

Enthalpy of Phase Change Materials as a Function of Temperature: Required Accuracy and Suitable Measurement Methods

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Abstract Phase change materials (PCMs) are thermal storage materials with a high storage density for small temperature range applications. In the design of latent heat storage systems, the enthalpy change of the PCM has to be known as a function of temperature with high precision. During dynamic measurements, the sample is not in thermal equilibrium, and therefore the measured value is not the equilibrium value. The influence of non-equilibrium on the measurement results can be quantified by doing measurements during heating and cooling with any measurement instrument. Measurements carried out by differential scanning calorimetry (DSC) and by the T-history method are presented and discussed. To characterize encapsulated PCM objects, measurements on the whole objects should be carried out. A measurement setup for this purpose is also presented. The obtained precision meets typical application requirements, and good agreement between results obtained with the different methods is demonstrated.

Keywords Differential scanning calorimetry · Phase change material · Salt hydrate · T-history method

1 Introduction

Phase change materials (PCMs) are thermal storage materials with a high storage density for small temperature range applications. In the design of latent heat storage systems, the enthalpy change of the PCM has to be known with high precision as a function of temperature.

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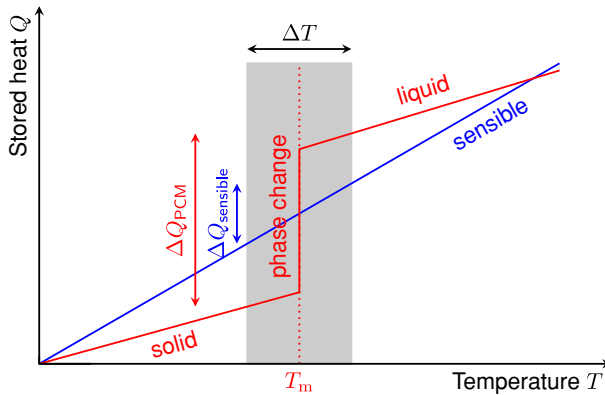


Fig. 1 Latent heat storage materials offer superior storage density ΔQ compared to sensible heat storage materials when used in small temperature intervals ΔT

In this paper, several problems that are typical for calorimetric measurements of PCMs are discussed. We compare different measurement methods and explain the observed differences in the results. Based on this, a recommendation on how to achieve and monitor suitable precision in a calorimetric measurement is given.

1.1 PCMs for Thermal Energy Storage

Thermal energy storage is a key technology in the efficient use of energy. The main applications are peak shifting, heat transport, and the management of fluctuating sources like renewable sources, waste heat, or natural cold [1,2]. PCMs offer a superior storage density compared to sensible heat storage materials when used in small temperature intervals around the melting temperature T_m . This is illustrated in Fig. 1.

An ideal material without phase change, i.e., a sensible heat storage material, heats up when heat is stored, and cools down when heat is released. Well-known examples of such materials for sensible heat storage are water or concrete. A material with a phase change does not change its temperature during the phase change but stores a large amount of energy. Only after the phase change is completed, the temperature starts to rise or fall. Due to this intrinsic buffer effect, latent heat storage is very interesting for applications where a temperature level shall be stabilized.

1.2 Goal of Calorimetry of PCMs

In order to be able to choose a good PCM, and successfully design a storage application, the properties of the material have to be known [3]. The most prominent property is the phase change temperature. The heat capacities c_p of the solid and liquid states are almost constant in small temperature ranges. The storage capacity of a PCM is then well defined via the four parameters c_p^{solid} , c_p^{liquid} , T_m , and the phase change enthalpy

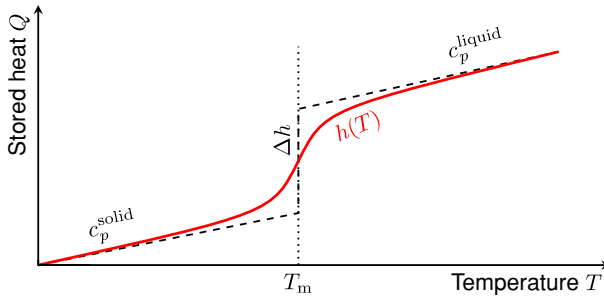


Fig. 2 The storage capacity $Q(T)$ of an ideal PCM (*dashed*) is characterized via four parameters, namely, c_p^{solid} , c_p^{liquid} , T_m , and Δh . Most real PCMs (*solid*) show a phase change region instead of a melting temperature, best represented by $h(T)$

Δh . However, many PCMs show a broadened melting range, i.e., the phase change enthalpy Δh is not attributed to a single temperature, but to a temperature range. Then, the shape of the enthalpy curve $h(T)$ describes the material with much better precision. This is illustrated in Fig. 2.

