**n-type to p-type crossover in quaternary BiₓSbᵧPb₂Se₃ single crystals**

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We report on the preparation and some physical properties of a quaternary system based on Bi₂Se₃ codoped with Sb and Pb. Single-crystal samples were prepared using the Bridgman technique and were characterized by measurements of the lattice parameters, electrical resistivity, Hall coefficient, Seebeck coefficient, and thermal conductivity. Atomic emission spectroscopy was used to find the concentration profiles of Sb and Pb along the single-crystalline ingots. Progressive codoping of the Bi₂Se₃ crystal lattice with Sb and Pb leads to a crossover of the initially n-type conduction to that of the p type. It is assumed that both Sb and Pb enter the Bi sublattice. Physical properties as well as the change in the dominant carrier type are discussed. © 2005 American Institute of Physics [DOI: 10.1063/1.1904158]

I. INTRODUCTION

Bismuth selenide (Bi₂Se₃) belongs to the family of narrow-band semiconductors \( A^{x+y}B^{1-x} (A=Bi,Sb \text{ and } B=Se, Te) \) with the tetradymite structure (space group \( D_{3d}^{1} \)) that form the base materials for room-temperature thermoelectric devices. Therefore, both the parent binary materials as well as their solid solutions are of theoretical and practical interest.

It is known that as-grown Bi₂Se₃ is a degenerate n-type semiconductor with electron concentration \( n=10^{19} \text{ cm}^{-3} \). Such a high electron concentration results from the predominance of one type of native defect—selenium vacancies \( (V_{Se}^{n}) \) that produce electrons—over another type—bismuth antisite defects \( (Bi_{Se}) \). Predominance of selenium vacancies makes it very difficult to prepare p-type Bi₂Se₃ and in spite of the considerable attention devoted to this compound and its solid solutions, there is little information about p-type materials based on Bi₂Se₃. According to Ref. 6, there is a noticeable decrease in electron concentration upon alloying Bi₂Se₃ with Sb₂Se₃, thanks to the suppression of native defects. Moreover, doping with Pb leads to a decrease in electron concentration via the creation of point defect Pb₂Bi. With the aim of preparing p-type single crystals based on Bi₂Se₃, we investigated the influence of double doping with Sb and Pb on the physical properties of the parent Bi₂Se₃. Changes in the free-carrier concentration and a crossover to the p-type conduction are discussed within the framework of point defects.

II. EXPERIMENTAL PROCEDURE

A. Preparation of single crystals

Single crystals of the quaternary system were pulled using a modified Bridgman technique described elsewhere. The crystals obtained (ingot length of 50 mm and diameter of 10 mm) cleaved easily along the (0001) planes. \( (Bi_{0.75}Sb_{0.25})_{2-}Pb_{y}Se_{3} \), with \( z \) varying from 0 to 0.04, was the nominal composition of all the crystals investigated.

B. Characterization of the crystals

The crystals were characterized by the x-ray diffraction (XRD) structural analysis and by the measurements of electrical resistivity \( \rho_{\perp} \), Hall coefficient \( R_{H}(B \parallel c) \), Seebeck coefficient \( \alpha(\Delta T \perp c) \), and thermal conductivity \( \kappa(\Delta T \perp c) \) in the temperature range 2-300 K. These experimental techniques are described elsewhere. The actual sample composition was determined using the atomic emission spectroscopy (AES) and is designated by the formula \( Bi_{x}Sb_{y}Pb_{z}Se_{3} \), where \( x+y+z=2 \). The same technique was used for the measurement of concentration profiles of the doping elements along the pulling axis.

III. RESULTS AND DISCUSSION

A. Lattice parameters

X-ray diffractograms for the parent Bi₂Se₃, the ternary sample \( (Bi_{0.75}Sb_{0.25})_{2}Se_{3} \), and the quaternary sample \( (Bi_{0.75}Sb_{0.25}Pb_{0.04})_{2}Se_{3} \) with the highest content of lead are depicted in Fig. 1. They indicate that no secondary phases
are present in the as-grown crystals. The lattice parameters are summarized in Table I. In agreement with Ref. 6, the unit-cell volume of the ternary system (Bi$_{0.75}$Sb$_{0.25}$)$_2$Se$_3$ is smaller than that of Bi$_2$Se$_3$. Upon doping with Pb, we observe no change in the unit-cell volume because the concentration of Pb is too small and the radii of Pb and Bi are comparable.

