SYNTHESIS AND CHARACTERIZATION OF THE BiTe$_{1-x}$Se$_X$I SOLID SOLUTIONS SERIES

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Nowadays, the bismuth tellurohalides and their derivatives are one of most studied and required materials in the condensed matter physics community thanks to giant-spin orbit Rashba-type spin-splitting in their free-electron-like surface states. This work describes the synthesis and characterization of the BiTe$_{1-x}$Se$_x$I solid solutions series based on the BiTeI, which is known as a giant- Rashba semiconductor. The existence of the BiTe$_{1-x}$Se$_x$I solid solutions series (γ_1 and γ_2) experimentally confirmed by powder *X*-ray diffraction (PXRD) and scanning electron microscope equipped with energy dispersive *X*-ray spectrometer (SEM-EDS). Phase diagram of the system were plotted based on experimental data from Differential Thermal Analysis (DTA).

Keywords: phase diagram; materials synthesis; bismuth selenoiodide; bismuth telluroiodide; solid solutions
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1. INTRODUCTION

Since the existence of giant three-dimensional (3D) bulk Rashba-type spin splitting has recently been reported in the polar layered non-centrosymmetric BiTeI [1-2], the bismuth containing tellurohalides became one of the much more attractive materials in condensed matter physics [3-6]. These materials have been reported to have a strong spin-orbit interaction effect that reveals new paths for the realization of spin-based electronic devices based on them. On the other hand, sulfo- and selenohalides of a group 15 metals have been intensively studied over the last four decades due to their intriguing ferroelectric, piezoelectric and semiconducting properties [7-11]. The growing interest to these materials steams from their intriguing electronic properties which make them perspective source materials for spin-based electronics and ferroelectric, thermoelectric, photovoltaic, etc., devices [1, 2, 9-11].

The rational design and elaboration of such ternary or quaternary new phases, in particular, solid solutions having a non-centrosymmetric crystal structure and variable chemical compositions by cation and anion substitutions is of significant interest from the point of view optimized properties. Considering increasing interest to this class of materials, the thorough investigation of phase diagrams for the respective element systems is of particular importance to find proper starting composition for the elaboration of materials with optimized properties [13-14].

Here, we present the experimental study of the phase BiTeI - BiSeI system. This study can shed light on the chemical design of the new phases with variable compositions based on the starting multifunctional compounds of the systems namely, BiTeI and BiSeI.

The ternary compound BiTeI was found in the Bi$_2$Te$_3$-BiI$_3$ system. This system includes only this compound melts congruently at 828 K and crystallizes in a hexagonal system with space group *P*3*m*1 and lattice parameters a =4.3392(1), c =6.854(1) *Å* and z =1 [15]. Another starting compound, BiSeI was reported along the quasi-binary Bi$_2$Se$_3$-BiI$_3$ system that has been investigated by different authors so far. The literature data on this binary system until 2004 were reviewed by Oppermann [16]. This compound melts incongruently at 818 K and crystallizes in the SbSI-type orthorhombic crystal system with space group *Pnma* and lattice a = 8.697(2), b = 4.221(1)*, c = 10.574(2) *Å* and z = 4 [17].

2. EXPERIMENTAL PART

2.1. Synthesis

Starting BiSeI and BiTeI were synthesized from the elements of a high purity grade (not less than 99.999%) in sealed (~10^{-3} Pa) silica ampoules at 850 K. Synthesis processes of the compounds performed in a split tube furnace by a specially designed method that takes into account of the high volatility of iodine. The syntheses were performed in an inclined three-zone furnace, with two hot zones kept at 850 K, whereas the temperature of the cold zone was 400 K. After the bulk of the iodine reacted, the ampoules were relocated such that the products melted at 850 K. The melts were stirred at these temperatures by slightly shaken of ampoules and then cooled in the furnace. Because of BiSeI melt by peritectic reactions, it was further annealed at 770 K for 250 h in order to complete homogenization. All the considered samples along the BiSeI- BiTeI (total mass = 0.5g) were prepared from preliminary synthesized ternary compounds. After melting, the alloys were annealed at 730 K for two weeks.

