IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 12, Issue 3 Ser. I (March. 2019), PP 73-76
www.iosrjournals.org

Character of Interaction in the $Cuinse_2$-Mnse System.

[1]MirzayevaRahilaJ., [2]Shukurova Guntakin M., [3] ГasanovaZivar T.,[4]Kurbanova Tarana R., [5]Mammadova Saadat O.,[6]Sultanova Samina Q., [7]Allazov Maxmud R.

[1,2,3,4,5,6,7]*Departmentof Chemistry,Baku State UniversityBakuAzerbaijan,*
Corresponding Author: MirzayevaRahilaJ.

Abstract: *The manganesemonoselenidesolubilityinα-$CuInSe_2$hasbeendeterminedbystudyingphaseequilibria in the $CuInSe_2$–MnSe system using differential thermal analysis, x-ray diffraction, microstructural analysis, and microhardness measurements. At room temperature, the α-$CuInSe_2$-based solid solution extends to 46 mol % MnSe.*

Keywords: *solid solution, eutectic, chalcogenide, microhardness*

Date of Submission: 04-03-2019 Date of acceptance: 20-03-2019

I. Introduction

The low-temperature chalcopyrite phase of the $CuInSe_2$ compound is widely used as a photosensitive material. It is also a promising substance for theconstruction of Wagner light diodes, solar cells and various nonlinear optics devices [1–3].

The electro-optical properties of photosensitive compounds are strongly dependent on the band structure, which is strongly influenced by dissolved foreign atoms, especially transition elements.The introduction of 3d transition metals into the $CuInSe_2$ structure greatly changes the electrophysical and optical properties of the matrix compound, for example, its electrical conductivity may increase by several orders of magnitude.

The introduction of 3d transition metals into the $CuInSe_2$ structure greatly changes the electrophysical and optical properties of the matrix compound, for example, its electrical conductivity may increase by several orders of magnitude.

Solubility of foreign atoms is related to themobility of the chalcopyrite structure of $CuFeSe_2$. $CuFeSe_2$ and $CuInSe_2$formacontinuousseriesofsolidsolutions[4,5], but the solubility of iron monoselenide in $CuInSe_2$is just 19 mol % [6], and those of cobalt andnickel selenides are even lower: 10 and 1 mol %,respectively [7].

Thethreeselenidescrystallizeinhexagonalsymmetry(NiAsstructure).Sincetheiron-groupmetalsare close in effective ionic radius (Fe^{2+}, 0.76; Co^{2+}, 0.74; Ni^{2+},0.72 Å), the large difference in the solubility of their monoselenides in $CuInSe_2$ can be rationalized in terms of polarizability. The polarizability in these monoselenides increases markedly in the orderFe→ Co →Ni, resulting in the formation of a narrow 3d band owing to the overlap of the wave functions of the metals in the binary selenides.

It is of interest to determine the MnSe solubility in $CuInSe_2$ since the polarizability in MnSe is even lower thanthat inCoSe and NiSe, as confirmed by its wide band gap and the nonmetallic behavior of its conductivity.

II. Results and its discussion

$CuInSe_2$–MnSealloys were prepared by reacting extrapure elements (electrolytic copper and manganese containing less than 0.001%, indium-0.001%, and selenium-0.001% impurities) in evacuated ($\sim 10^{-2}$Pa)silica ampules at 1370 K for 8 h. To prevent reaction between manganese and silica, the ampules were graphitized. The samples were equilibrated by homogenizing annealing for 100 h at 900 K, i.e., just below the temperature of the polymorphic transformation of $CuInSe_2$ -based solid solutions.

In differential thermal analysis (DTA), we used an N-307/1 XY potentiometer. The reference substanceused was calcined alumina. X-ray diffraction (XRD)patterns were collected on a“Bruker Д8 ADVANCE” powderdiffractometer (Cu $K_\alpha$radiation).