**B. Homogeneity of the crystals**

Since the Bridgman crystal growth is essentially a directional solidification, great attention was paid to mapping the concentration gradient of the component elements along the pulling direction. As described in Ref. 6, there is a gradient of Sb and Bi in (Bi$_{1−x}$Sb$_x$)$_2$Se$_3$ single crystals along the pulling direction. The concentration profiles of Sb and Pb along the pulling direction for a quaternary (Bi$_{0.75}$Sb$_{0.25}$)$_2$Pb$_{0.04}$Se$_3$ crystal are depicted in Fig. 2. One observes a practically constant concentration of the elements for the first 40 mm measured from the tip of the single crystal. It is only in the last 10–15 mm (the head of the single crystal) where concentrations of the dopants change markedly. This fact facilitates reproducible preparation of single crystals with the desired composition. The concentration profiles with a plateau are characteristic of these Bridgman technique-grown crystals. Interestingly, both Sb and Pb show the same tendency of increasing concentration from the tip to the head of single crystals. The head segment of single crystals crystallizes as a multiphased solid (x-ray diffraction data

![Image](76x548 to 270x742)

**FIG. 1.** X-ray diffractograms of Bi$_2$Se$_3$ ternary sample (Bi$_{0.75}$Sb$_{0.25}$)$_2$Se$_3$ and quaternary sample (Bi$_{0.75}$Sb$_{0.25}$)$_2$Pb$_{0.04}$Se$_3$, with highest content of Pb.

**TABLE I.** Lattice parameters (average value) of the (Bi$_{1−x}$Sb$_x$)$_2$Pb$_y$Se$_3$ single crystals.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$c/a$</th>
<th>$V$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Se$_3$</td>
<td>0.413 86(4)</td>
<td>2.862 0(2)</td>
<td>6.915(2)</td>
<td>0.424 50(5)</td>
</tr>
<tr>
<td>(Bi$<em>{0.75}$Sb$</em>{0.25}$)$_2$Se$_3$</td>
<td>0.412 15(2)</td>
<td>2.866 1(1)</td>
<td>6.954(2)</td>
<td>0.421 62(5)</td>
</tr>
<tr>
<td>(Bi$<em>{0.75}$Sb$</em>{0.25}$)$<em>2$Pb$</em>{0.04}$Se$_3$</td>
<td>0.412 20(3)</td>
<td>2.865 9(2)</td>
<td>6.953(2)</td>
<td>0.421 71(7)</td>
</tr>
<tr>
<td>(Bi$<em>{0.75}$Sb$</em>{0.25}$)$<em>2$Pb$</em>{0.04}$Se$_3$</td>
<td>0.412 10(3)</td>
<td>2.866 6(2)</td>
<td>6.954(2)</td>
<td>0.421 59(7)</td>
</tr>
</tbody>
</table>

**FIG. 2.** The concentration profiles for Sb and Pb along a single crystal of (Bi$_{0.75}$Sb$_{0.25}$)$_2$Pb$_{0.04}$Se$_3$. The drawing below represents the single crystal with segregated many-phase solid at the head of the crystal (shaded).

