PROVISIONAL ASSESSMENT OF CANDIDATE HIGH TEMPERATURE THERMAL CONDUCTIVITY REFERENCE MATERIALS

Presented by: Jiyu Wu

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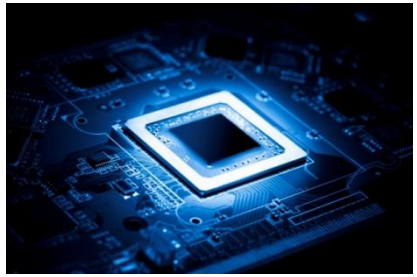
ACKNOWLEDGEMENTS

- EURAMET EMRP:
  - EMRP supports the collaboration of European metrology institutes, industrial organisations and academia through Joint Research Projects (JRPs). It is structured around European Grand Challenges in such areas as Health, Energy, the Environment & New Technologies.
- Contributions from a group of material scientists at NPL.
- Collaborations between funded partners of 'Thermo ' project (Metrology for Thermal Protection Materials): LNE, PTB, MKEH, CMI and NPL

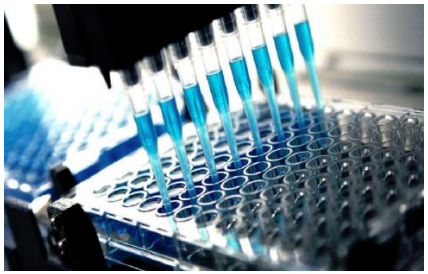
SI Units (2011 & 2012)

Environment (2010 & 2013)

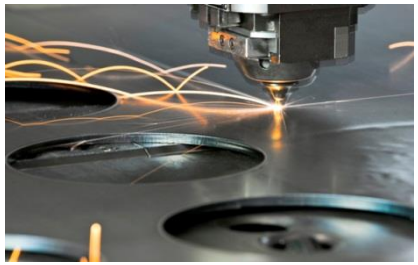
Energy (2009 & 2013)



New Technologies (2011)



Health (2011)



Industry (2010 & 2012)

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Outline

- Objectives
- Results of surveys
- Provisional assessments
- Conclusions

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Objectives

- One of the aims of this project is to develop reference materials with thermal conductivity in the range 0.02 $Wm^{-1}K^{-1}$ to 1 $Wm^{-1}K^{-1}$ and with a target maximum temperature of 800 °C.

- The first stage is the provisional assessment of candidate reference materials. The aim is to select one or two best candidate reference materials for further detailed assessment within the next stage.

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Results of Surveys

- Results of surveys at the beginning of the Thermo project

  Sixteen companies and organizations have contributed to the survey that leads to a shortlist of potential candidate materials:

  - Low density calcium silicate: ‘LDCaSi’
  - High density calcium silicate: ‘HDCaSi-N’
  - Amorphous silica: ‘AmSi’
  - Exfoliated vermiculite: ‘EV’

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Provisional Assessments

- Test Matrix

No.	Item	Owner
1	XRF for element composition of the material	NPL
2	XRD for material component	NPL
3	SEM for microstructure and bases for long term stability	NPL
4	Mechanical stability and isotropy aspect of the material via Thermal expansion	NPL
5	Chemical stability via TGA	NPL
6	Chemical stability via DSC	NPL
7	Uniformity of fresh material via density distribution	NPL

No.	Item	Owner
8	Heat treatment curve	NPL
9	Shrinkage/warp	NPL
10	Thermal cycling and compressive load tests at high temperatures	CMI
11	Heat treatment and machining trial tests	MKEH
12	Transparency	LNE
13	Material handleability	LNE
14*	Density distribution within heat treated specimens	PTB

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Provisional Assessments

- Material Composition – X-Ray Fluorescence Spectrometry (XRF)