Microhardness of polycrystalline samples wasmeasured with a PMT-3 tester. Microstructures were revealed by etching with a dilute (1:3) chromic acid mixture.

Data DTA and microhardness are presented in the table.

Table

Results of DTA and microhardness of the $CuInSe_2$-MnSe system

Composition of the sample			Thermal effects, 0C		Microhardnessof the conductive crystalline phase Hμ, MPa	
mol% MnSe	The number of $CuInSe_2$ and MnSe in the sample is 1 gram,		isothermal	polythermic		
	$CuInSe_2$	MnSe			stack phase	light phase
0	1,00000	0	810; 986	-	2200	-
5	0,97947	0,02053	-	795; 760; 985	2250	-
10	0,95763	0,04237	-	750; 720; 980	2300	-
20	0,90947	0,09053	-	650; 670;	2500	-
25	0,88283	0,11717	-	650;665	-	-
30	0,85423	0,14577	-	975; 990	2600	-
35	0,82345	0,17655	-	830;965;995	-	-
40	0,79024	0,20976	890	960 ; 990	2700	-
45	0,75428	0,24572	890	950; 975	2790	-
50	0,71522	0,28478	890; 950	985	2800	-
55	0,67265	0,32735	890;950	-	eutectic	
60	0,62608	0,37392	890; 950	990	-	830
70	0,51839	0,48161	890; 950	1090	-	830
75	0,45568	0,54432	895; 945	undefined		
80	0,3857	0,61430	890; 950	undefined	-	
90	0,21817	0,78183	-		-	
100	0	1,00000	1460±8[8]		-	830[9]

The phase diagram constructed using these characterization techniques is presented in Fig. 1a.

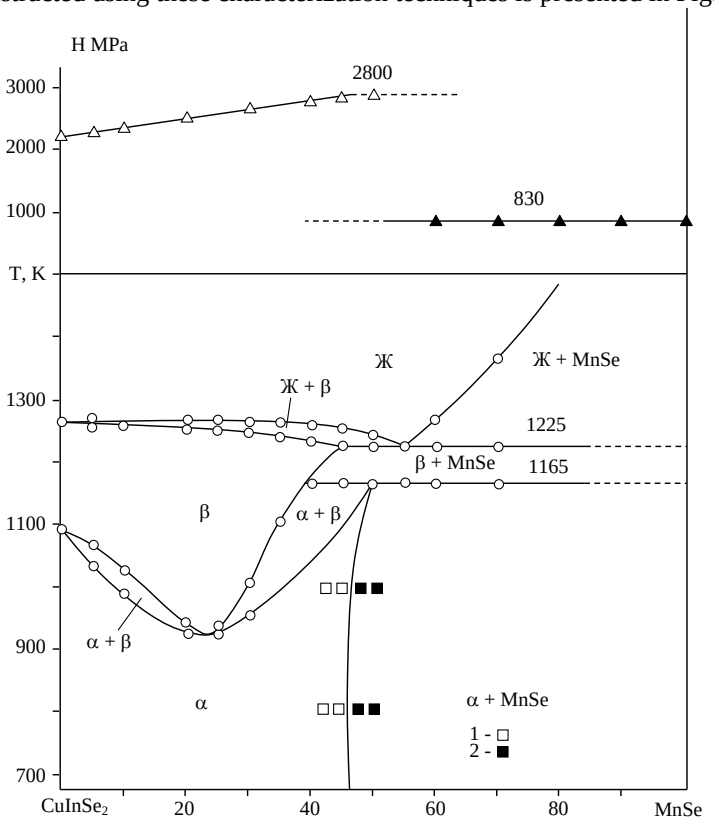

Fig. 1.(a) $CuInSe_2$–MnSephase diagram: (*1*) single- and(*2*) two-phase samples; (b) composition dependence of microhardness.

