioned, is that associated with heating especially above 500C and will be discussed in more detail below. From what has been said, the most challenging step to deal with is the second step since this work seeks to increase aerogel density, while minimizing shrinkage. Thus, significant changes to the Sol-Gel chemistry were made to minimize shrinkage associated with supercritical drying. First, Tetramethylorthosilicate (TMOS) was used in place of TEOS. Secondly, 325 mesh fumed silica powder was added along with granular (dense) silica powder. The procedure was nearly identical as was used for the TEOS sol and the specific concentrations of each constituent in the aerogel were as follows: 75 mg Silica aerogel, 20 mg/cc fumed silica and 55 mg/cc granular silica powder. The modifications to the Sol gel chemistry dramatically improved the reproducibility and eliminated cracking especially when working with higher density aerogel. The details as to why these modifications were made are not within the scope of this report and will be reported in future publications.

The combined effects of optimized Sol-gel formulation and coupon design are striking. The sublimation rates for n and p type Skutterudite coupons at the beginning-of-life (BOL) measure in the TGA are in the 10^{-4} g/cm^2·hours range **(Figure 9).** To improve accuracy and evaluate long term sublimation suppression a new test protocol was established. Extended period tests were implemented with out the use of the TGA apparatus. Samples requiring greater than 10 hour isotherms were impractical, thus a new protocol involving heating coupons in a quartz ampoule under high vacuum (10^{-6} torr) for week long intervals was implemented. The ampoules had an inner diameter of 2.54cm and were 200cm long. The ampoules extended out of the furnace such that half of the ampoule was heated in the furnace and half was not. As Sb vapor sublimed and escaped it

condensed on the colder walls of the ampoule. Between intervals, the encapsulated coupons were cooled and weighed to measure mass loss rates **(Figure 10).** With the exception of one data set, it is apparent that the sublimation rates for all samples significantly decreased during the first few days of heating. Most samples initially lost weight at rates ranging from the high 10^{-5} to low 10^{-4} g/cm^2·hours, but after approximately 3 days practically all samples were in the low 10^{-5} g/cm^2·hours range **(Figure 11).** The relatively high rates in the beginning of testing are typical and similar observations were made when testing SiGe sublimation rates. This could also be a result of slight oxidation of the Skutterudite coupons during the supercritical extraction process. The oxidation film burns off initially until the Skutterudite surface is exposed and the weight loss becomes constant. Regardless, the data clearly shows that aerogel can slow the sublimation rate of Skutterudite at 700C by approximately 3 orders of magnitude compared to the uncoated samples.

Thermal Stability

RTGs typically operate in a static thermal environment for extended (decades) periods of time. Thus, all components are expected to maintain their thermal and mechanical integrity for the life of the generator. A study was conducted to characterize the thermal stability of silica-based and non-silica based aerogel. The primary emphasis was on linear shrinkage associated with heating. As mentioned above, linear shrinkage in the range of <10% is considered acceptable. Cubic (2.5cm by 4cm by 3cm) and cylindrical (1.5cm diameter and 4cm long) coupons were prepared and heated to various temperatures in air and in high vacuum. One group of experiments involved heating a coupon for one hour at a certain temperature, cooling, measuring linear shrinkage and heating to the next higher temperature in air and under high vacuum (10^{-6} torr). Two types of aerogel were compared. Pure silica was evaluated and a composite of 15wt% colloidal alumina powder and silica aerogel made up 85 wt%. The addition of alumina has been shown to increase viscosity of aerogel, thus improving thermal stability(ref). The data for these are shown in **(Figure 12)** from which it is apparent that shrinkage for both aerogels was negligible up to 600C. The shrinkage appears to increase exponentially with increasing temperature and clearly is more pronounced in the samples heated in air above 700C. Post heating FTIR analysis indicates that the primary difference between samples heated in air versus vacuum indicates that the loss of Si-OH bonds causes accelerated sintering, which agrees with work done by s etal (Ref loss of water sintering). This will be explained in more detail in a later publication. Thermal stability as a function of time at 1000C was compared between a pure silica aerogel and silica/alumina composite aerogel (15wt% alumina/85 wt% silica) **(Figure 13)**. Both samples were heated in high vacuum at 1000C. In both cases, the linear shrinkage appeared to level off near the 10% shrinkage mark.