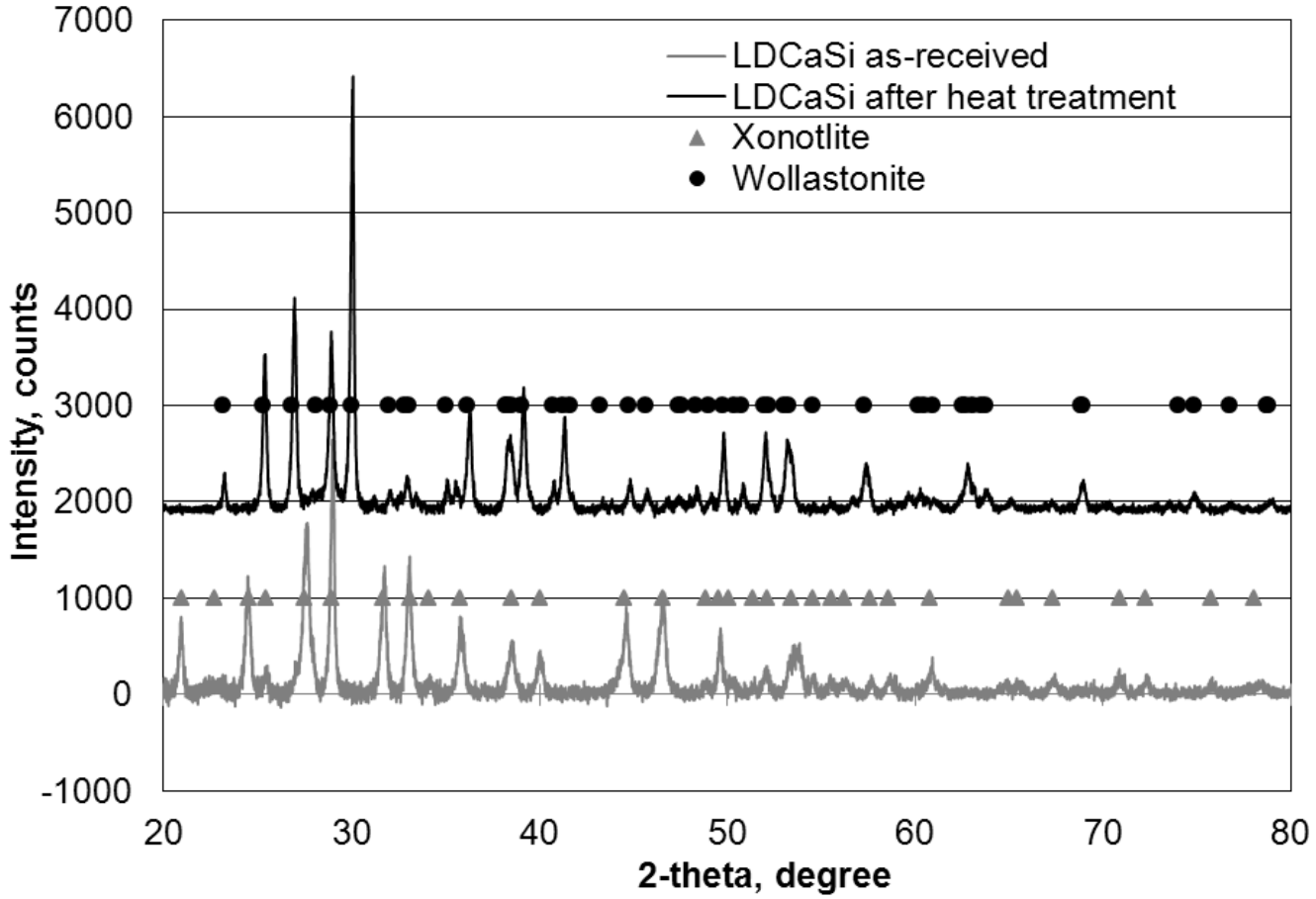
THE OXIDE COMPOSITION OF EACH MATERIAL

Result(s)		LDCaSi	AmSi	EV	HDCaSi-N	HDCaSi-B	HDCaSi-HT3B*
Sample Basis		Dried 110 °C	Dried 110 °C	Dried 110 °C	Dried 110 °C	Dried 110 °C	Dried 110 °C
Silicon Dioxide	SiO_2	45.72%	65.86%	46.98%	48.53%	54.05%	51.85%
Titanium Dioxide	TiO_2	0.01%	31.25%	0.36%	0.18%	0.06%	0.03%
Aluminium Oxide	Al_2O_3	0.15%	1.01%	10.20%	0.62%	0.59%	0.49%
Iron (III) Oxide	Fe_2O_3	0.10%	0.28%	5.13%	0.22%	0.45%	0.33%
Calcium Oxide	CaO	43.99%	0.01%	2.01%	44.12%	42.54%	45.62%
Magnesium Oxide	MgO	0.58%	<0.02%	20.47%	0.33%	0.17%	0.35%
Potassium Oxide	K_2O	0.12%	<0.01%	2.89%	0.28%	0.03%	0.15%
Sodium Oxide	Na_2O	<0.03%	<0.03%	2.73%	0.34%	0.04%	0.40%
Loss on Ignition		**8.16%**	**1.10%**	**8.53%**	**4.38%**	**2.02%**	**0.11%**
Loss on Ignition Temperature °C		1025	1025	1025	1025	1025	1025
Total		99.61%	99.90%	99.76%	99.68%	100.08%	100.08%
Sulphur Trioxide	SO_3	0.13%	<0.05%	<0.05%	0.10%	<0.05%	<0.05%
SiO_2/CaO Ratio		**1.04**			**1.10**	**1.27**	**1.14**

*: The HDCaSi-HT3B sample had been heated to 1100°C before sending for XRF analysis.

Provisional Assessments

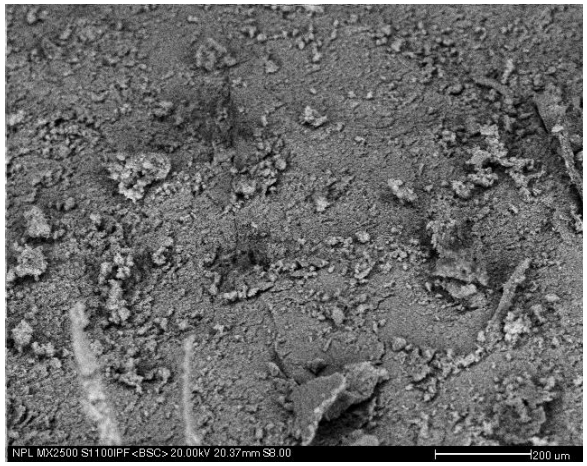
- Material Composition – X-ray Diffraction (XRD)



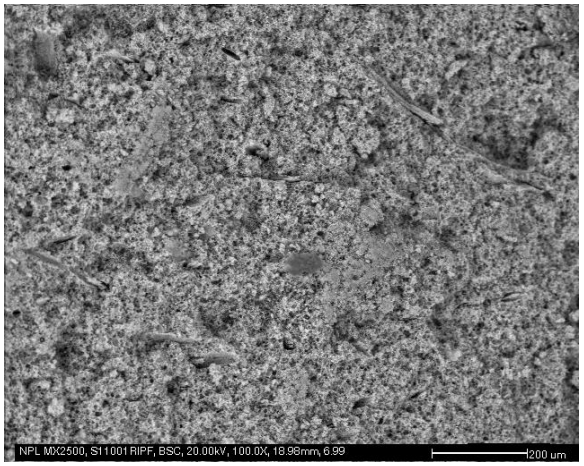
X-ray diffraction trace for LDCaSi showing the diffraction data before and after the heat treatment

Provisional Assessments

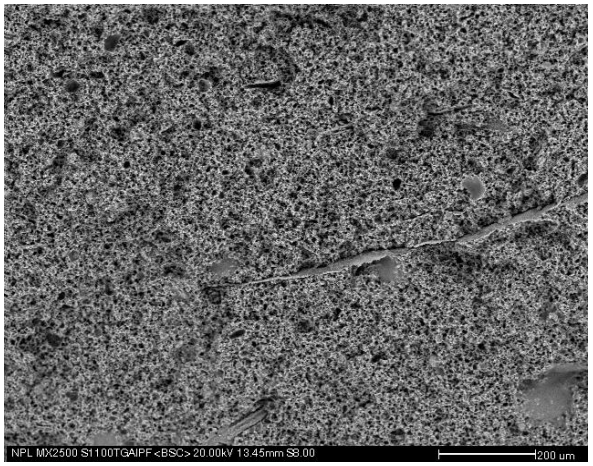
- Microstructure – SEM Micrographs



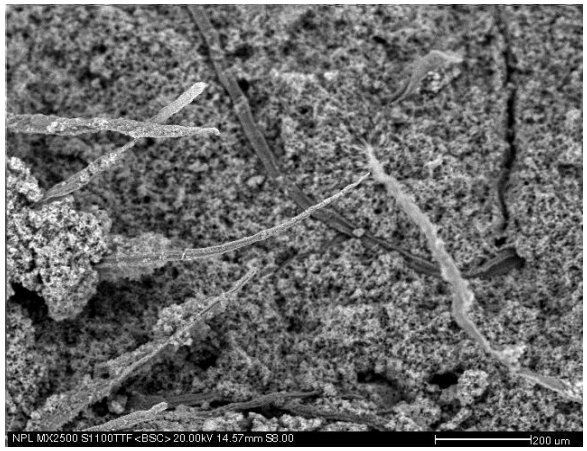
(a) as received, in-plane



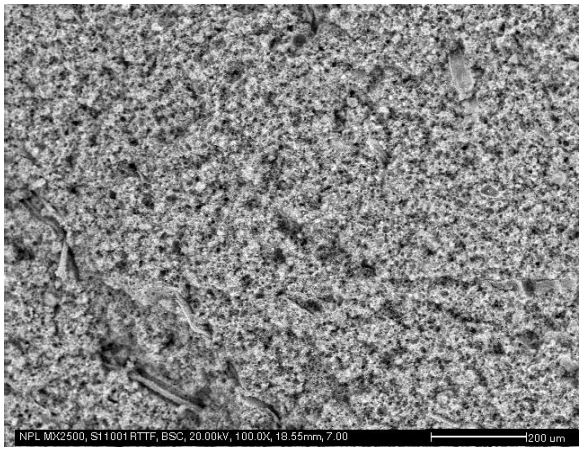
(c) after 1st HT at 850 °C for 24 hrs, in-plane



