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A sample-saving method for heat capacity measurements on powders using relaxation calorimetry

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ABSTRACT

An experimental method is described for determining the low-temperature heat capacity (C_p) of mg-sized powder samples using the Quantum Design “Physical Properties Measurement System” (PPMS). The powder is contained in an Al pan as an ~ 1 mm thick compressed layer. The sample is not mixed with Apiezon N grease, as compared to other methods. Thus, it is not contaminated and can be used for further study. This is necessary for samples that are only available in tiny amounts. To demonstrate the method various samples, all insulating in nature, were studied including benzoic acid, sapphire and different silicate minerals. The measurements show that the method has an accuracy in C_p to better than 1% at T above 30–50 K and ± 3 –5% up to $\pm 10\%$ below. The experimental procedure is based on three independent PPMS and three independent differential scanning calorimetry (DSC) measurements. The DSC C_p data are used to slightly adjust the PPMS C_p data by a factor $\left(C_p^{\text{DSC}}/C_p^{\text{PPMS}}\right)^{\text{at } 298 \text{ K}}$. This is done because heat capacities measured with a DSC device are more accurate around ambient T ($\leq 0.6\%$) than PPMS values and is possible because the deviation of PPMS heat capacities from reference values is nearly constant between about 50 K and 300 K. The resulting standard entropies agree with published reference values within 0.21% for the silicates, by 0.34% for corundum, and by 0.9% for powdered benzoic acid. The method thus allows entropy determinations on powders with an accuracy of better than 1%. The advantage of our method compared to other experimental techniques is that the sample powder is not contaminated with grease and that heat capacity values show less scatter at high temperatures.

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1. Introduction

A fundamental property of any substance is its heat capacity (C_p) and its measurement is required for various investigations in physics, chemistry, material research and Earth sciences. Dating back to the early 1900s, the standard and most accurate method for measuring low-temperature heat capacities is low-temperature adiabatic calorimetry (low-TAC) [1]. This technique has, however, several experimental disadvantages, namely: (i) it requires large sample masses at least on the order of several grams for measurement, (ii) it is time-consuming and the measurements are rather tedious and (iii) it requires complicated instrumentation. As a result, relatively few such calorimeters have been constructed and operated world-wide.

As reviewed by Stewart [2], new techniques and devices for small sample calorimetry (in the mg range) were developed in the 1970s. Based on this and later work [3] Quantum Design constructed a commercial relaxation calorimeter, implemented as the heat capacity option of the Physical Properties Measurement Sys-

tem (PPMS) [4]. Technical details of the instrument, as well its measuring procedures and performance, have been described [5,6].

The best accuracy and precision with the PPMS have been obtained for measurements using flat plate-like single crystals mounted directly onto the calorimeters' platform with a film of Apiezon N grease providing thermal contact. Experimental accuracy in this case can be better than 1% at $100 \text{ K} < T < 300 \text{ K}$, but it decreases at lower temperatures [5–7]. If the contact surface of the sample to the platform is polished, sample coupling, a measure of the quality of the thermal contact between sample and calorimeter platform, can be improved further [8,9].

In terms of measuring powdered samples with the PPMS, several preparation techniques, depending on the physical nature of the powder (i.e. insulating versus conducting, compressibility behavior, volatility, etc.), have been tested and applied. Experimental techniques that place the sample directly on the sample platform, as a paste mixed with grease [5], or as pressed pellet with grease on the bottom contact face [7], may be distinguished from those using a powder encapsulated in a container. The latter method has several variations including (i) a compressed pure powder sample in a sealed Al pan without internal grease [6], (ii) a powder mixed with grease and sealed in an Al pan [10], (iii) a powder held in a sapphire or epoxy container [11], and (iv) a mixture of powder

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and grease wrapped in a copper foil and together pressed to a pellet [12]. The accuracy of C_p data obtained from powder measurements using the PPMS is generally lower compared to single-crystal measurements. It is 1–2% for not too low temperatures [6,10,12] and critically depends on sample geometry and sample mass [7].