CONCLUSION

A new application for aerogel has been proposed and evaluated for use in thermoelectric technology. The inherently tortuous pore network of aerogel significantly slows the rate of sublimation of volatile metal vapors from the surface of Skutterudite materials and is likely to exhibit the same behavior in most thermoelectric materials such as PbTe, or TAGS. The sublimation of uncoated Skutterudite coupons was determined to be 2.15 x 10^{-2} g/cm^2·hours while coupons encapsulated with aerogel were reduced by a factor of more than 700 (~3 x 10^{-5} g/cm^2·hours). While preliminary calculations indicate that a sublimation rate in the 10^{-7} g/cm^2·hours is required, it is believed that further improvements to aerogel processing and the composition may approach the

suppression goal. Additionally, it is not unreasonable to think that conventional coatings can be combined with aerogel to further enhance sublimation suppression. The thermal stability of aerogel was also characterized and no significant degradation was observed up to 700C. Despite the high surface area, the aerogel resisted significant sintering up to 1000C in high vacuum. Altogether, the prospect of integrating aerogel into thermoelectric technology is appealing in that durability is improved without sacrificing performance and it is likely that aerogel may increase RTG performance by providing improved thermal insulation.

ACKNOWLEDGEMENTS

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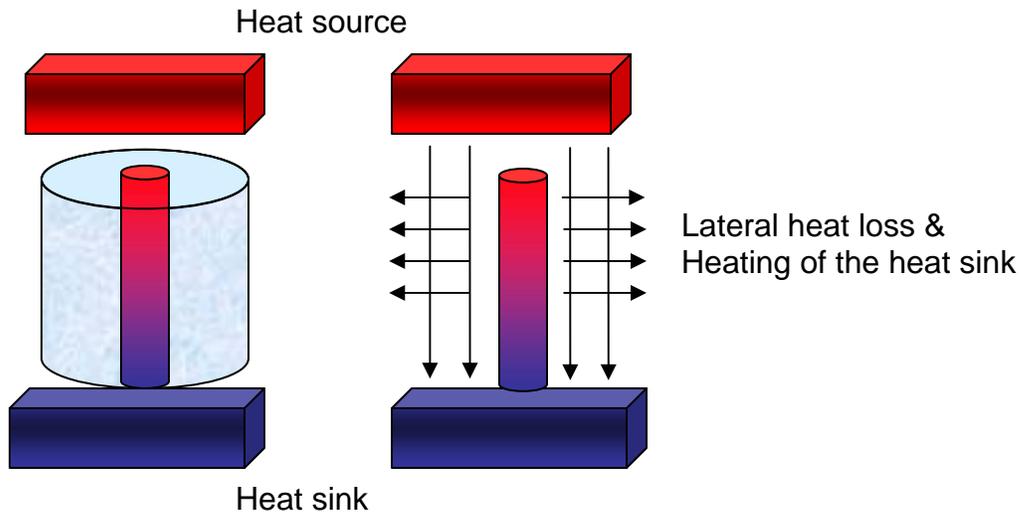
Figure 1. A typical thermoelectric device consists of heavily-doped semiconductor elements (the vertical elements above) a heat source and heat sink. The element on the left is encapsulated in aerogel, which channels heat through the thermoelectric element and prevents parasitic heat loss.
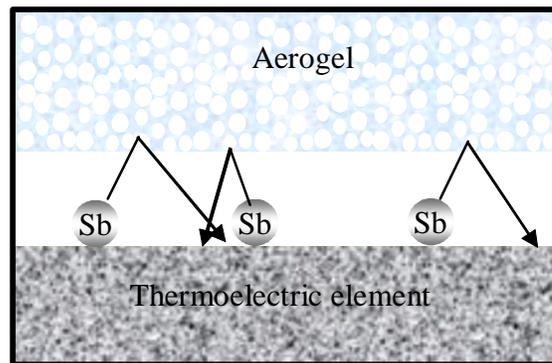
Figure 2. Under high vacuum (10^{-6} torr), the mean free path of most heavy metal vapor, like Sb, are far too long to penetrate the highly-tortuous, porous, aerogel network (not to scale). The Sb atoms are "reflected" back to the SKD surface, thus establishing a highly-localized, equilibrium environment..

