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Abstract

Metallurgy and thermal stability of Bi-Te thermoelectric modules

Nancy Y.C. Yang, Alfredo M. Morales, Peter van Blarigan, Bruce P. Mosier, April Nissen.

Sandia National Laboratories, 7011 East Ave., Livermore, CA 94550.
*Contact author: nyyang@sandia.gov, (925) 294-2680, fax (925) 294-3410.

We are developing a long lived power source based on the generation of electrical power from a heat source using a bismuth telluride thermoelectric device. Key to long lasting, reliable power output is a fundamental understanding of the material properties and potential failure modes of bismuth telluride. Specifically, the components in the power source will be subjected to elevated temperatures for brief of times during assembly followed by extended use at temperatures above room temperature. Any resulting materials changes in bismuth telluride must be understood and mitigated if necessary.

In this talk, we will present the metallurgy of commercial and custom made bismuth telluride devices, including microstructure, texture, mechanical properties, and the general thermoelectric device construction materials. We will then discuss the stability of bismuth telluride over time as a function of both its thermal history and its reactivity with other materials in the thermoelectric device.

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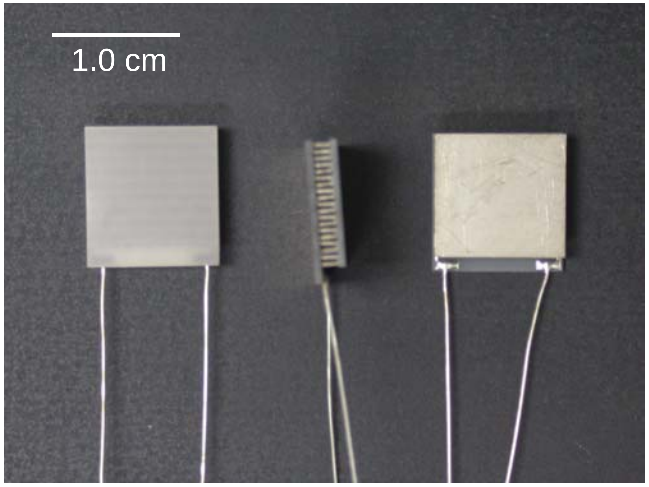
Samples background

Sample description of the Bi_2Te_3 thermoelectric (TEC) modules supplied by Thermix, Ukraine as follows:

-- The cover support plates are Aluminum nitride (0.02" thick)
-- Solder is SnSb, Melting Point is ~ 230 C

--The individual TEC elements ("Legs") are 1.27 mm long and 0.27 mm square for both P-types and N-type.
--Modules dimension is shown below



Experimental results

(I) Material design and construction of multi-layered modules

(II) Metallurgy of the Bi-Te thermal piles and materials for joining

--Microstructure

-- Mechanical properties and behavior

--Texture

(III) Thermal stability of the materials and integrity of the TEC modules

(I) Material design and construction of multi-layered modules

•Layered structure of the current TEC modules was examined through modules cross sections that were prepared by the conventional metallographic polishing and mounting processes

•Metallurgical/material science were investigated using advanced electron optical techniques:

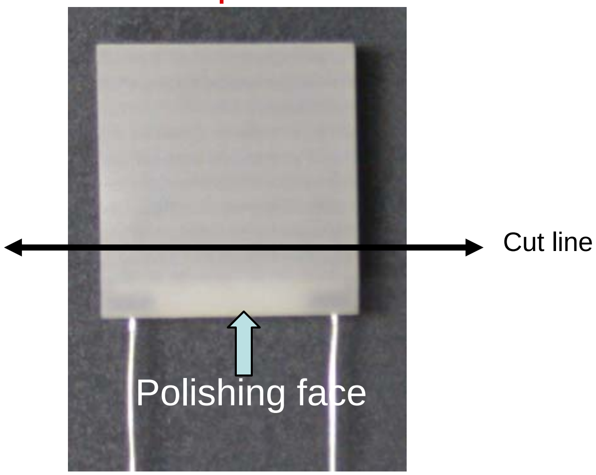
-- Optical metallographic

-- Scanning electron microscopy (SEM)

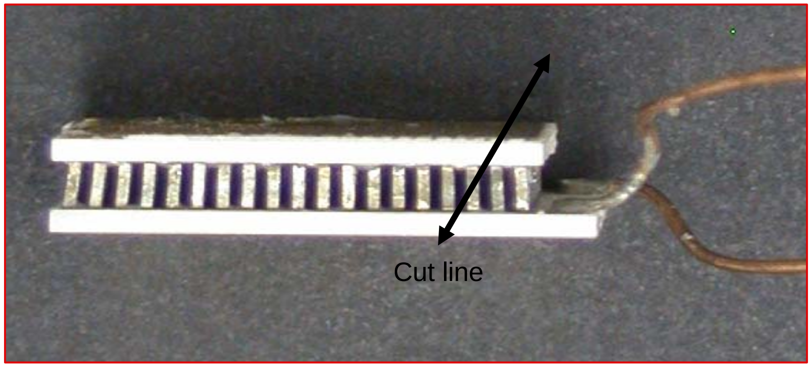
-- Electron probe microanalyses (EPMA)

Cross section samples prepared using standard metallographic mounting and polishing process

