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Composition, structure and properties of $PbSb_2Te_4$ crystals grown by the Chokhralsky method

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Abstract. This paper presents the results of X-ray diffraction and electrophysical studies of $PbSb_2Te_4$ crystals grown by the Chokhralsky method. The phase composition and crystal structure of ingots, including those doped with a donor admixture of copper, are discussed from the qualitative and quantitative perspectives. The samples are a periodic structure. They are multiphase, with $PbSb_2Te_4$ and Sb_2Te_3 as dominant phases. The presence of intrinsic electrically active point defects causes a high concentration of holes $p \approx 3.2 \times 10^{20}$ cm^{-3}. The temperature dependences of the kinetic coefficients indicate a complex structure of the valence band. Impurity atoms occupy vacancies in the metal sublattice during alloying and form chemical compounds with Sb and Te atoms.

Keywords: semiconductor, $PbSb_2Te_4$, thermoelectricity, topology insulator, tetradymites, doping, kinetic coefficients, nanocomposites, X-Ray diffraction analysis, temperature dependences of the Hall coefficient, valence band structure

Introduction

The research and development of materials exhibiting unique electronic properties is the most intensively developing field of solid-state physics. The integration of such materials into high-tech industries is the key to creating a new generation of devices with improved performance compared to existing ones.

A group of narrow-bandgap semiconductors with band gap inversion, so-called three-dimensional topological insulators (TI), is one of new electronics materials. These materials are characterized by the properties of an insulator (or semiconductor) in bulk, along with gapless states on the surface, which ensure the flow of spin-polarized current across the surface without energy loss. The use of unusual properties of the TI surface is promising in spintronic, magnetoelectric devices and for the quantum computing (Jayan Rakesh 2022; Wang et al. 2016).

Among the currently discovered materials with TI properties, binary layered compounds Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 are the most studied, both experimentally (Chen et al. 2009) and theoretically (Aguilera et al. 2013). A promising area of search for new materials with the ability to control their electronic structure are triple and quadruple compounds based on chalcogenides. Triple-layered tetradymite-like compounds $PbSb_2Te_4$ from the quasi-binary $A^{IV}B^{VI}$-$A^{V}B^{VI}$ system (A^{IV} — Ge, Sn, Pb; A^{V} — Bi, Sb; B^{VI} — Te, Se) are of particular interest. In such compounds, which have a layered structure formed by septuple layers, protected surface states can be localized in both surface and subsurface blocks (Hattori et al. 2023).

In addition, $PbSb_2Te_4$ could be used as a potential material for thermoelectric energy conversion. This material is the result of synthesis based on two main components of low- and medium-temperature thermoelectrics respectively, lead telluride PbTe and antimony telluride Sb_2Te_3. For effective utilization of such compound as a topological insulator and for thermoelectric energy conversion, a detailed study of the features of its electronic structure and current carrier scattering mechanisms is needed.

Modern theoretical calculations of the energy spectrum of ideal crystals are also important for assessing the potential use of these materials.

Papers studying the electronic structure of TI using first principles theoretical methods are most widely presented in literature (Menshchikova et al. 2013). Electronic structure is usually calculated using the formalism of density functional theory by the pseudopotential method and the full-potential method of linearized coupled plane waves. A generalized gradient approximation describes the exchange-correlation energy, taking into account scalar-relativistic corrections. The spin-orbit interaction is considered by the method of the second variation.

However, theoretical calculations do not take into account the characteristics of the grown tetradymite-like crystals. The high concentration of point defects, including vacancies along with the structural and phase complexity of massive samples obtained by the Czochralski peritectic reaction method, has a significant impact on the actual location of the Fermi level. It is also known that the gaps between septuple layers can serve as natural 'containers' for the accumulation of impurities during synthesis, which leads to fluctuations in their geometric dimensions. The magnitude of the fluctuation depends on the type of impurity and on the presence of conglomerates of impurity atoms in the gap. That is why the electronic structure of real $PbSb_2Te_4$ crystals cannot be understood without an experimental study of their structure and electrophysical properties.