Hot side

necking

Leg

Cold side
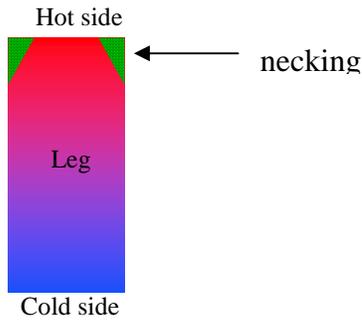
Figure 3. Practically all thermoelectric materials considered for use in RTGs are susceptible to sublimation. Typically, sublimation causes a reduction in effective cross-section causing a necking effect.
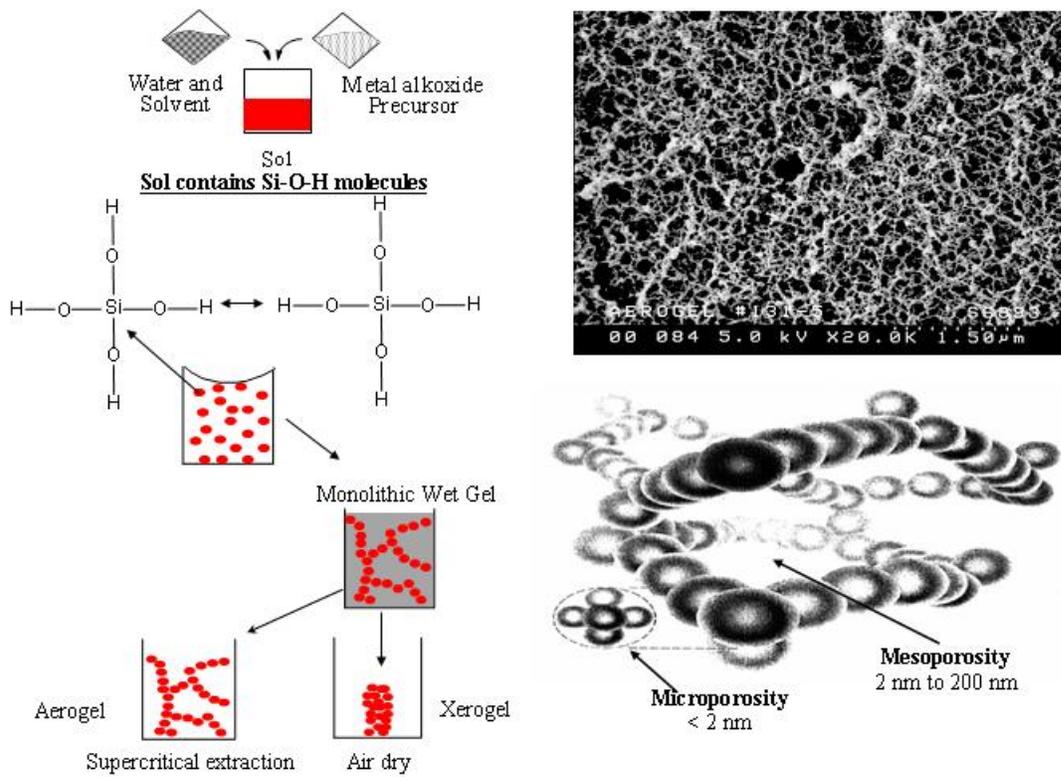
Figure 4. Silica aerogel is synthesized using Sol-Gel synthesis, which involves the combining of liquid precursors. The slight addition of water and acid causes hydrolysis of silica precursors such as TEOS or TMOS. Typically, base is added to cause hydrolyzed silica units to condense forming an interconnected network of silica. A majority of the volume is occupied by an expanding solvent. If the expanding solvent, such as acetonitrile, ethanol or methanol, is allowed to evaporate under ambient conditions, the capillary pressure associated