Annual Group Meeting 17th July 2019

INNOVATIVE OXIDATION PROTECTIVE COATINGS FOR THERMOELECTRIC MATERIALS (TE)

F. D'Isanto[1], M. Salvo[1], F. Smeacetto[2], F. Gucci[3] R. Zhang[3], K. Chen[3] , M. J. Reece[3] , Hans- Peter Martin[4]

[1] Institute of Materials Physics and Engineering, Department of Applied Science and Technology, Politecnico di Torino, Italy

[2] Department of Energy, Politecnico di Torino, Italy

[3] School of Engineering and Materials Science and Nanoforce Technology Ltd., Queen Mary University of London, UK

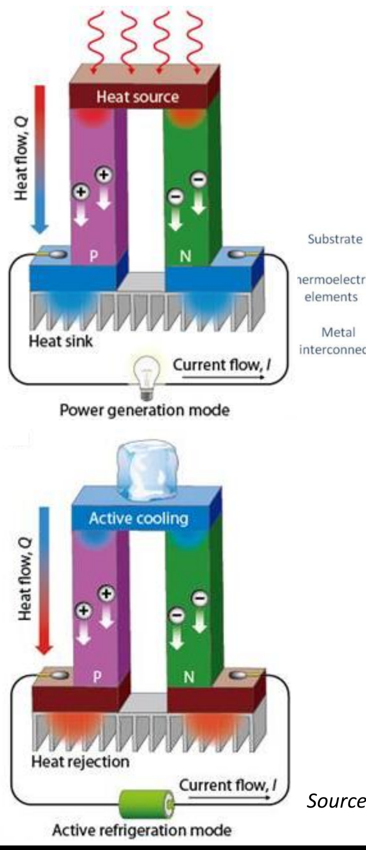
[4] Hans- Peter Martin, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany

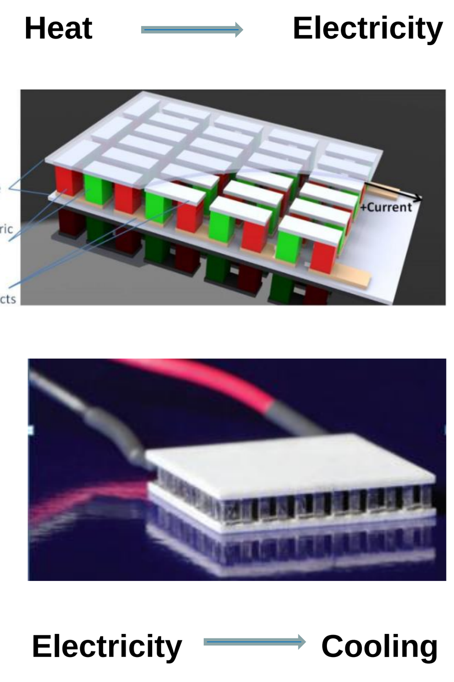
STATE OF ART AND AIM OF THE WORK

Thermoelectrics can convert thermal energy directly into electricity and vice-versa. They operate in the solid state.

Thermoelectric devices can be used either for **cooling (Peltier effect)** or for **power generation (Seebeck effect)** applications.

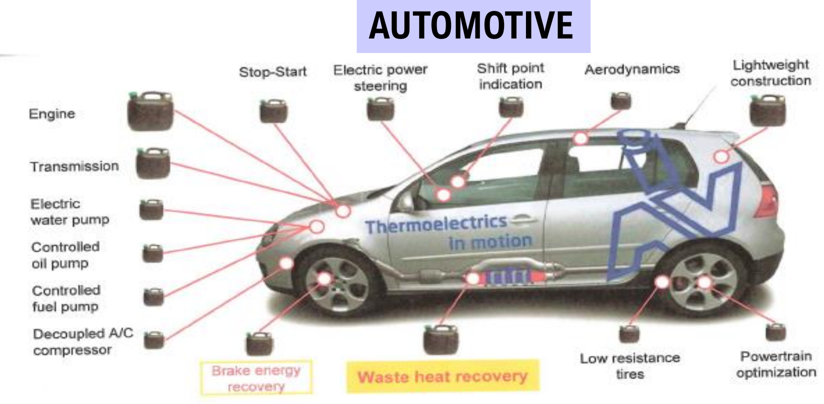
THEY CAN CONVERT WASTE HEAT INTO ELECTRICITY