Objects of research

The paucity of investigations into our material can be explained by the technological difficulties of obtaining it. The synthesis of crystals occurs through the peritectic reaction $PbSb_2Te_4 \rightleftarrows PbTe + Sb_2Te_3$ and is complicated by the need to maintain an equilibrium in a narrow temperature range. The first small samples of layered composite material were grown using the vertical Bridgman method by the team of L. E. Shelimova at the A. A. Baykov Institute of Metallurgy of the Russian Academy of Sciences (Shelimova et al. 2004). The Chokhralsky method with continuous feeding of the synthesized crystal made it possible to obtain samples of a larger size and higher perfection in the direction of the trigonal axis ($\bar{3}$). Cylindrical crystals with a diameter of 20 to 30 mm and a length of about 50–100 mm were grown in the direction of growth. Sufficiently large ingots were cut into samples up to 4×4×20 mm in size and oriented, respectively, in the cleavage plane and along the direction of the inversion-rotary axis $\bar{3}$. Cu-doped samples with $(PbTe+Sb_2Te_3)_{0.9995}Cu_{0.0005}$ and $(PbTe+Sb_2Te_3)_{0.999}Cu_{0.001}$ stoichiometry were also grown and later investigated.

Experimental results and their discussion

The obtained compounds were initially examined by the X-ray diffraction of the single crystal planes using an automatic diffractometer DRON-UM (CuKa-radiation). Finally, the $PbSb_2Te_4$ ingots have rhombohedral symmetry with an inversely rotated axis $\bar{3}$. However, a hexagonal unit cell containing three rhombohedra is more convenient to study (Fig. 1). It has the following parameters: a = 0.4350 nm and c = 4.1712 nm. The $PbSb_2Te_4$ compound has a 21-layer lattice and contains three seven-layer TeSbTePbTeSbTe packages, ordered in the direction of the hexagonal axis c (Shelimova et al. 2008), which is in good correlation with the results of numerical calculations of ideal crystals.

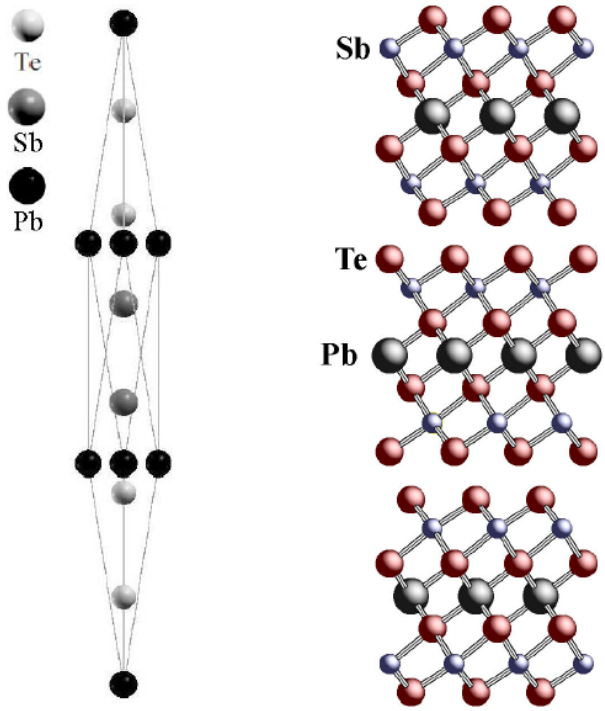

Fig. 1. The crystal structure of $PbSb_2Te_4$ in the form of a rhombohedral unit cell (left) and a hexagonal cell (right)

Further X-ray diffraction studies using a Bruker D8 Advance diffractometer in the Bragg–Brentano geometry (Cu-Ka radiation with a nickel filter) revealed the complex structure of the material and the existence of two phases: the basic $PbSb_2Te_4$ (70–80%) and Sb_2Te_3 (up to 20–30%) with rhombohedral symmetry, the spatial group R3m and the parameters of a hexagonal lattice about a = 0.426 nm, c = 3.045 nm. (Fig. 2). Also observed is the PbTe phase, mainly oriented perpendicular to the $\overline{3}$ axis, as well as traces of phases containing Sb and Te atoms.