with evaporation causes severe shrinkage and produces a xerogel (~50% porous). To eliminate the capillary pressure, the expanding solvent is extracted under supercritical conditions in an autoclave, which preserves the pore volume and produces aerogel. A typical microstructure imaged in an SEM reveals a homogeneous distribution of fine pores mesopores (40 mg/cc silica). Meso and micopores are typically present in aerogel.
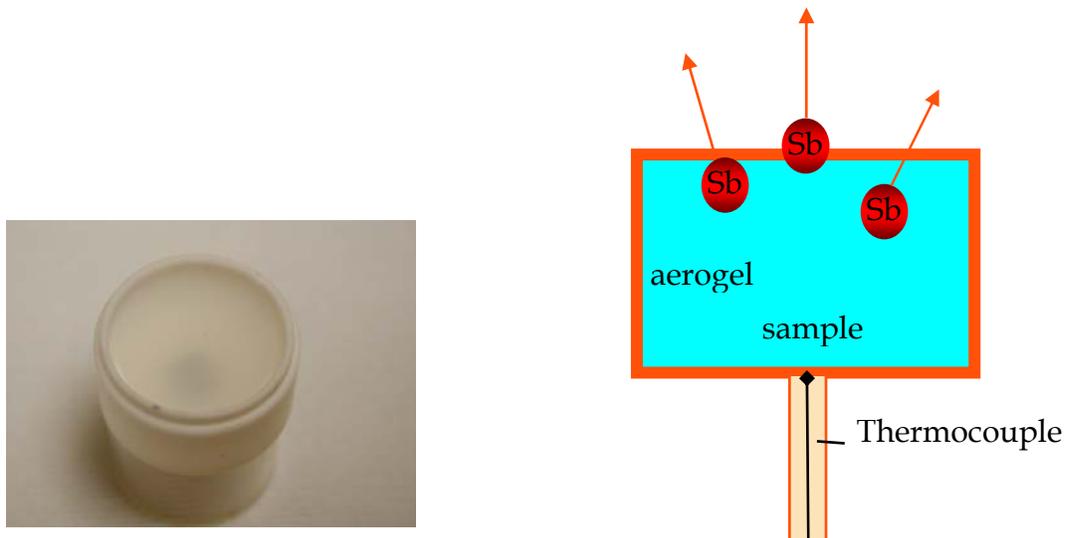
Figure 5. The first generation coupons consisted of a cube of Skutterudite encapsulated by aerogel, which was contained in an alumina TGA crucible.
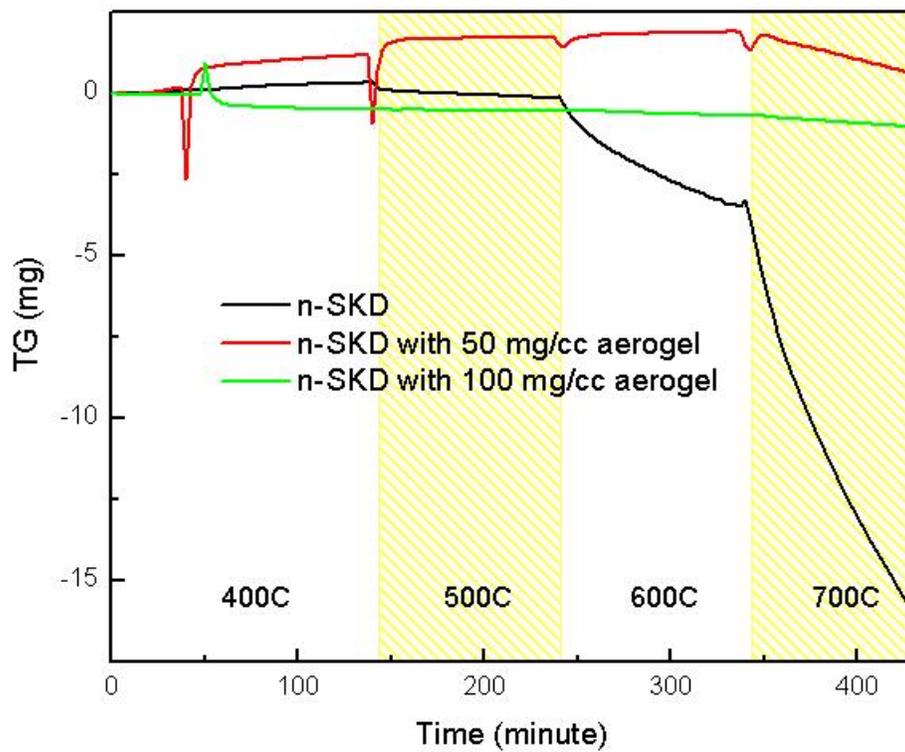
Figure 6. TGA data of first generation coupons (black-uncoated, red-50m/cc aerogel, green-100mg/cc aerogel).
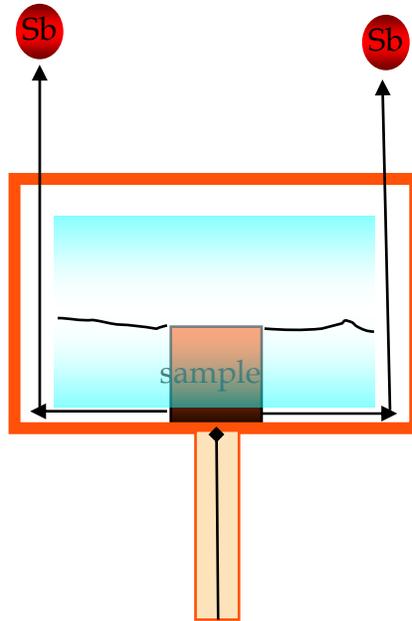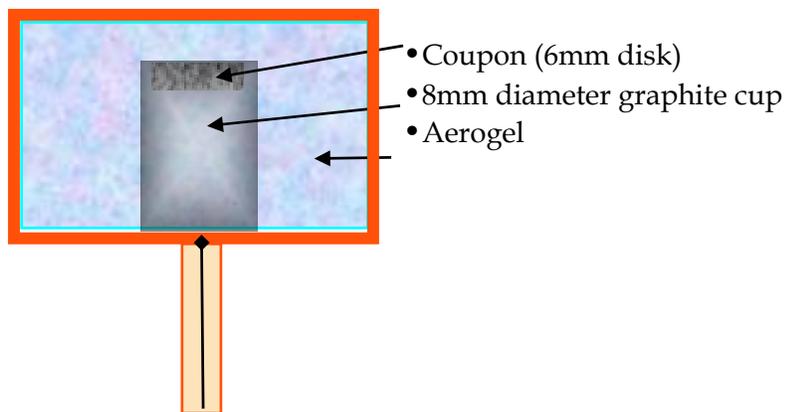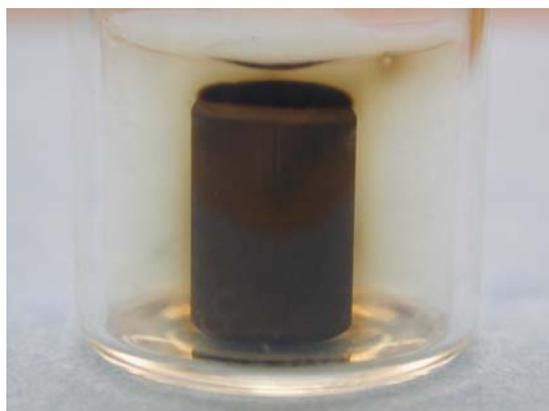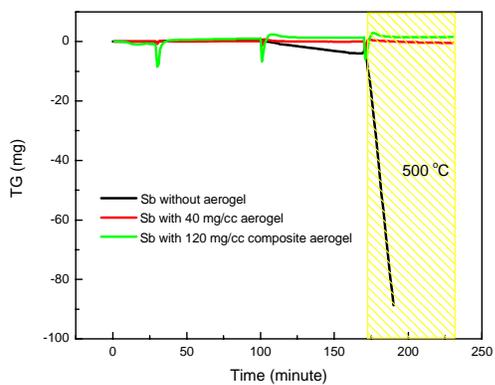
