ORIGINAL RESEARCH ARTICLE

Heat of Mixing of the Liquid Silver–Indium and Silver–Gallium–Indium Alloys

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Experimental studies of the multicomponent systems are necessary in the development of new materials which can be used in various industries. The literature review showed, that the liquid phase in the silver–gallium–indium system has not been studied yet. In the present work the heat of mixing of the liquid silver–indium and silver–gallium–indium alloys was studied using Calvet type MHTC96 calorimeter. Calorimetric measurements were carried out at the temperatures: 973 K, 1123 K and 1273 K for Ag–In alloys, and at 923 K, 1123 K and 1273 K along two cross-sections X_{Ag}/X_{Ga} = 1:1 and X_{Ga}/X_{In} = 1:1 for Ag–Ga–In alloys. Next, the Redlich–Kister–Muggianu formalism was applied in the mathematical description of the heat of mixing of the liquid silver–gallium–indium alloys. Experimental results obtained in this work are first, which provided information about the thermodynamic properties of the liquid phase in this ternary system.

https://doi.org/10.1007/s11661-023-07196-5
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I. INTRODUCTION

THE silver–gallium–indium system is used in modern technological applications related to medicine and industry. This ternary system was investigated for the use as electronic skin which can be connected to the human body or as a part of electronic devices.[1–3] Electronic skin can be used to monitor health, as a material with self-healing properties or as a component of capsules accelerating the wound healing process.[4] Recently, the novel methods for the production of this electronic skin in the form of a tattoo are developed.[5–7] This kind of electronic tattoo can be used in medical devices for monitoring: vital functions, neural connections, level of oxygen, sugar or energy in human body.[8–10] Moreover, the ternary Ag–Ga–In system is a candidate for ternary III to V semiconductor nanowires (NWs).[11,12] Taking into account that silver has similar properties but is cheaper than gold, (which is applied in Au-catalysed nanowires), the measurements of Ag-seeded III to V nanowires containing In and Ga can be interesting. Recently, in the literature appeared a description of a process of silver nanowires preparation which were grown in a solution using eutectic gallium–indium (EGaIn) seeds.[13] It is interesting to find out how silver nanostructures can be obtained by applying nontoxic reagents under ambient conditions.

The discovery of recent years are Ag–Cu–In–Ga (ACIG) and (Ag,Cu)(In,Ga)Se_2 (ACIGS) materials which can be applied in solar cells.[14,15] These materials are the next generation of Cu(In,Ga)Se_2 (CIGS) materials, which are expected to produce film solar cells. The ACIGS materials present less residual stress than CIGS ones, which is an important advantage in the view of flexible photovoltaic applications. The efficiency of ACIGS solar cell under laboratory conditions is about 20 pct and is obtained in a wider temperature range than in the case of CIGS cell.[16,17] In the solar cell preparation process, the control of deposition each element is important. Undeniably, the knowledge about thermodynamic properties and evolution of phase equilibria with temperature change in these materials is required. Moreover, the literature review shown that among lower-order systems which are components of ACIGS materials, the most unknown one is the Ag–Ga–In system.

On the basis of the above information, it can be performed that the new measurements in the silver–indium–gallium system should be conducted. To the best of our knowledge, experimental results of the heat of mixing of the liquid Ag–Ga–In alloys have been presented in this paper for the first time. Finally, the results of this work were described by Redlich–Kister–Muggianu formula.[18]

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Manuscript submitted March 27, 2023; accepted September 1, 2023.
Article published online September 24, 2023

II. LITERATURE REVIEW

Generally, thermodynamic description of the silver–gallium–indium system is missing in the literature despite of the fact that it will help to understand the optimal conditions the in development of these new materials. The two most popular monographs on phase equilibria in multicomponent systems[19,20] do not contain information about this ternary system as well as its properties. Up to this time, the silver–indium–gallium system was studied only by Campbell and Reynolds.[21] They reported experimental results obtained by applying thermal analysis, photomicrography, X-ray analysis as well hardness testing. These authors presented the phase relations in Ag-rich region in the Ag–Ga–In system at 298 K and also liquidus projection. More experimental results on the Ag–Ga–In system cannot be found in the literature.

Meanwhile, the experimental data and phase equilibria in the Ag–Ga, Ag–In and Ga–In systems which are components of this ternary system were published many times. Recently, the thermodynamic assessments of binary systems: Ag–Ga,[22] Ag–In[23] and Ga–In[24] were published. In them the following information about heat of mixing of these binary system were used.

The heat of mixing of the liquid silver–gallium system has been reported by many researchers who used various types of calorimeters.[25–31] These results are described in details together with the recent experimental data at 1223 K and 1323 K which were published in our previous paper.[32] All experimental values of the heat of mixing of the liquid Ag–Ga alloys reported in the literature[25,26,29–32] are negative. It is typical in systems having tendency to intermetallic phase formation. They are also temperature dependent *i.e.*, they become more negative at lower temperature.

In the past, the molar heat of mixing of the liquid silver–indium alloys was examined by many researchers applying calorimetric method. Different techniques were used at different temperatures. Heat of mixing was determined at 723 K using high-temperature calorimeter,[33] at 1243 K using adiabatic calorimeter,[26] at 773 K and 1028 K by applying direct calorimetry[30] and at 743 K and 1280 K[34] using drop calorimetry. Moreover, in work[35] the molar heat of mixing of this liquid alloy was determined at 1100 K. The experimental data reported in cited works have negative values and they agree with one another except for the values given in work[26] which are not so negative like the rest of them. The minimum values of the heat of mixing in the liquid silver–indium alloys are given for different mole fractions of indium at various temperatures: $X_{In} \cong 0.3$ at 1028 K,[30] $X_{In} \cong 0.4$. at 1243 K[26] and 1280 K.[30] In the literature, a dependence on temperature of the molar heat of mixing in the liquid Ag–In alloys is treated in a different manner. In the recent optimisations of Ag–In system Gierlotka[36] and then Muzillo and Anderson[37] accepted temperature dependence of the heat of mixing. Fischer *et al.*[21] assumed that the heat of mixing is not temperature dependent in this binary system. Taking into account the discrepancies mentioned above, the molar heat of mixing of the liquid silver–indium alloys was studied at 973 K, 1123 K and 1273 K in this work. Values obtained from the experiments will be used in the explanation of these differences. Moreover, they will be used in mathematical description of the molar heat of mixing of the liquid silver–gallium–indium alloys.

The molar heat of mixing of the liquid gallium–indium alloys was examined calorimetrically in the temperature range from 743 to 1423 K.[38–43] Reported $\Delta_{mix}H$ data are positive for all studied concentrations. It can be assumed that the heat of mixing of liquid Ga–In alloys is temperature independent.

III. EXPERIMENTAL PROCEDURE

The calorimetric studies were carried out in Calvet type MHTC 96 drop calorimeter (Setaram Instruments). This calorimeter and procedure of calorimetric measurements were described in details in previous works.[27,32,43] During our measurements the following materials: silver wire, gallium ingot, indium wire (all 99.999 wt pct, Alfa Aesar, Germany), argon (99.9999 wt pct, Air Products), sapphire rods NIST SRM 720 (99.95 wt pct, NIST) and alumina crucibles (95 wt pct, Powłoka, Poland) were used.

