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The Bridgman Method of $(BiAs)_2$ $(TeSe)_3$ Bulk Single Crystal Growth by Spontaneous Nucleation

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Abstract:

The $Bi_{0.5}As_{1.5}Te_{2.98}Se_{0.02}$ single crystal in 11 mm×80 mm size was grown using the Bridgman method. Energy dispersive spectrometry (EDS) analysis was used to determine the chemical composition of the studied samples, as well as for checking and confirming the homogeneity of the samples. Mobility, concentration of charge majority carriers and Hall coefficient of single crystal, were determined using a Hall Effec system based on the Van der Pauw method. Hall Effect was measured at room temperature with four ohmic contacts and at temperature of liquid nitrogen with silver contacts with an applied magnetic field strength of 0.37 T at different current intensities. The expected improvement in the mobility of obtained single crystal doped with this content of arsenic was not obtained.

Keywords*: Bulk single crystal; Bridgman method; EDS; Hall and Van der Pauw method; Doping.*

1. Introduction

The semiconductor compound materials are formed from special combinations of group III and group V elements. Binary compounds are formed by combining one group III and one group V element. It is difficult to obtain single crystals with good quality. We can also form ternary semiconductor compound. More complex semiconductors can also be formed that provide flexibility when choosing material properties.

Impurities can significantly change the properties of single crystals [1]. When doping single crystals, dopants are the desired impurities in it. It is necessary for the dopants to be evenly distributed in the single crystal.

The best-known commercially used thermoelectric material and semiconductor compound material in the bulk form for cooling and power generation applications at ambient temperature is bismuth telluride (Bi_2Te_3) [2].

As fabrication techniques of Bi–Te semiconductor bulk materials, there are the melting techniques based on the Bridgman [3-9], Czochralski [10, 11] and zone-melting [12] methods and also the powder metallurgy techniques such as hot-pressing [13] and hot-extrusion [14] methods. The products fabricated by these methods were often subjected to annealing in various atmospheres to raise the ZT value as high as possible [15].

Due to the application in electronics, the starting materials from which single crystals are obtained should be of high purity (from one impurity atom per million atoms of the starting element, the so-called 6N purity and more).

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Defects significantly degrades properties [16-20]. Research on thermoelectric materials is being carried out also in Serbia [21-35]. In the present work it is presented Bridgman method for growth of $Bi_{0.5}As_{1.5}Te_{2.98}Se_{0.02}$ bulk single crystal in order to clarify the effect of As-doping on the transport properties. By Bridgman method it can be obtain a single crystal of the desired orientation, with little or no dislocations, with a high degree of perfection of the crystal lattice and with uniform properties in the volume of the single crystal.

Research of the BiTe properties doped by arsenic has begun earlier by Đorđević et all [36]. In this investigation the focus was on improving transport properties by better control of the crystal stoichiometry and bulk single crystal obtaining.

2. Materials and Experimental Procedures

The high purity bismuth (Sigma – Aldrich, 99.999%), arsenic (Koch-Light Laboratories Ltd Colnbrook Bucks England, 99.999%), tellurium (Sigma – Aldrich, 99.999%) and selenium (Alfa Aesar, 99.999%) were prepared and merged in a stoichiometric relationship 2:3, namely with given compound formula of $Bi_{0.5}As_{1.5}Te_{2.98}Se_{0.02}$. The subscript indicates the fraction of the component element atomic number. Compound was synthesized by Bridgman method (spontaneous nucleation).

A furnace for crystal obtaining consists of several working parts: ceramic tubes, insulation, heaters and quartz ampoule (Fig. 1).

