Physico-chemical analysis of the sections of the ternary BiCl₃-LiCl-AgCl systems

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Abstract. Recently, the use of halogens and their compounds in industry and the national economy has increased. The halides of the ternary systems Ag – Bi – Li of are insufficiently studied. So, to create semiconductor materials on their basis, the analysis of this system has become very important. In this paper, the character of interaction of the binary sections in the BiCl₃-LiCl-AgCl ternary system is studied through a complex of methods of physical and chemical analysis, precisely by differential thermal and X-ray phase analyses. The analysis of the obtained data allowed to establish the eutectic character of interaction in the LiCl-AgBiCl₄ system. It was confirmed that the addition of AgBiCl₄ lowers significantly the melting point of the second component. Also, it was defined as the eutectic character of interaction with limited solubility of the components in the AgBiCl₄-LiBiCl₄ and AgBiCl₄-LiBi₄Cl₁₃ systems.

1. Introduction
The development of physical and chemical bases of halogenation is explained by the increasing role of halogens in various manufacturing processes of chemical raw materials to obtain pure and superpure materials. Halides of various metals appear to be non-conventional materials in this field.

2. Problem statement
The aim of this paper is to analyse binary sections of LiCl-AgBiCl₄, LiBiCl₄-AgBiCl₄, LiBi₄Cl₁₃-AgBiCl₄ in the BiCl₃-LiCl-AgCl ternary system using the complex methods of physical-chemical analysis: differential thermal and X-ray phase analysis [1, 2].

3. Scientific novelty
A quasi-binary section of LiCl-AgBiCl₄ and polythermal sections of LiBiCl₄-AgBiCl₄, LiBi₄Cl₁₃-AgBiCl₄ in the BiCl₃-LiCl-AgCl ternary system are studied firstly.

According to the literature data [3, 4, 5] the LiCl- AgCl binary system is characterized by a number of solid solutions; the BiCl₃-AgCl system is characterized by the formation of the AgBiCl₄ chemical compound at a ratio of 1:1; the BiCl₃ – LiCl system is characterized by the formation of chemical compounds at a ratio of 1: 1 and 1: 4, i.e. the LiBiCl₄ and LiBi₄Cl₁₃ compounds.

4. Materials and methods
To analyse the section of the LiCl-AgBiCl₄ compound the alloys of chemical compounds or solid solutions were taken.

Pre-weighed samples (3.0000 g) were thoroughly mixed and homogenized to bring into equilibrium at temperatures below the melting temperatures of the respective compositions and time regimes. The mixture of chlorides were vacuumed and sealed in the molybdenum vessels of Stepanov (5 cm³) and annealed to provide the equilibrium state. The vessels were then cooled to room temperature in a furnace.

Differential thermal analysis was carried out on a thermal analyzer (DTA-850), the heating rate of the samples was 1–25 deg/min. The standard was calcined aluminum oxide, HC model number. To stabilize the temperature, the required time was 10 minutes, after which the study began.

X-ray phase analysis was performed on XRD-7000 Maxima diffractometer manufactured by Shimadzu with vertical goniometer by a continuous flow method. The obtained diffractograms were identified and compared with the database of X-ray card index of PDF-2 2012.

The measurement process was completely controlled by the computer. Using the software, the measurement results were subjected to various profile processing (smoothing, background subtraction), peak parameters processing (peak search, systematic error correction, internal/external standard method).

The accuracy in determining the reflection angles Δ θ did not exceed 0.02 °C. The hygroscopic samples were protected from air contact by X-ray amorphous film. The original components were identified using X-ray card index ASTM, interplanar distances were found in the tables of Hiller J.L.

5. Discussion of results

The alloys from the area of formation of solid solutions or chemical compounds of the AgBiCl₄ – LiCl system are of practical interest as solid electrolytes [6-11]. According to the results of DTA a polythermal section was constructed. The melting temperature of the primary components are respectively equal to 100°C (AgBiCl₄) and 610 °C (LiCl). The following phases are found on the diagram of the analysed system: L, three double phases: L+ LiCl, L+ AgBiCl₄, LiCl + AgBiCl₄, two triple L+LiCl + AgCl, L+ AgCl + AgBiCl₄ phases. The analysis showed that the addition of LiCl increases the melting point of the alloys, while the addition of AgBiCl₄ lowers the melting point of the alloys; and this corresponds to the 1st Gibbs-Konovalov law. Interplanar distances are gradually increased for alloys, hence the solid phase of the analysed system is relatively rich in LiCl.

