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THEORETICAL BACKGROUND OF ALKALINE-FREE TIN CONTENT COATINGS ON CERAMICS IN THE SYSTEM RO-SnO_2-Al_2O_3-SiO_2

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Abstract. Theoretical calculations in the oxides systems RO-SnO_2-Al_2O_3-SiO_2, where RO – CaO, ZnO and BaO, have been done. Their structure has been established; eutectic and geometer-topological characteristics have been calculated. The process of the conodes adjustment at 1100 K has been revealed.

Keywords: systems, eutectic, geometer-topological characteristics, conodes adjustment.

1. Introduction

Recently in the technology of nonmetallic coatings for various purposes there has been a heightened interest in oxide of tin (IV) as a modifying component of glass matrix, which promotes a glass crystal structure due to the presence of valence electrons in shells s^2p^2. SnO_2 oxide has specific features, namely, it provides glass resistance to alkalis and increases the melts viscosity to a lesser extent than ZrO_2 [1]. Its usage is known in the development of opaque vitreous and glass ceramic materials and coatings for ceramics, due to the high value of its own refractive index [2].

In multicomponent oxide alloys hexagonal co-ordination SnO^{4+} is more stable. SnO_2 is easily recovered from the alloy in the form of cassiterite crystals [3]. While using this oxide glasscrystal composition acquires a number of unique thermomechanical features: the rate of expansion decreases at the exchange of SiO_2 for SnO_2 and thin uniform crystallization is stimulated. It is one of the conditions for the creating a material with high heat resistance, density and structural strength. Introduction of CaO, ZnO and BaO to the glass composition significantly reduces the tin oxide solubility in molten glass and plays an important role in obtaining white opaque irrigated surfaces. Materials based on SnO_2, Al_2O_3, BaO, ZnO, CaO oxides and their compounds are of interest both in the technology of special ceramic and refractory materials, and glass crystal materials technology.

The RO-SiO_2-Al_2O_3-B_2O_3-SnO_2 system (RO – oxides-modifiers among CaO, ZnO, BaO) was chosen as a basis for the investigations. Analysis of literature data has shown that the CaO-Al_2O_3-SnO_2, ZnO-Al_2O_3-SnO_2, BaO-Al_2O_3-SnO_2 systems were previously investigated insufficiently; some components of these systems are not yet studied substances [4, 5].

Thus, in order to predict the glass composition contents and their properties it is necessary to get information on the relationship of crystalline phases which are the part of the studied systems. It is a relevant and promising task of ceramics technology.

2. Experimental

Methods of the phase diagrams calculations correspond to those adopted in theoretical physico-chemical studies for multicomponent systems [6, 7]. To obtain the values of standard entropy S^0_{298} we used Yatsymirsky method; the values of standard enthalpy ΔH^0_{298} were calculated using Moraczewski and Sladkov method; the equation of heat capacity dependence on the temperature $C_p = f(T)$ [8, 9] was defined using Landiya method.

Modern thermodynamic data of the binary systems which form the researched three-components systems [10, 11] were involved as the initial data. The search showed that the available data on multicomponent tin-containing systems are very limited. Among the existing data on subsolidus status of the mentioned systems there is no information about alkaline-free tin-containing oxide systems with alkaline-earth oxide- [12-15].

In the literature there are data on the structure of two-component system Al_2O_3-SnO_2 [3], which is a simple eutectic system with the eutectic temperature of 1893 K. Eutectic is observed at 98 wt % SnO_2 and 1893 ± 5 K.

The small amounts of $SnAl_2O_4$ are formed while mixture quenching that indicates to the presence of a small proportion of SnO.

The binary system $CaO-Al_2O_3$ has been widely known in the technology of ceramics and carefully studied in the works of A. Berezhny [4]. The double phase diagrams of $ZnO-SnO_2$, $ZnO-Al_2O_3$ and $SnO_2-Al_2O_3$ systems were investigated in the works [10, 12, 13]. It has been found out that $2ZnO{\cdot}SnO_2$ (Zn_2SnO_4) is formed in the first case and $ZnO{\cdot}Al_2O_3$ ($ZnAl_2O_4$) – in the second one. Stable compounds are not formed in the $SnO_2-Al_2O_3$ system.

3. Results and Discussion

The initial data for thermodynamic calculations were taken from [3, 7, 15, 16] and are listed in Table 1. Gibbs energy was calculated in the temperature range of 1073–1773 K with intervals of 50 K, taking into account the phase transition of alumina $\gamma-Al_2O_3 \rightarrow \alpha-Al_2O_3$.

