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MODELING OF PHASE DIAGRAM OF THE SYSTEM BiI_3-Bi_2S_3-Bi_2Te_3

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Abstract. Using the 2D and 3D option of the computer Origin Lab, analytical dependencies of the liquidus temperatures on the composition for the binary and three-component phases of the system BiI_3-Bi_2S_3-Bi_2Te_3 were obtained, which allowed to visualize the crystallization surfaces of the Bi_2S_3, Bi_2Te_3, BiSI, $Bi_{19}S_{27}I_3$, BiTeI and Bi_2Te_2S separately and of all phases of the system BiI_3-Bi_2S_3-Bi_2Te_3 on one graph.

Keywords: *BiI_3-Bi_2S_3-Bi_2Te_3 system, 3D analytical modeling, liquidus surfaces.*

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1. Introduction

Chalcohalides of arsenic subgroup elements, in particular, bismuth chalcoiodides have been the focus of attention of researchers as valuable ferroelectric, thermoelectric, photovoltaic, magnetic, and optical materials (Koc *et al.*, 2017; Hahn *et al*., 2012; Khan *et al*., 2017; Ganose *et al.*, 2016). In the last few years, it has been determined that bismuth tellurohalides and phases on their basis also show the properties of a topological insulator and demonstrate 3D Rashba spin splitting, which opens up the possibilities to use them in spintronic devices (Ishizaka *et al*., 2011; Landolt *et al*., 2012; Eremeev *et al.*, 2017; Li *et al*., 2020; Wu *et al*., 2016; Maa *et al.*, 2016; Gennep *et al.*, 2014). The phase equilibria in Bi–S(Te)–I systems were studied, the projection of liquidus surfaces was constructed, melting character and primary crystallization regions of existing phases were determined (Aliev *et al*., 2014; Babanly *et al*., 2009). In Ahmadov, (2020) based on the results of the DTA and X-ray diffraction analysis, the phase equilibria in the BiTeI–BiSI system were studied and the *T–x* phase diagram was constructed. It was established that the system is stable in the subsolidus area and there are ~7–8 mol % and ~5 mol% solid solution areas based on BiTeI and BiSI compounds at room temperature, accordingly. The system is non-quasibinary. $Bi_{19}S_{27}I_3$ (0–33 mol % BiTeI) and tetradymite-Bi_2Te_2S (33–83 mol% BiTeI) phases primarily crystallize from the liquid phase in the wide composition ranges. In Ahmadov et al., (2021) phase equilibria in the quasi-ternary system Bi_2S_3–Bi_2Te_3–BiI_3 were studied by differential thermal analysis, powder X-ray diffraction analysis, and scanning electron microscopy. The isothermal sections at 300, 750, 800, and 850 K and some polythermal sections and a projection of the liquidus surface were constructed. The primary crystallization fields

and homogeneity regions of phases, and the types and coordinates of in- and monovariant equilibria were determined. It was shown that the system is characterized by the formation of limited regions of solid solutions based on bismuth sulfide and telluride, and also ternary compounds Bi_2Te_2S, BiSI, and BiTeI.

However, to date the phase diagram of BiI_3-Bi_2S_3-Bi_2Te_3system is not modeled. The analytical model of the phase diagram, in particular the 3D model of the crystallization surface of the phases, is very useful for choosing the optimal conditions for obtaining solid phases by crystallization of liquid alloys of the BiI_3-Bi_2S_3-Bi_2Te_3 system. The aim of this work is analytical 3D modeling of crystallization surfaces of all phases of the ternary system BiI_3-Bi_2S_3-Bi_2Te_3 based on the data of boundary systems and a small number of experimental DTA measurements.

2. Modeling Technique

For 3D modeling of crystallization surfaces in the BiI_3-Bi_2S_3-Bi_2Te_3 system, an analytical method was used, which was previously successfully tested in Yusibov et al., (2017, 2018). With regard to the three-component BiI_3-Bi_2S_3-Bi_2Te_3 system, the temperature dependences of the crystallization surface are determined as a function

$$T = f(x, y) \quad (1)$$

where: x -is the relative mole fraction Bi_2S_3: $y(Bi_2S_3/[y(Bi_2S_3)+ y(Bi_2S_3)]$ and y– is mole fraction of BiI_3 in ternary system BiI_3-Bi_2S_3-Bi_2Te_3.

