Development of Accelerated Aging Capabilities for Thermoelectric Materials and Metallic Contacts

Karla R. Reyes-Gil, Elizabeth Withey, Josh Whaley, Jeff Chames, Josh Sugar and Norman Bartelt

Sandia National Laboratories, 7011 East Ave, Livermore, CA 94551

Motivation

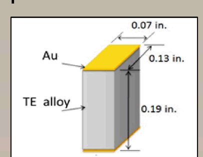
- The most important considerations for the selection of thermoelectric (TE) generator materials is the TE efficiency and stability at the target temperature gradient and during the expected lifetime that could be as long of several decades.
- The efficiency of the device is mainly governed by the transport properties of the thermocouples, which are sensitive functions of bulk material composition and microstructure.
- *Need # 1*: Accurate and reliable transport properties measurements are needed to calculate TE efficiency.
- *Challenge # 1*: Reliability Issues of Transport Properties of Bulk Thermoelectrics :
  - Significant gaps exist between literature ZT values and scalable materials.
  - IEA-AMT round-robin testing of bismuth teslluride transport properties showed significant measurement issues and highlighted need for standardization of measurements of thermoelectric materials properties.
  - Overall errors for ZT were from ±12 to 21%
- *Proposed Approach # 1*: In-house development of characterization capabilities.
- *Need # 2*: Aging studies are needed under realistic conditions to predict the lifetime of TE generators.
- *Challenge # 2*: A typical approach for device life testing is to expose the material to high temperatures for short period of time. This aging approach can changing or introducing new failure mechanisms and doesn't capture mechanisms driven by temperature gradient (such as Soret effect).
- *Proposed Approach # 2*: Development of novel aging capabilities to experimentally test under temperature gradient coupled with modeling lifetime predictions.

Development of Thermoelectric Characterization Capabilities at SNL

Sandia has dedicated several years on the development of reliable and reproducible in-house thermoelectric characterization capabilities. The developed capabilities have been used beyond thermoelectric for internal and external collaborations with industry and universities.

Figure of merit (Z_o and Z_{eff}) is calculated as function of temperature

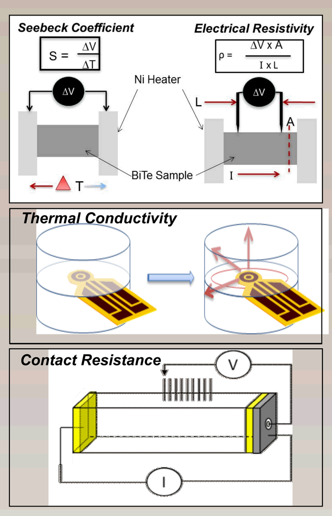
$$Z_o = \frac{S^2}{\rho.\kappa} \qquad Z_{eff} = Z_o\left(\frac{1}{1+\frac{2R_C}{R}}\right)$$



Dimensions of the polycrystalline p and n-type BiTe samples provided by a commercial supplier. Electroplated Au contacts at both ends (thickness of ~8-10 µm).

- Seebeck coeffiecient (S) and electrical resistivity (ρ) custom-built device
  - To measure resistivity, the sample is located between two heaters with two voltage probes in contact with the top surface. A known current is then sent through the material and a voltage recorded.
  - To measure Seebeck, a temperature gradient is set up across the material and the voltage recorded.
- Thermal conductivity (κ)
  - A new experimental procedure was designed using a commercial device called TPS 2500S Thermal Property System, where a sensor is used both as a heat source and as a dynamic temperature sensor. The heat generated dissipates through the sample at a rate dependent on the thermal transport characteristics of the material.
  - By recording the temperature versus time response in the sensor, thermal conductivity can accurately be calculated.
- Contact Resistance (Rc)
  - Contact resistance and bulk resistivity measurements by 4-point probe method using custom built in-house device
  - Current is injected across two faces of the sample while voltage measurements are taken at equal distances (400µm) on the top face.
  - By recording resistance versus distance from the contact, the resistivity is calculated rom the slope and contact resistance from the y-intercept.
- All the techniques were carefully tested using internal and NIST standards.