The molar heat of mixing of the liquid silver–indium alloys was studied at 973 K, 1123 K and 1273 K. At the beginning of the measurements, the molar heat of mixing in the liquid silver–indium alloys was determined by adding small pieces of silver (40 to 87 mg), to pure indium bath (approximately 0.50 g). After the addition of silver and standard α-Al_2O_3, the signal of the recorded heat effect returned to the baseline after 30 minutes. Next, the molar heat of mixing of the liquid ternary Ag–Ga–In alloys was determined at three temperatures 923 K, 1123 K and 1273 K and along two cross-sections X_{Ag}/X_{Ga} = 1:1 and X_{Ga}/X_{In} = 1:1.The initial value of the molar heat of mixing in the liquid gallium–indium alloys necessary for calculations in this ternary system for chosen composition X_{In} = 0.5 at 923 K, 1123 K and 1273 K was appointed using parameters given in our work.[43] Next, the initial data of the molar heat of mixing of liquid silver-gallium alloy for chosen composition X_{Ag} = 0.5, at 923 K, 1123 K and 1273 K were taken from the literature.[27,32] To ensure data reproducibility, the experiments for cross-section X_{Ga}/X_{In} = 1:1 at 1123 K and 1273 K have been performed two times.

After the end of calorimetric measurements, samples from obtained metallic alloys were studied by optical microscope in order to check dissolution of silver and indium pieces dropped into the bath. Also, selected ternary alloys were tested by X-ray fluorescence method. Total mass of the bath and samples added during experiments differed less than 1 pct from the mass of the obtained alloy after experiments.

IV. RESULTS AND DISCUSSION

A. *Experimental Data*

The molar heat of mixing in the liquid silver–indium system was measured at 973 K, 1123 K and 1273 K and one experimental run was performed at each

temperature. The partial and integral heats of mixing (together with standard uncertainty of the heat of mixing $u(\Delta_{mix}H)$) of liquid silver-indium alloys are gathered in Table I.

The c is the calorimeter constant ($J\mu V^{-1}\ s^{-1}$) which is calculated from the equation:

$$c = \frac{H_{Al_2O_3}^{T_S \to T_M} \cdot n_{Al_2O_3}}{Q_{Al_2O_3}} \quad [1]$$

Next, the heat of reaction, which was determined in liquid metallic systems, is given by the equation:

$$\Delta H_r = (Q_{i(i=Ag,In)} \cdot c) - (H_i^{T_S \to T_M} \cdot n_{i(i=Ag,In)}) \quad [2]$$

finally

$$\Delta_{mix}H = \frac{\sum \Delta H_r}{n_b + \sum n_{i(i=Ag,In)}}, \quad [3]$$

where $n_{Al_2O_3}$ is the number of moles of alumina oxide and n_i is the number of moles of silver or indium which were introduced into the bath, n_b is the number of moles which correspond to amount of bath (indium, silver–gallium or gallium–indium alloy) which was placed in the crucible (all of them given in mol). The T_S is the temperature of metals which were introduced into bath, and T_M is the measurement temperature (T_S and T_M are given in K). The $H_{Al_2O_3}^{T_S \to T_M}$ and $H_{i(i=Ag,In)}^{T_S \to T_M}$ is the heat content of alumina oxide, silver and indium, respectively. It is obtained from reference[44] given in $Jmol^{-1}$, $Q_{Al_2O_3}$ (μVs) is integral of the measured effect corresponding to the introduction of α-Al_2O_3 sample into the bath, $Q_{i(i=Ag,\ In)}\ c$ (J) is the heat effect corresponding to the introduction of metallic sample into the bath. Next, ΔH_r (J) is the heat of reaction and $\Delta_{mix}H$ ($Jmol^{-1}$) is the molar heat of mixing of liquid alloys. The partial heat of mixing ($Jmol^{-1}$) of liquid alloy is described by the expression:

$$\Delta_{mix}\overline{H}_{i(Ag,In)} = \frac{\Delta H_r}{n_{i(i=Ag,In)}} \quad [4]$$

as a consequence of small masses of metals which were added into the bath.

All values of the heat of mixing obtained at three temperatures in which the liquid silver–indium system was studied are negative. They are shown in Figure 1 and compared with the literature data.[26,30,33–35] A visible minimum of the molar heat of mixing of liquid alloys determined at each experimental temperature in this work was found near $X_{In} = 0.30$, in agreement with experimental data given in work.[30] It can be seen in Figure 1 that the values from this work agree well with the literature data,[30,33–35] except for one series of measurements at 1280 K from work,[34] and they create a consistent description of the liquid phase in this binary system. Experimental values reported in works[26,30] at 1243 K and 1280 K, respectively, are less negative than the values reported in studies[30,33–35] as well as in the present work. The molar enthalpy of mixing of liquid silver-indium alloys exhibits temperature dependence in the examined temperature range from 723 to 1273 K.

Next, the liquid Ag–Ga–In alloys were studied. The heat of mixing of liquid ternary alloys was measured at 923 K, 1123 K and 1273 K along two cross-sections X_{Ag}/X_{Ga} = 1:1 and X_{Ga}/X_{In} = 1:1 in eight separate experiments. Obtained experimental results are listed in Tables II and III (together with standard uncertainty of the heat of mixing $u(\Delta_{mix}H)$), and they are shown in Figure 2. The good reproducibility may be observed for the measurements performed along the cross-section X_{Ga}/X_{In} = 1:1 at 1123 K and 1273 K. The starting values of the heat of mixing in liquid silver–gallium system, necessary for the evaluation of results obtained along the cross-section X_{Ag}/X_{Ga} = 1:1, were taken from two previous works,[27,32] where the heat of mixing in this binary system was described by applying Redlich-Kister polynomial.[45] These experimental values for $Ag_{50}Ga_{50}$ alloys are following: $\Delta_{mix}H = -2730\ J\ mol^{-1}$ at 923 K,[27] $\Delta_{mix}H = -1923\ J\ mol^{-1}$ at 1123 K[27] and $\Delta_{mix}H = -1433\ J\ mol^{-1}$ at 1273 K.[32] For the cross-section X_{Ga}/X_{In} = 1:1, the heat of mixing in the liquid gallium-indium system required to perform calculations in the liquid ternary system was accepted from previous work.[43] The molar heat of mixing of the liquid gallium-indium system is temperature independent. In this case the value of heat of mixing for $Ga_{50}In_{50}$ alloys has the same value for each temperature and is equal to $\Delta_{mix}H = 1143\ J\ mol^{-1}$.

