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## Features of copper doping of $\text{PbSb}_2\text{Te}_4$ crystals

S. A. Nemov <sup>1</sup>, A. V. Povolotskiy <sup>2</sup>, V. D. Andreeva <sup>3</sup>, A. J. Aliabev <sup>1</sup>

<sup>1</sup> St. Petersburg State Electrotechnical University 'LETI' named after V. I. Ulyanov (Lenin),  
5F Professora Popova Str., St. Petersburg 197022, Russia

<sup>2</sup> Saint Petersburg State University, 7/9 Universitetskaya Emb., Saint Petersburg 199034, Russia

<sup>3</sup> Peter the Great St. Petersburg State Polytechnical University,  
29B Politekhnicheskaya Str., St. Petersburg 195251, Russia

### Authors

Sergei A. Nemov, ORCID: [0000-0001-7673-6899](https://orcid.org/0000-0001-7673-6899), e-mail: [nemov\\_s@mail.ru](mailto:nemov_s@mail.ru)

Alexey V. Povolotskiy, e-mail: [apov@inbox.ru](mailto:apov@inbox.ru)

Valentina D. Andreeva, e-mail: [avd2007@bk.ru](mailto:avd2007@bk.ru)

Aleksei J. Aliabev, e-mail: [alyabjev\\_au@mail.ru](mailto:alyabjev_au@mail.ru)

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**Abstract.** This paper presents the results of X-ray diffraction and Raman spectroscopy studies of Cu-doped  $\text{PbSb}_2\text{Te}_4$  crystals grown by the Czochralski method. Electrophysical properties such as carrier concentration and thermoelectric Q factor ZT are discussed. A rationale is provided for introducing a donor impurity to optimize the properties of crystals as a potential thermoelectric material, and doping features are observed. The Bramfitt heterogeneous nucleation model is applied to calculate disregistry between the parameters of the crystal lattices of the phases occurring in crystals during the growth process. Possible copper-rich phases are predicted. The presence of chemically bound copper atoms forming new phases and their predominant location in the van der Waals gap between the septuple and quintuple layers is confirmed experimentally.

**Keywords:** semiconductors,  $\text{PbSb}_2\text{Te}_4$ , thermoelectricity, Czochralski method, carrier concentration, doping mechanism, Bramfitt heterogeneous nucleation model, X-ray diffraction analysis, Raman spectra, septuple layers

### Introduction

Tetradymite-like ternary compounds  $\text{PbSb}_2\text{Te}_4$ , which belong to the homologous series  $n\text{PbTe}-m\text{Sb}_2\text{Te}_3$ , initially sparked interest among researchers as a basis for obtaining a medium-temperature thermoelectric material of p-type conductivity (Shelimova et al. 2004).

The compound has a complex structure formed from septuple layers ( $\text{TeSbTePbTeSbTe}$ ). The bonds inside the septuple packages are ion-covalent, and the bond between the packages is carried out mainly by weak van der Waals forces. The presence of heavy elements in the composition of the material and the effective scattering of phonons by potential barriers at the boundaries between the layer packages ensure a decrease in lattice thermal conductivity (Shelimova et al. 2008), which is important for achieving high thermoelectric Q-factor (ZT) values (Ioffe 1956).

More interest in these compounds is generated by theory assuming that an ideal periodic structure may have protected surface states that can be localized in both surface and subsurface blocks (Menshchikova

et al. 2013). Such unusual surface properties — the state of a topological insulator — ensure the flow of spin-polarized current without loss of energy, which has the potential for application in quantum computers, spintronics and magneto-electric devices (Jayan, Rakesh 2022).

The first massive single crystals of this compound were grown by the Czochralski method with liquid phase feeding from a floating crucible in the late 2000s at the Institute of Metallurgy of the Russian Academy of Sciences by a team led by L. E. Shelimova. The grown crystals had a diameter of 20 to 30 mm and a length of about 100 mm.

X-ray studies on a Bruker D8 Advance diffractometer in Bragg–Brentano geometry (Cu-K $\alpha$  radiation with a nickel filter) showed a complex crystal structure with the presence of two phases: the main  $\text{PbSb}_2\text{Te}_4$  (about 70–80%) and  $\text{Sb}_2\text{Te}_3$  (up to 20–30%). The main phase has rhombohedral symmetry and the spatial group R3m and the parameters of the hexagonal cell  $a = 0.435$  nm and  $c = 4.171$  nm (Nemov et al. 2024). The noted multiphase feature of the crystal structure is presumably caused by the fact that the synthesis of the compound  $\text{PbSb}_2\text{Te}_4$  occurs by a peritectic reaction.

