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Specific Heat Capacity Measurement of Single-Crystalline Silicon as New Reference Material

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We started to develop a new certified reference material for specific heat capacity measurement using a new type of cryogenic adiabatic calorimeter, applying a pulse-tube cryocooler in the temperature range from 50 to 350 K. A candidate certified reference material is single-crystalline silicon. To check the performance of the equipment, we measured the specific heat capacity of NIST SRM720, a type of synthetic sapphire. The relative expanded uncertainty of the measurement was estimated to be 0.65% at 350 K and 8.2% at 50 K, and the certified value of SRM720 was within the limits of uncertainty. In the next step, we measured the temperature dependence of the specific heat capacity of single-crystalline silicon. The result was compared with some reference data, and good agreement within 0.6% residual was found.
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1. Introduction

Specific heat capacity is one of the most important physical properties for evaluating the thermal characteristics of materials. Furthermore, it is necessary to calculate thermal conductivity from thermal diffusivity measured by transient methods. To measure the specific heat capacity of materials correctly, a reference material is essential. In the National Institute of Standards and Technology (NIST), USA, as is shown in Table I, three kinds of standard reference materials (SRMs) for enthalpy and heat capacity (SRM720: synthetic sapphire,[1–5] SRM781D2: molybdenum,[6–9] and SRM705a: polystyrene[10]) have been developed.[11] For SRMs measurement, however, the uncertainty was not fully evaluated because they were developed in the old days. The National Metrology Institute of Japan (NMIJ) started to develop a new certified reference material for specific heat capacity measurement that is based on the latest quality system, in compliance with ISO GUIDE 34. A candidate certified reference material is single-crystalline silicon. For certified reference materials, it is necessary that their certified value is stable during storage, and that they are homogeneous. Since silicon has high stability and high homogeneity, it is suitable as a certified reference material.

Table I. NIST SRM for Enthalpy and Heat Capacity.[11]

SRM	Description	Unit size	Temperature range (K)
781D2	Molybdenum	0.64 cm diameter 10 cm	273.15 to 2800
705a	Polystyrene	5 g	10 to 350
720	Synthetic sapphire	15 g	10 to 2250

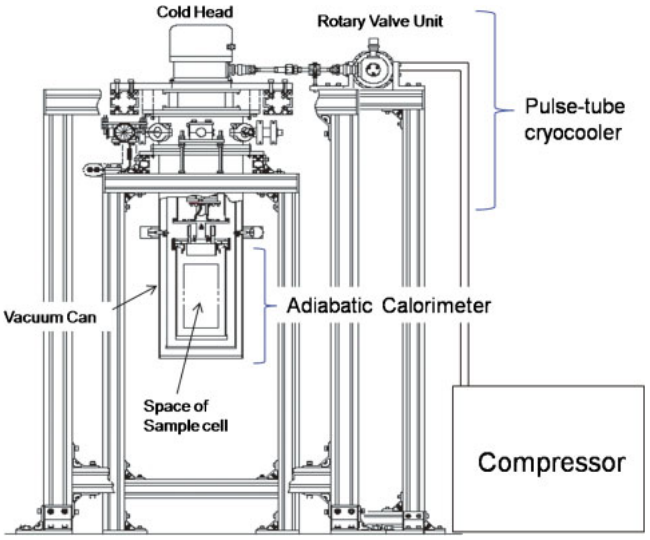

Fig. 1. (Color online) Cryogenic adiabatic calorimeter.

2. Experimental Procedure

2.1 Measurement method

The mesurement was performed by the adiabatic method. The specific heat capacity c_p at the temperature T_m can be expressed as

$$c_p(T_m) = \frac{\Delta Q}{m\Delta T} = \frac{C_p}{m}, \quad (1)$$

where ΔQ, ΔT, m, and C_p stand for the heat power applied to the sample, the temperature rise of the sample with heat power, the mass of the sample, and the heat capacity of the sample, respectively. T_m is given by $(T_i + T_e)/2$, where T_i and T_e are the temperatures before and after heating the sample, respectively. The thermal equilibrium state is kept at T_i, and the sample is heated from T_i to T_e under an adiabatic condition. The thermal equilibrium state is also kept at T_e. ΔT, which means $T_e - T_i$, is set at 1 or 2 K in the present measurement. The measurement was carried out by repeating the above process in the temperature range from 50 to 350 K.