The results of the measurements of temperature dependence of electrical resistivity $\rho_{\perp,c}$, Hall coefficient $R_H(B||c)$, Seebeck coefficient $\alpha(\Delta T \perp c)$, and thermal conductivity $\kappa(\Delta T \perp c)$ are depicted in Figs. 4–7. The curves are numbered according to Table II. From the changes of the Hall and Seebeck coefficients, it is evident that with the increasing content of Pb the concentration of electrons in the initially $n$-type material decreases and the system converts to $p$-type conduction at the highest content of Pb. The results of electrical resistivity also indicate this trend. The decrease in the peak value of the thermal conductivity and a shift of the peak towards higher temperatures indicate the increased influence of point defect scattering with the increasing concentration of Pb in the sample. The decrease in the concentration of electrons upon Pb doping could be explained in terms of point defects (see Sec. III D below). The sample of special interest is the intermediate sample 4, which shows $p$-type

![Image](316x63 to 556x133)

**FIG. 3.** Photograph of cleaved single crystal of (Bi$_{0.75}$Sb$_{0.25}$)$_2$Pb$_{0.04}$Se$_3$. Note the multiphase solid at the head of the crystal.
The concentration of V of Bi. In agreement with Ref. 12 this leads to the creation from stoichiometric melts reveals overstoichiometric content was the case of Bi$_2$Se$_3$. It is well known that Bi$_2$Se$_3$ grown the concentration and character of native point defects just as of Sb with native defects BiSe as well as selenium vacancies. This effect was explained by means of the interaction in a decrease of electron concentration. According to Refs. 6 and 13, this effect was explained by means of the interaction of Sb with native defects BiSe and 13, this effect was explained by means of the interaction in a decrease of electron concentration. Whereas higher concentrations result observed that low concentrations of Sb lead to an increase in concentration. We cannot exclude the interaction of Pb Bi$_2$Se$_3$. The curves are numbered according to Table II.

Next we suppose that Pb, just as Sb, is located exclusively on the sublattice of Bi. Comparison of the crystal radii $r$(Bi$^{+3}$) = 0.103 nm, $r$(Pb$^{+2}$) = 0.117 nm, and $r$(Se$^{−2}$) = 0.184 nm supports the idea. The first process that accounts for the decrease in electron concentration is due to Pb entering the Bi sublattice. In the process it creates negatively charged substitutional point defects Pb$_{Bi}^−$ that yield holes $h^+$ according to the following equation

$$2\text{Pb} + 3\text{Se} \rightarrow 2\text{Pb}_{Bi}^− + \text{Bi}_2\text{Se}_3 + 2h^+.$$

The holes recombine with electrons and decrease their concentration. We cannot exclude the interaction of Pb$_{Bi}^−$ defects with vacancies V$^*$, which is another process that might possibly explain the decrease in the concentration of electrons. The change in electron concentration $\Delta n$ as a function of Pb concentration $c_p$ at room temperature is plotted in Fig. 8. We define $\Delta n = n_0 - n$, where $n_0$ and $n$ are the concentrations of the electrons in the sample (Bi$_{0.75}$Sb$_{0.25}$)$_2$Se$_3$ and Pb-doped samples, respectively. We note that one atom of Pb produces approximately 0.25 holes, which contradicts Eq. (2). This apparent reduction in the activity of Pb can be explained in terms of the results presented in Ref. 14. Accordingly, elements of group IV (Ge, Sn, and Pb) produce the so-called seven-layer-lamellae structure B-A-B-M-B-A-B (where B = Te, Se; A = Sb, Bi, and M = Ge, Sn, Pb) in the tetradymite crystals. Thus, we assume that a large fraction of Pb atoms is incorporated in the crystal lattice as electrically inactive seven-layer-lamellae Se-Bi(Sb)-Se-Pb-Se-Bi(Sb)-Se. We

**TABLE II.** Actual composition of Bi$_x$Sb$_y$Pb$_z$Se$_3$ single crystals (estimated errors ±15%).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$x$</th>
<th>$y$/wt. %</th>
<th>$z$/wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6</td>
<td>0.40/7.9</td>
<td>0/0</td>
</tr>
<tr>
<td>2</td>
<td>1.63</td>
<td>0.37/7.2</td>
<td>0.001/2/0.039</td>
</tr>
<tr>
<td>3</td>
<td>1.63</td>
<td>0.37/7.2</td>
<td>0.0016/0.052</td>
</tr>
<tr>
<td>4</td>
<td>1.63</td>
<td>0.37/7.2</td>
<td>0.0018/0.059</td>
</tr>
<tr>
<td>5</td>
<td>1.59</td>
<td>0.41/8.1</td>
<td>0.0032/0.106</td>
</tr>
</tbody>
</table>