In non-cubic crystals most of the physical properties are tensor ones. The tensors of the main kinetic coefficients, such as electrical conductivity ( $\sigma$ ) and thermal conductivity ( $\kappa$ ), Seebeck coefficients ( $\alpha$ ) and Hall coefficients (R), are in particular characterized by two components, which are measured in the direction of the inversion-rotation axis of the third order  $\bar{3}$  and in the cleavage plane perpendicular to axis  $\bar{3}$ .

Both components of the Seebeck coefficient tensor in the studied crystals are positive in the temperature range of 77–450 K (Nemov et al. 2012), which corresponds to the hole-like nature of the conductivity. The hole concentration was determined from the larger component of the Hall coefficient tensor at a temperature of 77 K, as is usually done in the study of chalcogenides of elements in group V of the periodic table (Goltsman et al. 1972). It was found that the  $\text{PbSb}_2\text{Te}_4$  crystals have a hole concentration  $p \approx (eR)^{-1}$  equal to  $3.2 \times 10^{20}$  cm $^{-3}$ . Such a high concentration of holes in the  $\text{PbSb}_2\text{Te}_4$  indicates a large number of acceptor-type point defects in the crystal lattice caused by a deviation from stoichiometry. Such defects in chalcogenides are vacancies in the metal sublattice. Interestingly, the deviation from the stoichiometric composition of the compound does not lead to a noticeable change in the Hall concentration of holes.

An estimate of the thermoelectric Q factor  $ZT$  equal to  $ZT = \frac{\alpha^2 \cdot \sigma}{\kappa}$  gives the value of  $ZT \sim 0.3$  at 675 K (Shelimova et al. 2006), which shows that the hole concentration in  $\text{PbSb}_2\text{Te}_4$  is nonoptimal from the point of view of thermoelectric energy conversion. Therefore, to optimize the thermoelectric properties, a significant reduction in the hole concentration is required by modifying the  $\text{PbSb}_2\text{Te}_4$  crystals with electroactive impurities. Copper, which is a donor in lead chalcogenides, was chosen as such impurity. The effect of copper doping of  $\text{PbSb}_2\text{Te}_4$  crystals on their electrophysical properties is studied in this work.

## Experimental results and their discussion

As part of optimizing the electrophysical properties of the studied compound, a series of Cu-doped samples with the compositions  $(\text{PbTe} + \text{Sb}_2\text{Te}_3)_{0.9995}\text{Cu}_{0.0005}$  and  $(\text{PbTe} + \text{Sb}_2\text{Te}_3)_{0.999}\text{Cu}_{0.001}$  was synthesized and studied (Nemov et al. 2025). Introduction of copper slightly increases the lattice parameter to  $c = 4.173$  nm. At the same time, even a small amount of copper (0.5 atm.%) significantly increases both components of the Hall tensor. It results in almost half as much the concentration of holes compared to the non-doped crystal. Increment of the proportion of the dopant additive in the initial mixture does not lead to a reduced hole concentration.

This fact may be due to a change in the mechanism of the incorporation of dopant atoms into the structure of the initial crystals with dopant proportion. Copper atoms initially fill vacancies in the metal sublattice (Pb, Sb), which leads to a decrease in the hole concentration. With a further increase in the proportion of Cu atoms in the mixture, these atoms begin to settle in the gaps between the septuple and quintuple layers and react with weakly bound Te atoms (the outermost atoms in septuples and quintuples), forming new copper-containing phases.

To calculate the probability of phase formation in doped crystals containing copper chemically bound to the atoms composing the initial compound, as well as to analyze the crystal growth sequence on a temperature scale, we used the Bramfitt nucleation model (Bramfitt 1970) for high-temperature alloys. The Bramfitt heterogeneous nucleation model is a further development of the Turnbull–Vonnegut

approach for evaluating the crystallographic interaction at the phase boundary during growth. From the formula

$$\xi_{(hkl)_n}^{(hkl)_s} = \frac{1}{3} \sum_{i=1}^3 \frac{d_{[uvw]_s}^i \cos \theta - d_{[uvw]_n}^i}{d_{[uvw]_n}^i} \cdot 100\%$$

it is possible to determine the degree of disregistry between the parameters of the crystal lattices of the phases that occur in crystals during the growth process.

The formula uses the following notation:  $\xi$  is the lattice disregistry,  $(hkl)_s$  is a low-index plane of the substrate,  $(hkl)_n$  is a low-index plane of the nucleated solid,  $[uvw]_s$  is a low-index direction in  $(hkl)_s$ ,  $[uvw]_n$  is a low-index direction in  $(hkl)_n$ ,  $\theta$  is the angle between  $[uvw]_s$  and  $[uvw]_n$ ,  $d_{[uvw]_s}$  is the interatomic spacing along  $[uvw]_s$ , and  $d_{[uvw]_n}$  is the interatomic spacing along  $[uvw]_n$ .

According to the Bramfitt model, in copper-doped samples, only phases with copper compounds can be observed, the coefficient of disregistry of the lattices with the lattices of the main phases for which does not exceed 6.