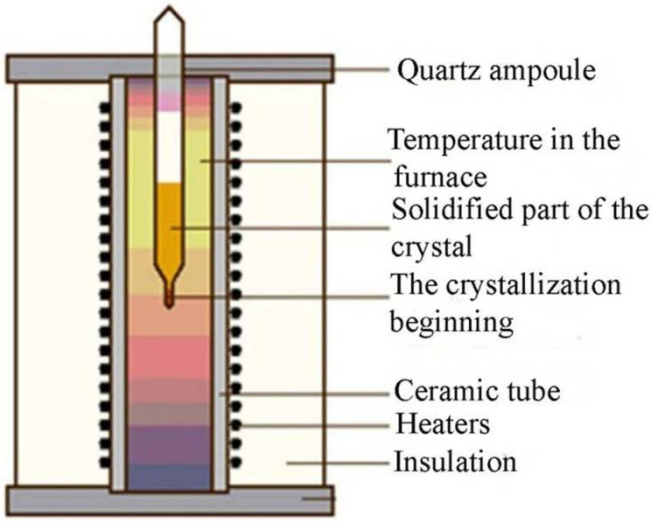

Fig. 1. Bridgman crystal growth [5-7]

Crystal growth was achieved in a closed quartz ampoule under a pressure of 10^{-5} Pa. The material from which the single crystal grows melts in a quartz ampoule which walls are coated on the inside with a thin film of graphite.

Graphitization was performed by wetting the walls of the ampoule and heating with a burner to 1000 °C. The top of the quartz ampoule is conical in shape due to easier seed formation, ie. center of crystallization.

The furnace in which the ampoule with the material is placed has its own „temperature profile“ (Fig. 1), which is very important for crystal growth. The temperature of the central part of the furnace is slightly higher than the melting temperature of the material. Before the single crystal growth, the solids were dissolved for 72 h at a temperature of 800 °C, after which the ampoule began to move the „colder“ area of the furnace.

The ampoule heating at the synthesis temperature lasted for 3 days. The ampoule was then on a stable temperature gradient for 14 days.
Then ampoule is lowered into the area of the furnace at a certain speed (0.8-1.5) mmh^{-1}. When it reaches the „colder“ area of the furnace, where the temperature is lower than the melting temperature of the material, a seed is formed and crystallization begins in the conical part of the ampoule.