The system is of the eutectic type, with a considerable MnSe solubility in $CuInSe_2$. Since the DTA curves were measured to 1400 K, the liquidus near manganese selenide was not determined (MnSemeltscongruentlyat1785±5K[10]).The eutectic is located at 55 mo l% MnSe and melts at 1225 K. At room temperature, the α-$CuInSe_2$- based solid solution extends to 46 mol % MnSe. The high MnSe solubility can be accounted for by the facts that indium and manganese are very close in ionic radius (In^{3+} – 0.92 Å; Mn^{2+} – 0.91 Å), both phases have cubic structures, and the metals in question are is ostructural: indium has a tetragonal structure of theγ- Mn type [11]. The MnSe solubility in the high - temperature phase α- $CuInSe_2$ is 45 mol % at the eutectic temperature. The α ↔β phase transition in the solid-solution has a minimum at 23.5 mol % MnSe.

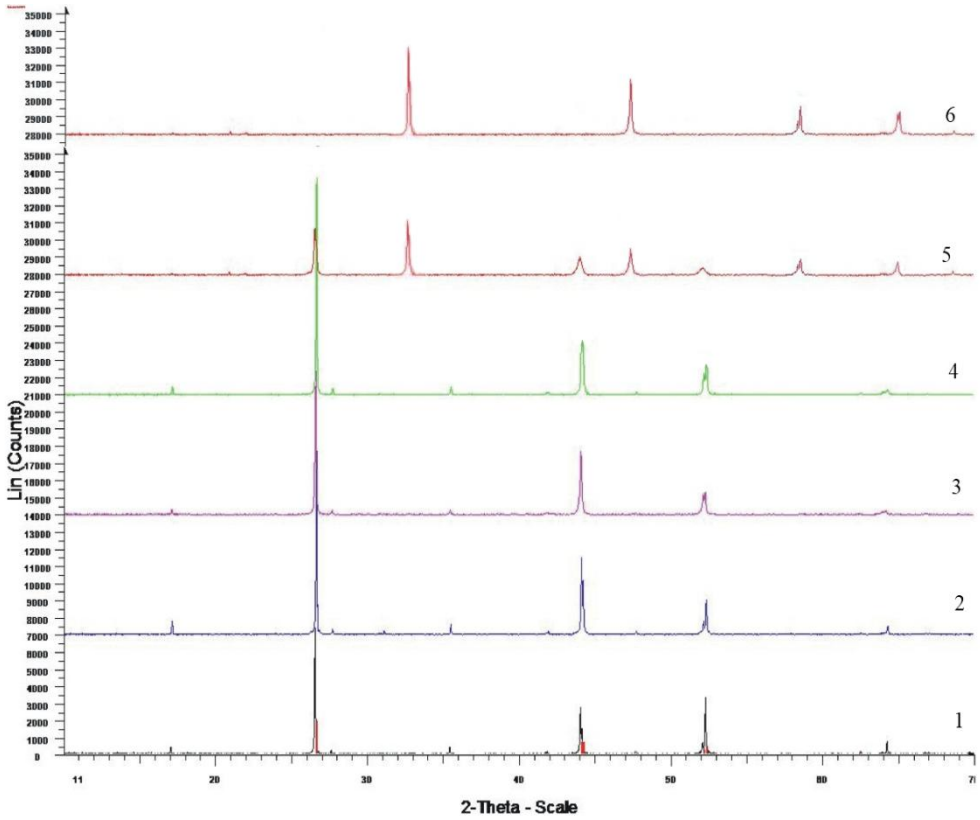

Fig. 2.XRD patterns of $CuInSe_2$ –MnSe alloys

The microhardness of the alloys was measured at an indentation load of 0.2 N using etched polished sections. The microhardness of $CuInSe_2$ has variously been reported as 2200 [12], 1060 [13], and 3370 MPa [14].

