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Heat Capacity Anomalies of $TlInS_2$ and $TlGaS_2$ Single Crystals Detected by Differential Scanning Calorimetry (DSC)

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Abstract

Specific heat capacity C_p anomalies of layered single crystals $TlInS_2$ and $TlGaS_2$ have been investigated using differential scanning calorimetry (DSC) as a new technique for such crystals. Special features of C_p have been revealed in the temperature range of the possible phase transitions of both crystals. A sequence of maximum values of C_p is obtained at 163, 174, 184, 193, 201, 212, 224, 254, and 259 K for $TlInS_2$. In the case of $TlGaS_2$, the temperatures of the obtained maximum C_p values at 177 and 241 K agree well with the intervals of the phase transition temperatures reported in the published data of $TlGaS_2$. As a result, it is remarked that DSC technique might have a particular potential for the thermal measurements of layered semiconductors.

Key Words: Ternary compounds, layered crystal, heat capacity, DSC, phase transition.

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1. Introduction

Heat capacity C_p is one of the basic properties for any material and the knowledge of C_p has particular importance for many scientific and engineering applications [1]. $TlInS_2$ and $TlGaS_2$ crystals are ternary thallium chalcogenides belonging to the III-III-VI_2 family of crystals having layered crystalline structures. To the best of our knowledge, there are a few studies [2–5] on heat capacity of the $TlInS_2$ and $TlGaS_2$ crystals as reported in the literature. However, DSC technique is used for the first time for this system to investigate heat capacity behavior of these types of thallium ternary compounds. Specific heat investigations in such crystals with a complex structure and obviously expressed chemical bond anisotropy are of interest to elucidate unique features of thermal oscillation dynamics in such complex layered semiconductors [5].

DSC has been used for over forty years to characterize thermal properties in materials. Using DSC, one can detect the temperatures and heat flows caused by changes in heat capacity by endothermic and exothermic processes of materials as a function of time and temperature [6]. It is used to study what we call the thermal reactions, which take place in a crystal during heating or cooling.

In the present work, the aim is to study specific heat capacities of $TlInS_2$ and $TlGaS_2$ single crystals using DSC method as a new technique for such crystals. In addition, the present study also intends to reveal the applicability of DSC for the comparison of the data of relevant compounds existing in literature.

2. Experimental

Single crystals of $TlInS_2$ and $TlGaS_2$ were synthesized from high-purity elements ($\geq 99.999\%$ pure) taken in stoichiometric proportions. The growth process was executed in evacuated quartz tubes by using modified Bridgman method. The quality of the samples and the orientation of the crystal planes were examined by X-ray diffraction measurement study. The crystals are found to be suitable to be cleaved into the plane parallel-plates along the (001) basal plane, which is perpendicular to the c-axis. The morphology of the crystal allows performing this operation. At room temperature, these thallium chalcogenides crystallize in a monoclinic structure with a space group of C2/c [7, 8] and the corresponding lattice parameters $a = 1.0942$, $b = 1.0484$ and $c = 1.5606$ nm and $\beta = 100.70°$ for $TlInS_2$; and $a = 1.031$, $b = 1.043$ and $c = 1.507$ nm and $\beta = 99.60°$ for $TlGaS_2$. XRD patterns of both the samples are shown in Figure 1.

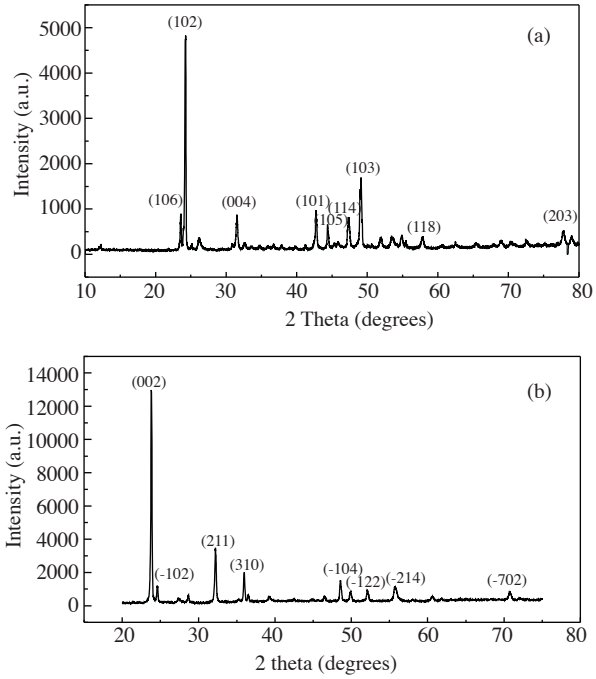

Figure 1. X-ray powder diffraction (XRD) patterns of (a) $TlInS_2$ and (b) $TlGaS_2$ single crystals.