The XRPD results confirm the presence of primary crystallization fields.

In the analysed AgBiCl₄ – LiBiCl₄ system a polythermal section is firstly built, in which there are no solid-phase transformations at the temperature below the solidus level.

The system has three single-phase areas: L, α – and β-solids solutions based on the initial components, there are three double areas: L + α, L + β, α + β and the area of L + α + β non-variant equilibrium. The solidus curve was calculated theoretically by the Schroeder – Le-Chatelier equation, and the experimentally obtained data are in good agreement with them. The analysis of XRPD data confirmed the absence of solid-phase transformations, which is a consequence of a monotonic change in the interplanar distance.

In the LiCl-AgBiCl₄, LiBiCl₄-AgBiCl₄ sections of the LiCl-AgCl-BiCl₃ system the analysis of peak intensities showed that the transition from 100 % of the AgBiCl₄ content to 100% of LiCl content in the alloys of the intensity and interplanar distances change monotonically, indicating the preservation of the structure of the samples (tabl. 1–2).
Table 1 The results of X-ray phase analysis of the LiCl – AgBiCl₄ section of the alloys

|                | 100 | 75  | 60  | 30  | 0   |
|----------------|-----|-----|-----|-----|-----|
| The contents of AgBiCl₄, mol % |
| d, nm | I  | d, nm | I  | d, nm | I  | d, nm | I  | d, nm | I  | d, nm | I  |
| 0.713  | 100 | 0.725 | 93 | 0.738 | 92 | 0.725 | 100 | 0.714 | 4  |
| 0.641  | 9   | 0.689 | 33 | 0.670 | 3  | 0.660 | 8   | 0.691 | 4  |
| 0.568  | 5   | 0.651 | 30 | 0.641 | 4  | 0.530 | 12  | 0.653 | 5  |
| 0.367  | 76  | 0.619 | 28 | 0.615 | 4  | 0.479 | 10  | 0.598 | 13 |
| 0.342  | 50  | 0.583 | 48 | 0.598 | 4  | 0.452 | 12  | 0.467 | 9  |
| 0.296  | 43  | 0.527 | 15 | 0.471 | 4  | 0.432 | 8   | 0.427 | 9  |
| 0.276  | 88  | 0.504 | 15 | 0.455 | 3  | 0.406 | 12  | 0.423 | 8  |
| 0.268  | 74  | 0.488 | 18 | 0.419 | 2  | 0.398 | 10  | 0.407 | 5  |
| 0.244  | 57  | 0.446 | 18 | 0.400 | 4  | 0.366 | 46  | 0.394 | 6  |
| 0.219  | 17  | 0.419 | 48 | 0.366 | 30 | 0.343 | 39  | 0.380 | 15 |
| 0.194  | 40  | 0.395 | 35 | 0.353 | 3  | 0.318 | 14  | 0.359 | 5  |
| 0.184  | 26  | 0.375 | 18 | 0.350 | 3  | 0.309 | 12  | 0.350 | 5  |
| 0.175  | 5   | 0.360 | 23 | 0.332 | 6  | 0.277 | 39  | 0.345 | 5  |
| 0.171  | 8   | 0.340 | 23 | 0.318 | 36 | 0.274 | 19  | 0.319 | 4  |
| 0.168  | 14  | 0.320 | 40 | 0.305 | 8  | 0.268 | 80  | 0.299 | 10 |
| 0.166  | 40  | 0.316 | 25 | 0.293 | 4  | 0.255 | 12  | 0.284 | 4  |
| 0.160  | 40  | 0.306 | 15 | 0.285 | 4  | 0.240 | 17  | 0.274 | 4  |
| 0.157  | 22  | 0.289 | 23 | 0.275 | 100 | 0.220 | 14  | 0.271 | 100 |
| 0.152  | 17  | 0.285 | 25 | 0.266 | 13 | 0.195 | 23  | 0.259 | 11 |
| 0.146  | 12  | 0.278 | 100 | 0.250 | 6  | 0.194 | 25  | 0.255 | 8  |
| 0.137  | 14  | 0.269 | 40 | 0.244 | 15 | 0.187 | 19  | 0.254 | 9  |
| 0.253  | 23  | 0.233 | 3  | 0.182 | 35 | 0.226 | 8   |
| 0.239  | 25  | 0.227 | 2  | 0.176 | 8   | 0.221 | 9   |
| 0.233  | 13  | 0.226 | 3  | 0.166 | 42  | 0.220 | 10  |
| 0.228  | 13  | 0.219 | 4  | 0.160 | 12  | 0.211 | 8   |
| 0.216  | 18  | 0.216 | 4  | 0.157 | 15  | 0.207 | 6   |
| 0.196  | 53  | 0.198 | 4  | 0.156 | 19  | 0.201 | 4   |
| 0.191  | 10  | 0.195 | 23 | 0.152 | 15  | 0.200 | 4   |
| 0.168  | 20  | 0.192 | 3  | 0.146 | 15  | 0.196 | 5   |
| 0.160  | 18  | 0.184 | 4  | 0.144 | 4   | 0.193 | 5   |
| 0.145  | 15  | 0.183 | 7  | 0.140 | 10  | 0.192 | 10  |
| 0.140  | 15  | 0.181 | 5  | 0.138 | 12  | 0.184 | 5   |
| 0.139  | 18  | 0.167 | 10 | 0.137 | 6   | 0.181 | 4   |
| 0.137  | 12  | 0.166 | 8  | 0.136 | 8   | 0.180 | 6   |
| 0.135  | 12  | 0.160 | 5  | 0.134 | 8   | 0.176 | 8   |
| 0.129  | 18  | 0.161 | 4  | 0.129 | 8   | 0.172 | 8   |
| 0.124  | 15  | 0.157 | 12 | 0.126 | 19  | 0.170 | 4   |
Table 2. The results of X-ray phase analysis of the LiBiCl₄–AgBiCl₄ section of the alloys