The calorimetric data of the molar heat of mixing of the liquid silver–gallium–indium system, obtained along the cross-section X_{Ag}/X_{Ga} = 1:1 at T = 923 K, 1123 K and 1273 K, show negative values. During the introduction of indium from silver-gallium side, the heat of mixing continuously increases towards pure In. The heat of mixing at 923 K for considered cross-section increases from − 2730 to − 372 J mol^{-1} for X_{In} varying from 0 to 0.67, while at 1123 K from about − 1923 to − 229 J mol^{-1} for X_{In} increasing from 0 to 0.68. It also increases at 1273 K from − 1433 to − 98 J mol^{-1} for X_{In} changing from 0 to 0.68.

Similarly the results of measurements along the cross-section X_{Ga}/X_{In} = 1:1 at T = 923 K, 1123 K and 1273 K, show negative values. Results obtained at 1123 K and 1273 K showed the minimum. The lowest obtained value of the heat of mixing in this work at 923 K is equal − 4819 J mol^{-1} for X_{Ag} = 0.61. The minimum of the heat of mixing at 1123 K is approximately equal to − 4850 J mol^{-1} for X_{Ag} in the range 0.73 to 0.76, and it is approximately equal to − 3540 J mol^{-1} for X_{Ag} from 0.74 to 0.76 at 1273 K. It can be seen that addition of Ag shows strong interaction with indium and gallium resulting in exothermic heat of mixing obtained during experimental measurements in the Ag–Ga–In system along considered cross-section. This is probably connected with the fact that in

Table I. Partial and Integral Molar Heat of Mixing of the Liquid Silver–Indium Alloys at 973 K, 1123 K and 1273 K

X_{Ag}	$\Delta_{mix}\overline{H}_{Ag}$/J mol^{-1}	$\Delta_{mix}H$/J mol^{-1}	$u(\Delta_{mix}H)$/J mol^{-1}
T = 973 K, c = (31.65 × 10^{-4} ± 0.50 × 10^{-4}) JμV^{-1} s^{-1}			
0.0908	− 5568	− 505	34
0.1728	− 6356	− 1033	63
0.2442	− 6870	− 1537	87
0.3056	− 9164	− 2158	106
0.3588	− 9092	− 2689	122
0.4049	− 9717	− 3193	135
0.4459	− 10238	− 3678	146
0.4830	− 11229	− 4184	155
0.5167	− 11691	− 4673	163
0.5480	− 12001	− 5148	169
0.5762	− 10292	− 5469	177
0.6013	− 10447	− 5764	184
0.6236	− 10239	− 6014	190
0.6439	− 8478	− 6147	198
0.6623	− 8899	− 6289	204
0.6791	− 9498	− 6449	209
0.6948	− 7117	− 6481	216
T = 1123 K: c = (28.17 × 10^{-4} ± 0.35 × 10^{-4}) JμV^{-1} s^{-1}			
0.0877	− 4673	− 410	32
0.1629	− 5324	− 815	59
0.2334	− 7512	− 1379	54
0.2990	− 9125	− 2041	76
0.3549	− 8965	− 2593	95
0.4070	− 9303	− 3136	112
0.4513	− 8647	− 3548	127
0.4908	− 8458	− 3901	141
0.5269	− 9489	− 4297	152
0.5582	− 9211	− 4622	163
0.5884	− 8853	− 4911	173
0.6148	− 8300	− 5128	182
0.6381	− 8201	− 5314	191
0.6588	− 7836	− 5459	198
0.6778	− 7261	− 5559	206
0.6946	− 7139	− 5641	212
0.7102	− 7266	− 5724	218
0.7249	− 5223	− 5699	226
0.7341	− 6214	− 5716	230
0.7431	− 5346	− 5704	234
0.7521	− 5443	− 5694	238
0.7606	− 2933	− 5600	243
0.7693	− 5388	− 5592	247
0.7775	− 4376	− 5549	252
0.7853	− 3450	− 5476	256
0.7929	− 3849	− 5418	260
0.8000	− 3478	− 5352	264
0.8068	− 2741	− 5263	269
T = 1273 K: c = (28.06 × 10^{-4} ± 0.32 × 10^{-4}) JμV^{-1} s^{-1}			
0.0809	− 4864	− 393	32
0.1581	− 4597	− 746	62
0.2275	− 7282	− 1286	87
0.2967	− 8598	− 1941	110
0.3565	− 9011	− 2541	130
0.4077	− 8894	− 3046	147
0.4520	− 8899	− 3484	162
0.4907	− 8406	− 3832	175
0.5267	− 7756	− 4110	188
0.5592	− 8236	− 4393	199
0.5887	− 7243	− 4583	210
0.6154	− 6961	− 4737	220
0.6392	− 6268	− 4832	229
0.6605	− 6107	− 4907	238
0.6801	− 6503	− 5000	246
0.6978	− 4703	− 4983	254

Table I. continued

X_{Ag}	$\Delta_{mix}\overline{H}_{Ag}$/J mol^{-1}	$\Delta_{mix}H$/J mol^{-1}	$u(\Delta_{mix}H)$/J mol^{-1}
0.7139	– 4899	– 4979	261
0.7287	– 4794	– 4969	268
0.7382	– 3729	– 4926	273
0.7473	– 3358	– 4871	277
0.7559	– 3562	– 4827	282
0.7641	– 2942	– 4764	286
0.7720	– 2381	– 4684	290
0.7798	– 2120	– 4596	295
0.7873	– 2176	– 4513	299
0.7945	– 2787	– 4455	303
0.8012	– 2986	– 4407	306
0.8077	– 1209	– 4302	311
0.8140	– 1541	– 4211	314
0.8201	– 1727	– 4131	318
0.8259	– 1819	– 4057	321

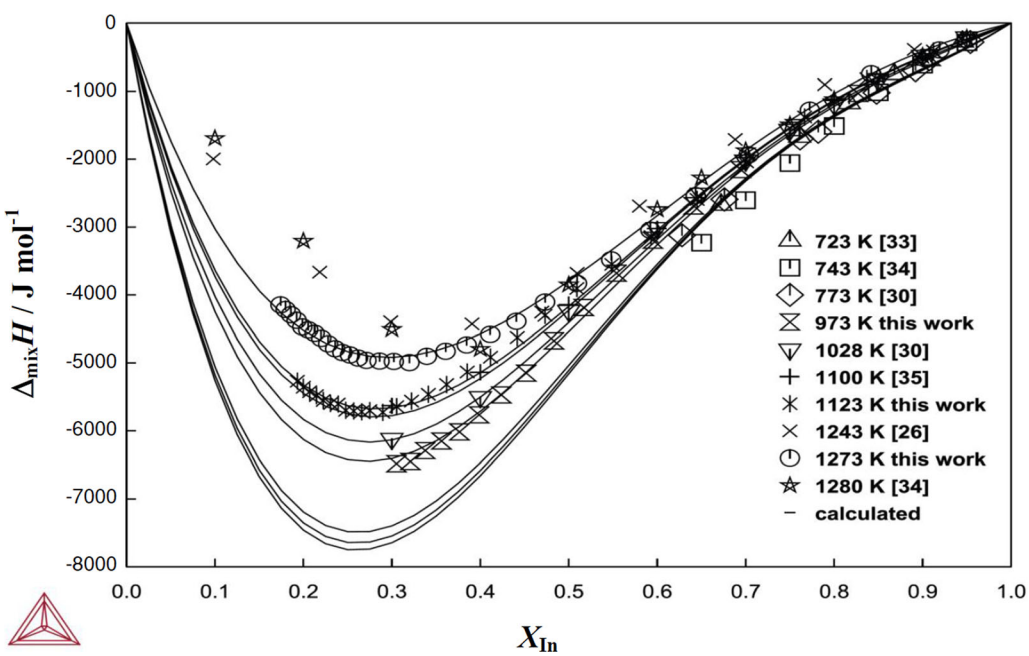


Fig. 1—Integral molar heat of mixing of the liquid Ag–In alloys.

the binary Ag–Ga and Ag–In systems, a minimum of $\Delta_{mix}H$ is located for X_{Ag} in the range 0.7 to 0.8. It corresponds to the existence of ζ phase in the solid state in both binary systems.

