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Phase equilibria in the solid state and colour properties of the CuO–In_2O_3 system

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Abstract Phase equilibria up to solidus line in CuO–In_2O_3 system have been investigated using XRD and DTA/TG methods. According to the results, only one compound of the formula $Cu_2In_2O_5$ formed in the system studied. Its thermal stability was determined in the air and argon proving that the compound did not melt but underwent decomposition. The decomposition of $Cu_2In_2O_5$ in the air atmosphere began at 1080 °C, while in argon at 835 °C. Additional studies were undertaken to determine the hitherto unknown colour properties of samples representing the CuO–In_2O_3 system in the equilibrium state.

Keywords CuO–In_2O_3 system · $Cu_2In_2O_5$ · DTA · Ceramic pigments · Optical properties

Introduction

The compounds admixtured with copper(II) oxide or/and indium(III) oxide and the phases formed as a result of reactions of these oxides with other ones are known to be attractive materials for industry as components for production of electrodes, solar cells, liquid crystal displays, and other products [1–5]. The physicochemical properties and structures of CuO and In_2O_3 are well known [6–11].

It is known that indium(III) oxide can occur in two polymorphous varieties H-In_2O_3 and C-In_2O_3 [6, 7]. Under normal pressure it occurs in the C-In_2O_3 variety crystallising in the regular system [6, 7]. The hexagonal H-In_2O_3 variety is obtained under a pressure of 65 kbar at 1,100 °C [8] and is considered a metastable form [9]. It has been reported that above 1,600 °C the regular C-In_2O_3 undergoes a polymorphous transition to a nonstoichiometric monoclinic variety of the formula $InO_{1.496}$ [7].

The other component, CuO, does not have polymorphous varieties. CuO crystallises in the monoclinic system [9], and above 1,100 °C it undergoes thermal decomposition to Cu_2O and O_2 [10, 11].

To the best of our knowledge, the phase equilibriums settling in solid state in the binary system CuO–In_2O_3 have not been studied and hence no phase diagram of the system made by these oxides is known. According to the hitherto published scarce data on this system, as a result of the reaction of CuO with In_2O_3 two compounds green $Cu_2In_2O_5$ and black $CuIn_2O_4$ are formed [12–15]. The compound $Cu_2In_2O_5$ has been obtained in two ways: by heating a mixture of CuO and In_2O_3 at the molar ratio of 2:1 at 950 °C for 36 h [13] and by heating the equimolar mixture of Cu_2O and In_2O_3 in the air atmosphere at a temperature from the range 700–1,150 °C for only 2 h [12]. The authors of [12, 13] practically agree that $Cu_2In_2O_5$ in solid state undergoes decomposition to Cu_2O and In_2O_3, but the temperatures of thermal decomposition given by the authors differ significantly. The authors of [13] claim that a slow decomposition of $Cu_2In_2O_5$ begins already at 1,000 °C, but according to [12] this compound starts decomposing above 1,100 °C. $Cu_2In_2O_5$ crystallises in orthorombic system [14] and does not have polymorphous forms.

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The other compound forming in the system CuO–In_2O_3 that is $CuIn_2O_4$ has been to the best of our knowledge the subject of only one paper. The compound $CuIn_2O_4$ was obtained by melting a mixture of oxides composed of 1.5 In_2O_3, 0.9 BaO, 0.01 K_2O, 2 SrO and 4 CuO [15]. From this mixture black crystals were obtained, claimed by the authors to be $CuIn_2O_4$ [15]. The crystal structure of these black crystals has been resolved, they crystallises in tetragonal system [15]. Thermal stability of this compound has not been determined in this work, neither temperature nor the mode of $CuIn_2O_4$ are known.

The lack of information on CuO–In_2O_3 has prompted us to study first of all the phase equilibriums in this system in solid state, which was expected to help identify which compounds really form in this system, what is the thermal range of their stability and what are the products of their melting or decomposition. Moreover, additional studies were undertaken to determine the hitherto unknown colour properties of samples representing the CuO–In_2O_3 system in the equilibrium state.

