

Phase transformation in the system $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$

K. Chrissafis¹, E. S. Vinga¹, M. Ozer^{1,2}, K. M. Paraskevopoulos*¹, and E. K. Polychroniadis¹

¹ Solid State Physics Section, Department of Physics, Aristotle University of Thessaloniki, GR 54124, Thessaloniki, Greece

² Dep. of Mathematics and Computer, Instabul Kultur University, Turkey

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TlBiTe_2 and TlBiSe_2 -that are ternary analogs of the IV-VI semiconductors-, although they crystallize in the same space group $R\bar{3}m$ (D_{3d}^5), exhibit different behaviour during heating. The observed phase transformation depends on Se content (x) in the system $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ and the transformation disappears by increasing Se content after a certain value ($x=0.25$). This dependence is examined through the analysis of the DSC non-isothermal measurements and an attempt for the explanation of the observed behaviour is undertaken through the consideration of off - center atoms.

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1 Introduction

TlBiTe_2 and TlBiSe_2 are narrow gap semiconductors belonging to the group of III-V-VI ternary compounds of the general type TlBiX_2 ($X=\text{Te}, \text{Se}, \text{S}$). They are ternary isoelectronic analogs of the IV-VI semiconductors and often referred to as pseudo-lead chalcogenides because of their close electronic relation to the compounds PbTe , PbSe and PbS (since Tl and Bi precede and follow Pb in the Periodic Table). The members of this family possess interesting properties and have found applications as optoacoustic detectors, IR detectors in thermoelectric devices and non-destructive switching and memory elements [1-5]. Both crystallize in $R\bar{3}m$ (D_{3d}^5) space group (rhombohedral structure) and can be considered as having a nearly fcc structure of the NaCl type, with an elongation along the cubic [111] direction. Crystallographically they can be described by a non-primitive, almost cubic, rhombohedral cell with lattice parameter $a=0.647\text{nm}$ and angle $\alpha=88.5^\circ$ for TlBiTe_2 [6] and with $a=0.616\text{ nm}$ and $\alpha=87.21^\circ$ for TlBiSe_2 . TlBiTe_2 exhibits a phase transformation from the rhombohedral (D_{3d} , low temperature phase) to the cubic (O_h , high temperature phase) symmetry [7]. The kinetic analysis of DSC measurements combined with the Electron Microscopy findings [8], supported also by FTIR spectroscopy ones [9], has proved that the phase transformation of TlBiTe_2 is a multiple-step displasive - martensitic type transformation. On the other side TlBiSe_2 presents no phase transformation with temperature.

$\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ system is an anion-substituted quaternary solid solution and from the preliminary studies of transport and optical properties [10] has been found that it presents an anomalous behavior at x with a value close to 0.25. It was found that all members of the family show a rather linear dependence of their properties on x , except for $\text{TlBi}(\text{Te}_{.75}\text{Se}_{.25})_2$ which deviates from this regularity both in its electrical and optical behavior [10].

The existence of phase transformation at the one end of the system ($x=0$) and its disappearance at the other end ($x=1$), as well as the above mentioned characteristic behavior of the quaternary system at a specific

* Corresponding author: e-mail: kpar@auth.gr

concentration, drove us to examine thoroughly this group of material, in order to understand the phase transition of $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ and find out how these are combined to the transport behavior of plasma shifting from one end to the other.

2 Experimental

$\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ compounds (crystals with different stoichiometries) were grown from the elements (of 99,999% purity) by the Bridgman – Stockbarger [5] method. Transmission Electron Microscopy (TEM) reveals always a single phase material. Its composition and homogeneity were confirmed by EDS analysis in a Scanning Electron Microscope (SEM). Accurate measurements of electron diffraction patterns taken from all above mentioned materials indicate that their lattice parameters follow the Vegards law. This indicates that the substitution of the Te atoms by the Se ones form a continuous series of solid solutions.

The thermal behavior of $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ was studied using a Setaram DSC 141 calorimeter. The temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and melting enthalpies of high purity standards, i.e. In, Sn and Zn. The $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ crystals were powdered and the samples, about 100 mg in weight, were thermally treated using aluminum crucibles under a constant nitrogen flow. All the DSC measurements were non-isothermal and consisted of a complete thermal cycle (heating and cooling) with the same heating/cooling rate (β). The rates varied from 2.5 to 18K/min in different measurements. The same sample was used for all the heating-cooling cycles. However, in order to testify the reproducibility of the results, the whole set of measurements was carried out on different samples.

