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Investigation of phase relationships in the $3CuO \cdot B_2O_3$ – ZnO system

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The paper presents the results of studying the interaction between the copper borate and zinc oxide, as well as some physical properties of the intermediate samples. It was established that the studied system is quasi-binary. With a 1:1 ratio of the initial components, the compound $3CuO \cdot B_2O_3 \cdot ZnO$ is formed in the system, which melts congruently at a temperature of 1253K. Since this compound is a glass former, the system is characterized by the formation of a wide range of glasses. The article also presents studies of the temperature dependence of thermo-EMF for alloys containing x=0.0-20.0 mol% of the ZnO in the temperature range of 573-1233 K. Using the extrapolation method, it was established that the compositions are compensated alloys with semiconductor properties. Within the experimental error, the value of thermoelectric power is close to the value obtained from the temperature dependence of electrical conductivity.
Keywords: semiconductor properties, thermo-EMF, glasses, electrical conductivity, dielectrics, alloys.

Дослідження фазових співвідношень у системі $3CuO \cdot B_2O_3$ - ZnO. *Л.А. Халілова, Ш.С. Ісмаїлов, С.І. Бананярлі*

У роботі представлені результати вивчення взаємодії борату міді із оксидом цинку, а також деякі фізичні властивості проміжних зразків. Встановлено, що система, що досліджується, є квазібінарною. При співвідношенні вихідних компонентів 1:1 у системі утворюється з'єднання $3CuO \cdot B_2O_3 \cdot ZnO$, яке плавиться конгруентно при температурі 1253К. Оскільки дане з'єднання є склоутворювачем, для системи характерне утворення широкого спектра скла. У статті також представлені дослідження температурної залежності термоЕРС для сплавів, що містять x=0,0-20,0 мол.% ZnO в інтервалі температур 573-1233 К. Методом екстраполяції встановлено, що склади є компенсованими сплавами з напівпровідниковими властивостями. У межах похибки експерименту значення термоЕРС близьке до значення, отриманого з температури температури електропровідності.

1. Introduction

Glass materials based on transition metals are widely used in advanced technology, namely lasers, electronics, luminescent devices, energy conversion and storage devices etc. [1-5]. On the other hand, materials based on metal oxides are widely used in various fields of science and technology [6–10].

The creation of materials that meet the requirements of advance technology is the main task of fundamental research in the field of inorganic synthesis. It is necessary to create materials capable of maintaining the necessary properties in different environments and different temperature ranges. This requires detailed experiments to explain the phenomena occurring in complex systems. In this regard, there is a growing interest in reliable information on phase diagrams of complex systems, which provide a logical connection between the physical and chemical properties of the material composition and its phase state [11-13].

Considering the prospects of research into oxide materials for their subsequent implementation and identification of the relationship between properties and composition, physicochemical studies of multicomponent borate systems were continued [14-16].

Previously, we presented the results of a study of phase equilibria and some physical properties of intermediate alloys of oxide glass-forming systems [17-21]. The $3CuO{\cdot}B_2O_3 - ZnO$ systems belong to the class of glassy oxide materials, which include $CuO{\cdot}ZnO$ as a semiconductor material and B_2O_3 as a filtering catalyst [21]. This study is part of a series of works devoted to the systematic study of the physicochemical and physical properties of $3CuO{\cdot}B_2O_3 - ZnO$ alloys and is aimed at searching for new materials for practical use.

Note that the physical properties of $3CuO{\cdot}B_2O_3 - ZnO$ alloys have not been fully studied and require further study. In our opinion, the complex temperature dependence of specific density is associated with the migration of zinc atoms to the place of copper atoms, and it can be assumed that as a result, a phase transformation occurs. The change in the $\rho = f(T)$ dependence is of interest for practical purposes, since the alloys of the systems under study can be used as a ceramic posistor in a self-regulating temperature sensor in the low temperature range. In this regard, the proposed materials based on $3CuO{\cdot}B_2O_3 - ZnO$ are of interest and can be used as self-regulating temperature sensors to control the current strength in a narrow temperature range.