Thus, the ingots are a periodic structure consisting of septuple and quintuple layers of $PbSb_2Te_4$ and Sb_2Te_3 compounds oriented along the trigonal axis $\overline{3}$.

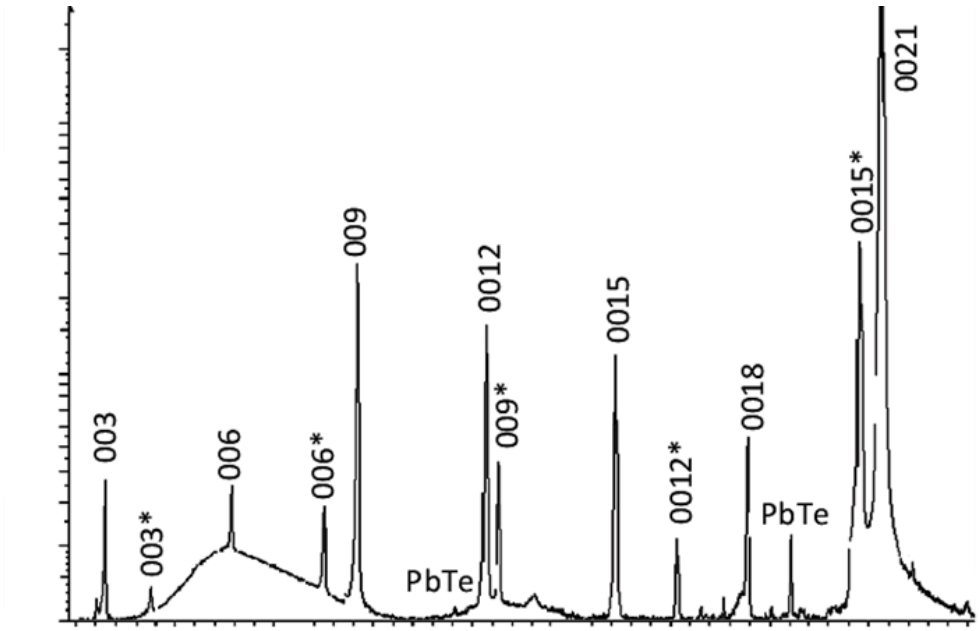

Fig. 2. Radiograph of the PbSb2Te4 ingot. Reflexes with the * sign and without * belong to the Sb_2Te_3 and $PbSb_2Te_4$ phases respectively

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Two main phases have very similar values of the unit cell parameter a in the cleavage plane. Summarizing the experimental data and the data available in literature, we can note that despite the polyphasicity of the $PbSb_2Te_4$ ingots grown by the Chokhralsky method, they are characterized by a rhombohedral symmetry.

Information about the electronic spectrum of the studied samples and the structure of the valence band was obtained from the measurements of kinetic coefficients — electrical conductivity, Hall, Seebeck coefficients and the transverse Nernst–Ettingshausen effect — in two crystallographic directions: parallel and perpendicular to the hexagonal c axis. The kinetic coefficient tensors have a significant anisotropy corresponding to the rhombohedral symmetry of the ingots. Both components of the thermopower tensor are positive, so holes are the main current carriers. Their concentration was estimated from the Hall coefficient from the larger component, as is usually made for compounds $A_2^V B_3^{VI}$:

$$p \approx \left(eR\right)^{-1},$$

As already noted, tetradymite-like materials contain a large number of point defects. The process of the defect formation in $PbSb_2Te_4$ has been poorly studied, but it is clear that vacancy defects prevailing in chalcogenides are positive charged acceptor levels and create holes in the valence band. Measured low values of the components of the Hall tensor ($R_{123} \approx 0{,}02$ cm^{-3}/K) of $PbSb_2Te_4$ crystals indicate a high concentration of holes in these compounds. The material has a p-type conductivity and a hole concentration of 3.2×10^{20} cm^{-3}. In chalcogenide materials, vacancies in the metal sublattice in materials with hole conductivity play an important role, providing, respectively, the maximum concentration of current carriers in p-PbTe at the level of 1×10^{19} cm^{-3} and in Sb_2Te_3 at the level of 1×10^{20} cm^{-3} (Lu et al. 2012).

