Bavarian Center for
Applied Energy Research (ZAE Bayern)

Principles of T-History measurements +

T-History Round Robin Test

Christoph Rathgeber

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Principles of T-History measurements

T-History Round Robin Test

Combined T-History and DSC measurements

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Principles of T-History measurements

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Motivation

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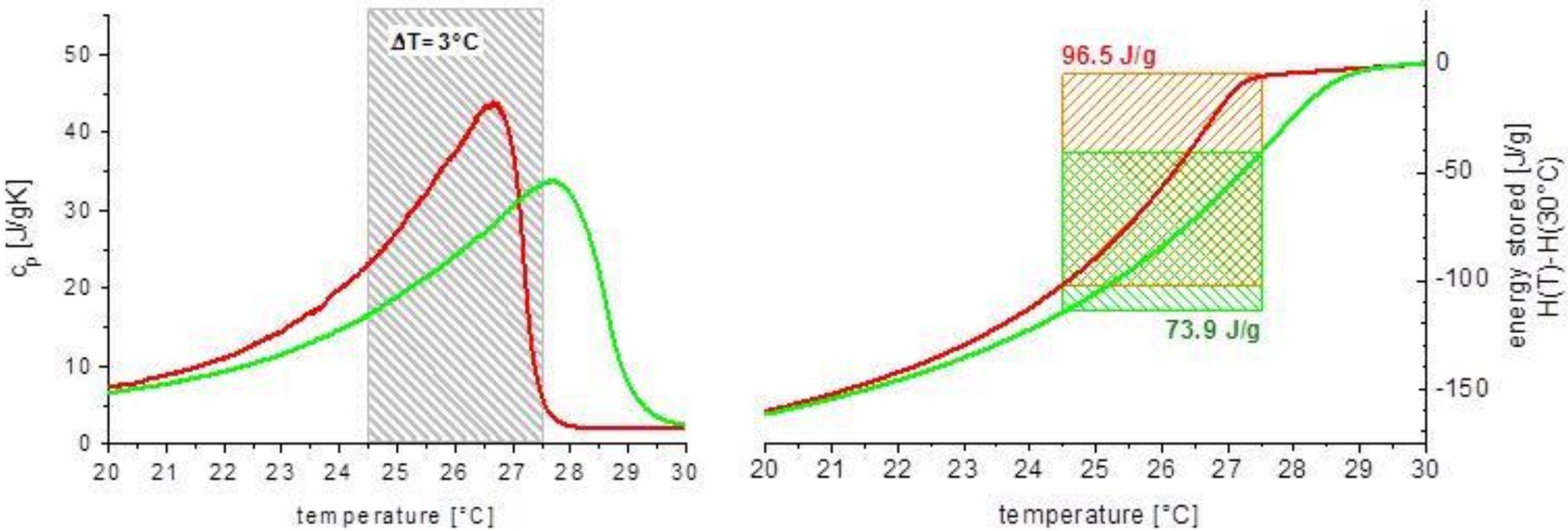
Enthalpy curves of PCM have to be measured with high accuracy to design efficient latent heat storages.

<u>Example:</u>

Enthalpy curves upon melting of one sample, measured with different heating rates

→ 23 % deviation of ΔT within ΔT = 3 °C



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RAL testing regulations defined by *PCM Gütegemeinschaft e.V.* (www.pcm-ral.de)

- uncertainty limits for the measurement of enthalpy curves
  - enthalpy ($\delta(\Delta h) < 10$ %)
  - temperature ($\delta T < 1$ K)

Measured enthalpy curves should be …

… close to thermodynamic equilibrium

→ the slower the larger the sample

… representative for the behaviour of bulk material in real applications

→ large samples

→ charging and discharging temperatures similar to applications

[Günther et al. 2009]

Motivation

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Measurement of enthalpy curves *h*(*T*) of PCM upon heating and cooling

Standard method: Differential scanning calorimetry (DSC)

- measurement of *h*(*T*)
- determination of transition temperatures (onset, peak) and latent heat
- fast screening of a large number of materials

Advantages of T-History compared to DSC:

- 1000x larger samples: ~ml (T-History) ↔ ~µl (DSC)
  - ➢ heterogeneous materials (salt hydrates, PCM mixtures)
  - ➢ materials with volume dependent behaviour (subcooling, phase separation, polymorphism)
- constant charging / discharging temperatures similar to applications

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Motivation: T-History sample size compared with DSC

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T-History: Typical setup and measured data

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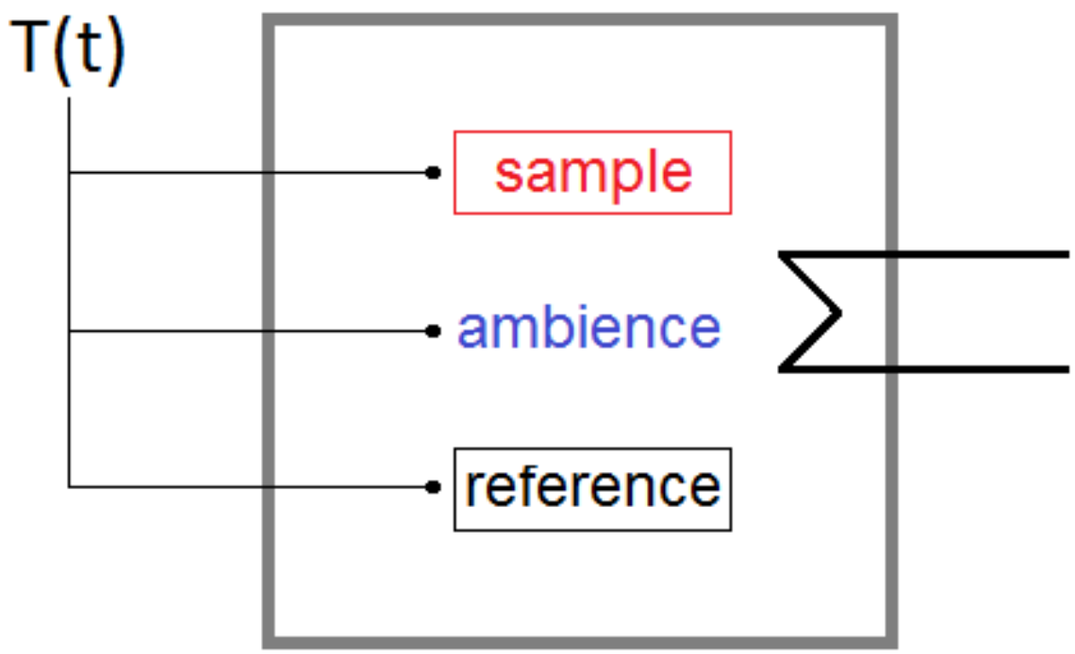

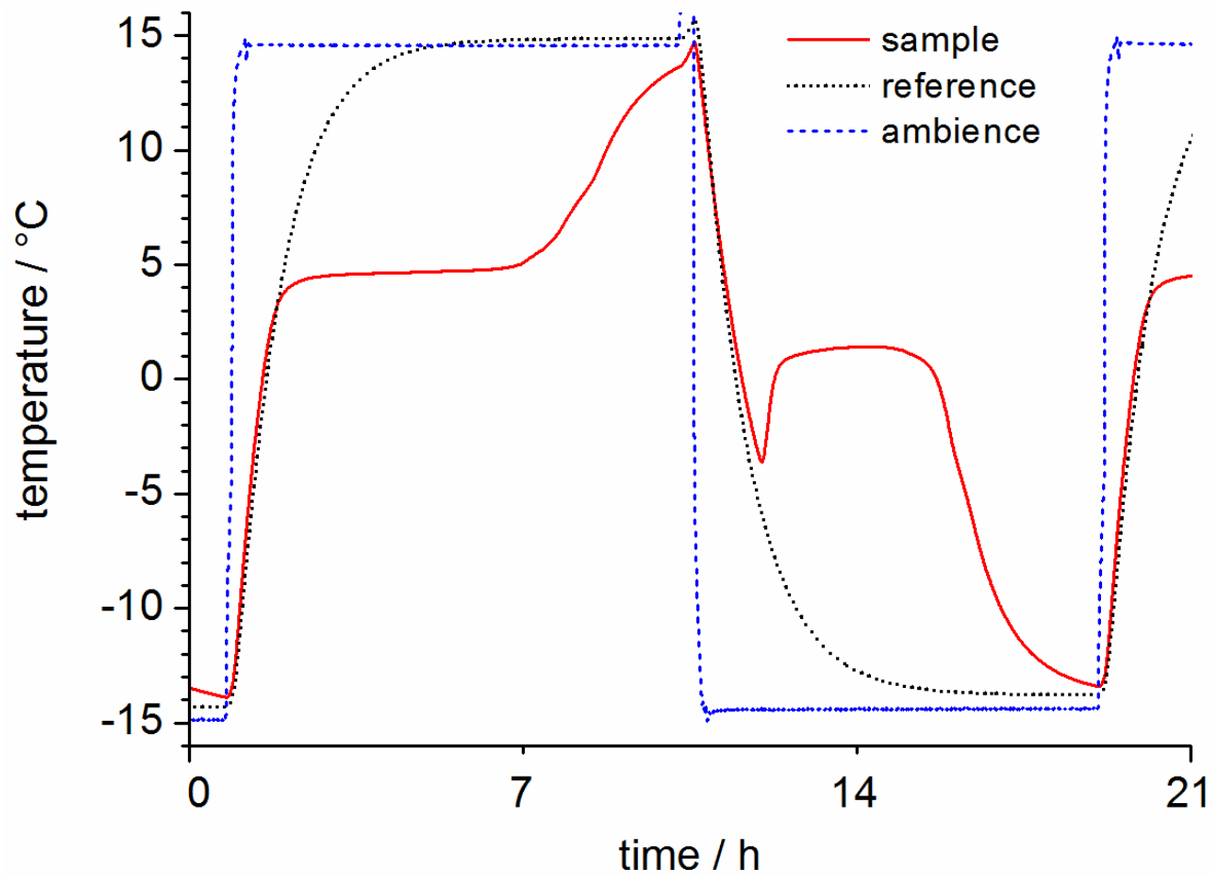

Example:
Temperature-time data of a salt-based, eutectic PCM melting around 4 °C
[Schmit et al. 2014]