Experimental

All samples were synthesised from mixtures of oxides containing In_2O_3 (p.a., Aldrich, Niemcy) and CuO (p.a., Fluka, Germany) by the conventional method of stage calcinations [16–19]. Mixtures of oxides of compositions specified in Table 1, were homogenised by grinding, formed into tablets and heated in air at stages from 700 to 900 °C. After the final heating all the samples were slowly cooled to room temperature, the tablets were ground and subjected to XRD and DTA/TG measurements.

In order to establish the type of phases coexisting with the liquid, selected samples were additionally heated above the solidus temperature for 2 h, then these samples were rapidly cooled to room temperature and their compositions were determined by the XRD method.

Phases occurring in the samples were identified on the base of the XRD study (diffractometer HZG4-A2, radiation CuK_α filter Ni). Identification of individual phases was performed by using the XRD characteristics given in the PDF files [20] and the data reported in [14].

The DTA/TG measurements were made with the use of a Paulik–Paulik–Erdey derivatograph Q-1500 (MOM, Budapest). The samples to be examined by this method, in portions of 500 mg, were placed in corundum crucibles. All measurements were performed in air, in the temperature increased in the range 20–1,300 °C, at a heating rate of 10°/min. The temperature accuracy was ±5 °C.

Some samples were subjected to DTA/TG studies on a TA Instruments SDT 2960. Measurements were conducted in corundum crucibles in argon on heating at the rate of 10°/min over the range 20–1,500 °C.

Table 1 Composition of samples prepared for research and phases detected in equilibrium samples

Lp.	Composition of initial mixtures/ %mol/		Heating conditions	Composition of equilibrium samples
	In_2O_3	CuO		
1	5.00	95.00	700 °C/12 h/ + 800 °C/12 h/ + 900 °C/4 × 12 h/	$Cu_2In_2O_5$ + CuO
2	10.00	90.00		
3	12.50	87.50		
4	15.00	75.00		
5	20.00	80.00		
6	25.00	75.00		
7	30.00	70.00		
8	33.33	66.67		$Cu_2In_2O_5$
9	40.00	60.00		$Cu_2In_2O_5$ + In_2O_3
10	50.00	50.00		
11	60.00	30.00		
12	70.00	30.00		
13	75.00	25.00		
14	80.00	20.00		
15	90.00	10.00		
16	95.00	5.00		

Selected samples were examined by means of an electron scanning microscope (JSM-1600, Jeol, Japan).

The powder samples were applied to an organic matrix in mass tone. The final paints were evaluated for colour change by measuring spectral reflectance in the visible region of light (400–700 nm) using a ColorQuest XE (HunterLab, USA) [21]. The measurement conditions were following: an illuminant *D65*, 10° complementary observer and measuring geometry *d*/8° [21]. The CIE 1976 $L^*a^*b^*$ colorimetric system was used as recommended the Commission Internationale de l'Eclairage (CIE), L^* is the lightness axis [black (0) to white (100)], a^* is the green to red and b^* is the blue to yellow axis. The parameter *C* (chroma) represents saturation of the colour, and $H°$ represents the hue angle. The chroma is defined as $C = [(a^*)^2 + (b^*)^2]^{1/2}$. The hue angle $H°$ is expressed in degrees and ranges from 0° to 360° and is calculated using formula $H° = \tan^{-1}(b^*/a^*)$.

