UDC546.56.86.22.15

PHYSICO-CHEMICAL INTERACTION OF THE COPPER AND ANTIMONY IODIDES

P.R.Mammadli

*Azerbaijan State Oil and Industry University, Azerbaijani-French University
M.Nagiev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan*

parvin.mammadli@ufaz.az

Received 09.10.2020

Accepted 11.12.2020

The character of the mutual interaction of the components in the CuI-SbI₃ system was studied by differential thermal analysis and X-ray phase analysis methods and its phase diagram was constructed. It was found that the system is quasi-binary and forms a monotectic phase diagram. The immiscibility region covers ~15-93 mol% SbI₃ concentration interval at the monotectic equilibrium temperature (~ 493°C). The temperatures of polymorphic transformations of the CuI compound in the system drop slightly and these phase transitions take place by metatectic reactions.

Keywords: *CuI-SbI₃ system, fast-ion conductor, phase diagram, differential-thermal analysis, X-ray phase analysis.*

doi

Introduction

Metal halides are of potential interest due to their application in semiconducting electronic devices, nanotechnology, optoelectronics, radiation detectors, etc. [1–3].

Copper (I) iodide CuI is earth-abundant non-toxic material possessing stable p-type electrical conductivity at room temperature and fast-ionic conductivity at high temperatures [4–7]. It has attracted much attention for its wide use as high-performance thermoelectric elements, transparent electrodes for solar cells, flat-panel displays, light-emitting diodes, etc. [8–13].

Antimony triiodide SbI₃ is a well-known wide gap semiconductor, considered to be a potential material for radiation detectors [14], as cathodes in solid-state batteries [15], in high-resolution image micro recording and information storage [16]. Additionally, crystalline SbI₃ exhibits the second-harmonic generation, which provides a variety of opportunities for optoelectronic devices [17, 18].

The search and design of new functional materials require investigation of the respective phase diagrams. Understanding the phase interaction in the corresponding systems is always helpful for the development of advanced materials [19–21].

There is no literary information about the phase relations in the Cu–Sb–I system. How-

ever, the formation of different ternary compounds has been reported in the A^I–B^V–I (A^I – Cu, Ag; B^V – As, Sb, Bi) type similar systems [1, 22–24]. In this regard, the present work is devoted to the study of the physicochemical interaction between the typical binary iodides of the Cu–Sb–I system: CuI and SbI₃.

Primary compounds of the CuI–SbI₃ system have been studied in detail. CuI melts at 606°C without decomposition. It has 3 modifications [25, 26]. The low-temperature γ -modification crystallizes in a surface-centered cubic lattice and transfers to the β -phase at 369°C. The β -CuI phase crystallizes in a trigonal lattice, exists in a small temperature range (~10K), and transforms into the α phase at 407°C [25]. The latter phase also crystallizes in a cubic lattice [26]. SbI₃ melts at a low (172°C) temperature [27] and crystallizes to the rhombohedral lattice with the space group $R\bar{3}$ [28].

Experimental part

Antimony and iodine elementary components, as well as, CuI binary compound of the *Alfa Aesar German* brand (99.999 % purity) were used in the course of experimental studies.

SbI₃ was prepared using elements of high purity grade in an evacuated (~10⁻² Pa) silica ampoule. Considering the high volatility of iodine, the specially designed method was used for the synthesis of the SbI₃ compound. The

process was carried out in a 3-zone inclined furnace. Temperatures of the 2 "hot" zones were kept at 470K and 750K, whereas the temperature of the "cold" zone was 400 K (the sublimation temperature of iodine is 386 K). After the main portion of iodine reacted at 470K, the ampoule inserted into the second hot zone where the product melted at 750K. After stirring the homogeneous liquid at this temperature the furnace cooled gradually. The purity and individuality of the obtained product were monitored using differential thermal analysis (DTA) and X-ray phase analysis (XRD) methods.

Two sets of samples (0.5 g each) of the CuI-SbI₃ system were prepared by co-melting of different proportions of the CuI and pre-prepared SbI₃ compounds in quartz ampoules. Thermal annealing of samples was carried out at ~400K (~20–30K below the solidus temperature) for 1000 hours in order to achieve complete homogenization.