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T-History: Evaluated enthalpy curves

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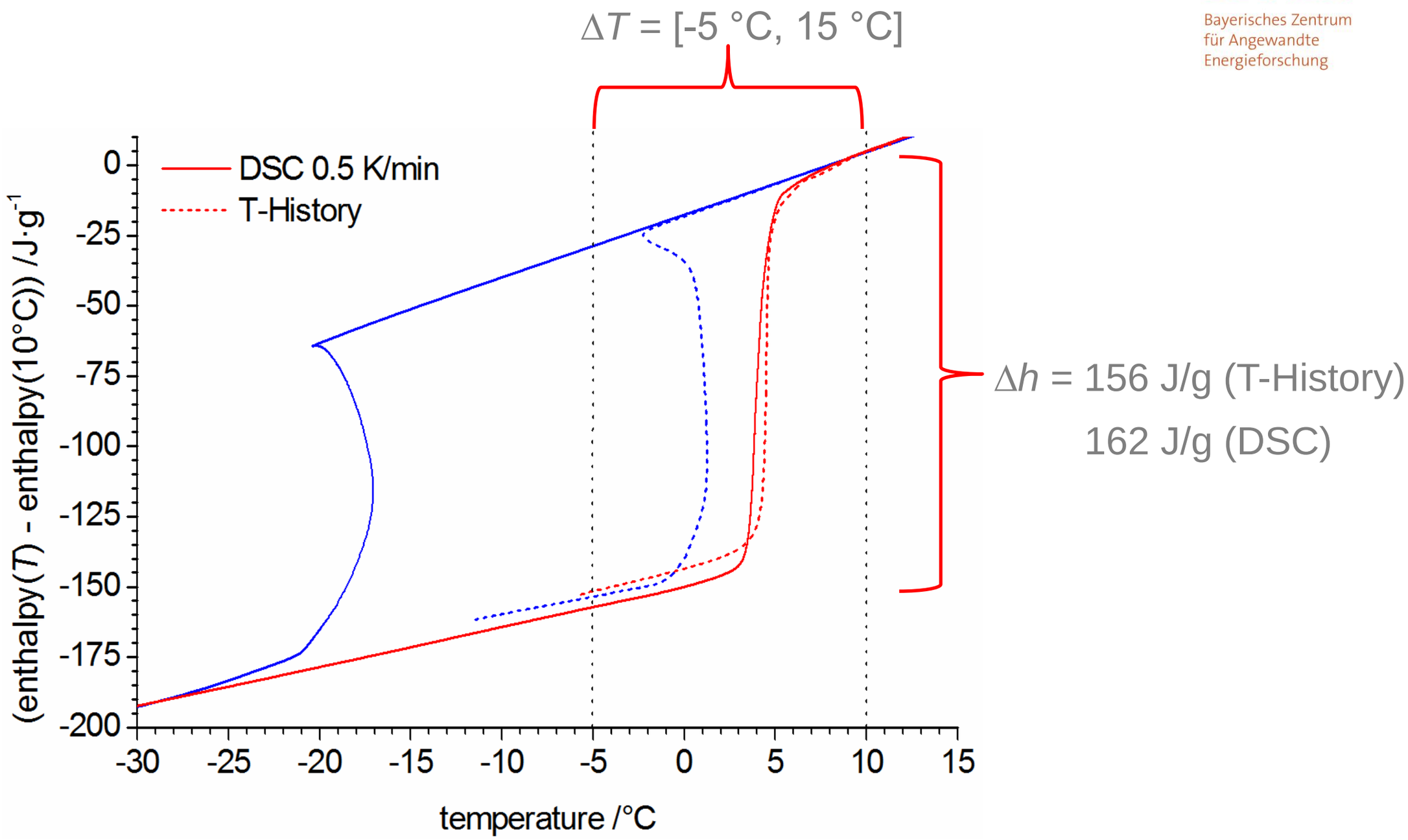

Example:

Enthalpy curves of a salt-based, eutectic PCM melting around 4 °C measured via T-History and DSC [Schmit et al. 2014]

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T-History calorimeters at our lab

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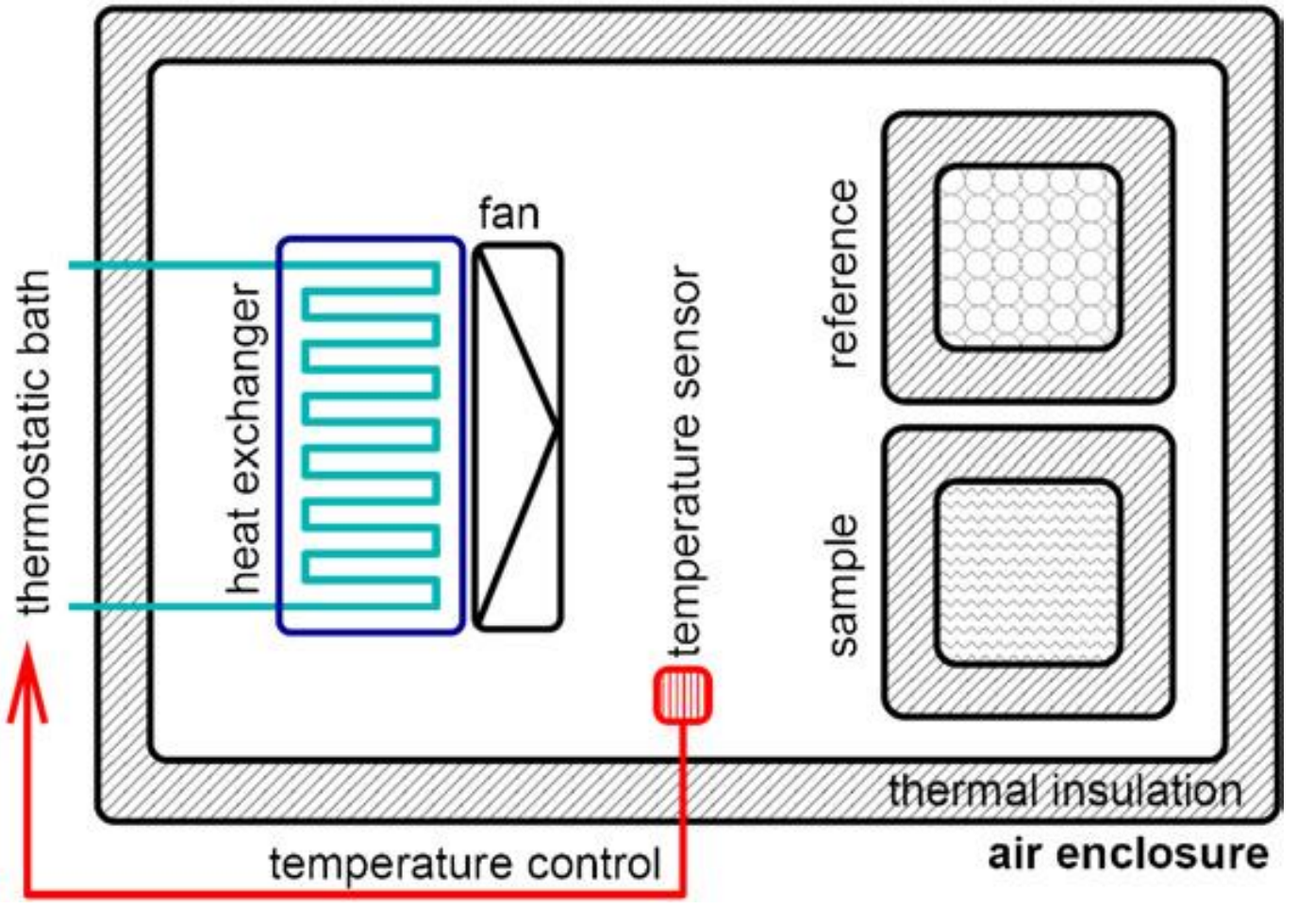
T-History 1

- -15 °C … +80 °C
- Calibrated with distilled water, gallium, copper



[Lázaro and Günther 2006]