Measurement Schematic



Device

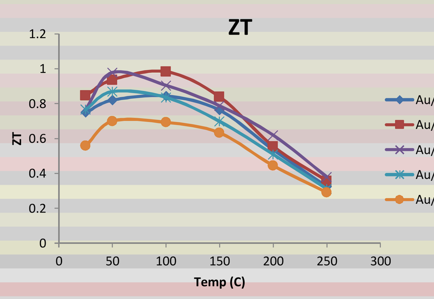
Isothermal Aging Studies

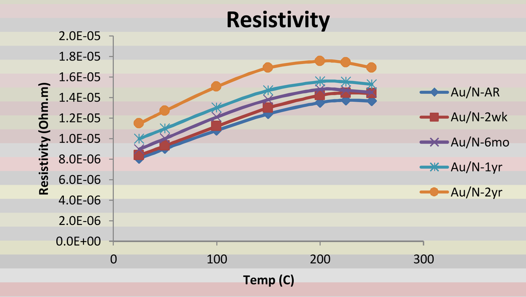
Due to difficulty of testing under real conditions, a typical approach for device life testing is to expose the material to higher temperatures (without changing or introducing new failure mechanisms).

- **Pros**- commercially available ovens, relativity inexpensive and large number of samples can be aged simultaneously for long periods of time.
- **Cons**- do not mimic operational conditions, and therefore interesting effects that can occurs only under temperature gradients (such as Soret effect) can be missed.

Experimental procedure:

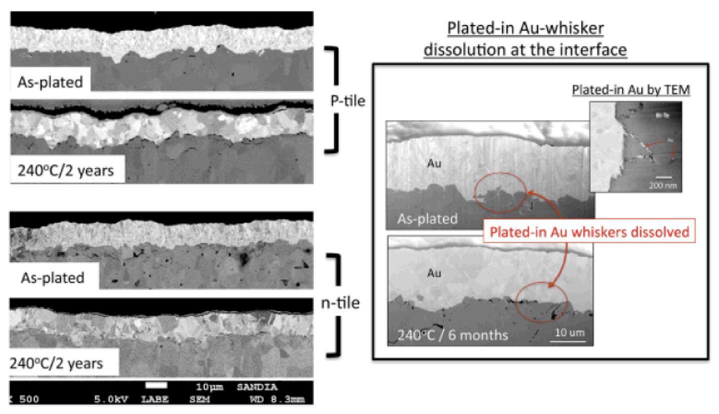
- Au plated samples were sealed in Ar filled quartz tubes and thermal exposed to 240ºC up to 2 years.
- In house capabilities were used to measure the individual transport properties (thermal conductivity, electrical resistivity and Seebeck coefficient) and ZT was calculated as function of temperature for the as received samples and thermal aged samples.





Results of 2-yr isothermal aging study in Ar atmosphere

- No significant change in th TE properties of Au plated p-type BiTe samples.
- A reduction of ~15-20% was found on the ZT of n-type BiTe samples, mainly due to an increase in electrical resistivity. Microscopy images revealed that changes of resistivity might be due of porosity changes.
- No changes of contact resistance were found.
- SEM images showed that after aging at 240C for 2yr in Ar there is no significant change in Au thickness, except for some minor Au dissolution in the interface.



SEM images are courtesy of Nancy Yang (Sandia National Labs)

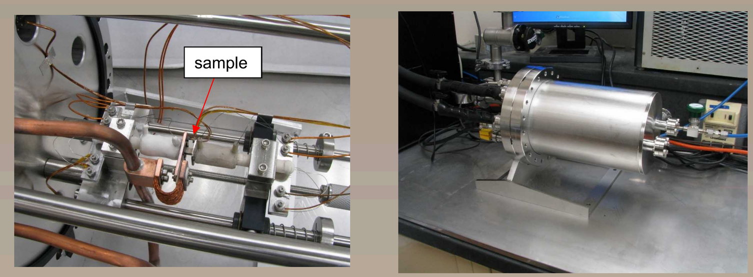
Temperature Gradient Aging Studies

Thermoelectric generators are operated under relative large temperature gradient and with flowing current. In addition to isothermal aging, aging under realistic operational conditions is important to characterize effects such as Soret effect and Electromigration. Soret effect (also known as thermodiffusion and themomigration) is a compositional redistribution driven by thermal gradients. This phenomenon is observed in mixtures of mobile particles where the different particle types exhibit different responses to the force of a temperature gradient.