The obtained analytical expressions for the ternary system the BiI_3-Bi_2S_3-Bi_2Te_3 and its binary boundary systems are given in Tables 1 and 2. The analytical dependences are presented in the form used by the Origin Lab computer program.

Modeling is carried out in this order. First, the temperature dependences on the composition are determined $T = f(x)$ and $T = f(y)$ for the liquidus of binary boundary systems. Next, on the basis of using the experimental ternary the BiI_3-Bi_2S_3-Bi_2Te_3 system defined function $T = f(x, y)$.

2.1. Binary boundary systems

The boundary quasi-binary constituents of the system BiI_3-Bi_2S_3-Bi_2Te_3 have been studied in detail (Aliev *et al*., 2014; Babanly *et al*., 2009; Yusa *et al*., 1979; Kuznetsov & Kanishcheva, 1970). In the system Bi_2S_3–BiI_3 (Fig.1), two ternary compounds, BiSI and $Bi_{19}S_{27}I_3$, form, which melt with decomposition by peritectic reactions at 808 and 990 K, respectively (Aliev *et al*., 2014). The compound BiSI crystallizes in the orthorhombic symmetry, and $Bi_{19}S_{27}I_3$ has a hexagonal lattice. In the system Bi_2Te_3–Bi_2S_3 (Yusa *et al.*, 1979; Kuznetsov & Kanishcheva, 1970), a variable-composition phase forms, the homogeneity region of which includes the mineral tetradymite Bi_2Te_2S. This compound melts congruently at 898 K and has a rhombohedral structure. The phase diagram of the system Bi_2Te_3–BiI_3 is characterized by the formation of the ternary compound BiTeI, which congruently melts at 828 K (Babanly *et al*., 2009) and has a trigonal structure.

The phase diagrams of the quasi-binary boundary systems BiI_3-Bi_2S_3, BiI_3-Bi_2Te_3 and Bi_2S_3-$Bi_2Te_3$and their analytical dependences for liquidus lines are shown in Table 1. Analytical dependencies are determined using the "analysis" option of the OriginLab computer program. From Fig. 1 it is shown that the obtained analytical dependence with

sufficient accuracy approximates the liquidus curve of compound BiTeI in the system BiI_3-Bi_2Te_3.

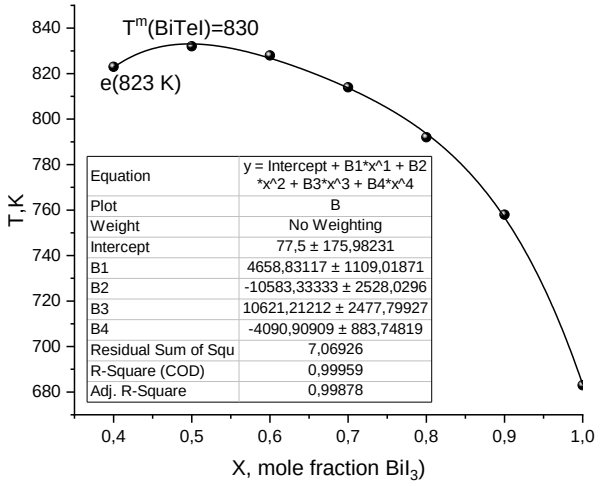
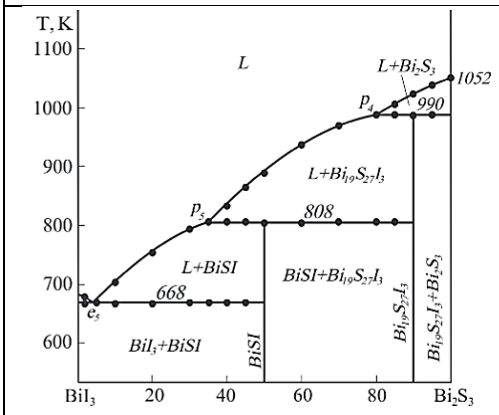
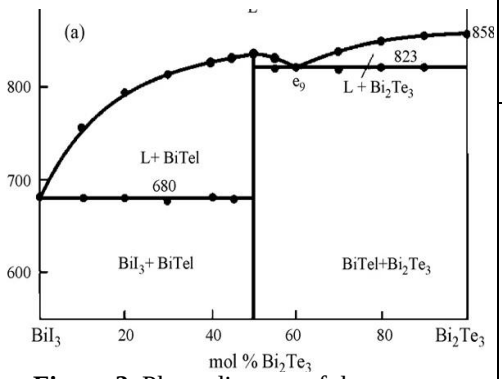