Based on the literature data the $CaO-Al_2O_3-SnO_2$ system triangulation was done by plotting sections of all possible pair interactions for this system. The probability of formation and coexistence of phases in the studied system was determined by the calculated values of Gibbs energy for the exchange reactions occurring in the temperature range of 600–1600 K. For the compounds $CaO{\cdot}SnO_2$ and $2CaO{\cdot}SnO_2$ only standard values of their enthalpy and entropy are known from the literature data [4-7]. In the absence of the heat capacity dependences on the temperature $C_p = f(T)$ their values were calculated in accordance with the method given in [6].

The diagram of the $CaO-Al_2O_3-SnO_2$ system and its topological graph are presented in Fig. 1. At the temperatures above 1100 K the changes of conodes structure take place, namely, the formation of such elementary triangles, the ratio between which can be described by the phase diagram and topological graph of the following view (Fig. 1). The coincidence of both graphs indicates the same interaction character in the system between its constituent phases and shows no complex phase transitions and unstable compounds.

Table 1

Thermodynamic constants of compounds

Compound formulas	Melting point, K	$-\Delta H^0_{298}$, *kcal / mol*	S^0_{298}, *cal / mol · grad*	$C_p = f(T)$		
				a	$b \cdot 10^3$	$c \cdot 10^{-5}$
$CaO-Al_2O_3-SnO_2$						
CaO	2898	151.9	9.5	11.67	1.08	-1.56
$\alpha-Al_2O_3$	2327	400.48	12.17	27.43	3.06	-8.47
$CaO{\cdot}6Al_2O_3$	1903	2549.4	73.8	138.736	96	-5.311
$CaO{\cdot}2Al_2O_3$	2123	957.06	42.5	66.09	5.48	-17.8
$CaO{\cdot}Al_2O_3$	2038	556.18	27.3	36.01	9.98	-7.26
$12CaO{\cdot}7Al_2O_3$	1878	4640.16	249.7	301.96	65.5	-55.3
$3CaO{\cdot}Al_2O_3$	1729	851	49.1	62.28	4.58	-12.09
SnO_2	1808	138.3	12.5	17.66	2.4	-5.16
$CaO{\cdot}SnO_2$	2073	305.2	18.6	26.574	5.246	-2.963
$2CaO{\cdot}SnO_2$	2073	456.6	28.8	35.978	7.774	-1.044
$ZnO-Al_2O_3-SnO_2$						
ZnO	2248	348.48	44.0	49.06	5.11	-9.13
$\alpha-Al_2O_3$	2327	400.48	12.17	27.43	3.06	-8.47
SnO_2	1903	579.48	52.375	74.0	10.06	-21.62
$2ZnO{\cdot}SnO_2$	2211	3197.14	150.25	82.83	206.93	15.64
$ZnO{\cdot}Al_2O_3$	2223	2069.86	100.31	427.38	355.73	-
$BaO-Al_2O_3-SnO_2$						
BaO	2193	558.15	70.29	53.3	4.35	-8.3
$\alpha-Al_2O_3$	2327	1675.61	50.92	114.77	12.08	-35.44
SnO_2	1903	579.48	52.375	74.0	10.06	-21.62
$BaO{\cdot}SnO_2$	2333	3260.15	146.52	39.40	202.47	16.02
$2BaO{\cdot}SnO_2$	2183	3678.65	159.64	78.37	219.24	17.01
$BaO{\cdot}Al_2O_3$	2088	2334.17	123.43	148.32	35.44	-29.25
$3BaO{\cdot}Al_2O_3$	2188	3537.91	267.78	247.86	48.53	-17.41
$BaO{\cdot}6Al_2O_3$	1893	10740.33	376.56	738.22	70.5	-221.75
$4BaO{\cdot}Al_2O_3$	1873	4014.49	329.99	275.85	56.89	-23.33
$8BaO{\cdot}Al_2O_3$	1923	6238.10	611.68	441.99	96.23	-25.31

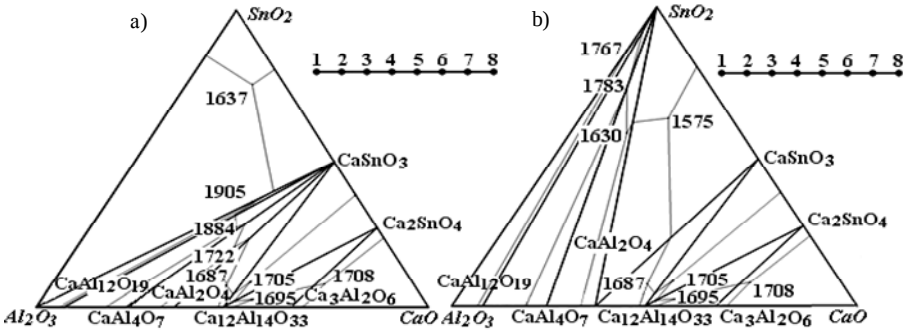

Fig. 1. Phase diagram and topological graph of the CaO-Al_2O_3-SnO_2 system: temperatures below 1100 K (a) and temperatures above 1100 K (b)