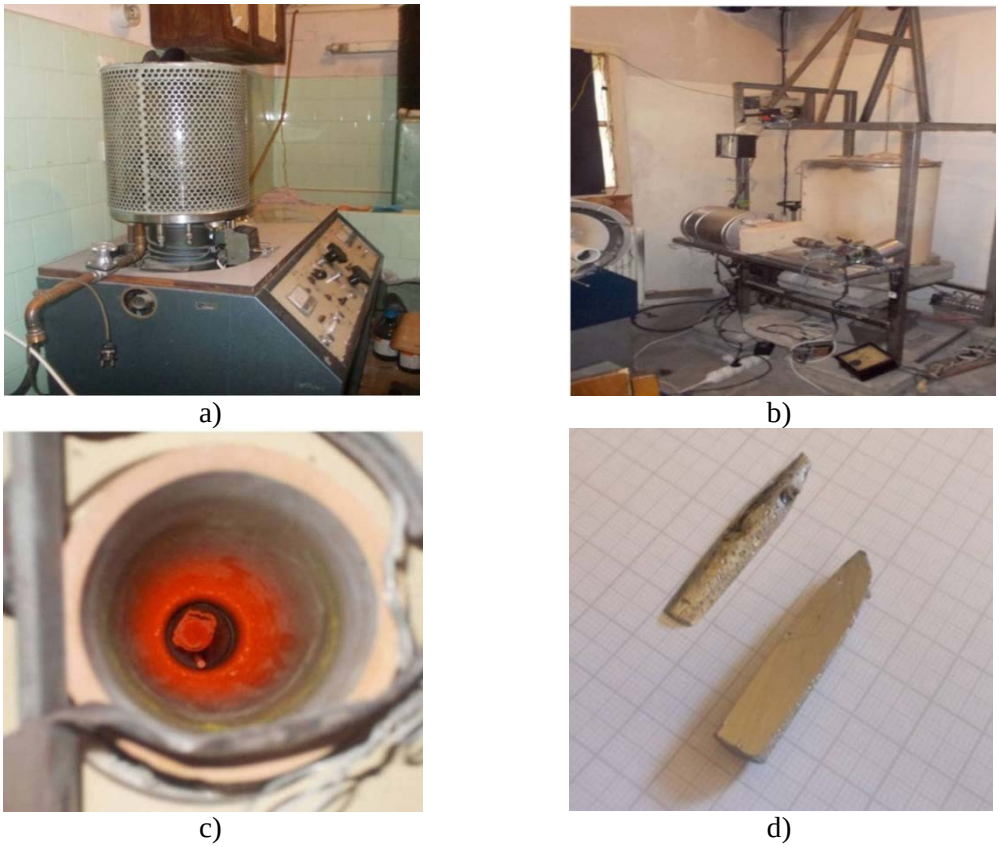

Fig. 2. Procedure for the single crystal $Bi_{0.5}As_{1.5}Te_{2.98}Se_{0.02}$ synthesis by Bridgman method: a) Vacuum system ampoules and steaming of thin films; b) Single crystal growth in the furnace; c) View of the sample in the furnace from below; d) Doped single crystal of bismuth telluride.

Fig. 3. Preparation of samples for characterization [5]; the inserted image in the upper right corner shows samples of circular cross-section

A single crystal formed in the capillary was used as the seed for crystallization. It is the seed with the most favorable orientation that has surpassed other seeds. The beginning of crystal growth occurs by spontaneous nucleation so that a single crystal of arbitrary orientation is obtained [37]. The ampoule was gradually lowered and the rest of the material hardened. After that the ampoule is cooled naturally to room temperature.

The crystal growth rate was 2.2 mmh^{-1}, and the final crystal length was 8 cm.

After single crystal synthesis, the samples were washed in acetone and allowed to dry. Samples of circular cross-section were cut with an ingot carborundum disc (Fig. 3).

The obtained samples were finally mechanically polished with diamond powder with a grain size of 3 μm, until a mirror-shiny surface was obtained.

3. Results and Discussion

The sample tested by the EDS method was cut from the ingot normal to the crystallization direction (⊥) and in the form of thin disc (Fig. 3). In the following, this pattern will be referred to as 5/3 (⊥). The same sample was also used for the Hall and Van der Pauw measurements.

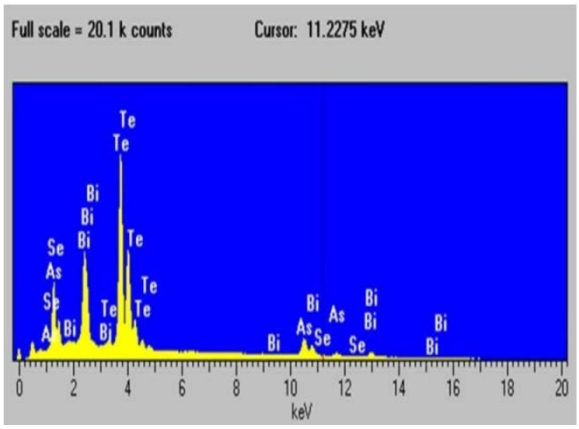

Fig. 4. EDS spectrum of sample 5/3 (⊥) [5, 7].

Energy dispersive spectrometry (EDS) analysis was used to determine the chemical composition and obtaining empirical formula of the compound. Concentrations of elements in studied point are function of the peak areas at EDS diagram (Fig. 4.). The experimental results of EDS chemical analysis of sample 5/3 (⊥) are shown in Table I. The table shows that selenium was not detected.

Tab. I The results of EDS analysis of sample 5/3 (⊥).

