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THERMOANALYTIC INVESTIGATIONS OF THE SEMICONDUCTOR $TlSbSe_2$

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SUMMARY

Differential thermal analyses (DTA), dilatometric, and X-ray powder diffraction studies of the semiconductor $TlSbSe_2$ show the existence of three phases. Between the high temperature (HT) phase with statistically distributed cations and the room temperature (RT) phase, an intermediate phase with partial cation order (PO phase) was found. The phase transition from HT to PO phase is of first order, where both displacement and atomic exchange processes occur. The phase transition from PO to RT is of higher order, accompanied by diffusion processes, which increase the order of the cations. The completely ordered RT phase can be obtained by long time annealing (e.g. four weeks at 350 °C). Another method to obtain the well ordered RT phase is to pass repeatedly the phase transitions without melting the material. The coefficients of thermal expansion have been measured for the temperature range from 25 to 300 °C.

INTRODUCTION

The compound $TlSbSe_2$ melts congruently at 450 °C (ref. 1) and performs two phase transitions. The orthorhombic HT phase (380 to 450 °C) is isotypic with TlI (B33 structure type). The Tl and Sb atoms are statistically distributed at the cation positions (ref. 2). Complete ordering of these atoms takes place in the RT phase, which crystallizes with a monoclinic superstructure. Both phases are separated by a third metastable phase which is envisaged to exhibit partially ordered cations (the PO phase). The occurrence of the latter phase strongly depends on the kinetics of the ordering. The lattice parameters a and b of the orthorhombic PO phase are doubled with respect to the corresponding parameters of the HT phase. X-ray diffraction patterns, which are displayed in Fig. 1, verify the existence of the three phases.

The phase transitions were investigated by DTA, dilatometric measurements, and X-ray powder diffraction.

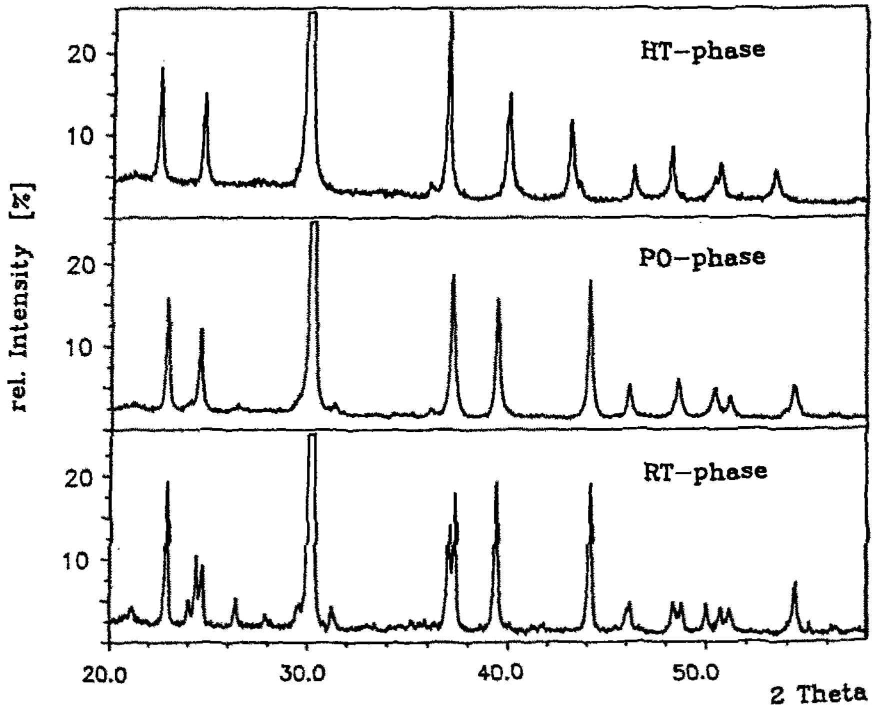

Fig. 1. Powder diffraction patterns of the HT, PO, and RT phase.