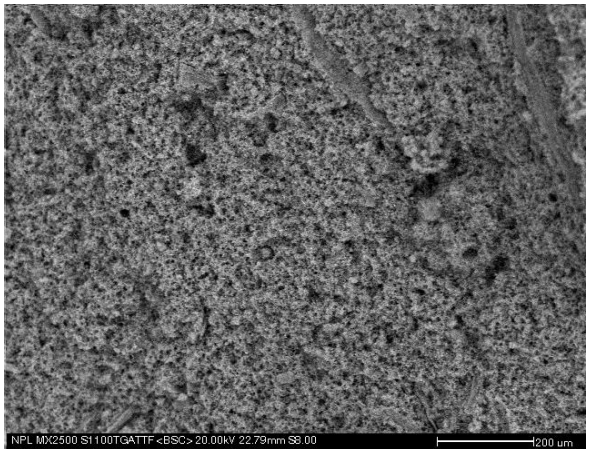
(e) post TGA, in-plane



(b) as received, through-thickness



(d) after 1st HT at 850 °C for 24 hrs, through-thickness



(f) post TGA, through-thickness

Backscattered electron images of fractured surfaces of LDCaSi

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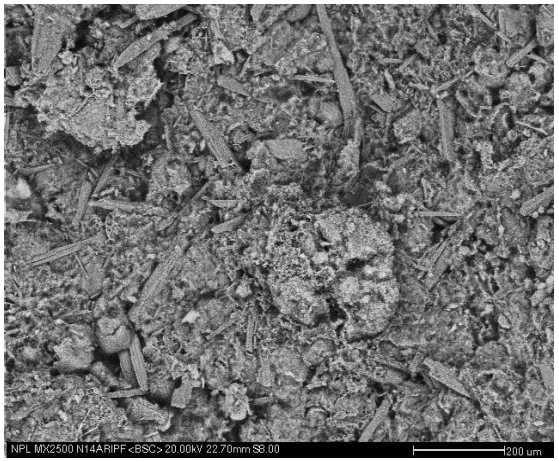
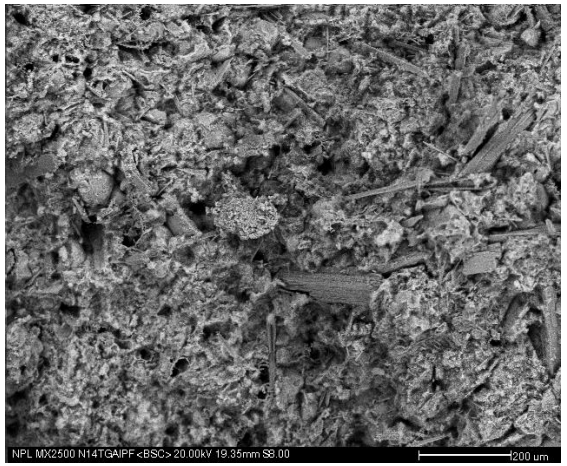
Provisional Assessments

- Microstructure – SEM Micrographs



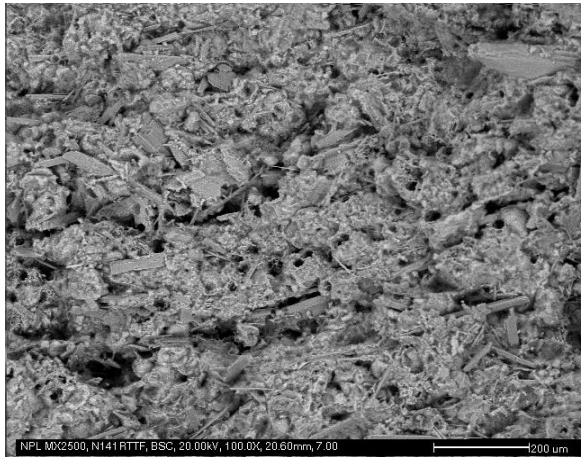
(a) as received, in-plane

(c) after 1st HT at 850 °C for 24 hrs, in-plane

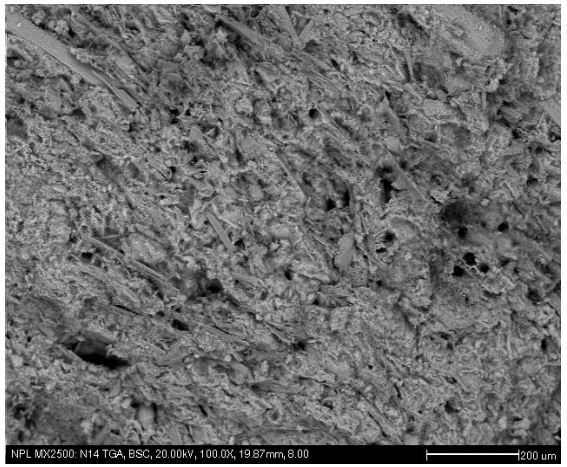


(e) post TGA, in-plane

(b) as received, through-thickness



(d) after 1st HT at 850 °C for 24 hrs, through-thickness



(f) post TGA, through-thickness

Backscattered electron images of fractured surfaces of HDCaSi-N

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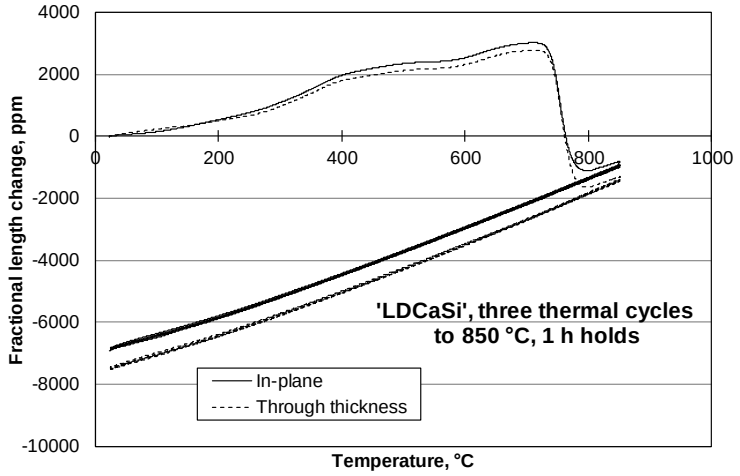
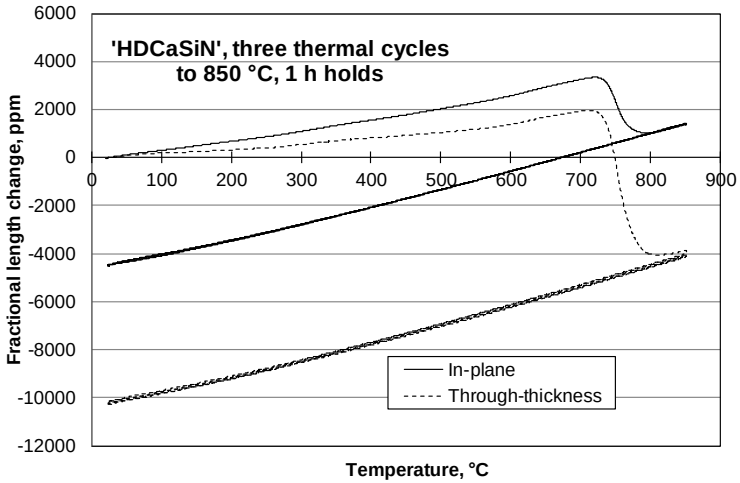
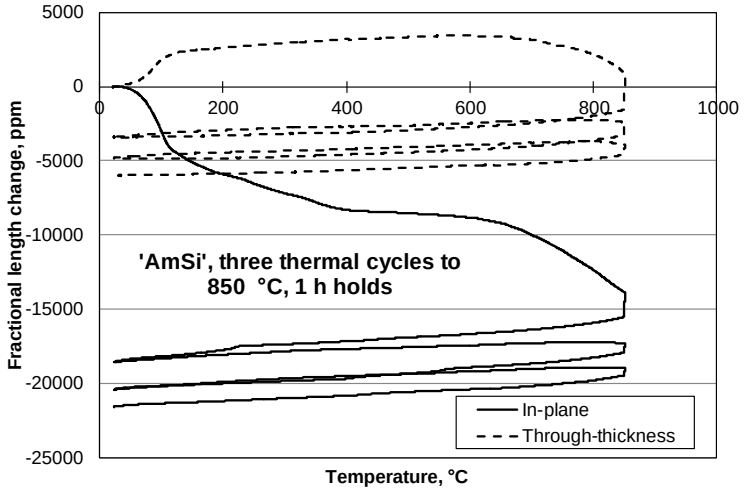
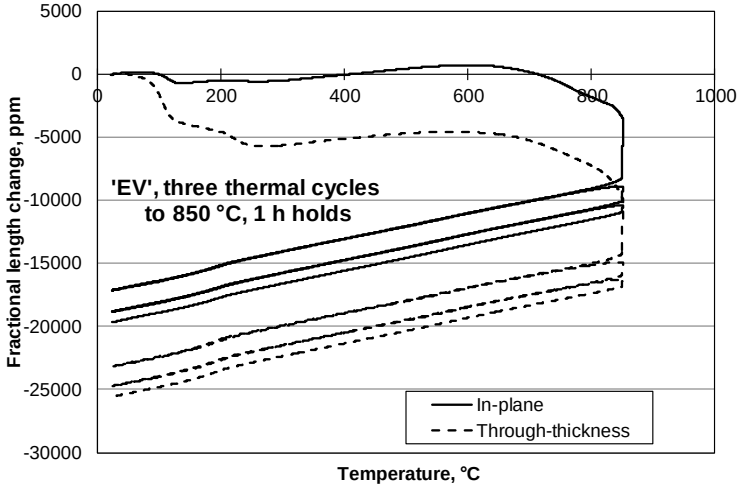
Provisional Assessments

- Mechanical and Dimensional Stability under Thermal Cycling and Isotropy Aspects – Thermal Expansion









Provisional Assessments

- Mechanical and Dimensional Stability under Thermal Cycling and Isotropy Aspects – Warp of Surfaces of Large Specimens (300 mm by 300 mm)

  After the first heat treatment at 850°C for 24 hrs: only the surfaces of the LDCaSi specimen remain flat and parallel within 0.03 mm.