2.2 Measurement system

An adiabatic calorimeter is a device with high reliability for specific heat capacity measurement. We have developed a new type of cryogenic adiabatic calorimeter applying a pulse-tube cryocooler[12,13] developed in collaboration with JECC Torisha and Tokyo Institute of Technology. In NMIJ, we started a SI traceable measurement service for specific heat capacity in 2008 in the temperature range from 50 to 350 K. A schematic view of the calorimeter is shown in Fig. 1. The calorimeter realized a liquid-helium-free cooling system using the pulse-tube cryocooler. Moreover, the effect

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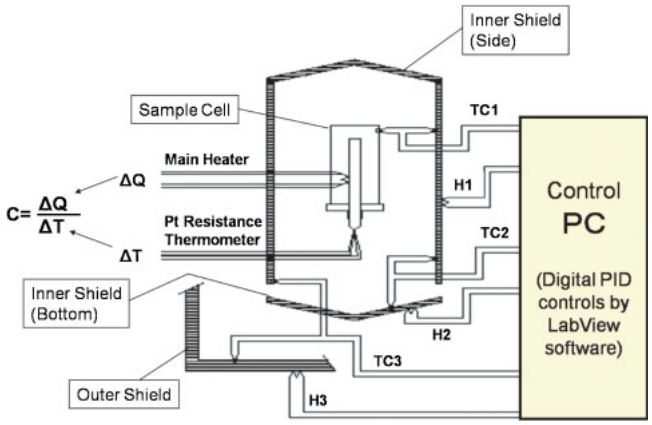

Fig. 2. (Color online) Adiabatic control system and sample cell in vacuum can.

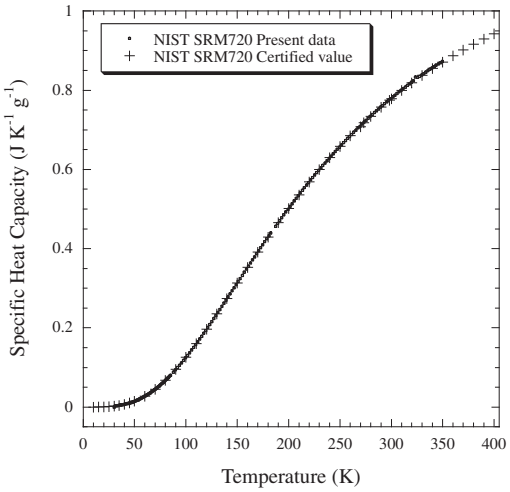

Fig. 3. Specific heat capacity of NIST SRM720, synthetic sapphire.

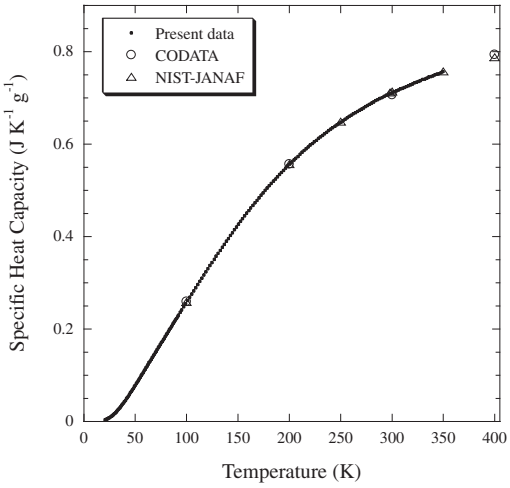

Fig. 4. Specific heat capacity of single-crystalline silicon.

of the vibration by the pulse-tube cryocooler was reduced by separating the rotary valve unit from the cold head. Therefore, the noise level of thermometry caused by the vibration was improved to a level better than the noise level caused by the vibration of a Gifford–McMahon (GM) refrigerator. Figure 2 shows the setup of a digital proportional integral derivative (PID) control system and a sample cell in a vacuum can. The PID control system enabled easy and safe operation, full automatization, and continuous long-term measurement. A double heat insulation shield comprising an inner shield and an outer shield was installed in surroundings of the cell, and the thermodynamic equilibrium situation between the cell and these shields was controlled using three differential thermocouples (TC1, TC2, and TC3) and three heaters (H1, H2, and H3).

