Doping with Organic Halogen-containing Compounds the Bi$_2$Te$_3$-Bi$_2$Se$_3$ Solid Solutions

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Abstract
Presently, Bi$_2$(Te, Se)$_3$ solid solutions used as an n-type legs for thermoelectric devices, are doped with inorganic halogen-containing compounds. However, most of these compounds are liable to dissociation when exposed to light, they are hygroscopic and tend to electrization when poured from one place to another. These factors often give rise to wrong dosing of dopants in conditions of commercial production. This paper describes opportunities for doping of Bi$_2$(Te,Se)$_3$ solid solutions with organic halogen-containing compounds. For practical application it is proposed to use hexachlorethane (C$_2$Cl$_6$), hexachlorbenzol (C$_6$Cl$_6$), dibrombenzol (C$_6$H$_4$Br$_2$), hexabrombenzol (C$_6$Br$_6$) and iodoform (CHI$_3$). The advantages of the latter are shown as compared to inorganic halogen-containing compounds.

1. Introduction

Doping (donor) effect on Bi$_2$(Te,Se)$_3$ solid solution can be produced by the foolowing [1]: point defects (tellurium vacancies); dissolved oxygen; metals of the second sub-group of the I group (Cu, Ag, Au); tellurium and selenium, if they are available in excess of stoicheiometry; halogens. In practice, use is made of inorganic halogen-containing compounds [2]. These are halides of metals of the second sub-group of the I group (AgCl, AgBr, CuI, etc.); halides of metals of the second sub-group of the II group (ZnCl$_2$, ZnBr$_2$, ZnI$_2$, CdCl$_2$, Hg$_2$Cl$_2$, CdBr$_2$, CdI$_2$, etc.); chlorides, bromides and iodides of antimony, bismuth and tellurium (SbCl$_3$, BiCl$_3$, SbBr$_3$, BiBr$_3$, TeI$_4$, SbI$_3$, BiI$_3$, etc.). However, inorganic halogen-containing compounds are liable to dissociation when exposed to light, they are hygroscopic and tend to electrization when poured from one place to another. Therefore, the necessity arises for the search of halogen compounds free from the above mentioned shortcomings.

2. Choosing a dopant

For the investigation polyfluoreethylene ([C$_2$F$_4$]$_n$), hexachloroethane (C$_2$Cl$_6$), hexachlorobenzol (C$_6$Cl$_6$), dibrombenzole (C$_6$H$_4$Br$_2$), hexabromobenzole (C$_6$Br$_6$) and iodoform (CHI$_3$) have been chosen. The considered organic halide-containing compounds are chemically stable, nonhygroscopic and do not tend to electrization. Table 1 presents basic characteristics of the chosen organic halogen-containing compounds compared to those of somes inorganic halogen-containing compounds (mercurous chloride, cadmium chloride). It is clear from the tabled data that halogen content by mass in organic compounds is 2-3 times higher that in inorganic ones, though their mole content is of the same level (for completely substituted compounds).

3. Thermodynamic analysis

In the development of the technology for the synthesis and zone melting for commercial production it is rather important to have quantitative estimates of the variation of the equilibrium of chemical reactions depending on the synthesis conditions [3]. The technique described in [4] has been used. Thermodynamic calculations of (Bi$_2$Te$_3$)$_{90}$(Bi$_2$Se$_3$)$_{10}$ with various dopants have been made for the following conditions.
The synthesis and the vertical zone-melting effected via the melting of the components with a stoichiometric ratio in evacuated sealed-off quartz ampoules with an inside pressure P=0.1Pa, under temperature T=1073K. The specific free volume of the material during a process amounted to 0.000314 m^3/kg. Calculation results are given in tables 2-4.

Table 1. Characteristics of organic and inoganic halogen-containing compounds.