  After grinding the surfaces of the heat treated specimens, they stay flat after being through two repeated thermal cycling up to 850 °C (or 750 °C for EV) at 1 °C min^{-1} rate, and held for 24hrs.

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Provisional Assessments

- Thermal cycling and compressive load testing at high temperatures

Overview of tests under compressive loads, each test at 850°C for 24 hours.
[a] specimen cracked during heat treatment

Specimen No.	Compressive Load (Pa)
IT-LDCaSi-1328202-NA-b3	4016[a]
IT-LDCaSi-1328202-NA-a3	2513; 4008; 5071
IT-N14-30639-NA-b-5	769; 5050
IT-N14-30639-NA-a-5	2509
IT-N14-30639-NA-a-13	4003

Provisional Assessments

- Thermal cycling and compressive load testing at high temperatures

Results of the weight measurements of some initial test specimens.

[a] heat treatment was carried out under compressive load

Specimen No.	Mass (g)					
	before HT	after 1st HT	after 2nd HT	after 3rd HT	after 4th HT	after 5th HT
IT-LDCaSi-1328202-NA-b3	1103.6	1012.7	1013.6	1012.9[a]		
IT-LDCaSi-1328202-NA-a3	1101.4	1010.5	1011.3	1011.6[a]	1011.4[a]	1010.5[a]
IT-N14-30639-NA-b-9	10323.6	9856.2				
IT-N14-30639-NA-b-5	3730.6	3553.8	3561.6[a]	3551.4[a]		
IT-N14-30639-NA-a-5	3504.9	3343.6	3349	3349.2[a]		
IT-N14-30639-NA-a-13	3744.0	3568.9	3573.7	3567.7[a]		

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Provisional Assessments

- Thermal cycling and compressive load testing at high temperatures

Results of the length measurements of some initial test specimens.

[a] heat treatment was carried out under compressive load

Specimen No.	Length (mm)					
	before HT	after 1st HT	after 2nd HT	after 3rd HT	after 4th HT	after 5th HT
IT-LDCaSi-1328202-NA-b3	299.4	297.4	297.4	297.3[a]		
IT-LDCaSi-1328202-NA-a3	299.8	297.8	297.7	297.7[a]	297.8[a]	297.7[a]
IT-N14-30639-NA-b-9	499.7	497.8				
IT-N14-30639-NA-b-5	299.7	298.5	298.5[a]	298.5[a]		
IT-N14-30639-NA-a-5	299.2	297.9	297.9	297.9[a]		
IT-N14-30639-NA-a-13	298.9	297.8	297.8	297.7[a]		

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Provisional Assessments

- Thermal cycling and compressive load testing at high temperatures

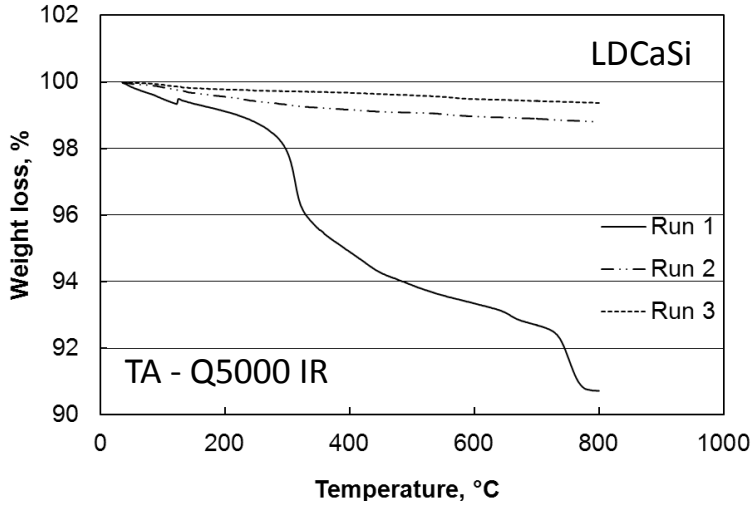
Results of the thickness measurements of some initial test specimens.

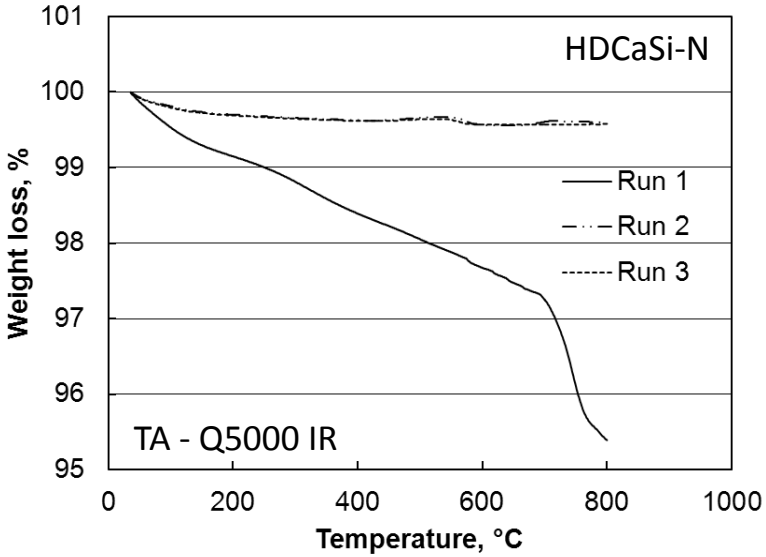
[a] heat treatment was carried out under compressive load

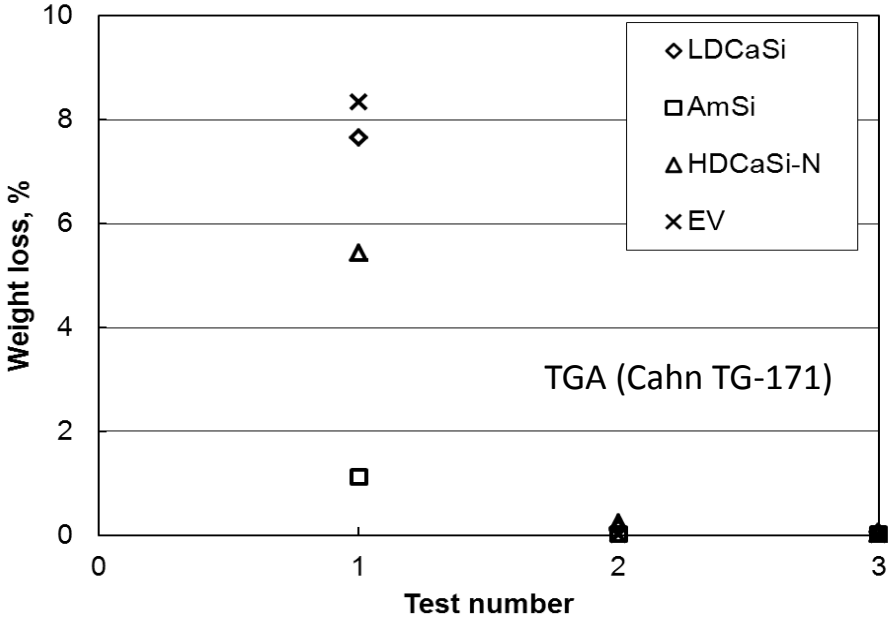
Specimen No.	Thickness (mm)					
	before HT	after 1st HT	after 2nd HT	after 3rd HT	after 4th HT	after 5th HT
IT-LDCaSi-1328202-NA-b3	46.7	46.4	46.4	46.3[a]		
IT-LDCaSi-1328202-NA-a3	46.9	46.6	46.5	46.5[a]	46.5[a]	46.5[a]
IT-N14-30639-NA-b-9	51.1	50.5				
IT-N14-30639-NA-b-5	50.5	49.9	49.9[a]	49.9[a]		
IT-N14-30639-NA-a-5	50.5	50.0	49.9	49.9[a]		
IT-N14-30639-NA-a-13	50.7	50.1	50.0	50.0[a]		