| d, nm | 100 | 80 | 50 | 20 | 0 |
|-------|-----|----|----|----|---|
| 0.569 | 0.661 | 0.660 | 0.660 | 0.660 | 0.542 |
| 0.367 | 0.640 | 0.640 | 0.640 | 0.640 | 0.511 |
| 0.342 | 0.610 | 0.619 | 0.619 | 0.619 | 0.461 |
| 0.297 | 0.550 | 0.550 | 0.550 | 0.550 | 0.410 |
| 0.276 | 0.535 | 0.550 | 0.530 | 0.530 | 0.369 |
| 0.268 | 0.519 | 0.530 | 0.520 | 0.520 | 0.334 |
| 0.244 | 0.480 | 0.520 | 0.519 | 0.519 | 0.297 |
| 0.219 | 0.475 | 0.519 | 0.485 | 0.485 | 0.294 |
| 0.194 | 0.450 | 0.484 | 0.469 | 0.469 | 0.257 |
| 0.184 | 0.428 | 0.466 | 0.450 | 0.450 | 0.229 |
| 0.175 | 0.415 | 0.445 | 0.415 | 0.415 | 0.197 |
| 0.171 | 0.390 | 0.428 | 0.370 | 0.370 | 0.185 |
| 0.168 | 0.380 | 0.415 | 0.360 | 0.360 | 0.170 |
| 0.166 | 0.370 | 0.388 | 0.340 | 0.340 | 0.153 |
| 0.160 | 0.360 | 0.370 | 0.319 | 0.319 | 0.151 |
| 0.157 | 0.340 | 0.360 | 0.300 | 0.300 | 0.151 |
| 0.152 | 0.320 | 0.345 | 0.295 | 0.295 | 0.151 |
| 0.146 | 0.289 | 0.330 | 0.289 | 0.289 | 0.151 |
| 0.137 | 0.285 | 0.300 | 0.278 | 0.278 | 0.151 |

The melting temperatures of the primary components are respectively equal to 100°C (AgBiCl₄) and 210°C (LiBi₄Cl₁₃).

The analysis of the results of XRPA for the samples section of LiBi₄Cl₁₃-AgBiCl₄ confirmed that the intensity of the reflexes corresponding to the solid solution based on AgBiCl₄ decreases with decreasing the relative content of this phase (tabl. 3).
Table 3. The results of X-ray phase analysis of the alloys of the LiBi$_4$Cl$_{13}$ – AgBiCl$_4$ section