The concentration of free electrons is given by the following equation

$$|e'| = 2[V_{Se}^*] - [Bi_{Sc}^−].$$

The influence of Sb on the transport properties of Bi$_2$Se$_3$ is indirect because Sb is isoelectronic with Bi and such substitution in itself produces no free carriers. Nevertheless, it is observed that low concentrations of Sb lead to an increase in electron concentration, whereas higher concentrations result in a decrease of electron concentration. According to Refs. 6 and 13, this effect was explained by means of the interaction of Sb with native defects Bi$_{Sc}^-$ and V$^*$. It was assumed that the increasing concentration of uncharged substitutional defects Sb$_{Bi}^0$ tends to suppress the negatively charged antisite defects as well as selenium vacancies.
note that a similar effect was observed in Ge-doped Bi$_2$Te$_3$.\(^\text{15}\)

The above arguments can qualitatively account for the behavior of all samples, except sample 4. Measurements of $\rho_{\perp,c}=f(T)$, $R_H(B\|c)=f(T)$, and $\alpha(\Delta T\perp c)=f(T)$ on this sample show an anomalous temperature dependence (Figs. 4–6), which can indicate a donor level activated at $T\approx70$ K. A drop in the Hall coefficient is also noticeable in samples 2 and 3, as detailed in Fig. 9. We cannot exclude a possibility that the anomalous behavior of the transport properties is connected with the formation of a defect in the crystal structure. One possible candidate is a complex defect consisting of a substitutional defect and a selenium vacancy (Pb$_2$Bi$_2$V$_2$Se$_6$).

However, the temperature dependence of the transport properties can also result from the band structure complexity of the material. Though the band structure of the studied quaternary crystals is not available in the literature, there are some evidence of splitting of the conduction and valence bands in the ternary crystals Bi$_{2-x}$Sb$_x$Se$_3$.\(^\text{16}\) The occurrence of light and heavy electrons and holes, respectively, can account for the different behavior of transport parameters. Based on the presented experimental results it is difficult to ascertain which of the above explanations is more plausible.

For completeness, in Fig. 10, we show a comparison of the Hall mobility of electrons (samples 1) and holes (sample 5). The Hall mobility of electrons is considerably higher than that of holes throughout the temperature range investigated even though the respective temperature dependences are similar.

### E. Figure of merit

As already noted, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ alloys are the materials of choice for room-temperature thermoelectric applications. The criterion by which one judges whether a material is useful as a thermoelectric is the so-called thermoelectric figure of merit $Z=\alpha^2/\rho k$, where $\alpha$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, and $k$ is the thermal conductivity. Often, the dimensionless figure of merit $ZT$ ($T$ being the absolute temperature) is being used because, fortuitously, the values of unity represent the state-of-art room-temperature performance. In Fig. 11 we display the dimensionless figure of merit of all the samples studied. It is clear that the best material is still the basic ternary compound. Upon doping with Pb, the figure of merit slightly decreases. It should be noted, however, that in this work we did not aim at optimizing the thermoelectric performance, and much higher figures of merit might be achieved with appropriate doping. In particular, it would be interesting to explore the possibility of forming $p$-type materials based on Bi$_2$Se$_3$.

### IV. CONCLUSION

Single crystals of quaternary Bi$_x$Sb$_y$Pb$_z$Se$_3$ compounds with the tetradymite structure were prepared by modified
Bridgman technique and were characterized by the detailed studies of the transport parameters such as electrical resistivity $\rho_{\|c}$, Hall coefficient $R_{H\|c}$, Seebeck coefficient $\alpha(\Delta T\perp c)$, and thermal conductivity $K(\Delta T\perp c)$. The measurements indicate that by incorporating Pb in Bi$_{2-x}$Sb$_x$Se$_3$ one lowers the concentration of electrons and, at high levels of Pb, a crossover to $p$-type conduction takes place. This behavior can be understood in terms of point defects Pb$_{\mathrm{Bi}}$ that produce holes.

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