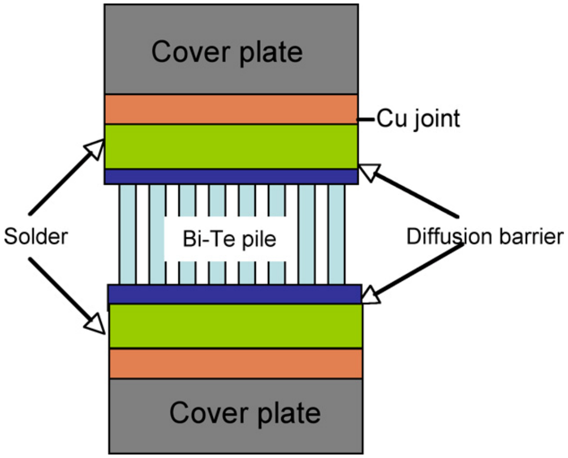
Top view



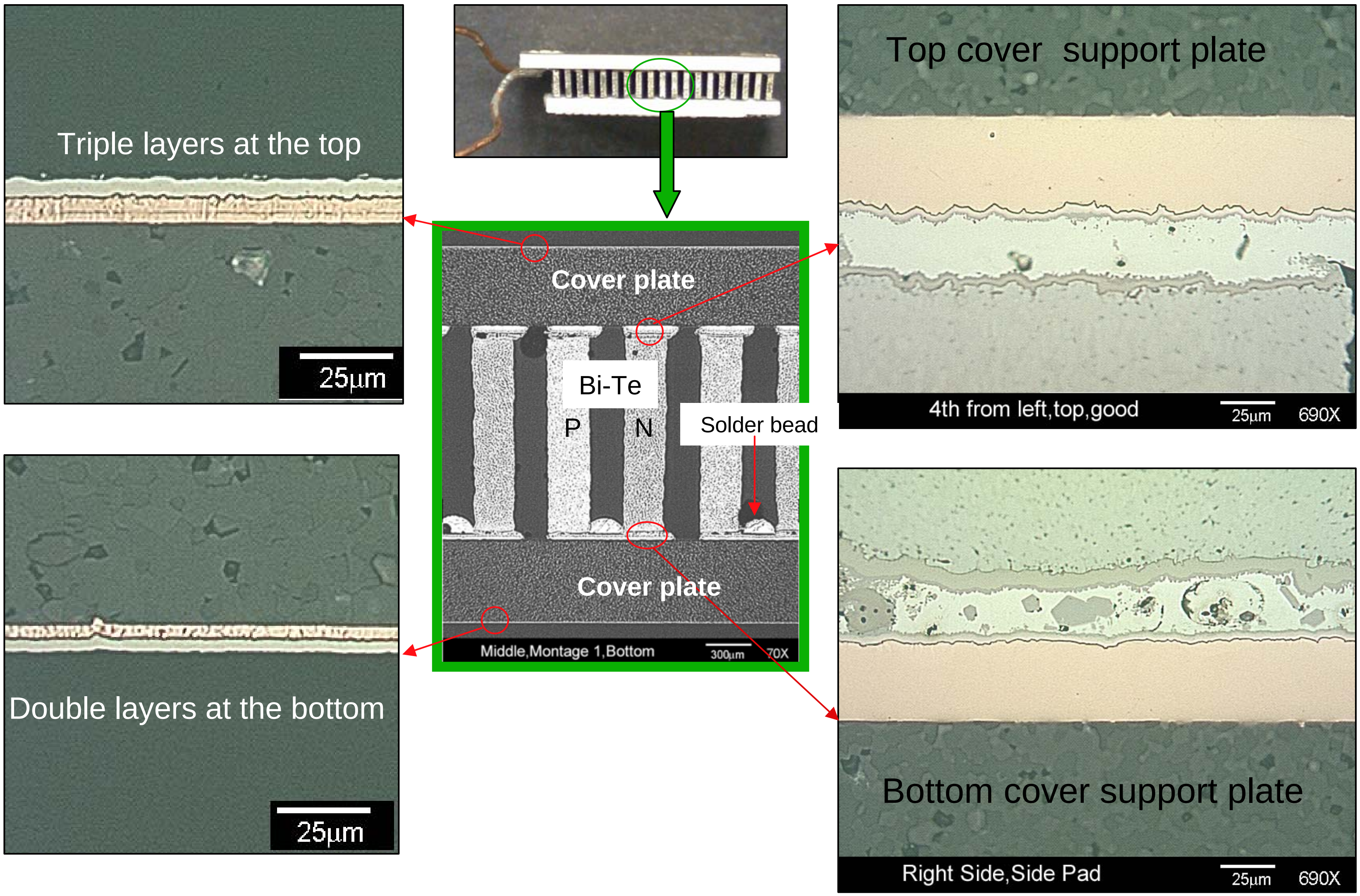
Side view



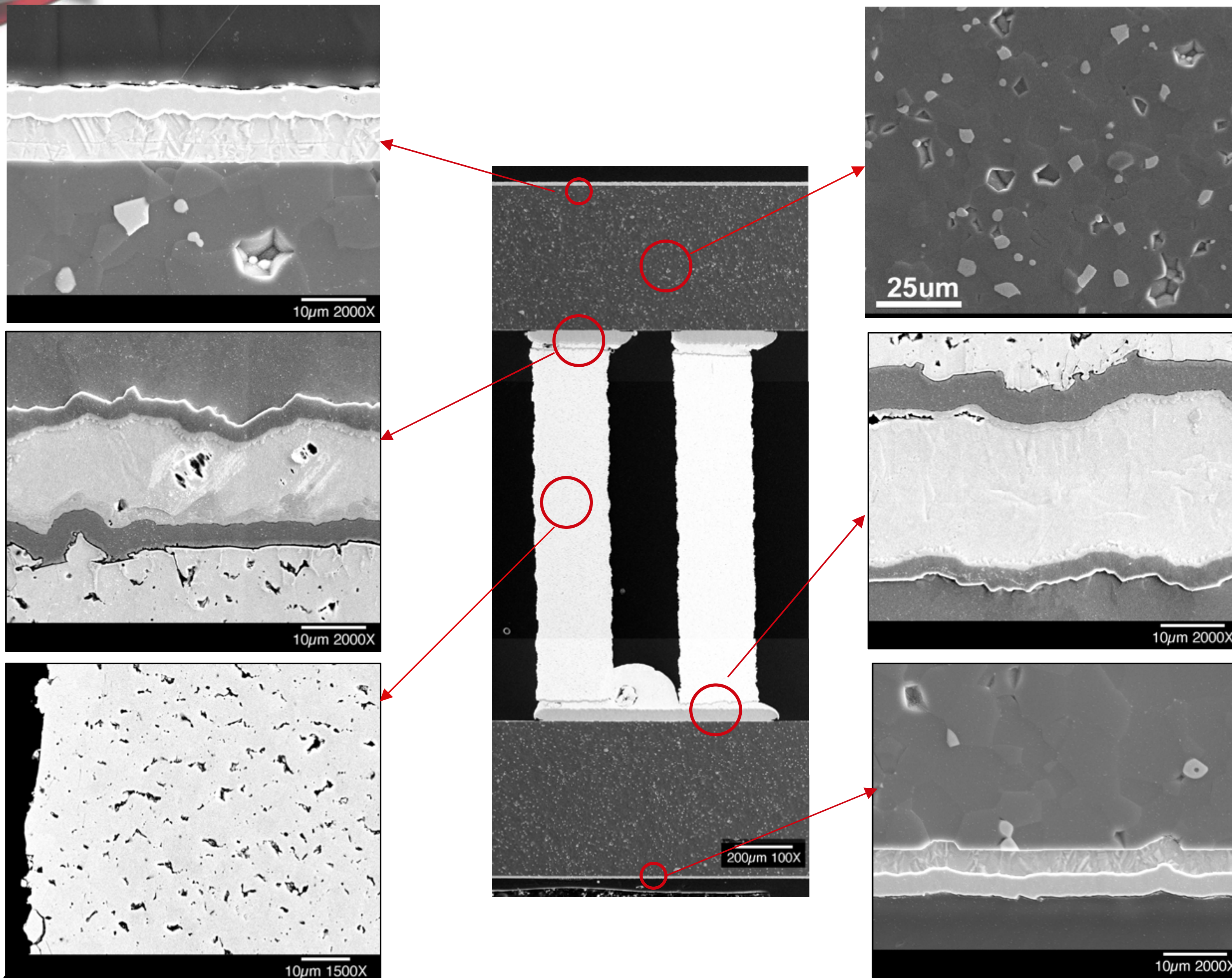
Schematic of multi-layered expected in the current TEC modules



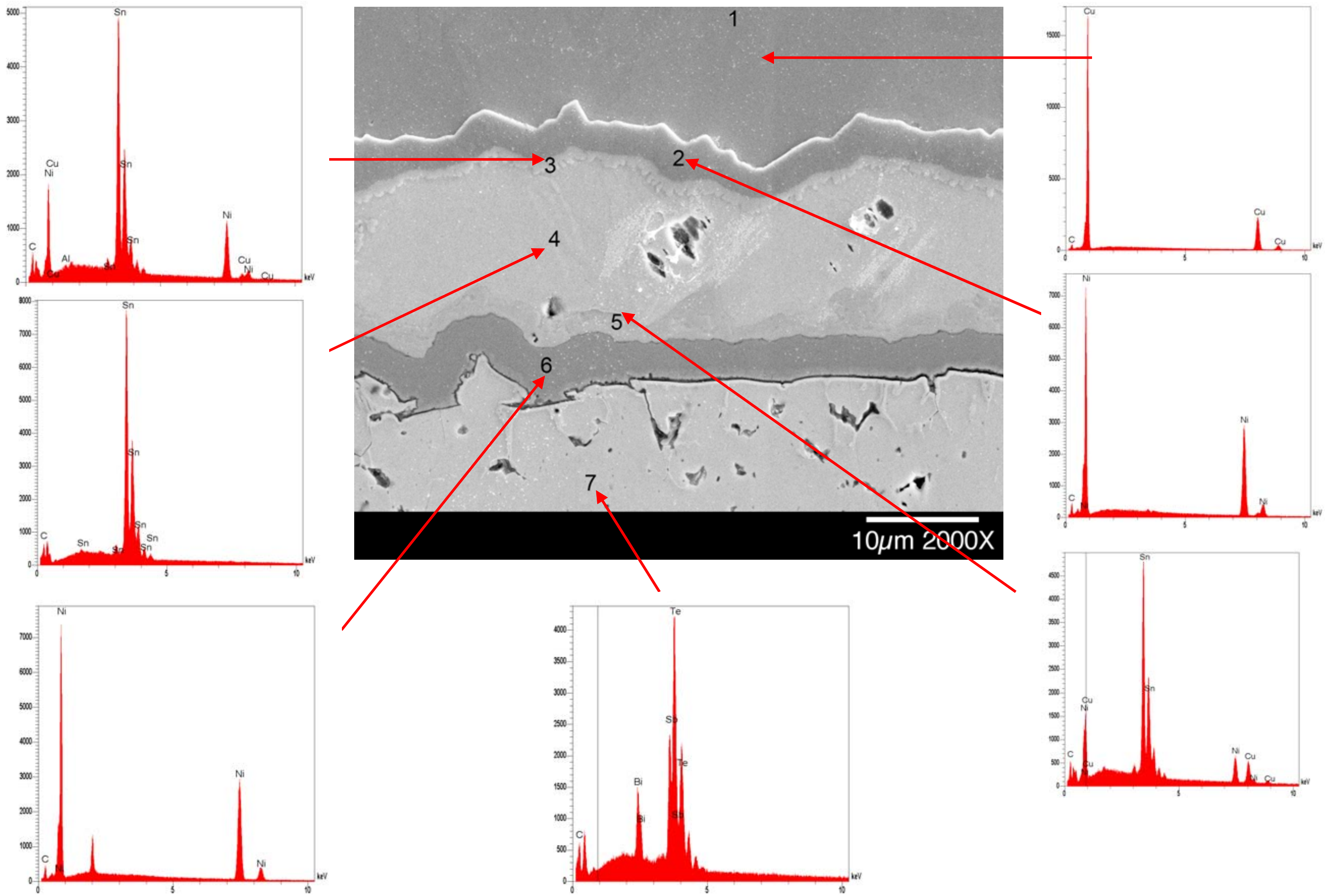
Multi-layered construction of the TE modules were revealed using optical imaging



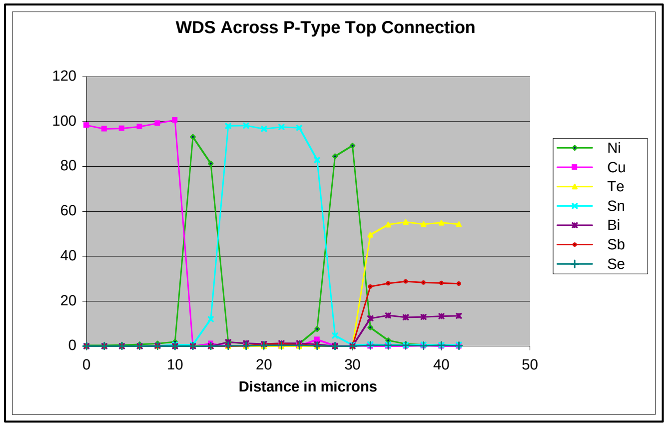
Multi-layered structure was confirmed using scanning electron imaging

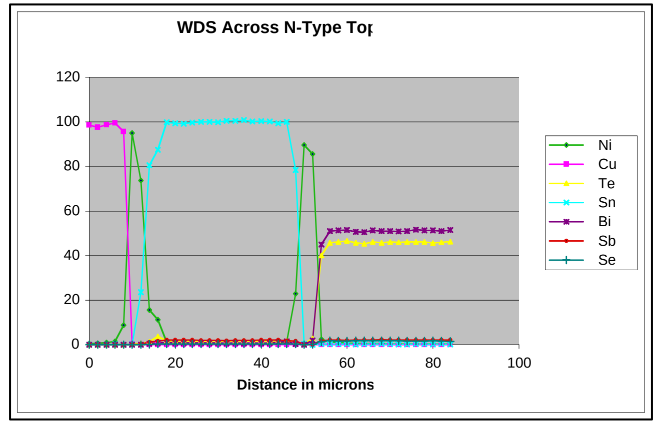


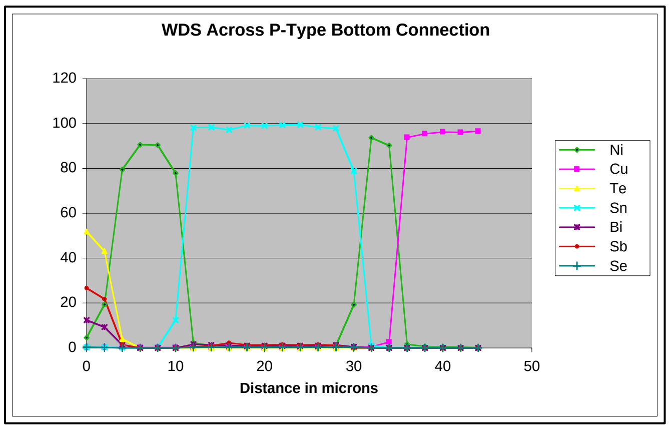
Chemical composition of each layer were qualitatively identified using Energy Dispersive X-ray Spectroscopy (EDS)

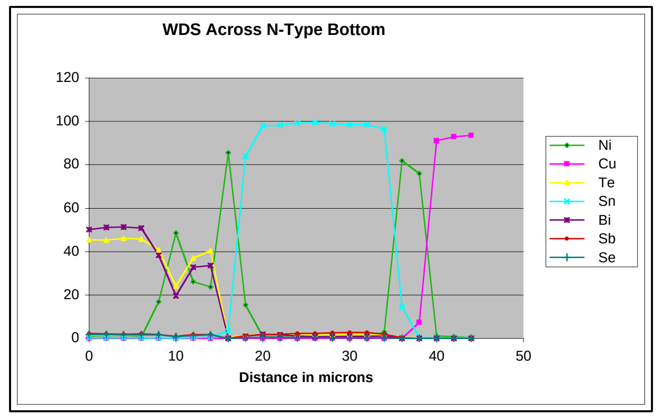


Chemical composition and its concentration profile across the layered structure were quantified using electron microprobe analyses (EMPA)









Chemical composition (wt%) measured using electron microprobe

Ni	P	Te	Sn	Bi	Sb	Se		
1.0		54.6	0.6	13.3	28.2	0.3	P-type	
0.4		46.0	0.3	51.1	2.1	1.7	N-type	
			99.0		1.0		Solder	
>99						Diffusion barrier Cu side		
90.0	10.0					Diffusion Barrier Bi-Te side		