T-History calorimeters at our lab

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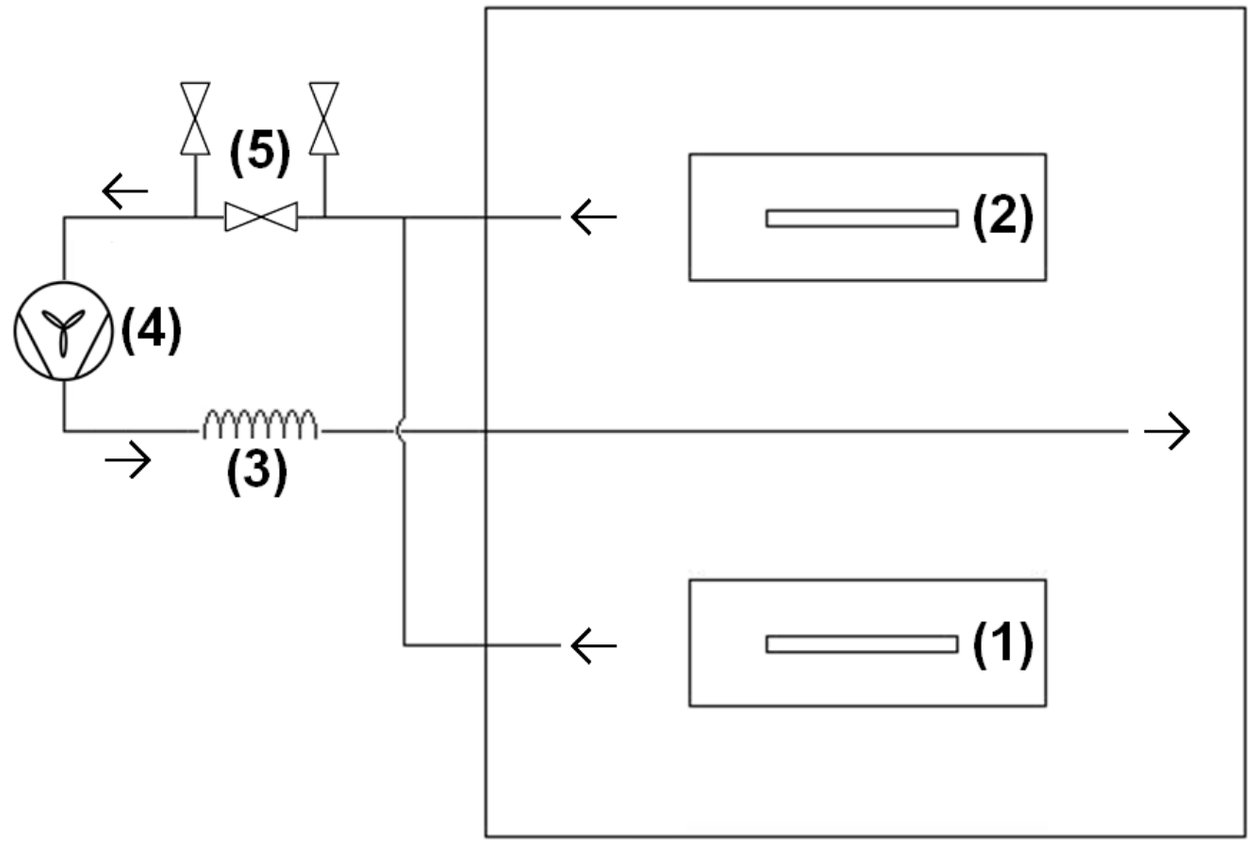

[Rathgeber et al. *Meas. Sci. Tech.* 2014]

T-History 2

- 40 °C … 200 °C
- Calibrated with Indium, copper, 3 pure organic PCM (stearic acid, DMT, D-mannitol)

T-History: Summary

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Advantages

- 1000x larger samples than in DSC & constant charging / discharging temperatures
→ $h(T)$ curves more representative for behaviour of bulk material in real applications
- determination of a suitable operating temperature range and the corresponding maximum storage capacity therein

What need's to be improved?

- determination of uncertainty
- standardisations (setup, reference, calibration etc.)
→ What is a T-History measurement?
- T-History measurements for temperatures > 200 °C

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Motivation

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T-History RRT aims at

- comparing T-History instruments from different institutes
- identifying the most appropriate / reliable / accurate calibration
- improving the accuracy of measured data

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RRT procedure

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First round of the RRT

- participants measure the enthalpy curves $h(T)$ of octadecane for melting and crystallisation according to their own procedure

- no standardisations in terms of
  - calibration
  - sample preparation
  - experimental setup
  - applied temperature profile

- comparison of
  - measured enthalpy curves $h(T)$
  - application relevant enthalpy changes Δh within suitable operating temperature ranges ΔT around the phase change
    (Δh = maximum storage capacity within ΔT)

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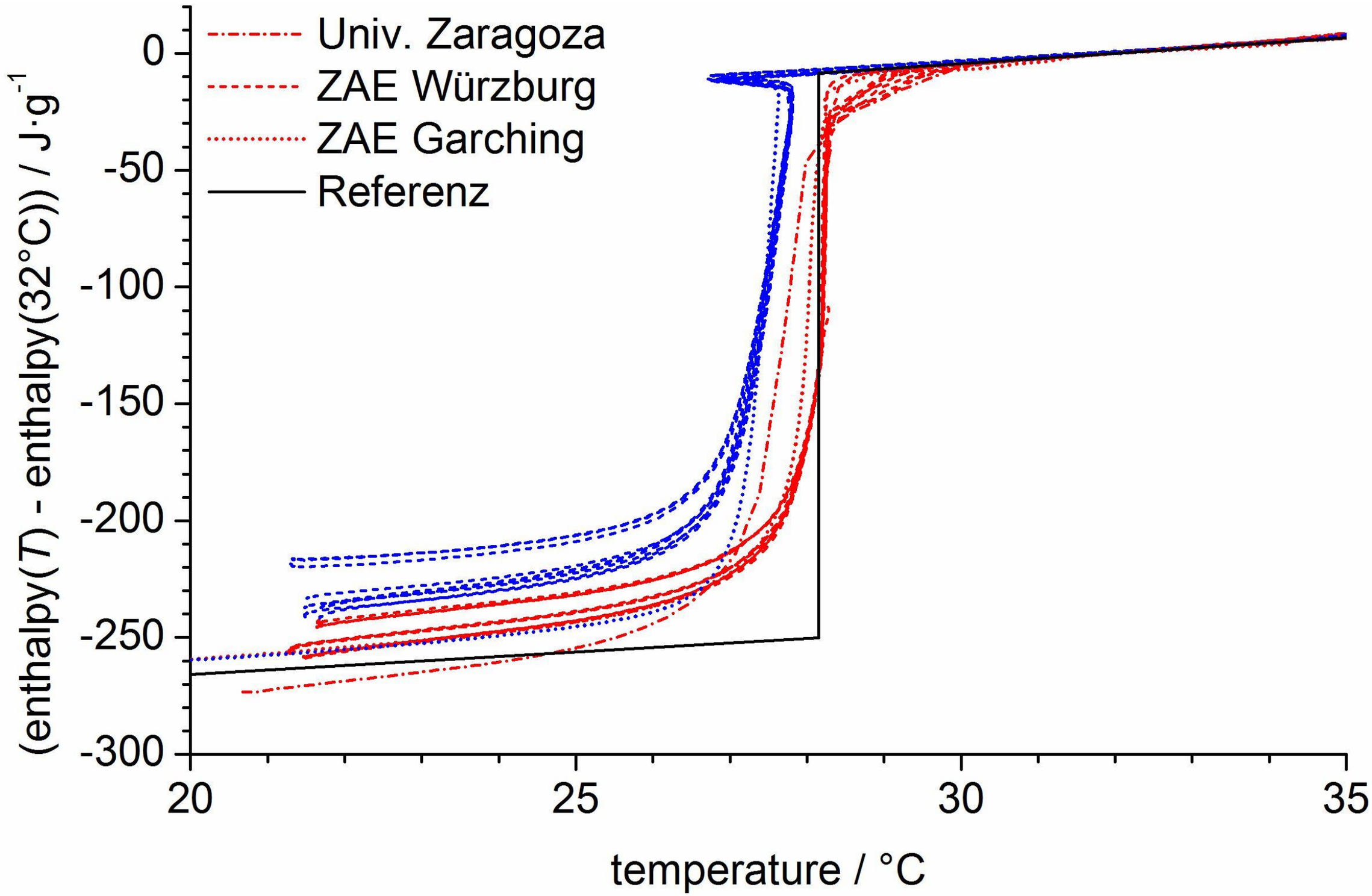
Results



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Results – Enthalpy curves for melting

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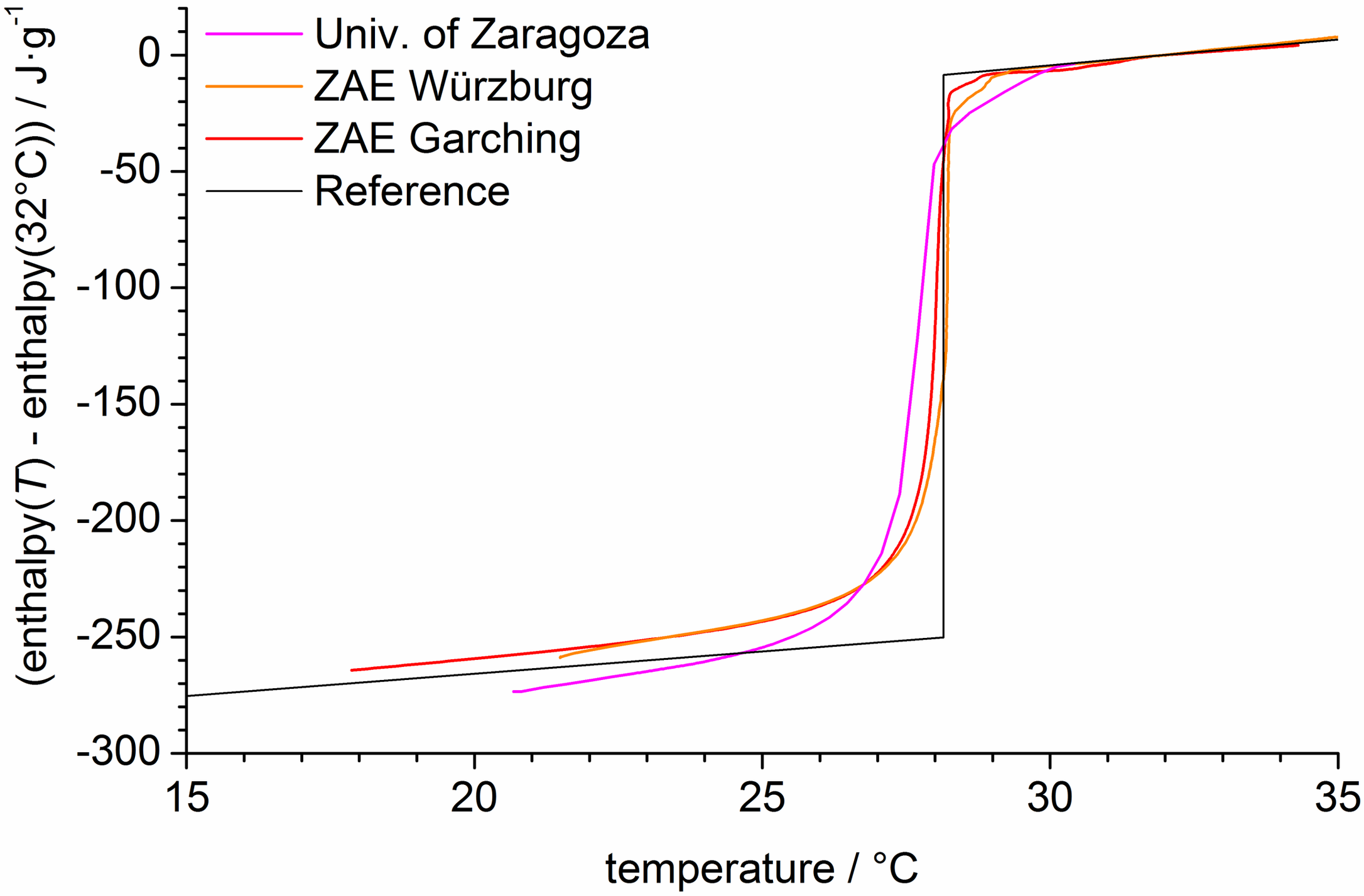