While in theory the goal of any measurement is to detect precise data, in practice every measurement is associated with some uncertainty. Also, higher precision in a thermodynamic measurement is often associated with longer measurement times and thus higher measurement costs. Therefore, a good measurement has to find a balance of tolerable uncertainty and reasonable costs and effort.

In order to define the tolerable uncertainty, the scope of the data to be acquired has to be known. If the data are used in the design of an application, the measurement data must be of sufficient accuracy to allow the design of an application that will satisfy its task.

Typical temperature ranges on PCM applications are in the order of ± 10 K around the phase change temperature of the PCM. An error in the overall phase change enthalpy in this temperature range is directly reflected in the storage capacity of the system. An error in the temperature slope of the enthalpy has more subtle consequences, which are illustrated in the following example. In order to assure sufficient loading and unloading power, a gradient of at least 1 K is assumed for the heat transfer. Then, the PCM is used in an interval of about 18 K. Assuming a phase change temperature in the middle of the operational temperature range, the available gradient for loading and unloading is 9 K each. In the case of an ideal PCM, the PCM is isothermal at T_m during most of the loading and unloading process. Then, if the measured melting temperature differs by 1 K from the real melting temperature, this would lead to an error of about 11 % in the power calculation. For real PCMs or different applications, the situation may be more or less severe, but in principle similar. Therefore, for most PCM applications, a reasonable design can be done if data uncertainty δ is in the range of $\delta \Delta h := \delta [h(T_{\text{max}}) - h(T_{\text{min}})] \leq \pm 10\%$ and $\delta T \leq \pm 1$ K.

A second important point is to study a possible influence of the sample size on its thermal behavior. Depending on the application, the amount of PCM used can vary from a few (milli)grams (e.g., cooling of electronic equipment) to many tons (e.g., stor-

age in a solar thermal power plant). Kinetic or statistic effects such as crystal growth, phase separation, and undercooling are dependent on the sample size and geometry. These effects should therefore be studied in samples of similar size as to be used in the application, as far as possible.

2 Determination of the Enthalpy as a Function of Temperature

In this section, we show with the help of experimental data and theoretical analysis why the use of standard DSC measurements is troublesome for PCM samples. Then, we show results of an alternative method for larger samples, the T-history method, that solves most of the problems. The sample material is a mixed linear alkane. We also introduce a simple setup to verify upscaling of sample mass and show results on a salt hydrate sample.

2.1 Differential Scanning Calorimetry (DSC)

The standard measurement method for thermal analysis is differential scanning calorimetry (DSC) [4]. Typical sample volumes are in the range of 10 μL to 50 μL . The sample and a reference are simultaneously subjected to a temperature program, a so-called *ramp*. The signal is proportional to the temperature difference between the sample and the reference. Dynamic mode and isothermal step mode are different operation modes, which are distinct in the shape of the ramp.

2.1.1 Dynamic Mode

The most common operating mode for DSC is a ramp with a constant heating rate [5]. Typical heating or cooling rates for the measurement of specific heat are 2 $\text{K} \cdot \text{min}^{-1}$ to 10 $\text{K} \cdot \text{min}^{-1}$. A typical signal and temperature plot during a heating ramp is shown in Fig. 3a.

Using three measurements with the same ramp but different crucible content (empty, standard substance, sample substance), the specific heat of the sample as a function of temperature $c_p(T)$ is then given by

$$c_{p,\text{sample}}(T) = c_{p,\text{standard}}(T) \cdot \left[\frac{U_{\text{sample}} - U_{\text{empty}}}{U_{\text{standard}} - U_{\text{empty}}} \right] (T) \cdot \frac{m_{\text{sample}}}{m_{\text{standard}}} \quad (1)$$

where m denote the masses of sample and standard material, and U denote the voltage signals of empty, standard and sample run.¹ This procedure results in a curve as shown in Fig. 3b. From those data, the storage capacity, Δh , can be derived by integration over T .

