

Physico-chemical analysis of Fe_2O_3 solution in the melt solvent $\text{PbO-B}_2\text{O}_3\text{-BaO-BaF}_2$

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The electroconductivity of iron (III) oxide solutions in the melted lead-boron-barium fluoride solvent has been studied. The pseudo-binary phase diagram of the $\text{Fe}_2\text{O}_3\text{-(PbO-B}_2\text{O}_3\text{-BaO-BaF}_2\text{)}$ system has been constructed. The dissociation scheme of iron oxide in the solution-melt is proposed. The dissociation degrees and constants are determined in the 1123–1373 K temperature range.

Исследована электропроводность растворов оксида железа (III) в расплаве свинцово-бор-барий-фторидного растворителя. Построена псевдобинарная диаграмма состояния системы состава $\text{Fe}_2\text{O}_3\text{-(PbO-B}_2\text{O}_3\text{-BaO-BaF}_2\text{)}$. Предлагается схема диссоциации оксида железа в растворе-расплаве. Определены степени и константы диссоциации в диапазоне температур 1123–1373 К.

The basic way to prepare the single crystal ferrite garnet films is liquid phase epitaxy (LPE) on nonmagnetic garnets single crystal substrates. For the recent years, $\text{PbO-B}_2\text{O}_3\text{-BaO-BaF}_2$ solvent with low lead content has been used to produce the garnet films [1]. The yttrium-iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) solutions are obtained by dissolution of garnet-forming oxides in a melt-solvent, therefore, the garnet-forming solution-melt can be represented as homogeneous mixture of the iron (III) and yttrium oxides solutions. In this paper, presented are the physico-chemical analysis results of iron (III) oxide solutions in $\text{PbO-B}_2\text{O}_3\text{-BaO-BaF}_2$ solvent with B_2O_3 content within 31–35 mol.% range, BaO — 30–35 mol.%, BaF_2 — 12–14 mol.%, the remainder being PbO described. The solvent studied corresponds in qualitative and quantitative composition to that described in [2].

The experiments were carried out in a shaft furnace, platinum equipment was used. The temperature control system consisted of a precision programmed temperature controller RIF-101, a platinum-platinorhodium thermocouple, and a F-283M1

digital voltmeter. The resistance of the melt measured by the multimeter E7-12, the cell was calibrated on melted potassium chloride [3]. The experiments were carried out within temperature range from 1123 to 1373 K.

The research basis of any crystallization process is the phase diagram. To construct the diagram in our experiments, three methods of phase transition temperature determination were used: examination of the melt conductance [4], thermal analysis, and microstructure method [5].

Fig. 1 represents the typical temperature dependences of electrical conductivity of the iron (III) oxide solutions-melts. At the temperatures above crystallization point, the polytherms of the solution-melt conductance are linear with a high correlation coefficient and small temperature gradients. By the equation:

$$\chi = A \cdot \exp(-W_a^\chi / R \cdot T), \quad (1)$$

where χ is electrical conductivity of the solution-melt; W_a^χ , activation energy of the

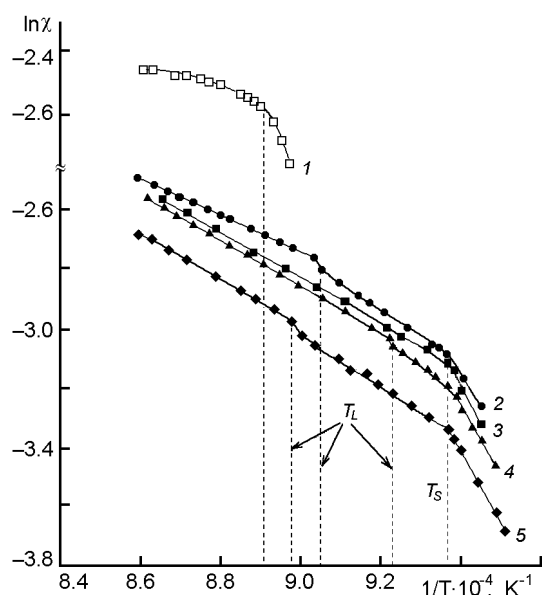


Fig. 1. Dependences of specific electric conductivity logarithm on inverse temperature: 1, pure solvent PbO–B₂O₃–BaO–BaF₂; 2, 2.5 mol.% Fe₂O₃; 3, 6.0 mol.% Fe₂O₃; 4, 7.0 mol.% Fe₂O₃; 5, 10.0 mol.% Fe₂O₃.

electrical conductivity; R , gas constant; T , temperature [6, 7], the activation energy of electrical conductivity for iron (III) oxide solutions in the melted solvent was calculated. The temperature and concentration of the solution-melt influence considerably the electric conductivity activation energy values (Table 1). The determined values of the electroconductivity activation energy for the iron (III) solutions exceed considerably the conductivity energy of well dissociated salt melts (alkali metal chlorides) [3], thus confirming the weak ionic structure of the oxide solutions-melts [8].

