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A new heat capacity measurement scheme based on the scanning relaxation method for the Si–N membrane microcalorimeter at high temperatures up to 700 K

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ABSTRACT

We present a sensitive heat capacity measurement method for use at temperatures between 300 and 700 K using a home-made calorimeter incorporating a Si–N membrane microcalorimeter and a commercial tube furnace. We employ a scanning relaxation method with the two relaxation times, in which temperature is scanned with a maximum speed up to ~30 K/min to measure the heat capacity of sub-mg single crystals. The heat capacity of the addenda composed of the Si–N membrane and thermal grease is measured to be as small as ~30 μJ/K. For the high temperature thermal grease, several materials such as In, Wood's metal, and silicone oil have been tested. We demonstrate the successful performance of this method with different scanning speeds by measuring the specific heat of Cu up to 620 K. A brief summary of advantages/disadvantages of this method vis-à-vis commercially available differential scanning calorimeters (DSCs) is given.

1. Introduction

Accurate measurements of the specific heat (C_p) have been essential in understanding physical properties of numerous materials. The C_p, for example, provides a direct evidence of a thermodynamic phase transition as well as entropy change involved in the phase transition. In particular, measurements of C_p above room temperature become increasingly important as numerous materials of interest have phase transitions in the high temperature region. To list a few examples, $BaTiO_3$ shows a ferroelectric to paraelectric phase transition around 408 K [1] while $Y_3Fe_5O_{12}$ exhibits a ferrimagnetic to paramagnetic transition around 553 K [2]. Identifying those phase transitions and extracting related entropy changes through C_p measurements have been common practice to understand the nature of the phase transition.

Even with such continual demands in various scientific subfields, high temperature C_p measurements usually become more challenging than at low temperatures due to several experimental restrictions encountered. For example, in the high temperature region, the contribution of the addenda heat capacity to the total can become quite large so that extracting the heat capacity of the sample using a conventional calorimeter is difficult. In addition, controlling the base temperature (T) within ±0.5 K of the target T in the high temperature region is challenging so that the application of a conventional relaxation method, which requires a stable T over a long period of time, becomes difficult. To overcome those technical hurdles, differential scanning calorimetry (DSC) has been frequently used. In the DSC scheme, a signal from a reference calorimeter is subtracted from that of the sample calorimeter to give a sensitive measure of the temperature variation due to the sample heat capacity. Furthermore, rather than relying on the isothermal condition, the DSC employs a scanning temperature mode with variable scanning speeds and as well can be utilized up to a pressure of at least 150 bar. One drawback of the conventional DSC technique, however, is in its sensitivity limit that is not still enough to measure a tiny heat capacity involved in micro- or nanometer scale materials. Progress toward improving these drawbacks has been recently made, for example, through the high-speed scanning microcalorimeter [3,4] and differential ac-chip calorimeter techniques [5]. These works have demonstrated high measurement speeds up to ~200,000 K/s [4] as well as very high sensitivity down to ~1 pJ/K [5].

On the other hand, applications of such high-speed techniques may be yet challenging when one wants to measure accurately C_p of a ~100 μg single crystal and to exchange samples repeatedly

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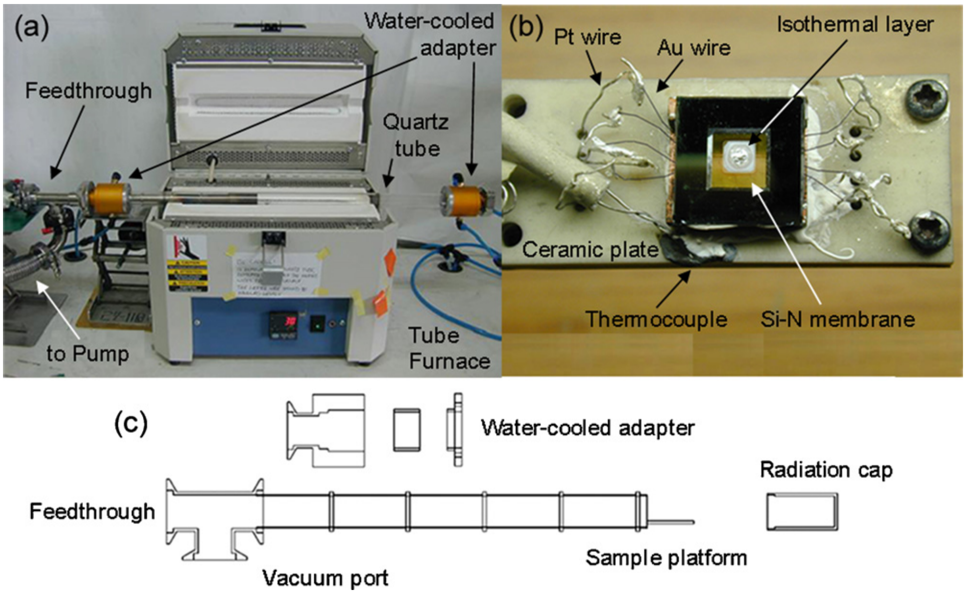