For differential scanning calorimetry (DSC) measurements, TA Instruments model DSC-2010 was employed. DSC-2010 is advanced equipment providing a fundamentally more accurate way of measuring heat flow. The heat sink is cooled with liquid nitrogen, the level of which is kept constant during the DSC measurements. In order to purge the system, helium gas is constantly passed through the heat sink and over the cells. In our DSC apparatus, there are two pans, identically positioned platforms and connected to a furnace by a common heat flow path. DSC 2010 has the reference and sample cells made of platinum-iridium alloy. These cells with a thermometer and a heater are mounted in an aluminum heat sink kept nearly at the temperature of the cooling bath. We put the sample in one pan, and the other pan left empty is used as a reference. Throughout the experiment, the heating rates through the pans are kept equal and stable. To obtain reasonable results, the calorimeter is calibrated. After calibration for temperatures and calorimetric sensitivity of the DSC equipment, the optimum heating rate is determined to be 10 K/min through the entire temperature range. The masses of $TlInS_2$ and $TlGaS_2$ are taken 14.5 mg and 8.5 mg, respectively. DSC measurements on both samples have been carried out in the temperature range of 140 to 280 K.

3. Results and Discussions

The DSC curves of $TlInS_2$ and $TlGaS_2$ are shown in Figures 2(a) and (b), respectively. In the whole temperature range, endothermic processes can be seen for both the crystals.

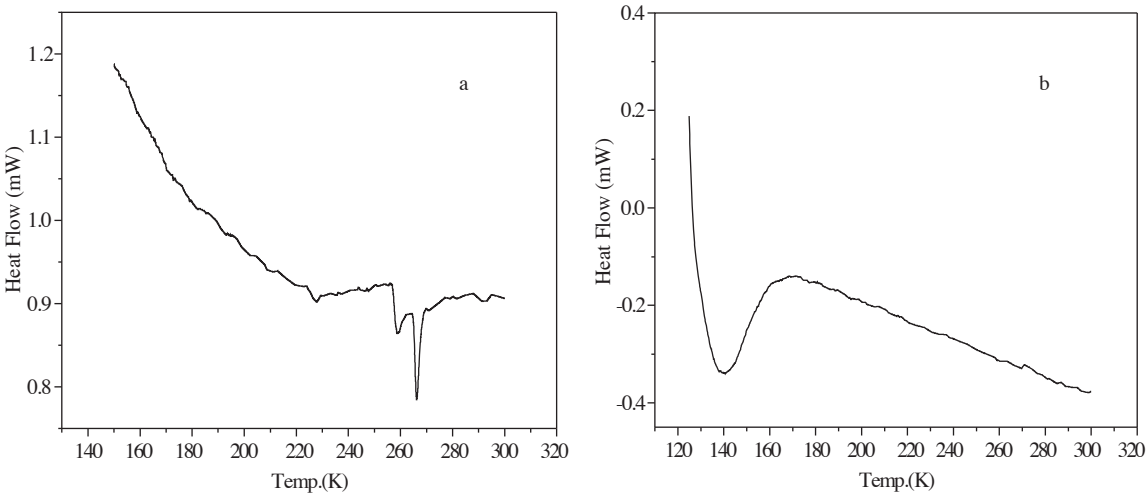

Figure 2. DSC curves of $TlInS_2$ (a), and $TlGaS_2$ (b).

The temperature dependence of C_p of the bulk $TlInS_2$ in the range of 140–280 K was determined and plotted in Figure 3. C_p values on both sides have been extrapolated with using the C_p data given in [4] in order to see the normal heat capacity curve progression, as shown in Figure 3. This range consists of anomalies some of which coincide with temperatures of phase transitions revealed by many elucidative experimental techniques.

