DTA measurements in the ternary Ag-Au-Ga system

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Abstract
In this work, the ternary Ag-Au-Ga system was studied experimentally by differential thermal analysis (DTA). Measurements were carried out along two chosen cross-sections determined by the ratio of mole fractions $X_{Ag}/X_{Ga}=1:1$ and $X_{Au}/X_{Ga}=1:1$ by applying Pegasus 404 apparatus form Netzsch. Experiments were performed at three rates: 1 K min$^{-1}$, 5 K min$^{-1}$ and 10 K min$^{-1}$. Next, the obtained experimental results were used to estimate the temperatures of liquidus by applying extrapolation to zero rate. Moreover, the temperatures of invariant reactions and other phase transformations were investigated from DTA measurements which were carried out with the rate 1 K min$^{-1}$. Finally, the experimental results were compared with the isopleths obtained from prediction and calculation of the phase diagram which were done by using CALPHAD method. Experimental data obtained in this work are in good agreement with the results of calculation.

Keywords: Ag-Au-Ga system; DTA measurements; CALPHAD method

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1. Introduction

Metals that are liquid at or near room temperature are the only materials that have both metallic and fluidic properties. Mercury is metal with the lowest melting temperature, but is toxic. The second one is gallium which provide low-toxicity alternatives and recently, its alloys are used in many areas. It was shown that the introduction of gallium into multicomponent alloys can decrease their melting temperature and facilitate the formation of proper interconnections between high melting transition metals [1]. Schmid–Fetzer [1] suggested that Ga-based amalgams with metals like Mo, V and even transition metals like Hf, Nb and Zr can be used for soldering in high temperature applications. Alloys containing gallium may find more interesting applications. Gallium has excellent wetting properties and decreases the temperature of melting [2]. Used as a solder alloy, the Cu-Ga system is a part of Cu-In-Ga-Se photovoltaics [3] and Cu-Ga-N semiconductor systems [4]. Moreover, gallium is the component of the following interesting alloys-shape memory (Ga-Mn-Ni alloys exhibit the giant magneto-mechanical effect) [5, 6]. The Au-Ga-In system is especially interesting in electronics in which it is encountered during the growth of Au-seeded III-V semiconductor nanostructures, so-called nanowires (NWs) containing Ga and In from group III) [7-10]. Some gallium alloys have a range of properties that make them an attractive option for stretchable and soft electronics [11, 12]. Gallium alloys are used in production of diodes [13], which are made of very thin layers of semiconductor materials. Gallium arsenide (GaAs), gallium phosphide and gallium arsenide phosphide are used for LED manufacturing. The semiconductor materials with different impurities result in different colors of light coming from LED. To complete the device, it is necessary to bring electricity to it and from it. Thus wires must be attached onto the substrate. These wires must stick to the semiconductor and be strong enough to withstand subsequent processing such as soldering and heating. Gold and silver compounds are most commonly used for this purpose, because they form a chemical bond with the gallium at the surface of the wafer.

The ternary Ag-Au-Ga system is quite interesting from practical point of view. Alloys based on noble metals with gallium are used mainly in three areas: medicine (especially in dentistry) [14], electronics (one among most interesting multicomponent possible lead free solder is quaternary Au-Ga-In-Śb system whose examination has just begun) [15], jewelry (special gold colors such as purple, blue, brown and black) [16-18] as well as part of lead-free solders [19]. Thus, to gain the necessary knowledge about the phase diagram and melting behavior of the Ag-Au-Ga system, new experimental data are needed.