EXPERIMENTAL

The DTA studies were performed using a HERAEUS TA 500 system. The material, enclosed in a quartz ampoule, was heated and cooled down with a rate of 5 K/min.

Dilatometric data were recorded by a NETZSCH 402 TMA system keeping the crystal in nitrogen atmosphere. We prepared rectangular crystals of the size 5 × 4 × 3 mm^3, orientated in the setting of the PO phase. To compare DTA and dilatometric measurements the same heating and cooling rate was used for both methods.

X-ray powder diffraction patterns were recorded by a STOE powder diffraction system, using CuKα_1 radiation. These examinations were carried out at room temperature. Diffraction patterns of HT and PO phase were obtained by quenching the material (enclosed in quartz ampoules) from higher temperature in liquid nitrogen.

EXPERIMENTAL RESULTS AND DISCUSSION

The lattice parameters of the quenched orthorhombic HT and PO phase were determined to a = 4.514, b = 11.958, c = 4.197 Å for the HT phase; and a = 9.137, b = 23.692, c = 4.102 Å for the PO phase. The RT phase crystallizes with a monoclinic structure, a = 9.139, b = 4.096, c = 12.745 Å, and $\beta = 111.7^{0}$.

Fig. 2 shows, additionally to the melting and solidification peaks, two thermal effects of one phase transition, in both the heating and cooling curves. The phase transition is strongly dependent on the cooling rate. For cooling rates of 1 K/min and 8 K/min the transformation from the HT phase to the PO phase occurs at 325 ^{0}C and 295 ^{0}C, respectively. The heating rate does not influence the temperature of the phase transition.

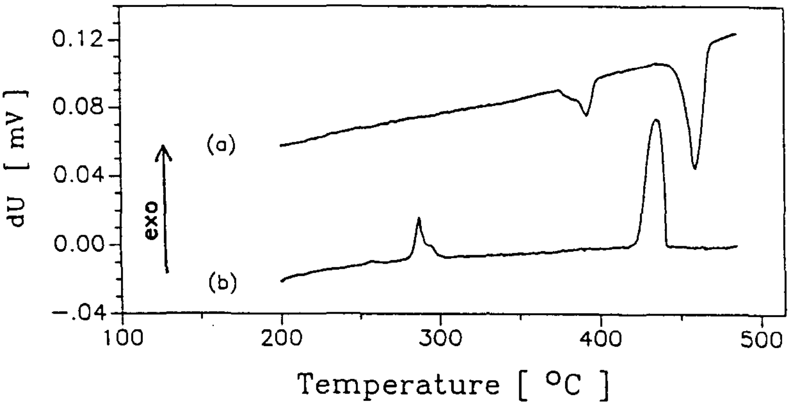

Fig. 2. DTA diagrams: (a) phase transitions and melting point; (b) solidification point and phase transitions.

We consider the main peak of the two thermal effects of this first order phase transition as a displacement of the structure, whereas we assume the smaller peak to be the result of cation exchange processes.

The diffusion process from PO to RT phase is not indicated by the DTA diagram. This process takes place in a continuous way and should be a phase transition of higher order.

Without melting the material, both observed effects are clearly separated from each other in the cooling curve (Fig. 3.1.b). In comparison to Fig. 2 the smaller peak is shifted to lower temperatures. Repeating the procedure (heating up to 410 ^{0}C and cooling down to 210 ^{0}C) the temperature difference between the adjacent thermal effects decreases. After 50 repetitions the two different peaks could not be resolved at all.

We correlate the position of the smaller peak with the degree of cation order. The shift of the small peak to the main peak in Fig. 3 is interpreted as an increased cation order which is accompanied by a decreased symmetry. Correspondingly the orthorhombic PO phase changes continuously into the monoclinic RT phase. This mechanism causes a characteristic line splitting, as represented in Fig. 4.