Modern DSC instruments assure high repeatability of a measurement. The calibration of the DSC for heating and cooling is well described by Gmelin and Sarge

¹ Alternatively, the empty line U_{empty} can be constructed using isothermal segments before and after the dynamic segments as suggested in ASTM E 1269 [6].

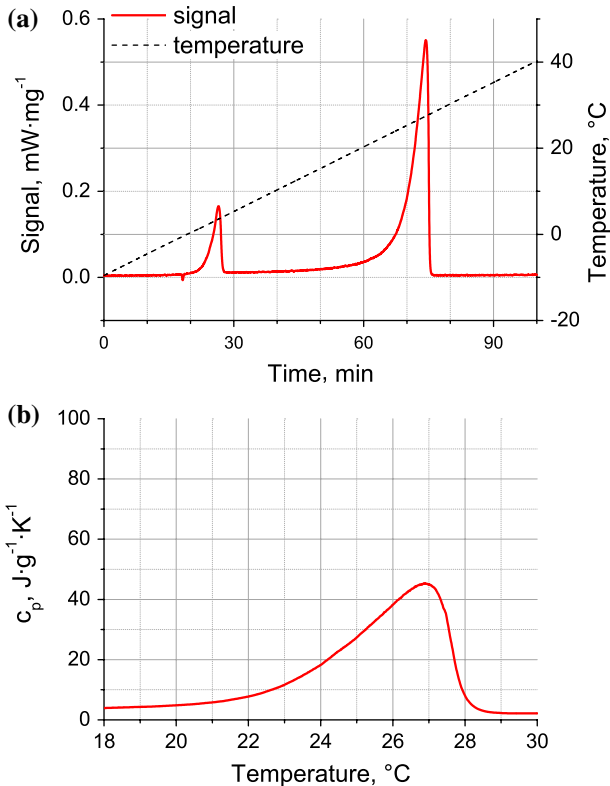


Fig. 3 Typical measurement ramp and signal of a dynamic DSC heating measurement, and the evaluated signal of the main peak

[7] and Sarge et al. [8]. The accuracy of DSC measurements of standard materials is discussed in detail by Richardson [5] and Rudtsch [9]. The precision of the temperature sensors is typically < 0.1 K, and the heat is determined with an uncertainty of typically $< 5\%$.

Repeating the measurement with different heating rates and different sample masses gives results as shown in Fig. 4. The results of the individual measurements differ considerably. While the result for one measurement configuration is highly reproducible, a change in the measurement configuration changes also the result. The integral of the curves and the onset of the peaks are found to have little dependence on the heating rate or sample mass. Therefore, for pure materials, the onset of the peak is commonly used to mark the melting temperature, and the integral of the peak denotes the melting enthalpy. However, in the context of PCM, this is not a useful approach, as the information needed is the slope of the curve $h(T)$ and not just the two punctiform values T_m and Δh . Obviously, the same sample should be characterized by one curve only. The question is, which curve represents best the properties of the sample? And, how large is the deviation from the real properties?

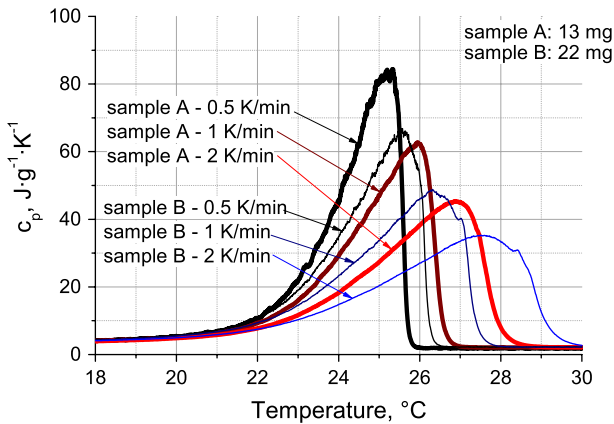


Fig. 4 Results of a dynamic DSC measurement on one substance vary when using different heating rates or sample masses

2.1.2 Source of Uncertainty in Dynamic Mode DSC

Focusing on the end of the peaks shown in Fig. 4, a clear trend can be observed. The peak is shifted toward higher temperatures as the mass or the heating rate increases. This can be explained by an increasing thermal gradient in the sample. When an initially isothermal sample is heated in a DSC, heat enters from the outside of the crucible and is absorbed by the sample. During a heating segment as shown in Fig. 3a, there is constantly heat supplied to the sample, and an internal gradient is created. This gradient increases with increasing heating rate or sample mass. The sample temperature is attributed to the sensor placed on the sample surface,² that means, the sample temperature is overestimated during a heating segment. As a consequence, the signal of the sample being attributed to too high temperatures, the shift of the melting peak increases with increasing gradient, i.e., heating rate or sample mass. This general effect is particularly strong for PCMs.

