Potential new reference materials for caloric measurements on PCM

Harald Mehling [1], Jan Leys [2], Christ Glorieux [2], Jan Thoen [2]

[1] Consultant, Weingartenstr. 37, 97072 Würzburg, harald.mehling@gmail.com

[2] Soft Matter and Biophysics, Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D box 2416, 3001 Leuven, Belgium

Introduction: Materials that are able to store and release a considerable amount of heat while undergoing a phase change are called Phase Change Material (PCM). Most PCM used undergo a phase change between solid and liquid, some between two solid phases. The ability to store and release a considerable amount of heat, while undergoing a phase change at small temperature changes, results in two main fields of use (Mehling et al. 2008): heat storage (or called thermal energy storage) with high storage density (per unit mass or volume) in a narrow temperature interval, and passive temperature stabilization (temperature control). PCM are used today mainly within the temperature range from about -40°C to 80°C, e.g. for heating and cooling in buildings or transport of temperature sensitive goods, but interest ranges from about -70°C, e.g. for storage or transport of vaccines, to about 400°C, e.g. for storage of process heat. For the determination of the heat stored as a function of temperature by calorimetric measurements a variety of methods and instruments exist, ranging from DSC with sample volume of some 20µl to some recently developed methods for up to 100 ml or more. Reference materials for temperature and amounts of heat are needed for calibration, testing, as well as relative / comparative measurements. Reference materials for temperature refer to a phase change temperature T_{pc}, for heat to a phase change enthalpy $\Delta_{pc}h$ or heat capacity c_p of solids or liquids. Reference materials being certified, meaning established as standard, are for T_{pc} and $\Delta_{pc}h$ e.g. the metals mercury, gallium, and indium, as well as other materials like cyclohexane, biphenyl, and naphthalene. Water is only certified for T_{pc}. This choice is insufficient for the required temperature range, and also for large samples size. Large amounts of mercury are dangerous; the other materials are expensive in the required high purity. For convenience, often materials where data are found in literature are used, for example octadecane. A review for octadecane (Faden et al. 2019) however shows that literature data range for the melting temperature from 298.5 K to 303.7 K, and for the melting enthalpy even from about 200 J/g to 260 J/g. This is insufficient, and thus the use of just some material is highly risky and not recommended.

Analysis: The common way of establishing reference materials is to find generally suitable materials, and then measure the desired property with high accuracy on very pure samples. The high purity is needed to assure that new samples are available of the material with the same composition, anywhere and anytime. But high purity leads to high cost for large samples. Therefore, a thorough analysis of what the requirements on reference materials are exactly, and what this means for PCM, is the start. What are the requirements for reference materials in general? Reference materials are materials with well known properties and well reproducible. In detail, this can be separated into three main topics. First, the selection of a material. For the measurement of the property by a wide range of instruments, parameters etc., the material must behave repeatable with regard to the property, meaning give the same result at same conditions, as well as reproducible, meaning at somewhat different conditions. E.g. the material must allow taking representative samples for a range of sample sizes. For practical reasons, a material should also not be hazardous or corrosive. And of course, it must also be available at the required composition, e.g. purity, at acceptable price. Second, the measurement of the property. The property of the material must have been measured by experts in the field, with highly accurate measurements, and a property value or value function accepted that includes the uncertainty. The uncertainty of a reference material must be significantly lower than the uncertainty needed in common measurements to be useful for calibration etc. It is important to test specifically reproducibility; e.g. regarding small variation in composition, large samples of high purity materials can have a high price.

Third, the presentation / communication of the property data. The presented / communicated property data must include the specification of the material (composition, preparation…), the value or value function of the property including uncertainty, and maybe also the measurement method used and a reference where further information is found. Some of these requirements on reference materials are closely related to the variety of methods and instruments they are meant to be used for. Therefore, requirements on reference materials for caloric measurements on PCM are specific. What are they? Regarding the selection of a material, specific requirements exist regarding that the material must be available in the required composition. Because of the large sample size of up to100 ml, sometimes even more, it is critical to know if a purity of let's say 98% or 99%, strongly related to the cost, is sufficient, or if the property value used (c_p, T_{pc}, or $\Delta_{pc}h$) changes. Because of the sample size, and the construction of the various instruments, a reference material should also have low vapor pressure e.g. to prevent the hazard of combustible vapors in large amounts. A reference material should also have a similar property value as the samples to be measured. For PCM this means $\Delta_{pc}h$ should be higher than 150 J/g or 150 J/ml, and T_{pc} in the range of interest. The thermal conductivity can be low; common liquid PCM have below 1 W/mK. Regarding the measurement of the property, for amounts of heat a measurement should have an uncertainty of ≤5%. The uncertainty of a reference material must be significantly lower, e.g. 3%; this could comprise a contribution of 1% from the sample (material) e.g. by its composition (e.g. purity), 2% from the measurement of the property, and 0% from the presentation / communication of the property data. For temperature, a measurement should have an uncertainty of ≤0.5°C. Assuming an uncertainty of 0.3°C at most for a reference material, this could e.g. comprise a contribution of 0.2 °C from the sample (material), 0.1°C from the measurement of the property, and 0.0°C from the presentation / communication of the property data. Regarding the presentation / communication of the property data, specific to PCM is how values of T_{pc} and $\Delta_{pc}h$ were read from the measured $c_p(T)$ or h(T) curve, meaning what given data refer to exactly. Different methods exist, e.g. for the phase change temperature the onset, peak, as well as offset temperature, and the different ways of data reading can lead to significantly different property values.

Results: Alkanes and water were investigated, by own measurements and also using literature data. The investigation shows that for calorimetric measurements on PCM, taking into account the specific requirements and the calorimetric methods used, water can be used as reference material also for $\Delta_{pc}h$. The sufficient purity is easily available, values from highly accurate measurements are available, and due to the sharp phase change at 0°C what the value refers to his well-defined. From the alkanes, dodecane C12, tetradecane C14, hexadecane C16, and octadecane C18 are suitable, covering the range from -10°C to 28°C. They have a single phase transition, and are available in sufficient purity, e.g. 98% or 99%, for a reasonable price. However, they do not have sharp phase change temperatures such that what values refer to is critical. And literature values with high accuracy are still rare for most of them. At higher temperatures, price and phase transition behavior are a problem. More details are discussed in Mehling et al. 2021, including also options for reference materials for c_p.

References

[Faden et al. 2019] M. Faden, S. Höhlein, J. Wanner, A. König-Haagen and D. Brüggemann: Review of Thermophysical Property Data of Octadecane for Phase-Change Studies. Materials, 12, 2974 (2019)

[Mehling et al. 2008] H. Mehling, L.F. Cabeza: Heat and cold storage with PCM. Springer, 2008, ISBN 978-3-540-68556-2

[Mehling et al. 2021] H. Mehling, J. Leys, C. Glorieux, J. Thoen: Potential new reference materials for caloric measurements on PCM. SN Applied Sciences (2021) 3:202, https://doi.org/10.1007/s42452-020-03929-y (open access)