2. Experimental

2.1. Materials and synthesis

The $3CuO{\cdot}B_2O_3 - ZnO$ section is located in the high-temperature part of the $CuO\text{-}B_2O_3\text{-} ZnO$ concentration triangle. The system was studied in the concentration range of 0-100 mol% ZnO with an interval of 5 mol%. Chemical grade CuO and H_3BO_3 as well as ZnO-analytical grade were used as initial materials. The samples were prepared by thoroughly grinding a mixture of the starting components, followed by melting in platinum crucibles in a muffle furnace for 8-10 hours at 1273-1373 K. The melts were then cast at room temperature onto a titanium plate. Analyses have shown that samples containing 5-70 mol% ZnO are crystalline. Glassy alloys were crystallized by heat treatment for 40-50 hours at a temperature of ~ 923K and then analyzed by DTA and XRD.

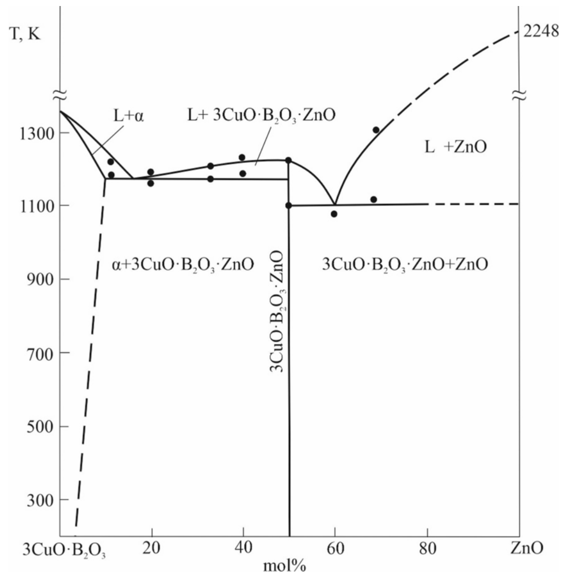

Fig. 1. Phase diagram of the $3CuO{\cdot}B_2O_3 - ZnO$ system

2.2. Methods

The phase relationships in the $3CuO{\cdot}B_2O_3 - ZnO$ system were studied using differential thermal analysis (DTA) and X-ray diffraction phase analysis (XRD) as well as the microhardness measurements.

The temperatures of the thermal effects were determined using a NETZCHSTA 449F3STA - 0836 derivatograph at room temperature and ~1400 K with a heating rate of 10 $K{\cdot}min^{-1}$ and accuracy of ±2 K. The phase composition of the powdered samples was identified by powder X-ray diffraction on a Bruker D2 diffractometer using CuK_α radiation in the angular range of $10° \leq 2\theta \leq 70°$ at room temperature.

Physical properties were measured using digital voltmeters B7-30 and B7-21A by compensation method [22] as the ratios of $(\Delta U)/(\Delta T)$, where ΔU is the voltage between the probes in the material if a temperature difference of $\Delta T = 6 \div 10°$ is maintained between them.

3. Results and discussion

3.1. Phase diagram

Based on the obtained DTA and XRD data, a phase diagram of the $3CuO{\cdot}B_2O_3 - ZnO$ system was constructed (Fig. 1).

It was established that the system is quasi-binary of the eutectic type. In the concentration range of 0-5 mol % ZnO, a region of solid solutions based on copper borate was found. When the component ratio is 1:1, a new phase $3CuO{\cdot}B_2O_3\text{-}ZnO$ is formed, which melts con-

