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GIBBS FREE ENERGY OF FORMATION OF $Cu_2In_2O_5$ TERNARY PHASE DETERMINED BY EMF METHOD

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Abstract

Employing electrochemical cells with the solid zirconia electrolyte:
Cu_2O*,* CuO */* O^{2-} */ air*
$Cu_2In_2O_5$*,* In_2O_3*,* Cu_2O */* O^{2-}*/ air*
In, In_2O_3 */* O^{2-}*/ Ni, NiO*
Gibbs free energy of formation of solid $Cu_2In_2O_5$ *phase, as well as that for* In_2O_3 *and CuO oxides, was determined in the temperature range from 973 K to 1372 K. The results obtained in this study were used to derive Gibbs free energy change of the reaction of formation of the ternary compound from respective oxides:*
$2CuO + In_2O_3 = Cu_2In_2O_5$
which is equal to: $\Delta G^0_{f,Cu_2In_2O_5} = 33905 - 41.50T(\pm 3600)$ *J mol*$^{-1}$*. Standard enthalpy of formation from elements* $\Delta H^0_{f,298}$ *and standard entropy* ΔS^0_{298} *derived for* $Cu_2In_2O_5$ *phase by Second Law sigma plot are -1211 (±15) kJ mol*$^{-1}$ *and 493.20 (±10) J (K*$^{-1}$ *mol*$^{-1}$*). Oxygen potential diagrams for the Cu–In–O system are also given at two temperatures.*

Keywords: *EMF method; Gibbs free energy; Formation of* $Cu_2In_2O_5$

1. Introduction

Transparent conductive oxides (TCO) are used as transparent electrodes which, depending on applications, require either n-type or p-type conductivity. The discovery of p-type conductivity in $CuAlO_2$ compound [1] stimulated an interest in the family of $CuMO_2$ delafossite compounds (where M =Al, Ga or In) of which $CuInO_2$ shows bipolar conductivity [2]. However, in spite of the technological interest in these materials, a little is known about their thermodynamic stability. Thermodynamics of $CuAlO_2$ and $CuAl_2O_4$ phases and phase equilibria in the system Cu_2O-CuO-Al_2O_3 were investigated by Jacob and Alcock [3]. They compared their results with published information on the stability of these compounds and also compared the results of calculations with available phase diagram. As a result of this work, a consistent picture of phase equilibria in Cu-Al-O system emerged. Recently, thermodynamic stability of two solid phases $CuGa_2O_4$ and $CuGaO_2$, which are known to exist in Cu-Ga-O system, was investigated [4]. In that paper the results were compared with existing thermodynamic data and suggested stability diagrams as $\log_{p_{O_2}}$ vs. composition representation at constant temperature.

Up to now, not too much is known about the thermodynamic stability of phases and phase equilibria in Cu-In-O system. It is suspected that depending on temperature and partial oxygen pressure three solid phases, namely $Cu_2In_2O_5$, $CuInO_2$ and $CuIn_2O_4$ may exist. The information about thermodynamic properties of $Cu_2In_2O_5$ is scarce. There is only one study cited by Tretyakov [5] which reports Gibbs free energy of formation of this phase. Chumilina et al. [6] measured its heat capacity in the temperature range 364-984 K. No more experimental information of this kind was found in the literature.

Green $Cu_2In_2O_5$ phase can be relatively easily synthesized by sintering copper (II) and indium (III) oxides at high temperature [7]. Formation of this phase from CuO and In_2O_3 oxides was recently confirmed by Lee et al. [8]. Recently, Makiura et al. [9] reported that among all the oxides derived from Cu-In_2O_3 system the $Cu_2In_2O_5$ phase is the most promising material which can be used in Fisher-Tropsch (FT) process using syngass, which includes hydrogen and carbon monoxide (CO) converted from captured CO_2. This is a method of efficient conversion of CO_2 to CO thought this process, reverse water-gas shift (RWGS) is a promising reaction that uses renewable H_2. Actually, the development of CO_2 capture techniques is an urgent task in the fight against global warming. Skaria et al. [10] reported

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deposition of $Cu_2In_2O_5$ thin films by the RF magneton sputtering technique. Annealing studies of $Cu_2In_2O_5$ thin films were performed at temperature ranging from 273 K to 1173 K (effects of structural, morphological and optical properties were studied). All films displayed high optical transmission of more than 70% in the wavelength region of 500–800 nm.

There is only one study [11] found in the literature concerning the formation of spinel $CuIn_2O_4$ phase. Despite of the fact that these compounds usually are easily formed at high oxygen pressure and temperature, under these conditions copper and indium oxides do not react to yield spinel phase. During experiments with the crystal growth of $Bi_2Sr_2CaCu_2O_8$ phase, after substitution of Bi with In, authors of this paper observed precipitation of a new, black phase, which was identified as $CuIn_2O_4$. Perhaps, this phase can be formed at temperatures around 1200 °C only from the melt.

