

# The Possibility of High-Temperature Heat Capacity Measurements by Differential Scanning Calorimetry<sup>1</sup>

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We have been conducting series of heat capacity measurements by differential scanning calorimetry (DSC) on various latent thermal storage materials such as NaOH-NaNO<sub>3</sub>. Our concern is now shifting to higher temperature applications of latent thermal storage: space solar dynamic power systems (solar thermal electric power generation systems in space) and so on. Such applications require storage materials which can be operated above 1000 K. Needs for heat-capacity measurements at higher temperatures are increasing. In the present paper, some results of our heat capacity measurements by DSC at intermediate temperatures are presented. Several items which should be considered in order to realize the heat capacity measurements above 1000 K by DSC are discussed.

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**KEY WORDS:** differential scanning calorimetry (DSC); heat capacity; high temperature; latent heat; thermal storage materials.

## 1. INTRODUCTION

We have been conducting research and development on latent thermal energy storage for various applications [1–10]: load following generation of nuclear power plants [6–9], solar heating, cooling, and hot water supply [2], space solar dynamic power systems [10], and so on. In order to investigate the performance of the latent thermal storage units, heat capacity as well as latent heat data are needed. They are also needed to design practical storage units.

Differential scanning calorimetry (DSC) is a powerful tool not only to investigate the thermal behavior of the storage materials, but also to determine their heat capacities and latent heats. At the beginning [11], DSC was considered as a simple method for heat capacity measurements but

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was not always recognized as a precise method comparable to other conventional calorimetric techniques. The reason for this seems due partly to its principle: dynamic method without adiabatic control. A substantial amount of heat capacity data have been generated since the commercialization of DSC by the Perkin Elmer Company. DSC is now widely used and accepted as a reasonably satisfactory technique for heat capacity measurements. Data with accuracies comparable to those obtained by adiabatic calorimetry have also been reported [12].

So far, reliable heat capacity measurements by DSC have been generally limited to the temperature range 100–1000 K. Drop calorimetry is usually used for heat capacity determination at high temperatures; however, it is time-consuming and heat capacity cannot be measured directly. Realization of heat capacity measurements at high temperatures by DSC is desirable. In the present paper, examples of our heat capacity measurements are presented. Extension of the measurements to temperatures above 1000 K is discussed.

## 2. PRINCIPLE OF HEAT CAPACITY MEASUREMENTS BY DSC

It is well known that there are two kinds of DSC: power-compensated DSC and heat flux DSC (a quantitative DTA). The principle of the heat capacity measurement by DSC is briefly summarized here. Figure 1 shows the configurations of the two types of DSC. In any type of DSC, a sample and a reference material are placed in thermally equivalent positions, and the temperature of the sensor (the sample holder) or that of the metal block is increased at a constant heating rate. Assuming a simple model, fundamental equations for the principle of the heat capacity measurements by DSC are written as follows.

For power-compensated DSC,

$$J_s - J_r = (C_s - C_r) dT/dt + J'_s - J'_r \quad (1)$$

For heat flux DSC,

$$(T_s - T_r)/R' = (C_s - C_r) dT/dt + J'_s - J'_r \quad (2)$$

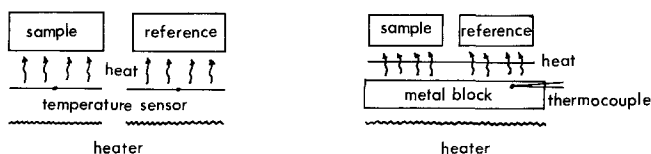


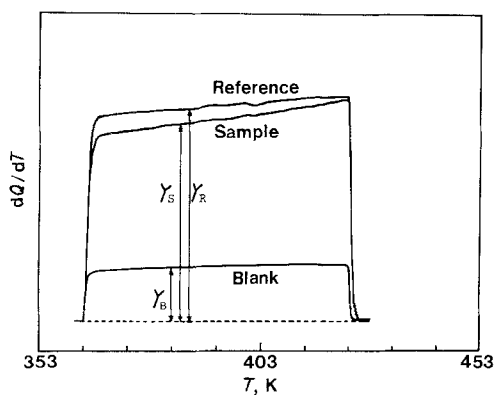
Fig. 1. Configurations of DSC. (a) Power-compensated DSC; (b) heat flux DSC.