Figure 1. Dependence of the liquidus temperatures of the compound BiTeI on the composition in the system BiI_3-Bi_2Te_3: curve-polynomial, symbol-experiment (Babanly *et al*., 2009).

Table 1. Phase diagrams and analytical dependencies for their liquidus line of the BiI_3-Bi_2S_3, BiI_3-Bi_2Te_3 and Bi_2S_3-Bi_2Te_3 systems (equations are presented in computer variation)

Phase diagram	System, region	Equations: T, K=f(x)	Eq. N
 **Figure 2.** Phase diagram of the system BiI_3-Bi_2S_3 (Aliev *et al*., 2014)	BiI_3-Bi_2S_3, liquidus BiSI, x=*x*(Bi_2S_3)=0.045÷0.35	634+800*x-860*x^2	1
	BiI_3-Bi_2S_3, liquidus $Bi_{19}S_{27}I_3$, x=*x*(Bi_2S_3)=0.35÷0.8	498+1094*x-600*x^2	2
	BiI_3-Bi_2S_3, liquidus Bi_2S_3, x=*x*(Bi_2S_3)=0.8÷1.0	-58+2110*x-1000*x^2	3
 **Figure 3.** Phase diagram of the system BiI_3-Bi_2Te_3 (Babanly *et al.*, 2009)	BiI_3-Bi_2Te_3, liquidus Bi_2Te_3, x=*x*(BiI_3)= 0÷0.4	858-42,7*x+ 121,4*x^2-583*x^3	4
	BiI_3-Bi_2Te_3, liquidus BiTeI, x=*x*(BiI_3)= 0.4÷1	14+5095*x-11667*x^2+11783*x^3 -4545*x^4	5

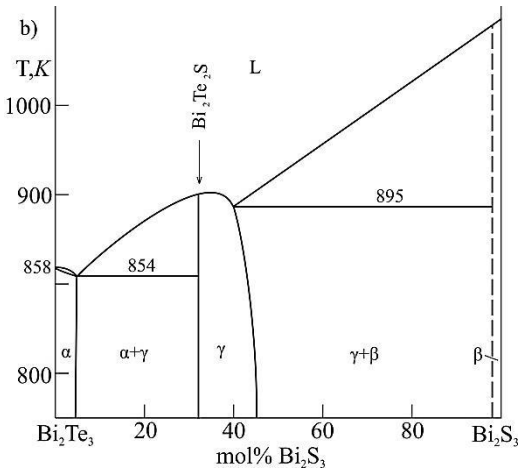


Figure 4. Phase diagram of the system Bi_2Te_3- Bi_2S_3 (Kuznetsov & Kanishcheva, 1970, refined in this work)

Bi_2Te_3- Bi_2S_3, liquidus Bi_2Te_3, x=*x*(Bi_2S_3)=0÷0.06	858-66.66*x	6
Bi_2Te_3-Bi_2S_3, liquidus Bi_2Te_2S, x=*x*(Bi_2S_3)=0.06÷0.4	809+973*x-4653*x^2+13416*x^3-16304*x^4	7
Bi_2Te_3-Bi_2S_3, liquidus Bi_2S_3, x=*x*(Bi_2S_3)=0.4÷1	748+405*x-101*x^2	9

2.2. System Bi_2I_3–Bi_2S_3–Bi_2Te_3

The analytical dependences for 3D modeling of the liquidus surfaces of the Bi_2S_3, Bi_2Te_3, BiSI, $Bi_{19}S_{27}I_3$, BiTeI and Bi_2Te_2S phases are given in Table 2 (equations 10-15). These equations allow visualizing the crystallization surfaces separately (Fig. 5) and on one graph of all phases (Fig. 6).