The reflectivity measurements in the plasma edge region were performed with the Bruker IFS113V spectrophotometer, using the reflectivity unit, and with the unpolarized light nearly perpendicular to the sample surfaces, that were freshly prepared.

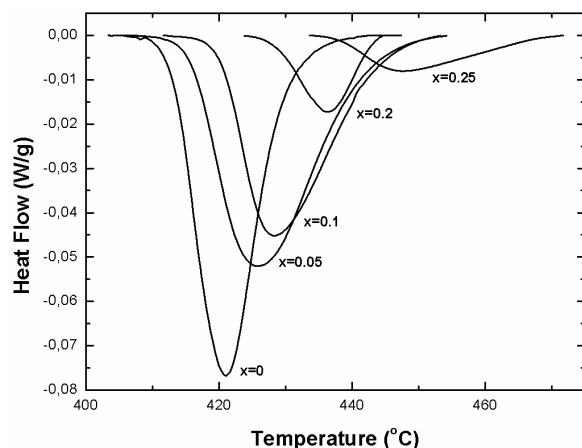


Fig. 1 Selenium content dependence of DSC curves of the $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ on heating ($\beta=18\text{K/min}$).

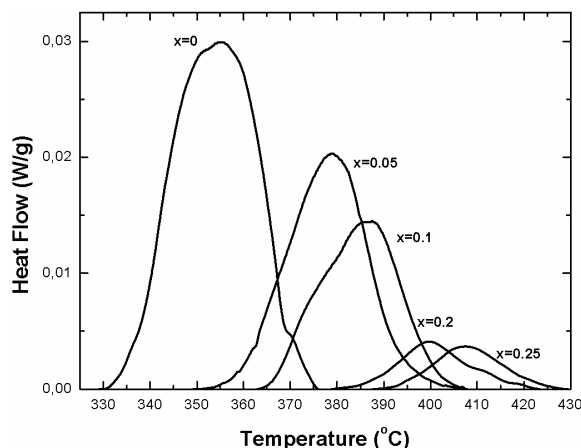


Fig. 2 Selenium content dependence of DSC curves of the $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ on cooling ($\beta=10\text{K/min}$).

3 Results and discussion

In all thermograms of the material $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ with Se concentration between $x=0.0$ and $x=0.25$ one peak was observed during heating and one during cooling process. During the heating procedure (Fig. 1) with the same heating rate for all the stoichiometries, it is observed that as the number of Se atoms -that substitute Te- increases, the phase transformation of the material shifts towards higher temperatures (for Se concentration $0 \div 0.25$, the shift in the transformation temperature comes up to $26\text{ }^\circ\text{C}$ from $421\text{ }^\circ\text{C}$ to $447\text{ }^\circ\text{C}$).

The same behavior is also observed during the cooling procedure (Fig. 2) where, as the number of Se atoms increases, the phase transformation appears at higher temperatures (e.g. when $0 \leq x \leq 0.25$ there is a shift towards higher temperatures that comes up to 50°C). At every DSC experiment with Se content larger than 0.25, no thermal phenomenon was recorded during either heating or cooling.

As in the case of the ternary compound TlBiTe_2 [7], the system $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ ($0 \leq x \leq 0.25$) during a complete heating-cooling cycle (and for a certain stoichiometry x) exhibits a hysteresis in the transformation temperature, which, for example, is about 53°C for the case of $\text{TlBi}(\text{Te}_{0.95}\text{Se}_{0.05})_2$ (Fig. 3 – heating cooling cycle).

It is observed (Table 1) that the hysteresis in the transformation temperature (T_h), for a constant heating-cooling rate, depends significantly on the content of Se atoms in the material, and decreases as the number of Se atoms substituting Te increases. In Fig. 4 are shown, the variation of the transformation temperature in relation to the Se concentration during heating T_{p-h} and cooling T_{p-c} , as well as the variation of the transformation temperature hysteresis (T_h) with stoichiometry. It is experimentally observed that the temperature of the phase transformation depends on the number of Se atoms substituting Te.