Provisional Assessments

- Chemical Stability under Thermal Cycling – TGA Results



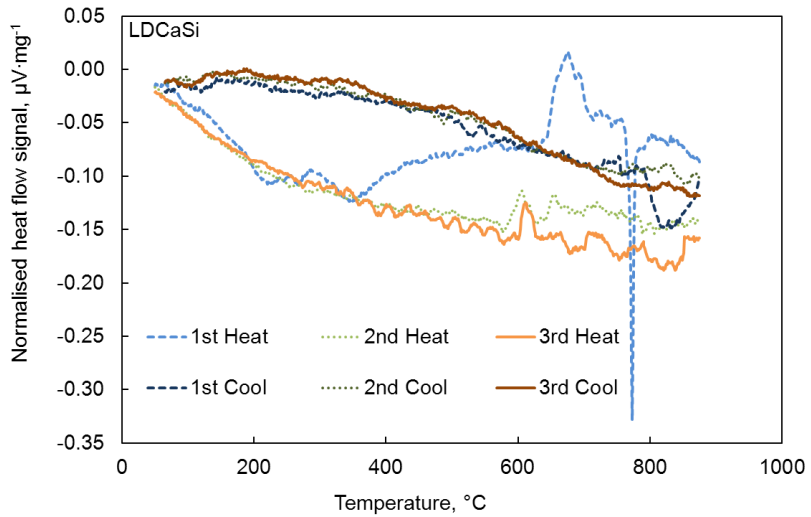


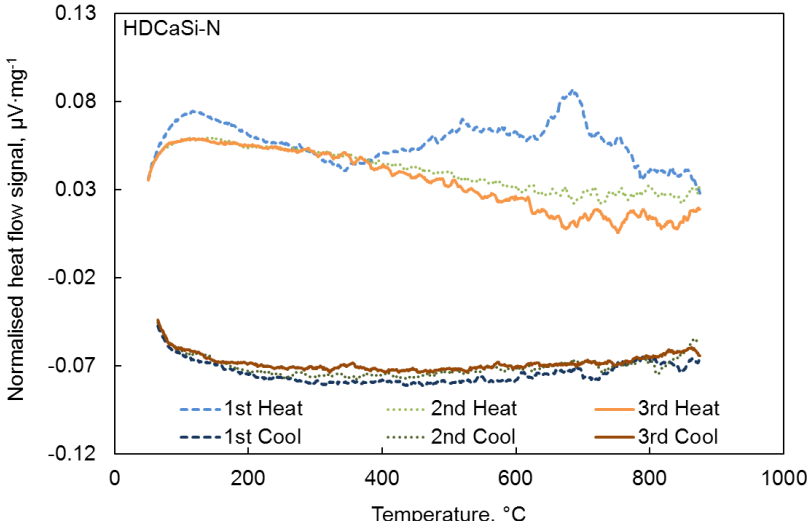


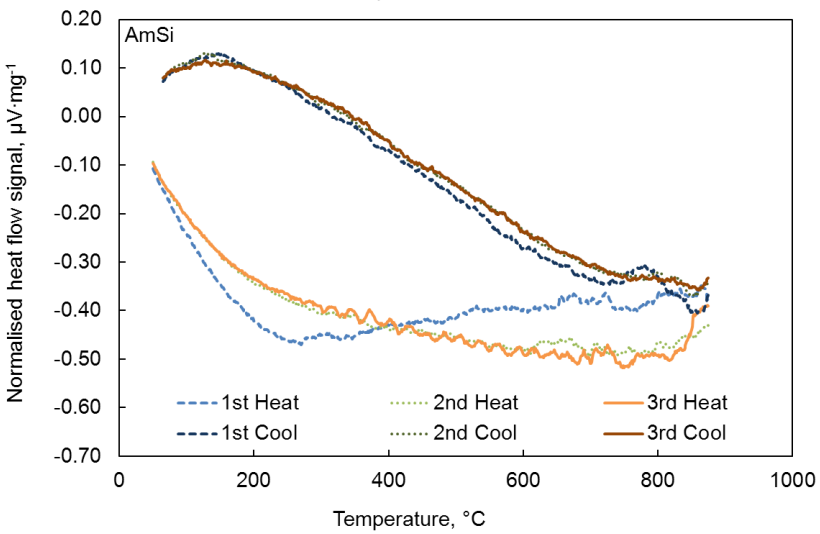
Weight loss after each run in the TGA (Cahn TG-171) where samples were held at 850 °C for 24 hours