Table 2. Analytical dependencies for phase diagram of the BiI_3-Bi_2S_3-Bi_2Te_3 system

Compound liquidus surface	T,K=f(x,y); x= y(Bi_2S_3/[y(Bi_2S_3)+ y(Bi_2S_3)]; y=y(BI_3); y_i=mole fractions BiI_3,Bi_2S_3,Bi_2Te_3	Eq.N.
BiSI	(634+800*(1-y)-860*(1-y)^2)*x^0.2: x=0.4-1; y=0.6-0.945	10
$Bi_{19}S_{27}I_3$	(498+1094*(1-y)-600*(1-y)^2)*x^0.18 x=0.3-1; y=0.2-0.65	11
Bi_2S_3	(748+405*x-101*x^2)*(1-y)^0.27 x=0.4-1; y=0-0.2	12
Bi_2Te_3	(858-42,7*y+121,4*y^2-583*y^3)*(1-x)^0.2; x=0-0.2; y=0-0.4)	13
BiTeI	(14+5095*y-11667*y^2+11783*y^3-4545*y^4)*(1-x)^0.2; x=0-0.3; y=0.4-1	14
Bi_2Te_2S	(809+973*x-4653*x^2+13416*x^3-16304*x^4)*(1-y)^0.25 x=0.13-0.5; y=0-0.8	15

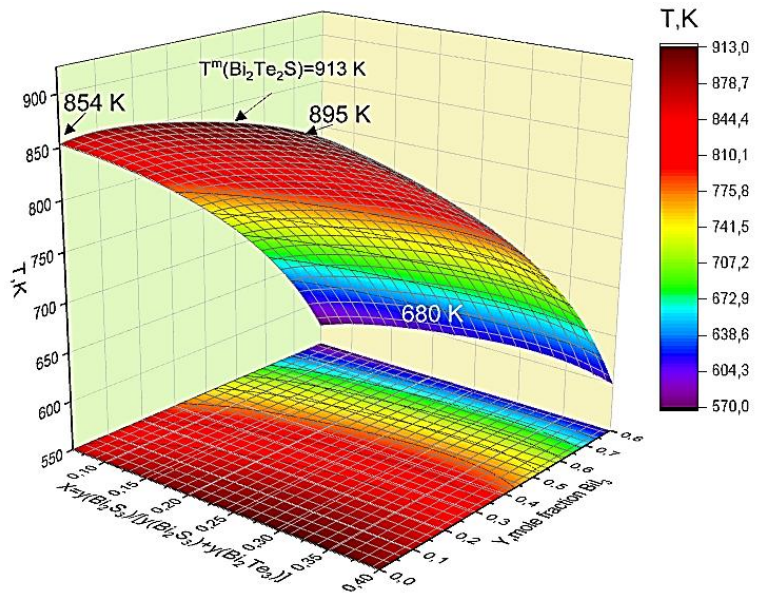


Figure 5. 3D model of crystallization surface Bi_2Te_2S, visualized by the equation 15 in table 2

The crystallization surfaces of all compounds in the BiI_3-Bi_2S_3-Bi_2Te_3 system are visualized in Fig. 6, where the 3D dimensional phase diagram of the system is viewed from the side of the BiI_3-Bi_2Te_3 system, from top to bottom.