PCMs are chosen as materials having a high thermal storage capacity, that is, they absorb a lot of heat per volume. Also, most PCMs have a low thermal conductivity λ . As a combined effect, the internal temperature gradient in PCMs is large compared to most other materials, including calibration standards [10].

Additionally, the large gradient is formed at temperatures close to the phase change temperature, where a high precision in the shape of the curve is desired and the slope of the $c_p(T)$ curve is highly nonlinear. For pure materials or calibration standards, the distortion of the signal can be corrected by calculations, but this is impossible for samples with an unknown thermal conductivity λ and an unknown shape of the phase change peak in c_p .

The consequences of the thermal gradient inside the sample can be experimentally quantified by reversing the ramp, i.e., by comparing heating and cooling measurements.

² In fact, the sensor is situated on the outer surface of the sample crucible, but the influence of the crucible is canceled out by measuring the differences between the sample and the empty reference crucible.

The gradient is reversed in a cooling ramp, i.e., the sample temperature is underestimated, and the true sample temperature is thus enclosed by the heating and cooling measurement data. If the difference between the results of heating and cooling is within the desired uncertainty range, then the gradient is small enough. If it is larger, a variation of the heating and respectively cooling rate can show whether the results are dependent on the measurement variables. If they are not, the difference can be considered a property of the material, i.e., a sort of thermal hysteresis. Using this approach, a suitable heating rate for dynamic DSC measurements can be found. However, for very small heating rates, the signal-to-noise ratio and the error in Δh increase [11]. This limits the use of the dynamic mode for calorimetry of PCMs.

2.1.3 Isothermal Step Mode

Another method to obtain data of the heat storage capacity is using a DSC in the isothermal step mode. In this case, the furnace is heated stepwise in given temperature intervals. The sample is following the steps with some time delay, and a signal is detected. When the signal goes back to zero, the sample and reference are isothermal, and there is no gradient in the sample. This is when the next step can follow. The area below a peak is proportional to the heat absorbed by the sample in the relevant step. For a pure material, this is schematically shown by Richardson [5]. For a PCM, an example of the ramp and signal is given in Fig. 5.

The absorbed heat is determined stepwise and attributed to the temperature interval of the respective step of the ramp. The heat storage capacity or enthalpy curve $h(T)$ is then obtained by adding the values of the steps. The temperature resolution of the acquired data is equal to the step size. The big advantage compared to the dynamic mode is that the uncertainty in the temperature is precisely known, as it is confined to the step size. A reduction of the step size leads to better temperature resolution. Again, for very small steps the signal will vanish and the precision in the measurement will be lost.

Results under varying conditions agree very well as shown in Fig. 6.

Still, for many PCMs, DSC measurements are unsuitable. If the PCM shows undercooling, i.e., the solidification starts at a temperature below the melting temperature, there are two problems: first, strong undercooling in a DSC deforms the cooling curve, making it difficult to quantify internal gradients by comparing heating and cooling curves. Second, undercooling is often stronger in small samples than in large samples, so the maximum undercooling determined in a DSC is not representative for the PCM in an application. But even for PCMs with negligible undercooling, one fundamental problem remains. Many PCMs contain nucleating agents, heat transfer enhancing additives, gelling materials, etc. Correct sampling of such materials in crucibles of typically 20 μL is problematic to impossible, because it cannot be assumed that the sample composition is equal to that of the material. Again, the solution to this problem is to use large samples.