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Results – Enthalpy curves for crystallisation

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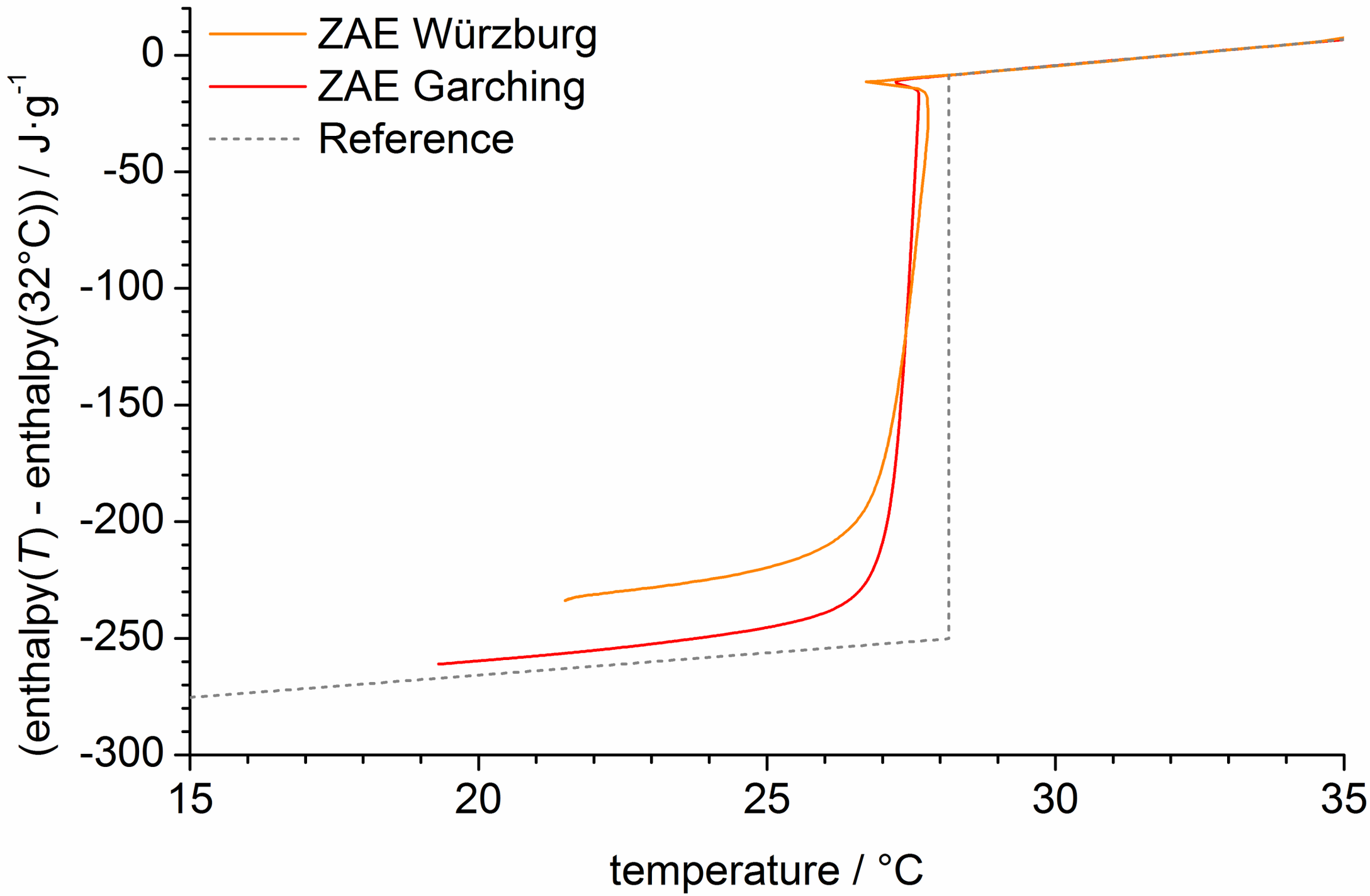

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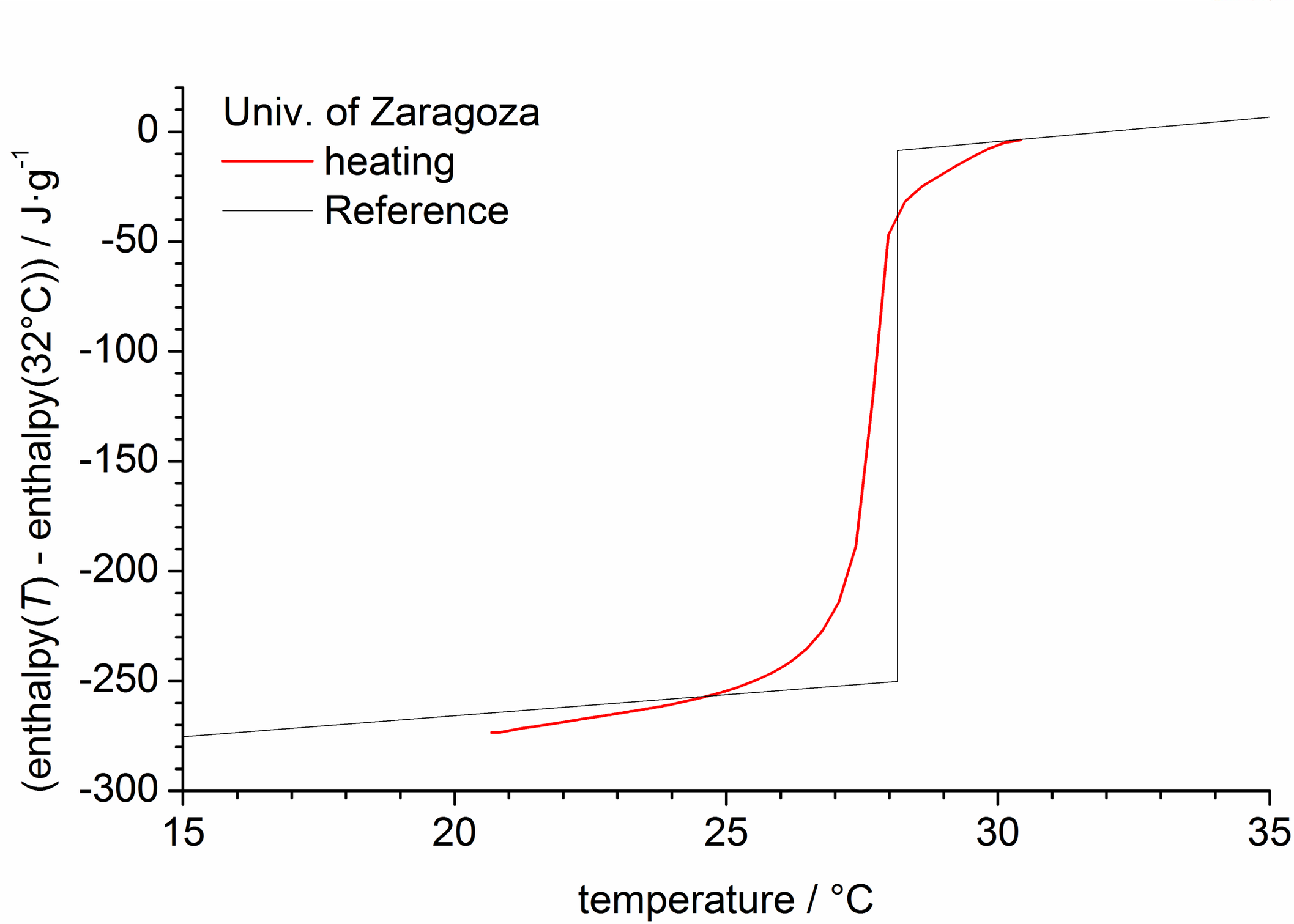