Figure 7. Cracks radiating from the edges of the coupon and shrinkage exposing the bottom of the coupon were likely the cause of the higher than expected sublimation rates.
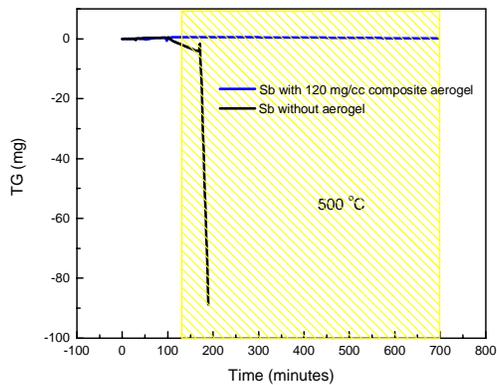
Figure 8. The second generation coupon design (a). Sb vapor appeared to condense above the Sb pellet and along the edges of the graphite cup (b). TGA plots for the uncoated, 40 mg/cc and 120mg/cc aerogel encapsulated coupons (c) and the extended test (d).
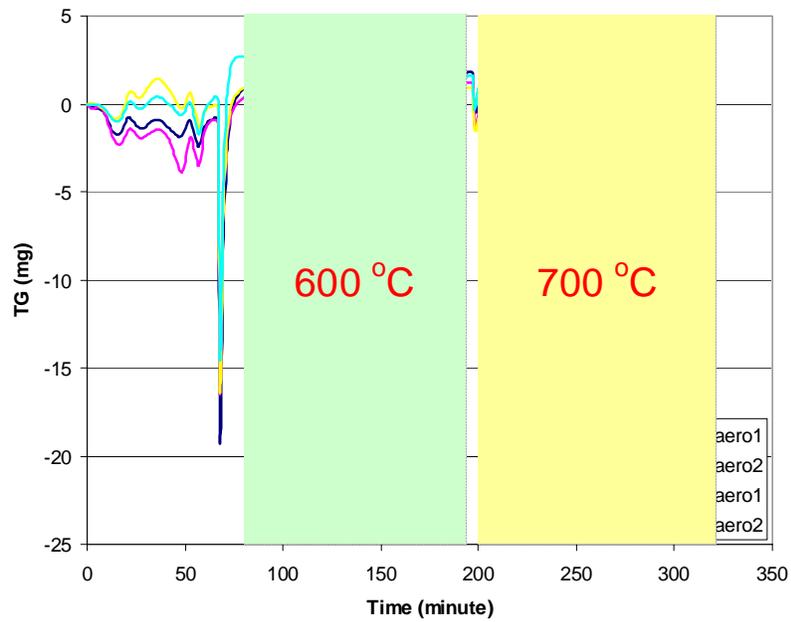
Figure 9. TGA data for two identical sets of coupons of n and p type Skutterudite encapsulated using the third generation scheme.
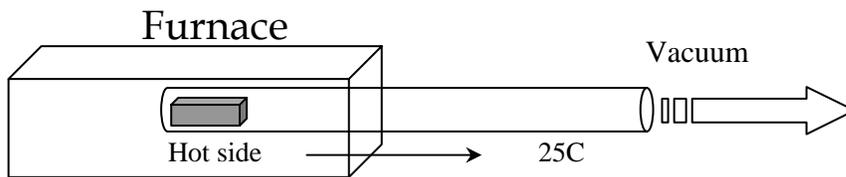
Figure 10. Coupons were placed in long ampoules, heated and evacuated.
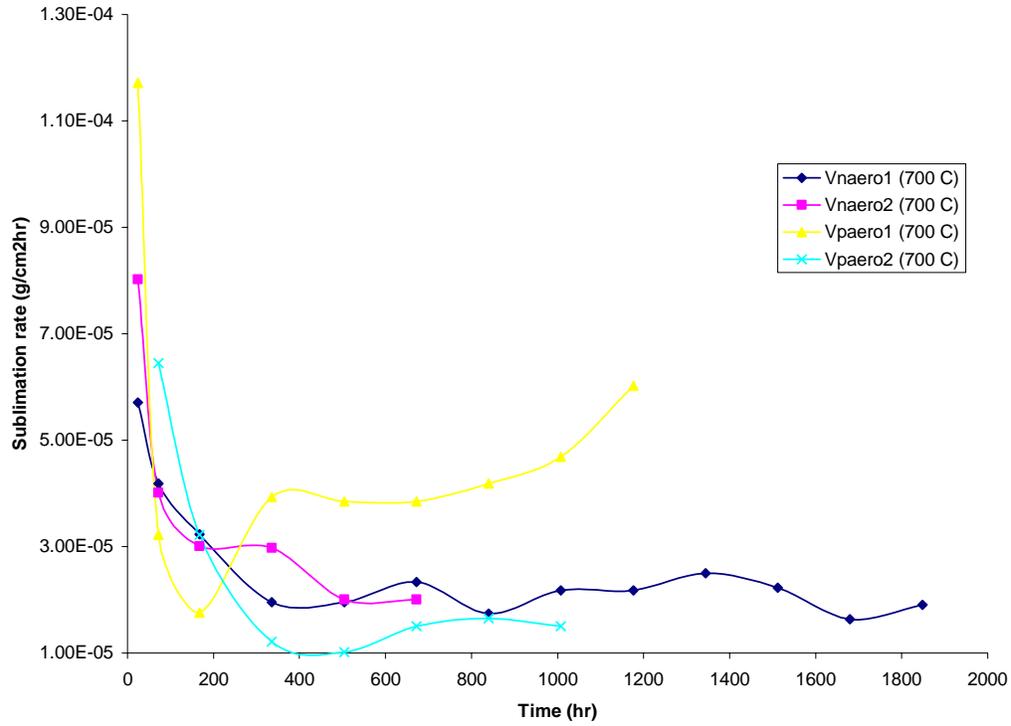
700 C