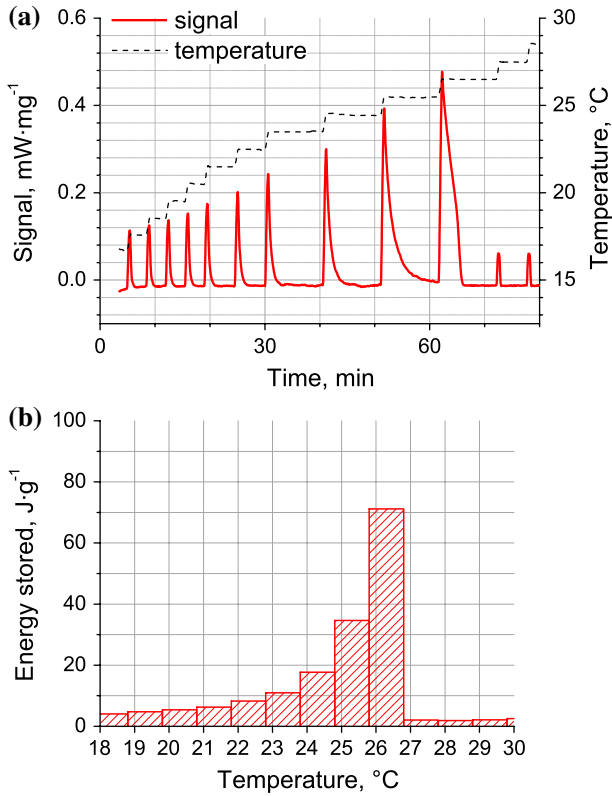


Fig. 5 Typical measurement ramp and signal of a DSC steps measurement, and the evaluated signal

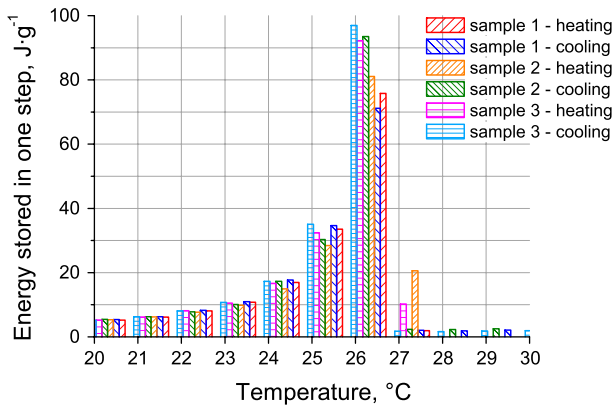


Fig. 6 Results of several DSC steps measurements. The sample mass and the steps program were varied. There are only minor variations in the results

2.2 T-history Method

The T-history method as proposed by Zhang et al. [12] and improved by Marín et al. [13], Hiebler [14], and Günther [15] is a method for the determination of $h(T)$ for larger samples. T-history installations are not available commercially, but can be assembled using standard laboratory components. The precision of a T-history installation can be verified using the methodology presented by Lázaro et al. [16]. The sample size in the installation used for this study is about 20 mL, i.e., increased by about a factor of 1,000 compared to the DSC sample.

The setup of our T-history installation and a typical measurement recording are shown in Fig. 7.

The sample and a reference material are simultaneously subjected to a sudden change in temperature in a symmetric setup. From the response of the reference, the heat flow as a function of crucible temperature is determined. Then, the heat flow to the sample is calculated and the enthalpy curve is determined. The measurement parameters are the temperature levels of heating and cooling. In order to assure a small gradient in the sample, temperature levels close to the melting temperature are chosen. Again, a variation of the temperature levels shows the impact of the gradient on the resulting data, and is used to find the optimal measurement parameters.

2.2.1 Comparison of Results Obtained with the Three Presented Methods

The results of dynamic DSC, step mode DSC and T-history measurements are shown in Fig. 8.

With the step method, the uncertainty in temperature has been reduced from 2 K, obtained by the slowest possible dynamic measurement, to about 1 K. The step method therefore fulfills the requirement for a measurement for a typical PCM application. The T-history method offers similar precision, but allows the investigation of large samples. This is crucial for heterogeneous materials such as compound PCMs or salt hydrates.