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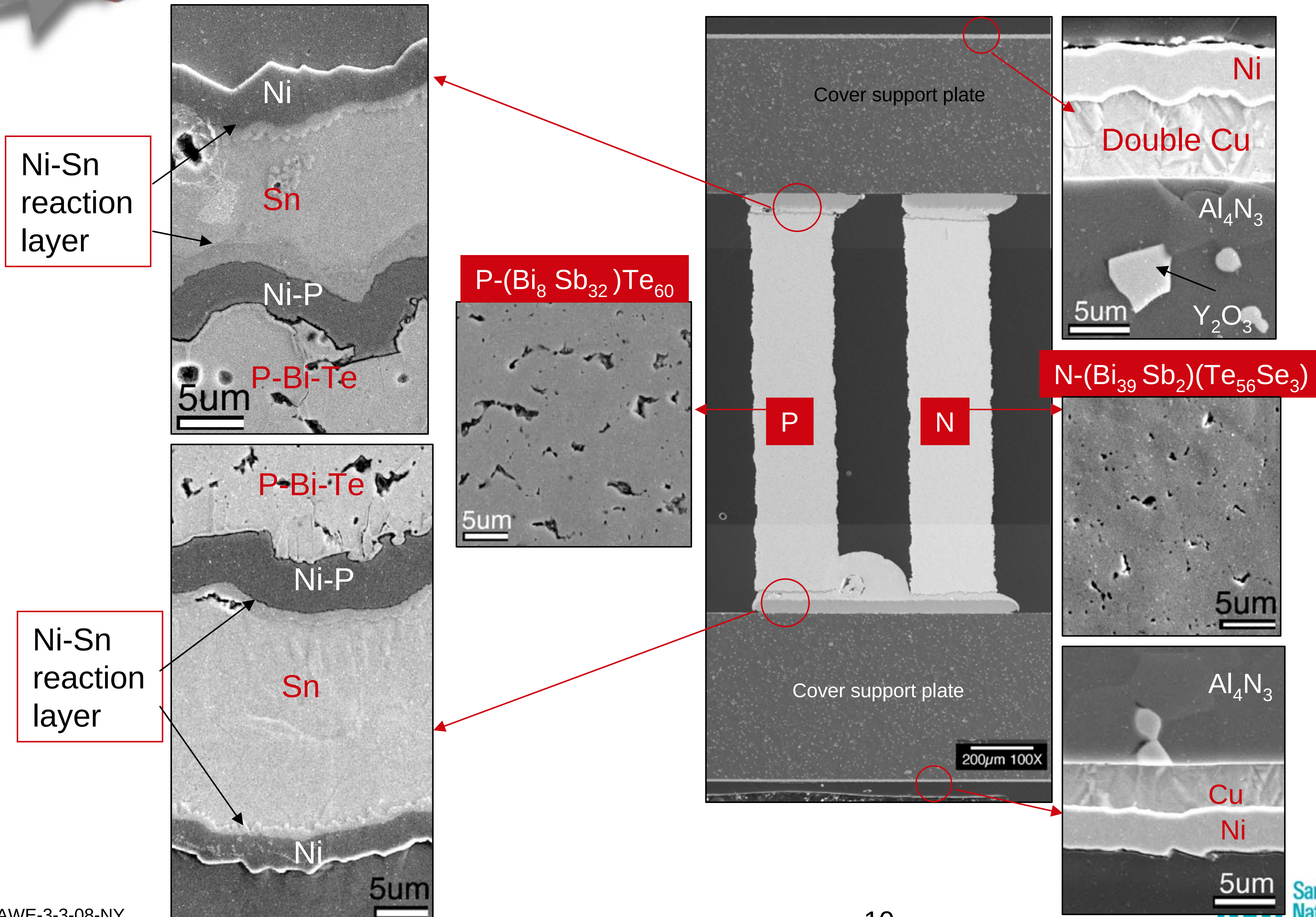
Summary of material design for the multi- layered TEC modules



(II) Metallurgy of the Bi-Te piles

Microstructure:

-- Optical metallography

-- Scanning electron microscopy (SEM)

Alloy composition

-- SEM with energy dispersive X-ray spectroscopy (EDS)

-- Electron probe microanalyses (EPMA)

Texture

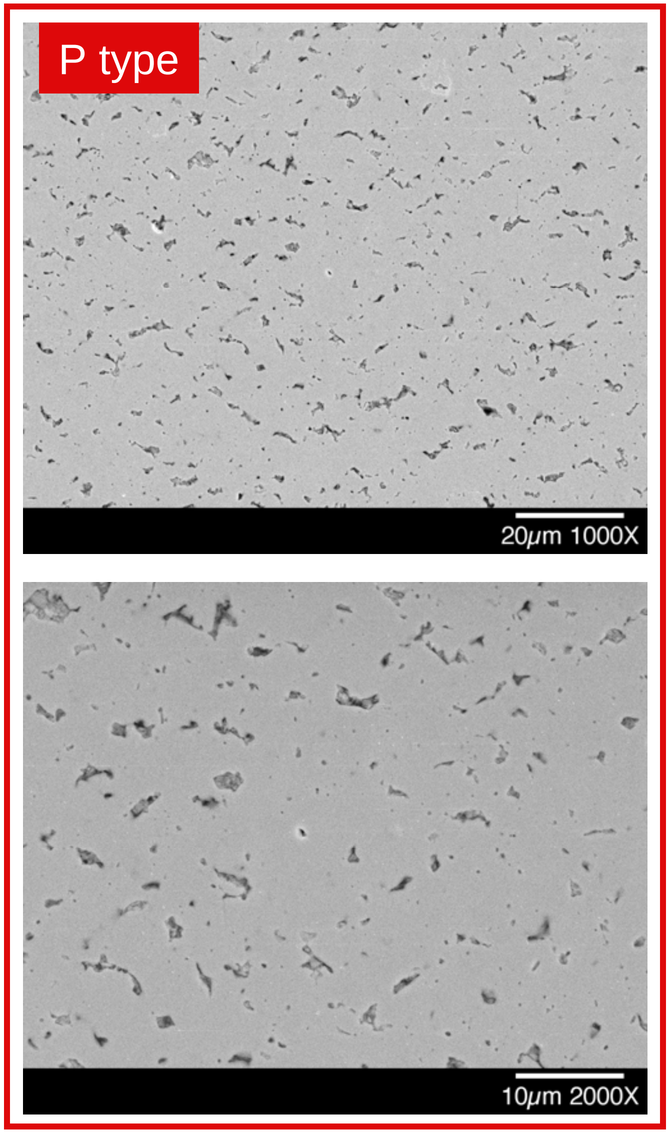
-- Backscattered electron diffraction pattern (EBSP)

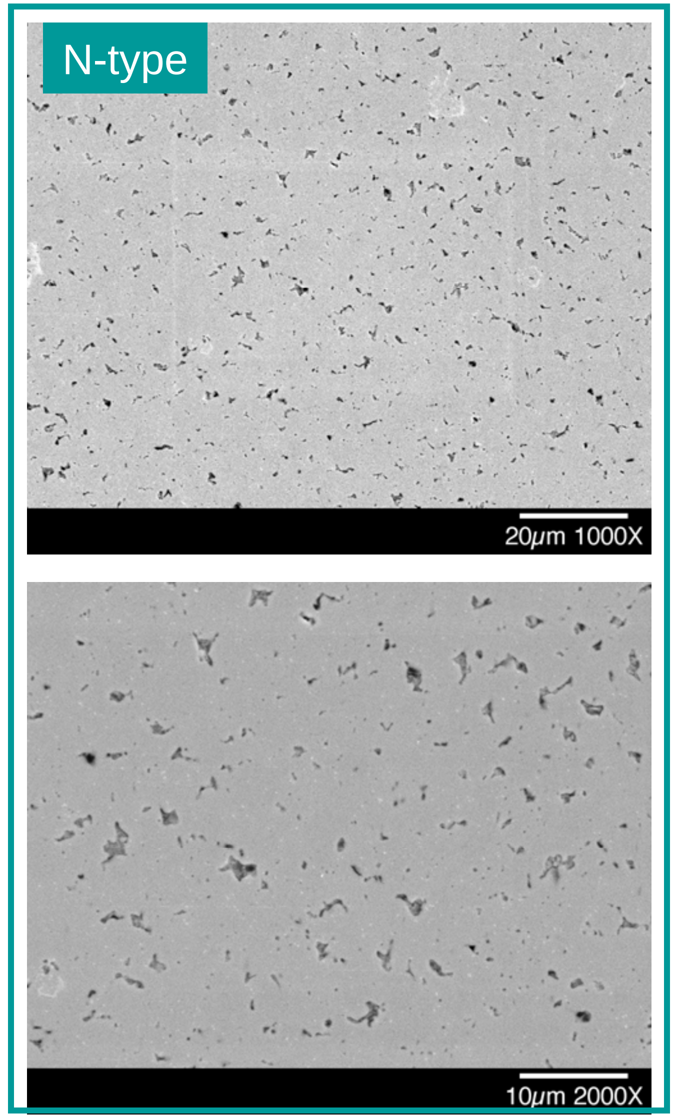
Mechanical properties and behaviors

-- Vickers microhardness diamond indentation

-- Nano-indentation

Typical microstructure with respect to defect, e.g. pore or inclusion?

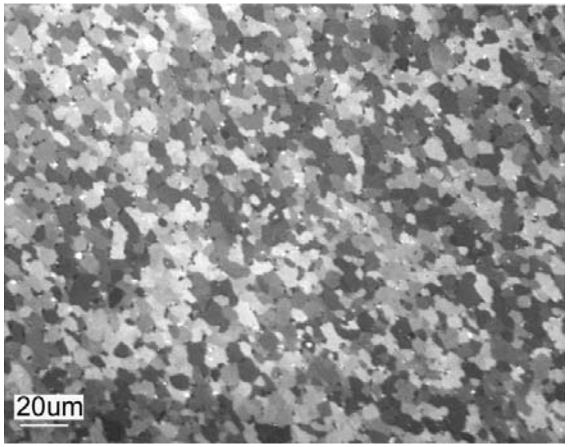




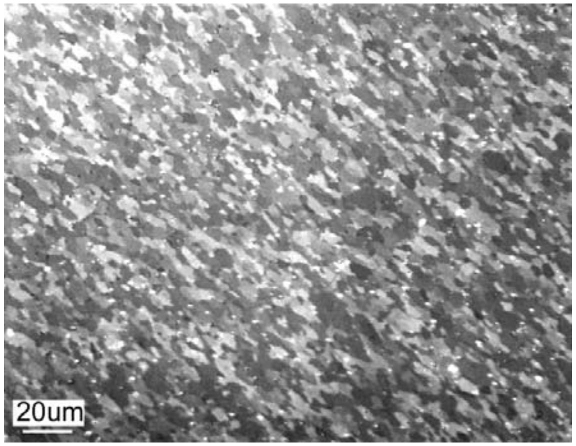
Defect Density is ≤1-5 vol. %

Typical Bi-Te grain structure is equi-axed in shape and ~5-10um in size. Grain size varies slightly between the P-type and N-type

P-type-Thermix

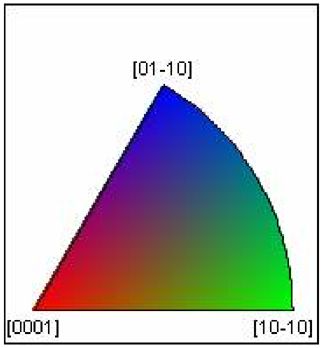


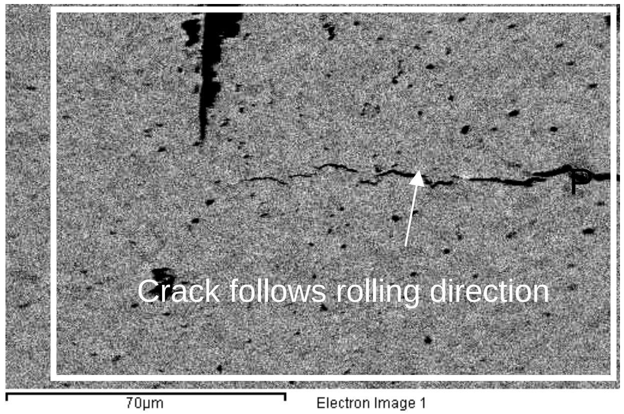
N-type

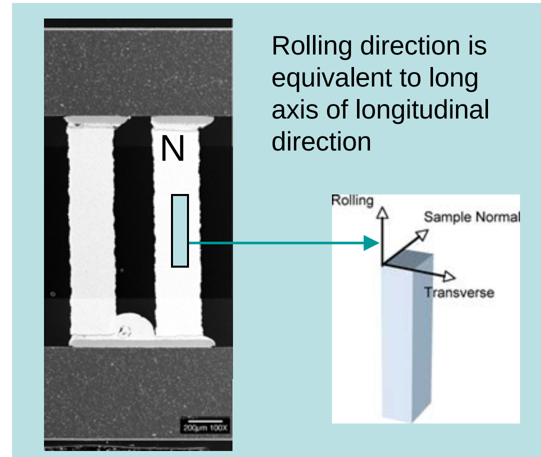


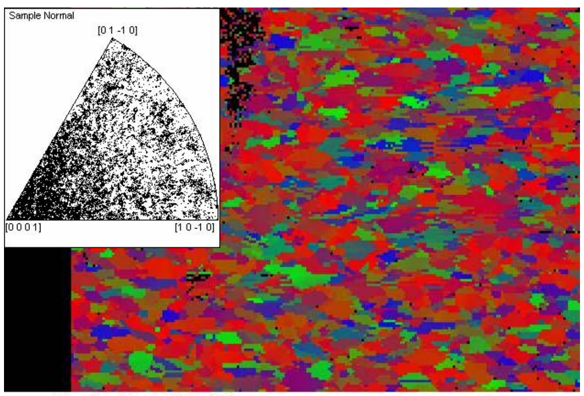
- P-type grains are equiaxed and ≤10um in diameter
- N-type grains are slightly elongated and ≤5um in width