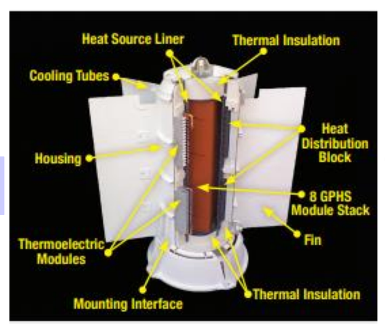
Source: Jing-Feng Li et al. NPG Asia Materials (2010) 2, 152–158

AUTOMOTIVE



Source: Thermoelectric Systems for Greener Vehicles, 2004, www.greencarcongress.com

SPACE



Multi-Mission Radioisotope Thermoelectric Generator (MMRTG).

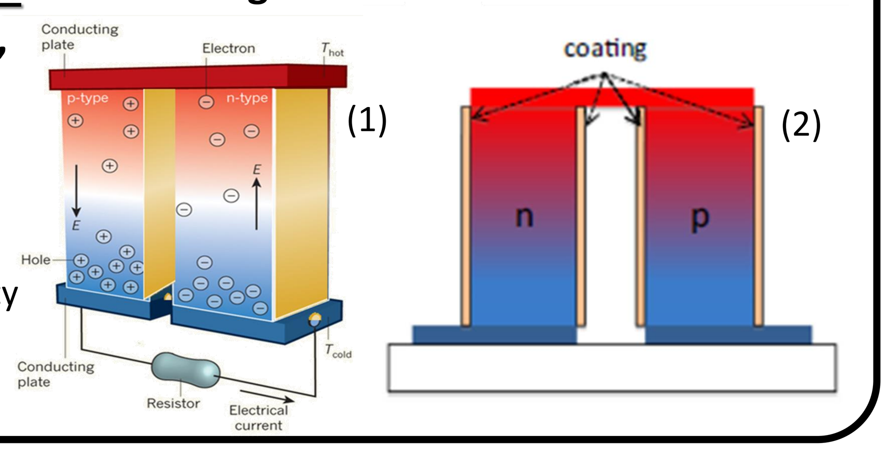
Source: www.mars.nasa.gov

Heat recovery in transport and industry

Source: www.esa.int/spaceinimages

NOVELTY OF THE RESEARCH: Glass and glass-ceramic based materials as OXIDATION PROTECTIVE COATINGS, because of:

- Low cost
- Thermal stability
- Low electrical and thermal conductivity
- Versatile composition
- CTE designing



MATERIALS and METHODS

TEs produced with Spark Plasma Sintering at Nanoforce Technology Ltd

$MnSi_{1.74}$ (HMS) [p-type]

Silica-based glass-ceramic with G11 composition (3) was deposited on Higher Manganese Silicide (4) at 700°C, 1h dwell, Ar flow.

Deposition on all faces → THERMAL CYCLING **(RT-600°C, 10 cycles, 1h dwell, Air)**

$Cu_{11.5}Zn_{0.5}Sb_4S_{13}$ (THD) [p-type]

Commercial water- based silicone resin was employed as hybrid coating . It was deposited and then thermal treated at low temperature (250°C) for 45 minutes under Ar flow.

Deposition on all faces → AGEING **(350°C, 48hrs dwell, Air)**

$Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ [n-type]

Preliminar tests for the characterization of the $Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ substrate and development of a **new oxidation protective glass (M3)** were carried out.

Deposition on all faces at 550°C , 1h dwell under Ar flow → AGEING **(500°C, 120hrs dwell, Air)**

TE produced at Fraunhofer Institute

TiO_x [n-type]

First proposal

Designing of a **new silica-based glass-ceramic (T1)** containing **titanium oxide,** to protect the substrate against oxidation for T ≥ 1000°C and to match TiOx thermal expansion (CTE ~ $8 \cdot 10^{-6}$ K^{-1})

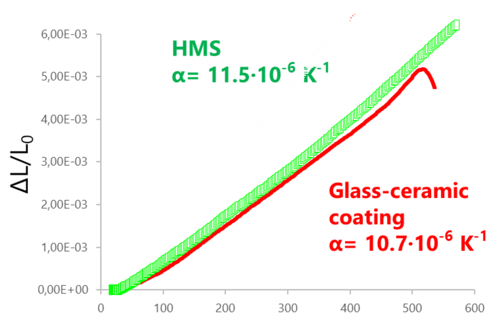
WORKING IN PROGRESS

Second proposal

Development of a **new glass-ceramic based composite** (CTE ~ $7.5 \cdot 10^{-6}$ K^{-1}) containing an **ytterbium monosilicate phase (Yb_2SiO_5)** embedded in a barium aluminium boron silicate glass.