The sample cell is a cylindrical form and has an effective volume of about 4 mL. The cell is made of oxygen-free copper and beryllium–copper plated with gold coating. The cell is filled with helium gas and sealed with indium. A 30 Ω platinum resistance thermometer provided by Minco Products, Inc. is calibrated to the International Temperature Scale of 1990 (ITS-90) and a main heater is installed at the center. The cell is suspended by nylon threads to suppress contact with heat outside.

3. Results and Discussion

In the first step, we measured the heat capacity of an empty cell. The mass of the cell was about 20 g. The cell contained helium gas. The measurement was performed by repeatedly measuring the temperature rise for 1200 s and the thermal equilibrium state for 3600 s. ΔT's were 1 K below 100 K and 2 K from 100 to 350 K. The empty cell was measured repeatedly three times in the temperature range from 50 to 350 K, and the residual from the average was less than 0.1%. This value was the same order as the measurement accuracy reported by Sterrett *et al.*[5)]

In the second step, we measured the specific heat capacity of NIST SRM720, a type of synthetic sapphire, to check the performance of the calorimeter. The sample specimen was 2–3 mm in diameter and 5–7 mm in height. The sample, which weighed 8.6834 g, was loaded into the cell. The heat capacity of the sample was obtained by subtracting that of the empty cell from the total heat capacity. The measurement conditions were the same as those for the empty cell. Figure 3 shows the present result and the certified value of SRM720. The uncertainties of the measurement were classified to five categories: joule heating, heat loss, temperature increase, correction of heat capacity, and mass of sample. The relative expanded uncertainty was estimated to be 0.65% at 350 K and 8.2% at 50 K with a coverage factor $k = 2$. The certified value of SRM720 was within the limits of uncertainty.

In the next step, we measured the temperature dependence of the specific heat capacity of single-crystalline silicon from 50 to 350 K. The sample specimen was extracted from the middle area of one silicon ingot 125 mm in diameter and 26.5 mm in height. The sample specimen was 5 mm in inner diameter, 17 mm in outer diameter, and 15 mm in height to fit the shape of the sample cell. The mass of the sample specimen was 7.2465 g. The measurement conditions were the same as those for the empty cell. The results are shown in Fig. 4 and Table II. We compared the result with the specific heat capacity of silicon in the NIST–JANAF thermochemical table[14)] and CODATA.[15)] These reference data were in good agreement with the result within 0.6%.

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Table II. Comparison with reference data.

Temperature (K)	Present data ($J K^{-1} g^{-1}$)	NIST–JANAF ($J K^{-1} g^{-1}$)	Residual (%)	CODATA ($J K^{-1} g^{-1}$)	Residual (%)
100	0.2586	0.2588	0.07	0.2592	0.24
200	0.5561	0.5567	0.12	0.5572	0.21
300	0.7110	0.7139	0.40	0.7070	−0.58

The relative expanded uncertainty of the present measurement was estimated to be 0.96% at 300 K with a coverage factor $k = 2$. We found that these reference data were within the limits of uncertainty.

4. Conclusions

To develop a certified reference material, the specific heat capacity of single-crystalline silicon in the temperature range from 50 to 350 K was measured using a cryogenic adiabatic calorimeter with a pulse-tube cryocooler. A performance check of the calorimeter was carried out by measuring the specific heat capacity of SRM 720, a type of synthetic sapphire. We estimated the uncertainty of the measurement and found that the certified value of SRM720 was within the limits of uncertainty. The specific heat capacity of silicon was compared with those in the NIST–JANAF thermochemical table and CODATA: it was found that these data were within the limits of uncertainty.

In the future, we will also discuss a homogeneity and stability study of single-crystalline silicon, which is required for the development of certified reference materials. The homogeneity study will be conducted by measuring four sample specimens extracted from different areas in the same silicon ingot. The stability study will be conducted by two methods: one is the determination of the long-term stability of the specific heat of silicon, and the other is that of the stability by thermal cycles. The uncertainties due to these evaluations will be compounded as the uncertainty of the reference material.

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