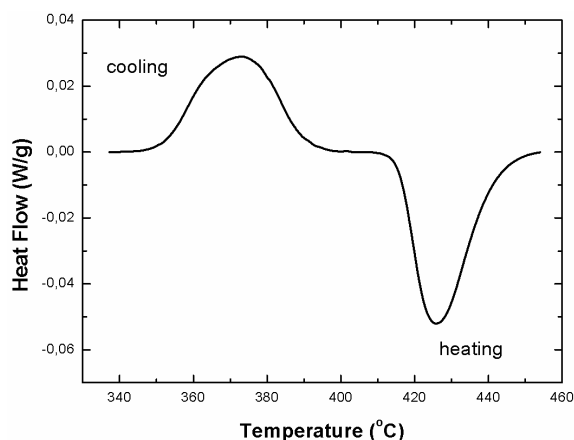


Fig. 3 Thermoanalytical curves of $\text{TlBi}(\text{Te}_{0.95}\text{Se}_{0.05})_2$ on heating and cooling with the rate of 18K/min.

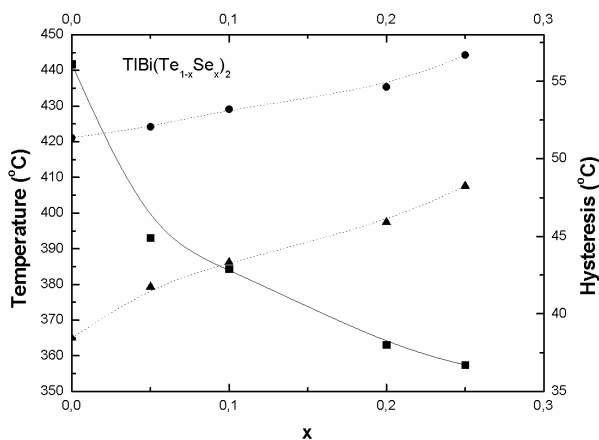


Fig. 4 Concentration dependence of transformation temperature during heating T_{p-h} (circles) and cooling T_{p-c} (triangles). The squares indicate the concentration dependence of the transformation hysteresis T_h .

Table 1 The hysteresis T_h of the peak temperature for a constant rate and the transformation enthalpy (ΔH_{tr}) for different solid solutions $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$.

Concentration (x)	Hysteresis T_h ($^\circ\text{C}$)	ΔH_{tr} (J/g)
0.00	56.1	3.6
0.05	44.9	3.0
0.10	42.9	2.5
0.20	38.0	0.5
0.25	36.7	0.45

On the other hand, for every concentration x , the hysteresis in the transformation temperature depends on the cooling rate, it is observed in all the complete cycles taken at different rates, and increases as the heating rate β increases.

In Fig. 5 are shown the DSC curves (endothermic peaks) of the typical $\text{TlBi}(\text{Te}_{0.95}\text{Se}_{0.05})_2$ samples obtained at different heating rates ($\beta=2.5, 5, 10$ and 18 K/min). It is observed that increase in the heating rate ($\beta=5 \div 18$ K/min) is not followed by a corresponding shift in the position of the peak maximum (T_{p-h}), the position of

the endothermic peak remains almost constant with increasing heating rate. Only, for small value of β (2.5 K/min) the peak maximum temperature (T_{p-h}) shifts slightly to lower temperatures with the rate decreasing. Consequently, as for heating rates higher than 5K/min the position of the endothermic peak remains constant with increasing heating rate, a first conclusion can be extracted directly from the DSC experimental results, that this phase transformation is almost an athermally-activated process during heating. The transformation enthalpy was evaluated from the area below the endothermic peak for each heating rate and its mean value for this concentration is found as 3.0 ± 0.3 J/g.