RESULTS and DISCUSSION

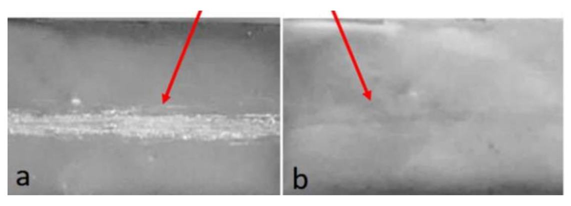
$MnSi_{1.74}$ (HMS) [p-type]



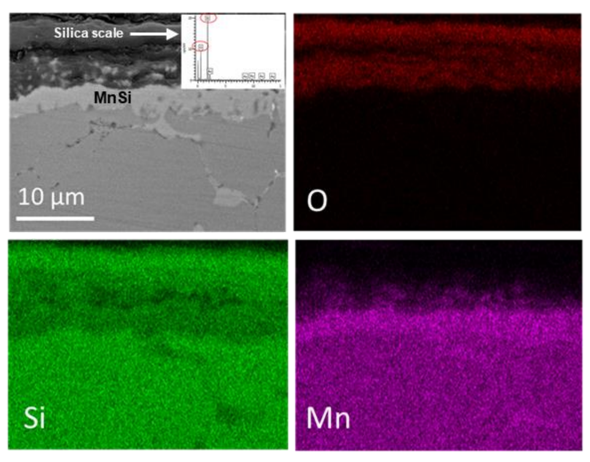
Dilatometry to test the thermo-mechanical compatibility between thermoelectric substrate and glass-ceramic

SELF-HEALING PROPERTIES

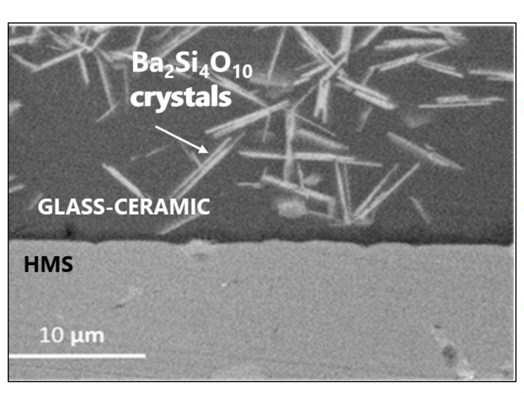
Scratch on the glass-ceramic coating before and after the heat treatment at T> softening point



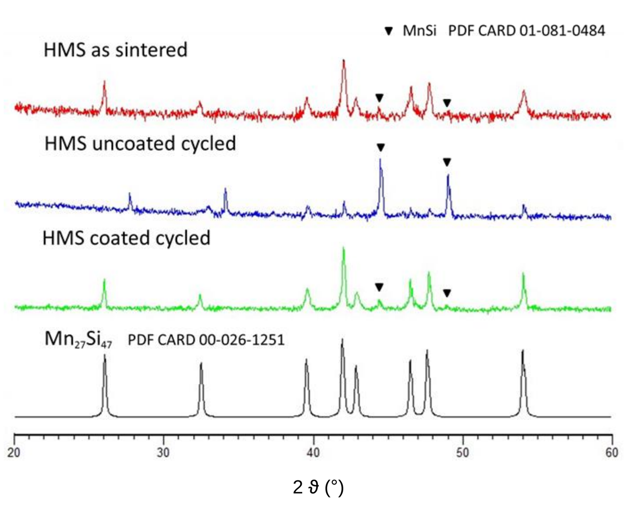
Silica layer due to the reaction between the HMS and oxygen, on Si-deficient layer (MnSi) formed on the top of the TE substrate