Similarly, synthesis of delafossite-type $CuInO_2$ phase is difficult by the solid state reaction. This phase was obtained first time by Gessner [12], who used cation exchange reaction between CuCl and $NaInO_2$. This method was next improved by Shimode et al. [13] who used $LiInO_2$ instead of sodium indate. Consequently, this route of synthesis was followed by Park and Keszler [14], Sasaki and Shimode [15], and Li et al. [16]. In each case the $CuInO_2$ phase was successfully formed. It looks that this phase is unstable and cannot be obtained at high temperature. First principles calculations performed by Liu et al. [17] indicate metastability of this phase. According to their study theoretical value of enthalpy change $\Delta H^0_{f,\mathrm{CuInO_2}}$, for the reaction: $Cu_2O+In_2O_3=2CuInO_2$ is about 5.4 kJ/mole. Thus, unless this phase is entropy stabilized, it cannot be stable at high temperature. Yao et al. [18] presented thermodynamic study on $CuInO_2$ preparation by solid reaction method. In their paper, the standard enthalpy, heat capacity at constant pressure and standard Gibbs free energy of formation were estimated by the application of two-parameter model. Five possible chemical reactions in Cu_2O-In_2O_3 mixture were studied in the preparation process of $CuInO_2$ by solid state reaction method. Similarly like in [17], theoretical value of enthalpy change $\Delta H^0_{f,\mathrm{CuInO_2}}$ was calculated for the same reaction and obtained value is equal -12.144 kJ/mol. It is obvious that the values obtained in papers [17, 18] are completely different.

The ranges of $CuInO_2$ stability (if any) are not known, which in fact is also true in the case of $Cu_2In_2O_5$ compound. Since this compound may exhibit interesting thermoelectric properties [19], its stability at higher temperature is of great importance.

Therefore, the purpose of this study is to provide new data on the Gibbs free energy of formation of $Cu_2In_2O_5$ phase and to determine its ranges of thermodynamic stability under visible oxygen potential pressure and temperature.

2. Experimental

2.1. Materials

Materials used in this study were the following oxides: CuO (99%) and Cu_2O (99%) obtained from Sigma Aldrich, Germany, while In_2O_3 (99.99%) obtained from Fluka AG, Germany. Platinum (99.99 %) was obtained from Mennica Polska, Poland. Solid ZrO_2 electrolyte stabilized 5 mass percent of Y_2O_3 (length 400 mm, outside diameter 8 mm), closed one end, was supplied by Friatec AG, Germany.

Pure CuO and In_2O_3 oxides at the molar ratio of 2:1 were mixed in a ball mill for 3 hours. Next, dark-green $Cu_2In_2O_5$ phase was synthesized by heating pressed pellets (weight 2 g) containing a mixture of CuO and In_2O_3 for 50 h in air at 1223 K with one intermediate grinding (ball mill for 3 hours). Temperature and time for synthesis of $Cu_2In_2O_5$ phase were chosen following literature information [7, 8]. Formation of the required compound was confirmed by an X-ray analysis (Fig.1). The prepared compound and respective oxides were used in the preparation of the working electrode for the electrochemical cell. Attempts to synthesize in the similar manner $CuIn_2O_4$ binary oxide failed. As a result of sintering process, oxide mixture with $Cu_2In_2O_5$ being predominant phase was always obtained.

2.2. EMF measurements

The electrochemical cells of the type:

$$Cu_2O,\ CuO\ /\ O^{-2}\ /\ air\ (p_{O_2} = 0.21atm) \qquad \text{(I)}$$

$$Cu_2O,\ In_2O_3,\ Cu_2In_2O_5\ /\ O^{2-}\ /\ air\ (p_{O_2} = 0.21atm) \qquad \text{(II)}$$

$$In,\ In_2O_3\ /\ O^{-2}\ /\ Ni,\ NiO \qquad \text{(III)}$$

were used for oxygen potential measurements.

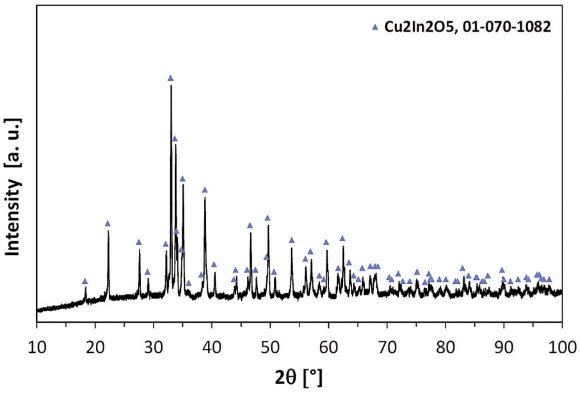

Figure 1. *XRD spectrum of synthesized $Cu_2In_2O_5$ phase*

Constructions of cells I and II differed from that used for cell III. A schematic diagrams of these cell assemblies were given in the earlier papers [20, 21]. In the experiments, yttria-stabilized zirconia (YSZ) was used as an electrolyte and dry air was used as the reference electrode. A sample consisting of mixed oxide powders was kept at the bottom of the long electrolyte tube. Electrical contact was made by using a platinum wire. Contact was assured by pressing an alumina shield with a flat base onto a sample. An inert atmosphere was maintained inside the cell by passing purified argon gas through the system. Experiments were performed in a vertical, resistance furnace. The cell was kept in the furnace in the constant temperature zone, and the sample at the bottom of the electrolyte tube was always placed in this zone. The construction of the cell III is different and it was described in the earlier study [21]. Short electrolyte tube was sealed with alumina cement inside alumina crucible which contained Ni+NiO powders mixture serving as a reference electrode. In order to provide electrical contact with liquid indium, the Kanthal™ wire was extended with Rhenium tip, welded to its end.