2. Literature review

The information about the ternary Ag-Au-Ga, as well as its properties is missing in the monographs of Villars et al. [20] and Petzow and Effenberg [21]. In the literature one can find four experimental works related to this ternary system. The first one, of Andronov et al. [2] provides information about wettability of the Ag-Au-Ga thin films. Consequently, the ternary Ag-Au-Ga system was studied as one of those who can be applied as a solder. The other one, published by Jendrzejczyk-Handzik [22], reported the results of calorimetric measurements of the enthalpy of mixing along two cross-sections of this ternary system, with $X_{Ag}/X_{Ga}$=1:1 and $X_{Au}/X_{Ga}$=1:1, as well as at two temperatures 1223 and 1323 K. The results obtained in that experimental work showed that the enthalpy of mixing in this ternary system does not have a temperature dependence. Next, Jendrzejczyk-Handzik [23] reported the results of EMF measurements from which the activity of gallium in liquid Ag-Au-Ga system was determined. Measurements were carried out along three cross-sections, with $X_{Ag}/X_{Au}$=1:2, 1:1 and 2:1 in the temperature range from 1023 to 1348 K. The activity of gallium shows negative deviation from Raoult’s law in the whole range of gallium concentration in which measurements were done. Next, the experimental data which were obtained from calorimetric and EMF
3. Experimental

Gold rod of 2 mm in diameter (99.99 mass%) were obtained from Mint of Poland. Metallic gallium piece and indium shots (every 99.999 mass%) were obtained from Alfa Aesar, Germany. The gas atmosphere was pure argon obtained from Air Products, of minimum mass fraction (99.9999 mass%). DTA measurements were carried out on Ag-Au-Ga alloys along two cross-sections, with $X_{Ag}/X_{Ga}=1:1$ and $X_{Au}/X_{Ga}=1:1$, and in the temperature range from 473 K to 1300 K. The experimental procedure of DTA measurements is the same like in the case of Au-Ga system [28], Ag-In-Sb system [31] and Ag-Cu-Ga system [32]. The samples of the alloys were prepared from pieces of pure silver, gold and gallium metals. The weight of samples used for DTA experiments the experiments were about 300 mg. These samples were prepared with the following compositions: $X_{Ag}/X_{Ga}=1:1$ for $X_{Au}$ from 0.1 to 0.8 and $X_{Au}/X_{Ga}=1:1$ for $X_{Ag}$ from 0.1 to 0.8. The samples were placed inside the self-made DTA quartz crucibles, and then they were sealed under vacuum. The melting and annealing process were performed in the operating furnace VMK22, Linn High Therm. The samples in quartz-ampoules were placed in alumina crucibles and they were held at the setting temperature 1373 K for nearly 6 h to make sure complete melting and homogenization. After this they were cooled slowly (2 K/min) to the temperature of 473 and annealed for 8 weeks to obtain thermodynamic equilibrium and then quenched in ice water. The overall compositions of all samples have been checked by using WD-XRF method and the differences between nominal and measured compositions were negligible. Homogeneity of chosen samples has been also checked by using optical microscope. After these analyses the samples were transferred to DTA apparatus. The measurements were performed on Pegasus 404 apparatus from Netzsch, Selb, Germany. This device is hooked up to PC in order to control all DTA procedures during the experiment by PROTEUS software, also obtained from Netzsch. The acquired data were recorded on PC. The calorimeter was calibrated by comparison of the melting temperatures of metallic In, Sn, Pb, Zn, Al, and Au (99.999 mass% purity) with tabulated values with accuracy of the melting temperature of ±2°C to establish an internal calibration file. The experiments were carried out at three rates: 1 K min⁻¹, 5 K min⁻¹ and 10 K min⁻¹ in two heating and cooling cycles. All measurements were carried out in temperature range from 473 K to 1273 K. The working side was a ternary alloy of the chosen composition sealed in self-made DTA quartz crucibles while the empty self-made DTA quartz crucible was the reference side. Next, the obtained results were used to estimate the temperature of liquidus by applying extrapolation to zero rate for the data obtained from heating and cooling cycles. Additionally, the temperature of phase transformations were estimated from thermal curves obtained from experiments which were carried out with the rate equal to 1 K min⁻¹. Based on the repeated DTA measurements the overall uncertainty of the determined phase transition temperatures was estimated to be ±2 °C.