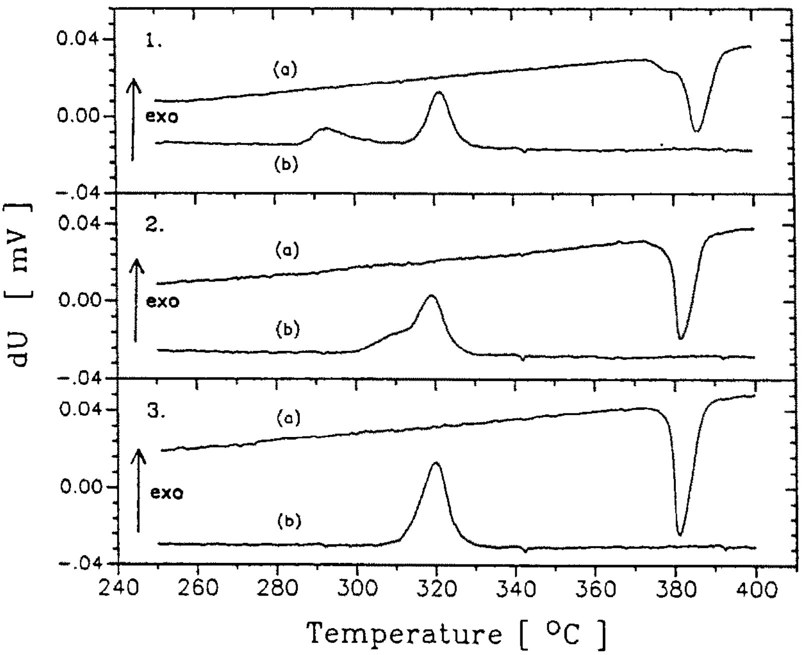

Fig. 3. DTA curves of the compound TLSbSe$_2$:
1. heating up and cooling down the material once;
2. heating up and cooling down the material twice;
3. after repeating this procedure 50 times.

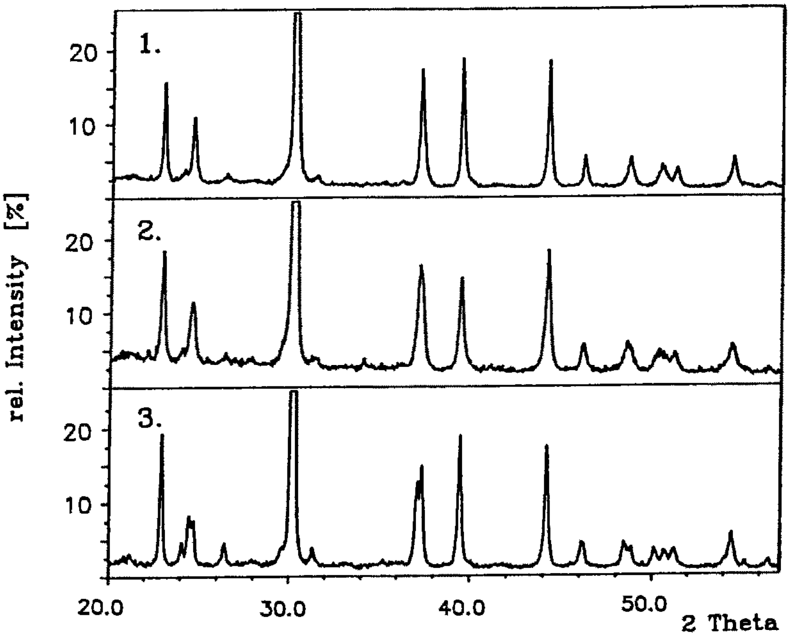

Fig. 4. Powder diffraction patterns of TlSbSe$_2$, corresponding to the processes of fig 3.

The dilatometric investigations show linearity of thermal expansion in the range from 25 to 300 °C. The expansion coefficients are determined to $\alpha_{11} = 34.9$, $\alpha_{22} = 22.4$ and $\alpha_{33} = 20.8$ $[10^{-6}/K]$.