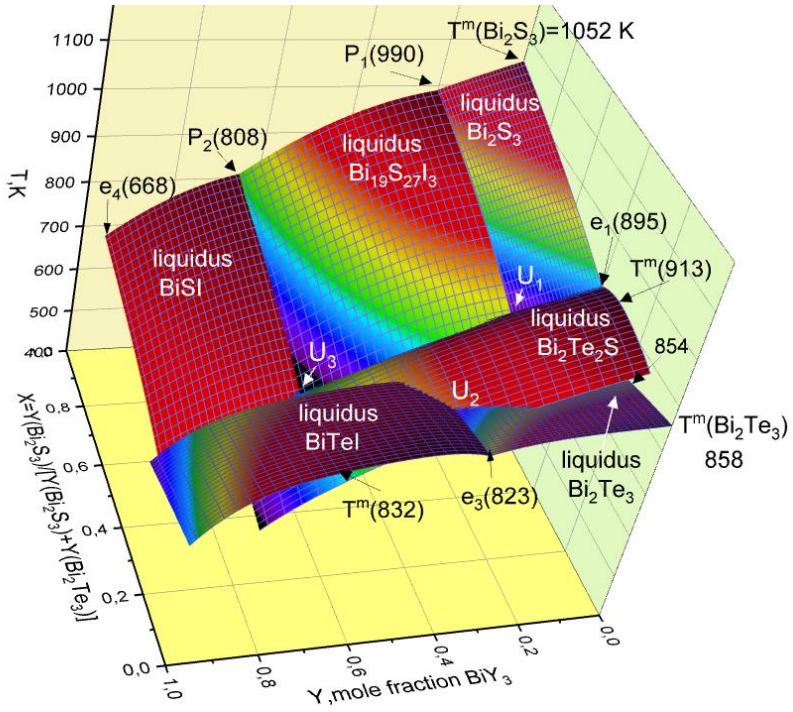


Figure 6. Multi-3D model of crystallization surfaces of the Bi_2S_3- Bi_2Te_3- BiI_3 system, visualized by the equations 10-15 in table 2

3. Conclusion

The obtained analytical dependences of the liquidus temperatures on the composition made it possible to visualize the crystallization surfaces of the Bi_2S_3, Bi_2Te_3, BiSI, $Bi_{19}S_{27}I_3$, BiTeI and Bi_2Te_2S separately and of all phases of the BiI_3-Bi_2S_3-Bi_2Te_3 system on one graph. Analytical dependences obtained using 2D and 3D option of the OriginLab program. 100x100 = 10,000 and 50x50 = 2500 tabular data in the form of matrices that can be used when choosing the optimal values of the composition, temperature for synthesis of binary and three-component phases BiI_3-Bi_2S_3-Bi_2Te_3 systems.

References

Ahmadov, E.J. (2020). Physico-chemical interaction in the BiSI–BiTeI system. *Azerb. Chem. J., 1,* 35-40.

Ahmadov, E.J., Aliev, Z.S., Babanly, D.M., Imamaliyeva, S.Z., Gasymov, V.A., Babanly, M.B. (2021). The Quasi-Ternary System Bi_2S_3–Bi_2Te_3–BiI_3. *Russ. J. Inorg. Chem., 66*(4), 538–549.

Aliev, Z.S., Musaeva, S.S., Jafarli, F.Y., Amiraslanov, I.R., Shevelkov, A.V., Babanly, M.B. (2014). The phase equilibria in the Bi–S–I ternary system and thermodynamic properties of the BiSI and $Bi_{19}S_{27}I_3$ ternary compounds. *J. Alloys Compd., 610,* 522–528.

Babanly, M.B., Tedenac, J.C., Aliev, Z.S., Balitsky, D.M. (2009). Phase eqilibriums and thermodynamic properties of the system Bi–Te–I. *J.Alloys Compd., 481*(1–2), 349–353.

Eremeev, S.V., Nechaev, I.A., Chulkov, E.V. (2017). Two- and three-dimensional topological phases in BiTeX compounds. *Phys. Rev. B., 96*(15), 1-9.

Ganose, A.M., Butler, K.T., Walsh, A., Scanlon, D.O. (2016). Relativistic electronic structure and band alignment of BiSI and BiSeI: candidate photovoltaic materials. *J. Mater. Chem. A., 4*(6), 2060-2068.

Gennep, D.V., Maiti, S., Graf, D., Tozer, S.W., Martin, C., Berger, H., Maslov, D.L., Hamlin, J.J. (2014). Pressure tuning the Fermi level through the Dirac point of giant Rashba semiconductor BiTeI. *J. Phys.: Condens. Matter., 26*(34), 342202-342208.