Results

Investigation of phase equilibriums reached in solid state in CuO–In_2O_3 system was made on 16 samples whose phase composition in the equilibrium state is as shown in Table 1. According to the data presented in this table, in the air atmosphere the components of the system studied are not inert towards one another. As follows from XRD analysis of the samples containing in the initial mixtures up to 33.33 mol% In_2O_3, in the equilibrium state the samples are biphasic and besides the unreacted CuO they contain $Cu_2In_2O_5$. The sample obtained from the initial mixture containing 33.33 mol% In_2O_3 and 66.67 mol% CuO, after the final stage of heating was monophasic and contained only $Cu_2In_2O_5$. The set of diffraction lines recorded on the diffractogram of this sample was fully consistent with the XRD pattern of this compound (PDF Card no. 70-1082). In the samples representing the remaining range of concentrations of the system components, the compounds identified were $Cu_2In_2O_5$ and In_2O_3. Thus, the phase composition of the samples in the state of equilibrium proves that in the system studied a reaction takes place leading to formation of one compound described by the formula $Cu_2In_2O_5$:

$$2CuO_{(s)} + In_2O_{3(s)} = Cu_2In_2O_{5(s)} \qquad (1)$$

As follows from the phase analysis on the basis of XRD data, performed for all samples studied after subsequent stages of heating, in CuO–In_2O_3 at none stage a compound of the formula $CuIn_2O_4$ whose formation was proposed in 1991, has been identified. Although the synthesis of $CuIn_2O_4$ (sample no. 8, Table 1) was performed by heating of the appropriate mixture of oxides in several stages and for a very long time (~200 h).

Figure 1a presents the DTA curve obtained for $Cu_2In_2O_5$ in the air atmosphere. This curve shows only one endothermic effect that started at 1080 ± 5 °C. This effect is accompanied by a mass loss detected on the TG curve of 2.8 mass%.

In order to establish the nature of the effect detected on the DTA curve, that is to identify the process to which it corresponds, the sample containing $Cu_2In_2O_5$ was subjected to additional heating at a temperature close to its maximum of the peak on the DTA curve, at 1105 °C for 3 h, and then the sample was rapidly cooled. After this additional heating stage, the sample changed the colour from green to brown and did not melt. The XRD pattern of this sample (additionally heated in air at 1,105 °C) revealed the XRD lines characterising $Cu_2In_2O_5$, In_2O_3 and Cu_2O. This result implies that $Cu_2In_2O_5$ does not melt but undergoes decomposition in the solid state, according to the reaction:

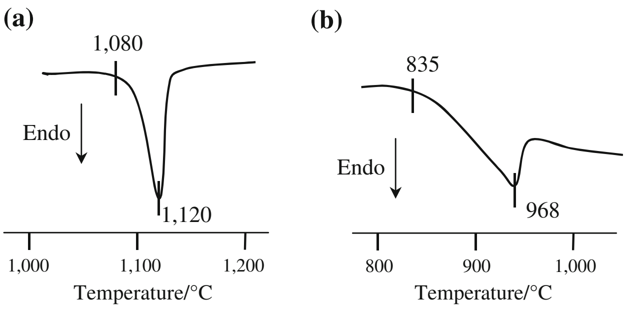

Fig. 1 DTA curves of $Cu_2In_2O_5$ in different atmospheres: **a** air, **b** argon