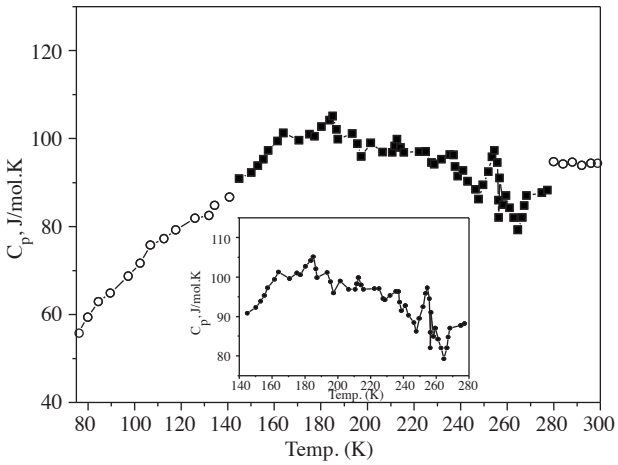

Figure 3. Temperature dependence of the specific heat of $TlInS_2$ single crystal, ○ indicates the values taken from [4] to extrapolate C_p curve in the range 80–300 K. C_p values determined using DSC are represented by ■.

We obtained C_p anomalies with the maxima at T = 163, 174, 184, 193, 201, 212, 224, 254, and 259 K. It is particularly constructive to compare these values with heat capacity anomalies of $TlInS_2$ reported in literature to realize C_p behavior measured by DSC in this temperature region.

For the heat capacity of $TlInS_2$, there exist a couple of published data in literature. In [4], the authors reported the measurements for a powder sample by the method of adiabatic calorimetry in the range of

5–300 K. Maximum values of heat capacity anomalies were obtained at the temperatures 173.4, 196.9, 206.1, 208, 210.9, 214.9 K. These values were deduced as a sequence of phase transitions explained by coexistence of long-period commensurate and incommensurate phases. The other published data [3] was obtained by the method of thermal relaxation in the temperature range 60–310 K. Maxima were obtained at T = 156, 166, 173, 192, 202, 207, 216, 222, 227.5, 244, 253, and 258.5 K for the single crystal form of $TlInS_2$. The temperatures of maxima that we obtained correspond to the values in the published data with differing by 1–3 K. The specific heat discontinuity of $TlInS_2$ amounted to approximately 10%; however, the other anomalies alter not only the maxima but also a small minimum by 4–5% of the regular values.

On the other hand, there are plenty of reports for the presence of the structural phase transitions in $TlInS_2$ as observed from the use of several experimental techniques. Firstly, dielectric constant measurements of $TlInS_2$ [9] established that $TlInS_2$ exhibits a sequence of structural phase transitions to incommensurate (IC) and commensurate (C) phases. The transition to the IC phase, according to neutron [10] and X-ray scattering investigations [11], occurs at ∼216 K. It is associated with condensation of a soft mode at the point in the Brillouin zone with q_i (δ, 0, 0.25), where δ is the incommensuration parameter (δ = 0.012). Also, $TlInS_2$ exhibits the IC–C phase transition at the temperature of $T_c \sim 204$ K with condensation of the soft mode at q_c = (0, 0, 0.25), which accompanied by the quadrupling of the unit cell volume along the direction of perpendicular to the layers.

Furthermore, the appearance of the ferroelectric soft mode with Curie temperature at about $T_c \sim 200$ K was understood from the result of submillimeter spectra and dielectric constant measurements [12]. A number of C_p anomalies that we determined from DSC measurements coincide with the aforementioned temperatures for the phase transitions.