Table

$3CuO\cdot B_2O_3$		$3CuO\cdot B_2O_3$ 85 mol%		$3CuO\cdot B_2O_3$ 65 mol%		$3CuO\cdot B_2O_3$ 55 mol%		$3CuO\cdot B_2O_3$ 50 mol%		$3CuO\cdot B_2O_3$ 45 mol%		$3CuO\cdot B_2O_3$ 35 mol%		ZnO	
1%		d, Å	1%	d, Å	1%	d, Å	1%	d, Å	1%	d, Å	1%	d, Å	1%	d,Å	1%
5.34	3	7.21	10	5.82	14	3.90	18	3.70	22	5.79	27	6.15	23		
4.95	3	4.29	7	5.53	14	2.88	55	3.39	18	5.15	22	5.35	36		
4.32	6	2.94	100	3.69	10	2.60	22	2.88	26	4.52	16	3.78	19		
3.93	6	2.86	83	2.92	100	2.53	22	2.53	42	3.01	27	3.56	36		
3.47	10	2.74	14	2.68	40	2.45	100	2.45	100	2.52	38	3.32	26		
3.16	2	2.45	66	2.63	14	2.30	40	2.30	42	2.46	100	3.17	40		
3.00	8	2.25	12	2.52	9	2.12	34	2.12	40	2.30	40	2.97	41		
2,938	100	2.13	19	2.46	56	2.04	23	1.50	30	2.12	45	2.88	37	2.81	71
2.876	100			2.42	17	1.86	23			2.00	27	2.75	26		
2.757	7			2.13	20	1.50	34			1.86	25	2.60	64	2.60	40
2.72	10									1.57	37	2.46	100	2.47	100
2.64	11									1.50	32	2.30	88		
2.605	7											2.12	42		
2.555	2											1.93	42		
2.525	4											1.50	40		
2,487	4														
2.426	6														
2.322	5														
2.264	5														
2.155	3														
1.7421	4														
1.6634	3														
1.5770	4														

gruently at 1253K. The density of this compound determined by hydrostatic weighing in distilled water is 4.50 g/cm^3. The formation of the new phase is confirmed by the appearance of new diffraction maxima in the X-ray diffraction patterns of alloys containing 50-55 mol% ZnO, in contrast to the original $3CuO\cdot B_2O_3$ and ZnO (Table). The ternary compound with the components of the system forms eutectics with compositions of 15 and 60 mol% ZnO, which melt at temperatures of 1193 K and 1103K, respectively.

Despite the fact that both components of the studied system are quite high-temperature (t_m= 1353K for $3CuO\cdot B_2O_3$ and t_m~ 2273K for ZnO), the liquidus temperatures of this system are low, which is probably due to the formation of a ternary glass-forming compound.

3.2. Electrical properties

When studying the electrical properties, it was discovered that glass alloys of the $3CuO\cdot B_2O_3$ – ZnO ternary system are mainly dielectrics, but in contrast to them, samples of the $3CuO\cdot B_2O_3$ – ZnO system are highly compensated materials.

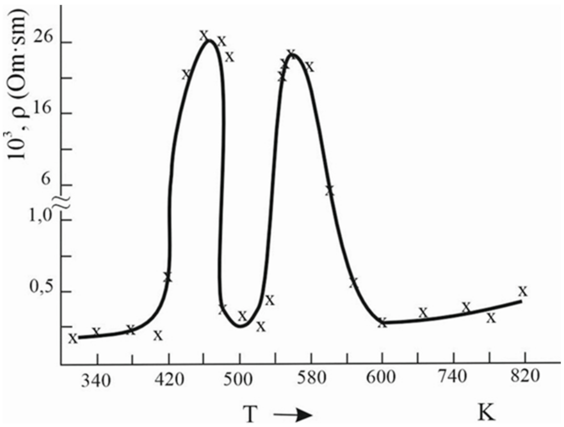

Fig. 2. Temperature dependence of the resistivity of the $3CuO\cdot B_2O_3$ ·ZnO compound

Figure 2 shows the temperature dependence of the resistivity of the identified ternary compound. From Figure 2 it is clear that the values of ρ change sharply with temperature, and in the temperature range of 400÷625K, starting from T=450K the resistivity changes twice from 148 to 26300 Ω·cm. At temperature T=460K it acquires its initial value and continues to be in this state until temperature T=510K; then the high-resistance state is repeated again.