After a constant temperature was reached, the cell was left overnight to attain an equilibrium state, and then the EMF was recorded with Keithley 2100 digital voltmeter. The temperature was cycled in the range 973 K to 1223 K, and the full run was completed after about one week. From time to time a small current from the external source was passed. The EMF returned to ±1mV of the original value in a few minutes depending on temperature. After the experiment the working electrode was checked by an XRD analysis (Fig. 2). This analysis confirmed that in the working electrode exchange reactions did not take place and all three phases: Cu_2O, In_2O_3, $Cu_2In_2O_5$ were present after experiment.

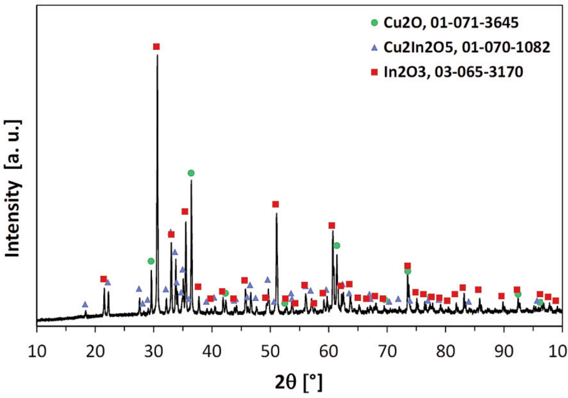

Figure 2. *XRD spectrum for working electrode ($Cu_2In_2O_5$, In_2O_3, Cu_2O) after measurement*

3. Results

At first, the electrochemical cell of the type:

$$CuO,\ Cu_2O\ /\ O^{2-}\ /\ air\ (p_{O_2} = 0.21 atm) \tag{I}$$

was assembled to check the performance of the whole experimental setup. All cells in this work are written in such a way that the right-hand electrodes are positive. Consequently, the net cell reaction for the cell (I) is:

$$Cu_2O + 1/2O_2 = 2CuO \tag{1}$$

Results (electromotive force values) were treated by the least-squares method and the EMF vs. temperature dependence is shown in Fig. 3a.

The obtained results can be represented by the following equation:

$$E_I = -0.00050T + 0.6375\ (\pm 0.0011)V \tag{2}$$

For the cell II:

$$Cu_2O,\ In_2O_3,\ Cu_2In_2O_5\ /\ O^{2-}\ /\ air\ (p_{O_2} = 0.21 atm) \tag{II}$$

the overall reaction is:

$$Cu_2O + \tfrac{1}{2}O_2 + In_2O_3 = Cu_2In_2O_5 \tag{3}$$

The measured EMF values can be described by the linear equation:

$$E_{II} = -0.00029T + 0.4618\ (\pm 0.0084)V \tag{4}$$

Similarly like in the previous case, obtained electromotive force values were treated by the least-squares method and the EMF vs. temperature dependence is shown in Fig. 3b.

The equilibrium oxygen potential over $In+In_2O_3$ two-phase mixture can be determined from EMF's measured by the cell III [21]. EMF's measured for the cell III were corrected by thermo-EMF Pt-Re(+ kanthal) and are shown in Fig. 3c. For the cell:

$$In,\ In_2O_3\ /\ O^{-2}\ /\ Ni,\ NiO \tag{III}$$

the overall cell reaction is:

$$3Ni + 2In = In_2O_3 + 3Ni \tag{5}$$

While EMF presented by the cell III can be described by the equation:

$$E_{III} = -0.0000931T + 0.3590\ (\pm 0.0013)V \tag{6}$$

The EMF of each cell is related to the oxygen partial pressure generated over respective having electrode through the equation:

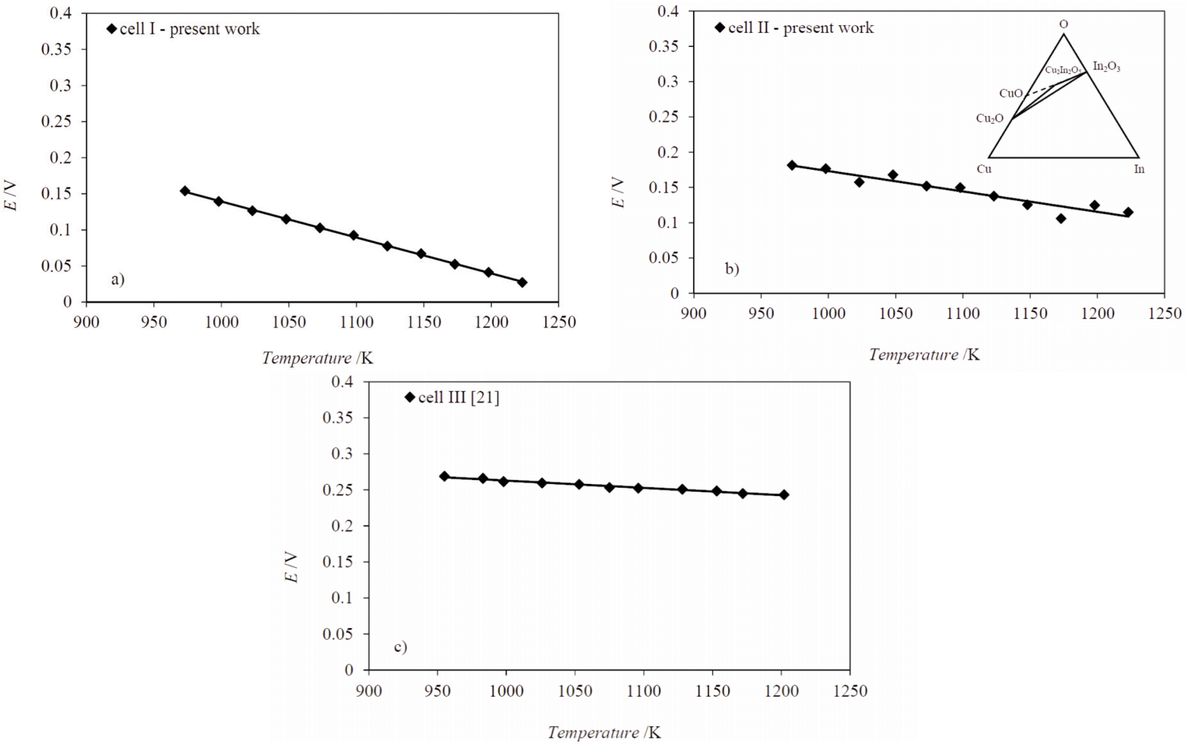

Figure 3. *Measured E as a function of temperature a) cell I, b) cell II, c) cell III. Showed area on Gibbs triangle (inset in Fig. 3b) corresponds to phase equilibria taking place in cell II*

$$E = (RT/4F)ln\{p_{O_2(reference)}/p_{O_2(working)}\} \quad (7)$$

where F is Faraday's constant 96485.34 C/mole, R is the gas constant 8.314 J/(mole×K), T is the temperature given in K, and p_{O_2} is oxygen partial pressure exerted by the electrodes, E is the measured EMF given in V. Thus, for each cell, oxygen partial pressure over investigated electrode is equal to:

$$lnp_{O_2(working)} = \ln p_{O_2(reference)} - (4FE/RT) \quad (8)$$

For cells I and II the reference electrode is air, and consequently $p_{O_2(reference)} = 0.21\ atm$. In the case of the cell III, the reference electrode was the mixture of Ni and its oxide, NiO. Corresponding equilibrium oxygen pressure as a function of temperature can be derived from $\Delta G^0_{f,NiO}$ and is equal to $\ln p_{O_2} = 2\Delta G^0_{f,NiO}/RT$. The Gibbs free energy of formation of NiO after Charette and Flengas was accepted [22].

Respective Gibbs free energy change for the reactions of formation (1, 3, 5) takes the following form:

$$\Delta G^0_{f,2CuO} = 1/2RT\ln p_{O_2(working)} = 1/2RT\ln 0.21 - 2FE_I = -123019 + 90.00T(\pm 2100)\ J\ mol^{-1} \quad (9)$$

$$\Delta G^0_{f,(3)} = 1/2RT\ln p_{O_2(working)} = 1/2RT\ln 0.21 - 2FE_{II} = -89114 + 49.49T(\pm 2700)\ J\ mol^{-1} \quad (10)$$

$$\Delta G^0_{f,In_2O_3} = 3/2RTlnp_{O_2(working)} = 3/2RT\ln p_{O_2(reference)} - 6FE_{III} = -911570 + 313.10T(\pm 1000)\ J\ mol^{-1} \quad [21] \quad (11)$$

4. Discussion

The Gibbs free energies change for the reaction of formation of 2CuO and In_2O_3 were compared with the literature data and they are shown in Fig 4. $\Delta G^0_{f,2CuO}$ values calculated from the experimental data given in the present work are shown and compared with the literature data in Fig. 4a. The difference between values obtained in the present work and the literature data [22-24] is in the range of 5% and with the data [4] is about 7%, so they are in fair agreement. Next, obtained $\Delta G^0_{f,In_2O_3}$ data represented by Eq. (11) are shown in Fig. 4b and are compared with the published data [21, 25-28]. A good agreement was found between results of different studies with the spread of results of the order of 16 kJ, which is about 3% of the measured value. Results [21] are in good agreement with those of Panek and Fitzner [25], Chatterji and Vest [28], while Kameda's values [26] are higher and those by Newns and Pelmore [27] are lower than the results of this study.

Good agreement between obtained results for $\Delta G^0_{f,2CuO}$ and $\Delta G^0_{f,In_2O_3}$ in this work with the literature data proved the proper operation of the cells (I) and (III) and reliability of the ΔG^0 determination for $Cu_2In_2O_5$.

The Gibbs free energy of formation of $Cu_2In_2O_5$ from oxides can be derived from the obtained data.

