The synthesis of n-type and p-type ZnSb compositions for thermoelectric applications

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Abstract. A two-step quenching schedule was applied for the synthesis of polycrystalline n- and p-type thermoelectric ZnSb. The charge, up to 500 g in weigh, contained in a sealed quartz capsule, was melted and solidified after switching the furnace off by a preliminary quenching in water. Then the capsule was put back in the furnace and cooled in it to the temperature of 700 K; next, the second quenching to the room temperature in water was made. The material showing the resistivity of 1–5 mΩ·cm and the thermopower of 175 μV/°C was reproducibly obtained.

1. Introduction
Thermoelectric effects are due to the interrelation between the electric and thermal processes in solids. The major characteristic of a thermoelectric material is its figure of merit ZT, which is given by the formula

$$ZT = S^2T/\rho k,$$

where $S$ is the Zeebeck (or thermopower) coefficient, $T$ is the absolute temperature, $\rho$ is the electrical resistivity, and $k$ is the thermal conductivity.

The availability of materials with high figures of merit is of great practical importance. For instance, materials with $ZT = 2$ promise a replacement of Freon in refrigerators, a progress in semiconductor electronics and fast cooling; thermoelectric power generators based on them would make it possible to utilize a huge amount of energy that is now dissipated with no use increasing the temperature of the surrounding medium.

Presently, Te and Sb compounds and solid solutions based on them are widely used in thermoelectric devices. Zinc antimonide ZnSb, the first compound in which thermoelectricity was revealed in early 19th century, is still a promising material as well as its analog CdSb that has a high thermopower coefficient.

The turnover of thermoelectric materials makes now about $6$ billion a year which suggests their mass production. An important requirement is their production cost, which limits severely the use of rare and trace elements.

There are also environmental safety restrictions concerning the use of materials with toxic components, such as Cd, Pb, Hg; these cannot be exported to the European countries.

For these reasons, the synthesis of ZnSb was used for the subject of this work.

In the temperature range of 50–60 at %, the Zn-Sb system has four individual phases, ZnSb, Zn₃Sb₂, Zn₅Sb₄, and Zn₅Sb₆ (figure 1).
The last two compounds are unstable, they exist in the temperature intervals 839–682 K and 765–800 K, respectively. The phases Zn$_3$Sb$_3$ and Zn$_3$Sb$_2$ crystallize directly from the melt, the temperatures of their congruent melting are 837 K and 839 K, respectively. The phase ZnSb forms by a peritectic reaction at 819 K.

Two phases, ZnSb and Zn$_4$Sb$_3$, are practically important for thermoelectric applications. Compared to Zn$_4$Sb$_3$, ZnSb has more simple and well-ordered structure (diamond-type cubic lattice) and higher thermoelectric performance; its Zeebeck coefficient of 150 µV/K is 1.5–2 times greater than that of Zn$_4$Sb$_3$. The experiments on the synthesis of Zn$_4$Sb$_3$ yielded the material whose thermopower varied with time, which is probably due to a solid-state transition at 765 K [1].

Among modern works on the synthesis of ZnSb with $ZT$ close to unity, those made at Oslo University ($ZT = 1.4$ at 673 K) [2] and at the AF Ioffe Physicotechnical Institute ($ZT = 0.8–1.0$ at $T = 635–700$ K) [3, 4] should be cited. Doping with I- and IV-group elements was used for increasing the electrical conductivity of the material [2, 3].

2. Experiment and results
In this work, ZnSb was synthesized by melting a charge of mixed components 99.99% purity in evacuated and sealed quartz capsules. The capsules were heated in a horizontal resistance furnace at a rate of 100–150 K/h to a temperature 100–150 K above the melting point (853 K). In the first trial experiments, the charges about 200 g in weight and the capsules 20 mm in diameter were used; later on, greater charges of 400–500 g and the capsules 30–50 mm in diameter were taken. Several runs with 70-mm-dia capsules and a vertical resistance furnace were also conducted.
To achieve a higher electrical conductivity, p-type dopants were added. These were I-group elements Cu, Ag (0.2–0.7 at.%) and IV-group elements Sn, Pb (1–2 at.%). To enhance the plasticity of the material, Bi was added in amounts of 1–6 at.% as an isoelectronic dopant.

In the trial experiments, the charge was melted, then cooled for a short time in water to obtain a polycrystal of a small grain size and cooled further in the furnace (which was already switched off) to room temperature. This annealing operation was applied to provide a relief of a mechanical strain that could lead to the ingot cracking. However, the material obtained under such cooling conditions showed the electrical resistivity as high as several tenths of Ohm-to-centimeter and had accordingly low figures of merit. It can be suggested that higher electrical conductivity could not be attained even at high p-type dope concentrations because of the formation of complexes and resulting self-compensation of defects. Our experience in the work with some other semiconductors tells us that complex formation proceeds at temperatures below 700K [4-11], which is an obvious result of a low bond energy between the particles forming a complex. With regard to this fact, the second quenching was conducted as follows: the capsule was put out of the furnace at $T = 700K$ and cooled in running water to room temperature.

The use of the second quenching from 700–750K allowed one to prepare in a reproducible manner the material with the resistivity of 1–5 $\mu\Omega\cdot cm$, or the electrical conductivity of several hundreds of reciprocal Ohm-to-centimeter. The material obtained showed the thermopower of 115–175 $\mu V/K$. Typical temperature dependences of the electrical conductivity at temperatures from 290 to 480K measured on the samples cut of three ingots are shown in figure 2. Temperature dependences of the figure of merit measured by the Harman method on the same samples are shown in figure 3. Based on these data, one can expect that the material obtained will show figures of merit of about unity at working temperatures.

![Graph](image_url)

Figure 2. Temperature dependences of the electrical conductivity (a) and the figure of merit (b) for the samples cut of the ingots 1–3.
Figure 3. Temperature dependences of the figure of merit for the samples cut of the ingots 1-3 measured by the Harman method.

3. Conclusions
An additional quenching in running water from the temperatures of 700-750K to room temperature was introduced in the procedure of preparing p-doped polycrystalline ZnSb; the aim was to prevent the formation of complexes and resulting self-compensation of defects. The effect was obviously attained, as the material with the resistivity of 1–5 m$\Omega$·cm and the thermopower of 175 μV/°C could be reproducibly obtained in the suggested synthesis process.

4. References
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