An important further criterion for choosing a specific measuring technique is given by the availability and the value of the sample in question. If it is available in only small amounts, mixing it with grease in order to improve the thermal conductivity might be undesirable, because the sample cannot be used for further experiments without considerable loss of material resulting from wet-chemical techniques applied to regain the pure substance. This is, for example, the case with Earth Science materials that can only be synthesized in small amounts at high pressures and temperatures in various devices like a piston-cylinder apparatus or a multi-anvil press.

The powder preparation technique used by Dachs and Bertoldi [6] is appropriate for such samples. Here, powders are compressed to an ~ 1 mm thick layer with no open space and without internal grease in Al pans of flat geometry, as used in differential scanning calorimetry (DSC – see details below). These workers concluded that C_p values so measured were systematically 1–2% too low at $T > \sim 50$ K [6]. This was determined by comparing PPMS C_p results on corundum (sapphire standard reference material 720) and the mineral sanidine to published C_p data obtained from low-TAC. Following this initial investigation, several studies using the same sample preparation technique were performed [8,13–35]. The accuracy of C_p values obtained with this method is generally in the $\pm 2\%$ range above ~ 50 K, as shown in Fig. 1 for the case where low-TAC data are available for comparison.

In order to improve the accuracy of our experimental calorimetric method further, we have developed a statistical technique based on multiple PPMS and DSC measurements. We demonstrate the methods suitability using benzoic acid, a poor thermal conductor, and various silicates relevant for the Earth sciences. With this new approach, we are able to determine heat capacity values that agree with reference values to within 1% at $T > 50$ K. We also derive standard entropy values accurate to better than 1%, even for insulating powders that were not mixed with grease.

2. Experimental

2.1. Samples and data sources

Samples used for this study, whose C_p s were already measured using the Dachs and Bertoldi PPMS technique for powders [6] and whose C_p s can be taken from published work, are the following: corundum (sapphire, Al_2O_3 , standard reference material 720) [6], and the silicate minerals tremolite amphibole ($\text{Ca}_2\text{Mg}_5(\text{OH})_2\text{Si}_8\text{O}_{22}$) [35], anorthite feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$) [29], albite feldspar ($\text{NaAlSi}_3\text{O}_8$) [29], forsterite olivine (Mg_2SiO_4) [22], grossular garnet ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and pyrope garnet ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) [15]. Results presented for hedenbergite pyroxene ($\text{CaFeSi}_2\text{O}_6$) are unpublished. Anorthite, albite, forsterite, grossular, pyrope and hedenbergite are synthetic phases. Powdered benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$, standard reference material 39j) was also measured for this study using the preparation technique of Dachs and Bertoldi. Reference data for all these substances exist from low-TAC measurements [36–45].

2.2. Measurements

Low-temperature heat capacities (5–300 K) were measured with the PPMS constructed by Quantum Design [4]. A complete PPMS experiment to measure C_p comprises an ‘addenda run’ and