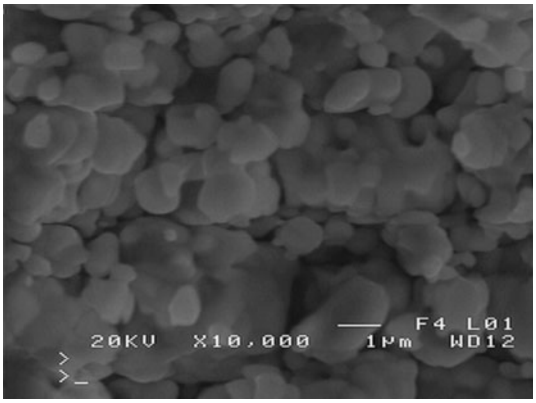

Fig. 2 SEM image of $Cu_2In_2O_5$

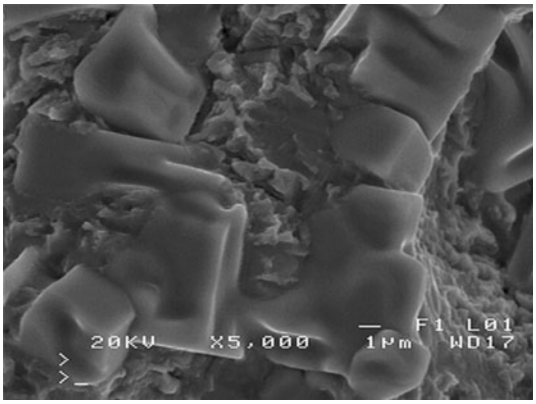

Fig. 3 SEM image of $Cu_2In_2O_5$ heated for 1.5 h at 1,150 °C and rapidly quenched

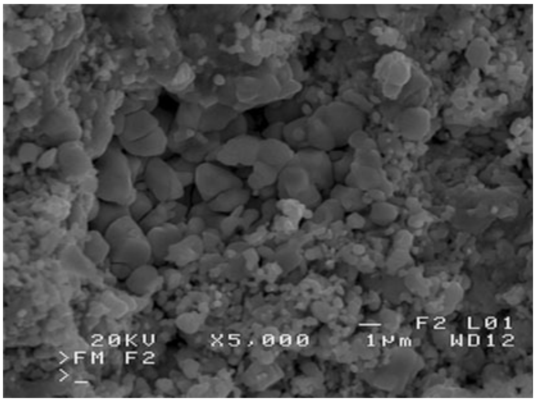

Fig. 4 SEM image of $Cu_2In_2O_5$ heated for 1.5 h at 900 °C in argon

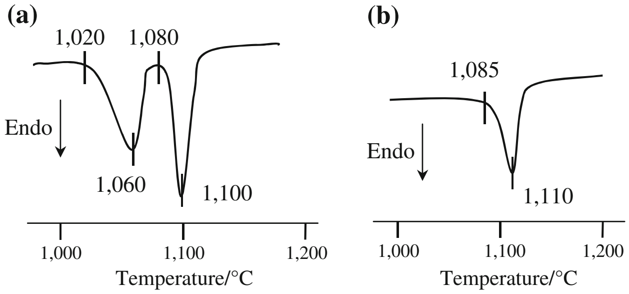

Fig. 5 DTA curves of selected samples at equilibrium: **a** 90 mol% CuO + 10 mol% In_2O_3 (which corresponds to the composition 12.5 mol% $Cu_2In_2O_5$ + 87.5% mol% CuO) **b** 50 mol% CuO + 50 mol% In_2O_3 (which corresponds to the composition 50 mol% $Cu_2In_2O_5$ + 50 mol% In_2O_3)

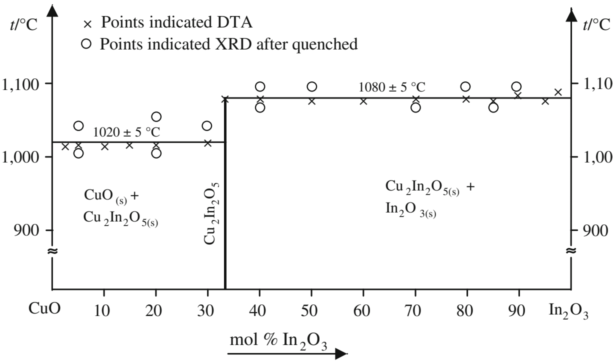

Fig. 6 Phase diagram of CuO–In_2O_3 system up to solidus line

$$Cu_2In_2O_{5(s)} \rightarrow In_2O_{3(s)} + Cu_2O_{(s)} + \tfrac{1}{2}O_{2(g)} \quad (2)$$

The mass loss of 3.66 mass% calculated from this formula is in a very good agreement with that of 3.49, recorded after heating $Cu_2In_2O_5$ at 1,150 °C for 12 h.

