Heat Capacity Anomalies of TlInS$_2$ and TlGaS$_2$ Single Crystals Detected by Differential Scanning Calorimetry (DSC)

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Received 04.10.2007

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.
PACS: 74.70.Dd, 65.40.Ba, 64.60.-i

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 (≥ 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 $\beta = 100.70^\circ$ for TlInS$_2$; and $a = 1.031$, $b = 1.043$ and $c = 1.507$ nm and $\beta = 99.60^\circ$ for TlGaS$_2$. XRD patterns of both the samples are shown in Figure 1.

![X-ray powder diffraction (XRD) patterns of (a) TlInS$_2$ and (b) TlGaS$_2$ single crystals.](image)

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).](image)

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 ■.](image)

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...
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 TlInS₂. 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 TlInS₂ 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 TlInS₂ as observed from the use of several experimental techniques. Firstly, dielectric constant measurements of TlInS₂ [9] established that TlInS₂ 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 $q_i (\delta, 0, 0.25)$, where $\delta$ is the incommensuration parameter ($\delta = 0.012$). Also, TlInS₂ 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 TlGaS₂ have been calculated from DSC data in the range of 130–260 K. Figure 4 shows the temperature dependence of heat capacity for TlGaS₂. 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 TlGaS₂ 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 TlGaS₂ occur at temperatures $T_l = 180-190$ K, $T_h = 240–250$ K.

![Figure 4](image_url). Temperature dependence of the specific heat of TlGaS₂ 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 TlInS$_2$ 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.

Acknowledgments

Laboratory portion of this work was carried out at Ankara Nuclear Research and Training Center. The author thanks to Dr. Sukru Cavdar and Mr. Haluk Yucel for their laboratory assistants.

References