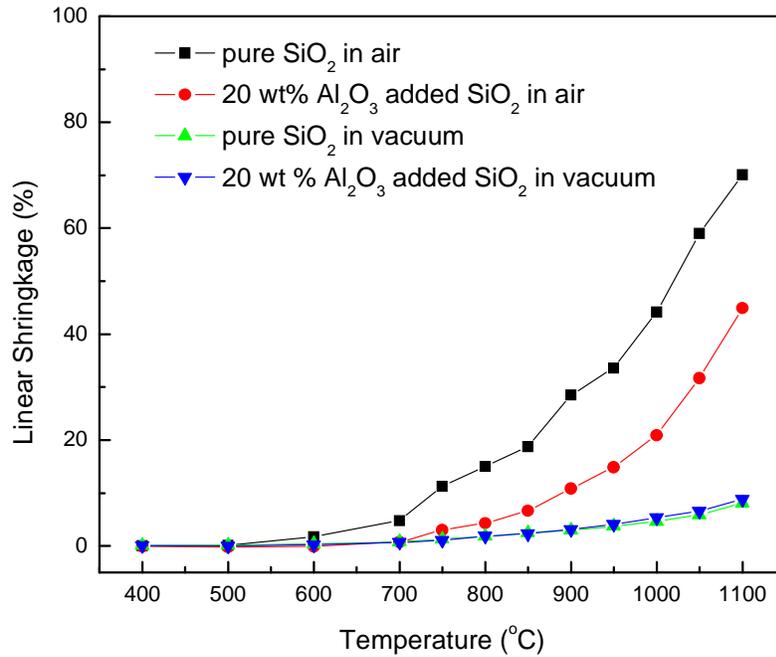**Figure 11.** Extended life test of aerogel encapsulated n and p-type samples.