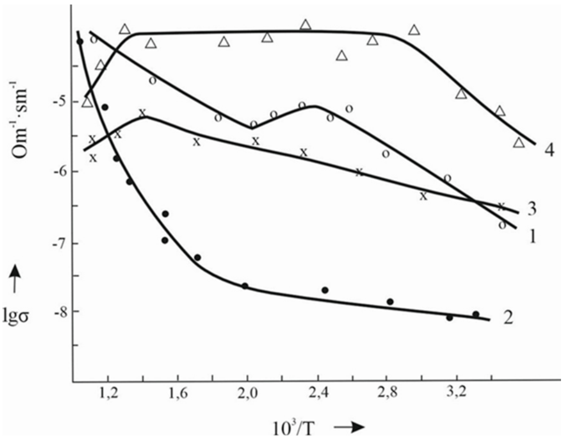

Fig. 3. Temperature dependences of electrical conductivity in samples: **1** – $3CuO \cdot B_2O_3$; **2** – 95.0 mol%$3CuO \cdot B_2O_3$ + 5.0 mol% ZnO; **3** – 90.0 mol %$3CuO \cdot B_2O_3$ + 10.0 mol% ZnO; **4** – 85.0 mol%$3CuO \cdot B_2O_3$ + 15.0 mol% ZnO

The analysis of the obtained results allows us to conclude that there is a strong compensation of charge carriers in the 5 mol% ZnO alloy, and at the same time, this composition has a semiconductor behavior in terms of electrical conductivity σ with temperature. From the temperature dependence of electrical conductivity lg σ =f(1/T) for a sample of 5 mol% ZnO, it was revealed that σ varies depending on *T* according to the following laws: in the range of 300-480K, $\sigma \sim T^{0.4}$; in the range of 530÷700K, $\sigma \sim T^{3.3}$ and in the range of 700÷960K, $\sigma \sim T^{9}$. The thermal band gap of the sample containing 5 mol% ZnO is 2.05÷2.15 eV.

A further increase in the ZnO content leads to an increase in electrical conductivity. Thus, for an alloy of 10 mol% ZnO, the change in σ versus *T* has almost the same character as for the initial $3CuO \cdot B_2O_3$ compound, and for alloys with 15 and 20 mol% ZnO, the value of electrical conductivity is higher and has a different dependence on *T*.

On curve 4, the dependence on temperature for the alloy 15 mol% ZnO has two regions in the range of 300÷380 K, σ increases sharply with increasing *T*, and the course of its change is close to the initial $3CuO \cdot B_2O_3$; above 380 K, the electrical conductivity changes (Fig. 3).

The analysis of the experimental data shows that the studied samples of the $3CuO \cdot B_2O_3$ – ZnO system are highly compensated materials. Of these alloys, the most interesting from the point of view of practical application is the eutectic alloy of 5 mol% ZnO with electrical conductivity $\sigma = 2.1 \cdot 10^{-9} \div 8.6 \cdot 10^{-8}\ \Omega^{-1} \cdot cm^{-1}$ and thermo-EMF α=2.08 mV/K at room temperature.

Previously, we studied thermo-EMF and electrical conductivity of this system, and it was found that some compositions have semiconducting properties [23, 24]. In [24], the electrical conductivity of alloys of the system $(3CuO \cdot B_2O_3)_{1-x}$ - $(ZnO)_x$ (x = 0-15.0 mol% ZnO), was measured, and it was revealed that some compositions in physical properties are close to semiconductors; they exhibit a characteristic increase in conductivity with increasing temperature in the temperature range of 300÷960K.