The values of four kinetic coefficients in cubic crystals are sufficient (Kaidanov et al. 1972) to determine the quadratic (parabolic) energy spectrum, including the effective mass of the density of states and the effective scattering cross section. A joint study of the temperature dependences of kinetic coefficients in the temperature range from 77 to 450 K makes an assessment of the efficiency of the mass density of states m^* and Fermi level ε_F at low temperature (T ≈ 120K):

$$m^* = \left(\frac{3}{\pi}\right)^{2/3} \cdot \frac{\hbar^2}{T} \cdot p^{2/3} \cdot \frac{e}{k_0} \cdot \left(S - \frac{Q}{R\sigma}\right),$$

$$\varepsilon_F = \left(\frac{3p}{8\pi}\right)^{2/3} \cdot \frac{h^2}{2m^*},$$

where p — holes concentration, $\hbar = h/2\pi$ — Planck's constant, k_0 — Boltzmann's constant and e — the electron charge module. These formulas are valid for the quadratic law of variance in the case of quantum statistics.

The effective mass $m^* \approx 0.5m_0$ (where m_0 is the mass of a free electron) and $\varepsilon_F \approx 0.15eV$ at room temperature. At the same time, as temperatures increase, both components of electrical conductivity (in the cleavage plane and along the trigonal axis $\overline{3}$) decrease monotonically, i. e. show behavior characteristic of metals.

An essential feature of the carrier transfer phenomena is the observed increase in both Hall coefficients with temperature, which indicates the complex structure of the valence band and the involvement of holes with different effective masses in the transfer phenomena. In the two-band model, it is traditionally assumed that the growth of the Hall coefficients is associated with the pumping of holes from the main extremum to an additional one located near the Fermi level (Askerov 1994) (Fig. 3).

The calculated values of the charge carrier concentration in $PbSb_2Te_4$ are not optimal for thermoelectric applications.

The addition of impurities to the initial mixture makes it possible to significantly modify the structure and properties of the resulting crystals. Given the high concentration of vacancy defects, it is interesting to study the samples of the compound $PbSb_2Te_4$, doped with a donor impurity, which is Cu.

We examined a series of Cu-doped samples as the formalism of the density functional theory using the pseudopotential method as well as the full-potential method of linearized coupled plane waves are rather limited in terms of calculating the defects of real crystals and the distribution of alloying impurities. The contribution of impurity atoms and defects in a real crystal can be considered by a change in the equilibrium carrier concentration.

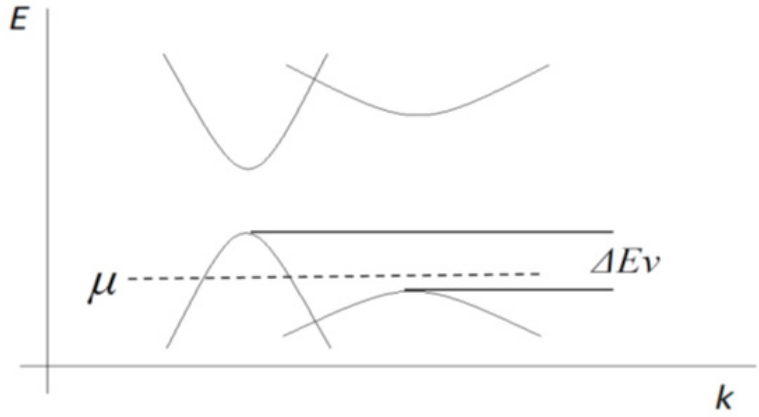

Fig. 3. $PbSb_2Te_4$ zone structure model. μ is the chemical potential, ΔEv is the energy gap between the unequal extremes of the valence band