Element	Measurement values (atomic %)							Average value
Bi	16.39	20.06	17.82	21.46	23.06	20.02	17.45	**19.46571**
Te	68.74	62.71	63.7	62.88	62.36	62.94	62.59	**63.70286**
As	18.89	19.63	21.28	17.82	16.36	19.56	22.72	**19.46571**
Se	**None**							

From Fig. 4. it can not be seen any other spectral peaks except Bi, As, Te and S_e which indicates the fine purity of the product. The average atomic ratio of Bi, Te and As is 19.47:63.70:19.47.

In order to clarify the effects of As-doping on TE (thermoelectric) properties of $Bi_{0.5}As_{1.5}Te_{2.98}Se_{0.02}$ the electronic transport properties were measured.

The samples tested by the Hall and Van der Pauw methods were cut from different parts of the ingot normally to the crystallization direction (⊥). In the following, these samples will be referred to as 5/3 (⊥) and 5/6 (⊥), respectively. The sample 5/3 (⊥) of circular cross-section is 1.5 mm thick and the sample 5/6 (⊥) of circular cross-section is 1.55 mm thick.

All samples were carefully inspected for cavities and scratches and polished if necessary. Measurements were carried out at room temperature (T = 300 K) with four ohmic contacts and at temperature of liquid nitrogen with silver contacts for sample 5/6 (⊥) only. The source of magnetic field applied perpendicular to the Hall element was a permanent magnet of 0.37 T. Hall effect measurements were done to obtain transport properties.

The first measurements were conducted with four ohmic contacts at room temperature and the obtained results were presented in Table II and III.

Tab. II The results of the Hall and Van der Pauw method for the sample 5/3 (⊥) at room temperature (T =300 K) with four ohmic contacts.

Current intesity I [mA]	Bulk carrier concentration n_b[/cm^3]	Sheet carrier concentration n_S [/cm^2]	Mobility μ [cm^2/Vs]	Average Hall coefficient R_H[cm^3/C]
0.1	$-3.033\cdot10^{18}$	$-4.550\cdot10^{17}$	$5.036\cdot10^{1}$	$-2.058\cdot10^{0}$
0.5	$-2.575\cdot10^{18}$	$-3.862\cdot10^{17}$	$7.030\cdot10^{1}$	$-2.424\cdot10^{0}$
1	$-3.044\cdot10^{19}$	$-4.566\cdot10^{18}$	$5.908\cdot10^{0}$	$-2.051\cdot10^{-1}$
5	$-2.442\cdot10^{19}$	$-3.662\cdot10^{18}$	$7.450\cdot10^{0}$	$-2.557\cdot10^{-1}$

Tab. III The results of the Hall and Van der Pauw method for the sample 5/6(⊥) at room temperature (T = 300 K) with four ohmic contacts.

Current intesity I [mA]	Bulk carrier concentration n_b[/cm^3]	Sheet carrier concentration n_S [/cm^2]	Mobility μ [cm^2/Vs]	Average Hall coefficient R_H[cm^3/C]
0.1	$-1.499\cdot10^{18}$	$-2.324\cdot10^{17}$	$6.180\cdot10^{2}$	$-4.164\cdot10^{0}$
0.5	$-5.412\cdot10^{18}$	$-8.388\cdot10^{17}$	$2.770\cdot10^{2}$	$-1.153\cdot10^{0}$
1	$-2.321\cdot10^{19}$	$-3.597\cdot10^{18}$	$7.999\cdot10^{1}$	$-2.690\cdot10^{-1}$
5	$-5.342\cdot10^{19}$	$-8.280\cdot10^{18}$	$4.230\cdot10^{1}$	$-1.168\cdot10^{-1}$