B. *Description of Mixing Enthalpy by Applying Mathematical Model*

The mathematical description of the molar heat of mixing of liquid silver–gallium, silver–indium and gallium–indium systems was performed using Redlich–Kister polynomial.[45] Parameters for Ag–Ga and Ga–In systems are accepted from works.[32,43] Considering this model, the heat of mixing of the silver–indium system is given by the expression:

$$\Delta_{mix}H_{Ag,In} = x_{Ag}x_{In}\sum_{v} {}^{v}W_{Ag,In}\left(x_{Ag} - x_{In}\right)^{v} = x_{Ag}x_{In}\sum_{v}\left({}^{v}a - {}^{v}cT\right)\left(x_{Ag} - x_{In}\right)^{v} \quad [5]$$

Table II. Partial and Integral Molar Heat of Mixing of the Liquid Ag–Ga–In Alloys at 923 K, 1123 K and 1273 K, Cross-section X_{Ag}/X_{Ga} = 1:1

X_{In}	$\Delta_{mix}\overline{H}_{In}$/ J mol^{-1}	$\Delta_{mix}H$ / J mol^{-1}	$u(\Delta_{mix}H)$ / J mol^{-1}
T = 923 K run I: c = (34.44 × 10^{-4} ± 0.14 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	− 2730	24
0.0637	3555	− 2330	30
0.1242	4817	− 1868	37
0.1802	3612	− 1517	43
0.2337	1914	− 1293	47
0.2840	899	− 1150	52
0.3270	2031	− 959	56
0.3681	1028	− 837	60
0.4071	432	− 759	63
0.4419	347	− 694	66
0.4737	658	− 617	69
0.5050	52	− 577	71
0.5331	225	− 532	73
0.5587	16	− 502	75
0.5821	216	− 464	77
0.6032	175	− 431	79
0.6225	− 89	− 415	81
0.6408	− 324	− 410	82
0.6578	332	− 375	83
0.6744	− 306	− 372	85
T = 1123 K run I: c = (28.84 × 10^{-4} ± 0.09 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	− 1923	30
0.0582	2751	− 1651	35
0.1122	3650	− 1347	41
0.1646	2620	− 1113	46
0.2129	1816	− 944	50
0.2608	1553	− 792	54
0.3054	827	− 694	58
0.3467	524	− 622	61
0.3845	494	− 557	65
0.4192	317	− 508	67
0.4551	142	− 468	70
0.4856	486	− 414	73
0.5118	261	− 380	75
0.5383	301	− 343	77
0.5626	148	− 317	79
0.5855	280	− 286	81
0.6069	120	− 265	83
0.6269	10	− 251	85
0.6456	18	− 237	86
0.6628	− 219	− 237	87
0.6787	− 85	− 229	89
T = 1273 K run I: c = (27.36 × 10^{-4} ± 0.06 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	− 1433	21
0.0596	4389	− 1086	24
0.1145	3612	− 812	27
0.1688	2005	− 639	30
0.2187	1384	− 517	32
0.2647	973	− 430	34
0.3075	1167	− 337	36
0.3472	781	− 273	38
0.3843	148	− 249	40
0.4192	417	− 211	41
0.4514	260	− 185	43
0.4825	40	− 172	44
0.5102	219	− 151	45
0.5364	332	− 125	46
0.5611	− 443	− 142	47
0.5843	17	− 134	48

Table II. continued

X_{In}	$\Delta_{mix}\overline{H}_{In}$/ J mol^{-1}	$\Delta_{mix}H$ / J mol^{-1}	$u(\Delta_{mix}H)$ / J mol^{-1}
0.6058	227	− 115	49
0.6254	− 114	− 115	50
0.6449	38	− 107	51
0.6630	− 41	− 104	52
0.6797	14	− 98	53

Parameters ${}^{v}W_{Ag,In}$ were determined from calculations performed using Thermo-Calc software[46] and are listed in Table IV. In these calculations, calorimetric data of the heat of mixing from this work at 973 K, 1123 K and 1273 K together with the data from works,[30,33–35] which were determined in the temperature range from 723 to 1028 K, were applied. Values obtained at 1243 K[26] and at 1280 K[34] are too positive in comparison with the results at 1273 K which are given in our work. Consequently, they were not taken into account in our calculations. The values of the molar heat of mixing of liquid silver-indium system obtained in this work are presented in Figure 1, and they are compared with the literature data together with the results of the model calculations in which Redlich–Kister polynomial[45] was used. The agreement among them is quite good and the heat of mixing of liquid Ag–In system exhibits temperature dependence.

Then, the molar heat of mixing of the liquid Ag–Ga–In system was described by the Redlich–Kister–Muggianu polynomial[18] for substitutional solutions. Considering this model, the heat of mixing of the ternary system is described by the following equation:

$$\begin{aligned}\Delta_{mix}H = {} & x_{Ag}x_{Ga}\sum_{v}{}^{v}W_{Ag,Ga}\left(x_{Ag}+x_{Ga}\right)\\ & +x_{Ag}x_{In}\sum_{v}{}^{v}W_{Ag,In}\left(x_{Ag}+x_{In}\right)\\ & +x_{Ga}x_{In}\sum_{v}{}^{v}W_{Ga,In}\left(x_{Ga}+x_{In}\right)\\ & +x_{Ag}x_{Ga}x_{In}\left({}^{v}W_{Ag,Ga,In}\cdot x_{Ag}\right.\\ & \left.+{}^{v}W_{Ag,Ga,In}\cdot x_{Ga}+{}^{v}W_{Ag,Ga,In}\cdot x_{In}\right)\end{aligned} \quad [6]$$

Parameters ${}^{v}W_{Ag,Ga,In}$ (enthalpic part of the interaction parameter from R–K–M polynomial) were calculated by applying Thermo-Calc software[46] and are listed in Table IV.

