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PHYSICO-CHEMICAL INVESTIGATION OF Pb(Ge)Te-$Bi_2(Sb_2)Te_3$ SYSTEM TERNARY COMPOUNDS FORMATION

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ABSTRACT

Formation regularities of Pb(Ge)Te-$Bi_2(Sb_2)Te_3$ system compounds were determined and temperature-time characteristics of their polycrystal synthesis were also detailed. The values of standard enthalpy of $PbBi_4Te_7$, $PbBi_2Te_4$, $Pb_2Bi_2Te_5$ formations were estimated.

INTRODUCTION

The interaction of bismuth (antimony) and lead (germanium) tellurides when their ratio is equal to 1:2(3), 1:1 and 2:1 leads to a formation of ternary intermediate phases ($GeBi_4Te_7$, $GeBi_2Te_4$, $Ge_3Bi_2Te_6$, $GeBi_4Te_7$, $GeSb_2Te_4$, $Ge_2Sb_2Te_5$, $PbBi_4Te_7$, $PbBi_2Te_4$ and $Pb_2Bi_2Te_5$) which are perspective for the application in the semiconductor devices. But physico-chemical conditions of their synthesis have been previously characterized insufficiently.

The purpose of this paper was to study the features of Pb(Ge)Te-$Bi_2(Sb_2)Te_3$ system ternary intermetallic compounds formation. The contents of the investigations made for Pb(Ge)Te-$Bi_2(Sb_2)Te_3$ systems are illustrated in detail below on the instance of PbTe-Bi_2Te_3 alloys formation.

MEASURING METHODS

We studied the features of the direct interaction processes at linear heating mode of pressed mixtures of alloy and metal powders (PbTe and Bi_2Te_3) with ternary compound compositions. Alloy characteristics obtained in such a way (as melting temperatures (T^m)and heats (ΔH^m) as compositions) were compared with corresponding data for samples synthesized by a traditional ampoule method by using a prolonged annealing (for 100 and more hours) and also by hardening the melts having ternary phase composition which was obtained by mixing PbTe with Bi_2Te_3 at 1250 K and Te with Bi-Pb at 725 K.

Investigations were carried out by a quantitative differential

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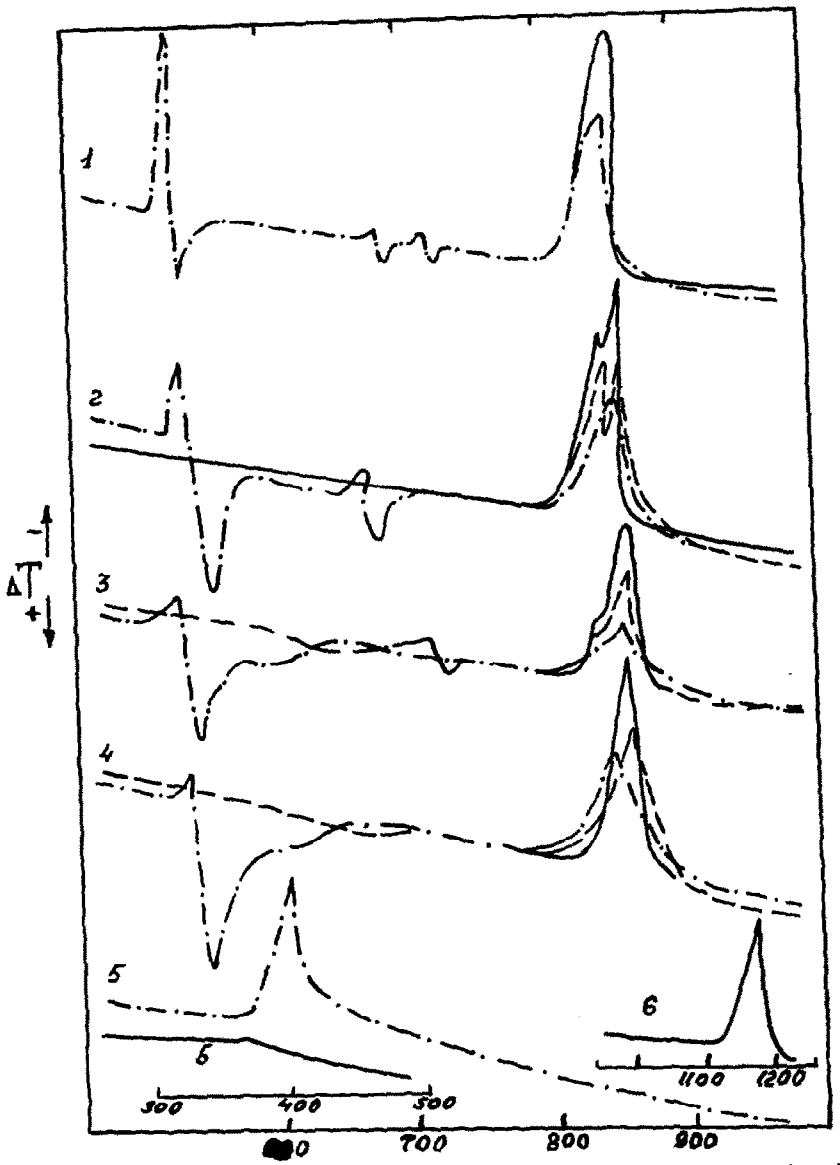
thermal (DTA) and X-ray phase analyses as previously in /1 /. All the experiments were done repeatedly, the error of definition reproduction of solidphase reaction heats (ΔH^s) and ΔH^m was equal to 5+7% and 2,5+3,0% respectively, in T^m - 0,1+0,2%. Material samples were prepared according to / 1 /.

