Thermophysical Properties of the CsPbCl₃ Single Crystal Using Pulse Transient Method[1]

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The main features of the pulse transient method are presented. The method gives the specific heat c and thermal diffusivity a for a single measurement, while thermal conductivity λ is calculated according to $\lambda = ca\rho$, where ρ is the density. The pulse transient method is a dynamic method based on the measurement of the temperature response to a heat pulse produced within a specimen. An apparatus operating in the temperature range from -40 to $100°C$ is described. Errors are discussed. The thermophysical properties of a CsPbCl₃ single crystal are determined using the pulse transient method for a temperature range between 10 and $65°C$ in the controlled heating and cooling regimes. The data show anomalies in the thermophysical properties around the phase transition temperature at $47°C$. Discrepancies in comparison with previously published data are discussed.

KEY WORDS: CsPbCl₃ single crystal; heat of transition; phase transition; pulse transient method; specific heat; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Technology optimization and material aging are of great interest in materials production. Thermophysical property measurements help to improve material reliability. Recently, dynamic methods have started to be used for measurements of the thermophysical properties [1–5]. Their advantage lies in measurements of the specific heat, thermal diffusivity, and thermal conductivity at a controlled temperature during heating or cooling of the specimen (thermal analysis regime). Such measurements give information regarding structural relaxation and phase transitions [1, 6].

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For the study of phase transitions in solids, various experimental techniques can be used and their reliability can be evaluated by different criteria. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are used for the investigation of the kinetics of the phase transition of first kind [7]. Information related to the kinetic parameters such as the Avrami exponent and the activation energy of the transition can be estimated. A measuring regime can be used that gives average values of the specific heat within temperature intervals of several tens of kelvins [8].

Adiabatic or drop calorimeters are used for the measurement of specific heat of both kinds of phase transition [9, 10]. These methods are not useful in the thermal analysis regime. Moreover, drop calorimetry induces nonequilibrium states in structures that undergo phase transitions due to rapid temperature changes.

The flash method is used for investigation of the thermal diffusivity in the region of phase transitions of both kinds [11]. It can be used in the thermal analysis regime. The measurement of the thermal conductivity near a phase transition is unreliable with a steady-state method due to the temperature gradient during the measuring process [12].

$CsPbCl_3$ is a Pb^{2+}-rich crystal in which mainly optical properties are studied because of their application for fast scintillation in high-energy physics and in some industrial applications. It has been reported that the crystal undergoes a succession of phase transitions: cubic (Pm3m)/tetragonal (P4/mbm) at 47°C, tetragonal (P4/mbm)/orthorombic (Cmcm) at 42°C, and orthorombic (Cmcm)/orthorombic (Pnma) at 37°C [13, 14]. The phase transition at 42°C is of second order and those at 47 and 37°C are of first order. The crystal has perovskite-type structure above 47°C. On lowering the temperature below 47°C, elastic instabilities connected with boundary motion of elastic domains can be found [15].

The present paper deals with the measurement of thermophysical properties—specific heat, thermal diffusivity, and thermal conductivity—of $CsPbCl_3$ single crystal by the pulse transient method. A detailed experimental study of the thermophysical properties in the temperature range from 10 to 60°C is performed. The reversibility of the phase transition is investigated using a controlled temperature during heating or cooling of the specimen (thermal analysis regime). The measured values of the specific heat are compared with previously published data.

2. EXPERIMENT

2.1. Specimen

The single crystal of $CsPbCl_3$ used for the measurement of thermophysical properties was grown from the melt by the Bridgman method [16].

It was formed by the frozen high-temperature cubic phase, and its dimensions were 20 mm in diameter and 50 mm in length. The density of the crystal is $4200 \text{ kg} \cdot \text{m}^{-3}$. A specimen was prepared from the crystal cut into three pieces along the a axis ($10 \times 10 \times 7 \text{ mm}^3$, $10 \times 10 \times 6 \text{ mm}^3$, and $10 \times 10 \times 7 \text{ mm}^3$) to insert measuring probes between the cut surfaces.