The calculated heat of mixing in the silver-gallium-indium system is plotted in Figure 2, suggesting good agreement with the experimental results obtained in this work. The biggest difference between calculated and experimental values is equal approximately ± 250 J mol^{-1} at 1123 K for X_{Ag} = 0.7493 along X_{Ga}/X_{In} = 1:1 cross-section. The results allow also to draw the conclusion that molar heat of mixing of liquid silver–gallium–indium system exhibits temperature dependence similarly as it was found in the case of the liquid Ag–Ga and Ag–In systems.

Three-dimensional plots of the integral heat of mixing calculated at temperatures: 923 K, 1123 K and 1273 K in the ternary silver–gallium–indium system are shown in Figure 3 together with the experimental results. These figures were created with Statistica 10.0 software.[47] They demonstrate that the minimum of the heat of mixing does not correspond to ternary composition, but it is located on the Ag–In side. It means that the strongest interactions between unlike atoms take place not in ternary but in the binary Ag–In solution.

If one assumes that negative value of the heat of mixing is connected with associates formation in the liquid solution[48,49] these associates should disintegrate with the temperature rise. It may explain the temperature dependence of $\Delta_{mix}H$. Moreover, since the most negative values of the heat of mixing are obtained in the binary Ag–In system, it can be suggested that the formation of the ternary phase is unlikely. The strongest interaction do not take place in ternary solutions. This conjecture is confirmed by the work[24] in which equilibrium diagram of the Ag-rich part of Ag–Ga–In system does not show the presence of ternary phases in the solid state.

The accuracy and correctness of the performed calorimetric measurements was confirmed by the determination of the heat of mixing at the intersection points for studied cross-sections. At these points the measured heat of mixing differs by 90 J mol^{-1} at 923 K, 70 J mol^{-1} at 1123 K, and by 40 J mol^{-1} at 1273 K, respectively. The biggest discrepancy is equal to 90 J mol^{-1} at 923 K. It allows to conclude that obtained results are reliable.

V. SUMMARY

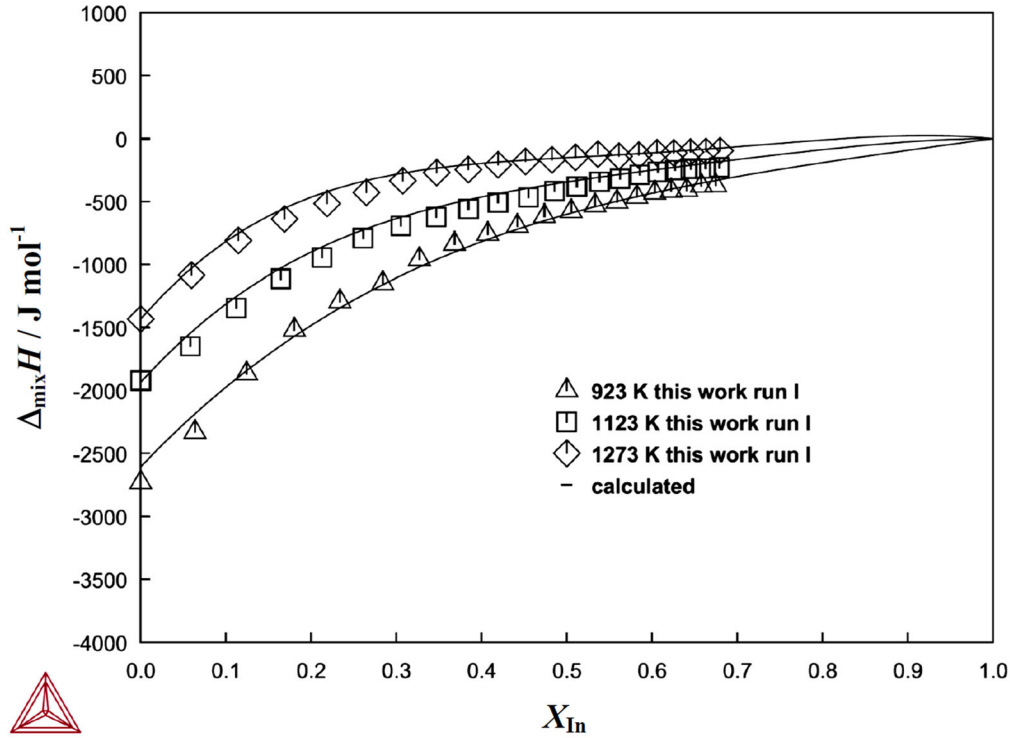
In this work, using the Calvet type calorimeter, the molar heat of mixing of the liquid silver–indium and silver–gallium–indium alloys was determined between 923 and 1273 K. The obtained results allow to conclude that heat of mixing in this system is temperature dependent. It is important information, which has direct influence on future optimization of the Ag–Ga–In system by applying CALPHAD method, in which evaluation of the Gibbs free energy of phases with temperature change is necessary. Furthermore, the experimental heat data were used to calculate parameters ${}^{v}W_{Ag,Ga,In}$ by application of mathematical model, which in this case was the Redlich–Kister–Muggianu polynomial.[18] The agreement between calculated and experimental results is very good. Finally, it should be pointed out that up to now no information about

Table III. Partial and Integral Molar Heat of Mixing of the Liquid Ag–Ga–In Alloys at 923 K, 1123 K and 1273 K, Cross-section X_{Ga}/X_{In} = 1:1