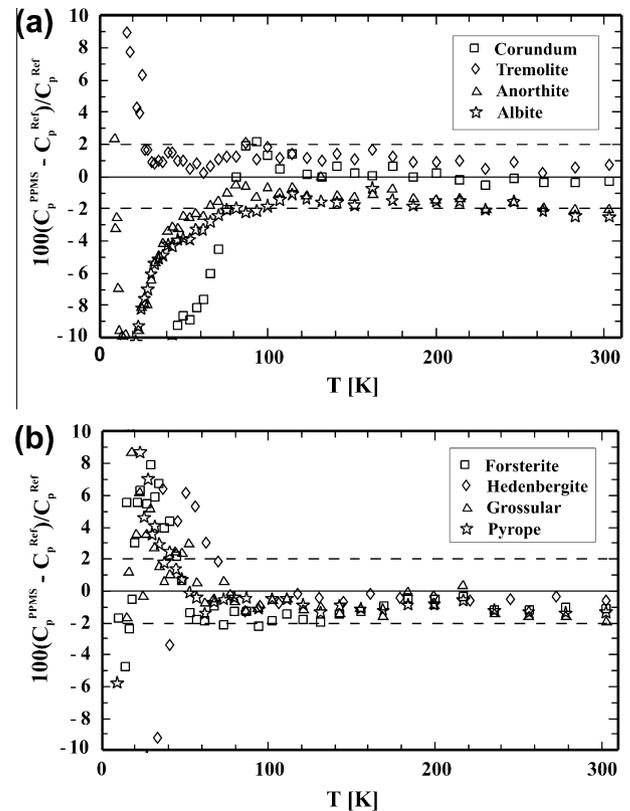


Fig. 1. Deviation of PPMS-measured heat capacities for (a) corundum (standard reference material 720 [6], tremolite [35], anorthite [29], albite [29], and (b) forsterite [22], hedenbergite, grossular [15] and pyrope [15] from published values obtained using adiabatic calorimetry [36–43]. The encapsulation technique for the powdered samples is that of Dachs and Bertoldi [6] as described in the text. Sample masses were in the range 20–27 mg.

a ‘sample run’. The first measurement determines the heat capacity of the empty sample platform (plus Apiezon N grease to facilitate thermal contact between the platform and the sample). In the second measurement, the sample is placed onto the platform and the heat capacity of the whole ensemble is measured. The net heat capacity of the sample is then given by the difference between both measurements. As the samples in this study are powders encapsulated in Al pans, the heat capacity of the pans must also be measured separately and their contribution subtracted from C_p^{total} .

As stated above, the sample encapsulation method applied here is that of Dachs and Bertoldi [6], where a powder is sealed in an Al pan (fabricated by TA Instruments – Part Nos. 900793 and 900794 for Al pan and lid, respectively). The pans and lids are 0.2 mm thick and weigh between 57 and 59 mg. The bottom of the pan has a diameter of 5 mm that slightly overlaps the quadratic 3.5×3.5 mm size sample platform. The sealing is done with a TA Instruments DSC sample press (Part No. 900685) such that the powder is compressed into an ~ 1 mm thick layer. There is an intimate contact with the walls of the Al pan and no open space. A picture of such an Al pan filled with powdered benzoic acid (13 mg) is shown in Fig. 2 (cut through the middle after sealing).

To calculate C_p^{sample} , and in order to minimize systematic errors related to $C_p^{\text{container}}$, the heat capacities of five different empty and sealed Al pans were measured with the PPMS and normalized to a mass of 57.5 mg. The mean C_p value was then subtracted from C_p^{total} taking into account the ratio between the normalized mass and the actual mass of the Al pan in the measurement. The empty Al pans and lid contribute $\sim 65\%$ to C_p^{total} around ambient T , increasing to $\sim 85\%$ at low temperatures in the case of powder samples

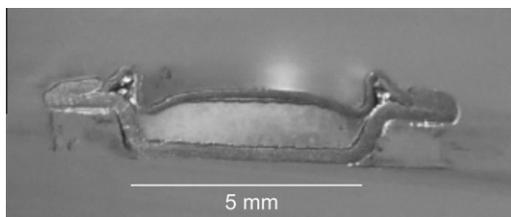


Fig. 2. Photograph of 13.6 mg powdered benzoic acid held in an Al pan and lid as described in the text and cut through the middle after PPMS measurement.

that have no heat capacity anomalies. PPMS measurements were performed at 60 different temperatures between 5 and 300 K with a logarithmic spacing and three replicates at each temperature. For benzoic acid three different powder samples were measured. For corundum, tremolite, anorthite, albite and grossular, in addition to previously published PPMS C_p data, some measurements with newly prepared powder samples were made in order to have, in total, three independent data sets for each substance. Sample couplings in the measurements were typically >99% at $T > \sim 100$ K and in the range 90–99% at lower temperatures.