As to the measurement and evaluation time, the T-history and DSC step mode methods require a similar effort. As shown in Fig. 7, the measurement of one

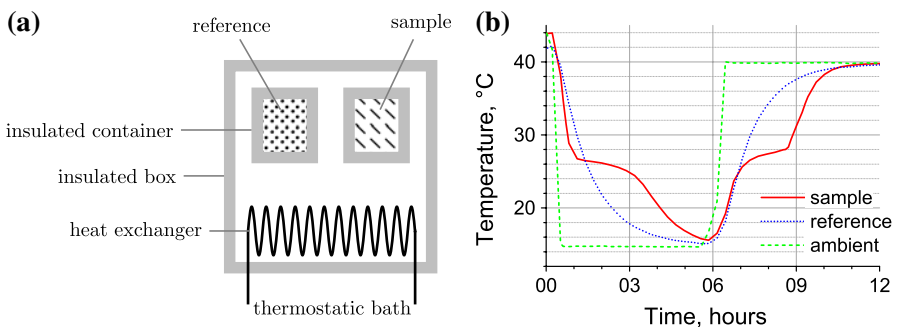


Fig. 7 Sketch of the T-history installation and typical measurement data during cooling and heating

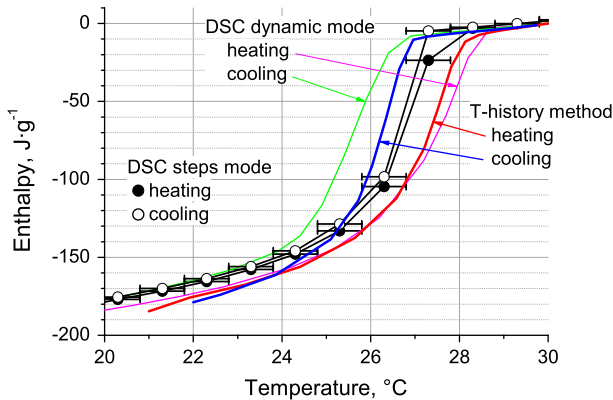


Fig. 8 Comparison of heating and cooling enthalpy curves of one sample material with different methods using optimized measurement parameters

heating–cooling cycle is carried out within a day. The measurement time for a typical DSC steps measurement in a range of 20 K with 15 min per step, step size of 1 K, is about 10 h for heating and cooling. With respect to the costs of other alternatives such as adiabatic calorimetry or Calvet DSC, both the DSC step and T-history methods are associated with a considerably lower effort.

2.3 Calorimetry of PCM Objects

In systems where the heat transport medium is air, heat transfer between storage and transport media has a strong impact on the system performance. Reliable data solely based on mathematical calculations are hard to obtain, so another experimental installation has been designed and set up. Figure 9 shows a sketch of the setup.

The central component of the installation is a test chamber, through which air of defined temperature and volume flow rate is blown. With the help of this installation, PCM components for air-based storages can be investigated concerning storage