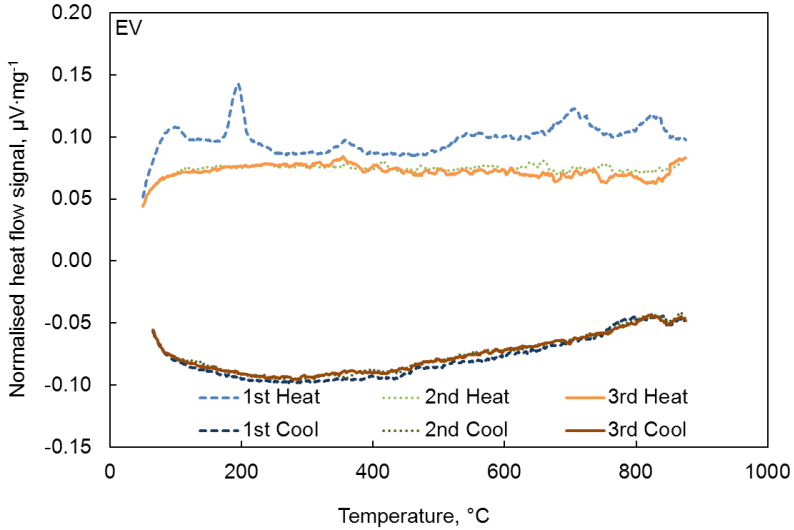
Provisional Assessments

- Chemical Stability under Thermal Cycling – DSC Results





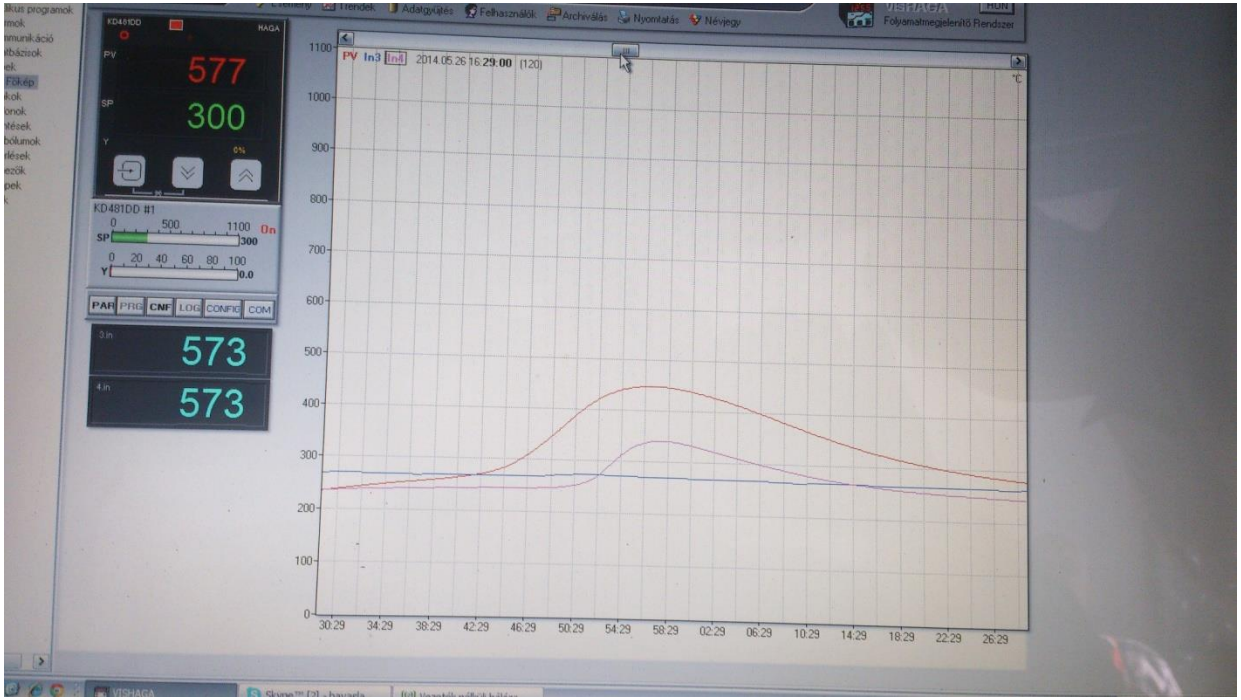




Provisional Assessments

- Heat treatment and machining trial tests

  Adjustment of heat treatment at large scale



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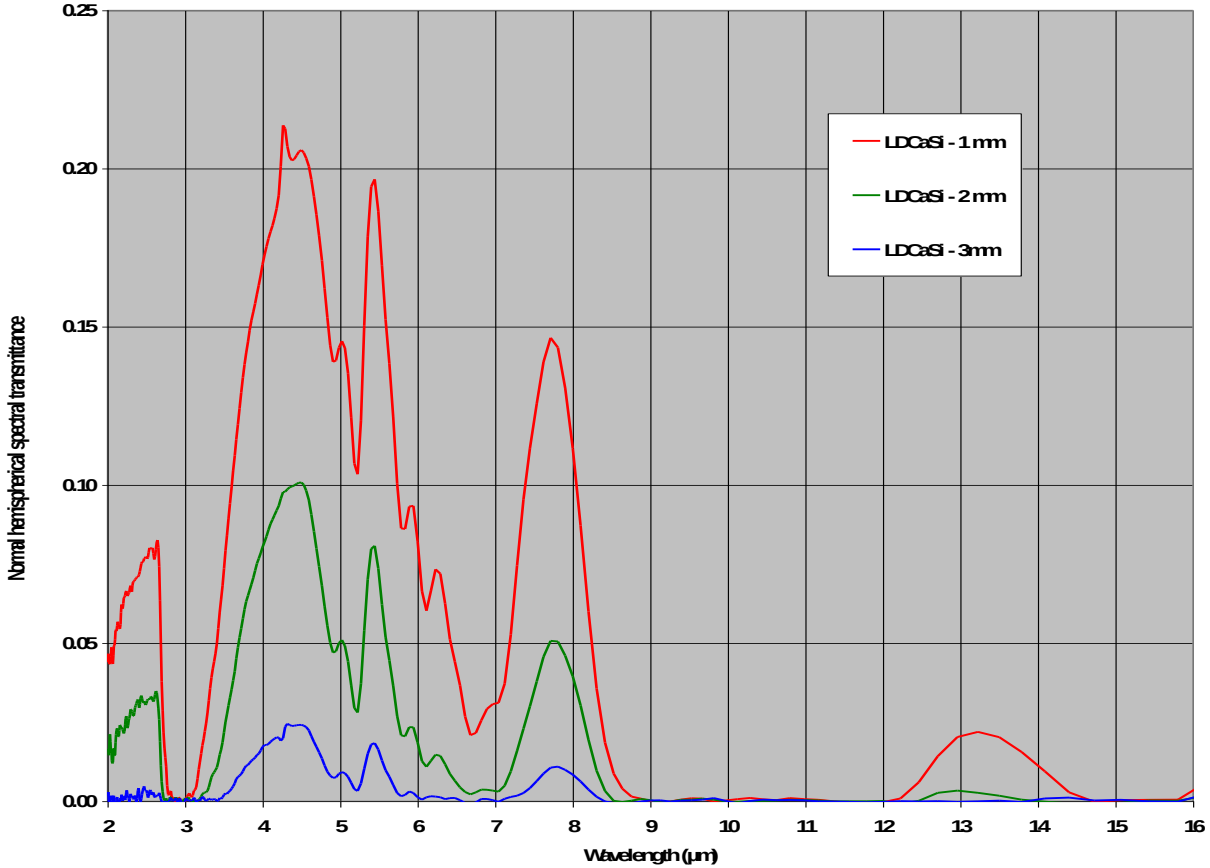
Provisional Assessments

- Transparency



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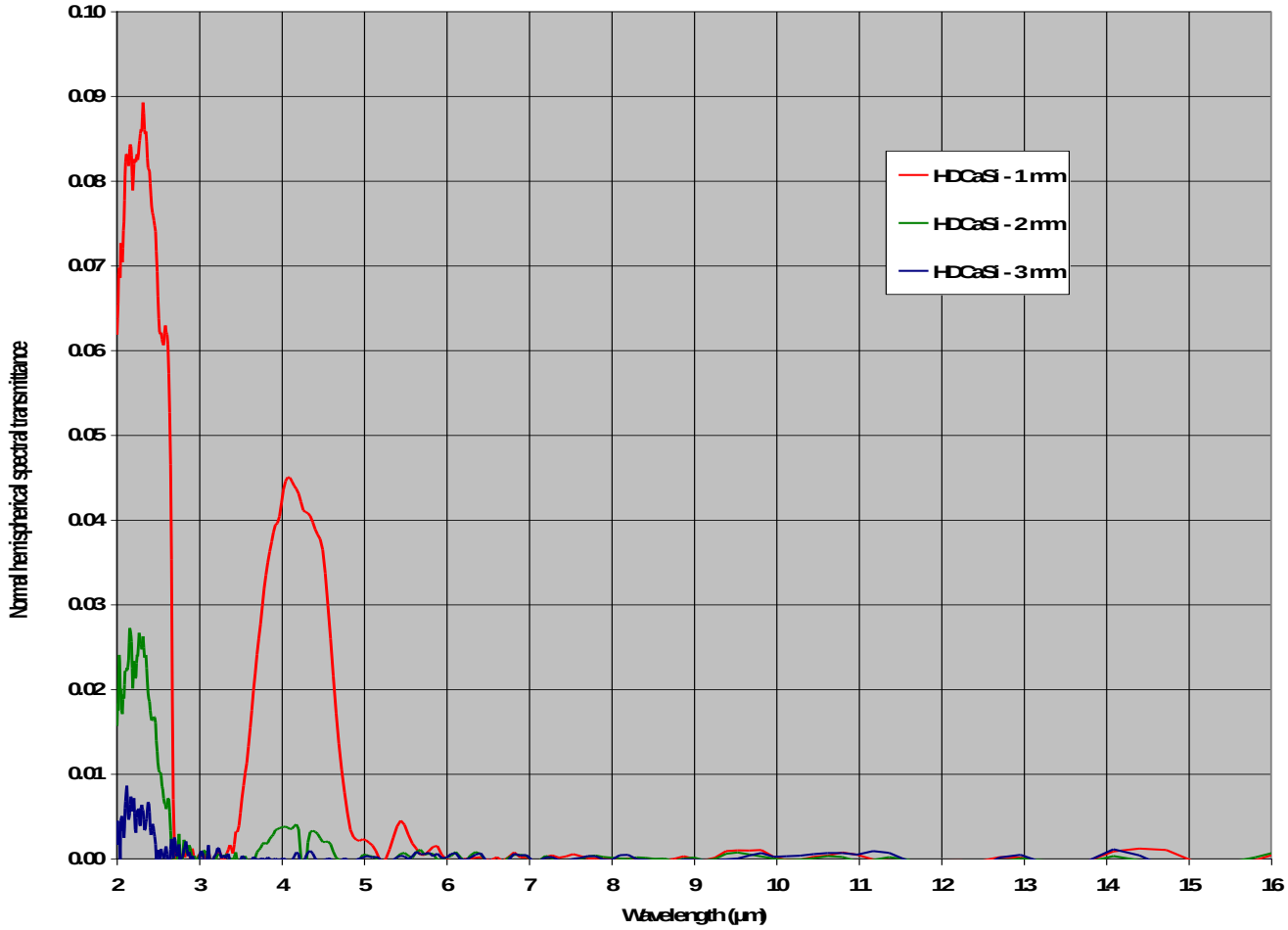