Heat capacities above ambient T were measured with a Perkin Elmer Diamond DSC using Perkin Elmer Al-pans and lids (kit No. 0219-0041) containing the loose powder sample. Benzoic acid was measured between 282 and 305 K and sapphire, tremolite, anorthite, albite, and grossular between 282 and 764 K. The measurements were performed under a flow of Ar gas and the calorimeter block was kept at a constant temperature of 243.3 K using a Perkin Elmer Intracooler. A flow of dried air avoided the growth of ice crystals on the calorimeter block. This flow was set to 200 ml/min and is lower than the factory setting (600 ml/min). Additionally, the cover heater was turned off. The heat-flow data were collected in the step-scanning mode with a heating rate of 10 K/min in temperature intervals of 100 K. Using a self-written Mathematica program, the heat capacity of the blank run was subtracted from that of the reference and sample measurement, respectively, following the method of Mraw [46, chapter 11.6.4.2]. This program is available as Supplementary material. We found that the accuracy of the DSC measurements, which is approximately $\pm 1\%$ for commercially available equipment [46], was improved applying the above mentioned technical changes and using this evaluation procedure. Each complete measurement includes three separate measurements: a blank, a reference and a sample measurement. Before each sample measurement, the DSC was calibrated with a reference run using a synthetic single crystal of corundum (31.764 mg) whose heat capacity values were taken from the National Bureau of Standards Certificate [36]. Each sample (15–25 mg of benzoic acid, sapphire, tremolite, anorthite, albite, grossular) was measured three to five times yielding mean relative uncertainties of 0.4%. Three different samples of each substance were prepared in order to obtain three independent DSC data sets on each substance similar to the PPMS measurements.

3. Improved experimental method based on combined PPMS and DSC measured heat capacities

The accuracy of three independent PPMS C_p measurements on powdered benzoic acid is within 2% above ~ 50 K and the deviations are approximately constant with temperature (Fig. 3a). Similar accuracies were obtained on various silicates (Fig. 1). At $T > 50$ K they amount to -1.4 , -0.6 and -1.1% on average for the three different measurements on powdered benzoic acid respectively. That is, the C_p values are too low by these amounts. For a PPMS measurement on a powdered sample for which no low-

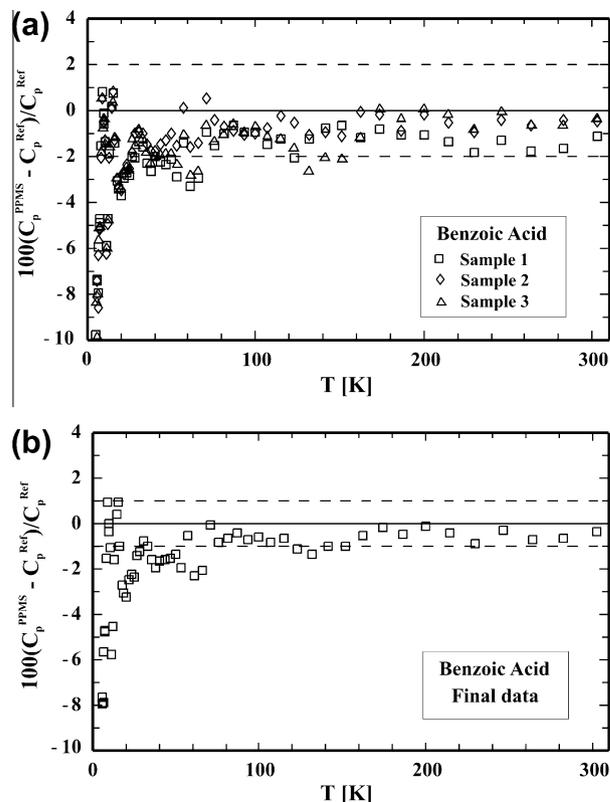


Fig. 3. Deviation of heat capacities for powdered benzoic acid (a) for three independent PPMS measurements (sample 1: 12.4 mg, sample 2: 13.6 mg, sample 3: 12.7 mg), and (b) resulting from the method presented in this study from published reference values [44,45].