| d, nm | 100 | 90 | 50 | 20 | 0 |
|-------|-----|----|----|----|---|
|       |     |    |    |    |   |
| 0.730 | 100 | 0.738 | 100 | 0.738 | 100 | 0.734 | 80 |
| 0.367 | 76  | 0.659 | 15  | 0.638 | 12  | 0.658 | 24 |
| 0.342 | 50  | 0.51  | 25  | 0.625 | 15  | 0.634 | 12  |
| 0.316 | 48  | 0.641 | 18  | 0.603 | 12  | 0.608 | 12  |
| 0.297 | 43  | 0.615 | 25  | 0.590 | 76  | 0.598 | 24  |
| 0.276 | 98  | 0.580 | 12  | 0.550 | 45  | 0.550 | 6  |
| 0.268 | 81  | 0.576 | 33  | 0.503 | 18  | 0.525 | 5  |
| 0.266 | 74  | 0.528 | 24  | 0.450 | 18  | 0.490 | 14  |
| 0.244 | 57  | 0.515 | 13  | 0.441 | 15  | 0.467 | 7  |
| 0.219 | 17  | 0.462 | 25  | 0.434 | 36  | 0.443 | 12  |
| 0.194 | 40  | 0.436 | 52  | 0.423 | 12  | 0.423 | 10  |
| 0.184 | 26  | 0.445 | 20  | 0.374 | 15  | 0.370 | 6  |
| 0.175 | 5   | 0.400 | 38  | 0.342 | 48  | 0.350 | 50  |
| 0.171 | 7   | 0.343 | 46  | 0.318 | 15  | 0.342 | 35  |
| 0.168 | 14  | 0.319 | 21  | 0.279 | 30  | 0.318 | 27  |
| 0.166 | 40  | 0.379 | 42  | 0.271 | 88  | 0.279 | 7  |
| 0.160 | 40  | 0.249 | 38  | 0.263 | 9   | 0.271 | 21  |
| 0.137 | 16  | 0.226 | 21  | 0.249 | 12  | 0.256 | 32  |
| 0.152 | 22  | 0.225 | 18  | 0.242 | 25  | 0.249 | 8  |
| 0.146 | 17  | 0.220 | 13  | 0.236 | 19  | 0.236 | 5  |
| 0.137 | 12  | 0.197 | 17  | 0.215 | 21  | 0.220 | 4  |
| 0.167 | 17  | 0.210 | 12  | 0.197 | 5  | 0.158 | 8  |
| 0.145 | 17  | 0.197 | 18  | 0.169 | 10  |
| 0.130 | 25  | 0.185 | 12  | 0.166 | 6  |

6. Conclusion
The AgBiCl$_4$ – LiBi$_4$Cl$_{13}$ system was analysed firstly, and a polythermal section was built. The melting temperatures of the initial components are respectively equal to 100°C (AgBiCl$_4$) and 224°C (LiBi$_4$Cl$_{13}$). The system has three single-phase areas: L, α – and β-solid solutions based on the initial components, two L + β, L + α double areas and a L + α + β triple area. The analysis of XRPA results showed that the intensity of reflexes corresponding to AgBiCl$_4$-based on the solid solution decreases with decreasing relative content of this phase.

In the analysed system it was made the projection of the liquidus surface of the BiCl$_3$-LiCl-AgCl ternary system. It consists of four fields of primary crystallization phases: BiCl$_3$, LiCl, AgCl, LiBi$_4$Cl$_{13}$ and solid solutions based on AgBiCl$_4$ and LiBiCl$_4$.

The XRPA results confirm the presence of primary crystallization fields.
Table 4 presents the non-variant equilibria.

Table 4. Non-variant equilibria

| The character feature of the point | t °C | Composition, mole. % | The equilibrium phases |
|-----------------------------------|-----|----------------------|-----------------------|
| E$_1$                             | 120.0 | 13.4 | 23.3 | 63.3 | L ↔ LiBi$_4$Cl$_{13}$ + AgBiCl$_4$ + BiCl$_3$ |
| E$_2$                             | 100.0 | 66.6 | 6.2 | 27.2 | L ↔ AgBiCl$_4$ + AgCl + LiBiCl$_4$ |
| E$_3$                             | 125.0 | 25.0 | 41.7 | 33.3 | L ↔ LiBi$_4$Cl$_{13}$ + AgBiCl$_4$ + AgCl |
On the basis of experimentally obtained data, the lines of joint crystallization were drawn and the coordinates of non-variant points were determined.

Thus, in the present paper, the phase equilibria in the BiCl$_3$-LiCl-AgCl ternary system were analysed utilizing the methods of differential thermal and X-ray phase analysis. The paper establishes that in the LiCl-AgBiCl$_4$ system the eutectic nature of the interaction is observed. The addition of AgBiCl$_4$ significantly lowers the melting point of the second component. The eutectic character of interaction with limited solubility of components in the AgBiCl$_4$-LiBiCl$_4$ and AgBiCl$_4$-LiBi$_3$Cl$_3$ systems is determined.

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