where  $J$  and  $J'$  are the heat generation rate at the heater and the heat flux to surroundings, i.e., heat loss not to be used to heat up the sample or the reference material.  $C$  and  $T$  are the heat capacity and the temperature. The subscripts  $s$  and  $r$  indicate the sample and the reference.  $R'$  is the heat resistance between the heater and the sample or the reference.

In the adiabatic calorimeter, the last term,  $J'_s - J'_r$ , is neglected since both  $J'_s$  and  $J'_r$  are controlled to become zero. DSC is not adiabatically controlled, but it is a twin-type calorimeter; the sample and the reference are placed in thermally equivalent positions. Although  $J'_s$  and  $J'_r$  are not negligible, the term  $J'_s - J'_r$  can become rather small due to the twin configuration. In order to obtain the heat capacity of the sample, three kinds of measurements, on the sample, the standard material (usually sapphire), and the blank, are needed. If the term  $J'_s - J'_r$  is almost the same for all three measurements, correction for this is possible because this term appears as a shift of the baseline, which is a DSC signal. These conditions can be satisfied at least below 1000 K provided that the measurements are carefully made considering the effects of temperature interval for one step, scanning rate, sample mass, reproducibility of setting the sample, and so on. The equation for the specific heat capacity determination is as follows [13] (Fig. 2):

$$c_S = \frac{W_R(\{Y_S - [c_P \Delta W_P(Y_R - Y_B)]/c_R W_R\} - Y_B)c_R}{W_S(Y_R - Y_B)} \quad (3)$$

where  $c_R$  and  $c_P$  are the specific heat capacities of the reference and the blank (empty pan), respectively.  $W_R$  and  $W_S$  are weights of the reference



**Fig. 2.** An example of DSC signals for an empty pan (blank), a pan with a reference (sapphire), and a pan with a sample (pentaerythritol).

and the sample, and  $\Delta W_P$  is the weight difference between the pan for the reference and that for the sample.  $Y_S$ ,  $Y_R$ , and  $Y_B$  are the DSC signals for the sample, reference, and blank, respectively.

### 3. HEAT CAPACITY AND LATENT HEAT MEASUREMENTS BY DSC ON LATENT THERMAL STORAGE MATERIALS

#### 3.1. Thermal Storage and Heat Capacity Measurements

We have measured latent heats and heat capacities of several latent thermal storage materials such as high-density polyethylene [14], pentaerythritol [13], and NaOH-NaNO<sub>3</sub> [15]. The data were used for screening the storage materials and for the heat transfer analysis. Computer simulation on the charge and discharge characteristics of a latent thermal storage unit requires the data on latent heat and heat capacity; even a storage unit with form-stable high-density polyethylene required temperature-dependent heat capacities to analyze the charge characteristics because its melting takes place over a wide temperature range. The heat capacity data measured by DSC was successfully used as shown in Fig. 3 [3].

#### 3.2. Conditions of Heat Capacity Measurements

In order to obtain accurate heat capacity data, conditions of the measurements should be carefully optimized. Among many items to be considered, only the heating rate and temperature intervals selected in our measurements are presented.

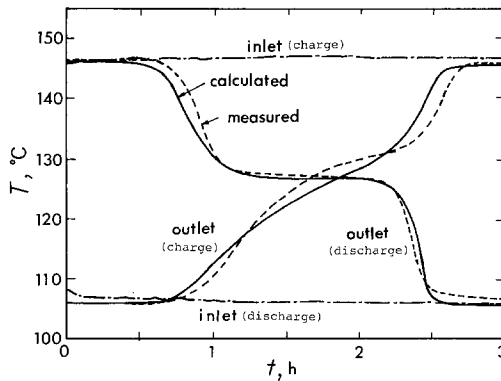


Fig. 3. Calculated charge and discharge characteristics of the HDPE storage unit. Comparison with the experiment.