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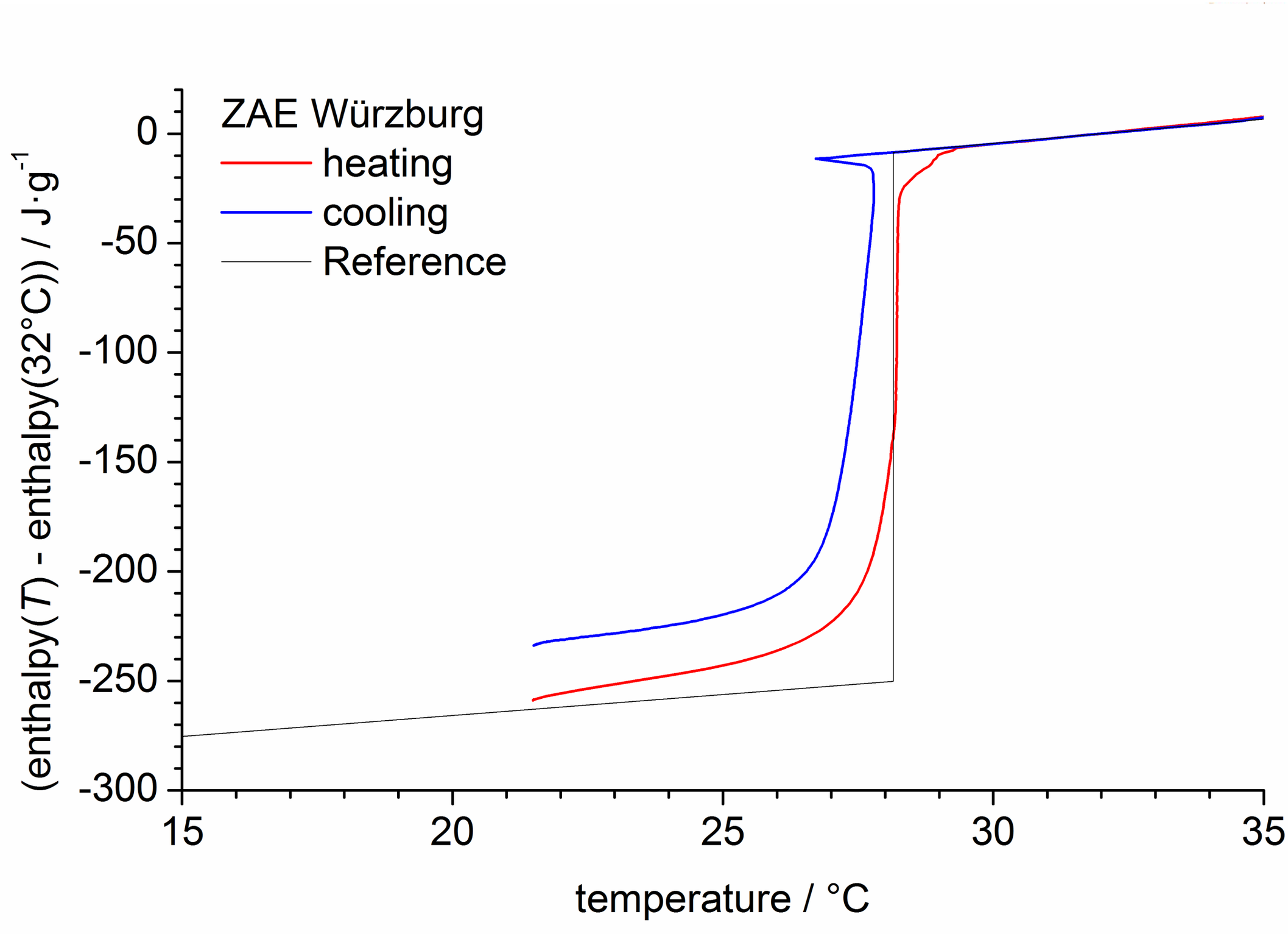

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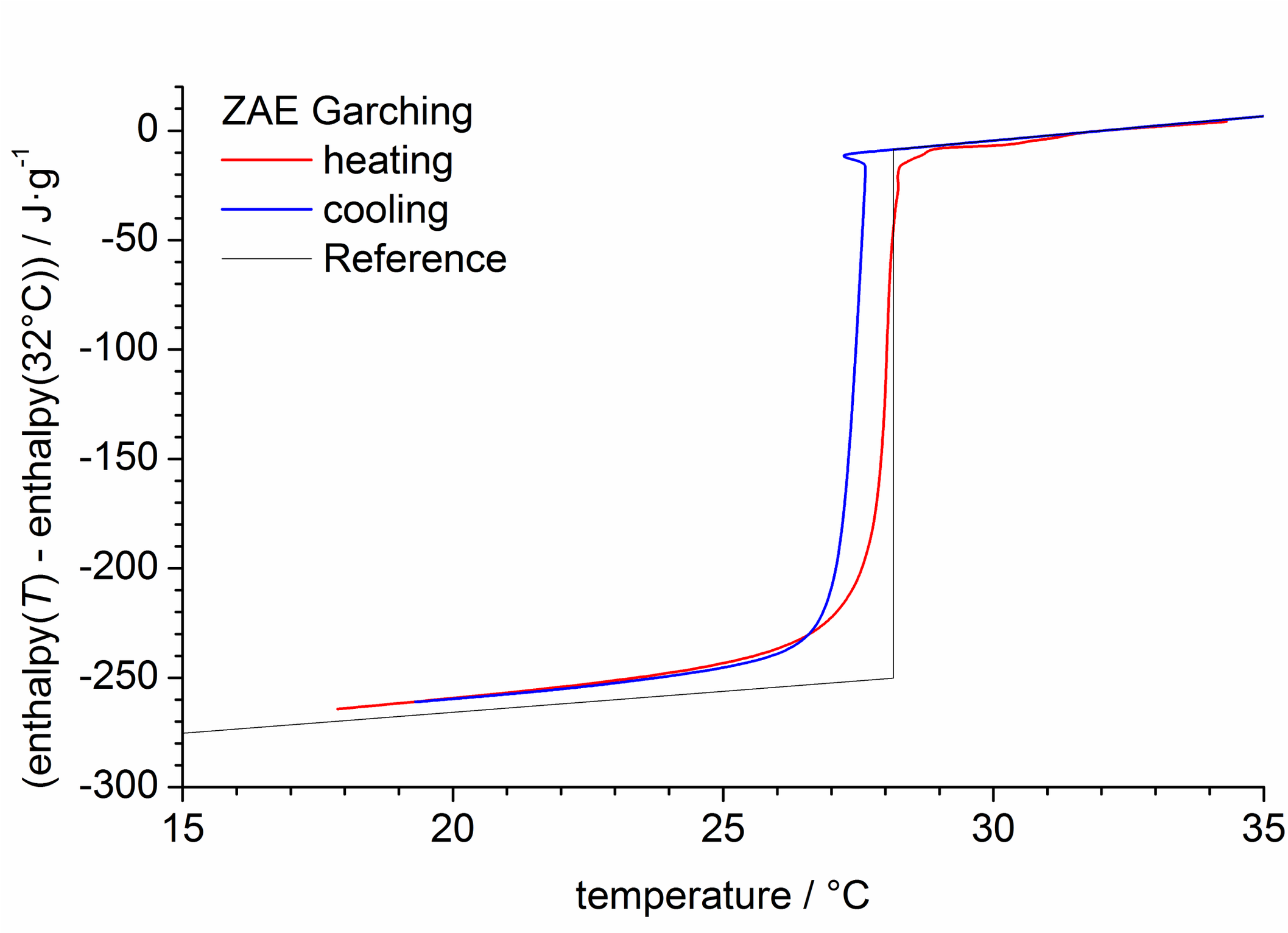
ZAE Garching



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Results after round 1

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Institution	Δh_{melt} (J/g) (measured)	Reference (NIST values) [Lázaro et al. 2013]	Δh_{cryst} (J/g) (measured)
University of Zaragoza	263 (22 → 30 °C)	258 (22 → 30 °C)	-
ZAE Bayern - Würzburg	256 (22 → 32 °C)	262 (22 → 32 °C)	231 (32 → 22 °C)
ZAE Bayern - Garching	254 (22 → 32 °C)	262 (22 → 32 °C)	255 (32 → 22 °C)
University of Lleida	T-History instrument not yet available		

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Octadecane: comparison T-History ↔ DSC

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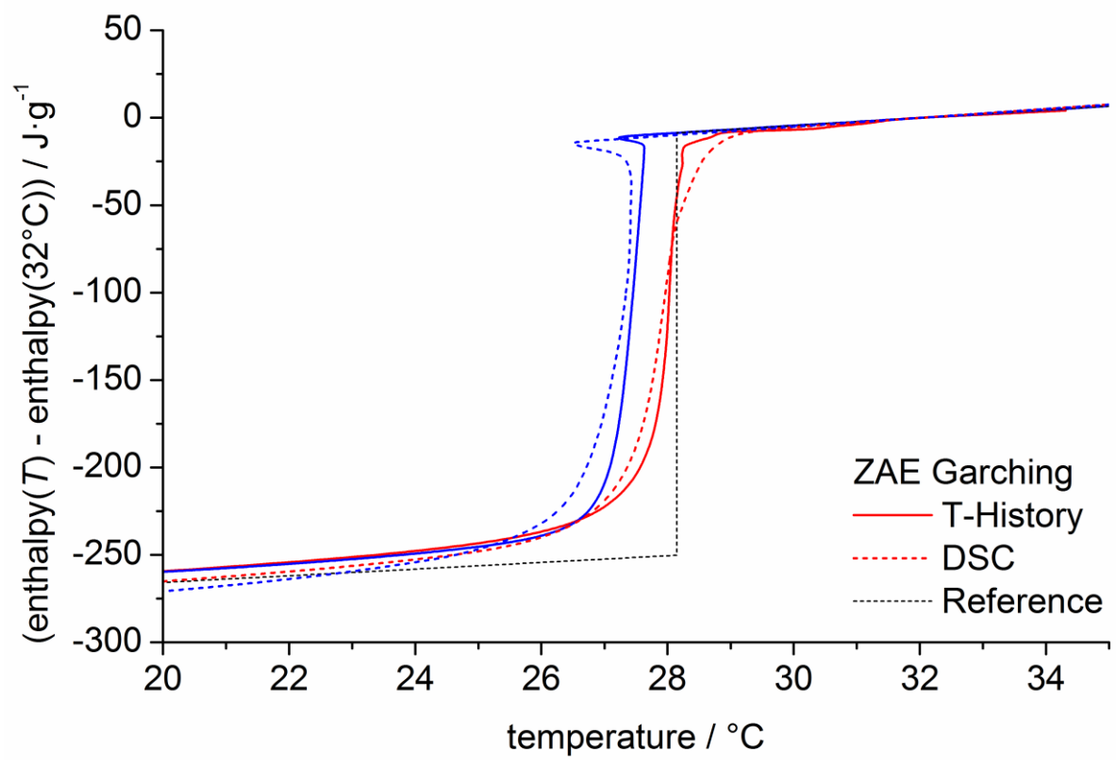