Figure 12. Linear shrinkage as a function of temperature for pure silica and alumina doped silica aerogel in air and in high vacuum.
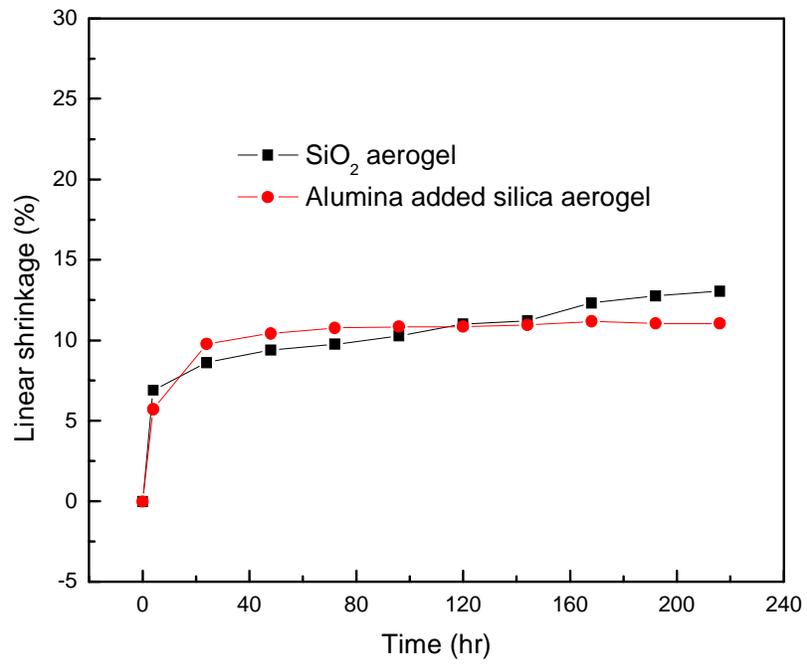
Figure 13. Linear shrinkage as a function of time at 1000C in high vacuum.