THE CONDITIONS OF OBTAINING OF HOMOGENEOUS MULTI-COMPONENT THERMOELECTRIC ALLOYS

F.K. ALESKEROV
Scientific-Production Association "Selen" NASA
Baku-1143, F. Agayev, 14

The review of the articles on the heterogeneity of low-temperature materials on the base of chalcogenides of bismuth and stibium, obtained by the different technological methods has been formed. The influence of the appearing samples at the doping of the heterogeneity on the properties (micro- and macro-heterogeneity), obtained by the methods of powder metallurgy and vertically directed crystallization has been established. The regions of eutectic and island structures have been found in heterogeneous alloys, created by the compounds Bi_2Te_3, Sb_2Te_3 and Sb_2Se_3.

Introduction

The treatment of high-effective thermo-electrics on the base of multi-component systems of solid solutions (Bi-Te-Se) <impurities> and (Sb-Te-Se-Bi) <impurities> leads to the creation and wide distribution of thermo-electric generators and refrigerators for the wide temperature interval. Nowadays the question is open: how we should change the compositions of solid solutions, in order to provide the high values of thermoelectric efficacy (Z) in wide temperature regions (100-700°K). Moreover, the material should have such concentration of current carriers, in order the optimal (including $Zmax$) values of thermoelectromotive force (α) and electroconductivity (δ) are supplied for the given temperature interval. That's why the task of the Z increase should be solved in the interconnection with the study of their structures and compound homogeneity. From other side, the knowing of component distribution allows to treat the technology of the obtaining of thermoelectric alloys of high quality.

First part of the given paper is dedicated to the short analysis of known experiment results on heterogeneity of alloys $A_2^VB_3^{IV}$, obtained by different methods of crystals of solid solutions on the base Bi_2Te_3 and Sb_2Te_3. In the second part of the paper the structures of the layers $Te^{(I)}$-$Te^{(I)}$ are given and analyzed.

Bi_2Te_3, Bi_2Te_3-Sb_2Te_3, Sb_2Te_3-Sb_2Se_3-Bi_2Te_3 are doped by impurities, created the optimal concentrations of current carriers.

First part

The heterogeneities in alloys obtained by the different methods

As the irregular distribution of the composition, so the possible creation of the strange phase at the synthesis (two-phase creations by eutectic type) influence on the properties of bismuth and stibium chalcogenides. The monograph [1], in which the characteristics are considered, influencing on the formation of micro- and macro-heterogeneous in growing sample was the one of the earliest works: the longitudinal and transversal layer heterogeneities, homogenization and introduced additions.

Many refs had been published in the further years in this direction, however, the wide review of authors [2], dedicated to the homogeneity of solid solutions $Bi_{1-x}Sn_xTe_{1-y}Se_y$ (x=0,01; y=0,06, 0,12), grown on the Chochralsky method with the replenishment of liquid phase from the floating crucible demands the special attention. The authors revealed the influence of tin atoms on the homogeneity distribution of main components: in monocrystals Bi_2Te_3 the tin increases the compound heterogeneity; the fluctuation of Sb and Te content increases on 0,3% in stibium telluride. The studying of electrophysical properties of the system $Bi_{2-y}Sn_yTe_{3-x}Se_x$ was the continuity of these investigations [3]. The methods of micro-analysis of the surface levels have been changed. Thus, the defects of crystalline structure and dislocation structure of bismuth telluride and above mentioned solid solution have been studied by the method of transmission electron microscopy. The dislocations, situated in basis plane (0001) are the dominant defect type in the given monocrystals, also the presence of the defects of the packing and very small dislocation loops is shown. As all investigated monocrystals are pronounced semiconductors, so the observable defects don't influence the significant influence on their electrophysical properties [3].

As a whole, heterogeneities and the structure unsoundness of material structures on the base of Sb_2Te_3 and Bi_2Te_3 influence on the obtaining of the optimal concentrations of the electrons and holes. Many publications are dedicated to these problems; some of them are [2,3,4-7]. At the investigation of the structure of these materials, the investigators [4-7] dispute in the relation to the presence of these or that defects. The different frequency and the composition of the initial materials, and also different conditions of alloy synthesis take place. The heterogeneities in them will be significantly differ because of the peculiarities of the growing technology of crystals by the type Sb_2Te_3, Bi_2Te_3 and their solid solutions.