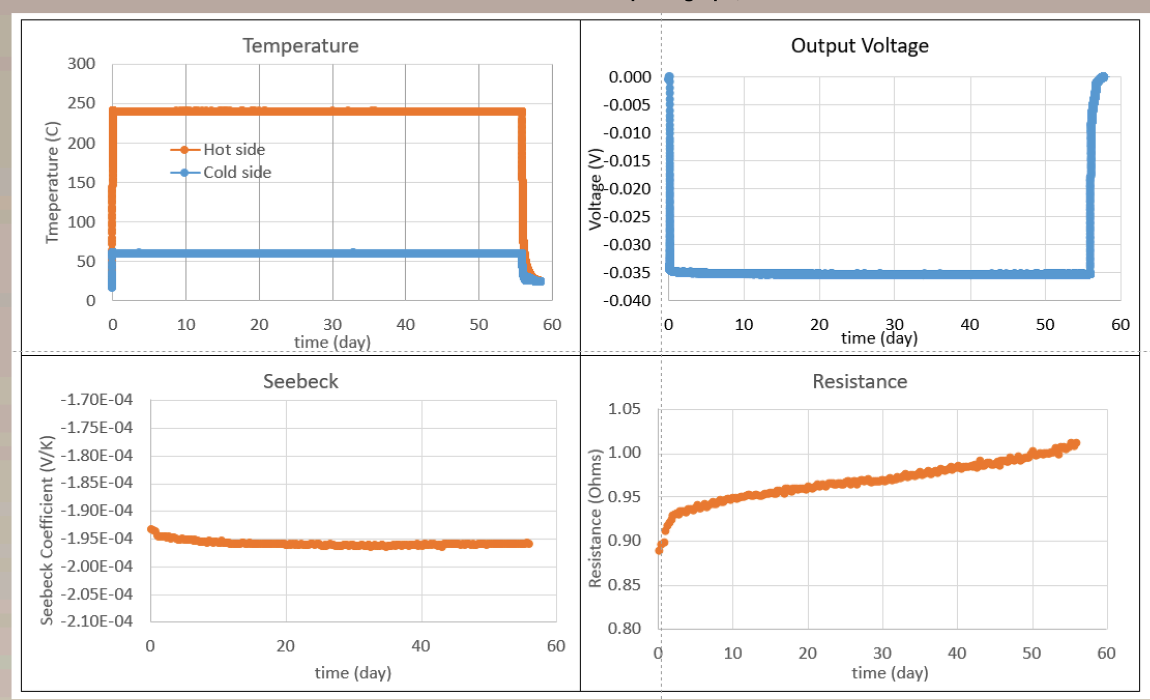
- Pros- realistic conditions, accurate failure mechanisms
- Cons- complex instrumentation, custom-built development, expensive, limited sample number can be tested.

New Capabilities at SNL

- A custom built in-house device was developed at Sandia to apply a temperature gradient and a current flow with in-situ measurements of the output voltage and electrical internal resistance of the thermoelectric materials.



Photographs of vacuum chamber: (left) inside view and (right) outside. In the inside view photograph, the red arrow indicates the location of the sample between the heaters.