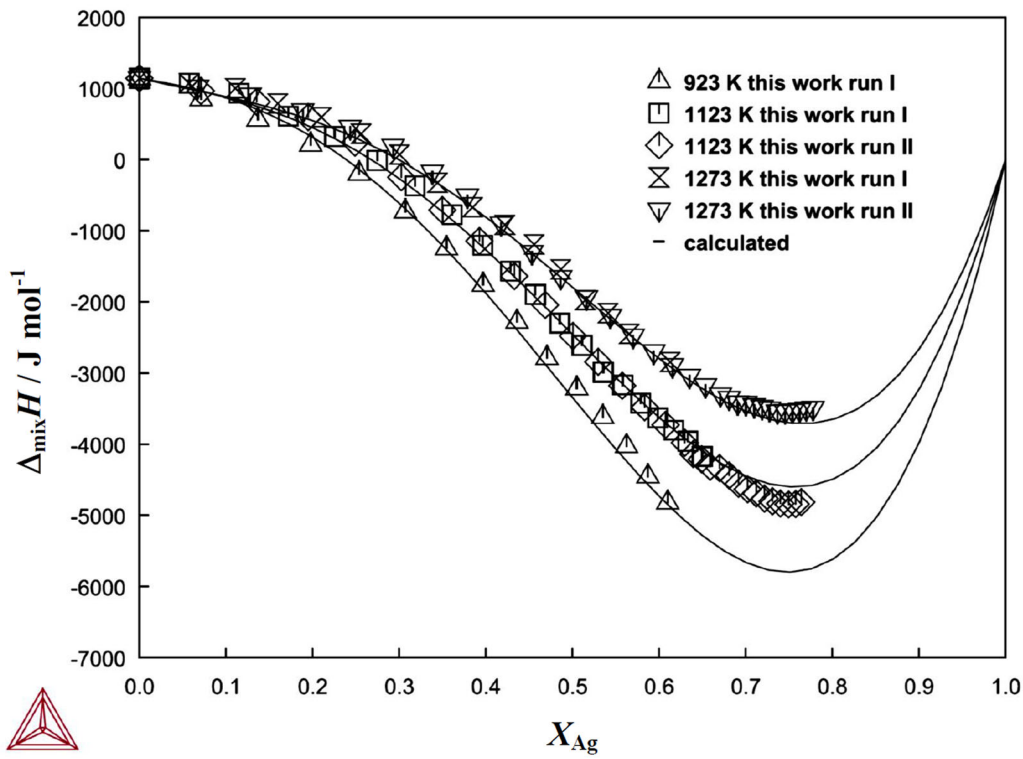
X_{Ag}	$\Delta_{mix}\overline{H}_{Ag}$/J mol^{-1}	$\Delta_{mix}H$/J mol^{-1}	$u(\Delta_{mix}H)$/J mol^{-1}
T = 923 K run I: c = (34.32 × 10^{-4} ± 0.18 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	1143	63
0.0715	− 2573	844	72
0.1372	− 3194	559	81
0.1982	− 4432	206	88
0.2543	− 5604	− 200	94
0.3076	− 7653	− 733	100
0.3553	− 8252	− 1250	104
0.3976	− 9064	− 1762	108
0.4367	− 9779	− 2281	111
0.4714	− 10514	− 2787	114
0.5059	− 9353	− 3215	117
0.5359	− 9833	− 3617	119
0.5633	− 10548	− 4026	121
0.5880	− 11578	− 4452	123
0.6107	− 11118	− 4819	124
T = 1123 K run I: c = (28.56 × 10^{-4} ± 0.15 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	1143	63
0.0578	470	1072	73
0.1148	− 1266	931	83
0.1723	− 4025	609	92
0.2256	− 3863	321	101
0.2746	− 4891	− 9	108
0.3185	− 5942	− 368	114
0.3615	− 6842	− 777	120
0.3969	− 8508	− 1205	124
0.4287	− 8159	− 1572	128
0.4575	− 8085	− 1900	132
0.4855	− 9704	− 2303	135
0.5112	− 8520	− 2614	138
0.5359	− 10080	− 2991	140
0.5583	− 6718	− 3171	144
0.5791	− 8527	− 3423	146
0.5987	− 7878	− 3631	149
0.6169	− 7473	− 3805	151
0.6337	− 7387	− 3962	153
0.6502	− 8693	− 4175	155
T = 1123 K run II: c = (28.79 × 10^{-4} ± 0.14 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	1143	63
0.0711	− 927	964	74
0.1354	− 1226	813	85
0.1948	− 2311	598	94
0.2490	− 4729	239	101
0.3024	− 6571	− 245	108
0.3498	− 7039	− 707	114
0.3927	− 7334	− 1143	119
0.4330	− 8594	− 1639	123
0.4687	− 8104	− 2045	128
0.5007	− 9285	− 2481	131
0.5298	− 8691	− 2843	134
0.5576	− 8507	− 3178	137
0.5835	− 8384	− 3482	140
0.6076	− 7744	− 3729	143
0.6298	− 8172	− 3981	146
0.6396	− 9939	− 4138	147
0.6493	− 6932	− 4213	148
0.6590	− 7927	− 4317	149
0.6699	− 4973	− 4338	151
0.6810	− 7439	− 4442	152
0.6919	− 7919	− 4561	154
0.7023	− 6860	− 4638	155
0.7123	− 6330	− 4695	156
0.7219	− 6856	− 4767	158

Table III. continued

X_{Ag}	$\Delta_{mix}\overline{H}_{Ag}$/J mol^{-1}	$\Delta_{mix}H$/J mol^{-1}	$u(\Delta_{mix}H)$/J mol^{-1}
0.7310	− 5955	− 4806	159
0.7402	− 5710	− 4837	160
0.7495	− 5208	− 4850	162
0.7577	− 4668	− 4844	163
0.7644	− 3915	− 4819	165
T = 1273 K run I: c = (27.54 × 10^{-4} ± 0.16 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	1143	63
0.0574	441	1069	76
0.1108	− 170	999	88
0.1599	− 2880	785	98
0.2103	− 2430	592	109
0.2562	− 3414	360	118
0.3005	− 4570	67	127
0.3443	− 6193	− 324	135
0.3849	− 5908	− 670	143
0.4221	− 4796	− 920	150
0.4559	− 5639	− 1195	156
0.4867	− 7410	− 1547	161
0.5150	− 9411	− 1980	165
0.5413	− 5349	− 2162	170
0.5657	− 7682	− 2456	174
0.6129	− 6053	− 2847	183
T = 1273 K run II: c = (27.35 × 10^{-4} ± 0.12 × 10^{-4}) JμV^{-1} s^{-1}			
0	0	1143	63
0.0673	− 76	1029	74
0.1280	− 737	914	85
0.1888	− 2273	692	94
0.2433	− 2781	459	103
0.2930	− 3591	193	111
0.3384	− 5491	− 173	117
0.3788	− 5651	− 507	123
0.4179	− 6693	− 897	128
0.4535	− 7525	− 1301	132
0.4866	− 7065	− 1651	137
0.5163	− 6564	− 1935	141
0.5439	− 6520	− 2197	144
0.5702	− 7025	− 2475	148
0.5941	− 6426	− 2695	151
0.6157	− 6297	− 2886	154
0.6352	− 5846	− 3036	157
0.6537	− 5643	− 3168	159
0.6710	− 5758	− 3297	162
0.6811	− 4920	− 3347	164
0.6908	− 5477	− 3412	165
0.7004	− 3582	− 3418	167
0.7099	− 4415	− 3449	168
0.7191	− 4198	− 3473	170
0.7277	− 4282	− 3498	171
0.7368	− 4716	− 3538	173
0.7457	− 3345	− 3532	175
0.7541	− 3341	− 3525	176
0.7624	− 3223	− 3515	178
0.7700	− 2911	− 3496	179
0.7778	− 3273	− 3488	181



(a)



(b)

Fig. 2—Integral molar heat of mixing of the liquid Ag–Ga–In alloys along cross-section: (*a*) X_{Ag}/X_{Ga} = 1:1, (*b*) X_{Ga}/X_{In} = 1:1.