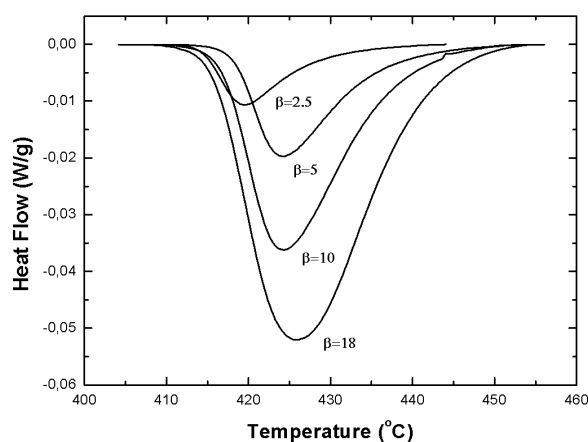


Fig. 5 The influence of the heating rate β on the thermoanalytical curves of $\text{TlBi}(\text{Te}_{0.95}\text{Se}_{0.05})_2$ ($\beta = 2.5 \div 18 \text{K/min}$).

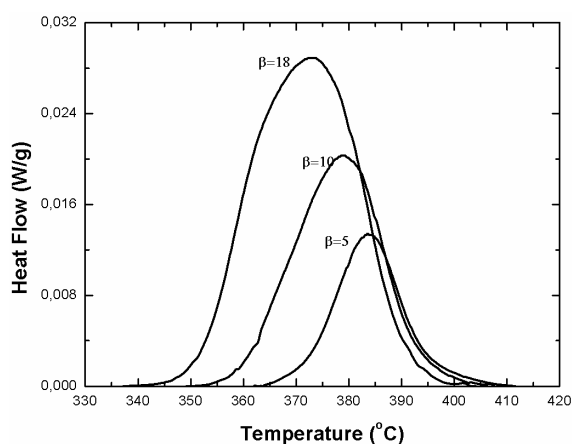


Fig. 6 Thermoanalytical curves of $\text{TlBi}(\text{Te}_{0.95}\text{Se}_{0.05})_2$ recorded at different cooling rates β ($\beta = 5 \div 18 \text{K/min}$).

In Fig. 6 are shown the thermograms (exothermic peaks) of the $\text{TlBi}(\text{Te}_{0.95}\text{Se}_{0.05})_2$ samples taken during cooling at different rates ($\beta = 5, 10$ and 18K/min) that correspond to the endothermic curves in Fig.5. It can be seen that there is a significant shift in the position of the peak maximum (T_{p-c}) towards lower temperatures with the increase of the cooling rate in contrary to the heating where the transformation temperature remains stable. The same DSC results (on both heating and cooling process) are also derived from all the examined stoichiometries ($0 \leq x \leq 0.25$).

It is clear that there is a different behaviour between the heating and the cooling process. An explanation could be that during cooling, the lattice distortion caused by the transformation from the cubic to the rhombohedral phase creates stresses, which are absorbed within a certain period of time. As the rate increases, the crystal has to undergo the same change in a shorter time period. The limited time dependent ability of the crystal to absorb the stresses creates most probably the shifting of the peak temperature during cooling.

The values of the transformation enthalpy ΔH_{tr} for every concentration are shown in Table 1. We observe that the transformation enthalpy decreases monotonically with the increase of the Se concentration, and when $x > 0.25$ it tends to zero, since no phase transformation can be traced any more.

The transformation can not be kinetically analyzed with the isoconversional method [12-14] or other similar methods which demand the existence of at least three different heating rates that exhibit a variation in the position of the transformation temperature. That is because the transformation of this system is basically an athermal one. For this reason, we investigated the possibility of defining the conversion function $f(\alpha)$ and the activation energy (E) with the "model fitting method" [15]. This model was applied for each rate independently.

The results of the fitting were good enough for all the heating rates and the form of the conversion function, obtained by fitting is $f(\alpha) = (1-\alpha)^n$, with exponent value n equal to 2.9 and the region of values of activation energy (E) were of the same order of magnitude for all the heating rates (about $E = 2500 \text{kJ/mol}$). However, the estimated value of the activation energy is too large to be accepted, and this fact may be related with the

inability of producing trustworthy results by the application of the model fitting method for just one heating rate. It is known [16] that in specific cases, single heating rate methods can give reasonable kinetic triplets (E , $f(a)$, A) but they are useless in the case when the actual reaction model differs from the assumed one or in the case of multi step reaction.

The conclusions made by the study of the thermograms for different heating and cooling rates for all the stoichiometries correspond to those made in the study of TlBiTe_2 [8].