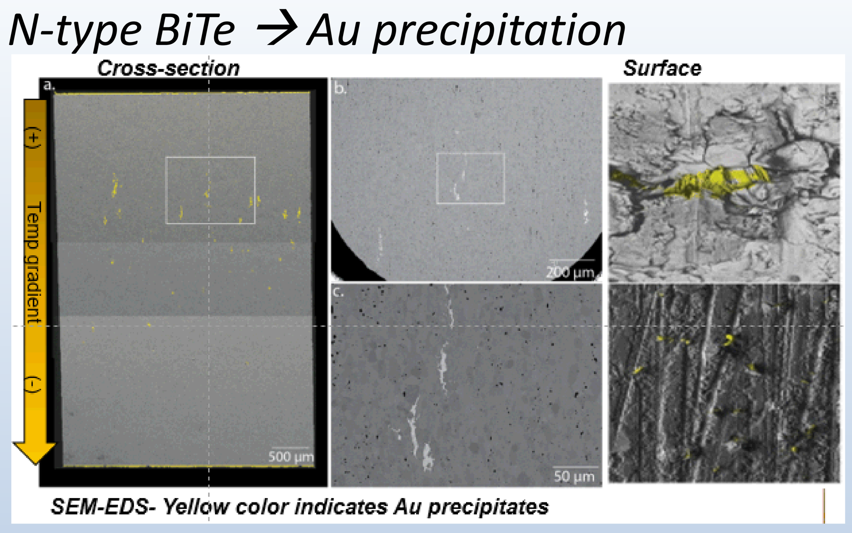
- **(Left) Temperature monitoring of the hot and cold side. One side of sample was kept at 240C and the other side at 60C.**
- **(Right) The output voltage was very stable during the 8-wk aging period. The output voltage is the sum of individual voltage contributions from Seebeck, resistivity and contact resistance.**

Every hour, the current was turned off and after a wait time, the short circuit current and open voltage were measured (8 readings each).

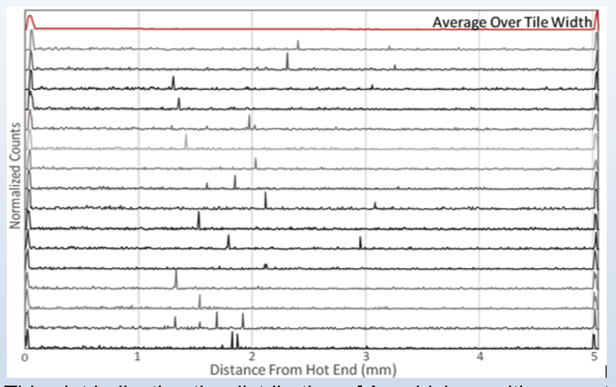
- **(Left) Seebeck coefficient was calculated by dividing the open circuit by the temperature gradient.**
- **(Right) The internal resistance was calculated as the ratio of the open circuit to short circuit current.**

The presented data is for n-type samples. The p-type samples had the similar results.

N-type BiTe → Au precipitation



SEM-EDS- Yellow color indicates Au precipitates

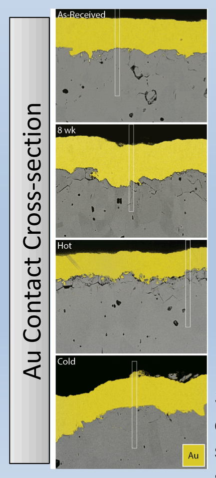


This plot indicating the distribution of Au whiskers with respect to distance from hot end. The Au whiskers start to appear after 1.0mm in from the hot end, and then the distribution decreases going toward the cold side.

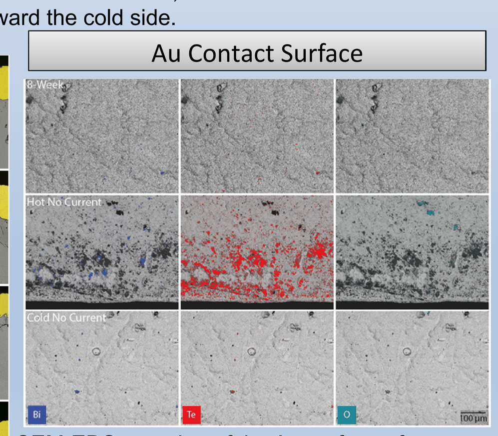
SEM and EDS montage of cross-section and surface of n-type tiles- Higher magnifications images of the cross-section revealed Au "islands" and of the surfaces revealed the Au precipitates to be whiskers and hillocks. Whiskers are fine "hair" like features that pushing through the tile surface under the action of compressive forces. Hillocks cover the whiskers until the whiskers can break through the surface of the tile.