The influence of the obtaining technology on the crystal heterogeneities (Bi-Te-Se) and (Sb-Bi-Te)

The micro-heterogeneities of the Bi_2Te_3-Sb_2Te_3 (x=0,3; 0,6) system have been formed in [8] after the sample synthesis from them, obtained by the methods of directed crystallization from the alloy, pressing, storage extrusion, investigated by roentgen-spectral analysis. The qualitative analysis of the distribution curves of Se and Te concentrations proves the data [1] and shows on the presence in the solid solutions, obtained by the directed crystallization and extrusion method, longitudinal layer heterogeneity. The solid solutions, prepared by the methods of powder metallurgy reveal the micro-heterogeneity, statistically distributed on the volume (micro-heterogeneities exceed 150 mcm). More homogeneous samples have been obtained by the directed crystallization. Such samples are called by directed crystals (DC). The less homogeneous crystals are pressed ones (here the sizes of heterogeneities change in the dependence on the grain sizes, used in the powders). The homogeneity of the extruded samples depends on the homogeneity of the initial storages. However, the extrusion process itself significantly homogenizes the material [2].

Bi-Sb-Te homogeneity. The more high homogeneity $Bi_{0,52}Sb_{1,48}Te_3$ is caused by the less temperature interval between the lines of liquidus and solidus in the system Bi_2Te_3-Sb_2Te_3, than in system Bi_2Te_3-Bi_2Se_3 in the comparison with $Bi_2Te_{3-x}Se_x$ [2]. The concentration heterogeneity, observable in the extruded samples $Bi_{0,52}Sb_{1,48}Te_3$ doesn't have the layer character, inherent in $Bi_2Te_{3-x}Se_x$.

Eutectic on Te base in the materials of n- and p-types

The eutectic containing the pure Te has been revealed by the authors in the alloy $Bi_2Te_{3-x}Se_x$ [8]. The quantity, structure and composition of it are defined by the method of sample obtaining. At the investigation of the layer surfaces of the crystals by the composition $(Bi_{0,25}Sb_{0,75})_2$ $(Te_{0,95}Se_{0,05})_3$ the eutectic had been revealed. It was situated between basis planes of solid solutions [2]. This two-phase system consisted on the pure Te and material disseminations of the composition $(Bi,Sb)_2(TeSe)_3$, in which the ratio of the concentrations Bi and Sb is close to 34:66mol.%. The solid solution in eutectics is strongly enriched by Te. The composition of the second phase, revealed in grown crystals on Bridgmen method and doped by Te excesses $(Bi_2Te_3)_{25}$ $(Sb_2Te)_{70}$ $(Sb_2Se)_5$, is defined as 90%Te with small quantity of Bi, Sb, Se, that corresponds with data [8].

The streaks, having the eutectic structures are created in two-phase region between crystals of solid solution $(Bi, Sb)_2Te_3$. The distribution heterogeneity of excess Te at the band recrystallization of solid solution $Bi_{1,6}Sb_{0,4}Te_3$ was also mentioned in [2]. The α change on the ingot and inversion of its sign is explained by this. The authors [9] inform about segregation of the doping impurity $CdCl_2$ in upper part of the ingot (90 mol% $BiTe_3$ – 10 mol% Bi_2Se_3) and change of the composition because of the significant evaporation of Te and Se.

The monocrystals of solid solutions (Bi_2Te_3-Bi_2Se_3) and (Sb_2Te_3-Bi_2Te_3), grown by Chochralsky method, are characterized by the most homogeneity in the comparison with other materials (obtained by other known methods) [2]. The $Bi_2Te_{2,7}Se_{0,3}$ samples have the less homogeneity, if they have been obtained by the methods of directed crystallization, extrusion and powder metallurgy.