EBSP/inverse pole figures shows moderate texture along all three crystallographic axes (logitudinal, transverse and normal) of N-type

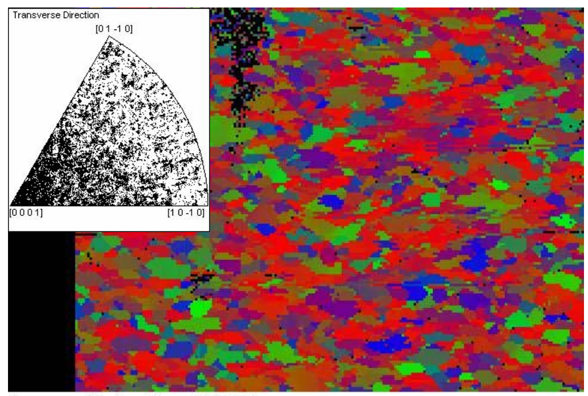




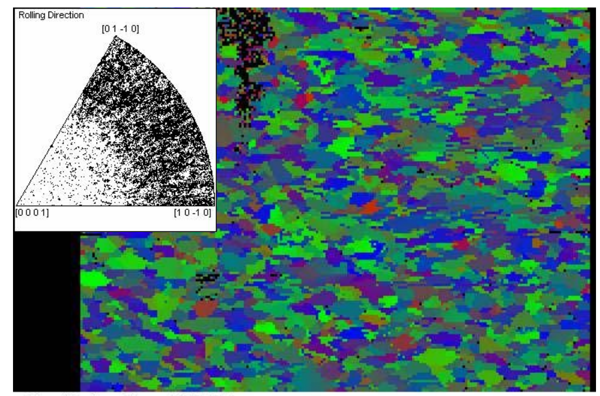




normal direction Phase: Bi2SeTe2



transverse direction Phase: Bi2SeTe2



rolling direction Phase: Bi2SeTe2

The crack in the SEM image above was an artifacts generated from the damage tolerance experiment by Vickers hardness indentation

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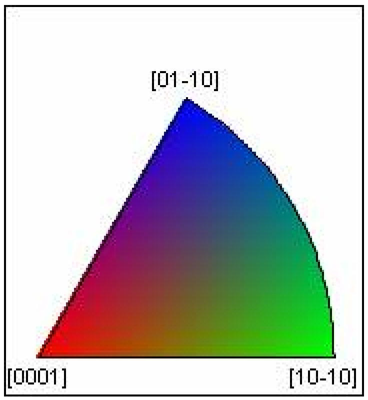
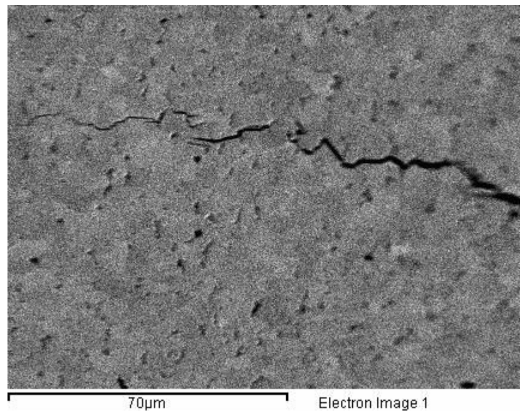
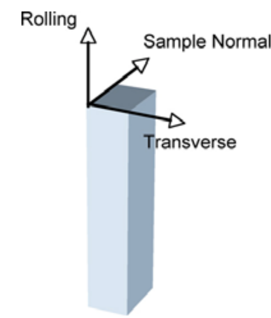
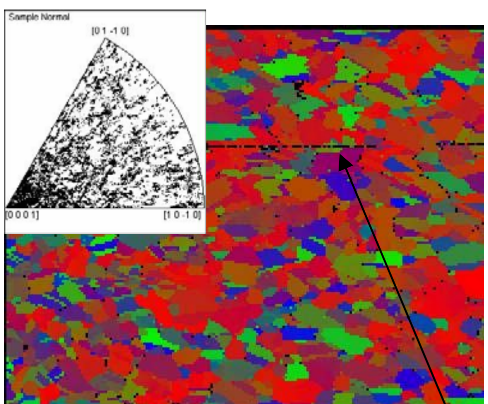
EBSP/inverse pole figures also shows similar texture along rolling, transverse and normal directions of the P-type Thermix device



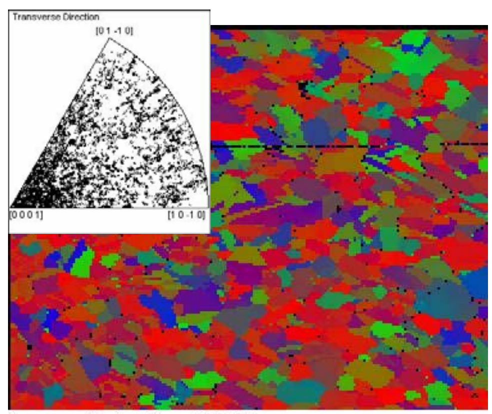


Rolling direction is equivalent to long axis of longitudinal direction

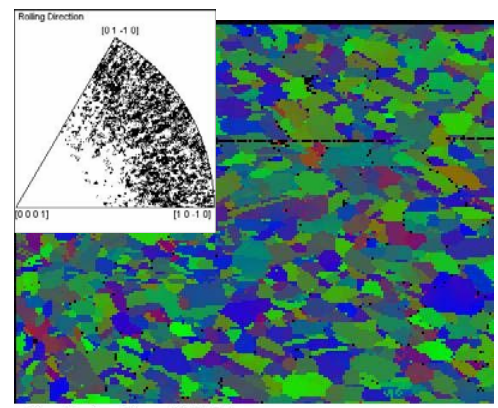




normal direction Phase: Bi2SeTe2



transverse direction Phase: Bi2SeTe2



rolling direction Phase: Bi2SeTe2

The dark line in the orientation maps is a artifacts due to minor sample charging

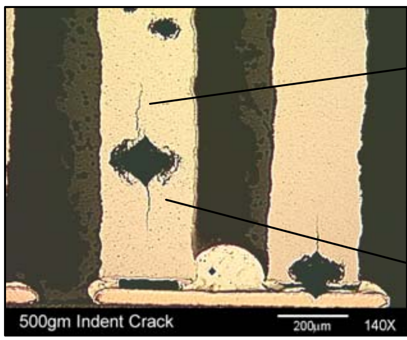
Mechanical properties and behaviors of the Bi-Te piles

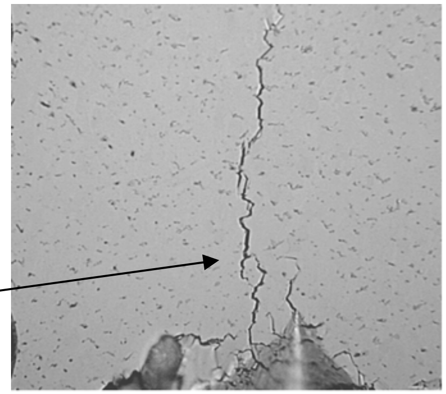
•Hardness was measured using Vickers diamond indentation and/or Nano indentation techniques at 5 grams-load and <<1gram (??) load respectively

•Modulus of the fine Bi-Te grains was measured using nano-indentation technique

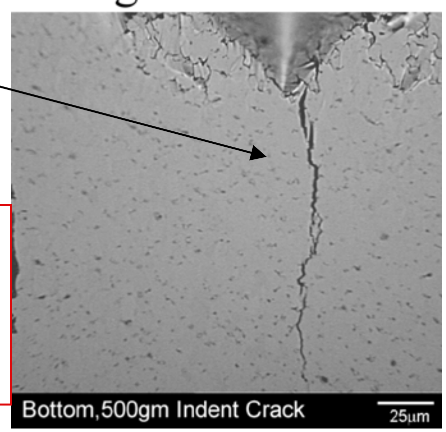
•Damage tolerance and fracture mode was examined using scanning electron microscopes (SEM) secondary electron image (SEI) and backscattered electron image (BEI). Fracture of the Bi-Te piles was intentionally created using Vickers diamond indentations at 500 grams-load.

Vickers diamond indentations show Bi-Te for both P-type and N-type are soft but brittle and the crack along the long axis of the pile.





500gm indent cracks



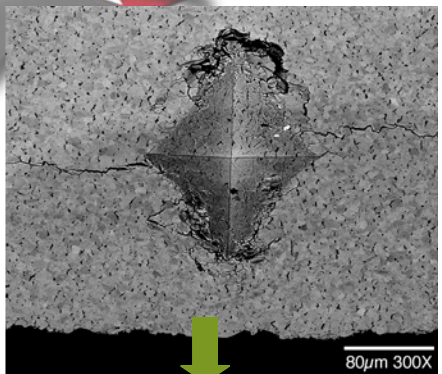
Cracks generated from 500 grams indent tend to propagated along longitudinal direction (Long axis of the P-type and N-type piles)

Hardness measured using Vickers microindentation		
Vickers Hardness (VHN) 5-gm load		Tensile strength (Gpa)** Calculated from VHN
Cu	57	0.171
Sn bead	19	0.057
P-Bi-Te	56	0.168
N-Bi-Te	65	0.195