At this stage of the study, it is highly probable that one of the products of thermal decomposition of $Cu_2In_2O_{5(s)}$ is copper(II) oxide which in the air atmosphere and at a temperature over 1,000 °C undergoes decomposition according to the following reaction [10, 11]:

$$2\ CuO_{(s)} \rightarrow Cu_2O_{(s)} + \tfrac{1}{2}\ O_{2(g)} \quad (3)$$

In order to confirm the above-proposed course of $Cu_2In_2O_5$ decomposition, in the next stage of this study the DTA/TG curves of this compound were recorded in the deoxidised argon atmosphere [22]. The DTA curve of $Cu_2In_2O_5$ recorded in the argon atmosphere (Fig. 1b) shows an endothermic effect beginning at 835 °C, which proves that in the oxygen-free atmosphere this compound is stable only up to this temperature. Moreover, the XRD pattern of $Cu_2In_2O_5$ sample heated in the argon atmosphere at 960 °C (maximum of DTA effect) for 12 h, revealed the sets of XRD lines characterising $Cu_2In_2O_5$, but also copper(II) oxide and copper(I) oxide. The presence of copper(II) oxide suggests that $Cu_2In_2O_5$ at first undergoes decomposition producing In_2O_3 and CuO, a then CuO contained in the products of decomposition undergoes further decomposition to Cu_2O with release of oxygen.

The acquired findings about the way of the decomposition of $Cu_2In_2O_5$ have been corroborated by SEM image. Figure 2 presents a SEM image of $Cu_2In_2O_5$. In order to show more clearly the shapes of the crystals of $Cu_2In_2O_5$ spinels, the image is presented in magnification of ×10,000. Figure 3 shows an image of the same $Cu_2In_2O_5$ sample heated additionally at 1,150 °C for 1.5 h and next rapidly cooled down. The temperature of 1,150 °C is higher than the maximum of the peak on the DTA curve (Fig. 1a). The SEM image reveals the molten phase. This is connected to the fact that the product of decomposition of $Cu_2In_2O_5$ is Cu_2O, which at 1,150 °C melts congruently [11]. Figure 4 shows the SEM image of the phase $Cu_2In_2O_5$, heated in an argon atmosphere at 900 °C for 1.5 h. This SEM image show that the sample is not molten and the crystals observed clearly differ from those of the pure $Cu_2In_2O_5$ phase.

At the next stage, all samples in the state of equilibrium (Table 1) were subjected to DTA/TG measurements in the air atmosphere. A few of the DTA curves obtained are

Table 2 The effect of composition of system CuO–In_2O_3 on colour properties

Sample of initial mixtures	Phase composition of sample in equilibrium state	*L**	*a**	*b**	*C*	*H°*
$1CuO + 9In_2O_3$	$0.5Cu_2In_2O_5 + 8.5In_2O_3$	63.42	−17.70	16.45	24.16	137.10
$2CuO + 8In_2O_3$	$1Cu_2In_2O_5 + 7In_2O_3$	57.04	−21.19	14.55	27.70	145.52
$3CuO + 7In_2O_3$	$1.5Cu_2In_2O_5 + 5.5In_2O_3$	52.74	−22.43	13.81	26.34	148.38
$4CuO + 6In_2O_3$	$2Cu_2In_2O_5 + 4In_2O_3$	48.39	−22.34	12.73	25.71	150.32
$5CuO + 5In_2O_3$	$2.5Cu_2In_2O_5 + 2.5In_2O_3$	46.32	−21.60	11.91	24.67	151.13
$6CuO + 4In_2O_3$	$3Cu_2In_2O_5 + 1In_2O_3$	43.05	−20.44	10.73	23.09	152.30
$7CuO + 3In_2O_3$	$1CuO + 3Cu_2In_2O_5$	38.96	−15.07	7.60	16.88	153.24
$8CuO + 2In_2O_3$	$4CuO + 2Cu_2In_2O_5$	34.69	−9.23	3.94	10.04	156.88
$9CuO + 1In_2O_3$	$7CuO + 1Cu_2In_2O_5$	32.26	−3.70	0.66	3.76	169.89
$2CuO + 1In_2O_3$	$Cu_2In_2O_5$	38.41	−16.70	8.40	18.69	153.30

shown in Fig. 5. The DTA curves recorded up to 1,500 °C for the samples that at equilibrium contained CuO with $Cu_2In_2O_5$ revealed two well-developed endothermic effects, the first beginning at 1,020 ± 5 °C, while the second at 1,080 ± 5 °C (Fig. 5, curve a).