2.2. Analysis

DTA, PXRD, and SEM-EDS techniques were employed to test the purity of the synthesized starting compounds and analyze the alloys. Thermal analysis was carried out using a NETZSCH 404 F1 Pegasus system from room temperature up to1000 K with a heating rate of 10 K min^{-1}. Temperatures of thermal effects were taken from the heating thermograms. The PXRD patterns were recorded on a Bruker D8 ADVANCE diffractometer with Cu-Kα_1 radiation within the range of 2 θ = 5° ÷75°. The microstructures and equilibrium compositions for the some selected samples were determined by Tescan Vega 3 SBH scanning electron microscope equipped with ThermoScientific UltraDry Compact EDS Detector.

3. RESULTS AND DISCUSSIONS

The phase diagram of BiSeI-BiTeI system was plotted based on the DTA, PXRD and SEM data of the equilibrated alloys (fig. 1). The system was found to be non-quasi-binary. Apparently, this section is represented by the liquidus surface of the β-phase in the wide range of composition (0-75 mol% BiTeI). The β- phase appears here due to this section is a qausi-binary part of the Bi_2Te_3-$BiSe_3$-BiI_3 system. The β- phase is a continuous solid-solution area of the Bi_2Se_3-Bi_2Te_3 system and can be shown as $Bi_2Se_{3-x}Te_x$ (0≤ x ≤1) [18]. The detailed investigation of the phase relationships of the different phases, including that β- phase along the Bi_2Te_3-$BiSe_3$-BiI_3 system is under investigation and will be published soon. In the subsolidus region, two wide solid-solution areas were revealed based on BiSeI (γ_1) and BiTeI (γ_2). The primary crystallization of the γ_2 -phase based on the