2.2. Principle of Method

The principle of the method is shown in Fig. 1. The specimen consists of three parts. A plane heat source is fitted between the first and second parts. A heat pulse is produced by passage of an electrical current through a planar electrical resistance. The heat pulse is produced due to the Joule heat in the planar electrical resistance. A thermocouple is fitted between the second and third parts. The thermocouple measures the temperature response to the heat pulse. The thermophysical parameters—specific heat, thermal diffusivity, and thermal conductivity—are calculated according to the following relations:

Specific heat

$$c = Q / \sqrt{2\pi e} \; \rho h T_m \tag{1}$$

Thermal diffusivity

$$a = h^2 / 2 t_m \tag{2}$$

Thermal conductivity

$$\lambda = a c \rho \tag{3}$$

Here $Q = R I^2 t_0$, R is the electrical resistance of the planar heat source, t_0 is the width of the current pulse, ρ is the density, and the other parameters are defined in Fig. 1.
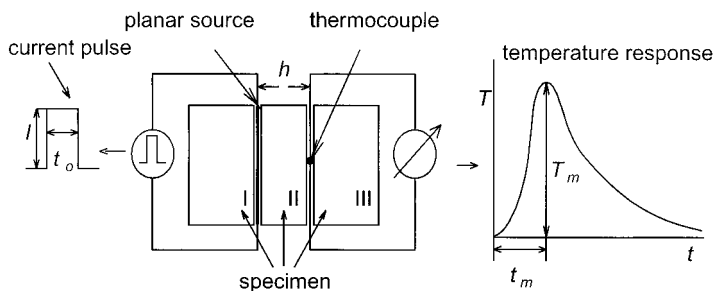

Fig. 1. Principle of the pulse transient method.

2.3. Experimental Arrangement

The experimental arrangement is shown in Fig. 2. A planar heat source made of a 20-μm-thick nickel foil was used. The heat source is etched as a series of loops to obtain higher electrical resistance. The electrical resistance of such a heat source is around 0.7 Ω. A K-type (chromel–alumel) thermocouple of diameter 50 μm was used to measure the temperature response to the heat pulse. A heat sink paste (Midland Silicones Barry Glamorgan) is used to improve thermal contact between the individual parts.

2.4. Experimental Apparatus

The experimental setup (Fig. 2) is fitted into the holder (Fig. 3). A thermostat with a precision of ± 0.05 K controls the temperature of the specimen holder. The measurements were performed in the temperature range from 10 to 65°C using heating and cooling rates of 0.04 K $\cdot$ min^{-1}. All measurements were performed in a vacuum of 0.1 Pa. A schematic diagram of the electronic devices is shown in Fig. 4. The heat pulse was produced with a programmable current source. The current intensity and the current pulse length were controlled by a microcomputer. The temperature response was scanned by a Keithley voltmeter. All units were synchronized by a PC that was used for data acquisition.

2.5. Measuring Cycle

The measurements were made in cycles consisting of operations required for the determination of the thermal diffusivity, specific heat, and thermal conductivity. A measuring cycle consists of the following operations: measurement of the specimen temperature, production of the heat
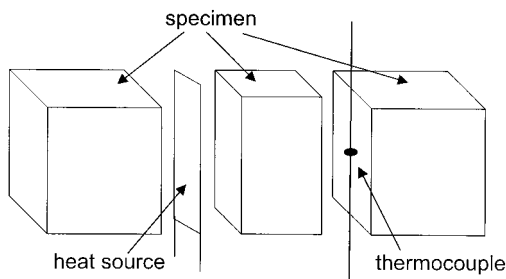