4. Results and discussion

4.1 Experimental data
As a result of DTA experiments, phase transition temperatures and the liquidus line along two selected cross-sections, namely $X_{Ag}/X_{Ga}=1:1$ and $X_{Au}/X_{Ga}=1:1$, were determined in the Ag-Au-Ga system. Temperatures of the liquidus and other phase transformations were taken from DTA curves for first heating and cooling cycles for every studied sample (the liquidus temperatures were taken from the peak maximum on heating and on cooling from the corresponding onset). Examples of DTA heating curves recorded for a chosen composition of the ternary Ag40Au20Ga40 alloy with various heating rates: 1 K min$^{-1}$, 5 K min$^{-1}$ and 10 K min$^{-1}$, are shown in Fig. 1. All of them showed clearly detected phase transitions. In the inset in Fig. 1 the dependence of the recorded liquidus temperature on the heating rate is shown. It demonstrated that, depending on the applied heating rate, determined liquidus temperature may vary by more than 20 K. The liquidus temperature is shifted with the increasing heating rate towards higher temperatures. This can be explained by process dynamics and by detection abilities of the instrument.

Fig. 1 DTA heating curves of Ag40Au20Ga40 alloy with various heating rates.

The data of liquidus temperatures obtained from DTA experiments which were carried out with three rates: 1 K min$^{-1}$, 5 K min$^{-1}$ and 10 K min$^{-1}$ for heating and cooling cycles were extrapolated to rate which is equal to zero. Finally, the temperature of the liquidus for every ternary alloy which was analyzed was determined. The obtained results from DTA experiments which were carried out with three different rates along chosen cross-section where $X_{Au}/X_{Ga}=1:1$ are shown in Figs. 2-4. Similar results were recorded for $X_{Ag}/X_{Ga}=1:1$ cross-section. All obtained results from DTA experiments are gathered in Table 1 where sample compositions, temperatures of liquidus from heating and cooling cycles and other effects from heating are given. According to the DTA results, two invariant reactions were identified, which are given in Table 2.
Fig. 2 DTA heating curves of Ag-Au-Ga alloys, \( X_{\text{Ag}}/X_{\text{Ga}}=1:1 \) with \( r=1 \text{ K min}^{-1} \).

Fig. 3 DTA heating curves of Ag-Au-Ga alloys, \( X_{\text{Ag}}/X_{\text{Ga}}=1:1 \) with \( r=5 \text{ K min}^{-1} \).
Fig. 4 DTA heating curves of Ag-Au-Ga alloys, $X_{\text{Ag}}/X_{\text{Ga}}=1:1$ with $r=10$ K min$^{-1}$. 
Table 1 Summary of measured thermal effects obtained in the Ag-Au-Ga system.