At the corresponding purity of the initial components the composition of given crystals becomes the homogeneous one. The monocrystalline sample, grown up from materials of 99,9999% purity, is the most homogeneous one. The thermo-elements, produced from such alloys and also the intercalationed crystals Bi_2Te_3 are more perfect; they are used in different scientific-technical aims [10-12].

Second part

Interlayer structure and electrophysical properties
Method of experiment

The monocrystals Bi_2Te_3, (Bi_2Te_3-Bi_2Se_3) и (Sb_2Te_3-Bi_2Te_3-Sb_2Se_3) had been obtained by Bridgmen method [13] and known method of vertically directed crystallization. In scientific investigations and industrial manufacturing the growing up the multi-component crystals by Bridgmen method has the set advantages [13]:

- repeatability and homogeneity of ingots, repeatability of the composition at the synthesis of multi-component crystals and solid solutions, the saving of the calculated components because of the system insularity, the possibility of crystal obtaining with microstructural characteristics and sizes of monocrystalline regions, which are acceptable for the studying of the properties.

Ampoules by the internal diameter 8-20mm, produced from the quartz glass, were washed firstly by nitric acid at the temperature ~350°K during 0,5 hours, further, by the distillated water many times. The degassing was carried out either in the stove, or in the flame of oxygen bumer at the continuous spooling.

The initial furnace was prepared from the components Te, Se, Bi, Sb of pure 99,9999% (treated by needed purity). The furnace components were weighted with the delicacy +- 0,005g, common mass of furnaces depends on the ampoule size and was from 100 till 200g. The opened ampoule after the preliminary heating at 400-600°K was put into upper low-temperature part of heated stove, where the temperature is lower on $\approx 70°K$, than liquidus temperature of furnace $T_{lic.}$, by conic part, and was lifted with the velocity 5 mm/h. At the sample obtaining by the method of directed crystallization the velocities 10, 20 and 30 mm/h were used.

The perfectness and heterogeneity of crystal structures were investigated by method of electron microscopy. The investigations were carrying out on the electron microscope JEM-35CX. The samples, cut from three parts of the crystal: initial, middle and final, had been investigated. The surface was obtained by the simple chipping on the planes before investigation (0001).

The results and their discussion

The sample heterogeneities, obtained by methods of Bridgmen and vertically directed crystallization had been analyzed. The samples, obtained by Bridgmen method were more perfect and in the middle region the regular distribution of the components took place Sb, Bi, Te, Se. The significant accumulations of the impurities were observed in the interlayer space of the samples, obtained by directed crystallization (we will call them, as it was mentioned - (DC)). The nonmonotonic change of component concentrations in crystallizing solid solutions P - ($Sb_2Te_3$70 mol% Sb_2Se_3·5 mol% - Bi_2Te·25 mol%) < impurities> has been established. The presence of two-phase region, appearing at the achievement of Te concentration and having the layered structure has been revealed by us. The streaks, having two-phase eutectic structures are clearly seen in two-phase region in the beginning of the ingot of samples by p-type with the additions of Te superstoichiometry (no more, than 3% weigh.). This is proved by electron-microscopic photos (fig.1). The analysis shows, that these planes are eutectic ones Sb_2Se_3-Se (having the composition on state diagram $SbSe_3$ 50 mol % - Se 50 mol %); they are situated on basis plane (0001) and very negatively influence on thermoelectromotive force. Thus, in the beginning of the ingot the thermoelectromotive force has the value $\alpha = +(130 \div 160)\dfrac{mcV}{C°}$, and in final has the value

$\alpha = +(230-240)\frac{mcV}{C^\circ}$. The middle part is more homogeneous one; the thermoelectromotive force oscillates in limits (195-205) $\frac{mcV}{C^\circ}$ at the value $\delta = (1300-1100)$ Om^{-1}cm^{-1}. The electron-microscopic photo (fig.2) of this compound by p-type of the surface of basis plane shows the significant quantity of lamination steep $Te^{(I)}$-$Te^{(I)}$ and its micro-crystal structure. Such dispersion along the length of this plane (~10-12mm) practically doesn't influence on thermoelectric parameters. The analogical micro-dispersion structures are observed in Bi_2Te_3 <Cu, In> and doped solid solution (Bi_2Te_3·95 mol % - Bi_2Se_3·5 mol %) <$CdCl_2$,Cu, In>.