On the other hand, specific heat data of $TlGaS_2$ have been calculated from DSC data in the range of 130–260 K. Figure 4 shows the temperature dependence of heat capacity for $TlGaS_2$. Again C_p values have been extrapolated on both higher and lower temperatures using the data in [5] for the normal heat capacity curve progression. As shown in figure 4, C_p rapidly decreases in 170–185 K range and stays almost stable in 185-200 K. Then the data show continuous increase in 210–240 K. We have obtained three maxima at 139, 177, and 241 K. In the previous studies, Krupnikov et al. [2] investigated the temperature-dependent of specific heat capacity of pure and doped single crystals of $TlGaS_2$ using relaxation method in the range of 60–280 K. They observed six anomalous at 73.5, 91, 101, 114, 133.5, and 187 K. In spite of this, Abdullaeva et al. [5], using adiabatic calorimeter method, observed no abrupt anomalies and stated a typical C_p behavior of layered semiconductors. Moreover, optical investigations [13] demonstrated anomalies in $TlGaS_2$ occur at temperatures T_l= 180-190 K, T_h= 240–250 K.

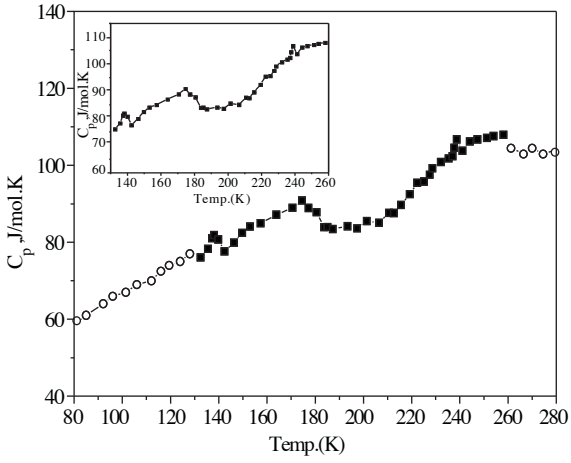

Figure 4. Temperature dependence of the specific heat of $TlGaS_2$ single crystal. ○ indicates the values taken from [5] to extrapolate C_p curve in the range 80–280 K. C_p values determined using DSC are represented by ■.

Our last two maxima temperatures are in agreement with the given intervals T_l and T_h in [13]. Authors of [13] considered that successive phase transitions occur around 180–190 and 230–260 K since the temperature ranges of the Raman line splitting, exciton absorption peak shift anomalies and the disappearance of the memory effect agree well. It is worth mentioning that no sufficient evidence have been revealed for phase transitions of $TlGaS_2$ up to now once we compare $TlGaS_2$ with its isostructural compounds, $TlInS_2$ and $TlGaSe_2$. On considering anomalies of the temperature dependence of C_p that we obtained in around 177, and 241 K, it may be supposed that some phase transformations occur in $TlGaS_2$ at these temperatures. At this point, it is important to state that the investigation of the structural phase transition in detail such as to give information about active atomic groups, local symmetry changes and possible atomic displacements during phase transformations at these compounds is beyond the scope of this study. In our previous work [14], we investigated structural phase transitions using electron paramagnetic resonance (EPR) technique and we observed that $TlInS_2$ crystal exhibits very interesting peculiarities around the mentioned phase transition temperatures above. Also we will publish our results of low temperature EPR study of $TlGaS_2$ in order to investigate the structural phase transitions in detail [15].

4. Conclusion

Heat capacities of $TlInS_2$ and $TlGaS_2$ have been investigated using DSC method as a new technique for these crystals. A sequence of oscillatory maxima has been observed on C_p behavior of $TlInS_2$ with little differences from the other published anomalies. These differences can depend on a couple of reasons; such as the quality of the crystal and growth conditions. It should be mentioned that the dependence of the modulation on temperature in the range of 190–220 K, where three maxima taking place, can be explained on the basis of assumptions of existing partial devil's ladders (long-periodic commensurable phases) in the vicinity of incommensurable phases [16, 17]. We should point out that, even though there is a fluctuation-type anomaly of C_p in the neighboring of incommensurate phase temperature and obvious maximum at commensurate phase temperature, it is not possible to obtain the profiles of the anomalies in reality. This is in coincidence with the theory that predicts a first order phase transition from a symmetric phase to an incommensurate phase and to a commensurate phase [18, 19]. On the other hand, C_p anomalies of $TlGaS_2$ we obtained have a good agreement with temperature intervals of the anomalies determined by optical investigations [13]. As a conclusion of all these obtained results and comparisons with published data, it can be stated that DSC technique might be considered as a potential method of studying thermal properties of the layered semiconductors.

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