In pre-eutectic zone, the first line bend corresponds to the starting temperature of of multicomponent solvent crystallization (Fig. 1, curve 2), while in the post-eutectic area, to the beginning of crystallization of the iron (III) oxide [4] (Fig. 1, curves 4, 5). The crystallization temperatures correspond to liquidus temperatures, T_L . The iron (III) oxide solutions hardened at temperature 1067 ± 2 K, which corresponds to solidus temperature, T_S . One more bend was observed on the temperature dependences 2–5. The dependence 3 corresponds to eutectic composition of the system (Fig. 1). The bend coordinates of the curves were determined by numerical differentiation. The phase change temperatures determined from

Table 1. Phase transition and activation energies of electric conductivity in the Fe₂O₃–(PbO–B₂O₃–BaO–BaF₂) system

Fe ₂ O ₃ concentration, mol.%	T_L , K	T_S , K	W_a^* , kJ/mol
0	1120*	–	47.2
1.0	1113	1067	56.0
1.5	1111	1067	56.0
2.0	1108	1068	55.4
2.5	1106	1067	50.2
3.0	1094	1066	62.8
4.0	1092	1069	63.9
5.0	1079	1066	66.1
6.0	–	1067	60.3
7.0	1085	1069	66.0
8.0	1093	1068	63.4
10.0	1113	1065	59.9
15.0	1187	1067	29.0
20.0	1221	1065	20.2

* melting temperature of the compound

conductance polytherms were confirmed by thermal and microstructure analysis of the system (temperature of the phase changes are presented in Table 1). The conductance grows considerably with raising the temperature at any composition of the solution-melt because of reduction of the medium viscosity [9], increase the mobility of the ions and the dissociation degrees of the solution-melt components.

Using the experimental data obtained, the limited pseudobinary phase diagram of the Fe₂O₃–(PbO–B₂O₃–BaO–BaF₂) system was constructed (Fig. 2). The studied solution-melt is represented as a simple eutectic system with eutectic composition 6 mol.% Fe₂O₃ at 1067 K. The system is described by the equation:

$$\ln X = -\frac{\Delta H_{melt}}{R \cdot T} + C, \quad (2)$$

where ΔH_{melt} is the melting heat; X , concentration of the crystallizing component, mole fraction; R , gas constant; C , a constant [10, 11]. From the slopes of linear dependences of the mole fraction logarithm on inverse temperature, the melting heats of the solvent crystals ($H = 18$ kJ/mol) and iron (III) oxide ones ($H = 75$ kJ/mol) in the solution-melt were calculated.

In the solution-melt, the yttrium-iron garnet is subjected to garnet-forming oxides, hence, the garnet dissociation mechanism should be considered as dissociation of the oxides. To determine the number of the new ions — products of the Fe_2O_3 dissociation, distinct from products of the solvent dissociation, the correlation of cryoscopic constants was used [11]. Theoretical cryoscopic constant was calculated as:

$$K_{theory} = \frac{RT_A^2}{\Delta H_{melt} \cdot 1000} \cdot M_A, \quad (3)$$

where R is the gas constant; T_A , melting temperature of the solvent; ΔH_{melt} , melting heat of the solvent crystals in the solution; M_A , the solvent molar mass. The constant is 82 K·kg/mol. The experimental cryoscopic constant, as determined by extrapolating the dependence of the molally reduction of the solution-melt solidification temperature on iron oxide molal concentration, equals 152 K·kg/mol. According to calculations, the number of the new ions practically equals two. Taking into account that the mole fraction of boron oxide is much less than the total one of barium and lead oxides (the melt basicity calculated in [12] is 10–27 mol.%), we propose the following oxide dissociation scheme:



in diluted solutions, iron (III) oxide dissociates into oxygen complexes that contribute to formation of the ferrite-garnet crystal lattice.