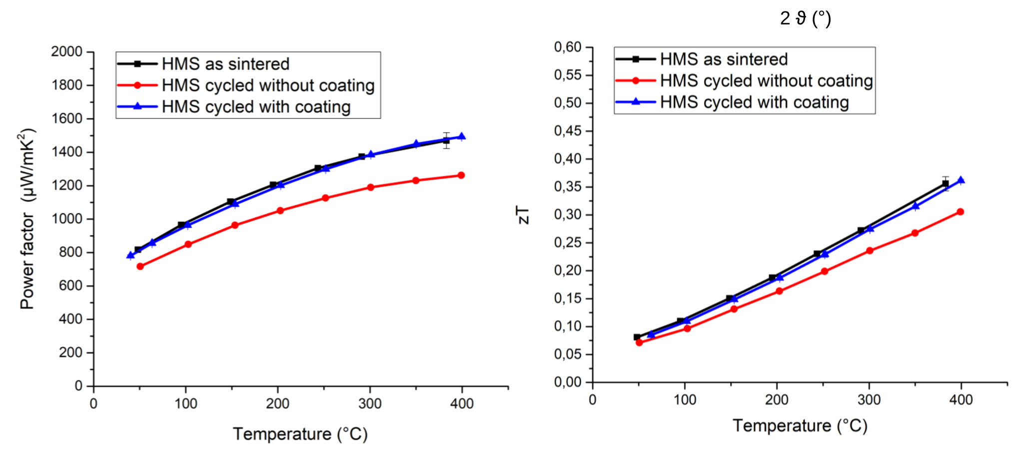


HMS uncoated cyled RT-600°C 1h, 10 cycles, Air flow



SEM of Glass-ceramic coated HMS, cyled RT-600°C 1h, 10 cycles, Air flow





Electrical properties

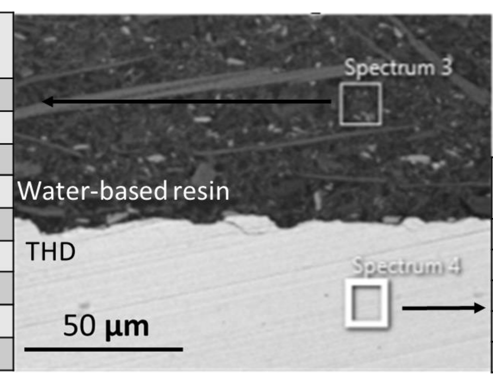
The coated sample shows a remarkably higher stability of the electrical properties compared to the uncoated HMS. The coated HMS shows an almost unchanged zT, electrical resistivity and power factor compared to the as-sintered TE.

Effective protection for HMS based thermoelectrics

Results published on: Salvo, Smeacetto, D'Isanto et al, *Journal of the European Ceramic Society* 2018, 39(1) 66-71

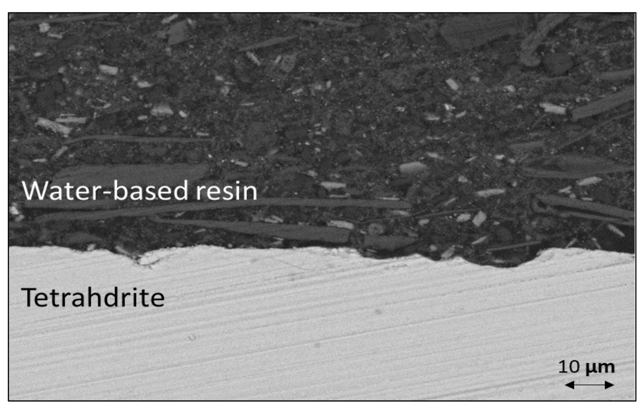
$Cu_{11.5}Zn_{0.5}Sb_4S_{13}$ (THD) [p-type]

Element	Atomic %
O	64.99
Mg	2.26
Al	8.59
Si	15.61
P	1.47
K	0.23
Ti	4.11
Zn	2.74
Total:	100.00