On the other hand, the DTA of the samples at equilibrium representing the remaining range of concentrations of the components of CuO–In_2O_3, that is the mixtures of $Cu_2In_2O_5$ and In_2O_3, in the same temperature range, showed a single endothermic effect beginning at ~1,080 °C (Fig. 5, curve b). The asymmetric shape of the thermal effects on the DTA curves of all samples at equilibrium and the mass loss accompanying the sample heating detected on the TG curves indicated that these effects were related to the thermal decomposition of the samples. In order to confirm the nature of these effects, sample nos. 2 and 10 (Table 1) at the state of equilibrium, were subjected to additional heating for 3 h at the temperatures close to those of DTA effects maxima, i.e., at 1,060 and 1,100 °C. The phase analysis (XRD) of these samples after their additional heating confirmed that the first effect beginning at ~1,020 °C was related to the decomposition of CuO (reaction 3), while the effect beginning at ~1,080 °C was related to decomposition of $Cu_2In_2O_5$ (reaction 2).

On the basis of XRD and DTA results collected for all samples in the state of equilibrium, a phase diagram of CuO–In_2O_3 has been constructed in the whole concentration range of its components up to the solidus line, i.e. to line at the temperature of the beginning of thermal decomposition of the samples (Fig. 6). The temperatures of the solidus lines were assumed to be those corresponding to the beginning of the first endothermic effects noted on the DTA curves. The temperature range of coexistence and types of solid phases at equilibrium were confirmed by XRD analysis of the frozen samples, i.e. the samples rapidly cooled to room temperature after 24 h of their heating at about 20° below the temperature of the solidus line determined from DTA curves. The sample compositions and temperatures of the freezing are given in Fig. 6.

The influence of sample composition on the colour properties of the system CuO–In_2O_3 was investigated. The colour properties of the prepared samples and applied into organic matrix in mass tone are given in Table 2. The hue $H°$ values of all samples prepared are in the range from 137 to 170 that corresponds to green colour. Analysis of the values of L^* has shown that with increasing content of CuO in the system CuO–In_2O_3 the lightness of the samples decreases and they get darkened. The values C (chroma) are in the range from ~4 to 28, the growing content of CuO is characterized by the increase of this value up to sample 2CuO + $8In_2O_3$, for another samples the value C decreases (Table 2). The samples containing from 4CuO to 6CuO have also similar values of chroma C in range approximately from 23 to 26. Another increasing content of CuO produces the decrease of C value. The best results were obtained for the sample 2CuO + $8In_2O_3$ and 3CuO + $7In_2O_3$ characterised by the highest value of C from all prepared samples.

Summary

The results of research allow the following statements:

- As a result of the solid-state reaction between CuO and In_2O_3 can be obtained only one phase, namely $Cu_2In_2O_5$.
- The compound $Cu_2In_2O_5$ is stable in the air atmosphere up to 1,080 °C, while in the argon atmosphere up to 835 °C and then it undergoes decomposition with release of oxygen to In_2O_3 and Cu_2O.
- In solid state at equilibrium $Cu_2In_2O_5$ co-exists with CuO up to 1,020 °C, while with In_2O_3 up to its decomposition temperature of ~1,080 °C.
- Considering that value $H°$ of these pigments lies from 137 to 170, the pigments are characterized by green hue. The increasing content of CuO in samples makes the decrease of value L^* (lightness) for all samples and they become the darkest. Sample 2CuO + $8In_2O_3$ and 3CuO + $7In_2O_3$ are characterized by intensive green colour.

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