We obtained a value close to that reported by Glazov and Vigdorovich [12]. The microhardness of MnSe in the alloys studied was 830 MPa, in accordance with that of pure manganeseselenide [10]. This indicates that the $CuInSe_2$ solubility in MnSe is insignificant. Figure 1b shows the composition dependence of microhardness for $CuInSe_2$ –MnSe alloys. MnSe dissolutionincreasesthemicrohardness of the α-phase from 2200 (pure CuInSe2) to 2800 MPa (alloy containing 45 mol % MnSe), which is characteristic of substitutional solid solutions.

References

[1]. Sovremenniye problemy polyprovodnikovoy fotoenergetiki(Modern problems of semiconductor photoenergy) Per. s angl../FonashS., Rotvorf A., Kazmerski L., et.all; Pod. red.T. Koutsa, J. Mikina./- M.: Мир, 1988.-307с.

[2]. Kawata, H. Kinoshita and T. Wada. Preparation of chalcopyrite-type $CuInSe_2$ and $CuGaSe_2$ by non-heating process.e-mrs. //Spring Meeting 2002 June 18-21, 2002.

[3]. Konstantin Gartsman, David Cahen.Extended stable junction regions in $CuInSe_2$ thin films byelectric field application E-MRS //Spring Meeting 2002 June 18-21, 2002.

[4]. Tverdyerastvory v poluprovodnikovykhsistemakh.Spravochnik(Solid Solutions in Semiconductor Systems;A Handbook), Moscow: Nauka, 1978.

[5]. Boltaks, B.I. and Tarnovskii, N.N., Electrical Properties of Chalcopyrite: Effect of Surface Processing on the Rectifying Properties of Crystals, Zh. Tekh. Fiz.1955, vol. 25, pp. 402–409.

[6]. Mirzoeva, R.J., Allazova, N.M., and Babanly, M.B., System $CuInSe_2$–FeSe, Vestn.Bakin.Gos. Univ., Ser. Estestv.Nauk, 2005, no. 1, pp. 20–25.
[7]. Mirzoeva, R.J. and Allazov, M.R., Phase Relationsbetween $CuInSe_2$ and Cobalt Selenide, Vestn.Bakin.Gos. Univ.,, Ser. Estestv. Nauk, 2007, no. 1, pp. 37–41.
[8]. Desk Handbook : Phase Diagrams for Binary Alloys, Second Edition, H. Okamoto. ASM International Materials Park, Ohio 44073-0002, 2010, 809 p.
[9]. БабаеваБ. К., АллазовМ. Р. Диаграммасостояниясистемы$MnSe$ -In_2Se_3. / Сб. Исследования в областинеорг.и физ. химии. Баку: Элм, 1977, с. 70-73.
[10]. Fiziko-khimicheskie svoistva poluprovodnikovykh veshchestv. Spravochnik(Physicochemical Properties ofSemiconductors: A Handbook), Novoselova, A.V. andLazarev, V.B., Eds., Moscow: Nauka, 1979.
[11]. Bokii, G.B., Kristallokhimiya(Crystal Chemistry), Moscow: Nauka, 1974.
[12]. Glazov, V.M. and Vigdorovich, V.N., Mikrotverdost'metallov i poluprovodnikov(Microhardness of Metals and Semiconductors), Moscow: Metallurgiya, 1969.
[13]. Zargarova, M.I., Babaeva, P.K., and Azhdarova, D.S., Systems $CuInSe_2$–InSe ($SnSe_2$, Bi_2Se_3), Neorg. Mater.,1992, vol. 31, no. 2, pp. 282–283.
[14]. Constantinidis, C., Tomilson, R.D., and Neumann, H., Microhardness of $CuInSe_2$, Philos. Mag. Lett., 1988, vol.57, no.2, pp. 91–97

MirzayevaRahilaJ. "Character of Interaction in The Cuinse2-Mnse System." IOSR Journal of Applied Chemistry (IOSR-JAC) 12.3 (2019): 73-76.