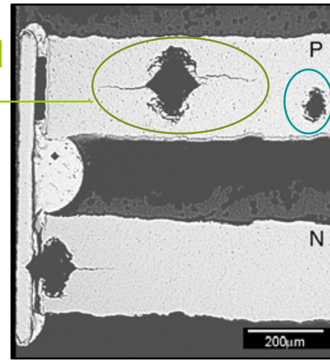
** VHN*3/1000

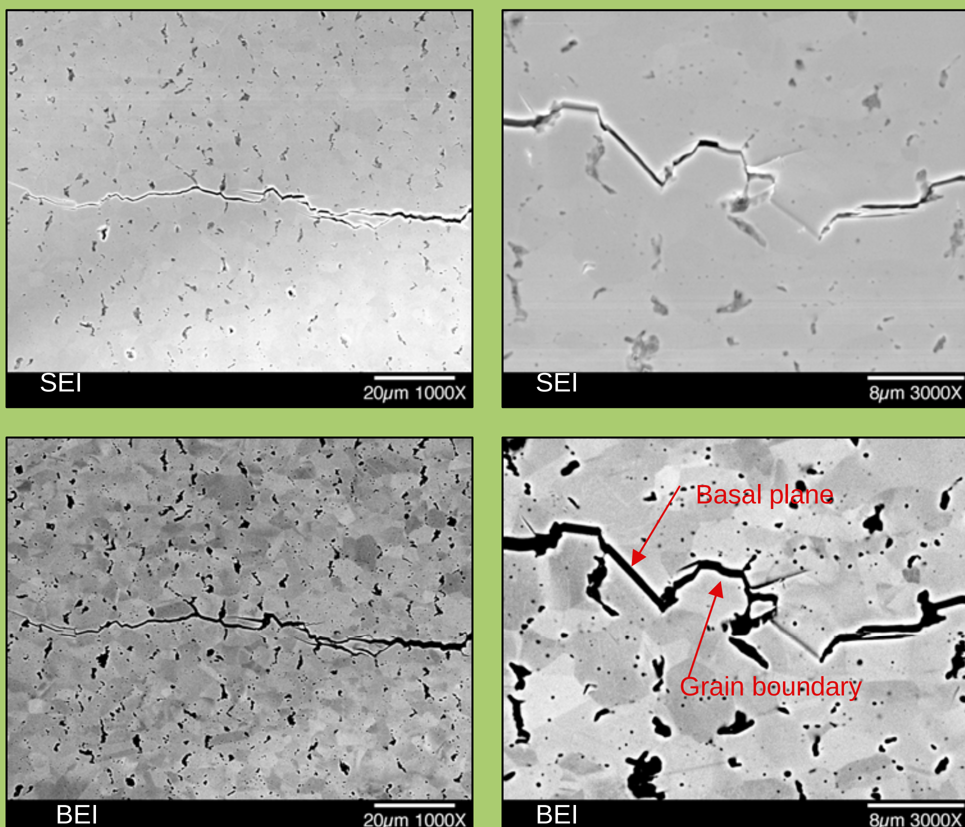
Hardness and Modulus stability using nanoindentation			
	As-received	**160°C/2hrs**	**200°C/2hrs**
Modulus(Gpa)			
P-type	1.2	1.2	1.1
N type	1.0	1.2	1.1
Hardness (Gpa)			
P-type	32.0	35.0	35.0
N-type	32.0	32.0	33.0

Crack propagation of P-type, at 500 grams-load in general is along grain boundaries and/or basal plane of hexagonal lattice.

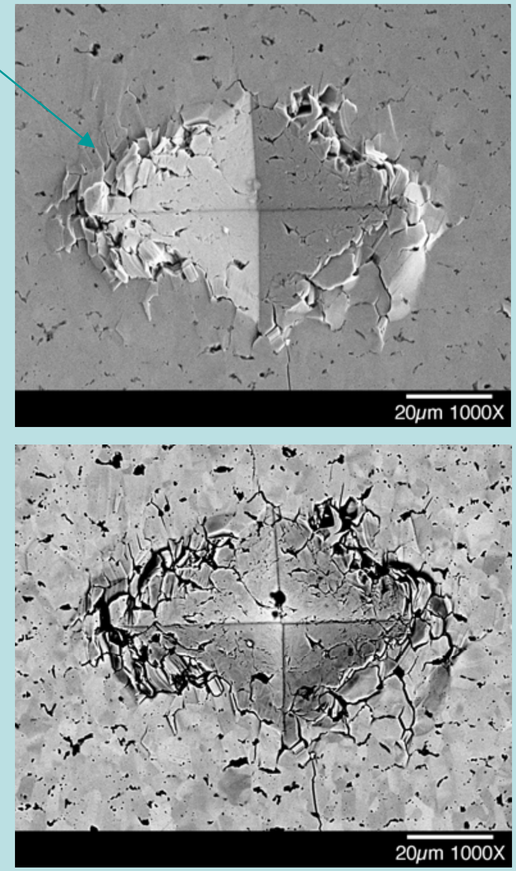


500gm-load





100gm-load (90 CCW rotation)



- At ≤100gm load Bi-Te exhibits intergranular brittle fracture without preferred direction
- At ≥500gm, both P and N type fractured and propagated along longitudinal direction

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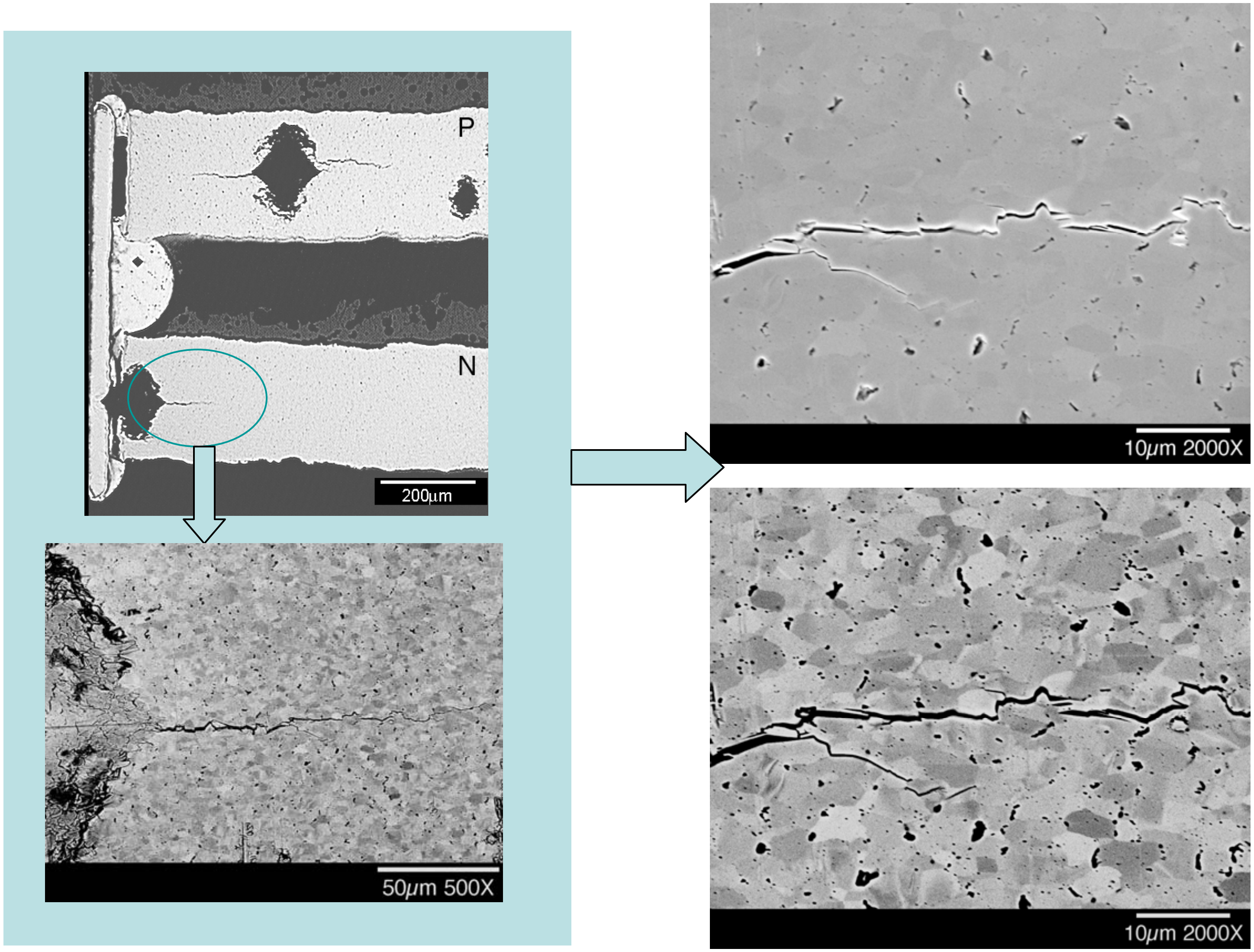
Damage tolerance/brittle crack of the N-type is comparable to those seen in the P-type described above



(III) Thermal stability of the TEC modules that consists of Bi-Te piles, solders, diffusion barriers and cover supports

Microstructure:

-- Optical metallography

-- Scanning electron microscopy (SEM)

Solder melting/elemental diffusion/alloy phase transformation

-- SEM with energy dispersive X-ray spectroscopy (EDS)

-- Electron probe microanalyses (EPMA)

-- Thermal Mechanical Analyses (TMA **) using Q400EM Thermomechanical Analyzer from TA Instruments

Mechanical properties behavior

-- Vickers microhardness diamond indentation

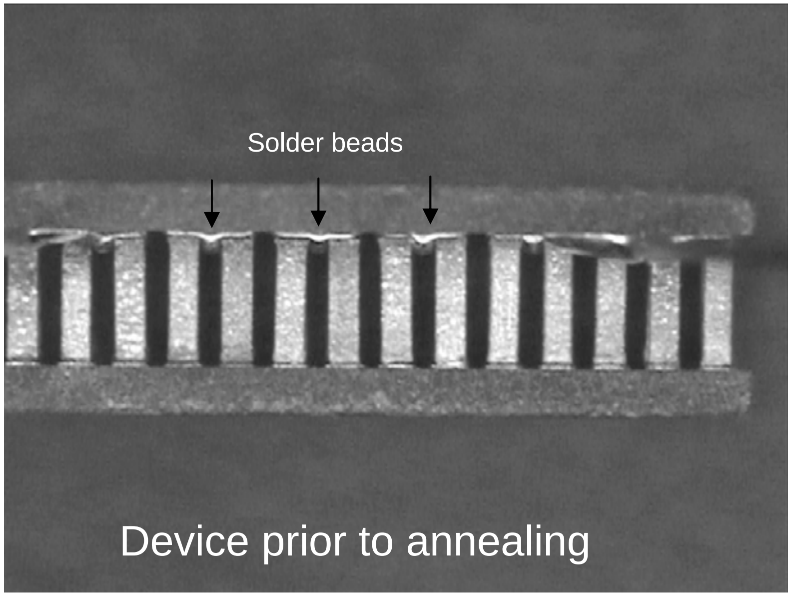
-- Nano-indentation

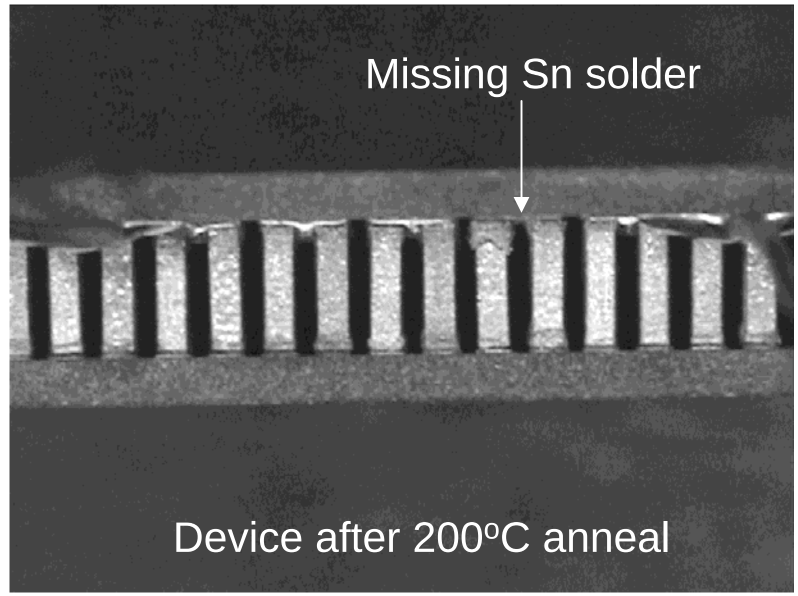
Texture

-- Backscattered electron diffraction pattern (EBSP)