Fig. 2. Experimental arrangement of the specimen and measuring probes.
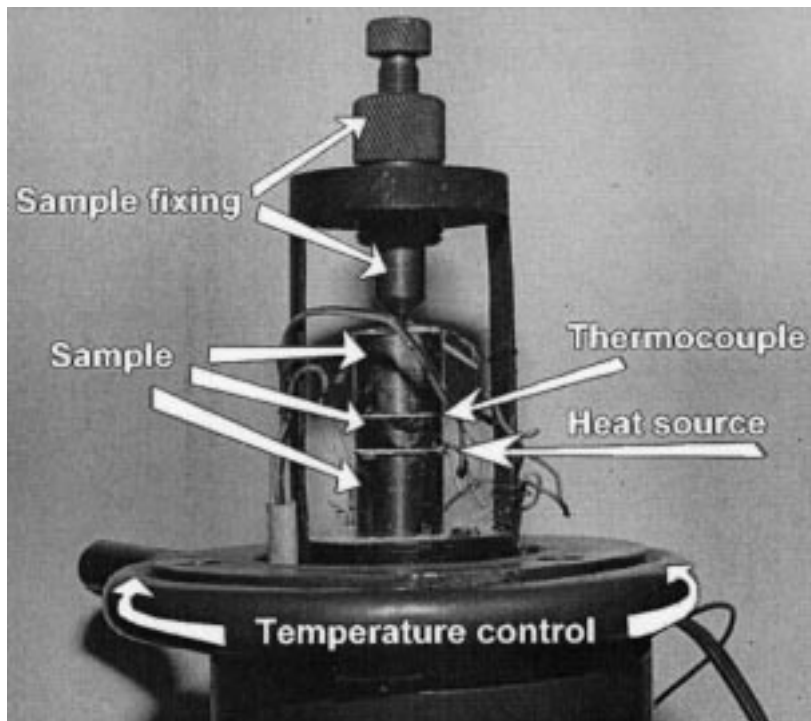
Fig. 3. Apparatus for measurements in the temperature range from -40 to $100°C$.
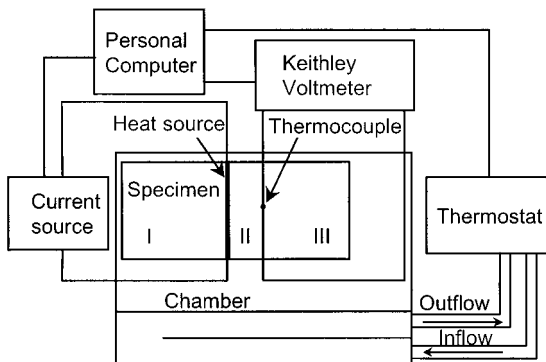

Fig. 4. Electronics arrangement of the pulse transient method.

pulse, measurement of the energy of the heat pulse, scanning of the temperature response, calculation of the thermophysical parameters, and stabilization of the specimen temperature. The length of the measuring cycle and the heating or cooling rates are the important parameters related to the measurement. The lower the heating or cooling rate, the more data that can be obtained in the region of the phase transition provided that the length of the measuring cycle is the same for all heating or cooling rates.

2.6. Measurement Error

The measurement error consists of the following components:

- the error components resulting from the difference between the idealized model and the actual experimental arrangement,

- the error component resulting from the nonreproducible fitting of the sample and the measuring probes into the holder, and

- the error component resulting from the imperfection of the instruments.

The first component can contribute considerably to the overall measurement error. This component is responsible for data shift. The error can be minimized by fulfilling the criterion of the ideal model, which represents the experimental arrangement where the influence of the heat source, the thermometer, and the thermal contacts on the data are negligible. Moreover, the ideal model represents an infinite body, i.e., the specimen surfaces do not influence the measuring process. A set of additional parameters needs to be estimated when the criterion of the ideal model is not satisfied. A theoretical analysis gives the following criteria of the ideal model [9]:

• To suppress the specimen surface influence on the measuring process, the following relations between the thickness of the second part of the specimen (Fig. 1) and the diameter of the specimen should be fulfilled:

$$h > 0.2D, \qquad hH/\lambda < 0.1$$

where h is the distance between the planar heat source and the thermometer (Fig. 1), D is the diameter of the specimen, and H is the coefficient of the heat loss from the specimen surface.

• The heat capacity of the heat source should be negligible in comparison to the specimen to suppress the properties of the heat source and

the contact thermal resistance between the heat source and the specimen,

$$\frac{hc\rho}{2bc_0\rho_0} > 500$$

where b is the thickness of the planar heat source and c_0 and ρ_0 are the specific heat and density of the heat source, respectively.

- The width of the heat pulse (Fig. 1) should fulfill the relation

$$t_0 < 0.1t_m$$

Correction factors have to be used when the criteria are not fulfilled.