Element	Atomic %
S	44.90
Cu	39.61
Zn	1.42
Sb	14.07
Total:	100.00

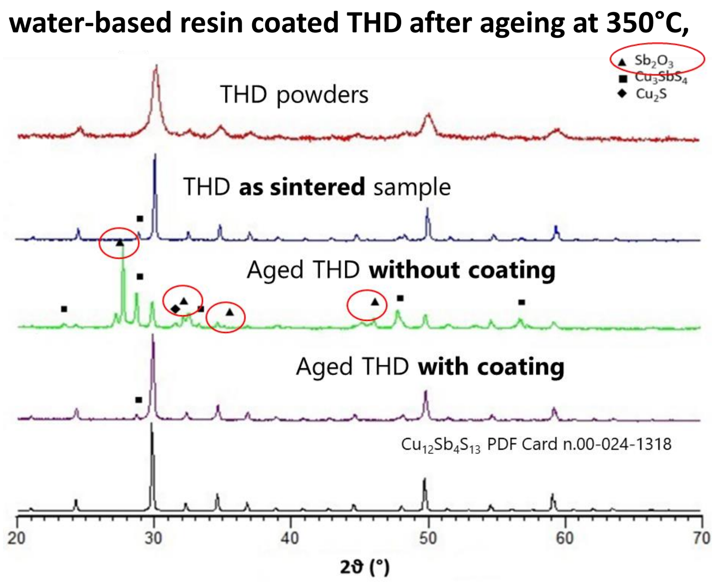
SEM image and EDS analysis : cross-section of the water-based resin coated THD

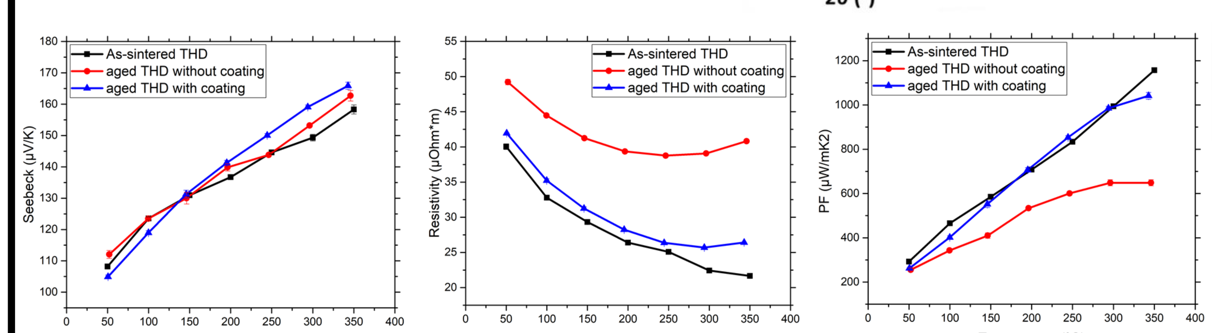


- **No cracks**
- the coating is well-adherent to the substrate also after the thermal treatment.
- **No oxidation layers at the coating/THD interface**

SEM image of cross-section of water-based resin coated THD after ageing at 350°C, for 48hrs, in air

- **No changes** between Aged THD with the coating and as sintered one.
- **Antimony Oxide** as main phase in the Aged THD without the coating





Electrical properties

The Power Factor of the uncoated sample decreases if compared to as-sintered THD, while the coated sample maintains a similar value.

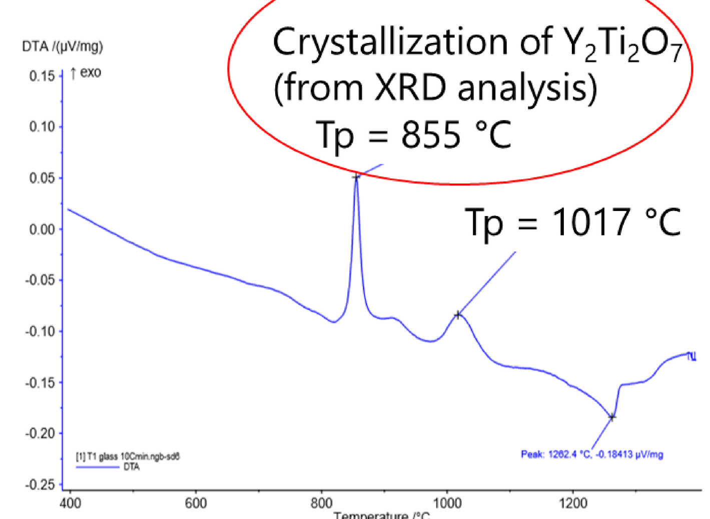
The hybrid coating provides effective protection against the oxidation at 350°C