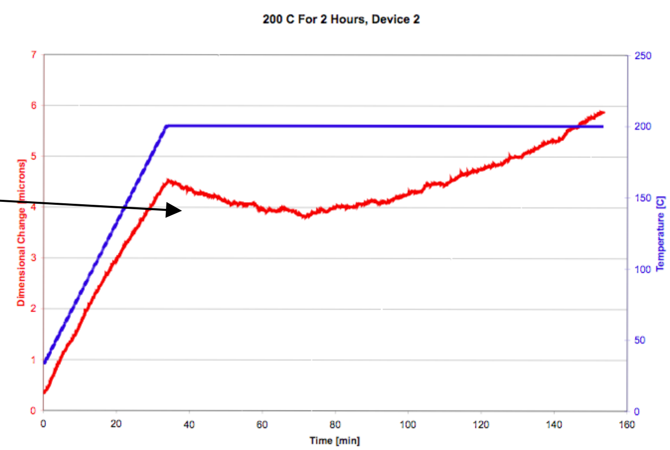
***A ThermoMechanical Analyzer (TMA) measures small sample dimensional displacement under conditions of controlled temperature, time, force, and atmosphere.*

Sn solder melting is evident after being TMA tested annealed up to 200°C and the melting appeared to start ~160°C

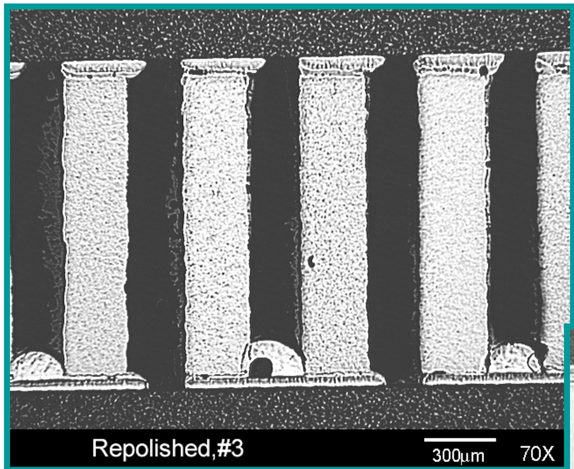




TMA analyses results of the 200°C annealed show drastic dimensional changes at 160°C. This large displacement is indicative of solder melting



Optical image show lost integrity at 160^{o}C and 200^{o}C of the TEC modules



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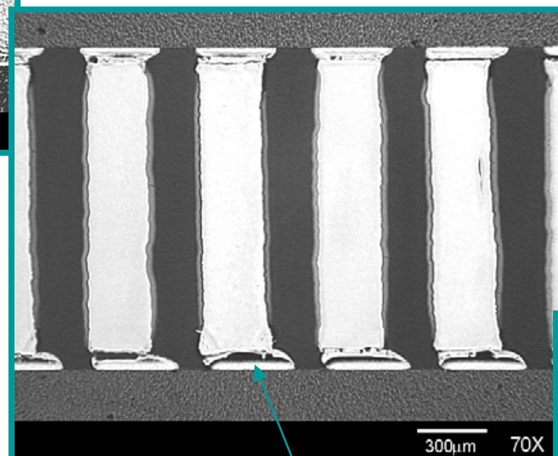
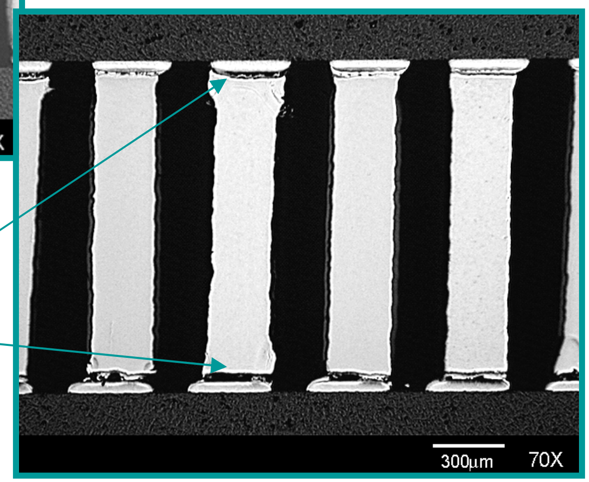
160^{o}C



200^{o}C



Sn solder melted at ≥160^{o}C

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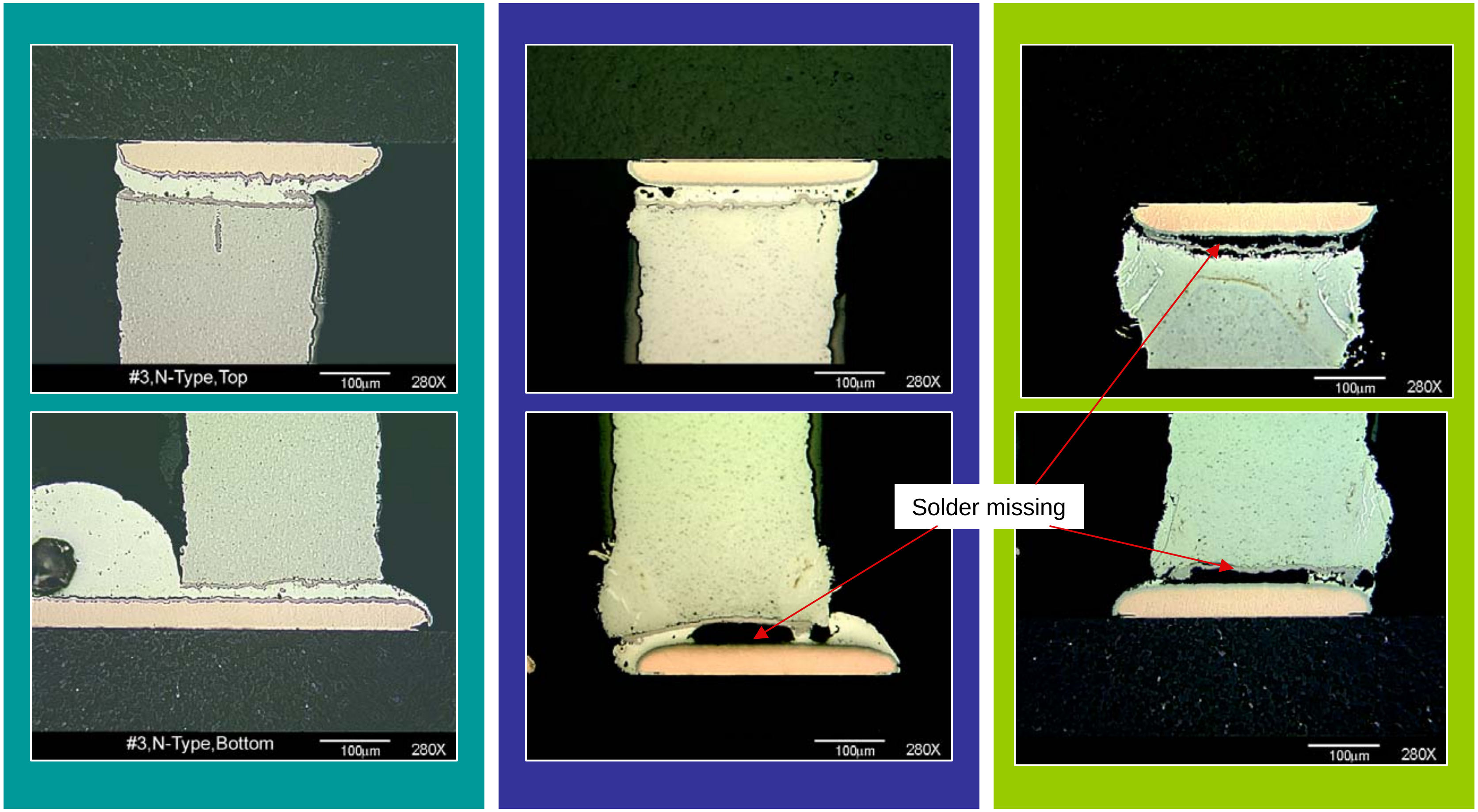
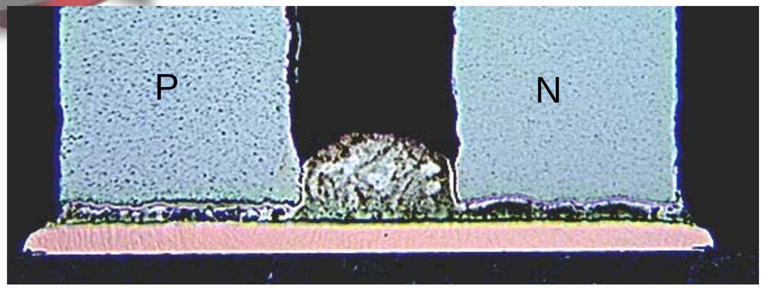
Optical images show thermal instability of the Sn solder beyond 160^oC

AR 160^oC 200^oC



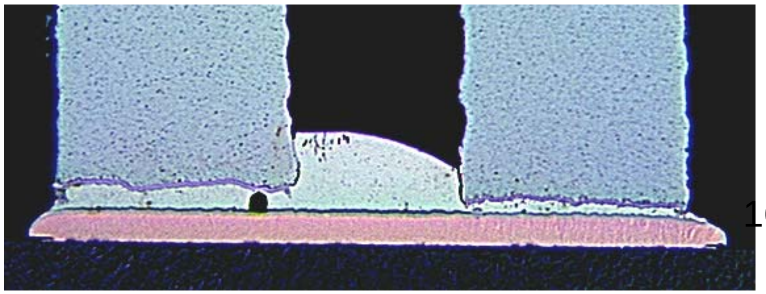
Solder melted at ≥ 160^oC and lost integrity is clearly revealed

Optical image show the layered structure losing integrity at 180°C and 200°C due to inter-elemental diffusion between Sn solder and Bi-Te

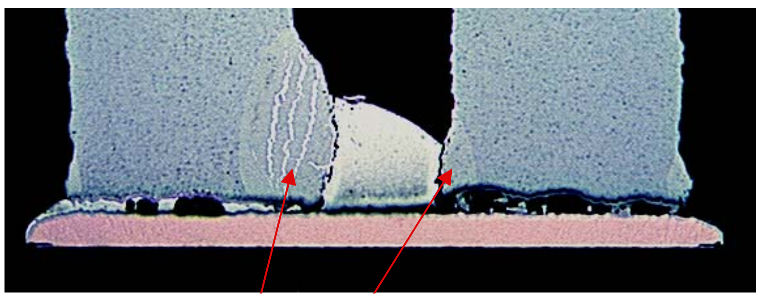


AR

- At 180°C and beyond, Sn solder diffused into P and N to form a reaction zone and lost integrity
- The reaction zone seems to be more pronounce on the sideway where the excess Sn-solder had a directly contact with Bi-Te pile directly without Ni-diffusion barrier