Table 1. Bramfitt phase lattice disregistry parameters of the  $PbSb_2Te_4:Cu$  system

Phase	$PbSb_2Te_4$	$PbSb_2Te_4$	$Sb_2Te_3$	PbTe	PbTe	$Cu_2Te$	$Cu_2Te$	$Cu_7Te_4$	$(CuSb)Te_2$
Symmetry	R-3m	R32	R-3m	Fm-3m	Pn-3m	F4-3m	P6/mmm	P3m1	R-3m
Cell type	Rhombohedral			cubic			hexagonal		rhombohedral
d	4.35	4.35	4.25	4.57	5.04	4.364	4.25	4.32	4.22
$T_{melt}$	800		622	924		900		773	
$\xi$ %	4.7 on PbTe Fm-3m	13.5 on PbTe Pn-3m	2.3 on $PbSb_2Te_4$ Fm-3m	–	–	4.5 on PbTe Fm-3m	7.0 on PbTe Fm-3m	5.4 on PbTe Fm-3m	7.54 on PbTe Fm-3m
			7.0 on PbTe Fm-3m	–	–	13.5 on PbTe Pn-3m	15.8 on PbTe Pn-3m	13.3 on PbTe Pn-3m	16.3 on PbTe Pn-3m
			13.5 on PbTe Pn-3m	–	–	-0.3 on $PbSb_2Te_4$	2.3 on $PbSb_2Te_4$	7.0 on $PbSb_2Te_4$	3.0 on $PbSb_2Te_4$

Calculations of the disregistry parameter for the main and copper-containing phases are shown in Table 1. Phases with a value of  $\xi$  more than 6, the existence of which is possible based on the phase diagram, could be detected on radiographs in significantly smaller quantities.

The results of X-ray diffraction analysis are shown in Fig. 1. Calculated disregistry values allowed us to estimate the probability of formation of phases with copper that correlates with the experimental results.

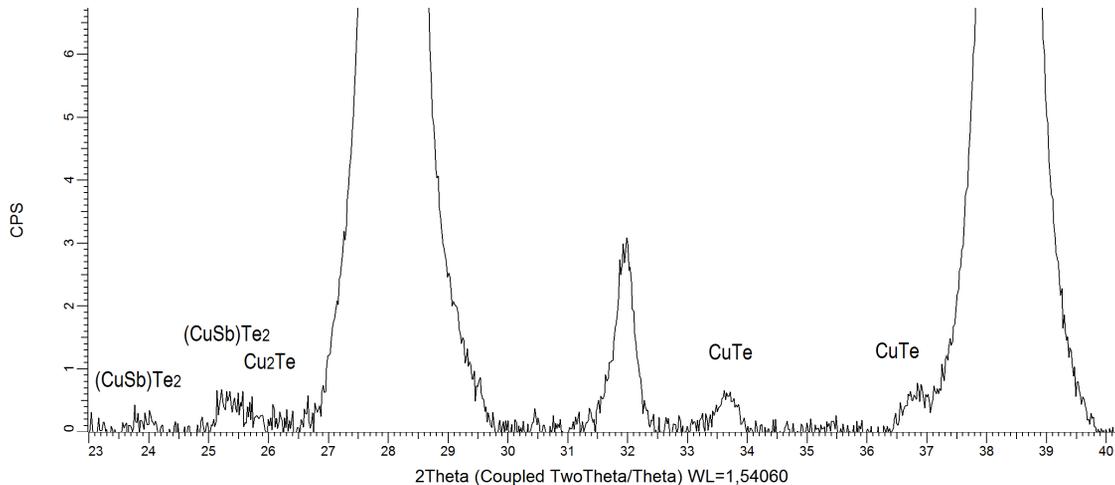


Fig. 1. Radiograph of the  $PbSb_2Te_4:Cu$  system

The reflexes of the copper-containing phases, despite their significantly lower intensity than those of the main phases  $\text{PbSb}_2\text{Te}_4$  and  $\text{Sb}_2\text{Te}_3$ , are determined on the radiograph and interpreted using the ICDD PDF-2 powder database and the Rietveld method using Bruker TOPAS4 software. The sizes of the coherent scattering regions were determined using the Scherrer formula:  $\text{Cu}_2\text{Te}$  up to 120 nm,  $\text{CuTe}$  up to 95 nm and  $(\text{CuSb})\text{Te}_2$  up to 75 nm.

Since copper-containing phases are recorded on the X-ray at the trace level, measurements of the Raman spectra were performed to confirm the existence of additional copper-containing phases in the crystals.