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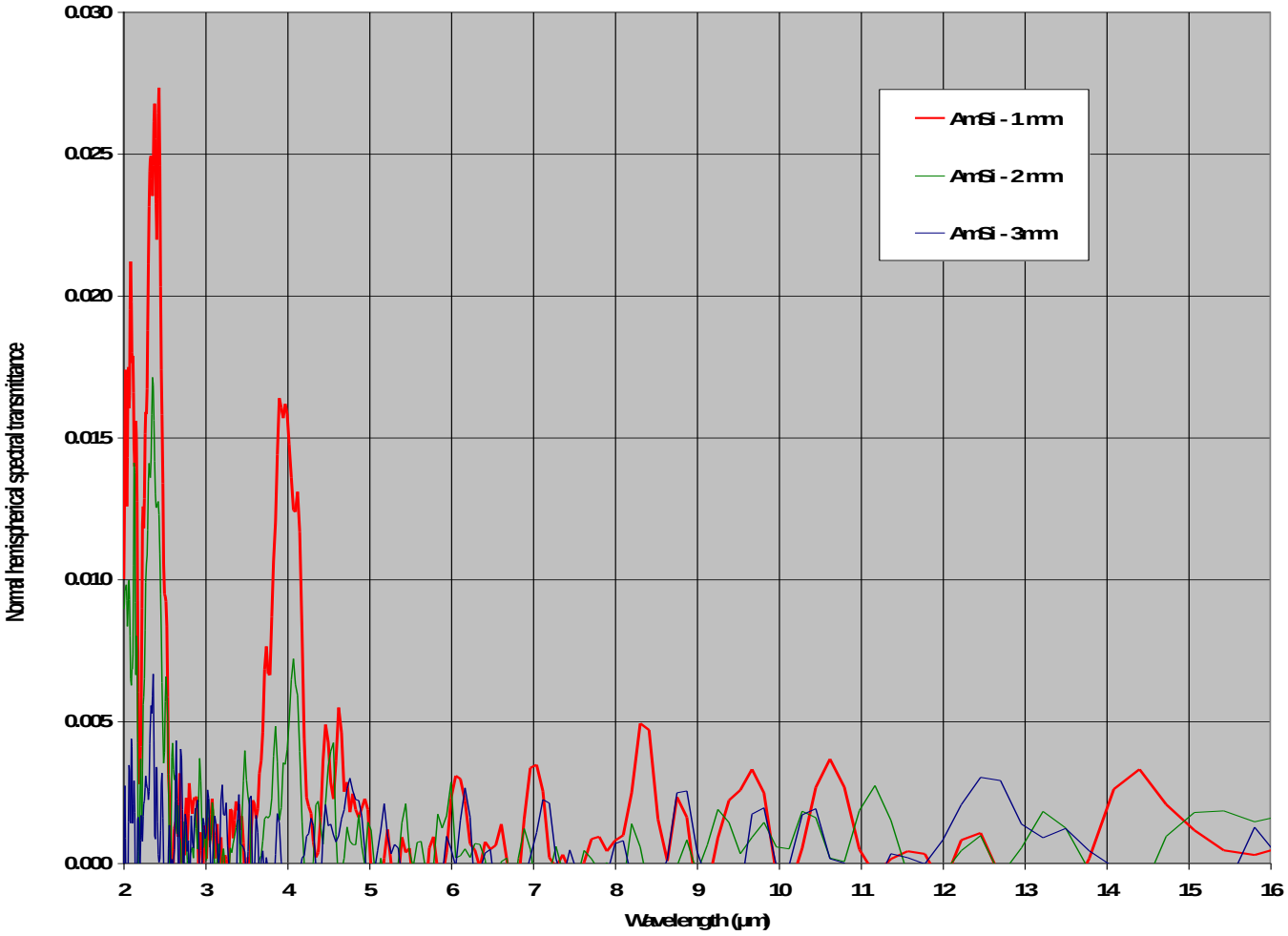

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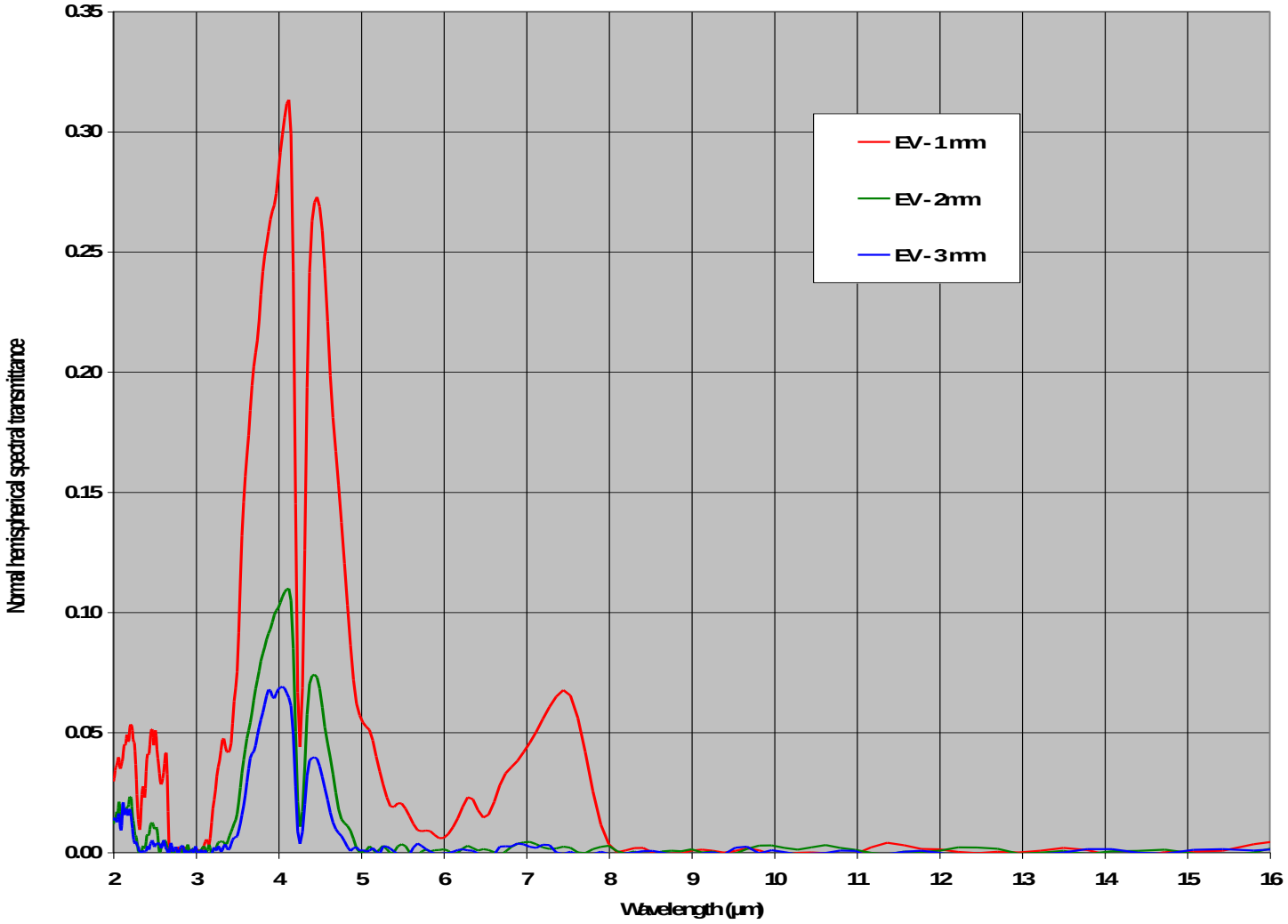