BiTeI occurs in the BiTeI-rich part of the system. A horizontal line at 760 K reflects the invariant transition reaction (*U*) L + β ↔ γ_1 + γ_2 that leads to the formation of biphasic γ_2 + γ_1 area in the subsolidus region. The expansion of this biphasic area was measured to be 30-45 mol% BiTeI at 760 K. The existence of these mono- and biphasic areas along this section were confirmed by PXRD and SEM micrographs (figs. 2 and 3 *a-c*). Fig. 2 displays the PXRD patterns of the selected alloys along the BiSeI-BiTeI section. Evidently, the PXRD patterns of alloys #1 and #2 are qualitatively similar to BiSeI, whereas the patterns of samples #5, #6 and #7 are entirely composed by diffraction peaks of BiTeI. On the other hand, it was observed that upon increasing the BiTeI content in both the γ_1- and γ_2- phases, there is negligible sifting in the peak positions on respective XRD patterns (alloys #1, #2 and #5, #6, #7) towards smaller angles. This fact is typical for the systems containing wide solid-solutions areas, and further confirms the existence and homogeneity areas of the γ_1- and γ_2- phases. The PXRD patterns for the alloys #3 and #4 display their biphasic content with clearly observed diffraction peaks typical for both starting BiTeI and BiSeI (distinguished by black triangles and blue circles in fig. 2, respectively). The phase constitutions of the BiSeI- BiTeI alloys are further confirmed in SEM micrographs of the alloys #2, #4 and #5 (figs. 3 *a-c*). Obviously, mono- and biphasic microstructures were observed in the SEM images for the alloys #2, #5 and #4, respectively. The microstructure of the alloy #4 (fig. 3 *b*) displays clearly co-crystallized γ_1- and γ_2- phases whereas, alloys #2 and #5 (Figs. 3 *a, c*) were found to be single phase according to pure γ_1- and γ_2- phases, respectively.
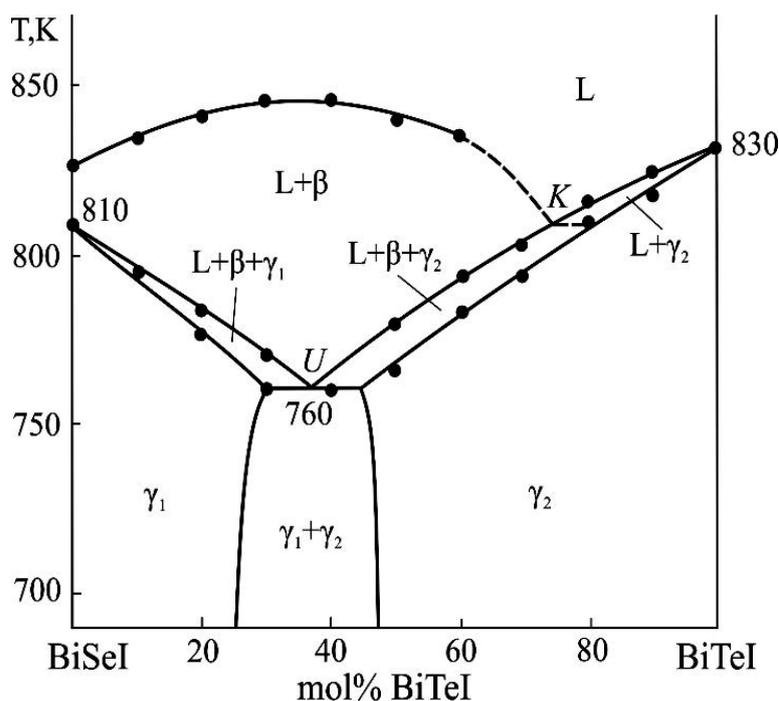
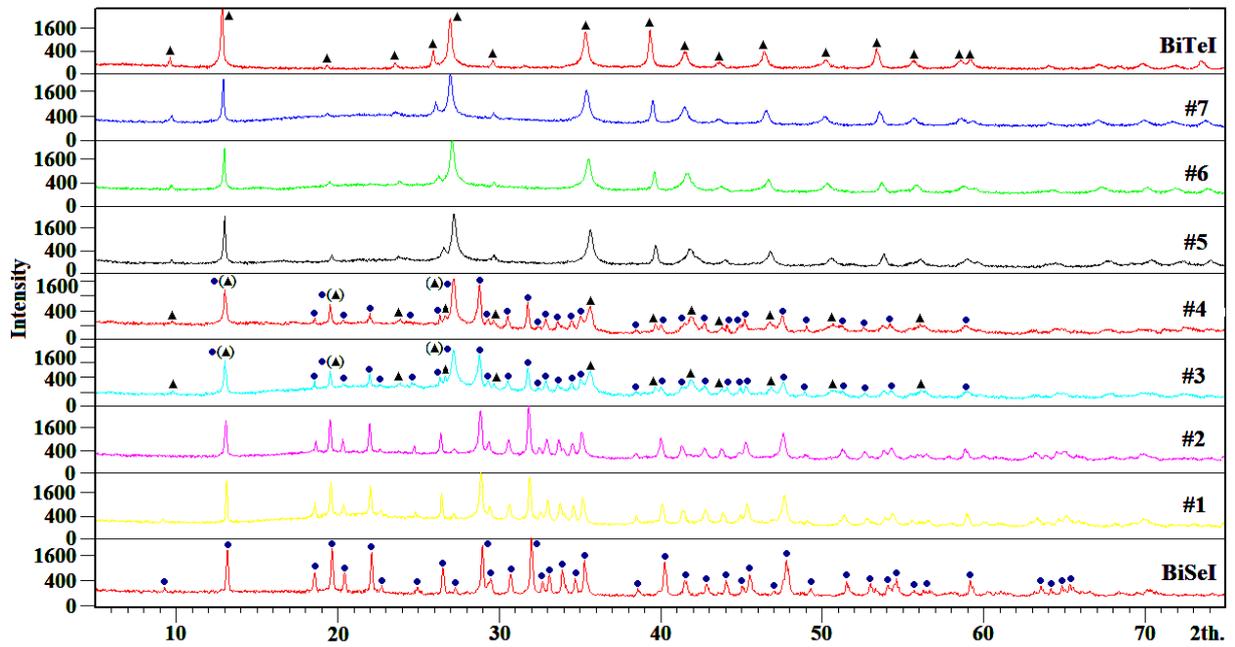*Fig. 1.* The phase diagram of the BiSeI – BiTeI system