In our heat capacity measurements, a heating rate of  $0.0833 \text{ K} \cdot \text{s}^{-1}$  is usually used. The measurement is made at every 1 K in the normal region and at every 0.0833 K in the transition region. For special purposes, such as detection of transitions within a small temperature range, a much slower heating rate should be selected. Figure 4 shows the heat capacity of  $\text{NaNO}_2$  measured at  $0.00521 \text{ K} \cdot \text{s}^{-1}$ . The data were taken every 0.025 K in this case. Although the scatter of data is rather large because of low S/N due to lower heat supply, two peaks corresponding to the ferroelectric-to-antiferroelectric and the antiferroelectric-to-paraelectric transitions are clearly seen. It should be noted that DSC can be used for heat capacity measurements with a high sensitivity comparable to the conventional adiabatic calorimetry [16] and ac calorimetry [17].

In order to obtain the stability of the isothermal baseline signal, a temperature interval for each measurement should be properly selected. We usually use a 40–50 K interval at the heating rate of  $0.833 \text{ K} \cdot \text{s}^{-1}$ . In this case, the initial data points for the first 10 K are omitted, since a steady state is not achieved yet; therefore, the next step of the measurement is overlapped by 10 K as shown in Fig. 5.

### 3.3. Latent Heat Measurement with Sapphire as a Standard Material

Takahashi [18] proposed the use of sapphire as a standard material for latent heat measurements as well as heat capacity measurements. The merits of this approach are as follows.

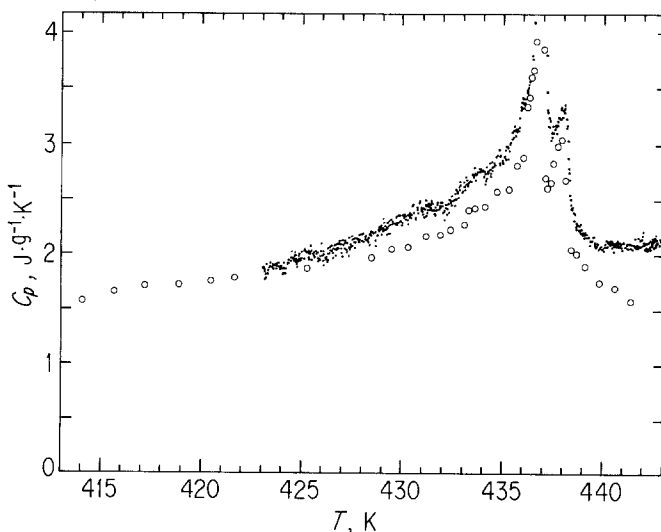


Fig. 4. Heat capacity of  $\text{NaNO}_2$ . (.....) This work; (○) Sakiyama et al. [16].

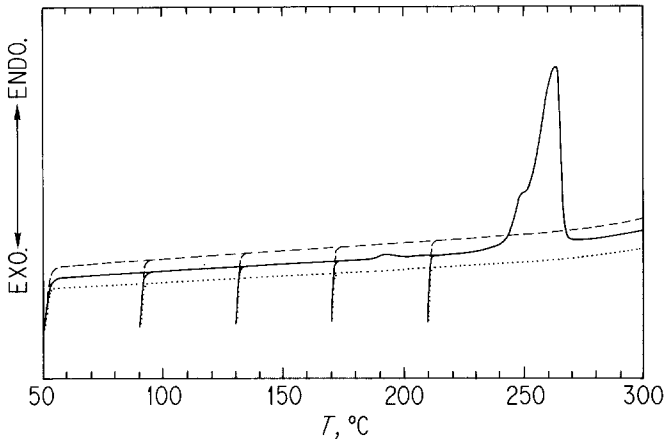


Fig. 5. An example of measured baselines for series of heat capacity measurements. (—) Sample; (-----) reference; (.....) blank.