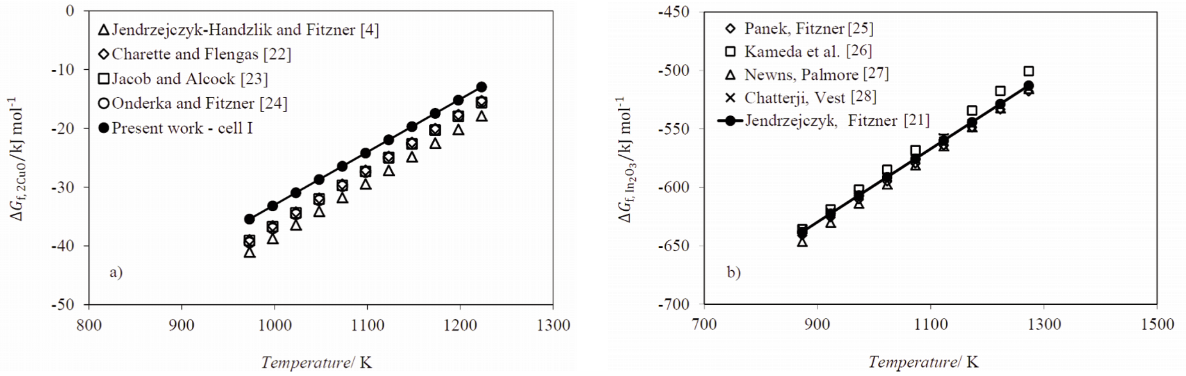

Figure 4. *The Gibbs free energies change as a function of T a) for the reaction of formation of 2CuO, b) for the reaction of formation of In_2O_3*

Namely, by combining reactions (1) and (3) the following reaction could be obtained:

$$2CuO + In_2O_3 = Cu_2In_2O_5 \qquad (12)$$

In the similar manner, by combining respective equations obtained for Gibbs free energy change, the expression was obtained:

$$\Delta G^0_{(f,Cu_2In_2O_5)} = 33905 - 41.50T(\pm 3600)J\ mol^{-1} \qquad (13)$$

for the formation of $Cu_2In_2O_5$ from oxides.

This result indicates that the phase is an entropy stabilized, and should be formed from oxides above 877 K. In Fig. 5 results obtained from the present work are shown and compared with the literature data given by Tretyakov [5] who cited unpublished data without experimental details from PhD Thesis presented at Moscow University. The results obtained in this study are different from those given by Tretyakov [5], whose experimental data are more positive and have different temperature dependence.

Having $\Delta G^0_{f,Cu_2In_2O_5}$ as a function of temperature, it is possible to derive $\Delta H^0_{f,298}$ for reaction (3) and ΔS^0_{298} for $Cu_2In_2O_5$ phase using Second Law method by sigma plot. This method was described by Gokcen [29] and it is used in this work.

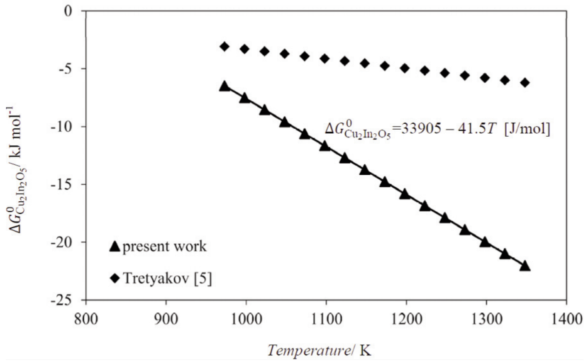

Figure 5. *The Gibbs free energy change of $Cu_2In_2O_5$ as a function of T*

If the heat capacities of all substances taking part in the reaction (3) are given in the form:

$$C_p = a + bT + cT^{-2} \qquad (14)$$

then the sigma *Σ* function assumes the following form:

$$\Sigma = -\frac{\Delta H^0_0}{T} + I = RT\ln K_{(3)} - \Delta a\ln T - \Delta bT + \frac{\Delta c}{2T^2} \qquad (15)$$

where $I = \Delta S^0_0 - \Delta a$

Constants a, b and c in respective C_p equations were accepted after Kubaschewski and Alcock [30].

A plot of -*Σ* vs.1/*T* yields the straight line shown in Fig.6

From this line, the values of ΔH_0^0 and *I* are obtained using least squares method.

Next, making use of the relations:

$$\Delta H^0_T = \Delta H^0_0 + \Delta aT + \frac{\Delta bT^2}{2} - \Delta cT^{-1} \qquad (16)$$

and

$$\Delta S^0_T = \Delta S^0_0 + \Delta a\ln T + \Delta bT - \frac{\Delta cT^{-2}}{2} \qquad (17)$$

the values of $\Delta H^0_{298,Cu_2In_2O_5}$ and $\Delta S^0_{298,Cu_2In_2O_5}$ can be calculated from Eqs. 16 and 17 for *T*=298 K. They are equal to -117.60 k*J mol*$^{-1}$ and 202.50 *J (K*$^{-1}$ *mol*$^{-1}$*)*,