Hahn, N.T., Rettie, A.J.E., Beal, S.K., Fullon, R.R., Mullins, C.B. (2012). n-BiSI Thin films: selenium doping and solar cell behavior. *J. Phys. Chem. C., 116,* 24878–24886.

Ishizaka, K., Bahramy, M.S., Murakawa, H., Sakano, M., Shimojima, T., Sonobe, T., Koizumi, K., Shin, S., Miyahara, H., Kimura, A., Miyamoto, K., Okuda, T., Namatame, H., Taniguchi, M., Arita, R., Nagaosa, N., Kobayashi, K., Murakami, Y., Kumai, R., Kaneko, Y., Onose, Y., Tokura, Y. (2011). Giant Rashba-type spin splitting in bulk BiTeI. *Nat. Mater., 10*(7), 521-526.

Khan, W., Hussain, S., Minar, J., Azam, S. (2017). Electronic and Thermoelectric Properties of Ternary Chalcohalide Semiconductors: First Principles Study. *J. Elec. Materials, 47*(2), 1131-1139.

Koc, H., Palaz, S., Mamedov, A.M., Ozbay, E. (2017). Optical, electronic, and elastic properties of some $A^5B^6C^7$ ferroelectrics (A=Sb,Bi; B=Te,S,Se; C=I,Br,Cl): First principle calculation. *Ferroelectrics, 511,* 22–34.

Kuznetsov, V.G., Kanishcheva, A.S. (1970). X-ray study of alloys of the Bi_2Te_3-Bi_2S_3 system. *Neorg. Mater., 6,* 1268-1271.

Landolt, G., Eremeev, S.V., Koroteev, Y.M., Slomski, B., Muff, S., Neupert, T., Kobayashi, M., Strocov, V.N., Schmitt, T., Aliev, Z.S., Babanly, M.B., Amiraslanov, I.R., Chulkov, E.V., Osterwalder, J., Dil, J.H. (2012). Disentanglement of Surface and Bulk Rashba Spin Splittings in Noncentrosymmetric BiTeI. *Rew. Phys. Rev. Letters., 109*(11), 1-5.

Li, X., Sheng, Y., Wu, L., Hu, S., Yang, J., Singh, D.J., Yang, J., Zhang, W. (2020). Defect-mediated Rashba engineering for optimizing electrical transport in thermoelectric BiTeI. *Npj. Comput. Mater., 6*(1), 107-113.

Maa, H., Bentmann, H., Seibel, C., Tusche, C., Eremeev, S.V., Peixoto, T.R.F., Tereshchenko, O.E., Kokh, K.A., Chulkov, E.V., Kirschner, J., Reinert, F. (2016). Spin-texture inversion in the giant Rashba semiconductor BiTeI. *Nat. Commun.,7*, 11621-11627.

Wu, L., Yang, J., Zhang, T., Wang, S., Wei, P., Zhang, W., Chen, L., Yang, J. (2016). Enhanced thermoelectric performance in the Rashba semiconductor BiTeI through band gap engineering. *J. Phys.: Condens. Matter., 28*(8), 085801-085807.

Yusa, K., Sugaki, A., Kitakaze, A. Phase relation of some sulfide systems. (1979). *J. Jpn. Assoc. Min., 74*, 162.

Yusibov, Yu.A., Alverdiev, I.Dzh., Ibragimova, F.S., Mamedov, A.N., Tagiev, D.B., Babanly, M.B. (2017). Study and 3D Modeling of the Phase Diagram of the Ag–Ge–Se System. *Rus. J. Inorg. Chem., 62*(9), 1223–1233.

Yusibov, Yu, A., Alverdiev, I.Dzh., Mashadieva, L.F., Babanly, D.M., Mamedov, A.N., Babanly, M.B. (2018). Experimental Study and 3D Modeling of the Phase Diagram of the Ag–Sn–Se System. *Russ. J. Inorg. Chem., 63*(12), 1622–1635.