Results published on : F, Gucci, F. D'Isanto, Zhang, M Reece, F. Smeacetto and M. Salvo. *Materials* 2019, 12(4), 573

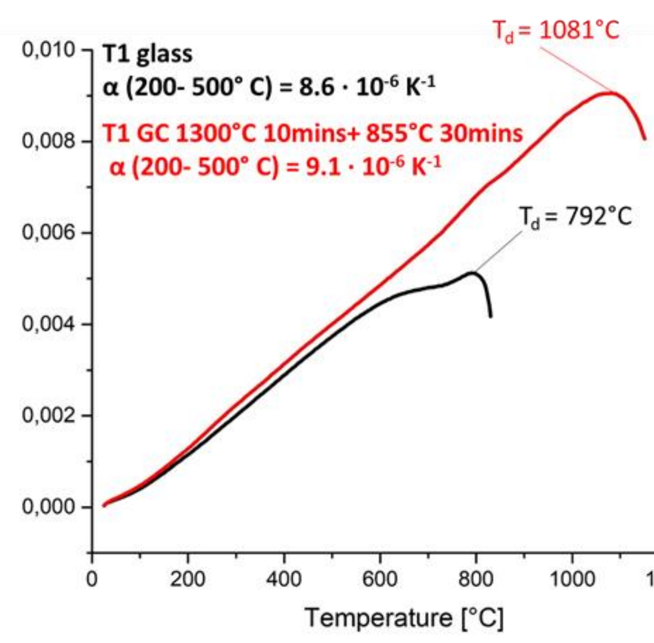
WORKING IN PROGRESS : Oxidation test at 400°C, dwelling time 120hrs

TiO_x [n-type]