Experimental studies were conducted by using DTA and XRD methods. The DTA was carried out using the differential-scanning calorimeter "NETZSCH 404 F1 Pegasus system" (heating speed of 10 K/min), and XRD – by means of the Bruker D8 diffractometer (CuK α radiation) at $2\theta = 5^\circ - 75^\circ$.

Experimental results and discussion

The powder X-ray diffraction patterns of the thermally treated CuI-SbI₃ alloys are given in Figure 1. As can be seen, the diffraction patterns of samples in the full composition range consist of the diffraction peaks of the low-temperature modification of CuI and SbI₃. Diffraction lines of the alloys do not displace relative to the pure components (Figure 1). It proves that there are no solid solution areas based on the initial compounds of the system. This can be explained by the fact that the nature of the chemical bond in these substances is very different.

The T - x phase diagram of the system (Figure 2) was constructed using DTA results (Table). Here, the symbols HT2, HT1, and LT indicate high, intermediate, and low-temperature modifications of CuI, respectively. Solid solutions based on them are indicated in the bracket.

It was established that the system is quasi-binary and forms a phase diagram of a monotectic type. Monotectic equilibrium

is observed at 493⁰C temperature. The immiscibility region at 493⁰C ranges at the 15–93 mol% SbI₃ concentration interval.

DTA results of the CuI-SbI₃ system

Composition, mol% SbI ₃	Thermal effects, ⁰ C
0 (pure CuI)	369; 407; 606
5	167; 367; 391; 493; 493–567
10	168; 367; 391; 494; 494–525
15	168; 366; 392; 492
20	168; 366; 390; 492
30	168; 368; 392; 494
40	168; 367; 390; 493
50	167; 387; 391; 494
60	167; 367; 390; 493
70	168; 367; 392; 493
80	168; 366; 391; 494
90	169; 367; 391; 492
95	167; 167–450
100 (pure SbI ₃)	170

A slight decrease in the phase transition temperatures of the CuI compound in the system indicates the existence of solubility areas based on its HT1 and HT2 modifications, and that the phase transitions occur by metatectic reactions.

Isotherms corresponding to the temperatures 391 and 367⁰C on the phase diagram, respectively reflect

metatectic equilibria.

Eutectic has a ~97 mol% SbI₃ composition and melts at 167⁰C by the reaction:

As mentioned before, there is practically no solubility in the solid state between the low-temperature modification of CuI and SbI₃.

The Tamman triangle, constructed based on the intensities of the thermal effects related to monotectic equilibrium, made it possible to determine the presence of up to ~ 3 mol% solubility based on the (HT2-CuI), as well as to define the mutually saturated compositions of the L₁ and L₂ immiscible liquids.

Fig. 1. X-ray images of different alloys of the CuI-SbI₃ system: 1 – SbI₃, 2 – 90 mol.% SbI₃, 3 – 80 mol.% SbI₃, 4 – 60 mol.% SbI₃, 5 – 50 mol.% SbI₃, 6 – 40 mol.% SbI₃, 7 – 20 mol.% SbI₃, 8 – 10 mol.% SbI₃, 9 – CuI.

Fig. 2. T - x phase diagram of the CuI-SbI₃ system.

Conclusion

For the first time, the nature of the physicochemical interaction of copper and antimony iodides was determined by DTA and X-ray methods. It is shown that, in contrast to similar systems consisting of copper and silver halides, ternary compounds are not formed in the CuI-SbI₃ system. There is a wide immiscibility area in the system. Phase transitions of copper (I) iodide occur by metatectic reactions.