TAC reference data are available for comparison it is, a priori, not clear how accurate this measurement will be within the observed range of 2%.

An improvement to the accuracy of the PPMS C_p values can be made by considering them in combination with C_p s measured around ambient T via DSC. The C_p values at 298 K on sapphire and benzoic acid and four silicates, obtained from three independent DSC determinations, where each represents the mean of 3–5 DSC measurements, are accurate to within 0.3% on average with a maximum deviation of 0.6% (Table 1). Thus, it seems reasonable to adjust the PPMS data using the DSC results because of the better accuracy of the latter. The adjustment is given by:

$$\left(C_p^{\text{PPMS}}\right)_{\text{corrected}} = C_p^{\text{PPMS}} * \left(C_p^{\text{DSC}}/C_p^{\text{PPMS}}\right)^{\text{at } 298 \text{ K}} \quad (1)$$

where $\left(C_p^{\text{DSC}}/C_p^{\text{PPMS}}\right)^{\text{at } 298 \text{ K}}$ is typically in the range 0.98 and 1.02. It is >1 , if the PPMS C_p values are less than the DSC C_p values and <1 in the opposite case. It is applied to all PPMS heat capacities because their deviation to reference data is nearly constant between 50 and 300 K, as discussed above (Fig. 1 and Fig. 3a). We apply this adjustment procedure in a statistical manner, i.e. to all possible combinations of the different PPMS and DSC data sets. This minimizes systematic error. Thus, each of the three PPMS C_p data sets is corrected according to Eq. (1) using each of the three DSC data sets. This results in nine adjusted PPMS heat capacity data sets in total that are averaged to give the final heat capacity.

4. Results and discussion

The accuracy of our low-temperature heat capacities, resulting from our modified procedure, is shown in Fig. 3b for benzoic acid

Table 1

Accuracy of the standard entropy (S^0) and the heat content ($H^{298\text{K}} - H^{0\text{K}}$) for various insulating powder samples measured by the PPMS method of this study (deviation in % from published reference values, i.e. $100(S^{\text{PPMS}} - S^{\text{ref}})/S^{\text{ref}}$, analogous for heat content). The accuracy of the DSC heat capacity values at 298.15 K is also given for three different series, each consisting of the mean C_p value from 3 to 5 repeated measurements. Data sources are cited in the text.

	S^0 % deviation	$H^{298\text{K}} - H^{0\text{K}}$ % deviation	$C_p^{298\text{K}}$ measured by DSC % deviation		
			Series 1	Series 2	Series 3
Corundum	-0.34	-0.43	-0.35	0.05	-0.60
Benzoic Acid	-0.85	-0.65	-0.48	-0.55	-0.58
Tremolite	0.11	-0.03	0.34	0.15	-0.22
Anorthite	-0.10	-0.08	-0.52	0.35	0.12
Albite	0.21	0.29	0.15	-0.22	0.21
Grossular	0.19	0.07	-0.27	-0.05	-0.10

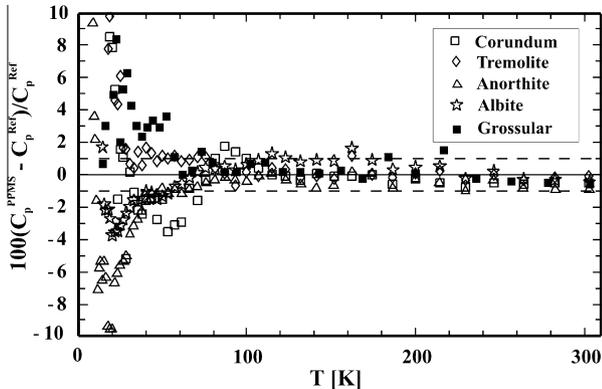


Fig. 4. Deviation of the heat capacity of corundum and tremolite, albite, anorthite and grossular resulting from the method presented in this study from published reference values [36–39,42].

and in Fig. 4 for sapphire, tremolite, anorthite, albite, and grossular. Following the adjustment procedure given above, heat capacities are accurate to within 1% above 30–50 K. Accuracy decreases at lower temperatures with possible deviations up to 5–10%. A correct determination of systematic errors in C_p behavior is difficult at low temperatures, however, because low-TAC is also less accurate below ~20 K [12].