Halogen	F	Cl				Br		I
Compounds	(C$_2$F$_4$)$_n$ organic	C$_2$Cl$_6$ organic	C$_6$Cl$_6$ organic	Hg$_2$Cl$_2$ inorganic	CdCl$_2$ inorganic	C$_6$H$_4$Br$_2$ organic	C$_6$Br$_6$ organic	CHI$_3$ organic
Molecular mass	50 (on chain)	236.7	284.7	472.2	183.3	235.8	551.4	393.7
Halogen content, mass.%	76.00	89.87	74.74	15.04	38.68	67.77	86.94	96.70
Halogen content, mole%	66.7	75	50	50	66.7	16.7	50	60
Factor of distribution of halogen in Bi$_2$Te$_3$ [5]	-	1.2	1.2	1.2	1.2	1.0	1.0	0.86

Table 2. The composition of gas-vapour and condensed phases at synthesis of $(Bi_2Te_3)_{90}(Bi_2Se_3)_{10}$ without doping and doped with inorganic compound - calomel (Hg_2Cl_2).

Components	Components, %mole			
	Without doping		0,125% Hg_2Cl_2	
T, K	1073	293	1073	293
Gas-Vapour Phase				
Se	0.0164	-	0.0188	-
Te	0.1577	-	0.1994	-
TeSe	0.0238	-	0.0273	-
Bi	$2.36 \cdot 10^{-6}$	-	$2.35 \cdot 10^{-6}$	-
BiCl	0	-	0.0116	-
$BiCl_3$	0	-	0.1297	-
BiSe	$5.01 \cdot 10^{-4}$	-	$4.81 \cdot 10^{-4}$	-
BiTe	$4.29 \cdot 10^{-4}$	-	$4.13 \cdot 10^{-4}$	-
Hg	0	-	0.4068	-
HgCl	0	-	$7.82 \cdot 10^{-7}$	-
$HgCl_2$	0	-	$6.50 \cdot 10^{-3}$	-
Condensed Phase				
Te	0	0.6928	0	0,4846
$BiCl_3$	0	0	0	0,1375
Bi_2Se_3	10,1927	10,1615	10,1356	10,1337
Bi_2Te_3	89,6085	89,1457	89,0635	88,8316
HgTe	0	0	0	0,4126

It is clear from table 2 that on doping of thermoelectric material with inorganic halogen-containing compound (Hg_2Cl_2), a corresponding bismuth halogenide $(BiCl_3)$ is formed in a synthesized material. Metal telluride (HgTe) as compound is known to be a p-type semiconductor and its presence in n-type material can affect the properties of the latter. Besides, a small amount of excess tellurium appears in synthesized material. As it is seen from table 3, the doping mechanism of organic halogen-containing compounds are similar to the mechanism of inorganic galogen-containing compounds. In synthesis and zone-melting of material the formation of the corresponding bismuth halide $(BiF_3, BiCl_3, BiBr_3, BiI_3)$, which on cooling transforms into a condensed phase and a small amount of tellurium appears. It should be noted, that formed bismuth fluoride (BiF_3) is in a condensed phase even at synthesis temperature.

Bismuth fluoride is a compound with high enthalpy of formation (ΔH^o_{293}): $2Bi+3F_2 \rightarrow 2BiF_3-904$ kJ/mole. In this case, probability of its dissociation in $Bi_2(Te,Se)_3$ solid solution is rather insignificant. Therefore, this compound cannot have any noticeable effect on thermoelectric properties. It should be noted that $BiCl_3$, $BiBr_3$, BiI_3 are characterized by rather low enthalpy of the formation (ΔH^o_{293}): -379 kJ/mole, -276 kJ/mole, -150 kJ/mole accordingly. Dissociation of these compounds in $Bi_2(Te,Se)_3$ solid solution takes place, which dielectric constant is similar to that of water ($\varepsilon=80$). In this case, halogens acquire an opportunity of releasing electrons to the zone of conductivity.

Table 3. The composition of gas-vapour phases at synthesis and zone-melting of n-$(Bi_2Te_3)_{90}(Bi2Se_3)_{10}$, which is doped with organic halogen-containing compounds, in which hydrogen is substituted for haloid completely.