- (1) Sapphire is much more stable than reference metals used for the conventional method, in which a proportionality coefficient is determined from the latent heat measurements on the reference metals.
- (2) Since the proportionality coefficient is not always constant with changing temperature, it has to be determined as a function of temperature before the measurements. For this purpose, sapphire

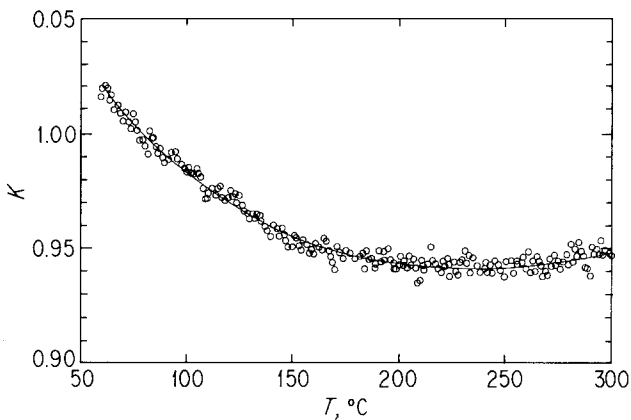


Fig. 6. Temperature dependence of the proportionality coefficient of the instrument.

is quite suitable because of the available reliable data, while the conventional method needs many stable reference materials with reliable literature data.

The proportionality coefficient of our instrument determined with sapphire as a standard is shown in Fig. 6 [18]. Temperature dependence in this temperature range is rather strong. The latent heat measurement by the proposed method is demonstrated in Fig. 7 [13]. Heat capacity and latent heat can thus be determined by the same experiment using sapphire as the standard material.

### 3.4. Sample Pan Made of ptfe for Alkali Metal Hydroxide

When molten salts are measured, an appropriate sample pan should be considered; they are sometimes very corrosive and tend to creep up the wall of the sample pan. We used a pan made of ptfe (polytetrafluoroethylene) for alkali metal hydroxides and their mixtures [13, 15, 19, 20]. Since the thermal conductivity of ptfe is much lower than that of metals such as aluminum, its effect on the data was first examined. Figure 8 [18] shows the apparent specific heat capacities of indium measured with aluminum sample pans and ptfe. As can be expected, the slope of the initial part of curve 2 for the ptfe pan is smaller than other curves for the aluminum pans because of its high thermal resistance. The enthalpies of fusion obtained by integrating the heat capacities in the melting region are almost the same for all the cases. Furthermore, heat capacities of sodium hydroxide and platinum measured with the ptfe pan were in good agreement with the literature values.

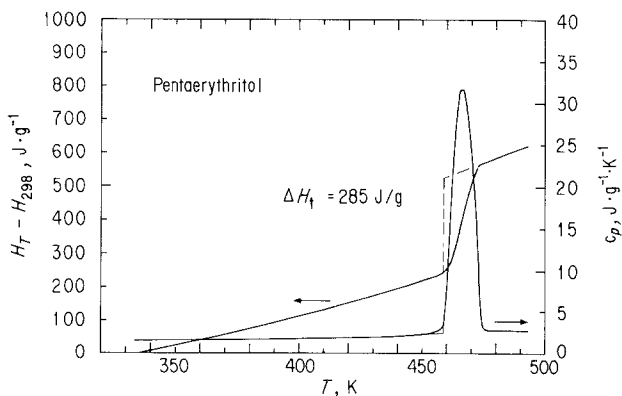


Fig. 7. Specific heat capacity data and the enthalpy change calculated from the data on pentaerythritol.