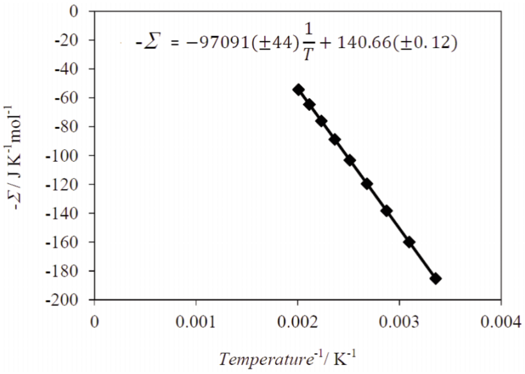

Figure 6. *Sigma plot vs.1/T*

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respectively. Having these values, the enthalpy of formation $\Delta H^0_{f,298}$ of $Cu_2In_2O_5$ from the elements was obtained as:

$$\Delta H^0_{f,298} = \Delta H^0_{298,Cu_2In_2O_5} + \Delta H^0_{f,In_2O_3} + \Delta H^0_{f,Cu_2O} = \\ -1211(\pm 15)kJmol^{-1} \text{ and } -135\ kJ\ (at^{-1}mol^{-1}) \tag{18}$$

Finally, since $\Delta S^0_{298} = \Delta S^0_{298,Cu_2In_2O_5} - \Delta S^0_{298,In_2O_3} - \Delta S^0_{298,Cu_2O} - 1/2\Delta S^0_{298,O_2}$, the standard entropy of $Cu_2In_2O_5$ phase was obtained, and it is equal to 493.20 (±10) *J* $(K^{-1}\ mol^{-1})$ and 54.80 *J* $(at^{-1}\ mol^{-1})$. The respective values of thermochemical data used in these calculations were taken from [30]. The obtained value of the standard enthalpy of formation can be compared with the value assessed by Grzanna and Migge [31] which is equal to ≈-1218 (±13) *kJ* mol^{-1}. The study [31] provided information about $Cu_2In_2O_5$, which were calculated only from table data, and not from the experiment. Additionally in this work the $Cu_2In_2O_5$ phase was formed from CuO and In_2O_3 oxides, which is different reaction which was analyzed in this work (Eq.3). In this situation data from work [31] were recalculated for the same reaction like in the present work and in this time the standard enthalpy of formation is equal to -2475 *kJ* mol^{-1}. It can be seen that this value is two times lower than value obtained in present work. It must be remembered that in this study, in order to calculate this value, not only table data were used, but the experimental results from work [6] were taken into account. In the same research [31], standard entropy of $Cu_2In_2O_5$ phase was estimated to be equal to 208.2 (±11) *J* $(K^{-1}\ mol^{-1})$. This value has to be recalculated for the reaction given by Eg. (3). This time the value of standard entropy of $Cu_2In_2O_5$ phase is equal to 313 *J* $(K^{-1}\ mol^{-1})$. It can be seen that value of standard entropy, which is determined in present work, is higher for about 60%. In order to decide which result is correct, the obtained value of the standard entropy of $Cu_2In_2O_5$ should be verified by low temperature heat capacity measurements.

Obtained set of data enabled the calculation of $\log p_{O_2}$ vs. composition stability diagrams for fixed *T*. In Figs. 7 and 8 such diagrams are shown for temperatures 873 and 1173 K (partial pressure is given in atmosphere). In calculation of these oxygen potential diagrams for the Cu-In-O system, the results of this study (Eqs. 9, 10, 13) and literature data [21, 22] were used.