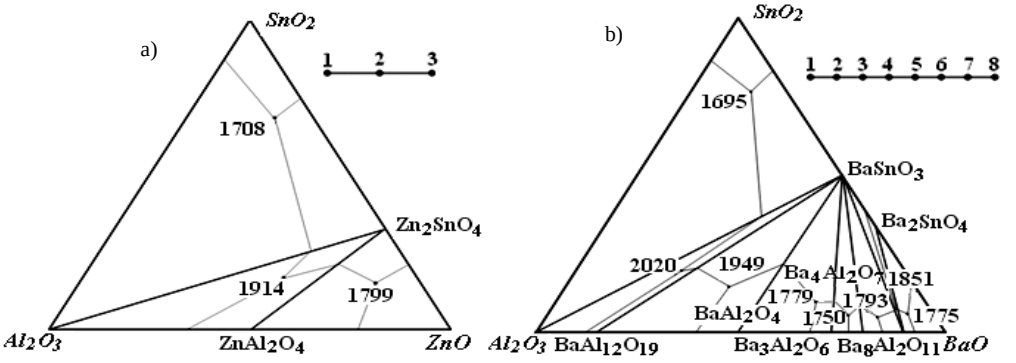

Fig. 2. Phase diagram and topological graph of the systems ZnO-SnO_2-Al_2O_3 (a) and BaO-SnO_2-Al_2O_3 (b)

To triangulate the ZnO-SnO_2-Al_2O_3 and BaO-SnO_2-Al_2O_3 systems we calculated enthalpy, entropy and constants of heat capacity dependence on temperature for zinc stannate and barium stannate (Zn_2SnO_4, $BaSnO_3$ and Ba_2SnO_4), as well as entropy values for $ZnO{\cdot}Al_2O_3$.

As a result of investigations the subsolidus structure of ZnO-SnO_2-Al_2O_3 and BaO-SnO_2-Al_2O_3 system was determined. Its phase diagram is represented in Fig. 2a.

We did not find the information about the structure of the BaO-SnO_2-Al_2O_3 system. Data retrieval concerning the two-component systems [17] has shown that two compounds are formed in the BaO-SnO_2 system: $BaO{\cdot}SnO_2$ ($BaSnO_3$) and $2BaO{\cdot}SnO_2$ (Ba_2SnO_4). There is also information about the existence of $3BaO{\cdot}SnO_2$ ($Ba_3Sn_2O_7$) compound but its formation is possible only under special conditions, that is why during the triangulation it was not taken into account.

Among 8 barium-aluminate compounds which may be formed in this two-component system at the triangulation in the BaO-SnO_2-Al_2O_3 system we consider only phases stable at 1673 K: $BaAl_2O_4$, $Ba_3Al_2O_6$, $BaAl_{12}O_{19}$, $Ba_4Al_2O_7$ and $Ba_8Al_2O_{11}$. As it was mentioned above, in the system SnO_2-Al_2O_3 the stable compounds are absent.

Taking these data into account the triangulation for three-component BaO-SnO_2-Al_2O_3 system also was done using the calculation method. On the basis of literature data the conodes sections characterizing all possible pair interactions in this system were plotted. Diagram and topological graph of the BaO-SnO_2-Al_2O_3 system as a result of triangulation is represented in Fig. 2b. It gives some information about the conodes location and phase interaction. The geometer-topological characteristics and eutectics of elementary triangles obtained as a result of triangulation are represented in Table 2.

The information about the structure of oxide systems containing SnO_2 is very limited. But it is needed to analyze the behavior of oxide compositions at heating in the process of thermal treatment of materials. The investigation of alkaline-earth oxides effect on phase formation in tin-containing oxide compositions is of great importance, because they significantly affect the processes of crystallization and glass formation [18].

4. Conclusions

As a result of theoretical studies the location of elementary triangles in the experimental systems has been established, their geometer-topological characteristics and

eutectics parameters have been specified. The data have been used to determine the oxide compositions field in the in the CaO-BaO-ZnO-SnO_2-Al_2O_3-SiO_2 system.