Sample	Area (µm²)	Length (µm)	Thickness (µm)
AR N Side 1	44088.732	3215.823	13.710
AR N Side 2	45437.652	3294.233	13.793
8wk N Side 1	41609.251	3308.087	12.578
N Soret Hot Left	25828.482	3332.911	7.750
N Soret Cold Left	35075.853	3271.831	10.721

Measurements of the Au thickness on both contacts of the Soret-tested tile under flowing current indicated a sharp decrease in thickness on the hot- contacts. The hot-side contact lost nearly half of its thickness and the cold-side ~20% of its thickness compared to a less than 10% decrease in the 8-week isothermally aged tile.



Au Contact Surface



SEM-EDS mapping of the Au surface of n-type sample exposed to temperature gradient. The hot side contact showed large amounts of Te precipitation, with some small amount of Bi and O.

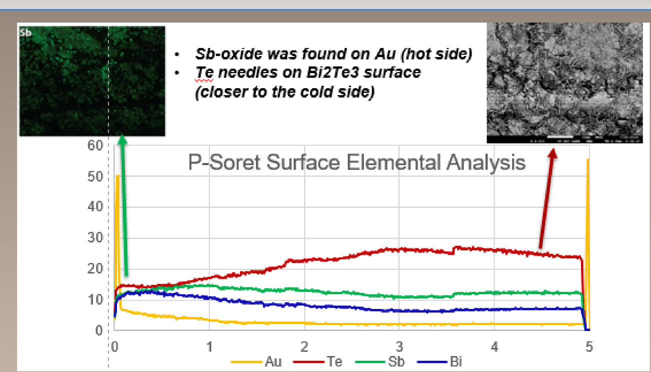
P-type BiTe → No Au precipitation

(under this conditions)

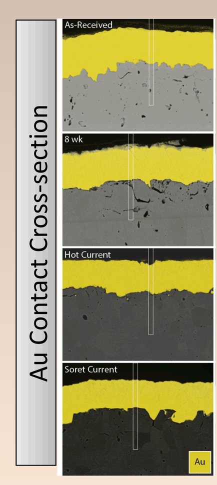
SEM and EDS montage of cross-section and surface of p-type tiles- Unlike the n-type sample aged under the same conditions, at this magnification the p-type tile does not exhibit any Au precipitates on the p-type surface or in the bulk of the tile.

Sample	Area (µm²)	Length (µm)	Thickness (µm)
AR P Side 1	44440.305	3303.024	13.787
AR P Side 2	48855.062	3459.916	14.120
8wk P Side 1	42640.127	3254.008	13.104
P Soret Cold	45789.759	3273.980	13.986
P Soret Hot	40793.884	3327.368	12.260

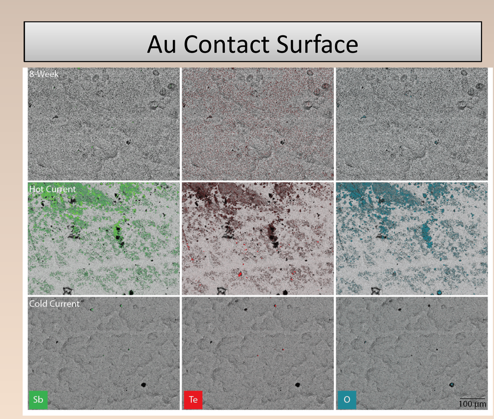
Au contact thickness did not change much in the p-type tile compared to the n-type tile under the same conditions. These differences in behavior between n- and p-type tiles is likely due to differences in Au diffusivity between the two materials and a good agreement with absence of Au precipitation.



The surface of the tile aged under thermal gradient was very different from its cross-section and the 8-week isothermal tile showing a clear variation in the concentration of Bi, Sb, and Te from the hot end to cold end in between the Au contacts

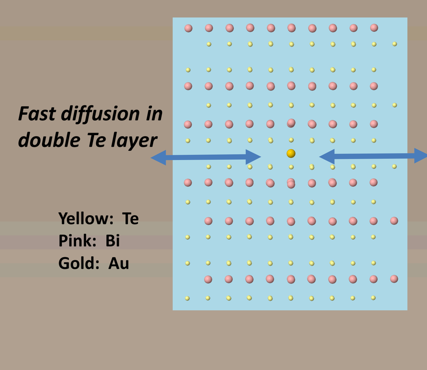


Au Contact Surface



Careful examination with analysis of EDS signal data, reveal a surface layer of Sb oxide with well distributed Te precipitates across the hot contact of the p-type Soret sample. Te precipitates can be also seen in the isothermal samples.