Components	Components, %mole							
	0.020%$[C_2F_4]_n$		0.026%C_2Cl_6		0.031% C_6Cl_6		0.0493% C_6Br_6	
T, K	1073	293	1073	293	1073	293	1073	293
Gas-Vapour Phase								
Br	0	-	0	-	0	-	$6.885 \cdot 10^{-5}$	-
Se	$4.018 \cdot 10^{-2}$	-	$3.932 \cdot 10^{-2}$	-	$1.941 \cdot 10^{-2}$	-	$3.913 \cdot 10^{-2}$	-
Te	0.9009	-	0.8625	-	0.2201	-	0.8566	-
TeSe	$2.869 \cdot 10^{-2}$	-	$2.810 \cdot 10^{-2}$	-	$2.816 \cdot 10^{-2}$	-	$2.793 \cdot 10^{-2}$	-
Bi	$2.053 \cdot 10^{-6}$	-	$2.092 \cdot 10^{-6}$	-	$2.34 \cdot 10^{-6}$	-	$2.095 \cdot 10^{-6}$	-
BiF_3	$4.028 \cdot 10^{-3}$	-	0	-	0	-	0	-
BiCl	0	-	0.01236	-	$1.237 \cdot 10^{-2}$	-	0	-
$BiCl_3$	0	-	0.1665	-	0.1655	-	0	-
BiBr	0	-	0	-	0	-	$5.571 \cdot 10^{-2}$	-
$BiBr_3$	0	-	0	-	0	-	0.12026	-
BiSe	$4.708 \cdot 10^{-4}$	-	$4.745 \cdot 10^{-4}$	-	$4.759 \cdot 10^{-4}$	-	$4.741 \cdot 10^{-4}$	-
BiTe	$4.039 \cdot 10^{-4}$	-	$4.071 \cdot 10^{-4}$	-	$4.088 \cdot 10^{-4}$	-	$4.066 \cdot 10^{-4}$	-
CF_4	$3.229 \cdot 10^{-6}$	-	0	-	0	-	0	-
Condensed Phase								
Te	0	0.9977	0	0.9452	0	0.9398	0	0.8927
BiF_3	0.2027	0.2066	0	0	0	0	0	0
$BiCl_3$	0	0	0	0.1706	0	0.1685	0	0
$BiBr_3$	0	0	0	0	0	0	0	0.1389
Bi_2Se_3	10.0674	10.088	10.0878	10.11	10.1211	10.076	10.0633	10.0912
Bi_2Te_3	88.4452	88.3976	88.6318	88.604	88.9233	88.311	88.4202	88.4611
C	0.3101	0.3100	0.1706	0.1706	0.5090	0.5056	0.4159	0.4161

The results of thermodynamic calculation of products content in material synthesis doped with organic compounds, where not all hydrogen atoms are substituted for halogen are given in table 4.

Table 4. The composition of gas-vapour and condensed phases in synthesis of n-$(Bi_2Te_3)_{90}(Bi_2Se_3)_{10}$, which is doped with organic halogen-containing compounds, in which hydrogen is substituted for haloid only partially.

Compo-nents	Components, %mole			
	0.0633% $C_6H_4Br_2$		0.0773%CHI_3	
T, K	1073	293	1073	293
P, Pa	29400	0.1	33097	0.1
Gas-Vapour Phase				
H_2	0.1739	-	$6.02\ 10^{-2}$	-
I	0	-	$1.07\ 10^{-4}$	-
HI	0	-	$2.32\ 10^{-3}$	-
Br	$7.71\ 10^{-6}$	-	0	-
HBr	0.3943	-	0	-
Se	$1.60\ 10^{-2}$	-	$4.73\ 10^{-2}$	-
HSe	$7.17\ 10^{-5}$	-	$5.09\ 10^{-5}$	-
H_2Se	$3.18\ 10^{-2}$	-	$1.32\ 10^{-2}$	-
Te	0.1528	-	1.2365	-
HTe	$4.86\ 10^{-5}$	-	$3.46\ 10^{-5}$	-
H_2Te	$4.63\ 10^{-5}$	-	$1.91\ 10^{-5}$	-
TeSe	$2.32\ 10^{-2}$	-	$3.36\ 10^{-2}$	-
Bi	$2.31\ 10^{-6}$	-	$1.81\ 10^{-6}$	-
BiBr	$1.43\ 10^{-2}$	-	0	-
$BiBr_3$	$1.55\ 10^{-3}$	-	0	-
BiI	0	-	0.4524	-
BiI_3	0	-	$7.81\ 10^{-7}$	-
BiSe	$4.93\ 10^{-4}$	-	$4.51\ 10^{-4}$	-
BiTe	$4.23.10^{-4}$	-	$3.87\ 10^{-4}$	-
CH_4	$5.18\ 10^{-3}$	-	$6.18\ 10^{-4}$	-
CH_3Br	$1.54\ 10^{-6}$	-	0	-
Condensed Phase				
Te	0	0.8905	0	0.9185
$BiBr_3$	0	0.1378	0	0
BiI_3	0	0	0	0.152574
Bi_2Se_3	9.9941	10.0285	10.0201	10.11455
Bi2Te3	87.9571	87.9094	87.9817	88.6618
C	1.2347	1.0338	0.1510	0.1144