The introduction of copper leads to a slight increase in the lattice parameter c. The obtained value of c = 4.1733 nm for the doped compound slightly exceeds the value of c = 4.1712 nm for the undoped $PbSb_2Te_4$. The addition of a copper impurity initially leads to an almost twofold increase in both components of the Hall tensor, which indicates a twofold decrease in the concentration of holes compared with an undoped crystal. However, a more significant decrease in the concentration of the main carriers was not achieved even with a twice increase in the proportion of the alloying additive in the initial mixture $(PbTe+Sb_2Te_3)_{0.9995}Cu_{0.0005}$. This effect can be explained if we assume the presence of several mechanisms for the incorporation of alloying additive atoms into the structure of the initial crystals. At the first stage, small amounts of copper atoms fill the vacancies. Filling such vacancies, in addition to reducing carrier concentration, should reduce phonon scattering and increase their mobility. With a further increase in the proportion of Cu atoms, these atoms presumably begin to settle in the interlayers between the septuple and quintuple layers, forming new copper-rich phases. Such inclusions should effectively scatter phonons along the hexagonal axis, reducing the lattice thermal conductivity.

When a donor copper impurity is introduced in a larger amount $(PbTe+Sb_2Te_3)_{0.999}Cu_{0.001}$ in addition to the main phases, the following components presumably could be identified in the samples: CuTe (ortho-rhombohedral lattice, a = 0.346 nm, c = 0.699 nm); Cu_3Sb (ortho-rhombohedral lattice, a = 0.550 nm, c = 0.435 nm); $Cu_{10}Sb_3$ (hexagonal lattice, a = 0.992 nm, c = 0.432 nm); Cu_7Te_4 (hexagonal lattice, a = 0.832 nm, c = 0.726 nm) and Sb_2Te (hexagonal lattice a = 0.418 nm, c = 1.747 nm).

To confirm the phase structure of the samples, additional measurements, such as Raman spectra, are needed and are currently underway.

According to the small size of Cu atoms (R_{Cu} = 0.116 nm) and the types of crystal lattices of the proposed minor phases, it can be assumed that, at least partially, these phases could be embedded in the Van der Waals gaps between the layers of the main phases.

The anisotropy of the Nernst–Ettingshausen coefficient observed when measuring the kinetic coefficients of the doped samples, viewed in a sign change during the transition from a component in which the carrier flow occurs exclusively in the cleavage plane to components in which the trajectory of the carrier flow intersects the cleavage plane, indicates a significant difference in the contributions of the dominant scattering mechanisms in different crystallographic directions. We can talk about the predominance of acoustic hole scattering in the cleavage plane and the significant influence of impurity scattering along the trigonal axis, which confirms the assumption of impurity localization between the septuple and quintuple layers of the main phases.

Conclusions

Our study of a series of samples of $PbSb_2Te_4$ crystals grown by the Chokhralsky method discovered that ingots are periodic structures oriented along a trigonal axis which are multiphase with dominant phases $PbSb_2Te_4$ and Sb_2Te_3.

The experiments on the doping of $PbSb_2Te_4$ crystals have shown that small amounts of Cu atoms are likely to occupy vacancies in the metal sublattice. As the amount of copper in the initial mixture increases, impurity atoms presumably enter into a chemical bond with Sb and Te atoms.

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The charge transfer phenomena were also investigated. Based on the measurements of four kinetic coefficients in the temperature range of 77–450 K, the parameters of the band spectrum of current carriers were estimated. The growth of the Hall coefficient indicates the involvement of several types of holes in the transfer phenomena.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

S. A. Nemov designed and directed the project; V. D. Andreeva performed the measurements and analysed the spectra, A. Yu. Aliabev processed the experimental data, performed the analysis, drafted the manuscript and designed the figures. All the authors discussed the final work and took part in writing the article.

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