Model Development for Au Mobility



Au equilibrium solubility in Bi_2Te_3 has been measured and it is small enough that it will not immediately affect electrical properties or cause significant contact loss.

However, Au whiskers grow on the surface of n-type samples after heating in a thermal gradient! Whiskers do not form during isothermal tests. Au precipitates also form inside the n-type Bi_2Te_3.

Is this precipitation affecting the equilibrium solubility?
Why do these precipitates form?
How do they grow in time?
Does the growth saturate?

"Soret" or "thermomigration" effect: Atomic flow can be caused by a thermal gradient:

$$J = -D(T)\, c\, (\nabla \ln(c) + Q^{*}\nabla T/k_B T^2)$$

c is the dissolved Au concentration, *D* is Au diffusivity and *Q** is the "heat of transport" of Au in Bi_2Te_3.

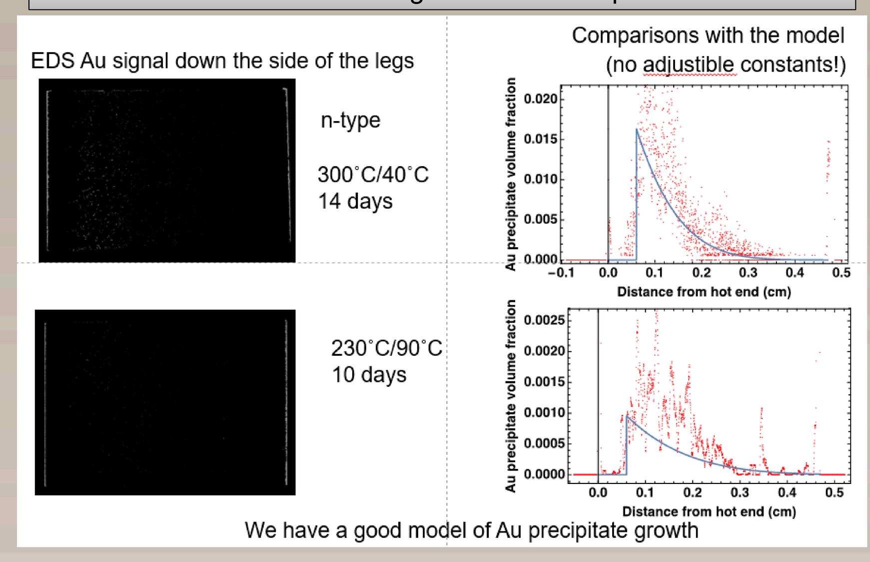
Without the formation of Au precipitates or whiskers, this equation predicts that J ≈ 0 at long times because the ∇c term will build up to cancel the ∇T term.

Au precipitate formation does not allow ∇c to build up causing a huge increase in Au diffusion

Predicted time and spatial dependence of number of Au atoms in the precipitates assuming that dissolved Au is in local thermal equilibrium with the precipitates:

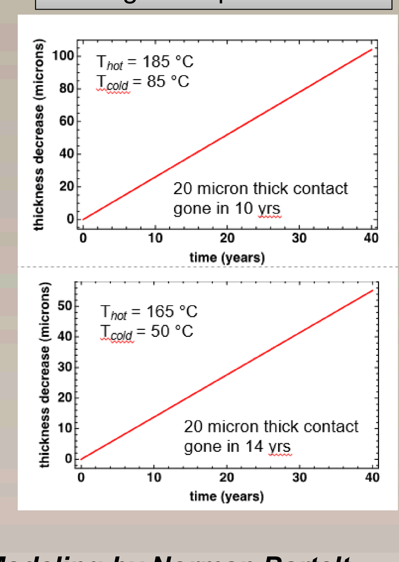
$$N(x,t) = \left(\frac{T_{hot} - T_{cold}}{L}\right)^2 \frac{D_0 c_o}{k^2 T^4}(\Delta H + Q^*)(\Delta H + Q - 2kT)\exp\left(-\frac{\Delta H + Q}{kT}\right)t$$