The concentration of the carriers and the mobility(⊥) at room temperature (T = 300 K) of the charge carriers for the studied samples 5/3 (⊥) and 5/6 (⊥) are given in Table II and Table III. Measurements were made at currents of: 0.1; 0.5; 1; and 5 mA. The concentration of charge carriers of both samples ranges from 10^{18} to 10^{19} cm^{-3}. The values of the Hall coefficient are negative, indicating that the samples are n-type and that the majority of charge carriers are electrons. The fact that the samples are n type is also confirmed by the hot spot method. The mobility of the majority charge carriers μ is less than the value of the mobility of bismuth telluride n type which is 1200 cm^{2}V^{-1}s^{-1} [16]. A large dependence of the mobility of majority charge carriers is observed on the change in current intensity, so that the mobility decreases with increasing current intensity. The samples are n type and the transport parameters refer to electrons as majority carriers.

Hall effect measurements at a temperature of liquid nitrogen were carried out with 0.05; 0.1; 0.5; 1; 5 and 10 mA current intensities. All calculated data from Hall measurements at temperature of liquid nitrogen for sample 5/6 (⊥) is presented in Table IV.

Sheet carrier concentrations was found to be from 10^{16} to 10^{18} cm^{-2}. Bulk carrier concentrations increas as current intensity increases from 10^{17} to 10^{19} cm^{-2}. Mobility decreases as current intensity increases from 1907 cm^2/Vs to 300.5 cm^2/Vs.

Tab. IV The results of the Hall and Van der Pauw method for the sample 5/6 (⊥) at temperature of liquid nitrogen with silver contacts.

Current intesity I [mA]	Bulk carrier concentration n_b[/cm^3]	Sheet carrier concentration n_S [/cm^2]	Mobility μ [cm^2/Vs]	Average Hall coefficient R_H[cm^3/C]
0.05	$3.847x10^{17}$	$6.155x10^{16}$	$1.907x10^{3}$	$1.623x10^{1}$
0.1	$1.997x10^{18}$	$3.195x10^{17}$	$1.772x10^{3}$	$3.126x10^{0}$
0.5	$-5.009x10^{18}$	$-8.015x10^{17}$	$9.366x10^{2}$	$-1.246x10^{0}$
1	$-7.553x10^{18}$	$-1.208x10^{18}$	$9.534x10^{2}$	$-8.265x10^{-1}$
5	$-2.036x10^{19}$	$-3.257x10^{18}$	$3.967x10^{2}$	$-3.066x10^{-1}$
10	$6.140x10^{19}$	$9.825x10^{18}$	$3.005x10^{2}$	$1.017x10^{-1}$

4. Conclusion

The main objective of this study was to obtain $(BiAs)_2(TeSe)_3$ bulk single crystal and to have good stoichiometry control. The crystal was characterized with Hall and Van der Pauw method and grown using the Bridgman method by spontaneous nucleation. Crystal up to 11 mm in diameter was grown (Fig. 2d). The elemental composition of the compound obtained by energy dispersive spectrometry (EDS) analysis made it possible to obtain empirical formula of this compound. The obtained empirical formula does not deviate from the given compound formula. After As-doping on Bi-side with this amount, the mobility could not be enhanced.

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Сажетак: *Монокристал* $Bi_{0.5}As_{1.5}Te_{2.98}Se_{0.02}$ *величине 11×80 добијен је Брицман методом. За одређивање хемијског састава проучаваних узорака, као и проверу и потврђивање хомогености узорка, коришћена је анализа енергетске дисперзивне спектрометрије (ЕДС). Покретљивост, концентрација већинских носилаца наелектрисања и Холов коефицијент монокристала, одређивани су коришћењем Холовог ефекта заснованог на Ван дер Пауовој методи. Холов ефекат мерен је на собној температури са четири омска контакта и на температури течног азота са сребрним контактима уз јачину магнетног поља од 0.37 T при различитим интензитетима струје. Очекивано побољшање покретљивости добијеног монокристала допираног овим садржајем арсена није добијено..*

Кључне речи*: Масивни монокристал, Брицман метода, ЕДС, Холова и Ван дер Паува метода, допирање.*