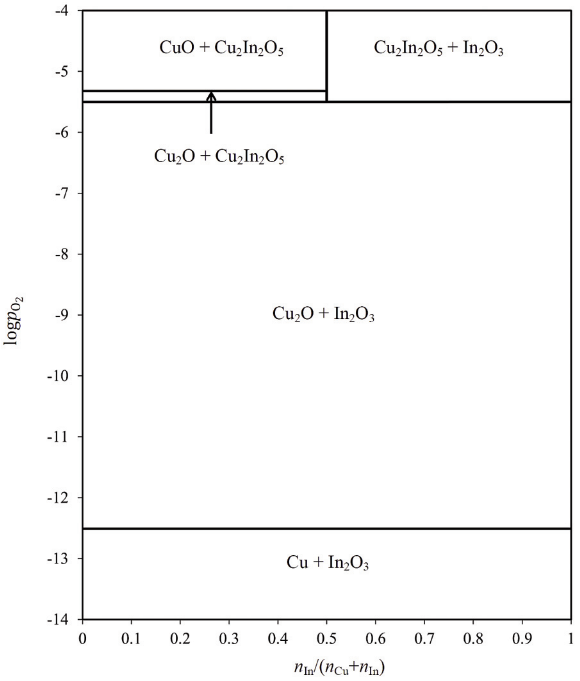

Figure 7. *Cu-In-O stability diagram at T=873 K*

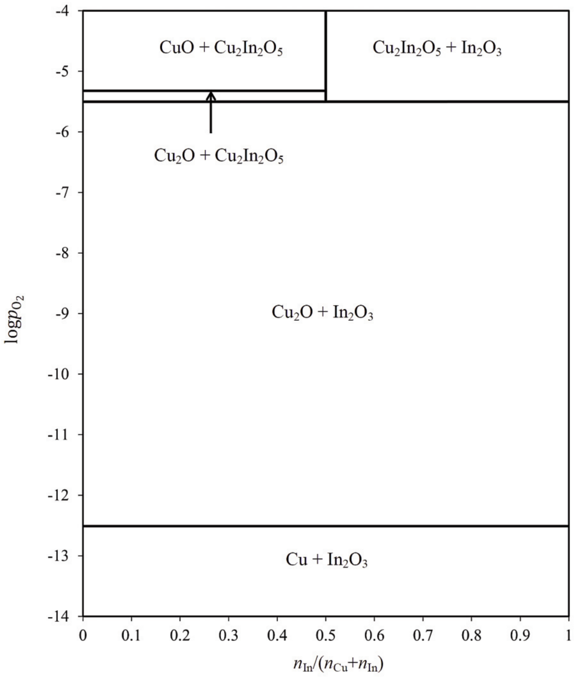

Figure 8. *Cu-In-O stability diagram at T=1173 K*

The most controversial problem relevant to Cu-In-O phase equilibria is the existence of delafossite phase $CuInO_2$. In her PhD thesis Novikova [32] excluded the existence of $CuInO_2$ phase, obtaining in her experiments in each case only the mixture of In_2O_3 and $Cu_2In_2O_5$. This result is compatible with the work of Bosacka et al. [33], who concluded that only one phase $Cu_2In_2O_5$ can be obtained by solid state reaction between copper and indium oxides. However, Sasaki and his group [34] developed a method based on cation exchange reaction leading to the $CuInO_2$ synthesis. In the first stage, $LiInO_2$ was prepared by the solid state reaction. Next, $LiInO_2$ powder was mixed with CuCl and this mixture was heated in evacuated silica capsules in the temperature 623-873 K. Reactions product proved that a new phase identified as $CuInO_2$ was obtained.

Formation of this delafossite phase was also observed during pulsed laser deposition of thin films. Teplin et al. [35] used pulsed laser deposition to obtain single-phase undoped and Ca-doped $CuInO_2$ thin films, which were deposited onto fused silica substrates at different oxygen partial pressure and substrate temperatures. Oxygen partial pressure was adjusted by varying composition of oxygen-argon gas mixture. The phase was successfully obtained under oxygen pressure 7.5 mTorr and at 823 K. At a little higher oxygen pressure of 15 mTorr the phase $Cu_2In_2O_5$ was found. The results of this study indicated that $CuInO_2$ phase may exist in the temperature range 673-873 K, and for pressures 1–15 mTorr. However there is no proof that this phase is thermodynamically stable.

Lee et al. [36] fabricated $CuInO_2$ thin films using Cu_2O-In_2O_3 composite targets prepared through the solid state reaction. These mixture powders were sintered in the temperature range 973-1423 K in air. Next, using samples with the highest density, thin films of $CuInO_2$ were grown on sapphire by pulsed laser deposition. Growing conditions were selected to be 823 K, 30 min and oxygen partial pressure of 10 mTorr. X-ray confirmed $CuInO_2$ formation. Similar study was conducted by Chadwick et al. [37], who also used pulsed laser deposition technique. $CuInO_2$ was obtained, but TEM micrographs showed the presence of some amorphous material. The study showed that the result of synthesis depended on the oxygen partial pressure, and the delafossite phase could appear only in films prepared under pressure range from $5x10^{-4}$ to $1x10^{-2}$ mbar. For the pressure lower than 10^{-4}, copper may appear, while for higher pressure than 10^{-2}, Cu^+ transforms into Cu^{2+} cation. Thus the range of existence of $CuInO_2$ seems to be very narrow.

Taking into account the processes which lead to the formation of $CuInO_2$ phase, it seems that this phase is formed in an nonequilibrium process as an intermediate and it is trapped by encountered external conditions being in fact a metastable phase.

One may attempt to prove it by considering possible relation between Gibbs free energy of formation of ABO_2 phases (B=Al, Ga, In) and their structure. Delafossite of ABO_2 type exhibits A^{1+} cation with coordination number equal 2, and B^{3+} cation with coordination number equal 6. This particular structure has remarkable bidimensional electrical properties. Marucco [38] suggested that the range of stability of delafossite phase depends on mutual relation of the size of A and B cations. It can be supposed that for A=Cu, the energy of formation will depend on the size of cation B. Thus, there should be a relation between this energy for $CuBO_2$ (B=Al, Ga, In) and the radius of cations B^{3+}.

Based on the literature data: ionic radius for cations Al^{3+}, Ga^{3+} and In^{+3} [39] together with the Gibbs free energies of formation of solid $CuAlO_2$ [3, 40] and $CuGaO_2$ [3, 4] phases, the Gibbs free energy of the solid $CuInO_2$ can be estimated. First, the dependence of the enthalpy change as a function of ionic radius for Al^{3+}, Ga^{3+} was constructed and it is shown in Fig. 9. These literature data were described by linear equation obtained by the last square method which is given ΔH_f^0=2133r_{ion}-145752 in $J\ mol^{-1}$. Then, from the obtained equation the enthalpy change for solid $CuInO_2$ phase ($r_{In}^{3+} = 80\ pm$) was calculated and is equal 24888 $J\ mol^{-1}$. Finally, the plot of entropy change as a function of enthalpy of formation change was constructed similarly like in the previous case taking into account literature data [3, 4, 40] for $CuAlO_2$ and $CuGaO_2$ phases, and it is shown in Fig. 10. These literature data were described by the linear equation obtained by the last square method which is given as ΔS_f^0 =0.00035 ΔH_f^0 -3.46 in $J\ (K^{-1}\ mol^{-1})$. Taking into account the value of the enthalpy formation change of $CuInO_2$ phase obtained above, the entropy change of $CuInO_2$ was determined and is equal to 5.25 $J\ (K^{-1}\ mol^{-1})$.