Table IV. Parameters Used in Mathematical Description of the Heat of Mixing in the Liquid Ag–Ga–In System (See Also Electronic Supplementary Data File)

System	Source	Parameters/J mol^{-1}
Ag–Ga	[32]	${}^{0}W_{\mathrm{Ag,Ga}} = -22802.5 + 13.41T$ ${}^{1}W_{\mathrm{Ag,Ga}} = -40272.9 + 16.58T$ ${}^{2}W_{\mathrm{Ag,Ga}} = -21660.7 + 9.06T$
Ag–In	This work	${}^{0}W_{\mathrm{Ag,In}} = -27807.8 + 9.92T$ ${}^{1}W_{\mathrm{Ag,In}} = -49442.2 + 24.58T$ ${}^{2}W_{\mathrm{Ag,In}} = -36901.7 + 24.21T$
Ga–In	[43]	${}^{0}W_{\mathrm{Ga,In}} = 4573.5$ ${}^{1}W_{\mathrm{Ga,In}} = -36.3$
Ag–Ga–In	This work	${}^{0}W_{\mathrm{Ag,Ga,In}} = 68134.8 + 30.40T$ ${}^{1}W_{\mathrm{Ag,Ga,In}} = 111340.9 - 73.46T$ ${}^{2}W_{\mathrm{Ag,Ga,In}} = -7465.6 + 7.77T$

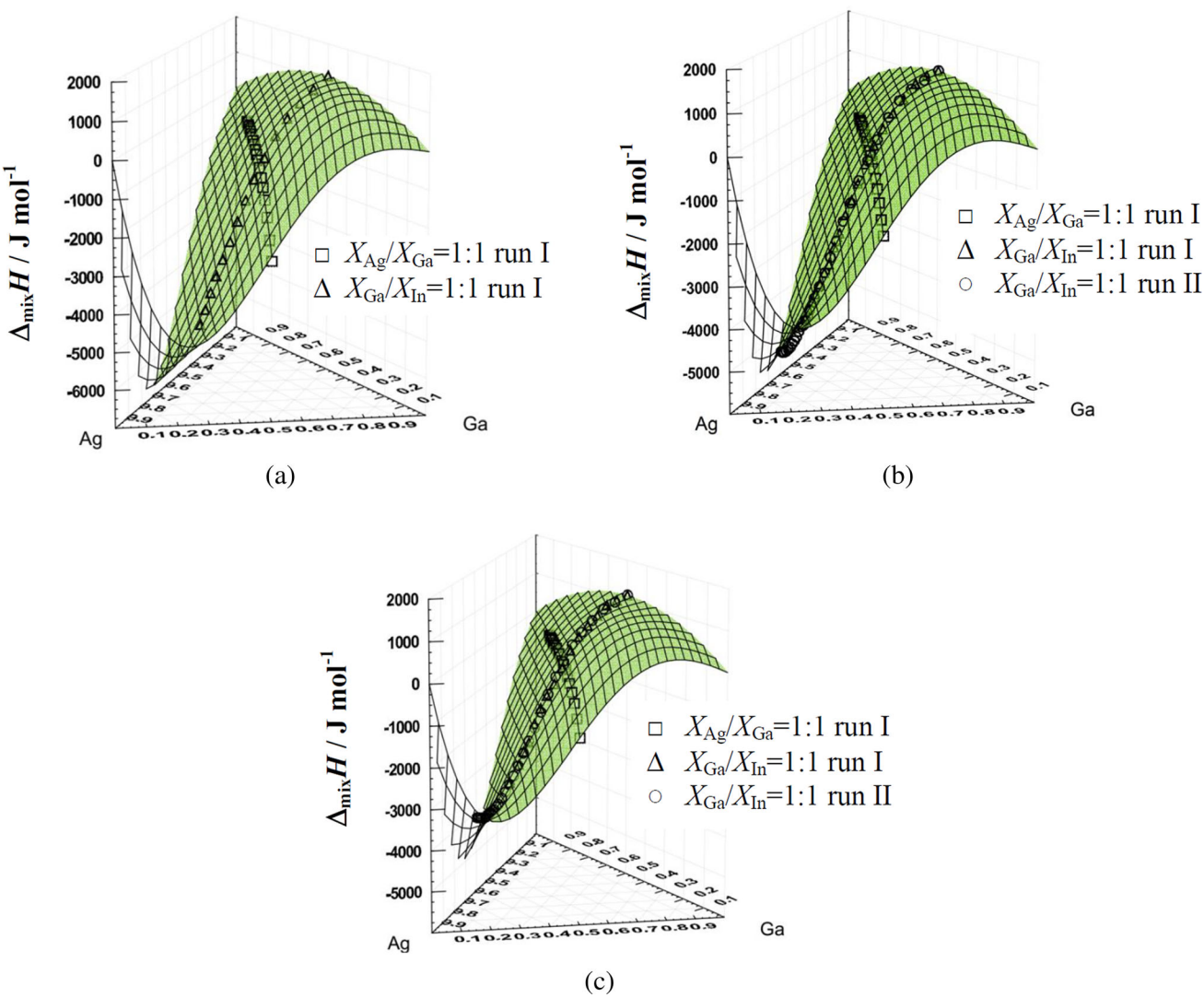


Fig. 3—Three-dimensional visualization of the integral molar heat of mixing of the liquid Ag–Ga–In alloys: (*a*) T = 923 K, (*b*) T = 1123 K, (*c*) T = 1273 K.

thermodynamic properties of the liquid phase in this ternary system has been reported in literature.

ACKNOWLEDGMENTS

This work realized at AGH University of Science and Technology, Faculty of Non-Ferrous Metals under grant number 16.16.180.006 was supported by the Polish Ministry of Education and Science. Authors thank to D. Michalski for his help in experiments.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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SUPPLEMENTARY INFORMATION

The online version contains supplementary material available at https://doi.org/10.1007/s11661-023-07196-5.