In Fig. 7 is presented the dependence of the plasma frequency ω_{p1} on Se content. The plasma frequency decreases with increasing Se content till the characteristic Se value ($x=0.25$) providing evidence for the lowering of the free carriers concentration (number) and then proceeds in the opposite direction increasing ω_{p1} value with increase of Se content. The same behaviour has been observed at the material of the IV-VI type, especially in quaternary alloy $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ [17]. By Hall measurements on these materials for the calculation of the carrier concentration in relation to the stoichiometry, it was observed that the carrier concentration exhibits a minimum at a characteristic Se content value x_c .

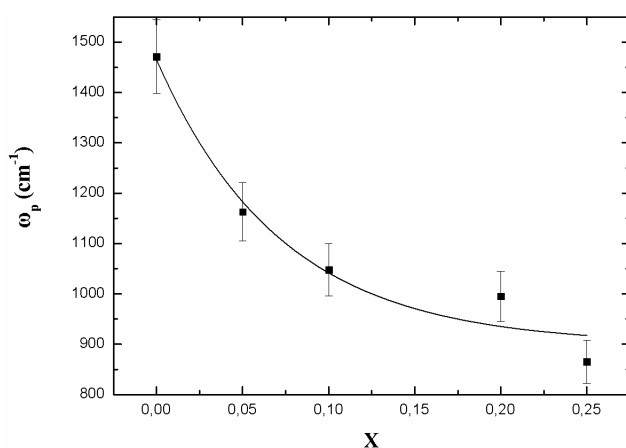


Fig. 7 Dependence of the plasma frequency ω_{p1} on Se content in $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$. Bars indicate deviations due to measurements on different samples of the same temperature.

The results obtained in this work enable us to understand better the mechanisms by which the introduction of the Se atoms (replacing the Te ones) influence the phase transition in TlBiTe_2 . The dependence of T_{p-h} on the Se content in $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ is shown in Figure 4. Taking into account that ionic radii of Se^{2-} is smaller than the Te^{2-} one ($r_{\text{Te}^{2-}} = 2.11 \text{ \AA}$, $r_{\text{Se}^{2-}} = 1.93 \text{ \AA}$) [18] it can be considered that in their entering in the Te sites, Se atoms become noncentral (off-center), and as in analogy to the S atoms in $\text{PbTe}_{1-x}\text{S}_x$ [19] the substitutional Se ions are unstable to the displacement from the regular anion sites. This is due to the smaller ionic radius of the Se^{2-} compared with that of the Te^{2-} . The main reason for the off-center instability of small atoms in ionic crystals is the instability of the decreased repulsive forces to oppose the action of the polarization forces that tend to displace the ion from its centrosymmetric position. It is known that off-center ions may be displaced from a lattice site to several energetically equivalence positions, between which thermal and tunnel jumps occur. The local dipoles produced by off-center Se ions mutually interact through the lattice polarization field (optical phonons) of the TlBiTe_2 medium as well as via the pure dipole-dipole coupling. If the overlap of wave functions of different off-center positions is large, the tunneling may depress the phase transition completely. In the theory of phase transitions this situation is described qualitatively by Ising model with tunneling.

To explain the shift of T_{p-h} with increasing substitutional disorder we suppose that Se in TlBiTe_2 (as off-center atom) is moving in the multi-well potential with low height of barrier separating different minima. The substitutional disorder can influence not only the energies of different potential wells of off-center ions, but also the distance and potential barrier height between different off-center positions. The substitution of large neighboring atoms with smaller ones increases both the distance between different positions of off-center atom and the height of the barrier, thus decreasing the tunneling rate of off-center Se ion and resulting in T_{p-h} increase.

The observed behavior in the plasma frequency in the $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ solid solution where each off-center atom polarized by its local environment, can be attributed to a competition that occurs between indirect dipole-dipole interaction that orders dipoles and random fields that act in the opposite way. When the random fields are strong they can destroy the long range order completely and the dipolar disorder state appears [20].

4 Conclusions

The phase transformation in the system $\text{TlBi}(\text{Te}_{1-x}\text{Se}_x)_2$ occurs only within the region of $0 \leq x \leq 0.25$ and is an almost athermal activated process. In this system the Se atoms entering in the Te sites become non-central and unstable to the displacement from the regular ion sites. The complete depress of the phase transition is attributed to the tunnelling as the overlap of wave functions of different off-center positions is large.

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