Predicted Gibbs free energy of formation of the solid $CuInO_2$ phase is described by following dependence $\Delta G^0_{f,CuInO_2} = 24888 - 5.25T\left(\pm 3600\right) J\ mol^{-1}$

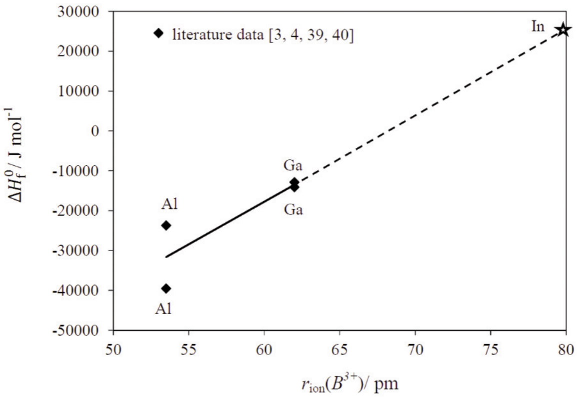

Figure 9. *Enthalpy values* ΔH_f^0 *as a function of cation* B^{3+} *radius.*

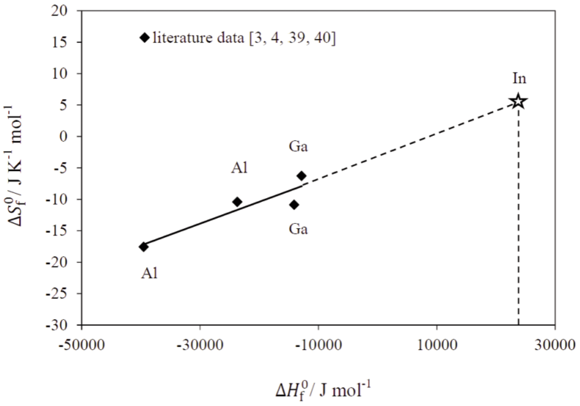

Figure 10. *Entropy values* ΔS_f^0 *as a function of* ΔH_f^0 *for* $CuBO_2$

The obtained temperature dependence suggests that the $CuInO_2$ phase is an entropy stabilized compound. Results obtained in the present work were compared with the data given by Liu et al. [17]. Comparison with this study shows that $\Delta H^{0}_{f,CuInO_2}$ determined in the present work is much more positive. Moreover, the results indicate that $CuInO_2$ phase may not be stable even at room temperature. The result obtained in the present study established the basis for the derivation of oxygen potential diagrams under different conditions imposed by the choice of *T* and variables. This may help to optimize proper conditions for the preparation of the chosen compound.

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Conflict of interest statement

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

Author's contributions

Dominika Jendrzejczyk- Handzlik: Conceptualization, Methodology, Validation, Resources, Investigation, Supervision, Writing – original draft, Writing - review & editing.

Piotr Handzlik: Conceptualization, Formal analysis, Visualization, Writing - original draft, Writing - review & editing.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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GIBSOVA SLOBODNA ENERGIJA FORMIRANJA $Cu_2In_2O_5$ TERNARNE FAZE ODREĐENA EMF METODOM

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Apstrakt

Korišćenje elektrohemijskih ćelija sa elektrolitom od čvrstog cirkonijuma:
Cu_2O, CuO / O^{2-} / *air*
$Cu_2In_2O_5$, In_2O_3, Cu_2O / O^{2-}/ *air*
In, In_2O_3 /O^{2-}/ *Ni, NiO,*
Gibsova slobodna energija formiranja čvrste $Cu_2In_2O_5$ *ternarne faze, kao i za okside* In_2O_3 *i CuO, određena je u temperaturnom opsegu od 973 K do 1372 K. Rezultati dobijeni u ovom istraživanju su korišćeni za dobijanje Gibsove slobodne energije reakcije formiranja ternarnog jedinjenja iz odgovarajućih oksida:*
$2CuO + In_2O_3 = Cu_2In_2O_5$
koja iznosi: $\Delta G^0_{f,Cu_2In_2O_5} = 33905 - 41.50T$ *(±3600) J* mol^{-1}.
Standardna entalpija formiranja iz elemenata $\Delta H^0_{f,298}$ *i standardna entropija* ΔS^0_{298} *dobijena za* $Cu_2In_2O_5$ *fazu pomoću Drugog zakona sigma dijagrama iznose -1211 (±15) kJ* mol^{-1} *i 493.20 (±10) J* (K^{-1} mol^{-1})*. Takođe su dati dijagrami potencijala kiseonika za Cu–In–O sistem za dve temperature.*

Ključne reči: *EMF metoda; Gibsova slobodna energija; formiranje* $Cu_2In_2O_5$

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