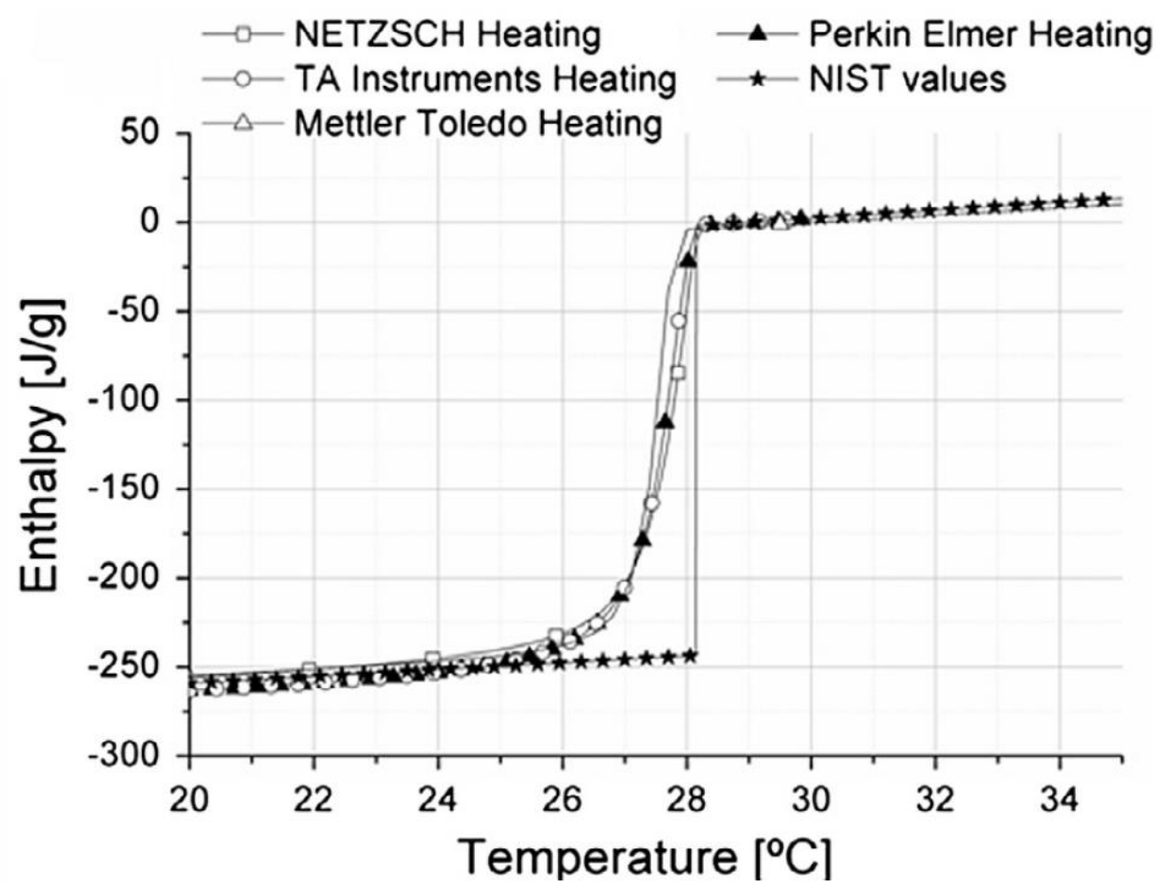

[Lázaro et al. 2013]

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Questionary for RRT contributors to inquire and compare main parts of each T-History instrument

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Description of T-History instrument (components, sample handling, temperature control etc.)						
Reference	Material					
	Solid?		Powder?		Liquid?	
	Mass (g)					
	$c_p(T)$ (J $g^{-1}K^{-1}$)					
Sample / reference container	Material					
	Dimensions (mm)					
	$c_p(T)$ (J $g^{-1}K^{-1}$)					
	Single use?		Multi use?			
Sample / reference insulation *	Available?					
	$c_p(T)$					
	Dimensions (mm)					
Biot number						

* maybe not applicable to all T-History calorimeters

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Questionary for RRT contributors to inquire and compare main parts of each T-History instrument

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Ambience	Box dimensions (mm)	
	Heat transfer medium	
	Accessible temperature range (°C)	
	Switching times (min) *	
	Isothermality (°C)	
Temperature sensors	Type	
	Dimensions (mm)	
	Accuracy (°C)	
	Position	
Evaluation	Basic assumptions	
	Basic equations	
	Software	
Calibration	Measured calibration substances (reference values used)	
	Corrections obtained via calibration	Temperature correction
		Enthalpy correction

* maybe not applicable to all T-History calorimeters

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RRT procedure

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Proposal for round 2

<u>Sample</u>	
Mass:	~ 10 g *
Preparation:	1. Melt the material as received from Stefan in an oven at 50 °C
	2. Mix the liquid material (shaking)
	3. Put the liquid material in the sample container
<u>Temperature program</u>	
Heating	Increase ambient temperature from 8 °C to 38 °C *
Cooling	Decrease ambient temperature from 47 °C to 17 °C *
# of cycles	3 per sample
<u>Number of samples</u>	3

* maybe not applicable to all T-History calorimeters

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RRT procedure

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Proposal for round 2

Data evaluation

Should be done according to the participants own evaluation procedure.
Zero point for enthalpy curves: $h(32\ °C) = 0$

Export data as Excel or Origin file in a table as follows:

t / s	T_{sample} / °C	$T_{reference}$ / °C	$T_{ambience}$ / °C	$(h(T) - h(32\ °C))$ / $J \cdot g^{-1}$
…	…	…	…	…
…	…	…	…	…
…	…	…	..	…

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Principles of T-History measurements

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Combined T-History and DSC measurements

25.09.2014 christoph.rathgeber@zae-bayern.de

Application-oriented characterisation of PCM

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Combined DSC and T-History measurements:

- separation: intrinsic material properties ↔ sample properties
- improved estimation of the behaviour of bulk material in applications
- validation of measured enthalpy curves via two independent instruments

Recommendation for the measurement of enthalpy curves:

1. dynamic DSC measurement (medium scanning rate, e.g. 2 K/min)

   → classification of the phase change behaviour

2. a) material with little subcooling and a single transition: slow dynamic DSC measurement (e.g. 0.5 K/min) or DSC step measurement

   b) material with significant subcooling or multi-stage phase change transitions: slow dynamic DSC measurement (e.g. 0.5 K/min) + T-History measurement

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T-History + DSC → T4229 database (https://thermalmaterials.ise.fraunhofer.de/)

[Rathgeber et al. *Meas. Sci. Tech.* 2014, Rathgeber et al. *Appl. Energ.*]

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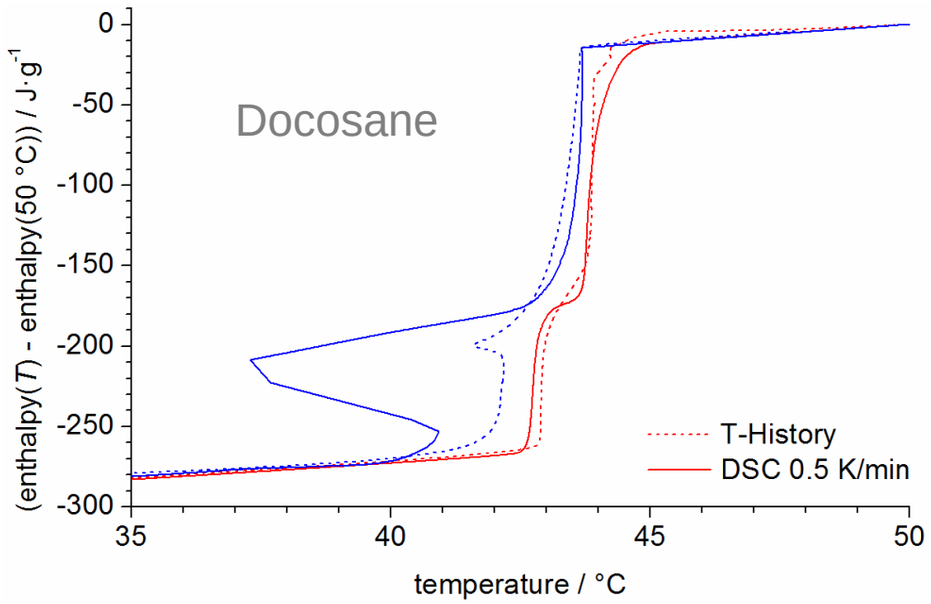