Fig. 2. PXRD patterns for different alloys in the BiSeI- BiTeI section: #1, 10 mol % BiTeI; #2, 20 mol %; #3, 30 mol %; #4, 40 mol %; #5, 50 mol %; #6, 60 mol %; #7, 80 mol
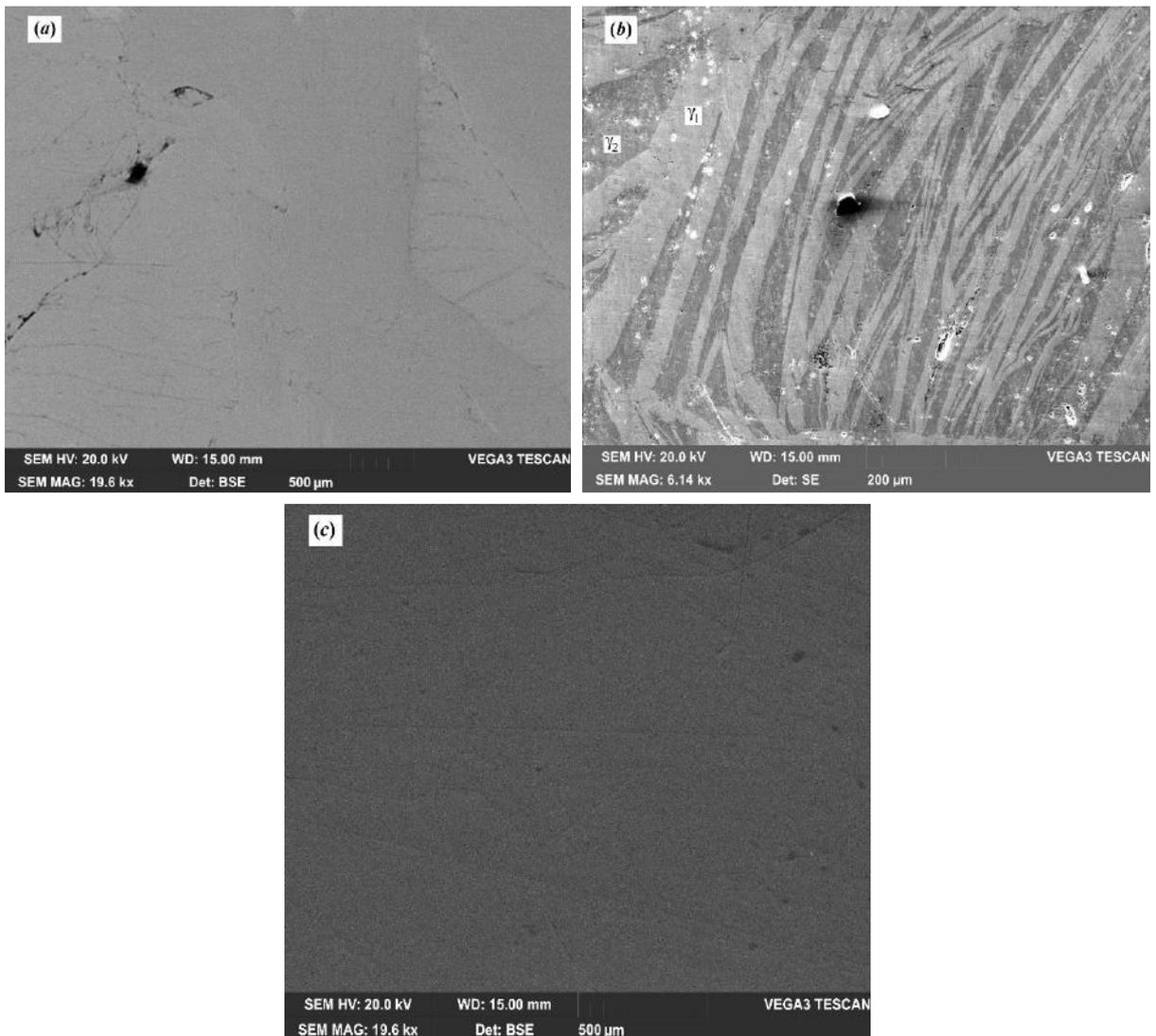

Fig. 3. SEM micrographs of the selected alloys #2 (a); #4 (b) and #5 (c) in the BiSeI- BiTeI section

4. CONCLUSION

The phase equilibrium in the BiSeI- BiTeI system was studied experimentally, shown that it is a non-quasi-binary one and features by wide solid solution areas based on the starting BiSeI and BiTeI compounds, respectively. The obtained data collected in this work, provides very valuable information for optimizing the synthesis and growth conditions of newly obtained materials. Particularly, the considered system is of significant importance in terms of the rational design of new $BiTe_{1-x}Se_xI$ solid solutions (γ_2-phase), which are expected to exhibit Rashba type spin splitting in the electronic structure similar to undoped BiTeI, which is known as a giant- Rashba semiconductor.