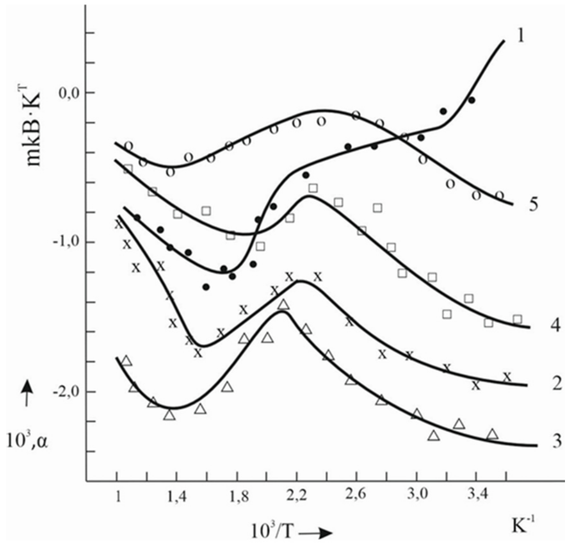

Fig. 4. Temperature dependence of thermo-EMF of the alloys $(3CuO \cdot B_2O_3)_{1-x}$ - $(ZnO)_x$: **1** – $3CuO \cdot B_2O_3$; **2** – 95.0 mol%$3CuO \cdot B_2O_3$ + 5.0 mol% ZnO; **3** – 90.0 mol %$3CuO \cdot B_2O_3$ + 10.0 mol% ZnO; **4** – 85.0 mol%$3CuO \cdot B_2O_3$ + 15.0 mol% ZnO; **5** – 80.0 mol%$3CuO \cdot B_2O_3$ + 20.0 mol% ZnO

The temperature dependence α=*f*(*T*) was plotted according to the results of thermo-EMF (α) measurements (Fig. 4). As can be seen, with an increase in the ZnO concentration (Fig. 4, curves 2, 3), the absolute value of the thermo-EMF initially increases. A further increase in the ZnO concentration leads to a decrease in the α value (Fig. 4, curves 4, 5), which is in good agreement with the results of [24]. It is also clear from the figure that for all the alloys, in contrast to the initial compound $3CuO \cdot B_2O_3$ (Fig. 4, curve 1), that the minimum observed on the α=*f*(*T*) curves in the temperature range of 417÷556 K shifts towards low temperatures with increasing ZnO concentration. With a further increase in temperature, the value of α for all the alloys gradually decreases, but the rate of the decrease in α is not the same. The research results show that, depending on the ZnO content, the electrical conductivity and thermo-EMF change naturally.

For a sample containing 5 mol% ZnO, the activation energy of current carriers was estimated from the graph $lg\sigma = f(\frac{10^3}{T})$ at $10^3/T \to 0$; and the resulting value $(E_d)_\sigma$ = 2.05÷2.15 eV was obtained. The obtained value $(E_d)_\sigma$ = 2.05÷2.15 eV was compared with the activation energy calculated in [24] by the formula $lg\sigma = f(\frac{10^3}{T})$. The discrepancy between $(E_d)_\alpha$ and $(E_d)_\sigma$ is insignificant within the measurement error.

So, the study of the temperature dependence $lg\sigma = f\left(\frac{10^3}{T}\right)$ of alloys $3CuO{\cdot}B_2O_3$–ZnO confirms the conclusions of [24] that these alloys have semiconductor properties in the temperature range of 300÷960K and belong to compensated materials.

4. Conclusion

For the first time, phase equilibria in the $3CuO{\cdot}B_2O_3$–ZnO system are presented. It has been established that the expansion of the glass formation region towards non-glass-forming boundary binary systems is associated with the formation of new ternary glass-forming compounds in them. It has been shown that the alloys of the $(3CuO{\cdot}B_2O_3)_{1-x}$–$(ZnO)_x$ system in terms of their electrical properties belong to compensated materials. With increasing ZnO content in the system, electrical conductivity increases. The temperature dependence of the electrical conductivity of the alloy with x = 5.0 mol% ZnO obeys an exponential law characteristic of semiconductor crystals. The results of the study of the phase equilibria in the $3CuO{\cdot}B_2O_3$–ZnO system are presented. It is shown that the system belongs to the simple eutectic type. Using the extrapolation method in the temperature range of 300-960 K, it was determined that the intermediate compositions have semiconductor properties (300÷960K) and belong to compensated materials. An alloy composition with semiconductor properties based on copper, zinc and boron oxides has been developed.

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