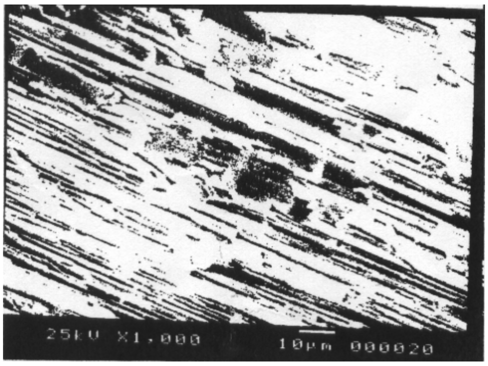

Fig.1. The electron-macroscopic photo of two-phase eutectic Sb_2Se_3-Se.

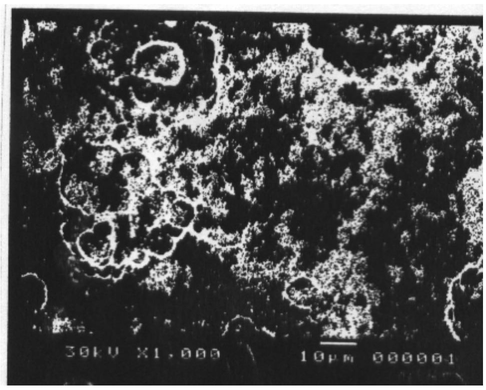

Fig.2. The electron-macroscopic photo of crystal of the system (Sb2Te$_3$·75 mol % - Bi_2Te·25 mol %)<3·0 weight Te>.

The electron-microscopic image of pure Bi_2Te_3 < In, Cu is given on the fig.3, and the island distribution of the impurity in the solid solution by n-type (doped by Cu and In) is shown on the fig.4. Such islands, situated on the surface of the plane (0001) along the layers $Te^{(I)}$-$Te^{(I)}$ in the middle part of ingots doesn't negatively influence on the electrophysical parameters (DC). At this it is seemed, that electric resistance of the islands changes the optimization conditions of parameters of such multi-layered structures in the comparison with earlier considered cases of the layers, having the normal conductivity (δ). The complex impurities (B, Cu, $CdCl_2$, Te, Sb, $SbCl_3$) at well their quantitative ratio, one play the donor roles, other have acceptor functions, allowing to obtain the needed concentrations of current carriers (including α and δ).

Fig.3. The electron-macroscopic photo Bi_2Te_3, doped by complex impurity In(0,05 weight%) и Cu(0,05 weight%).

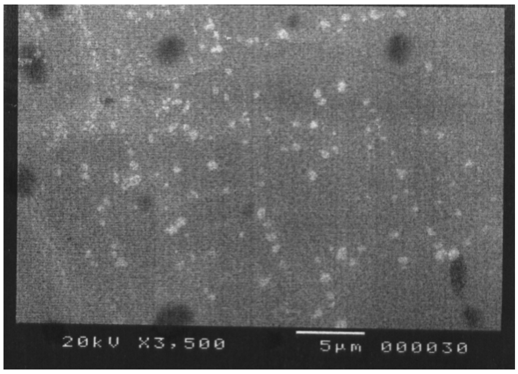

Fig.4. The islands steps of Cu on basis plane (0001) of bismuth telluride.

The investigations of the heterogeneities and elements distributions on the length and cross-section of given chalcogenides (DC) Sb and Bi (doped by impurities) were carried out by us mainly for the definition of the interconnection of conditions of obtaining and homogeneity. Here, in small degree the influence of this or that impurity heterogeneity on their thermoelectric parameters is reflected. The unit point of view on model of the introduction mechanism is absent and the complex character of introduction of impurity atoms in crystalline lattice on the base of which it could be possible to describe qualitatively the observable experimental facts. The formation of island structures in thin films and island layers $Te^{(I)}$-$Te^{(I)}$ of the crystals by type Bi_2Te_3 and Sb_2Te_3 causes the special interest of many investigators. The theory, developed in [14] can be accepted by us in the following explanations of island structures, obtained by us in the interlayers. Such the kinetics of phase impurity exfoliation in adsorbent layer on the mechanism of increased diffusion in segregation process of impurities from sample width had been investigated by authors. It is shown, that in the case of gravitation between the impurities they reveal the tendency to the formation in adsorbent layer of surface structure [14]. The main characteristics of these structures change with time by nonmonotonic way.