The resulting standard entropy values have an accuracy of $\leq 0.21\%$ for the silicate samples, 0.34% for corundum, and 0.9% for powdered benzoic acid. Similar accuracies are obtained for heat content values (Table 1). The method is therefore suitable for entropy determinations with an accuracy of better than 1% despite the noted uncertainty at low temperatures. This is because the entropy contribution from low temperatures is small for substances where the C_p only results from lattice vibrations. Our methodology originates back to the study of Benisek and Dachs [47]. They calculated the uncertainty in the standard entropy of several substances by propagating the errors involved in a PPMS measurement using a Monte Carlo technique. It was found that the relative deviations in the heat capacities values of empty Al pans were approximately constant as a function of temperature. Heat capacities in later studies on feldspar [29,33,34] were adjusted according to Eq. (1) using just a single PPMS and DSC data set.

The improved experimental method described herein leads to heat-capacity values that have less scatter (1%) at $T > 250$ K compared to heat capacities determined using encapsulation techniques in which the powder is mixed with grease [10,12]. This is demonstrated using the results of this study on benzoic acid [Fig. 3b] and those of Shi et al. [12] (their Fig. 6) and Mariott et al. [10] (their Fig. 2). Data scatter in the two latter studies is ~2% and ~4% at $T > 250$ K. As discussed by Shi et al. [12], this scatter is probably caused by irreproducible effects related to heat capacity anomalies arising from the Apiezon N grease at 220–

290 K [48] that were attributed to a glass transition [49]. Scatter can also arise from the state of Apiezon N grease, that is, whether it occurs as a thin film or forms a lump [50]. An advantage of our method is that these complications do not come into play, because Apiezon N grease is only used as a thin film to obtain conduction between the Al container and sample platform. It is not mixed with the sample.

Shi et al. [12] measured the C_p of a pressed pellet of benzoic acid having a copper foil covering with no grease included. They claim that such an assembly “mimics” the experimental setup of Dachs and Bertoldi [6]. The heat capacity values they measured were ~3–10% too low going from low to ambient temperatures (their Fig. 5). These deviations are clearly larger than those resulting from our measurements, which are <2% above 50 K (Fig. 3a). The reason why the assembly used by Shi et al. does not mimic the preparation technique of Dachs and Bertoldi is mainly due to the different sample geometries involved. This results in thermal conduction paths within the powders and heat flows that are different between the two experimental configurations. In the Dachs and Bertoldi method the encapsulated powder is a compressed layer only of ~1 mm thickness (Fig. 2) with a cross sectional area of ~20 mm² (Al pans have a bottom contact diameter of 5 mm). The samples of Shi et al. have a smaller diameter of 2.8 mm (6.2 mm² cross sectional area). Thus, they are thicker by a factor of about three compared to the samples in our encapsulation method (no information on the thickness of their pellets is given). Additionally, heat flow will reach the powder layer via the lid more efficiently in our method, because the Al pan is thicker by a factor of almost 10 (0.2 mm thickness compared to 0.025 mm thickness of the Cu foil). If thermal paths through a powdered sample are relatively short, relaxation effects within the sample should be minimized and it is not necessary to mix it with grease to obtain C_p values accurate to within 2%, even for insulating materials. Concluding, the Dachs and Bertoldi method for powdered samples, which is improved upon here, can be used for standard entropy determinations with an accuracy of better than 1%. It has the advantage that the sample does not need to be mixed with grease.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cryogenics.2011.04.011.

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