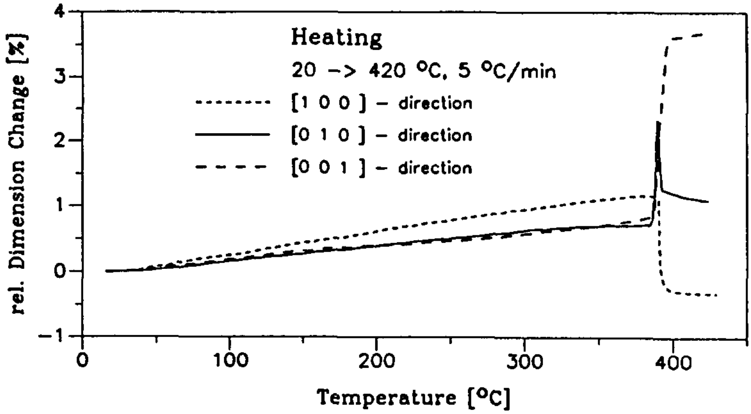

Fig. 5. Dilatometric diagrams of heating $TlSbSe_2$ in different directions.

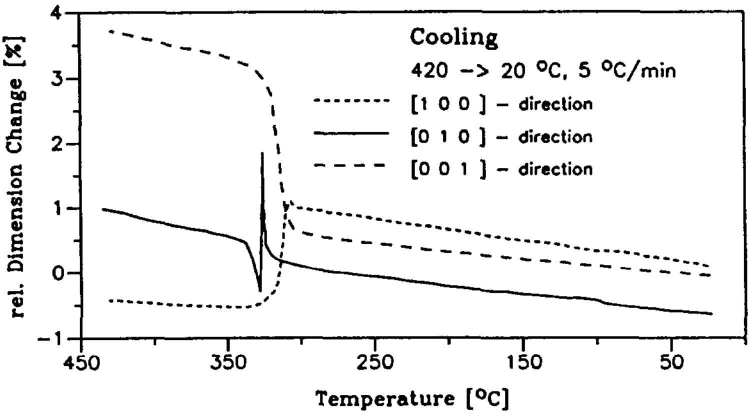

Fig. 6. Dilatometric diagrams of cooling $TlSbSe_2$ in different directions; all measurements were performed in the orthogonal main directions.

In the heating procedure the lattice dimensions decrease in [1 0 0] and increase in [0 0 1] at the phase transition temperature of 380 °C. Perpendicular to the atomic layers ([0 1 0] direction) an unusual behaviour is discovered.

During the cooling procedure the lattice dimensions increase and decrease in [1 0 0] and in [0 0 1] at 320 °C, respectively. Again an unusual behaviour in [0 1 0] can be noticed. The temperature where it appears (335 °C) is supposed to be in accordance with the main peak of the DTA cooling curve (3.1.b).

The changes in the dimension of the $\vec{a}$ and $\vec{c}$ directions correspond with the results, which we received by X–ray analysis of the HT and RT phase (ref. 3).

CONCLUSIONS

Thermoanalytic and X–ray results prove, that the compound $TlSbSe_2$ has both first and higher order phase transitions. The phase transition of first order shows two different effects: displacement of the lattice and atomic exchange processes. We connect the main peak of these two DTA effects with a displacement of the lattice. The smaller peak is supposed to be the result of starting ordering effects. These atomic exchange processes could explain the kinetic inhibition of the retransformation from the HT to the PO phase. At the re–transformation the influence of the process time shows to be important. That can be seen in the delayed dimension changes in [1 0 0] and [0 0 1] after change in [0 1 0]. The phase transition from PO to RT phase is a transition of higher order, which cannot be observed in the DTA diagrams, but can be proved by the line splitting in the X–ray powder diffraction patterns (decrease of symmetry).

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