Thus, in our case in "closed" interlayer space $Te^{(I)}$-$Te^{(I)}$ the accumulation of the impurities is bigger, than in other defect centers (vacancies from Te, in layers $Te^{(I)}$-Bi and $Te^{(I)}$-Sb, grain limits, on external surface) takes place. In real crystals (especially in layered materials by type of bismuth and stibium chalcogenide), consisting Se, tin, Cu, Ni, Fe, B, the distribution on the ingot (on the length and cross-section) is quite irregular. The one of the reason of this space heterogeneity can be segregation processes, caused by chemical interaction of impurities with atoms and matrix (Bi_2Te_3-Sb_2Se_3-Sb_2Te_3) – Te, Se, Bi and Sb.

The eutectic phases Sb_2Se_3-Se (fig.1) and island layers from Cu and In (fig.3 and 4) are observed in the investigated by us electron-microscopic photos (fig.1-4). Rather on the fig.3,4 in basis plane (0001) Bi_2Te_3 the created islands are the Cu layers. It is known, that Cu because of small ion radius "settles" in interlayer space $Te^{(I)}$-$Te^{(I)}$ more, than in layers $Te^{(I)}$-Bi и $Te^{(I)}$-Sb, creating the many layers and finally the islands (fig.4).

The similar phenomena are observed at the formation of film coverings created from the gas phase on massive substrates. For example, in [14] the results of direct observation of growing kinetics of island film Cu on the carbonic are analyzed. The growing of the islands is considered by them as multistage process, including in itself: diffusion of atoms on the substrate (in layered structure Bi_2Te_3 – in Van der Waals crack) $Te^{(I)}$-$Te^{(I)}$, the transfer through potential barrier on island bounder, diffusion on island surface and joyance to the elementary capture centers on the surface (the quintets $Te^{(I)}$-$Te^{(I)}$ are the surfaces in the considered variant Bi_2Te_3).

In conclusion let's consider the possible creations of eutectic alloys in the systems Bi_2Te_3, Sb_2Se_3, Sb_2Te_3 and in their solid solutions. The task is the creation of eutectics between the layers. Such layer had been revealed by us on eutectic base Sb_2Se_3-Se in basis plane (fig.1) of the system (Sb_2Te_3-Sb_2Se_3-Bi_2Te_3). This eutectic at the composition 50 at.% of Se melts at the temperature 820°K. In the conditions of high pressures its melting point can be closer to the melting point of solid solution (till 910°K) and this can be the one from the possible reasons of the simultaneous growth (DC) of solid solution and eutectic (having very low thermo-electric parameters).

In this connection the thought about the undesirability of the use of complex solid solutions, the one of the component of which can be stibium selenide.

Conclusion

From all possible heterogeneities two heterogeneity in solid solutions on the base of Bi and Sb chalcogenides have been revealed. The one heterogeneity, connected with the creation of eutectic streak from Sb_2Se_3-Se negatively influences on thermoelectric parameters of the alloy on the beginning stages of growing (DC). The other heterogeneity connects with the creation of island layers in basis plane (0001) of layered crystal by type Bi_2Te_3. The growing perspective of such multi-layered structures on the base of the multi-component alloys doesn't cause the doubts.

[1] *B.M. Goltsman, V.A. Kudinov, I.A Smirnov.* Monografiya - Poluprovodnikovie termoelektricheskie materiali na osnove Bi_2Te_3. M.: Nauka, 1972, 320 s.

[2] *I.V.Gasenkova, V.A.Chubarenko, E.A.Tyavlovskaya, T.E.Svechnikova*. J. Poverkhnost. Rentgenovskie, sinxrotronnie i neytralnie issledovaniya, 2003, № 3, s.32-41.