The Raman spectra were measured using a LabRam HR800 spectrometer (Horiba) equipped with a confocal microscope. The use of a single monochromator in the spectrometer caused the introduction of an edge filter into the recording channel, cutting off the laser excitation line, which limits the possibility of measuring spectra in the region of less than  $100\text{ cm}^{-1}$ . A continuous laser with a wavelength of 488 nm and a power of 100 mW was used as the source of exciting radiation. The laser radiation was focused on the sample surface using a 50x micro lens in an area of about  $4\text{ mm}^2$ . Each spectrum was recorded with an accumulation of 30 seconds and averaged over 9 spectra. To measure the Raman spectra, fresh fragments were prepared along the planes of layered structures.

Raman spectra of two types were obtained (Fig. 2): in the cleavage plane and in the plane perpendicular to the cleavage plane (the end face). The two peaks at  $121\text{ cm}^{-1}$  and  $139\text{ cm}^{-1}$  are known as  $A^1$  and  $E^2$  vibrational modes of Te respectively (Lal et al. 2020). The peak at  $161\text{ cm}^{-1}$  is closely related to the  $\text{Sb}_2\text{Te}_3$   $A^1$  mode (Guo et al. 2016). The wide peak with a maximum of about  $268\text{ cm}^{-1}$  which refers to the vibrational modes of the  $\text{CuTe}$  or  $\text{Cu}_2\text{Te}$  crystal phase (Park et al. 2011) is clearly visible, clearer on the spectrum taken from the end surface.

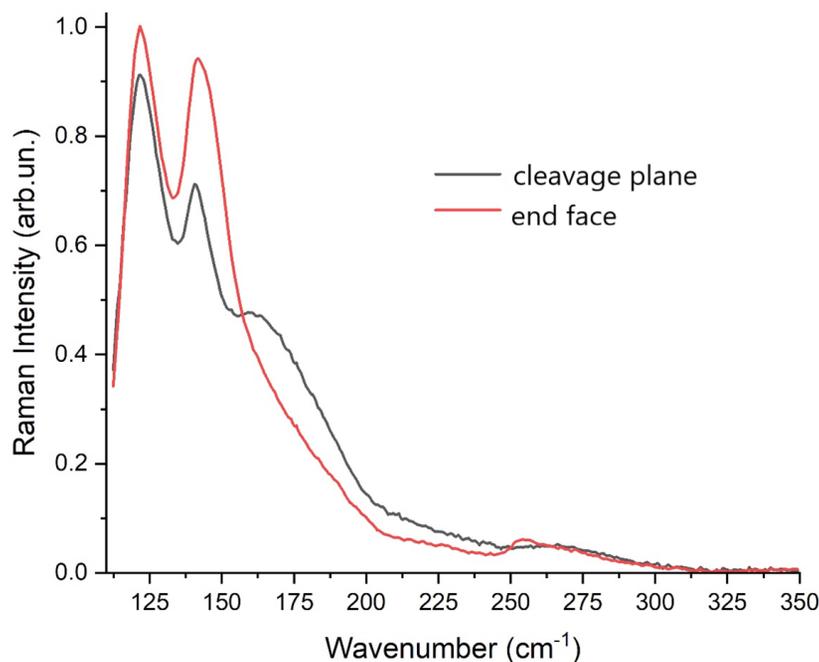


Fig. 2.  $\text{PbSb}_2\text{Te}_4:\text{Cu}$  crystals Raman spectra

The presence of a peak related to a copper-containing phase on the Raman spectra of the samples confirms that the studied crystals contain chemically bound copper atoms. Clearly expressed maximum when measuring the spectrum from the end surface confirms the assumption of localization of the phase with copper mainly in the van der Waals gap between the septuple and quintuple layers.

## Conclusions

The mechanism of the copper doping of  $\text{PbSb}_2\text{Te}_4$  crystals has been studied. X-ray diffraction analysis and Raman spectroscopy have shown that copper phases are present in doped crystals, the formation of which indicates the chemical bonding of copper atoms to Te atoms. With a relatively low copper content, there is a decrease in the concentration of holes, associated with filling vacancies in the metal sublattice. As the concentration of the alloying additive increases, copper atoms chemically bond

to Te atoms to form new phases, which does not lead to a decrease in carrier concentration. The assumed location of CuTe ( $\text{Cu}_2\text{Te}$ ) phase in the van der Waals gaps between the septuple and quintuple layers is validated by the Raman spectra of the end surface of the  $\text{PbSb}_2\text{Te}_4\text{:Cu}$  crystalline samples.

We would also like to note that the complex multiphase composition of  $\text{PbSb}_2\text{Te}_4$  crystals grown by the peritectic reaction by the Czochralski method and doped with copper, in our opinion, indicates that the melt is apparently structured and contains all the phases observed by us. The resulting crystals are a ‘frozen melt’.

### 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 X-ray measurements and analysed the spectra; A. V. Povolotskiy performed the Raman spectra measurements, analysed the spectra and reviewed the overall text; 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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