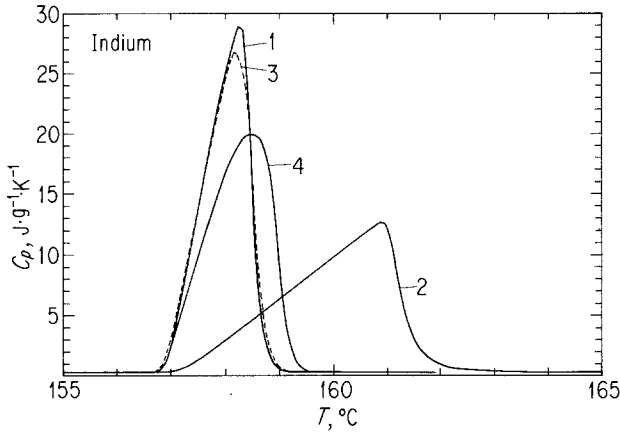


Fig. 8. Apparent specific heat capacity of indium from different sources with different sample pans. (1) Supplied by Rigaku Denki Co., Ltd. (Al pan); (2) 99.999% (ptfe pan); (3) 99.999% (Al pan); (4) granular sample supplied by NBS (Al pan).

### 3.5. Measurement of a Powder Sample Having a Low Thermal Conductivity

Another example is the measurement on cesium iodide, which is not a storage material, near room temperature [21]. The data obtained were connected well to the low-temperature data [22] by adiabatic calorimetry and the high-temperature data by drop calorimetry [21]. This compound is difficult to prepare dense material; therefore, it was hard to apply laser flash calorimetry.

## 4. EXTENSION OF PRECISE DSC MEASUREMENTS UP TO THE HIGH-TEMPERATURE REGION

The power compensated DSC is widely used below 1000 K, although there does not exist any commercialized apparatus of this type above 1000 K. Although heat flux DSC which works above 1000 K is available, it is usually used only for qualitative analysis.

With increasing temperature, the difficulty in measuring heat capacity drastically increases. The main reasons for the difficulty are increase in radiation heat loss, low S/N, and instability and poor reproducibility of the baseline signal as a result. Some of the above items are also the reasons for the difficulty in the latent heat measurements; therefore, we first tried to measure latent heat of LiF of various grades by heat flux DSC: Perkin Elmer DTA1700. In order to prevent LiF with creeping up, it was sealed



**Table I.** Thermal Properties for Different LiF Specimens

	99.9 % LiF <sup>a</sup>	99.999 % LiF <sup>a</sup>	>99.99 % LiF <sup>b</sup>
$T_m$ (°C)	845	845	845
$\Delta H_m$ (kJ · kg <sup>-1</sup> )	991	1,008	1,015

<sup>a</sup> Provided by Rare Metallic Co., Ltd.

<sup>b</sup> Provided by Aldrich Chemical Co.

into a gold capsule and the capsule was placed in an alumina crucible usually used as a sample pan for this instrument. The results are shown in Table I. It was made clear that the impurity affects the value of the latent heat of fusion. For this purpose, the heat flux DSC was confirmed to be used at high temperatures.

This, however, does not mean that heat capacity measurements above 1000 K can be performed easily. It shows only its possibility. What is most important is the stability and reproducibility of the baseline signal. At high temperatures, the heat losses,  $J'_s$  and  $J'_r$ , increase drastically. It causes instability and poor reproducibility of the baselines. Apparatuses with an outer heater make it difficult to determine the final isothermal baselines after the heating due to slow response. To obtain the stability of the baseline, the temperature interval of each measurement should be small. We are going to try not only the scanning method but also the enthalpy method, in which the area between the DSC signal during heating and the interpolated isothermal baseline gives the enthalpy change between the initial and the final temperatures.

## 5. CONCLUDING REMARKS

In the present paper it is pointed out that DSC can be conveniently used for precise measurements of heat capacity for a variety of samples, at least below 1000 K; our measurements on latent thermal storage materials are given as examples. In relation to the extension of the measurements to higher temperatures, we have just begun the work. The efforts in this area might be fruitless; however, should it be successful, it will greatly contribute to the advancement of thermal engineering and energy technology.

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