| Composition $X_i$ (i=Ag or Au) | mass of sample [g] | $T_{\text{effect heating/K}}$ |  |  |  |  |  |  |  |  |  |
|------------------------------|-------------------|-------------------------------|  |  |  |  |  |  |  |  |  |
|                              |                   | $T_{\text{Liquidus heating/K}}$ r=1 K min$^{-1}$ | r=5 K min$^{-1}$ | r=10 K min$^{-1}$ | r=0 K min$^{-1}$ | |  |  |  |  |
|                              |                   | $T_{\text{Liquidus cooling/K}}$ r=1 K min$^{-1}$ | r=5 K min$^{-1}$ | r=10 K min$^{-1}$ | r=0 K min$^{-1}$ | |  |  |  |  |
| $X_{\text{Ag}}/X_{\text{Ga}}$:1:1 |                   | $X_{\text{Ag}}/X_{\text{Ga}}$:1:1 |  |  |  |  |  |  |  |  |  |
| 0.1                          | 0.295             | 588, 661                       | 709 | 711 | 712 | 708 | 710 | 710 | 710 | 710 |
| 0.2                          | 0.298             | 677, 683, 688                  | 734 | 744 | 757 | 732 | 694 | 694 | 694 | 694 |
| 0.3                          | 0.293             | 668,679, 685                  | 736 | 759 | 760 | 738 | 684 | 719 | 726 | 686 |
| 0.4                          | 0.305             | 670, 678                      | 761 | 762 | 763 | 760 | 678 | 695 | 723 | 671 |
| 0.5                          | 0.294             | 612, 621                      | 776 | 778 | 782 | 775 | 696 | 713 | 715 | 697 |
| 0.6                          | 0.287             | 612                           | 908 | 911 | 939 | 900 | 908 | 910 | 912 | 907 |
| 0.7                          | 0.294             | 681                           | 1069 | 1101 | 1125 | 1064 | 1072 | 1075 | 1075 | 1075 |
| 0.8                          | 0.303             | 684                           | 1157 | 1166 | 1167 | 1157 | 1164 | 1174 | 1175 | 1164 |
| $X_{\text{Au}}/X_{\text{Ga}}$:1:1 |                   | $X_{\text{Au}}/X_{\text{Ga}}$:1:1 |  |  |  |  |  |  |  |  |  |
| 0.1                          | 0.301             | 669, 675                      | 703 | 709 | 724 | 699 | 659 | 666 | 683 | 645 |
| 0.2                          | 0.298             | 668, 679                      | 691 | 692 | 706 | 688 | 636 | 644 | 659 | 632 |
| 0.3                          | 0.301             | 669, 672                      | 713 | 749 | 762 | 713 | 680 | 682 | 695 | 677 |
| 0.4                          | 0.295             | 667, 670                      | 804 | 805 | 812 | 802 | 742 | 747 | 766 | 737 |
| 0.5                          | 0.299             | 667, 677                      | 843 | 844 | 847 | 842 | 812 | 857 | 858 | 816 |
| 0.6                          | 0.298             | 667, 684                      | 987 | 987 | 994 | 985 | 986 | 987 | 987 | 986 |
| 0.7                          | 0.297             | 684                           | 1069 | 1070 | 1077 | 1067 | 1074 | 1075 | 1077 | 1074 |
| 0.8                          | 0.302             | 837                           | 1144 | 1147 | 1149 | 1144 | 1143 | 1144 | 1144 | 1143 |
4.2 Thermodynamic Calculation

Prediction of ternary Ag-Au-Ga diagram by applying CALPHAD method was done by using Pandat 2017 software [33] and is compared with the experimental data obtained in this work. At first, this prediction was based on the existing information about assessed binary systems: Ag-Au [27], Au-Ga [28] and Ag-Ga [30]. The binary thermodynamic parameters used for the prediction of phase equilibria in the ternary Ag-Au-Ga system were taken from the previous work [26]. Then, a new set of thermodynamic parameters for the liquid phase of the Ag-Au-Ga system was evaluated by using the following experimental data taken from the literature. The heat of mixing data obtained along two cross-sections where \( x_{\text{Ag}}/x_{\text{Ga}}=1:1 \) and \( x_{\text{Au}}/x_{\text{Ga}}=1:1 \) at two temperatures 1223 K and 1323 K [22], activities of gallium determined from the EMF method by using solid oxide electrolyte in the temperature range from 1023 to 1348 K [23], as well as experimental data taken from the present work. To each piece of the selected information was given a certain weight based on experimental uncertainty. The optimization was carried out step by step in agreement with Schmid-Fetzer's et al. [34] guideline. Ternary interaction parameters were calculated by using ThermoCalc 2019 software [35].

The description of the thermodynamic parameters of the liquid phase was carried out in the following manner. The substitutional solution model was used to express the Gibbs free energy of the liquid solution in the following form:

\[
G^M = x_{\text{Ag}}G^0_{\text{Ag}} + x_{\text{Au}}G^0_{\text{Au}} + x_{\text{Ga}}G^0_{\text{Ga}} + RT(x_{\text{Ag}}\ln x_{\text{Ag}} + x_{\text{Au}}\ln x_{\text{Au}} + x_{\text{Ga}}\ln x_{\text{Ga}}) + G^E
\]  