It is clear from table 4, that in using not-completely substituted organic halogen-containing compounds, the character of doping procedure is the same as with doping of completely substituted compounds. However, due to hydrogen presence in molecules of dopants while sinthesizing materials in a gas-vapour phase, the formation of a number of byproducts and intermediate products, for example H_2Te, H_2Se, the traces of which could be present in a final product is possible. As we see in tables 3 and 4, nearly all amount of carbon emitted in the process of organic halogen-containing compounds, is in condensed phase (graphite). The amount of graphite emitted in the process of thermal decomposition of the dopes under consideration, is

sufficient for the formation of a continuos film on the surface of the ampoules. The letter can be considered a favourable indicator, as it allows to eliminate the stage of quartz ampoules graphitization in the technological process.

4. Thermoelectric properties

All measurements of properties have been taken in parallel to the growth direction of ingots of 30mm diameter and about 220mm length. The results of conductivity measurements along ingots of zone-melting material doped with organic halogen-containing compounds are represented in figure 1.
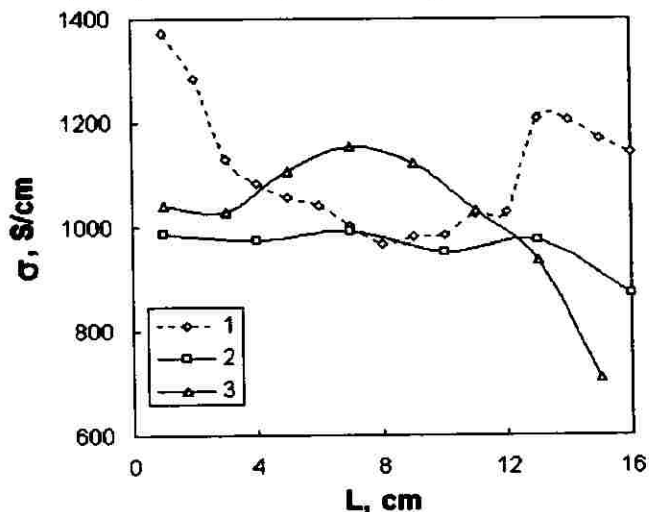
Figure 1. The dependence of conductivity (σ at 25°C) distribution along the ingot of n-$(Bi_2Te_3)_{90}(Bi_2Se_3)_{10}$ on the nature of the dopant: 1-C_2Cl_6; 2-C_6Br_6; 3-CHI_3.

As one can see, the most equal distribution of conductivity along the ingots is achieved with application of hexabromobenzene as a dopant.
The dependencies of conductivity and Seebeck coefficient n-$(Bi_2Te_3)_{90}(Bi_2Se_3)_{10}$ on the concentration of introduced organic halogen-containing compounds are shown in figure 2.
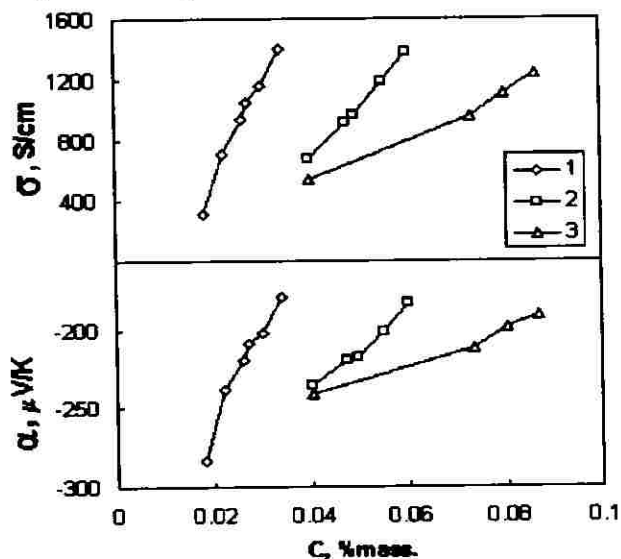
Figure 2. The dependence of conductivity (σ at 25°C) and Seebeck coefficient (α at 25°C) of n-$(Bi_2Te3)_{90}(Bi_2Se_3)_{10}$ on dopant content: 1-C_2Cl_6; 2-C_6Br_6; 3-CHI_3.