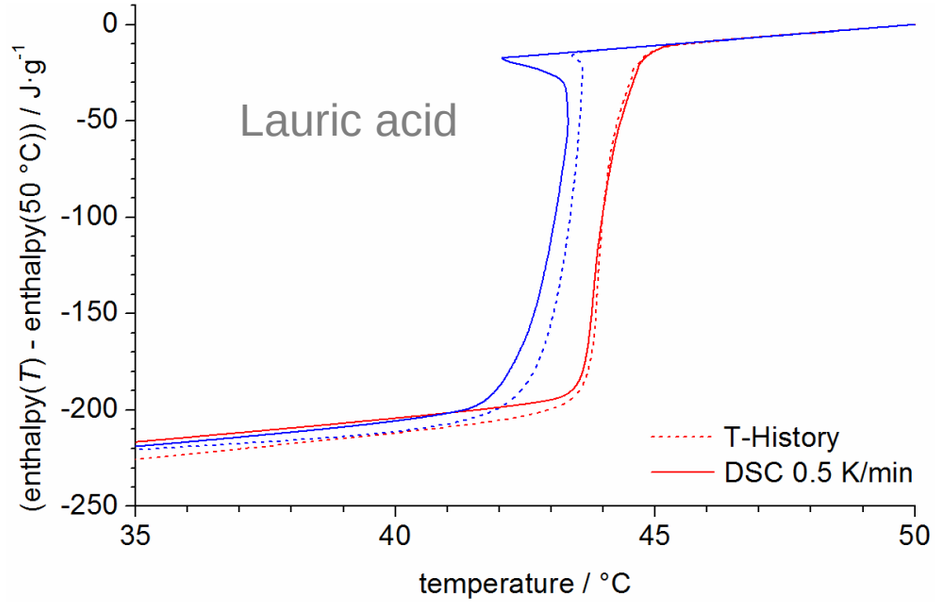

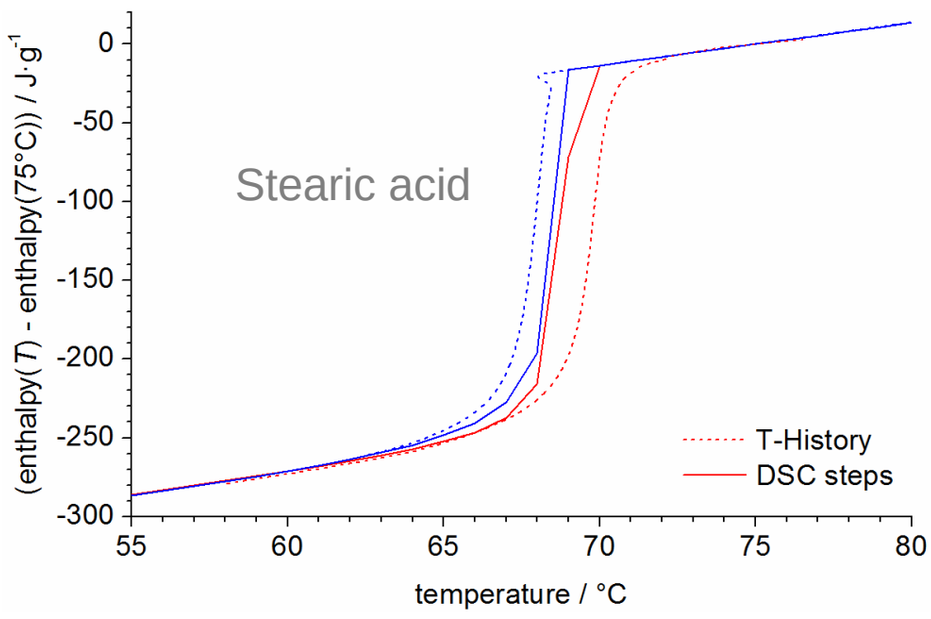

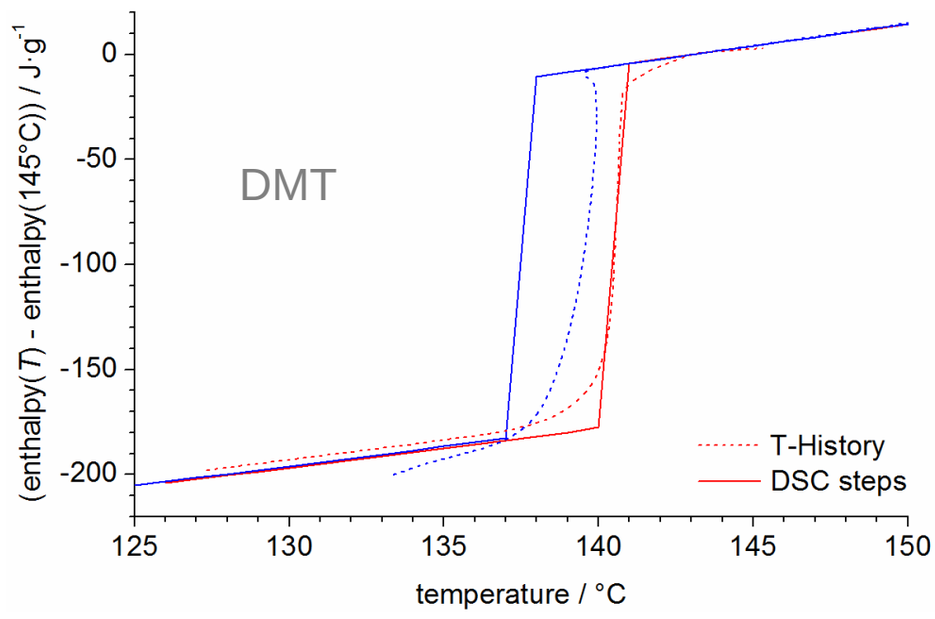

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[Rathgeber et al. *Meas. Sci. Tech.* 2014, Rathgeber et al. *Appl. Energ.*, Schmit et al. 2014]

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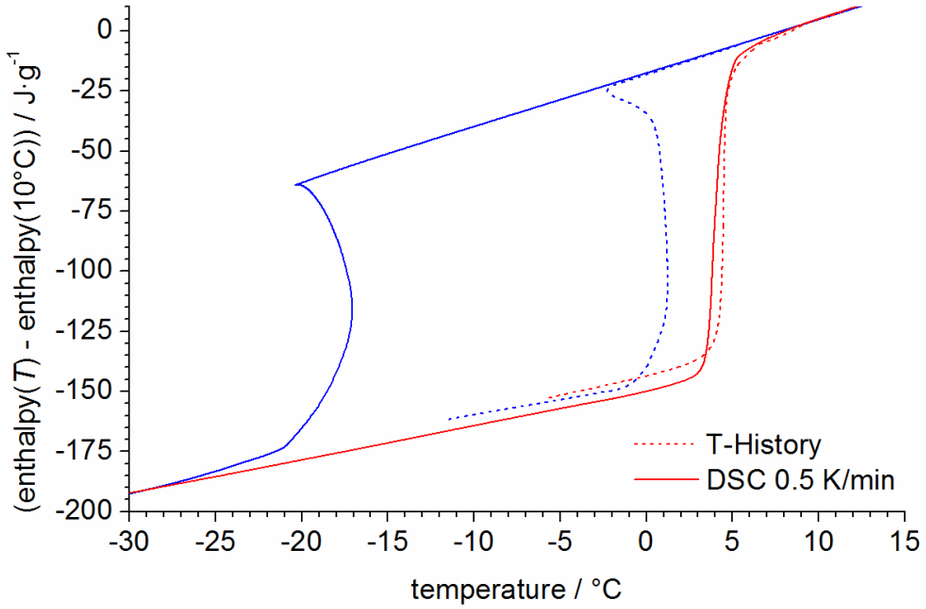
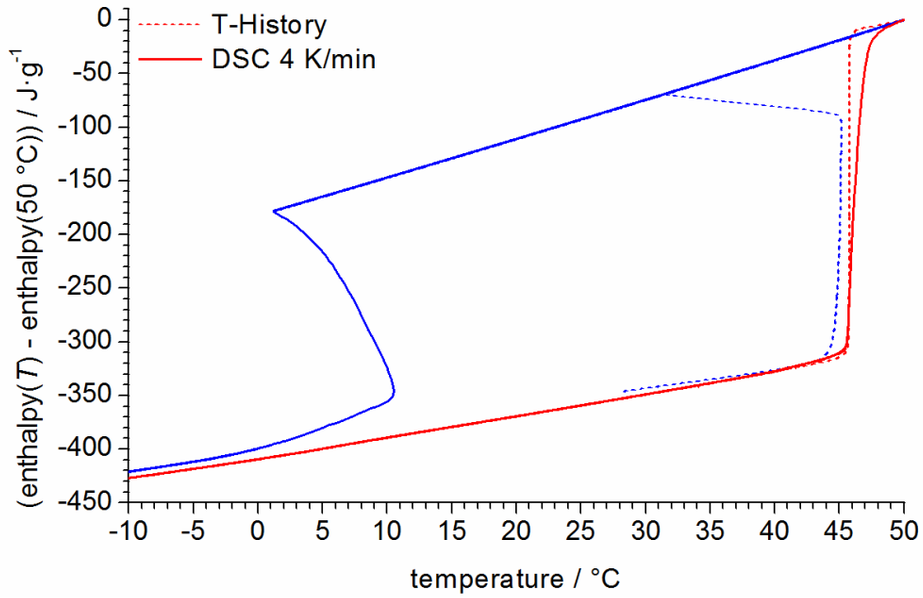
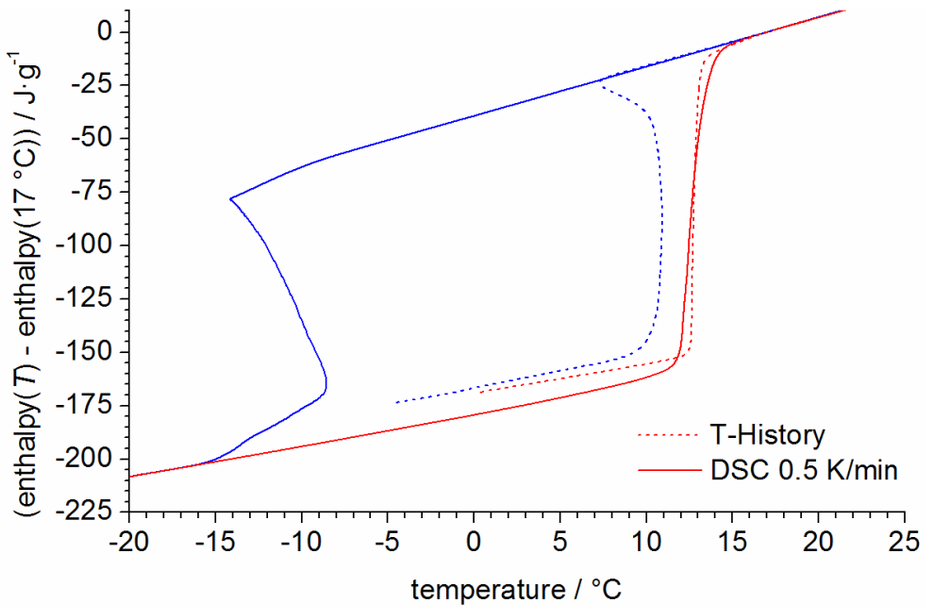
$Mn(NO_3)_2 \cdot 6H_2O + NH_4NO_3$ 73/27 mass%