Criteria for the ideal model and correction factors for the experimental setup used (Fig. 2) are given in Table I. It is assumed that the difference in parameter estimation for rectangular and cylindrical shapes of the specimen is negligible. The conditions of the ideal model listed in Table I were not met. Corresponding correction factors were calculated according to theory [1]:

- the measurements were performed in vacuum to suppress the heat loss from the specimen surface (f_a, $f_c \to 1$; see Table I), and
- data were corrected considering the finite length of the heat pulse according the procedure published elsewhere [1].

However, correction factors corresponding to nonideal heat source were not used. Thus, data for the specific heat might be shifted by 2% to higher values and data for the thermal diffusivity to lower values.

Table I. Parameters of Experimental Setup

Parameter	Theory	Experiment[a]		
			f_a	f_c
Thickness of specimen[b] (mm)	<2	6	1.5[c] (1[d])	0.8[c] (1[d])
Diameter of specimen[b] (mm)	>30	10		
Heat source thickness (μm)	<5	20	0.98	0.98
Heat pulse width (s)	<3.6	4	0.9	1

[a] f_a, correction factor for thermal diffusivity $a = a_{\mathrm{meas}}/f_a$; f_c, correction factor for specific heat $c = c_{\mathrm{meas}}f_c$.
[b] The estimation of the thickness and diameter is bounded.
[c] Air environment.
[d] Vacuum.

3. RESULTS AND DISCUSSION

Experimental results are shown in Fig. 5, where the temperature, thermal diffusivity, and specific heat are plotted as a function of measuring time. The specimen temperature is a linear function of time. Low scatter was observed. Anomalies of the specific heat and the thermal diffusivity were found during heating as well as during cooling. No hysteresis of the specific heat exists near the phase transition. An anomaly was also found for the thermal diffusivity around 47°C, and it has a more complicated structure. While the specific heat gives information related to the energy of the system, the thermal diffusivity is a transport parameter that is related to the sound velocity and free path of phonons. The thermal conductivity is a product of the specific heat, density, and thermal diffusivity [Eq. (3)]. Thus, determination of the thermal conductivity includes several properties.

The anomaly in the thermophysical parameters will be discussed and the specific heat data given by adiabatic calorimetry [17, 18] will be compared with the data obtained by the present measuring technique.

The nature of the phase transition is based on the freezing or condensation of the rotation modes of $PbCl_6$ octahedral phase in combination with atomic displacements of Cs atoms of the cubic sublattice when lowering the temperature from 50°C [19]. A ferroelastic phase is created below
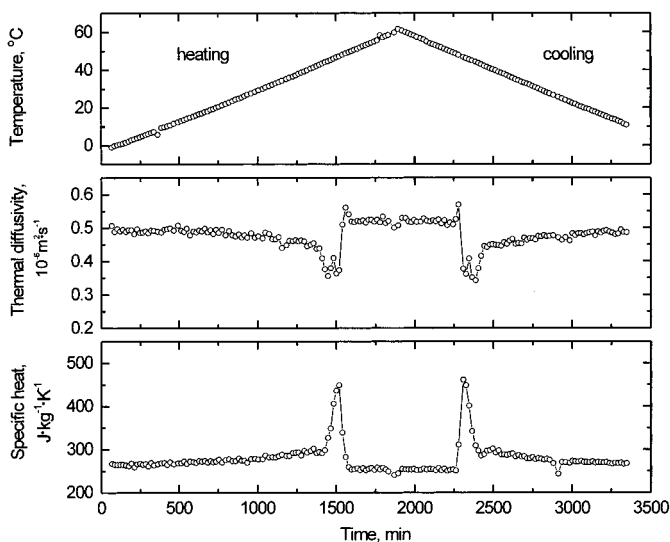

Fig. 5. Experimental data for the thermophysical properties of $CsPbCl_3$ single crystal.

the phase transition [15]. Any structural defect or temperature gradient inducing microstresses influences the domain structure.

Temperatures of the anomalies found by different authors are given in Table II. Sound velocity shows a broad dip around 40°C [13, 14]. Elastic compliance has a broad peak around this temperature [17]. Considerable acoustic attenuation is observed in this temperature range [15]. Soft modes were found by neutron scattering [19]. Anharmonicity of the structure should exist [15]. Expansion shows abrupt changes at 47°C [19].