References

- Ivanov-Shchitc A.K., Moorein I.V. Ionika tverdogo tela. V 2-kh tomakh. T. 1. SPb.: Izd-vo S.-Peterb. un-ta. 2000. 616 s.
- Guo Z., Li J., Pan R., Cheng J., Chen R., He T. All-inorganic copper(I)-based ternary metal halides: promising materials toward optoelectronics. *Nanoscale*. 2020. V. 12. P. 15560-15576.
- Ahn D., Park S.-H. Cuprous halides semiconductors as a new means for highly efficient light-emitting diodes. *Sci. Rep.* 2016. V. 6. № 1. P. 20718–20726.
- Sirimanne P.M., Soga T., Kunst M. Observation of microwave conductivity in copper iodide films and relay effect in the dye molecules attached to CuI photocathode. *J. Solid State Chem.* 2005. V. 178. No 10. P. 3010–3013.
- Chen D., Wang Y., Lin Z., Huang J., Chen X., Pan D., Huang F. Growth strategy and physical properties of the high mobility p-type CuI crystal. *Crys. Growth Des.* 2010. V. 10. No 5. P. 2057–2060.
- Wang J., Li J., Li S. Native p-type transparent conductive CuI via intrinsic defects. *J. Appl. Phys.* 2011. V. 110. No 5. P. 054907-054911.
- Grundmann M., Schein F.-L., Lorenz M., Böntgen T., Lenzner J., Wenckstern H. Cuprous iodide – a p-type transparent semiconductor: history and novel applications. *Phys. Status Solidi A*. 2013. V. 210. No 9. P. 1671–1703.
- Yadav M.K., Sanyal B. First-principles study of thermoelectric properties of CuI. *Mater. Res. Express*. 2014. V. 1. No 1. P. 015708–015514.
- Yang C., Souchay D., Kneiß M., Bogner M., Wei H.M., Lorenz M., Oeckler O., Benstetter G., Fu Y.Q., Grundmann M. Transparent flexible thermoelectric material based on non-toxic earth-abundant p-type copper iodide thin film. *Nat. Commun.* 2017. V. 8. No 16076. P. 1–7.
- Koyasu S., Umezawa N., Yamaguchi A., Miyauchi M. Optical properties of single crystalline copper iodide with native defects: Experimental and density functional theoretical investigation. *J. Appl. Phys.* 2019. V. 125. No 11. P. 115101–115111.
- Wang P., Zhang J., Zeng Z., Chen R., Huang X., Wang L., Xu J., Hu Z., Zhu Y. Copper iodide as a potential low-cost dopant for spiro-MeOTAD in perovskite solar cells. *J. Mater. Chem. C*. 2016. V. 4. No 38. P. 9003-9008.
- Christians J.A., Fung R.C.M., Kamat P.V. An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide. *J. Am. Chem. Soc.* 2014. V. 136. No 2. P. 758–764.
- Mohamed S.A., Gasiorowski J., Hingerl K., Zahn D.R.T., Scharber M.C., Obayya S.S.A., El-Mansy M.K., Sariciftci N.S., Egbe D.A.M., Stadler P. CuI as versatile hole-selective contact for organic solar cell based on anthracene-containing PPE-PPV. *Sol. Energy Mater. Sol. Cells*. 2015. V. 143. P. 369–374.
- Onodera T., Baba K., Hitomi K. Evaluation of Antimony Tri-Iodide Crystals for Radiation Detectors. *Sci. Technol. Nucl. Install.* 2018. V. 2018. No 1532742. P. 1–7.
- Suthanthiraraj S.A., Sarojini S. Ionic transport and surface morphological studies on SbI₃-Ag₂WO₄ mixed system for solid state battery applications // *Chem. Sci. Trans.* 2012. V. 1. No 1. P. 13–22.
- Mohan D.B., Philip A., Sunandana C.S. Iodization of antimony thin films: XRD, SEM, and optical studies of nanostructured SbI₃. *Vacuum*. 2008. V. 82. No 6. P. 561–565.
- Kępińska M., Starczewska A., Bednarczyk I., Szala J., Szperlich P., Mistewicz K. Fabrication and characterisation of SbI₃-opal structures. *Mater. Lett.* 2014. V. 130. P. 17–20.
- Guo S.-P., Sun Z.-D., Chi Y., Xue H.-G. Adduct-Type IR Nonlinear-Optical Crystal SbI₃·(S8)₃ with a Large Second-Harmonic Generation and a High Laser-Induced Damage Threshold. *Inorg. Chem.* 2018. V. 57. No 17. P. 11282–11288.
- Babanly M.B., Chulkov E.V., Aliev Z.S., Shevelkov A.V., Amirasanov I.R. Phase Diagrams in Materials Science of Topological Insulators Based on Metal Chalcogenides. *Russ. J. Inorg. Chem.* 2017. V. 62. No 13. P. 1703–1729.
- Babanly M.B., Mashadiyeva L.F., Babanly D.M., Imamaliyeva S.Z., Tagiev D.B., Yusibov Y.A. Some Issues of Complex Studies of Phase Equilibria and Thermodynamic Properties in Ternary Chalcogenide Systems Involving Emf Measurements (Review). *Russ. J. Inorg. Chem.* 2019. V. 64. No 13. P. 1649–1671.
- Babanly D.M., Tagiyev D.B. Physicochemical aspects of ternary and complex phases development based on thallium chalcogenides. *Chemical Problems*. 2018. V. 16. No 2. P. 153-177.
- Mashadiyeva L.F., Aliev Z.S., Shevelkov A.V., Babanly M.B. Experimental investigation of the Ag-Bi-I ternary system and thermodynamic pro-