Fig. 1. (a) A picture of the high temperature heat capacity measurement setup. Water-cooled vacuum seal adapters are placed at both ends of the quartz tube. The left vacuum port of the adapter is attached to a stainless steel tee that has two vacuum ports to connect a turbo-molecular pump and an electrical feedthrough. (b) An enlarged view of the ceramic holder with the microcalorimeter attached. The microcalorimeter is placed on top of a Cu holder, which is glued to the ceramic holder. (c) Drawings for the tee, the radiation cap, and the water-cooled adapter, which are all made of stainless steel (SUS304). Three layers of ceramic plates are placed on top of the stainless steel holder to hold the microcalorimeter and to electrically insulate the Pt wires and the thermocouple.

by reusing the same calorimeter without further sensor calibration efforts. For this specific purpose, utilizing the conventional relaxation method can be also advantageous as it allows one to measure C_p of many samples repeatedly with a single calibration. Moreover, it can provide absolute C_p values in a broad temperature window once the addenda composed of the membrane platform and thermal grease is premeasured. Even with these advantages, however, the relaxation method has been rarely used in the temperature region above 300 K, mainly because of the several hurdles described above such as temperature stability and sensitivity limit that must be overcome.

Recently, we have demonstrated in the use of the Si–N membrane microcalorimeter that employing a numerical least square fitting schemed based on the relaxation method with the two-relaxation times, called as the curve fitting method (CFM) [6], can produce absolute C_p data at low temperatures from 20 to 300 K with a sensitivity of ~0.01–0.1 μJ/K with a resolution of $\Delta C_p/C_p < 0.01$ [7–9]. The relaxation method considers the so-called τ_2 effect and it has been also termed as the lumped τ_2 model in the original literature [10]. The same microcalorimeter could be repeatedly used for many samples as well. In this report, by extending our previous work, we present a new C_p measurement scheme that works at high temperatures from 300 to 700 K based on the CFM. In particular, we have developed a custom-made probe with the Si–N membrane microcalorimeter loaded, which is then adapted into a commercial tube furnace. The new measurement scheme can produce absolute C_p data in a broad temperature window from 300 to 700 K with a sensitivity of ~1 μJ/K while the base T is linearly scanned up and down with a maximum speed up to ~30 K/min. Commercially available DSCs have a sensitivity more in the range of 0.5 mJ/K in the same temperature range, along with a much larger ‘background’ or addenda contribution to the specific heat. AC calorimetry (see [11] for the discovery work) can resolve changes in the specific heat of 1 part in 10^4 but is less often used for absolute measurements. The microcalorimeter described in the present work can be repeatedly used as well without further sensor calibration to get absolute C_p data. We demonstrate the successful performance of the method by presenting the C_p data of several materials such as In, Wood’s metal and Cu using different scanning speeds. The present work owes much to the pioneering works [12] by the Hellman group, see also [13] for their recent design. In those previous works, the authors have used similar type of the microcalorimeter as ours that can be extendable up to ~700 K in principle. However, in practice, real published data using the relaxation method are only available in the temperature window below 300 K so far [12,13].

2. Experimental

2.1. Measurement probe and experimental conditions

Since the C_p measurement scheme based on the CFM uses a lock-in amplifier operating at f = 1–2 kHz for measuring the temperature sensor resistance, the electrical shielding of the apparatus is essential in the calorimeter probe design. Thus, we have fabricated a tube-shaped C_p measurement probe made of stainless steel (SUS304) for electrical shielding. The C_p measurement probe consists of an electrical feedthrough, a vacuum port, and a sample holder on which the Si–N membrane microcalorimeter is mounted (Fig. 1). The enlarged picture of the sample holder is shown in Fig. 1(b). There are 8 Pt wires (0.01 in. diameter) for electrical connection to the microcalorimeter and a type-B thermocouple (Pt–30%Rh versus Pt–6%Rh) for measuring the block T. All the Pt wires are covered with ceramic tubes for insulation. The gold wires (0.005 in. diameter) were first fixed into the sensor/heater pads by use of a silver epoxy cured at 420 K for 10 min. Then, the gold wires were electrically connected to the Pt wires in the sample holder using a conductive silver paste. We have used the “type III” microcalorimeter that has been proved to have measurement errors less than ±5% in a temperature region from 20 to 300 K [8,9]. After the microcalorimeter is properly mounted, an Al foil was wrapped over the membrane area for radiation shielding. Then the sample holder is covered with a radiation shield made of the stainless steel (SUS304). The probe is then inserted into a long cylindrical quartz tube with water-cooled vacuum seal adapters and evacuated by