Detailed plots of the specific heat and thermal diffusivity around the phase transition for heating and cooling are shown in Fig. 6. Anomalies of sound velocity and elastic compliance from Refs. 17 and 19 are noted for comparison. Although the start and end of the anomalies coincide with the thermal diffusivity anomalies, no significant change in data can be found within the dip and peak of sound velocity and elastic compliance, respectively. Data on thermal diffusivity might be influenced by anharmonicity when the measurements are performed on polydomain crystals. Clearly, in our case, anharmonicity plays a negligible role, as measurements were performed on a nearly monodomain crystal. Data on specific heat show a small, broad peak around 40°C similar to that found in the literature [17]; however, it is questionable to ascribe it to a phase transition.

Comparing heating data with cooling data (Figs. 6a and 6b), one can see that good reproducibility of anomalies exists. Data scatter on heating is larger than on cooling. This is connected with the defreezing of the microstructural processes. A similar statement is valid for the anomaly of the thermal diffusivity at 37°C, where the anomaly associated with heating is more profound than that with cooling. It should be noted that no heat treatment was performed before the measurements started.

Table II. Characteristics of the Phase Transition of CsPbCl₃

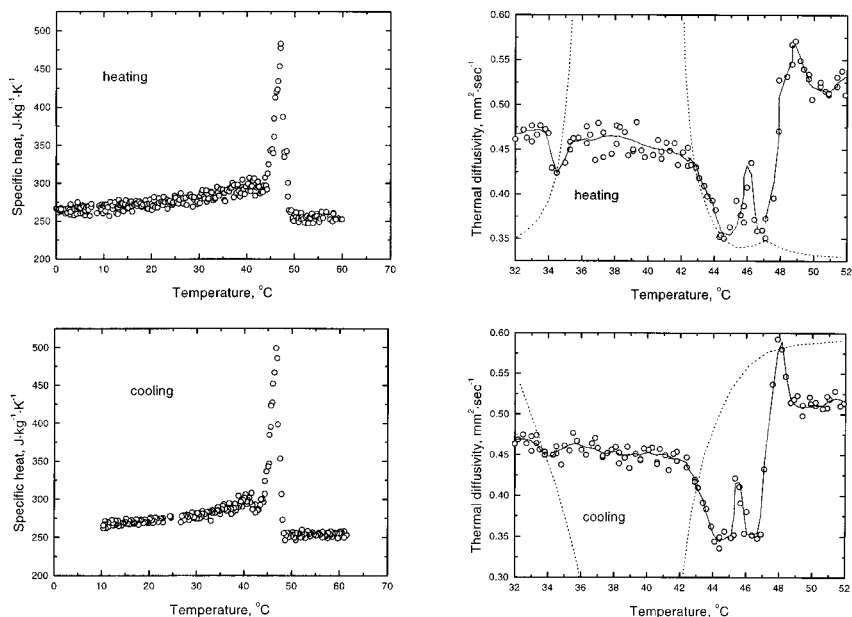|	Anomaly temperature (°C)			
Measured parameter	Orthorombic orthorombic	Orthorombic tetragonal	Tetragonal cubic	Reference
Sound velocity	Broad dip at 40		—	14
Elastic compliance	Broad peak at 40		—	16
Expansion	—	—	47	16
Specific heat	37	41.7	46.5, 47.9	17
Specific heat	Broad peak at 40		47	16
Specific heat	—	—	47.1	Present work
Thermal diffusivity	35	44.5	46.9	Present work

Fig. 6. Detailed plots of the specific heat and thermal diffusivity for heating and cooling around the phase transition.

A comparison of our specific heat data around the phase transition was made with published values [17, 18]. The heat of transition, specific heats at 25 and 50°C, as well as the shape of the specimen and the measurement method are listed in Table III. In Ref. 18, the area just under the peaks is given as 60 to 100 J · mol^{-1}. Adiabatic calorimetry in a sophisticated measuring regime was used to find several narrow peaks.