First proposal

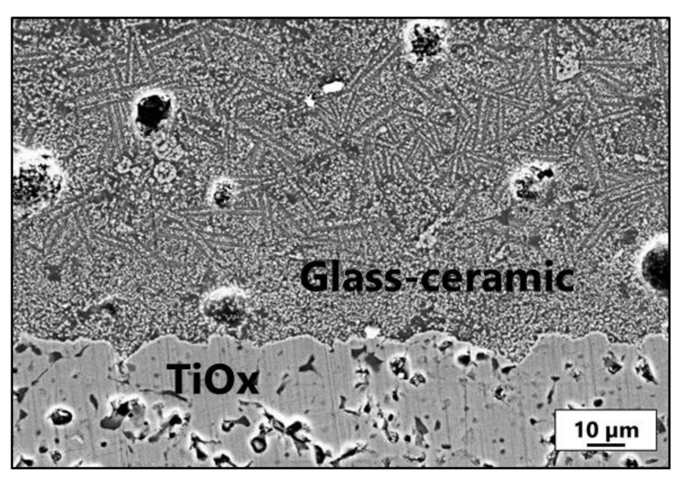


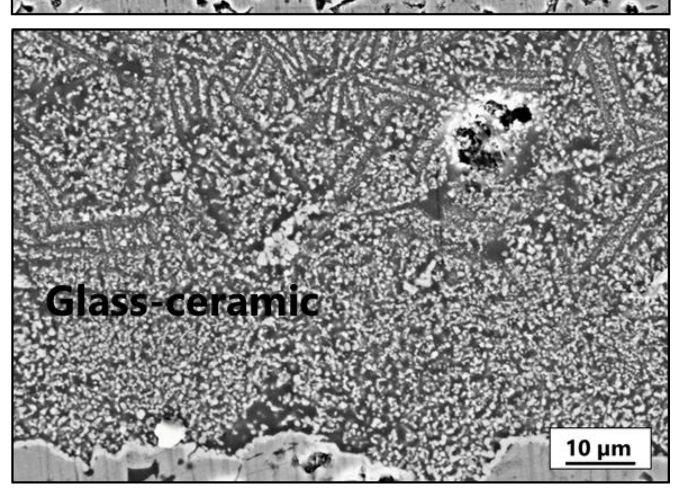
DTA analysis



Dilatometry

- Increase of the softening point during the sinter- crystallization





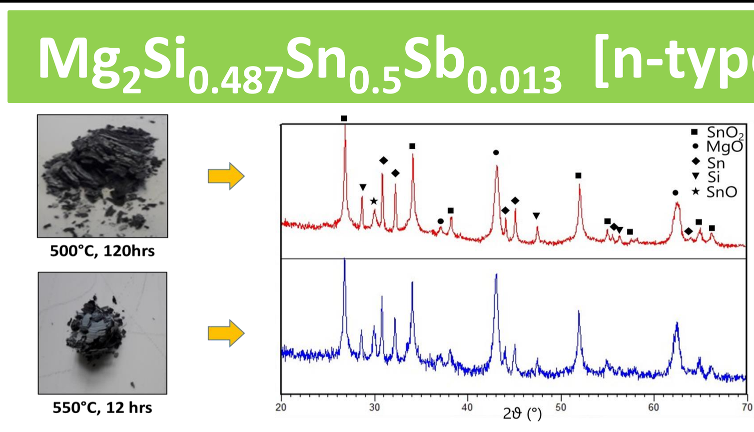
SEM image of cross-section of T1 glass- ceramic coated TiOx , after sinter- crystallization at 1300°C for 10mins + 855°C for 30mins, Ar flow

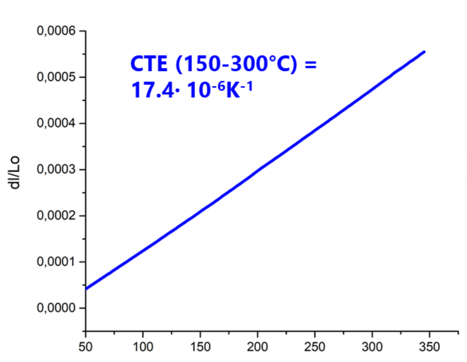
- No cracks
- Good wettability

UNPUBLISHED RESULTS

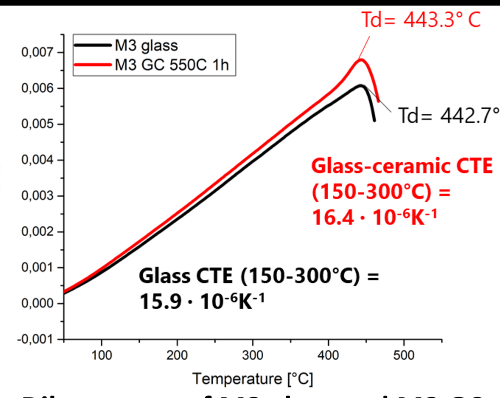
WORKING IN PROGRESS : EDS and TEM analysis to identify crystalline phases

$Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$ [n-type]

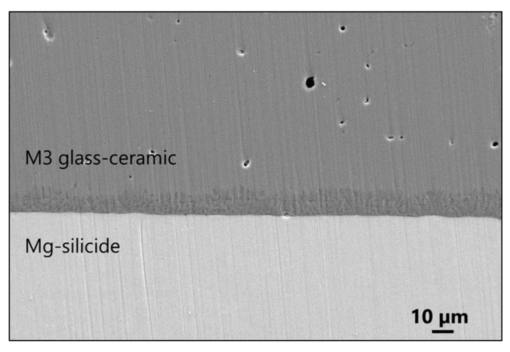




Dilatometry of Mg-Silicide



Dilatometry of M3 glass and M3 GC



SEM of M3 Glass-ceramic coated Mg-silicide, 550°C 1h, Ar flow

WORKING IN PROGRESS : Oxidation test at 500°C, dwelling time 120hrs

UNPUBLISHED RESULTS

Acknowledgments

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 642557

References

1) J. Heremans, Thermoelectricity: *The ugly duckling*, Nature 508 (2014) 327–328.
2) Y-S Park, T. Thompson, Y. Kim, J. R. Salvador, J. S. Sakamoto, *Protective enamel coating for n- and p-type skutterudite thermoelectric materials,* J Mat Sci 50 (2015) 1500-1512.
3) F. Smeacetto, M.Salvo, A. Ventrella, S. Rizzo, M. Ferraris, *Durable glass-ceramic coatings for Foam Glass*, Int J App Glas 3 (2012) 69-74.
4) H. Ning, M. J. Reece, F. Smeacetto and M. Salvo, *Oxidation protective glass–ceramic coating for higher manganese silicide thermoelectrics*, J Mater Sci 51 (2016) 9484–9489.