RESULTS AND DISCUSSION

Experimental date obtained are represented in a graphical form in the figure and results of their processing are given below.

DTA and X-ray result analyses of compounds and corresponding mixtures permits to draw a conclusion , that at linear heating of the pressed powder mixtures 2Bi+3Te, Pb+4Bi+7Te, PbTe+2Bi_2Te_3, Pb+2Bi+4Te, PbTe+Bi_2Te_3, 2Pb+2Bi+5Te, 2PbTe+Bi_2Te_3, Pb+Te at the rate not exceeding 5 K/min the formation of Bi_2Te_3, $PbBi_4Te_7$, $PbBi_2Te_4$, and $Pb_2Bi_2Te_5$ takes place, but the formation of PbTe is not observed at such condition (as it is seen from DTA curves 5 and 6). Morever, thermal stimulator interaction of components in 1(1,2)Pb+ 4 (2,2)Bi+7(4,5) Te systems starts mainly after bismuth being melt and occures at the temperature range of 550-640 K. The presence of the peak with a variable sign in the range of 640-730 K is connected with incomplete tellurium reaction with other componens at a lower temperature stage of the process. Decreasing samples heating rate down to 2,5-3,0 K/min brings to their disappearance. In case of the thermal stimulated reaction of alloying elements it is impossible to fix exactly the process beginning temperature and the temperature of exopic maximum on DTA curve is in the range of 630-700 K. The comparison of ΔH^m, T^m and X-ray data for ternary compounds sythesized as a result of the direct interaction of components during a linear heating regimes and obtained by using a prolonged annealing make possible to draw a conclusion that in the first case they are cha racterized by a homogenous but a disordered structure. Ternary phase samples obtained by hardening the melts with ternary compounds(as a result of mixing PbTe liquid with Bi_2Te_3 and Te with Bi-Pb) have a similar structure. Note that two-stage annealing during 5-6 hours at 700-750 and 400-420 K of ternary tellurides samples obtained by metals and binary compounds interaction leads to their preferential ordering. For intermetallic samples obtained as a result of hardening the melts a full homogenizing at indicated temperature conditions of annealing is reached after 10-20 hours. The given temperature-time parameters of PbTe-Bi_2Te_3 system ternary compounds syn -



DTA curves typical elements (heating rate - 5 K/min) of alloy formation process at the temperature up to 1300 K.

I -for pure compounds; II- for metal mixtures
III -binary compounds mixtures

1-Bi_2Te_3, 2-$PbBi_4Te_7$, 3-$PbBi_2Te_4$, 4-$Pb_2Bi_2Te_5$,
5 and 6 -PbTe . (I- ——— ; II- —·—;III- – – –)

thesis at different coditions would give the representation of op-regimes with the help of which one can obtain their polycrystals.

Since the calculation of thermal effect values to which sign variable peaks on DTA curves correspond is difficult, according to the previouly suggested method /1/(location of indifferent material with demanded quantity of bismuth in the reference cell) we have extracted the thermal effect component for the heating rate of 2,5 K/min that corresponds to the direct chemical interaction of the metals leading to the ternary compound formations. Using this date and also the values of ternary compounds and pure metals / 2/ melting heats /3/ we calculated their standard formations enthalpies (ΔH^{o}_{298}). Analogous calculations were made by using H^{s} for binary compounds. Values of ΔH^{o}_{298} (kJ/mol) calculated from (Pb+Bi+Te) and ($PbTe-Bi_2Te_3$) solidphase reaction heats were found to be -220(210), -140(160) and -230(220) for $PbBi_4Te_7$, $PbBi_2Te_4$ and $Pb_2Bi_2Te_5$ respectively. It should be noted that H^{o}_{298} calculated by this method for Bi_2Te_3 (-75$\pm$kJ/mol) is agreed with a calorimetric value (-78 kJ/mol /4/) and for $PbBi_4Te_7$ with the value of -223$\pm$ 4 kJ/mol /2/ which have been determined by means of a high temperature solution calorimeter in liquid tin. This suppors a high reliability of the given values.

Established regularities of alloy formation in $PbTe-Bi_2Te_3$ system are in agreement with the results of our investigations of analogous $GeTe-Bi_2Te_3$ and $GeTe-Sb_2Te_3$ systems though some differences and typical features have been revealed.

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