Table III.   Comparison of Data for CsPbCl$_3$[a]

Heat of transition (J · mol^{-1})	Specific heat (J · kg^{-1} · K^{-1})		Material/method	Reference
	25°C	50°C		
180	540	144	Powder/adiabatic calorimetry	16
500 (60?)	310	131	Several pieces of crystal/adiabatic calorimetry	17
185 508	272	250	Single crystal/pulse transient	Present data

[a] Dulong–Petit value of 270 J · kg^{-1} · K^{-1}.

Table IV. Measured Thermophysical Properties of CsPbCl₃ at 50°C

Parameter	Result	Uncertainty (%)
Specific heat $(J \cdot kg^{-1} \cdot K^{-1})$	272.10	2.7
Thermal diffusivity $(m^2 \cdot s^{-1})$	4.85×10^{-5}	4.3
Thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$	0.55	5.8

There is a difference between the results obtained for powder and bulk specimens. Data on heat transition obtained from a powder specimen give $\sim 180 \, J \cdot mol^{-1}$, while data from a bulk specimen give $\sim 500 \, J \cdot mol^{-1}$. Moreover, specific heat data differ for powder and bulk specimens. The specific heat of the powder is considerably higher than that of the bulk at 25°C. Powder was prepared by grinding a crystal. It is supposed that a polydomain structure was created by this procedure due to introducing numerous defects into the powder particles. This could be a reason for the differences at 25°C. The Dulong–Petit limit of the specific heat is given in Table III. It is not clear why specific heat by adiabatic calorimetry is significantly higher in comparison to this limit when the measurements were performed far from phase transition below 37°C [17, 18]. However, numbers on specific heat above the phase transition, i.e., at 50°C, should agree. Nevertheless, data in Table III show discrepancies. More detailed comparisons of measurements need to be made to find the reason for these discrepancies.

Our data show that one anomaly of the specific heat and one dip of the thermal diffusivity exist at 47°C. The dip has more complicated structure since it is induced by the anisotropic properties of the crystal structure. The shape of the specific heat anomaly [17, 18] (Fig. 6a) supports the hypothesis that one phase transition of order–disorder in combination with the displacive one exists [19].

Table IV gives data on the specific heat, thermal diffusivity, and thermal conductivity of the CsPbCl₃ at 50°C, i.e., above the phase transition to avoid any discrepancies caused by heat treatment. We believe that a deviation from equilibrium (frozen disordered structure) can appear below 47°C due to inappropriate cooling of the crystal.

4. CONCLUSION

The pulse transient method was used for the measurement of the specific heat, thermal diffusivity, and thermal conductivity of CsPbCl₃ single crystal in the temperature range from 10 to 60°C. The temperature

was controlled during heating and cooling of the specimen (thermal analysis regime). The data on the thermophysical parameters of the $CsPbCl_3$ single crystal show a λ anomaly of the specific heat and a dip of the thermal diffusivity around 47°C. The dip has a more complicated structure. No hysteresis was found during the temperature cycling in the temperature range studied.

Comparison of the specific heat and the heat of transition was made. Specific heat values depend on the specimen preparation. Powdered $CsPbCl_3$ shows significantly higher specific heat in comparison with the bulk below the phase transition. Two different values of the heat of transition were found depending on how the value is calculated. While area just under the peak gives a value around $\sim 180 \text{ J} \cdot \text{mol}^{-1}$, the value calculated from a broader temperature range gives $\sim 500 \text{ J} \cdot \text{mol}^{-1}$.

Data on specific heat, thermal diffusivity, and thermal conductivity at 50°C were also collected. The measurement error was influenced by the differences between the ideal model and the experimental arrangement. While the effect of the heat loss from the specimen surfaces is suppressed due to the vacuum environment, the finite length of the heat pulse changes the value of the thermal diffusivity by about 10%. Therefore, corresponding correction factors were applied [1]. The difference between the ideal and real heat source shifts the data for the specific heat by 2% to higher values and data for the thermal diffusivity by 2% to lower values. Data uncertainty caused by temperature stability is within 2.7% for specific heat, 4.3% for thermal diffusivity, and 5.8% for thermal conductivity.

ACKNOWLEDGMENT

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