Table 2

The eutectics composition and temperature

Elementary triangle	Eutectics composition, mas %			Eutectics temperature, K
Al_2O_3-SnO_2-CaO system				
Temperatures below 1100 K	Al_2O_3	SnO_2	CaO	
Al_2O_3-SnO_2-$CaSnO_3$	22.28	65.58	12.14	1637
Al_2O_3-$CaAl_{12}O_{19}$-$CaSnO_3$	63.04	26.68	10.28	1905
$CaAl_{12}O_{19}$-$CaAl_4O_7$-$CaSnO_3$	63.14	23.39	13.47	1884
$CaAl_4O_7$-$CaAl_2O_4$-$CaSnO_3$	39.48	38.80	21.72	1722
$CaAl_2O_4$-$Ca_{12}Al_{14}O_{33}$-$CaSnO_3$	43.34	15.81	40.85	1687
$Ca_{12}Al_{14}O_{33}$-Ca_2SnO_4-$CaSnO_3$	35.96	22.44	41.60	1705
$Ca_{12}Al_{14}O_{33}$-$Ca_3Al_2O_6$-Ca_2SnO_4	42.93	7.78	49.29	1695
$Ca_3Al_2O_6$-Ca_2SnO_4-CaO	17.45	25.39	57.16	1708
Temperatures above 1100 K				
Al_2O_3-SnO_2-$CaAl_{12}O_{19}$	77.15	16.31	6.54	1767
$CaAl_{12}O_{19}$-SnO_2-$CaAl_4O_7$	75.20	13.92	10.88	1783
$CaAl_4O_7$-SnO_2-$CaAl_2O_4$	53.78	26.41	19.81	1630
$CaAl_2O_4$-SnO_2-$CaSnO_3$	15.47	67.82	16.71	1575
$CaAl_2O_4$-$Ca_{12}Al_{14}O_{33}$-$CaSnO_3$	43.34	15.81	40.85	1687
$Ca_{12}Al_{14}O_{33}$-Ca_2SnO_4-$CaSnO_3$	35.96	22.44	41.60	1705
$Ca_{12}Al_{14}O_{33}$-$Ca_3Al_2O_6$-Ca_2SnO_4	42.93	7.78	49.29	1695
$Ca_3Al_2O_6$-Ca_2SnO_4-CaO	17.45	25.39	57.16	1708
ZnO-SnO_2-Al_2O_3 system				
	ZnO	SnO_2	Al_2O_3	
SnO_2-Al_2O_3-Zn_2SnO_4	27.99	53.79	18.22	1708
Al_2O_3-Zn_2SnO_4-$ZnAl_2O_4$	40.07	25.39	34.54	1914
Zn_2SnO_4-$ZnAl_2O_4$-ZnO	55.74	26.30	17.96	1799
BaO-SnO_2-Al_2O_3 system				
	BaO	SnO_2	Al_2O_3	
Al_2O_3-SnO_2-$BaSnO_3$	27.55	54.13	18.32	1695
Al_2O_3-$BaAl_{12}O_{19}$-$BaSnO_3$	26.04	12.99	60.97	2020
$BaAl_{12}O_{19}$-$BaSnO_3$-$BaAl_2O_4$	34.59	11.48	53.93	1949
$BaSnO_3$-$BaAl_2O_4$-$Ba_3Al_2O_6$	67.81	13.56	18.63	1779
$BaSnO_3$-$Ba_3Al_2O_6$-$Ba_4Al_2O_7$	76.40	9.62	13.98	1750
$BaSnO_3$-$Ba_4Al_2O_7$-$Ba_8Al_2O_{11}$	84.10	6.50	9.40	1793
$BaSnO_3$-$Ba_8Al_2O_{11}$-Ba_2SnO_4	80.60	14.30	5.10	1851
$Ba_8Al_2O_{11}$-Ba_2SnO_4-BaO	86.97	7.55	5.48	1775

The calculations of necessary thermodynamic constants ($C_p = f(T)$) have been done, phase diagrams of oxide systems have been plotted and the eutectics parameters in ternary diagrams have been defined.

The eutectic temperatures increased depending on oxide in such a sequence: CaO–ZnO–BaO. The phase diagrams show the lowest temperature of eutectics relates to the elementary triangles with enhanced content of SnO_2. Two other components formed chain-like bonds. Most of the bonds for CaO and BaO have been found. The obtained theoretical correlation of oxide ratio can be used for design of opaque tin-containing coatings with enhanced density and heat-resistance in the CaO-BaO-ZnO-SnO_2-Al_2O_3-SiO_2 system.

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ТЕОРЕТИЧНІ ОСНОВИ БЕЗЛУЖНИХ ОЛОВОВМІСНИХ ПОКРИТТІВ ПО КЕРАМІЦІ В СИСТЕМІ RO-SnO_2-Al_2O_3-SiO_2

Анотація. *Проведено теоретичні розрахунки в системах оксидів RO-SnO_2-Al_2O_3-SiO_2 , де RO – CaO, ZnO та BaO, встановлена їх будова, розраховані евтектики та геометро-топологічні характеристики. В залежності від перебудови конод за температури 1100 К виявлено можливості застосування складів композицій в різних технологіях.*

Ключові слова: *система, евтектика, геометро-топологічні характеристики, перебудова конод.*