REFERENCES

1. X. Huang, Y. Liu, G.W. Kong, J.H. Seo, Y. Ma, K.I. Jang, J.A. Fan, S. Mao, Q. Chen, D. Li, and H. Liu: *Microsyst. Nanoeng.*, 2016, vol. 2, pp. 16052–60.
2. S. Xu, Y. Zhang, L. Jia, K.E. Mathewson, K.I. Jang, J. Kim, H. Fu, X. Huang, P. Chava, R. Wang, S. Bhole, L. Wang, Y.J. Na, Y. Guan, M. Flavin, Z. Han, Y. Huang, and J.A. Rogers: *Science*, 2014, vol. 344, pp. 70–74.
3. T. Yokota, P. Zalar, M. Kaltenbrunner, H. Jinno, N. Matsuhisa, H. Kitanosako, Y. Tachibana, W. Yukita, M. Koizumi, and T. Someya: *Sci. Adv.*, 2016, vol. 2(e1501856), pp. 1–8.
4. B.J. Blaiszik, S.L.B. Kramer, M.E. Grady, D.A. McIlroy, J.S. Moore, N.R. Sottos, and S.R. White: *Adv. Mater.*, 2012, vol. 24, pp. 398–01.
5. P.A. Lopes, H. Paisana, A.T.D. Almeida, C. Majidi, and M. Tavakoli: *ACS Appl. Mater. Interfaces*, 2018, vol. 10, pp. 38760–68.
6. Y. Sohn and K. Chu: *Mater. Lett.*, 2020, vol. 265, pp. 127223–226.
7. P.A. Lopes, D.F. Fernandes, A.F. Silva, D.G. Marques, A.T. Almeida, C. Majidi, and M. Tavakoli: *ACS Appl. Mater. Interfaces*, 2021, vol. 13, pp. 14552–61.
8. D.H. Kim, N. Lu, R. Ma, Y.S. Kim, R.H. Kim, S. Wang, J. Wu, S.M. Won, H. Tao, A. Islam, K.J. Yu, T.I. Kim, R. Chowdhury, M. Ying, L. Xu, M. Li, J.H. Chung, H. Keum, M. McCormick, P. Liu, Y.W. Zhang, F.G. Omenetto, Y. Huang, T. Coleman, and J.A. Rogers: *Science*, 2011, vol. 333, pp. 838–43.
9. C. Dagdeviren, B.D. Yang, Y. Su, L.P. Tran, P. Joe, E. Anderson, J. Xia, V. Doraiswamy, B. Dehdashti, X. Feng, B. Lu, R. Poston, Z. Khalpey, R. Ghaffari, Y. Huang, M.J. Slepian, and J.A. Rogers: *Proc. Natl. Acad. Sci.* , 2014, vol. 211, pp. 1927–32.
10. I.R. Minev, P. Musienko, A. Hirsch, Q. Barraud, N. Wenger, E.M. Moraud, J. Gandar, M. Capogrosso, T. Milekovic, L. Asboth, R.V. Torres, N. Vachicouras, Q. Liu, N. Pavlova, S. Duis, A. Larmagnac, J. Voros, S. Micera, Z. Suo, G. Courtine, and S.P. Lacour: *Science*, 2015, vol. 347, pp. 159–63.
11. A.D. Kimberly and P. Caroff: *Nanoscale*, 2014, vol. 6, pp. 3006–022.
12. M. Ghasemi, E.D. Leshchenko, and J. Johansson: *Nanotechnology*, 2021, vol. 32, pp. 072001-1–72020.
13. C.W. Lin, L.A. Stewart, S. Zhao, G. Akopov, R. Mohammadi, M.T. Yeung, P.S. Weiss, and R.B. Kaner: *Z. Anorg. Allg. Chem.*, 2022, vol. 648, e202200067.
14. Y. Tauchi, K. Kim, H. Park, and W.N. Shafarman: *IEEE J. Photovolt.*, 2003, vol. 3, pp. 467–71.
15. S. Soltanmohammad, L. Chen, B. McCandless, and W.N. Shafarman: *IEEE J. Photovolt.*, 2017, vol. 7, pp. 237–80.
16. S.-C. Yang, J. Sastre, M. Krause, X. Sun, R. Hertwig, M. Ochoa, A.N. Tiwari, and R. Carron: *Sol. RRL*, 2021, vol. 5, pp. 2100108-1–100116.
17. S. Essig, S. Paetel, T.M. Friedlmeier, and M. Powalla: *J. Phys. Mater.*, 2021, vol. 4, pp. 024003-1–24009.
18. Y.J. Muggianu, M. Gambino, and P.J. Bros: *J. Chim. Phys.*, 1975, vol. 22, pp. 83–88.
19. P. Villars, A. Prince, and H. Okamoto: *Handbook of Ternary Alloy Phase Diagrams*, ASM International, Metals Park, 1995.
20. G. Petzow and G. Effenberg: *Ternary Alloys A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams*, Verlag Chemie, Weinheim, 1988.
21. A.N. Cambel and W.F. Reynolds: *Can. J. Chem.*, 1962, vol. 40, pp. 37–45.
22. W. Gierlotka and D. Jendrzejczyk-Handzlik: *J. Alloys Compd.*, 2011, vol. 509, pp. 38–42.
23. E. Fischer, K. Gajavalli, G. Mikaelian, P. Benigni, J. Rogez, A. Decreton, and M. Barrachin: *Calphad*, 2019, vol. 64, pp. 292–05.
24. S.R. Reddy and J.P. Hajra: *Calphad*, 1993, vol. 17, pp. 151–56.
25. B. Predel and D.W. Stein: *Acta Metall.*, 1972, vol. 20, pp. 515–22.
26. K. Itagaki and A. Yazawa: *J. Jpn Inst. Met.*, 1968, vol. 32, pp. 1294–300.
27. D. Jendrzejczyk-Handzlik and K. Fitzner: *J. Chem. Thermodyn.*, 2011, vol. 43, pp. 392–98.
28. D. Jendrzejczyk-Handzlik, P. Handzlik, and K. Fitzner: *Calphad*, 2014, vol. 44, pp. 39–47.
29. R. Beja (PhD Thesis), Université Aix-Marseille, 1969.
30. R. Beja and M. Laffite: *C. R. Acad. Sci. Paris C*, 1968, vol. 267, pp. 123–26.
31. D. Li, S. Delsante, W. Gong, and G. Borzone: *Thermochim. Acta*, 2011, vol. 523, pp. 51–62.
32. D. Jendrzejczyk-Handzlik: *J. Chem. Thermodyn.*, 2017, vol. 107, pp. 114–25.
33. O.J. Kleppa: *J. Phys. Chem.*, 1956, vol. 60, pp. 846–52.
34. R. Castanet, Y. Claire, and M. Laffitte: *J. Chim. Phys. Phys.-Chim. Biol.*, 1970, vol. 67(4), pp. 789–93.
35. W.A. Badawi and A.M. Oun: *Bull. Chem. Soc. Jpn.*, 1989, vol. 62, pp. 304–08.
36. W. Gierlotka: *J. Electron. Mater.*, 2012, vol. 41, pp. 86–108.
37. C.P. Muzillo and T. Anderson: *J. Mater. Sci.*, 2018, vol. 53, pp. 6893–10.
38. J.P. Bros: *C. R. Acad. Sci.*, 1966, vol. 263, pp. 977–80.

39. J.P. Bros, R. Castanet, and M. Laffitte: *C. R. Acad. Sci.*, 1967, vol. 264, pp. 1804–06.
40. B. Predel and D.W. Stein: *J. Less-Common Met.*, 1969, vol. 18, pp. 49–57.
41. L.A. Mechkovskii and A.A. Vecher: *Zh. Fiz. Khim.*, 1969, vol. 43(5), pp. 1346–48.
42. I. Ansara, M. Gambino, and J.P. Bros: *J. Cryst. Growth*, 1976, vol. 32, pp. 101–10.
43. D. Jendrzejczyk-Handzlik and P. Handzlik: *J. Mol. Liq.*, 2019, vol. 293, 111543.
44. I. Barin and O. Knacke: *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Berlin, 1973.
45. O. Redlich and A.T. Kister: *Ind. Eng. Chem.*, 1948, vol. 40, pp. 345–48.
46. J.O. Andersson, T. Helander, L. Höglund, P.F. Shi, and B. Sundman: *Calphad*, 2002, vol. 26, pp. 273–12.
47. Statistica 10.0, www.statsoft.com.
48. F. Sommer: *Z. Metallkde.*, 1982, vol. 2, pp. 73–76.
49. F. Sommer: *Z. Metallkde.*, 1982, vol. 2, pp. 77–86.

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