[3] *I.V. Gasenkova, T.E. Svechnikova*. Neorganicheskie materiali, 2004, t.40, № 6, s.663-668.

[4] *N. Frangis, S. Kuypers, C. Manolikas et al.*, J. Solid State Chem, 1989, v. 69, N 8, p.817-819.

[5] *N. Frangis, C. Manolikas, S. Amelinckx*. Phys. Status. Solidi. A. 1991, v.125, p.97-106.

[6] *N. Frangis, Kuypers, C. Manolikas et al.* J. Solid. State Chem. 1990, v.84, p.314-334.

[7] *D. Maier, D. Eyidi, O. Eibl*. Stoichiometric Varlations and Strain Fields in (Bi, Sb)$_2$(Se, Te)$_3$ Peltier Material. Proc. of the Sixth Eur. Workshop on Thermoelectrics. Freiburg im Breisgan, 2001, p.32-35.

[8] *K.G. Gartsman, T.T. Dedergaev, A.S. Barat*. J. Neorganicheskie materiali. 1977, t.13, № 7, s.1210.

[9] *Heon Phil Ha, Dow Bin Hyun. Young Whan Cho, Jac Dong Shim*. Proc. XIV Int. Conf. on Thermoelectrics. 1995. St. Petersburg.: A.F. Ioffe Physical-Technical Institute, 1995, p.104.

[10] *J. Bludska, S. Karamazov, J. Navratil, I. Jakubec, J. Horak,* Copper intercalation into Bi_2Te_3 single crystals, Solid State Ionics 171 (2004) 251-259.

[11] *Osami Vamashita and Shoichi Tomiyoshi*, High performance n-type bismuth telluride with highly stable thermoelectric figure of merit, Journal of Applied Physics, v.95, N 11, 2004.

[12] *D.A.Pshenay-Severin, Yu.I.Ravich, M.V.Vedernikov*. J. Fizika i texnika poluprovodnikov, Rossiya, 2000, t.34, t.10, s.1265-1269.

[13] *V.I. Shtanov.* J. Kristallografiya, 2004, t.49, № 2, s.343-349.

[14] *L.I. Stefanovich, E.P. Feldman, V.M. Yurchenko*. J.Metallofizika. Noveyshie texnologii, 2002, t.24, № 8, ss.1103-1122.

F.K. Ələsgərov

BİRCİNSLİ ÇOX KOMPONENTLİ TERMOELEKTRİK MATERİALLARIN ALINMASININ TEXNOLOJİ ŞƏRTLƏRİ

Bismut və antimonun xalkogenidlərinin əsasında yaradılmış metodlarda qeyribircinsli termoelektrik materiallarının elmi ədəbiyyatda verilən məlumat göstərilir. Şaquli yönəlmiş kristallizasiya və toz metallurji metodu ilə alınmış nümunələrinin xassələrinə təsir edən legirə qeyribircinslilik müəyyən edilmişdir. Bi_2Te_3, Sb_2Te_3 və Sb_2Se_3 qeyribircinsli ərintilərdə eftektik və adalı strukturlar tapılmışdır.

THE CONDITIONS OF OBTAINING OF HOMOGENEOUS MULTI-COMPONENT THERMOELECTRIC ALLOYS

Ф.К. Алескеров

УСЛОВИЯ ПОЛУЧЕНИЯ ОДНОРОДНЫХ МНОГОКОМПОНЕНТНЫХ ТЕРМОЭЛЕКТРИЧЕСКИХ СПЛАВОВ

Установлено влияние возникающих при легировании макро- и микронеоднородностей на свойства образцов, полученных методами порошковой металлургии и вертикальной направленной кристаллизацией. Из двух исследованных неоднородностей одна связана с возникновением слоя эвтектики Sb_2Se_3-Se в системе (Sb_2Te_3-Sb_2Se_3-Bi_2Te_3), другая связана с неоднородным распределением островковых примесей в базисной плоскости $Te^{(I)}$-$Te^{(I)}$ слосистого кристалла Bi_2Te_3.

Received: 15.12.05