where parameters \( G_i^0 \) denote free energy of pure component "i" taken from the SGTE database [36]. The function \( G^E \) denotes the excess free energy and is described by the Redlich-Kister-Muggianu formula:

\[
G^E = x_{\text{Ag}}x_{\text{Au}}^0 L_{\text{AgAu}}^{\text{Liquid}} + x_{\text{Ag}}x_{\text{Ga}}^0 L_{\text{AgGa}}^{\text{Liquid}} + x_{\text{Au}}x_{\text{Ga}}^0 L_{\text{AuGa}}^{\text{Liquid}} + x_{\text{Ag}}^2 L_{\text{AgAg}}^{\text{Liquid}} + x_{\text{Au}}^2 L_{\text{AuAu}}^{\text{Liquid}} + x_{\text{Ga}}^2 L_{\text{GaGa}}^{\text{Liquid}} + x_{\text{Ag}}x_{\text{Au}}x_{\text{Ga}}(x_{\text{Ag}}L_{\text{AgAg}}^{\text{Liquid}} + x_{\text{Au}}L_{\text{AuAu}}^{\text{Liquid}} + x_{\text{Ga}}L_{\text{GaGa}}^{\text{Liquid}})
\]

(2)

Parameters \( L_{\text{AgAu}}^{\text{Liquid}} \) are dependent on temperature and are given in J mol\(^{-1}\). Evaluated thermodynamic parameters are gathered in Table 3. Using this optimized parameters the Ag-Au-Ga system was calculated. Finally, experimental results obtained from DTA measurements were compared with the results of prediction and optimization, and are shown in Figs 5-6.
Table 3 Binary and ternary interaction parameters for liquid phase.

| Phase          | Thermodynamic parameters /J mol⁻¹                                                                 | Ref  |
|----------------|-----------------------------------------------------------------------------------------------|------|
| Liquid         |                                                                                                 |      |
|                | $^{0}_{L_{\text{AgGa}}} \text{Liquid} = -16402 + 1.14 \cdot T$                                  | [27] |
|                | $^{0}_{L_{\text{AgGa}}} \text{Liquid} = -19643.799 + 63.659 \cdot T - 8.620 \cdot T \cdot \ln(T)$ | [30] |
|                | $^{1}_{L_{\text{AgGa}}} \text{Liquid} = 38747.760 + 140.716 \cdot T - 16.112 \cdot T \cdot \ln(T)$ | [30] |
|                | $^{2}_{L_{\text{AgGa}}} \text{Liquid} = -25745.683 + 140.455 \cdot T - 17.417 \cdot T \cdot \ln(T)$ | [30] |
|                | $^{0}_{L_{\text{AuGa}}} \text{Liquid} = -64836.418 - 1.669 \cdot T$                            | [28] |
|                | $^{1}_{L_{\text{AuGa}}} \text{Liquid} = -26517.288 + 8.315 \cdot T$                            | [28] |
|                | $^{2}_{L_{\text{AuGa}}} \text{Liquid} = -12480.212 + 14.248 \cdot T$                           | [28] |
|                | $^{0}_{L_{\text{AgAuGa}}} \text{Liquid} = 28623 - 18.65 \cdot T$                               |      |
|                | $^{1}_{L_{\text{AgAuGa}}} \text{Liquid} = -114876 + 93.69 \cdot T$                            |      |
|                | $^{2}_{L_{\text{AgAuGa}}} \text{Liquid} = 119584 - 63.5 \cdot T$                               |      |

Fig. 5 Experimental data compared with the calculation of the Ag-Au-Ga system given for isoplethetical section with $X_{\text{Ag}}/X_{\text{Ga}}=1:1$. 

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AgGa₂ + AuGa₂ + L → \( \alpha \) + \( \beta' \) - Au₂Ga₃ + \( \alpha \)
Fig. 6 Experimental data compared with the calculation of the Ag-Au-Ga system given for isoplethal section with $X_{Au}/X_{Ga}=1:1$.