Model validation using accelerated experiments



We have a good model of Au precipitate growth

Long- term predictions

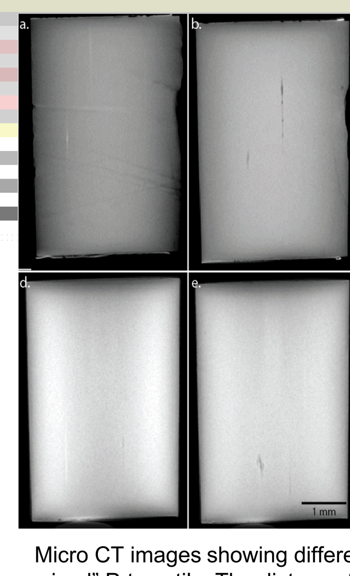


Modeling by Norman Bartelt

Future Developments

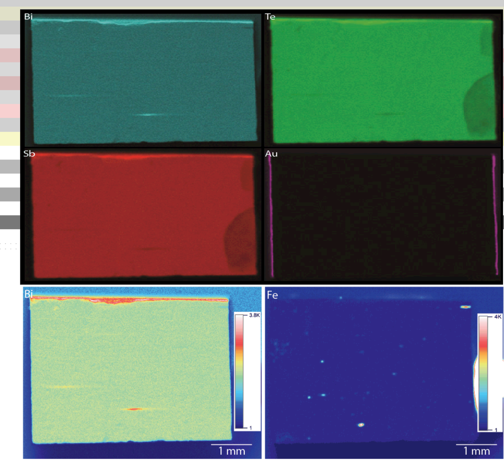
Elemental diffusion, in particular Au, behaves in different ways on p and n-type samples and under isothermal and thermal gradient conditions. Au diffusion in Bi_2Te_3 was evidenced for n-type samples, but the performance has not been significantly affected. Longer experiments together with modeling are needed to determined long-time effects. This work answered some questions, but open new ones. Here, we present future developments that would help to better understand this interesting phenomena.

- **Longer aging-** 6-month aging under temperature gradient was recently concluded. The samples are under analysis. This data will help to validate the model.
- **Experimental and Modeling efforts**- New capabilities for temperature gradient exposure have been successfully used to validate Au diffusion models. This experimental/modeling effort can be used to predict long-time effects and validate accelerated aging with larger temperature gradients. Also, the model can be expanded for diffusion of Bi, Sb and Te.
- **Diffusion barrier characterization and aging**- Diffusion barriers are currently under development. The same techniques used for aging thermoelectric materials and their characterization discussed in this work should be used to study the top diffusion barriers candidates.
- **Aging evolution by microCT**- As-received samples had existing features related to manufacturing, including discontinuous Au coverage and delamination, porosity gradients, iron oxide inclusions, cross-contamination between p- and n-type materials, and cracks, among others. As the majority of the microstructural characterization is destructive (such as cross-section SEM-EDS analysis), it is not possible to follow the same sample throughout the aging process. It is difficult to determine if some features observed in the aged samples were present before aging. The figures below shows that micro CT combined with XRF can detect important features (such as voids, cracks, Au delamination, high Z inclusions (such as Bi enriched zone) and low Z inclusions (such as Fe). With the development of a custom-built holder to avoid damage to the sample, a single sample can be analyzed before and during at different intervals to follow the evolution of multiple microstructural features. In addition, non-destructive techniques, such as micro CT, can also be used for diagnostic evaluation of thermoelectric modules.



Micro CT images and X-ray Fluorescents Maps are courtesy of Bernice Mills (Sandia National Labs)

Micro CT images showing different slices of an "as received" P-type tile. The distance from the surface was a) 10, b) 77, C) 300, d) 574, and e) 929 µm.



X-ray maps of Bi, Te, Sb, Au and Fe

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