Different slopes of curves for different dopant additions in figure 2 are responsible for the differences in their molecular weights and correspondingly by differences in mass concentrations at equimolar content (by a halogen).

The influence of composition n-$Bi_2(Te,Se)_3$, doped with hexabromobenzene (C_6Br_6), on its temperature dependence of figure of merit was investigated. Temperature changes for materials with varying content of bismuth selenide are shown in figure 3.
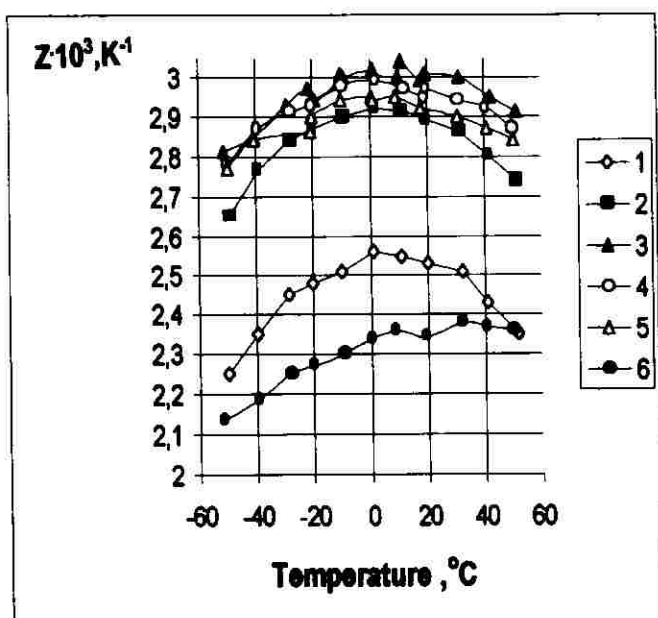

Figure 3. Temperature dependence of figure of merit for n-(Bi_2Te_3)(Bi_2Se_3) doped with hexabromobenzol (C_6Br_6) at various content of bismuth selenide (Bi_2Se_3, %mole):
1-0%; 2-4%; 3-6%; 4-8%; 5-10%; 6-20%.

It is clear from figure 3, that material containing 6% mole of bismuth selenide (Bi_2Se_3) and 0.049% mass. C_6Br_6 on doping, has conductivity 970-1000 S/cm, Seebeck coefficient 210-215 μV/K and mostly figure of merit z=3.0·10^{-3} K^{-1}.

5. Conclusions
Through the method of thermodynamic analysis the advantages of organic galogen-containing compounds for the doping of $Bi_2(Te,Se)_3$, as compared to inorganic ones are proved.

As a practical example, the experimental research into the doping ability of hexachloroethane (C_2Cl_6), hexaclorobenzol C_6Cl_6), dibromobenzol ($C_6H_4Br_2$), hexabromobenzol (C_6Br_6) and iodoform (CHI_3) has been effected.

The most equal distribution of conductivity along the zone-melting ingots n-$Bi_2(Te,Se)_3$ is achieved with application of hexabrombenzol (C_6Br_6) as a dopant.

The most figure of merit in the interval $\pm 50°C$, simultaneously with the most equal distribution of conductivity along zone-melting ingots is achieved in the solid solution Bi_2Te_3-Bi_2Se_3 doped with hexabrombenzol (C_6Br_6), containing 6% mole of bismuth selenide (Bi_2Se_3).

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