- perties of the ternary phases. J. Alloys Compd. 2013. V. 551. P. 512–520.
23. Bahari Z., Thévet F., Rivet J., Dugué J. Contribution à l'étude expérimentale du système ternaire Bi-Cu-I: Description du triangle CuI-BiI₃-I. JEEP. 2009. P. 20-23.
 24. Koedtruad A., Goto M., Patino A.M., Tan Z., Guo H., Nakamura T., Handa T., Chen W.-T., Chuang Y.-C., Sheu H.-S., Saito T., Kan D., Kanemitsu Y., Wakamiya A., and Shimakawa Y. Structure-property relations in Ag-Bi-I compounds: Potential Pb-free absorbers in solar cells. J. Mater. Chem. A. 2019. V. 7. No 10. P. 5583–5588.
 25. Shan Y., Li G., Tian G., Han J., Wang Ch., Liu Sh., Du H., Yang Y. Description of the phase transitions of cuprous iodide. J. Alloys Compd. 2009. V. 477. No 1–2. P. 403–406.
 26. Yashima M., Xu Q., Yoshiasa A., Wada S. Crystal structure, electron density, and diffusion path of the fast-ion conductor copper iodide CuI. J. Mater. Chem. 2006. V. 16. No 45. P. 4393–4396.
 27. Rolsten R.F. Iodide Metals and Metal Iodides. New York. John Wiley & Sons, Inc. 1961. P. 322.
 28. Trotter J., Zobel T. The crystal structure of SbI₃ and BiI₃. Z. Kristallogr. Cryst. Mater. 1966. V. 123. No 1–6. P. 67–72.

MİS VƏ STİBİUM YODİDLƏRİNİN FİZİKİ-KİMYƏVİ QARŞILIQLI TƏSİRİ

P.R.Məmmədli

DTA və RFA üsulları ilə CuI–SbI₃ sistemində komponentlərin qarşılıqlı təsir xarakteri tədqiq edilmiş, onun faza diaqramı qurulmuşdur. Müəyyən olunmuşdur ki, sistem kvazibinar olub monotektik tipli faza diaqramına malikdir. Monotektika temperaturunda (~493⁰C) təbəqələşmə sahəsi ~15–93 mol% SbI₃ qatılıq intervalını əhatə edir. Sistemdə CuI birləşməsinin polimorf çevrilmə temperaturları bir qədər aşağı düşür və bu faza keçidləri metatektik reaksiyalar üzrə baş verir.

Açar sözlər: CuI-SbI₃ sistemi, superion keçirici, faza diaqramı, differensial-termiki analiz, rengtenfaza analizi.

ФИЗИКО-ХИМИЧЕСКОЕ ВЗАИМОДЕЙСТВИЕ ИОДИДОВ МЕДИ И СУРЬМЫ

П.Р.Мамедлы

Методами ДТА и РФА изучен характер взаимодействия компонентов в системе CuI–SbI₃ и построена ее фазовая диаграмма. Показано, что система является квазибинарной и образует фазовую диаграмму монотектического типа. При температуре монотектики (493⁰C) область расслаивания охватывает интервал ~15–93 мол.% SbI₃. Температуры полиморфных превращений соединения CuI в системе несколько понижаются и протекают по метатектическим реакциям.

Ключевые слова: система CuI–SbI₃, суперинные проводники, фазовая диаграмма, дифференциально-термический анализ, рентгенофазовый анализ.