To determine the dissociation degrees and formal dissociation constants of the garnet-forming oxides, it is expedient to use not specific, but molar conductivity of the solution. The molar electrical conductivity of the electrolyte solutions depends on two factors: degree of the electrolyte dissociation and electrical interaction between ions. In diluted solutions of weak electrolytes, electrostatic interaction between ions

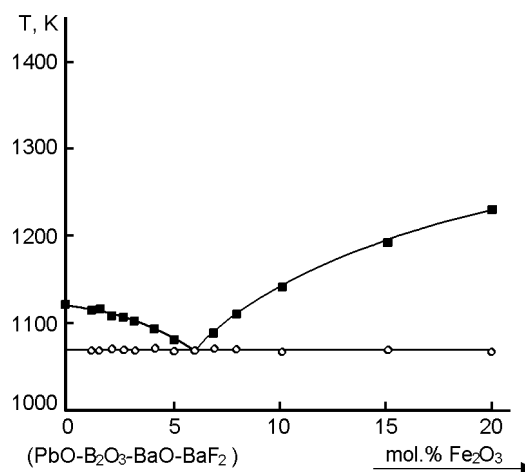


Fig. 2. Pseudo-binary phase diagram of the Fe_2O_3 –(PbO – B_2O_3 – BaO – BaF_2) system.

is insignificant and the following equation will be valid:

$$\alpha = \lambda / \lambda_\infty, \quad (4)$$

where α is the dissociation degree, λ , molar electric conductivity of the solution, λ_∞ , molar electric conductivity of the infinitely diluted solution. According to the dissociation scheme presented above, iron oxide is dissociated into univalent complex ions with low dissociation degrees, and in the diluted solution of the weak uni-univalent electrolyte, the dissociation constant is expressed as:

$$K = \frac{c \cdot \alpha^2}{(1 - \alpha)}. \quad (5)$$

The calculated dissociation degrees and constants of iron oxide in the diluted solution are presented in Table 2, the values thereof confirm weak ionic nature of the investigated solution-melt.

Thus, in this work, the conductance of iron (III) oxide solutions in the melted solvent PbO – B_2O_3 – BaO – BaF_2 has been studied. On the basis of the experimental data, the pseudo-binary phase diagram of Fe_2O_3 –(PbO – B_2O_3 – BaO – BaF_2) system has been con-

Table 2. Dissociation degrees and constants of the ferrum (III) oxide in the melt-solution on the basis of PbO – B_2O_3 – BaO – BaF_2

Dissociation degrees constants at $c(\text{Fe}_2\text{O}_3) = 1$ mol.%	Temperature, K					
	1123	1173	1223	1273	1323	1373
α	0.588	0.590	0.593	0.597	0.599	0.602
K	0.328	0.329	0.330	0.331	0.332	0.332

structed, the melting heats of the solvent and iron (III) oxide crystals in the solution-melt have been determined. On the basis of cryoscopic calculations, the dissociation scheme of the iron (III) oxide in the used solvent is proposed, dissociation degrees and constants in the working temperature interval are calculated.

References

1. E.I.Nikolaev, I.A.Krasin, *Kristallografia*, **33**, 478 (1988).
2. USSR Author's Cert. 1,604,871, C 30 B 19/02, C 30 B 29/28 (1988).
3. D.Dobosh, *Electrochemical Constants, Reference Book for Electrochemists*, Mir, Moscow (1980) [in Russian].
4. O.M.Konovalov, M.Ya.Konovalova, in: *Single Crystals and Engineering*, 1th Issue, VNIIM Publ., Kharkov (1970), p.21 [in Russian].
5. V.Ya.Anosov, M.I.Ozerova, Yu.Ya.Fialkov, *Principles of Physico-Chemical Analysis*, Nauka, Moscow (1976) [in Russian].
6. Ya.I.Frenkel', *Kinetic Theory of Liquids*, Nauka, Leningrad (1975) [in Russian].
7. Yu.K.Delimarsky, *Chemistry of Ionic Melts*, Naukova Dumka, Kiev (1980) [in Russian].
8. P.De Gasperis, R.A.Marcelli, *Mat. Res. Bull.*, **22**, 235 (1987).
9. V.V.Morenko, A.V.Belyi, *Dop.NANU*, **4**, 137 (2001).
10. V.A.Timofeeva, *Crystal Growth from Solutions-Melts*, Nauka, Moscow (1978) [in Russian].
11. L.M.Vitting, *High-Temperature Solutions-Melts*, MGU Publ., Moscow (1991) [in Russian].
12. Yu.K.Delimarsky, L.P.Barchuk, *Applied Chemistry of Ionic Melts*, Naukova Dumka, Kiev (1988) [in Russian].

Фізико-хімічний аналіз розчину Fe_2O_3 у розплаві розчинника $\text{PbO}-\text{V}_2\text{O}_3-\text{BaO}-\text{BaF}_2$

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Досліджено електропровідність розчинів оксиду заліза (III) у розплаві свинцево-бор-барій-фторидного розчинника, побудовано псевдобінарну діаграму стану системи складу $\text{Fe}_2\text{O}_3-(\text{PbO}-\text{V}_2\text{O}_3-\text{BaO}-\text{BaF}_2)$. Запропоновано схему дисоціації оксиду заліза у розчині-розплаві, визначено ступіні та константи дисоціації у діапазоні температур 1123÷1373 К.