4.3 Discussion

In the case of liquidus temperatures which were determined in the present work by extrapolation of obtained experimental data to $r=0$ K min$^{-1}$, the experimental values are in good agreement with the results of calculations in which the liquid phase was optimized. The biggest difference between liquidus temperatures obtained from the experimental results and this calculation is found for the sample from cross-section $X_{Au}/X_{Ga}=1:1$, where silver concentration is 0.4 mole fraction. The obtained experimental value for $X_{Ag}=0.4$ is 802 K while the calculated temperature is 779 K. In case of the second cross-section the biggest difference between temperatures of liquidus obtained from the experimental results and this calculation is found for the sample $X_{Au}=0.6$, where experimental value is 985 K while the calculated temperature is 955 K. However, in the case of other samples the difference between experimental liquidus temperatures and the calculation is less than 20 K. The comparison of liquidus temperatures obtained in the present work by extrapolation to $r=0$ K min$^{-1}$ with calculation of isopleths from only binary systems data, shows that the difference is much larger. It must be remembered that in this prediction the ternary interactions were not taken into account. The comparison of experimental liquidus temperatures which were determined in the present work from cooling cycles with both calculations gives the following result. For alloys with following compositions: along cross-sections $X_{Ag}/X_{Ga}=1:1$ for $X_{Au}$ which is in the range from 0.1 to 0.5, and along cross-sections $X_{Au}/X_{Ga}=1:1$ for $X_{Ag}$ which is in the range from 0.1 to 0.5, the supercooling effect is present. For the rest of ternary alloys the experimental liquidus temperatures are in good agreement with the calculation which was done by optimization of liquid phase. The determined temperature of invariant reaction $\zeta'+L=\text{AuGa}_2+\text{Ag}_3\text{Ga}_2$ is based on one sample for $X_{Au}=0.1$ from the cross-section
$X_{Ag}/X_{Ga}=1:1$. This invariant reaction was found at 588 K. The calculated temperature of this invariant reaction from information taken only from binary systems is 575 K. While, the calculated temperature of this invariant reaction was determined with the optimized liquid phase and it is equal to 580 K. The analysis of the experimentally determined values given in Table 3 shows that in case of this alloy the obtained temperature of this invariant reaction is higher than that obtained from both calculations. Next, the temperature of the invariant reaction $\text{Au}_7\text{Ga}_2+\text{L}=\alpha+\text{Au}_7\text{Ga}_3$ was determined from the DTA analysis of two samples: $X_{Au}=0.5$ and 0.6, while $X_{Ag}/X_{Ga}=1:1$. It is equal to 612 K. In turn, the predicted temperature of this invariant reaction from only binary systems is 617 K, while from calculation with optimized liquid phase is 614 K. It can be seen from Figs. 5-6 that in the case of the above listed invariant reactions the obtained experimental results are in good agreement with the results of both thermodynamic calculations of this ternary system.

6. Conclusions

The phase equilibria in the Ag-Au-Ga system have been experimentally investigated by using differential thermal analysis. The analyses of sixteen samples, along two cross-sections ($X_{Au}/X_{Ga}=1:1$ and $X_{Ag}/X_{Ga}=1:1$) gave information about liquidus temperatures, invariant reactions, as well as other phase transitions. The comparison of these experimental results with calculations of the Ag-Au-Ga system leads to the following conclusion: it seems that the real liquidus surface is located in good agreement with the one obtained from the calculation in which thermodynamic properties of the liquid phase as well as the data from the present work are taken into account. Experimentally determined temperatures of two invariant reactions are close to those obtained from the calculations. The comparison of temperatures of other phase transitions obtained from the experiment with the results of calculations showed some discrepancy.

Experimental DTA results obtained in the present work together with the other existing experimental results [22, 23, 26] will be used in the near future in the final optimization of the phase diagram of the ternary Ag-Au-Ga system by applying CALPHAD method.

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Figure Captions

Fig. 1 DTA heating curves of Ag40Au20Ga40 alloy with various heating rates.
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