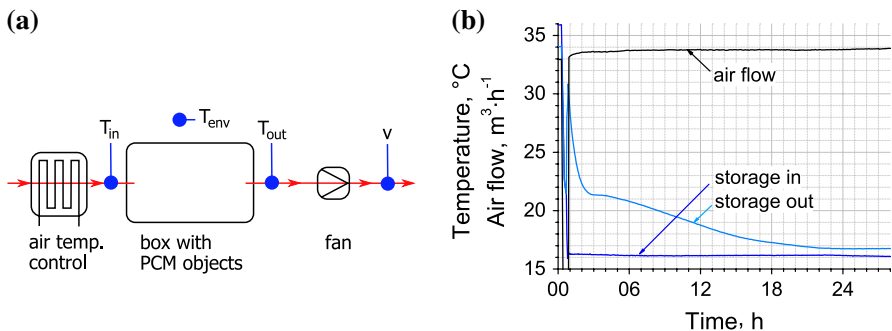


Fig. 9 Setup of the air flow method installation and typical measurement data

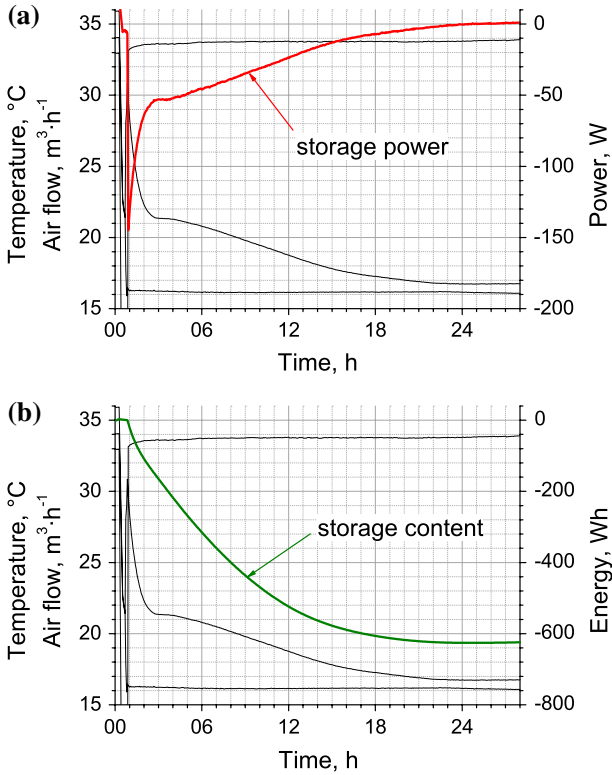


Fig. 10 Power and heat content evaluation of the data presented in Fig. 9. Here, the PCM is intended for a cooling application. Therefore, the storage is charged during a cooling experiment and the storage power is negative

capacity and power performance. Possible effects of undercooling on power output can be observed directly.

However, this can only be a verification of overall storage capacity, because a loss in temperature precision has to be expected as a trade-off of the increased sample size at a realistic measurement time. A typical data recording of a cooling run is shown in Fig. 9.

Using the measured temperatures at the storage inlet and outlet, combined with the measured air flow, the thermal power of the storage content is derived; see Fig. 10. Integrating this value, the storage content is determined, as shown in Fig. 10. The storage content divided by the sample mass is then a measure of the sample enthalpy in the investigated temperature range. The temperature resolution is given by the starting and end temperatures of the experiment. In Fig. 11, the storage content results of a measurement with the air flow chamber are compared to material data as acquired with the T-history method.

The mass of the sample was increased from about 15 g, in the T-history measurement, to about 500 g in the air flow chamber. As a first check, the total heat content during cooling and heating air flow experiments are compared. Here, it is $190 \text{ J} \cdot \text{g}^{-1}$

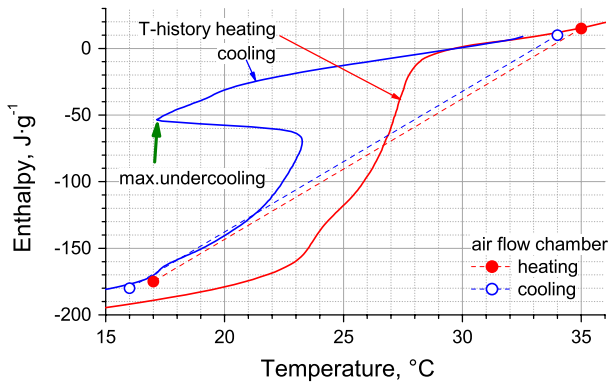


Fig. 11 Results of the air flow chamber compared to a T-history measurement. Maximum undercooling to 17 °C was observed in the T-history measurement. The high resolution in temperature of the calorimeter cannot be obtained with the air flow apparatus. However, the overall heat content as determined by the T-history method is successfully verified for real size samples

for heating and cooling each, in the temperature range 17 °C to 35 °C for heating and 34 °C to 16 °C for cooling, i.e., the same content is measured, as expected. The comparison with the results from the T-history measurement shows very good agreement of the overall storage capacity, too. In the T-history measurements, an undercooling to about 17 °C was observed. In the air flow measurements, the undercooling is not seen due to the averaged temperature at the air outlet sensor. As judged from the power plot in Fig. 10, undercooling in the real size samples was not observed to have a significant impact on the performance of the storage.

3 Conclusions

For typical PCM applications, the shape of $h(T)$ has to be known with a temperature uncertainty $\delta T < 1$ K. We showed that the precision of a measurement can be quantified by comparing results from heating and cooling measurements.

Measurements using differential scanning calorimetry in the dynamic mode are not in general suitable to determine $h(T)$ of PCMs. This is due to the characteristic properties of phase change materials. However, using the same instrument, an alternative measurement mode, the isothermal step mode, offers sufficient precision. Due to its small sample size, DSC in general is not suitable for heterogeneous materials. For these PCMs, the T-history method can be used to determine $h(T)$ data with sufficient precision. Additionally, we present an air flow chamber for calorimetric measurements of PCM objects, and compare results to T-history measurements. Good agreement between results obtained with the different methods used in our study is demonstrated.

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