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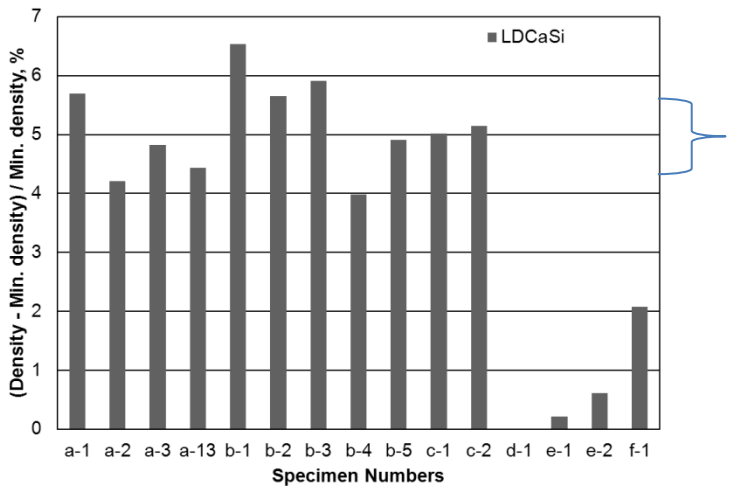
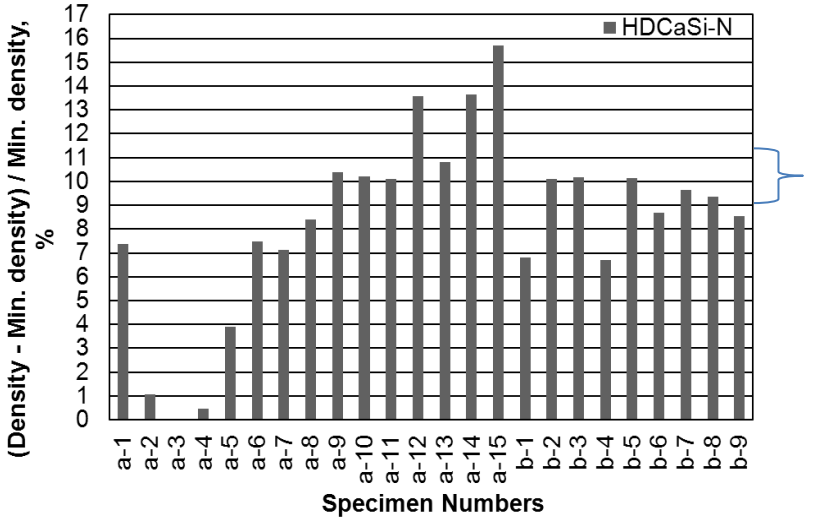
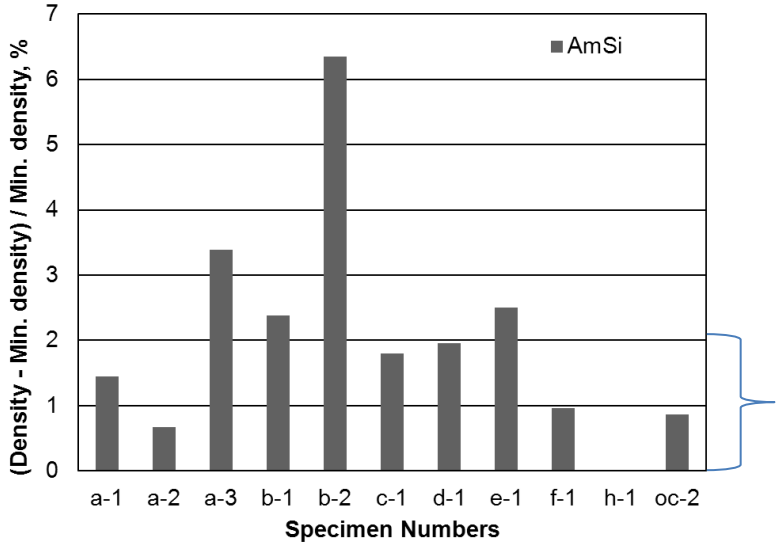
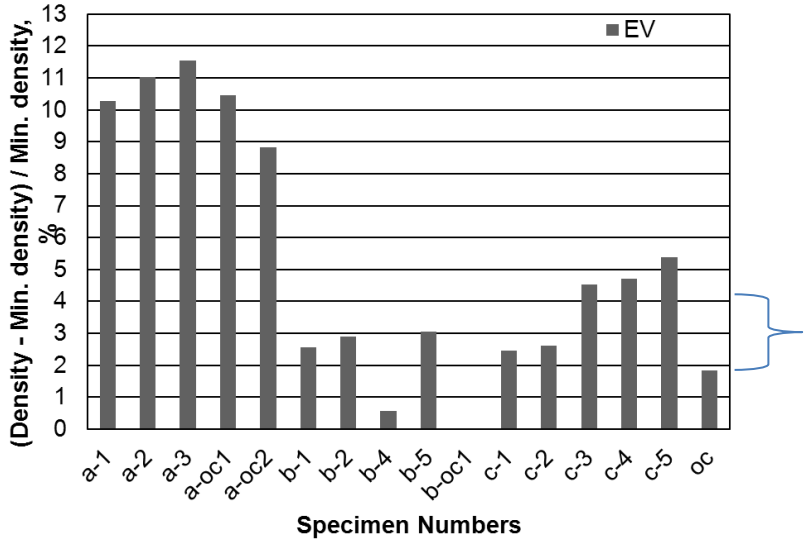
Provisional Assessments

- Material Uniformity – Density Distribution









Conclusions

- The two most promising candidate materials, LDCaSi and HDCaSi-N will be further developed into high temperature thermal conductivity reference materials in the next stage.
- Although permanent changes were observed during the first heat treatment, these two materials are dimensionally, mechanically and chemically stable after the first heat treatment.
- The microstructures of these two materials remain stable, and they are more robust and easier to handle.
- The dimensions and mass of the two candidate materials remain stable after thermal cycling and compressive load testing at temperatures up 850°C and pressure up to 5050Pa.
- The heat treatment curves have been adjusted after the trial tests at large scale.
- Not expecting any transparency issues for 50mm thick specimens. The normal hemispherical spectral transmittance of a 3mm thick HDCaSi-N is less than 0.01, and that of a 3 mm thick LDCaSi is less than 0.025.
- However, it is important that the specimens of reference materials meet the requirement for material uniformity, i.e. density varies within 2 %, hence, there need to be a stringent selection process to ensure the material uniformity.