[1] *K.Ishizaka, M.S.Bahramy, H.Murakawa, M.Sakano, T.Shimojima, T.Sonobe, K.Koizumi, S.Shin, H.Miyahara, A.Kimura, K.Miyamoto, T.Okuda, H.Namatame, M.Taniguchi, R.Arita, N.Nagaosa, K.Kobayashi, Y.Murakami, R.Kumai, Y.Kaneko, Y.Onose, Y.Tokura.* Nat. Mater. 10, 521, 2011.

[2] *G.Landolt, S.V. Eremeev, Yu. M. Koroteev, B.Slomski, S.Muff, T.Neupert, M.Kobayashi, V.N. Strocov, T.Schmitt, Z.S. Aliev, M.B. Babanly, I.R. Amiraslanov, E.V. Chulkov, J. Osterwalder, J.H. Dil.* Phys. Rev. Lett. 109, 116403 2012.

[3] *M.S. Bahramy, B.J. Yang, R. Arita, N.Nagaosa.* Nature Commun. 3, 679, 2012.

[4] *G.Landolt, S.V. Eremeev, O.E. Tereshchenko, S. Muff, B. Slomski, K.A. Kokh, M. Kobayashi, T.Schmitt, V.N. Strocov, J.Osterwalder, E.V. Chulkov* and *J.H. Dil.* New J. Phys. 15, 085022, 2013.

[5] *S.Fiedler, T.Bathon, S.V.Eremeev, K.A.Kokh, O.E.Tereshchenko, E.V.Chulkov, P.Sessi, H.Bentmann, M.Bode, F.Reinert.* Phys. Rev. B 92, 235430, 2015.

[6] *M.S. Bahramy, N.Ogawa.* Adv. Mater. 29, 1605911, 2017.

[7] *A. Audzijonis, R. Sereika R. Žaltauska.,* Solid State Commun. 147, 88-89, 2008.

[8] *K. Łukaszewicz, A. Pietraszko, M. Kucharska,* Ferroelectrics. 375,170-177, 2008.

[9] *A.Audzijonis, G.Gaigalas, L.Žigas, R.Sereika, R.Žaltauskas, D.Balnionis, A.Rėza.* Phys. Status Solidi B 246, 7, 1702–1708, 2009.

[10] *A.Audzijonis, R.Zaltauskas, R.Sereika, L.Zigas, A.Reza,* J. Phys. Chem. Solids 71, 884–891, 2010.

[11] *A.M.Ganose,K.T.Butler,A.Walsh, D.O.Scanlon.* J.Mater. Chem. A, 4, 2060-2068, 2016.

[12] *H. Zhang, C.X. Liu, X.L. Qi, X. Dai, Z. Fang, S.C. Zhang.* Nat. Phys. 5, 438–442, 2009.

[13] *G.Gottstein.* Physical Foundations of Materials Science. Springer. XIV, p. 502, 2004.

[14] M.*B. Babanly, E.V. Chulkov, Z.S. Aliev, A.V. Shevelkov, I.R. Amiraslanov.* Russ. J. Inorg. Chem., 62, 1703–1729, 2017.

[15] *A.V.Shevelkov, E.V.Dikarev, R.V.Shpanchenko, B.A. Popovkin.* J. Solid State Chem. 114, 379-384, 1995.

[16] *H.Oppermann,U.Petasch,P.Schmidta,E.Keller, V.Kramer.* Z.Naturforsch. 59b, 727 –746, 2004.

[17] *T.P. Braun, F.J. DiSalvo.* Acta Crystallogr. C 56, e1- e2, 2000.

[18] *H.G. Bouanani, D.Eddike, B.Liautard, G.Brun,* Mater. Res. Bull. 31, 2, 177-187, 1996.