160°C/2hrs

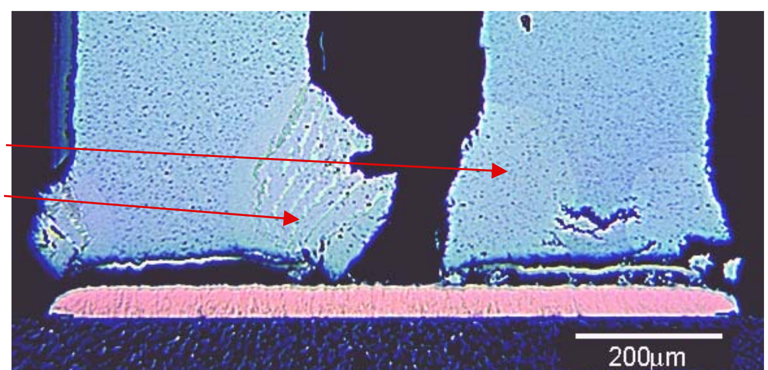


180°C/20hrs

P N

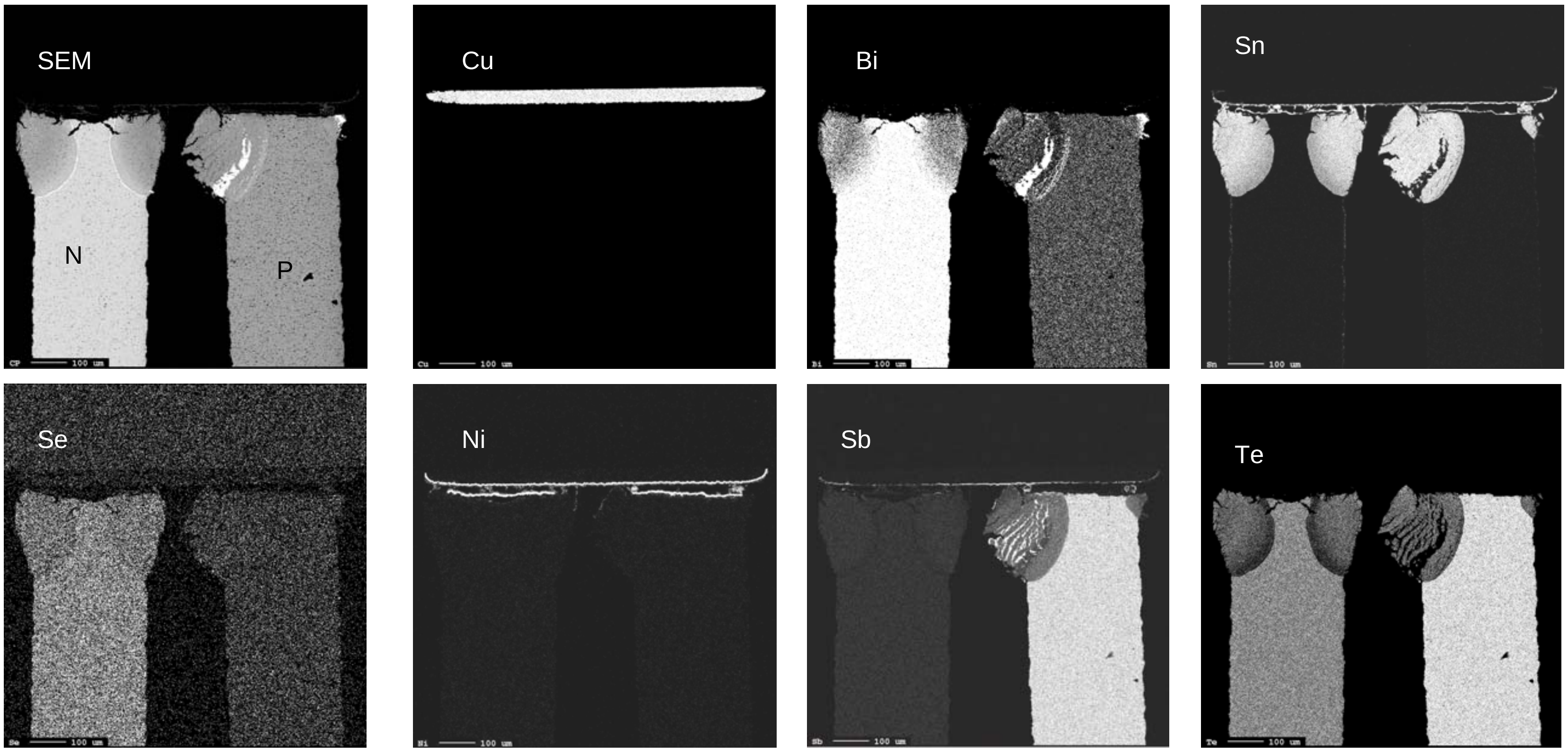
Reaction zones

N P



200°C/2hrs

Elemental X-ray maps show a reaction zone derived from Sn-diffusion into both P and N near the bond lines



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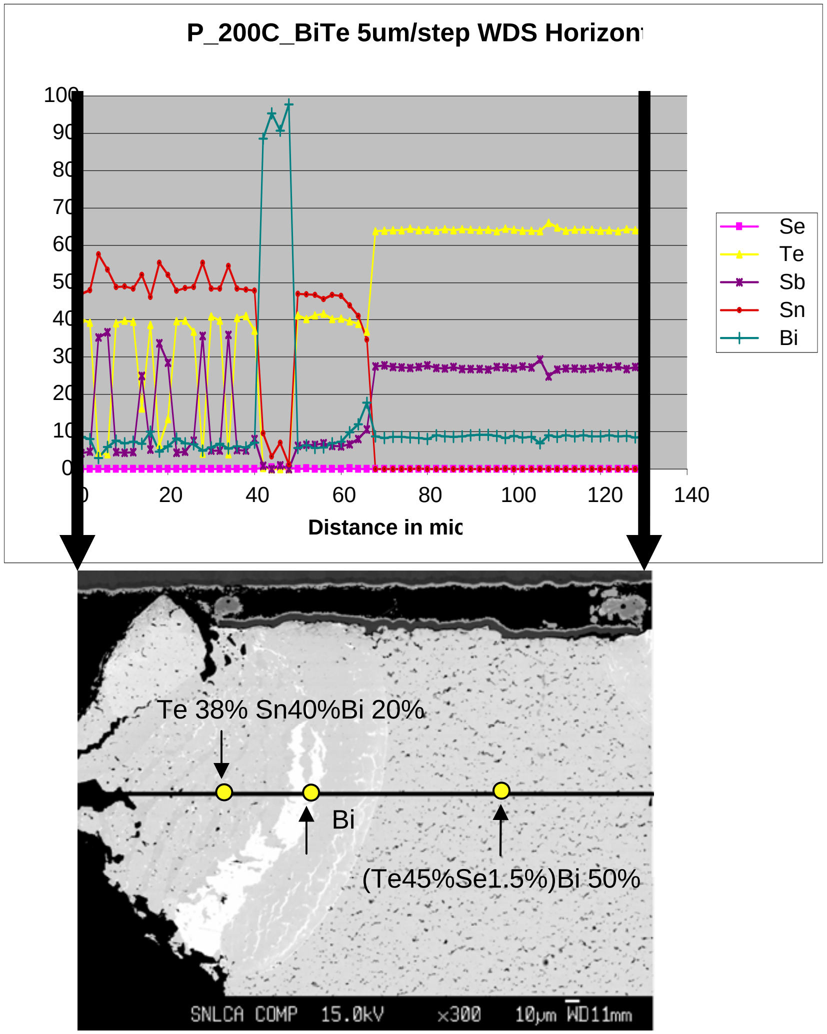
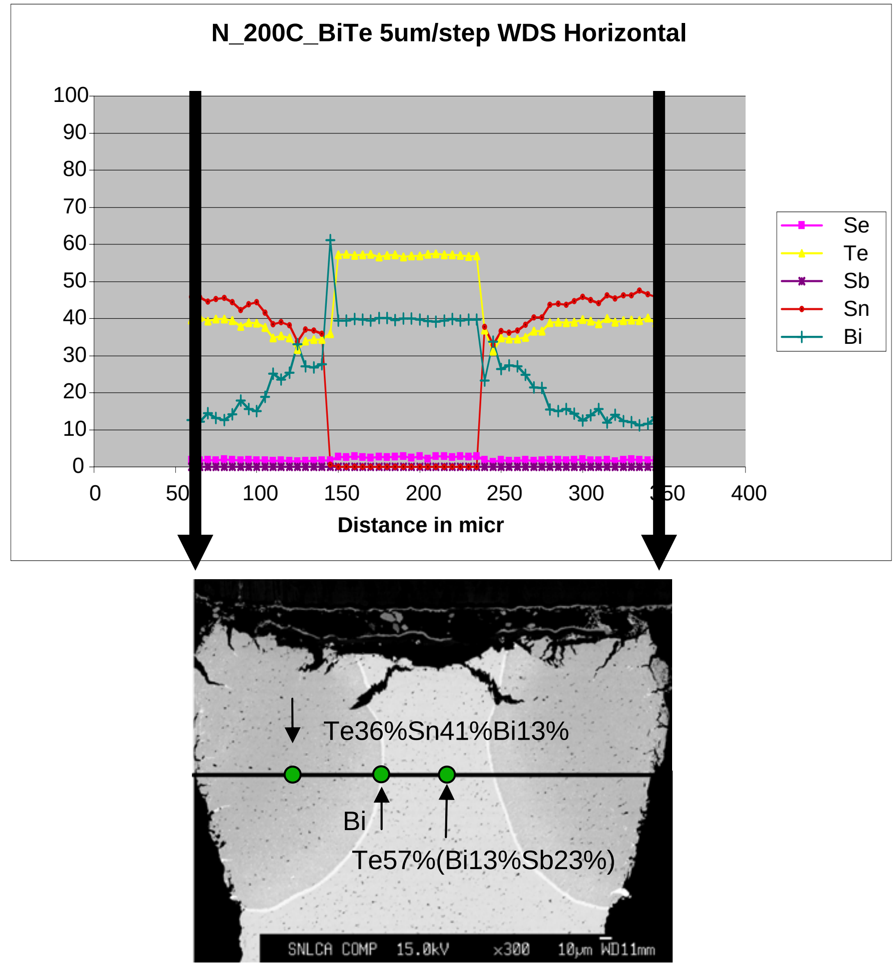
Chemical composition profile across Sn-Te-Bi reaction zone





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Bi-Te were relative soft and both hardness and modulus appeared to be thermally stable up to 200^{o}C without evidence of recrystallization

Hardness & Modulus stability using nanoindentation			
	As-received	**160^{o}C/2hrs**	**200^{o}C/2hrs**
Modulus(Gpa)			
P-type	1.2	1.2	1.1
N type	1.0	1.2	1.1
Hardness (Gpa)			
P-type	32.0	35.0	35.0
N-type	32.0	32.0	33.0
Vicker's hardness (VHN)			
P	*57.9*	*57.4*	*55.6*
N	*59.8*	*68.9*	*62.4*

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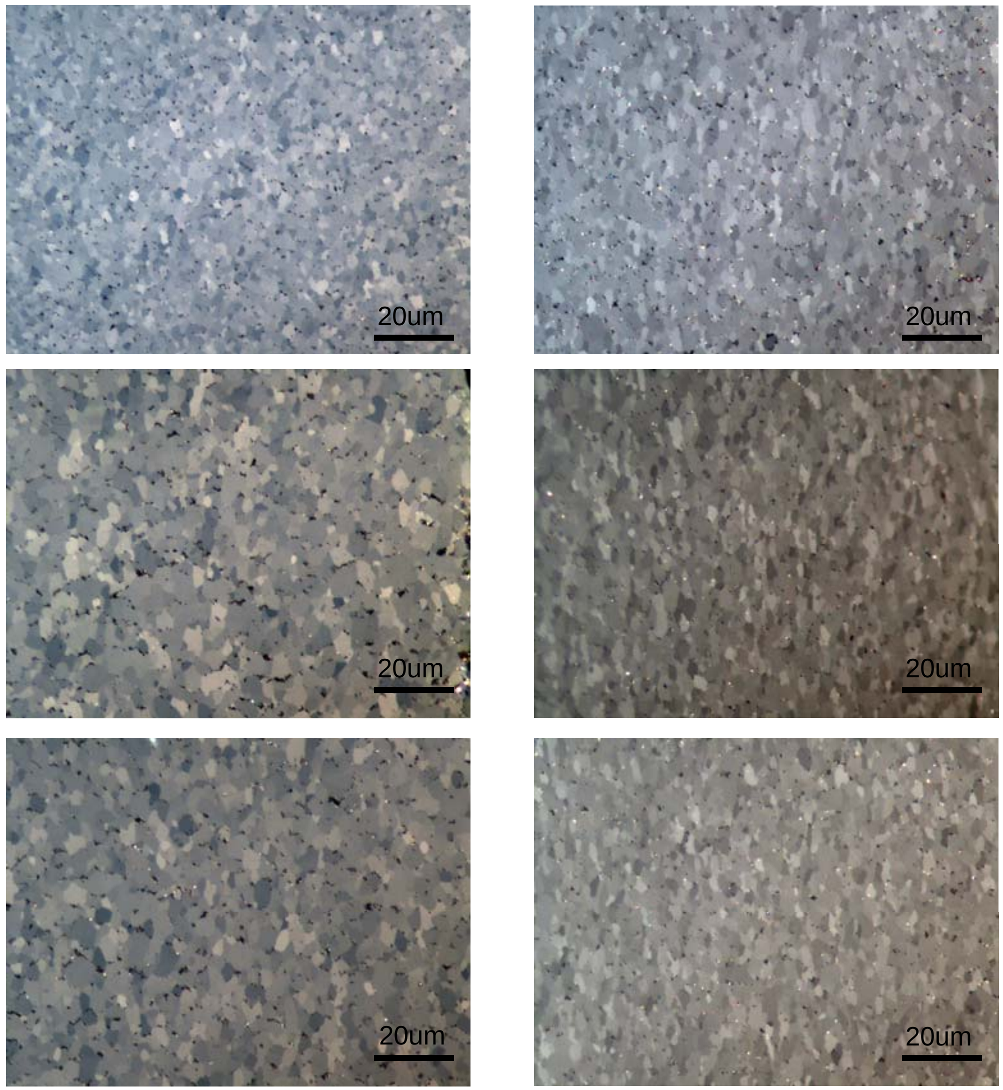
Grain structure of the Bi-Te is relatively stable up to 200^{o}C. Recrystalliztion was not evident