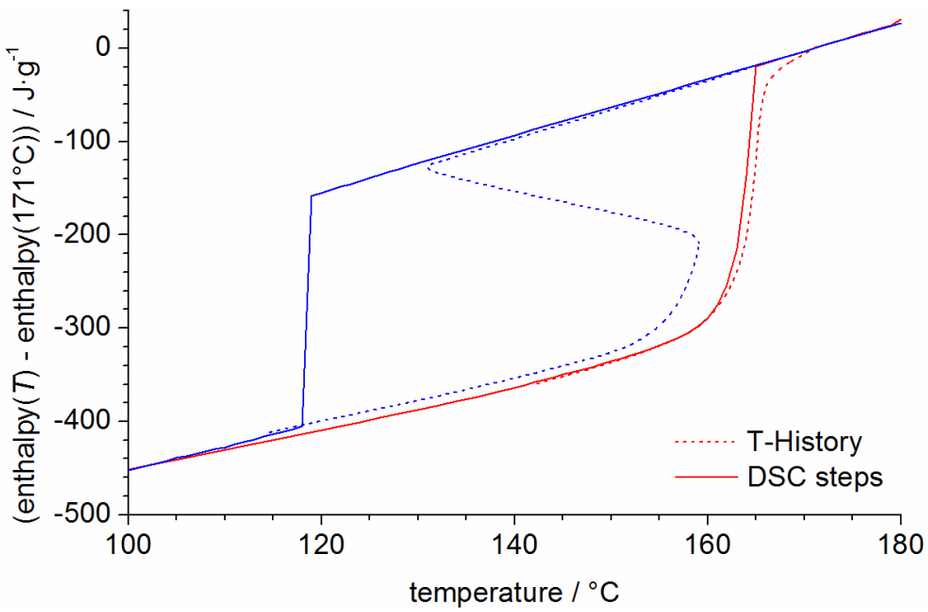
Pinacone hexahydrate



$Zn(NO_3)_2 \cdot 6H_2O + NH_4NO_3$ 75/25 mass%



D-mannitol



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T-History + DSC: $MgCl_2 \cdot 6H_2O$

[Rathgeber et al. *Thermochim. Acta*]

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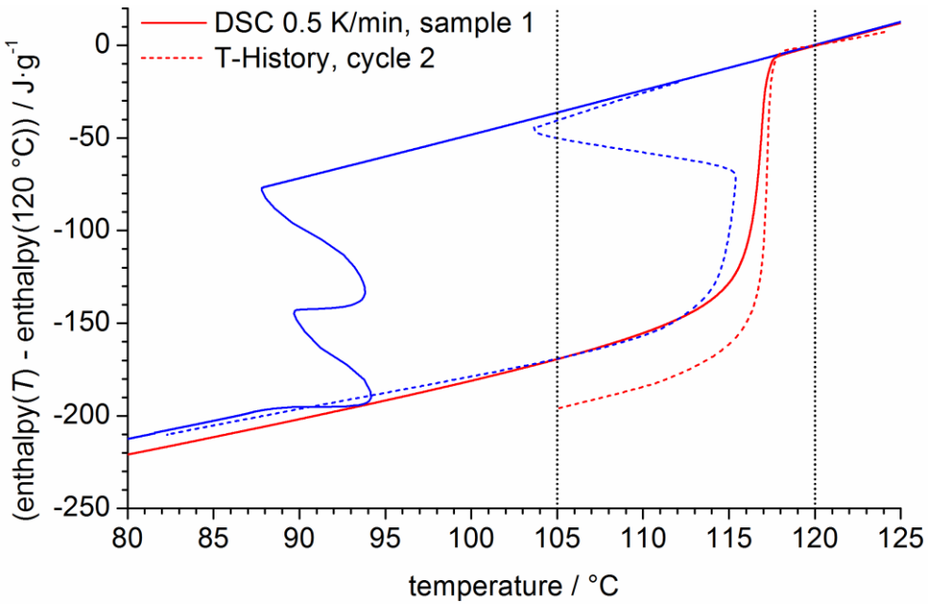
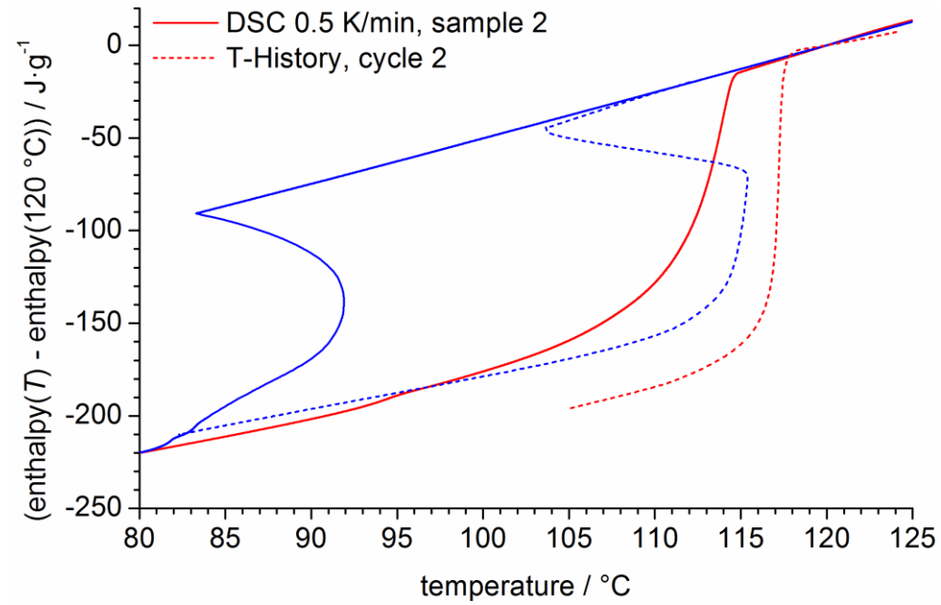
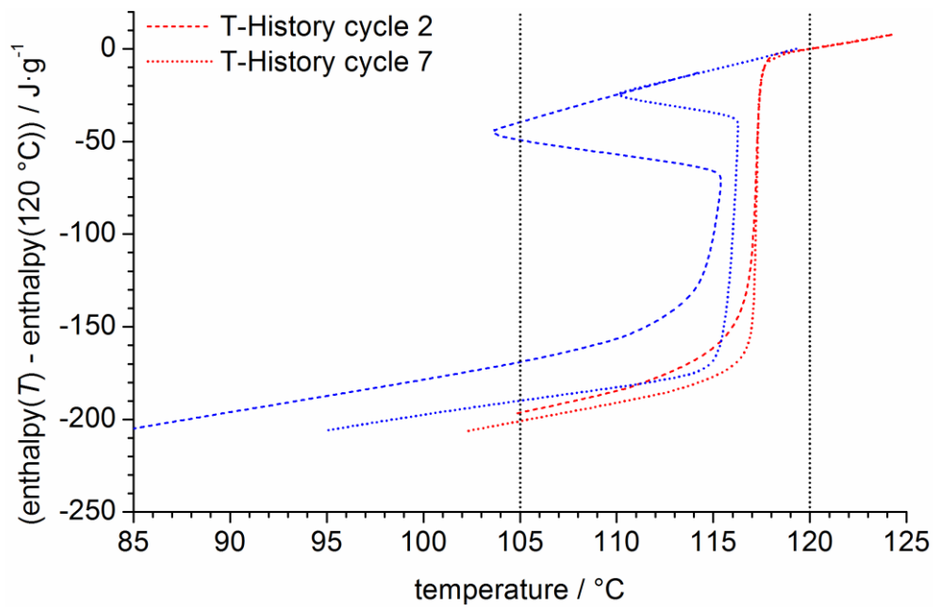
These figures are confidential!
(manuscript under review)







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Thank you for your attention!

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