P N

AR

160^{o}C

200^{o}C



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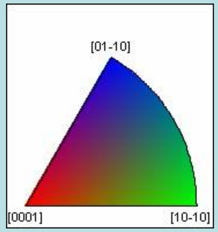
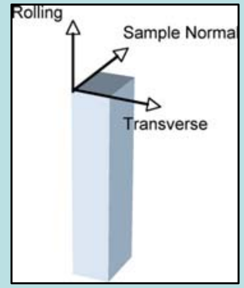
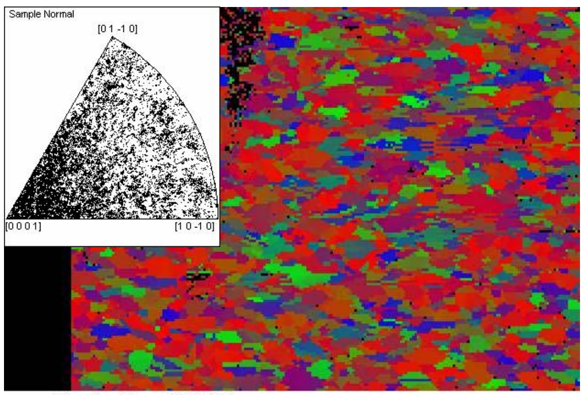
EBSP also show comparable texture of N-type pile after being annealed at 200°C

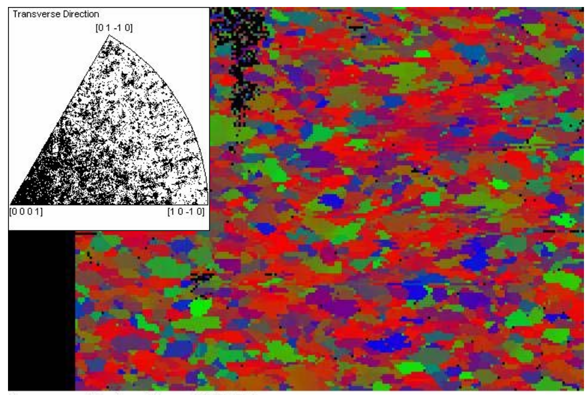




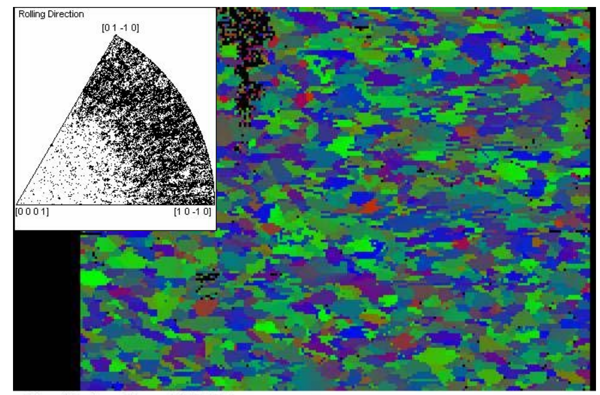
Rolling direction is equivalent to long axis of longitudinal direction



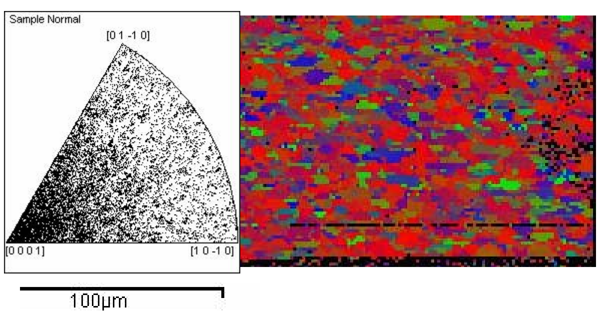
normal direction Phase: Bi2SeTe2

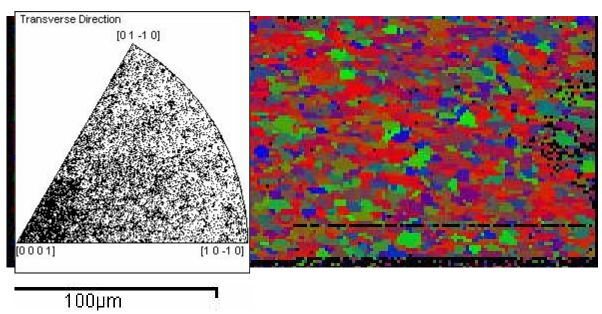


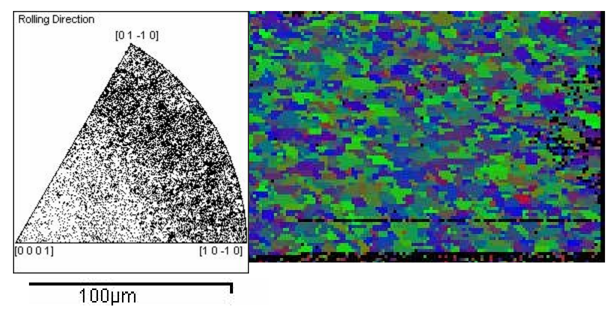
transverse direction Phase: Bi2SeTe2



rolling direction Phase: Bi2SeTe2







Sandia National Laboratories

$N\text{-}(Bi_{39} Sb_2)(Te_{56}Se_3)$

Summary

•Current TEC modules was constructed with $P\text{-}(Bi_8 Sb_{32})Te_{60}$ and $N\text{-}(Bi_{39} Sb_2)(Te_{56}Se_3)$ thermal piles. Material selections for the cover support plates, diffusion barrier and solder were, Al-Nitride/Cu, Ni/Ni-P and Sn-Sb (≤1.0 wt%) respectively.

•Bi-Te thermal piles were relatively soft and brittle contain. Both P and N piles possess fine grains, ≤5 um with moderate texture along all three axis.

•Physical metallurgy with respect to grain structure, hardness and texture of both P- and N-piles appeared to be thermally stable up to 200^{o}C, the temperature interest

•Modulus of the Bi-Te piles is ~1Gpa. Damage crack under Vicker's diamond indentation load usually propagated along the long axis of the pile either through grain boundaries hexagonal basal planes

• The TEC modules with Sn-rich solder lost its integrity at 180^{o}C and beyond due to solder melting and inter-elemental diffusion

•The inter-diffusion between Sn solder and to Bi-Te piles changes local thermal pile composition withTe-Sn-Bi phase near the solder joint. The composition change is especially pronounce near the solder joint where Sn-solder is in direct contact with the Bi-Te pile on the sideway. This diffusion induced composition changes could lead to mechanical and/or poor electrical failure performance

Future work

•Establish process-structure-property-TE performance relationship

• Research and develop materials, solder in particular, that possess suitable thermal stability and aging characteristics of the applications on hand.

Executive Summary: Scientific Study of Bi-Te Thermal Electric Modules

Issue:

Material science/design/construction and their implication to Bi-Te thermal electric (TE) module performance remains to be understood.

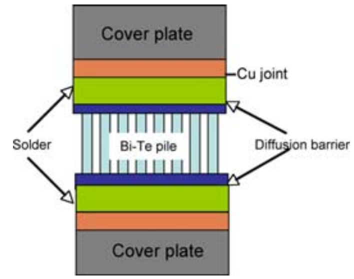
Approach:

•Characterize material science/module design and construction of TE modules supplied by two Vendors, Marlow and Thermix Inc.
•Investigate thermal stability and aging of the modules after being subjected to the temperatures (ambient to 200ºC), relevant to application.

Recent Results:

Material science and module design/construction of two TE modules were characterized in a great detail. The key findings up-to date-are:
• Bi-Te alloy is thermally stable and maintains its desirable metallurgical characteristics at 200ºC.
• TE modules constructed with Sn-Sb(≤1wt%) lost its integrity at ≥160ºC due to solder melting. At the same temperature range (≥160oC), the TE module constructed with Sn-Pb solder appeared to stable and maintain its integrity

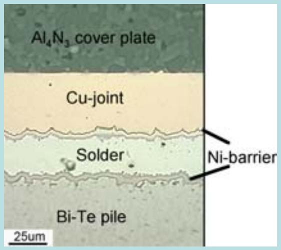
Schematic of TE module



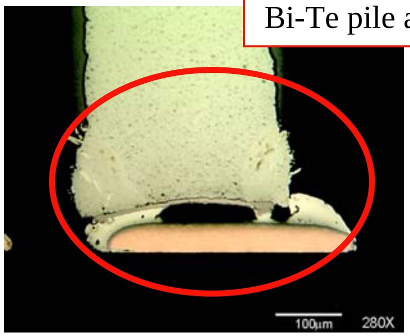
Physical metallurgy of Bi-Te is stable up to 200ºC

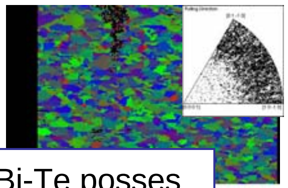
	As-received	160ºC/2hrs	200ºC/2hrs
Modulus(Gpa)			
P-type	1.2	1.2	1.1
N type	1.0	1.2	1.1
Hardness (Gpa)			
P-type	32.0	35.0	35.0
N-type	32.0	32.0	33.0

Optical image of TE module design/construction by Thermix



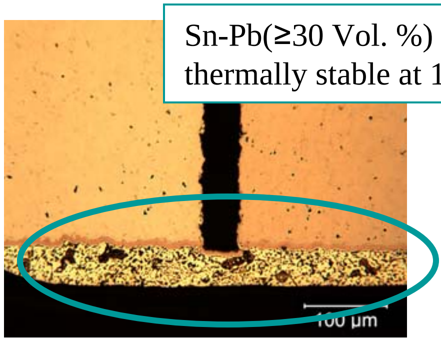
Sn-Sb(≤1%) solder melted and reacted with Bi-Te pile at 160ºC





Bi-Te posses strong texture

Sn-Pb(≥30 Vol. %) is thermally stable at 160ºC



Impact:

Selection of solder material coupled with module design/construction is a critical factor affecting thermal stability and aging of Bi-Te TE module.