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Simulation of the Mechanism of Formation of Solid Solutions in the System $In_2O_3 - TiO_2$ When Heated in Air

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On the basis of mathematical models of the formation of solid solutions in the $In_2O_3 - TiO_2$ calculated ionic radius of the cations: indium, titanium, anion and anionic vacancies on the scale of Templeton and Deben. A phase transformation in the oxide of indium was related with disorder of anionic vacancies in the lattice type C. The formation of solid solutions in this system proceeds on the basis of the disordered phase of type C[1]. The system formed limited solid solutions such as: subtraction – substitution – inculcation of a range of concentrations (0 – 2% TiO_2), subtraction – substitution of concentrations (0.5 – 2% TiO_2), higher concentrations of these compounds present in the mixture of In_2TiO_{5}-x – rhombic modification, which is formed during sintering the samples at 1100 °C in air. The type solid solution systems in the $In_2O_3 - TiO_2$, depend on the size of cation bases and additives. The energies of formation: solid solution subtraction – substitution – introduction, solid solution subtraction – substitution were determined and shows that the conductivity of the current, concentration and mobility of the charge carriers depends on the type of the solid solution and not on the valence of the dissolved additive.

Keywords: Indium oxide, Titanium dioxide, Solid solution, Conductivity, Phase transformations.

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1. INTRODUCTION

Search for materials with high conductivity of carriers and their resistance at high temperatures in air and a vacuum is an unsolved problem of materials science, physics and chemistry of solids. The crystal structure of the oxide Me_2O_3 (Sc_2O_3; In_2O_3 ,Y_2O_3, Ce_2O_3 , and so on can be added to them and Ti_2O_3) refers to the structure of pyrochlore C and contains 25% natural ordered anion vacancies, which are elements of the structure. Electronic structure of oxide Me_2O_3, MeO_2 - has a valence of 2P, and the conduction band they differ. The conduction band of In_2O_3 is 3d - state, TiO_2 - 4 d - state. The conductivity of the oxide materials, depending on the structure, phase transformations during heating in a variety of environments, when an electric field is: ion, electron, proton and mixed. Of these materials by sintering powders may be prepared thermistors micro thermistors. Thermistors are widely used in measuring equipment for measuring the temperature, and to compensate for temperature changes in the parameters of the electric fields. This small current flow through the thermistors and the thermistors is practically not heated and its temperature is determined by the ambient temperature. Thermistors are used to stabilize the voltage, power measurement electromagnetic waves as starting relays and timers. Micro-thermistors are used for the study of heat transfer processes in the leaves of plants, for the early diagnosis of various diseases [1,2].Materials based on In_2O_3 with the addition of TiO_2 are of practical interest as materials having conductivity. Such materials can be used in various fields of engineering and agriculture: in the form of solar energy converters, as sources of energy, solid fuel, materials for electronics [3].

Defects that are structural elements are combined with impurity atoms to form defect complexes as donor - acceptor pairs. Accumulation of such defects leads to a change in the polymorphic transformation temperature, change in the physical properties of a solid solution [4]. Thermodynamic calculation of solid solutions on the basis of a pyrochlore structure with defects in the structure of a complex process of choosing the right models for the formation of a solid solution as a model of a solid solution specifies the record of the thermodynamic potential, and thus the final result. Calculate energy coefficients determining the internal energy of the crystal, cannot be made with sufficient accuracy and finding appropriate by comparison with experimental data The presence of defects, impurities in the same crystalline states lead to the formation of cations with different charges, the exchange of electrons between neighboring ions of low energy exchange. All the electrons or holes that can move from one ion to another can be considered as free charge carriers [5].

The aim of this work is to develop proper models of mechanisms of formation of solid solutions of systems of $In_2O_3 - TiO_2$.

2. RESULTS AND DISCUSSION

2.1 Mathematical model for determining the radius of the atoms in compounds In2O3, TiO2

To build the right model based solid solution of indium oxide with the addition of titanium dioxide is necessary to determine the exact values of the ionic radius of the cations indium and titanium, forming a solid solution.

The reason for this lies in the fact, that values of the ionic radii not can be regarded as absolute, and each scale is apparently suitable only to describe cer-

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tain structural types. The criterion for this suitability can serve as a linear dependence of the lattice parameters of the compounds of the radius of the cations (for a fixed anion) contained in this scale, and received, depending on the geometry of the structure, subject to the availability of close packing.

The cubic structure of indium oxide type C - close to the pyrochlore type MeO_2 and differs from it in the vacant equal to one quarter of anionic positions and twice parameter of the lattice. Vacant and occupied the position alternate in natural. For one octant of the unit cell of the ordered structure of type C, we can write the lattice parameter of indium oxide by ionic radii as follows

$$\frac{a}{2} = D_c(r_k + \frac{3}{4}r_a + \frac{1}{4}r_{v(O)}) \tag{1}$$

where a – lattice parameter; Dc = 2.336 – the coefficient of cubic structures of rare-earth oxides on a scale of Templeton and Deben; r_k - the radius of the cation; r_a – ionic radius of oxygen; $r_{v(O)}$ – radius of the anion vacancy. The values of the ionic radii of indium and titanium can to find in this scale. Radius of the cation of indium on this scale can be determined by the value of the lattice parameter of indium oxide (a = 1.0120 nm), which is on the linear relationship, built on the known values of the parameters of lattice of the compounds of the type Me_2O_3 from the values of the radius of the cations (Fig. 1) [6] . Cationic radius of indium $r_k = 0.0763$ nm; oxygen radius $r_{(O)} = 0.1374$ nm, the radius of the anion vacancy, defined by the formula (1) is $r_{v(O)} = 0{,}1380$ nm. The cationic radius (Ti_2O_3) $r_k = 0.069$ nm, for (TiO_2) $r_k = 0.064$ nm. [7]. Since the interaction between the ions in a cubic lattice of type C is central, the directions of the displacements caused by the difference of the radius of the oxygen ion and anion vacancies are the directions [110], [111], [100]. The packaging atoms in the structure of type C is of the ordered phase in the plane (110) with the determined of the values radius cation indium, oxygen, anion vacancies was considered. It represents the distribution of atoms in an irregular of hexagon. The oxygen atoms and ordered anion vacancies form a distorted prism of six oxygen atoms and two ordered anion vacancies, which are centered cations of the indium or free. The tetragonal structure of titanium dioxide with unit cell parameters (a = 0.3733 and the tetragonal structure of titanium dioxide with unit cell parameters a = 0.3733 and with a =0,937 nm, c / a = 2, 51) there is to a temperature 1850 °C [7].

Point values of the radius: cations indium and titanium, oxygen, anion vacancies can build a model of solid solutions in the system $In_2O_3 – TiO_2$, given the known oxide and phase transformations in them within a given temperature range.

2.2 Models formation of solid solutions in the In_2O_3 - TiO_2 in the temperature range 1000 – 1450 °C in air

The samples fore research of the interaction in the system $In_2O_3 – TiO_2$ were prepared from powders of In_2O_3 special purity grade, TiO_2 – chemically pure grade. Additives introduced in the indium oxide in an amount of 0.5 – 50 mole.% TiO_2. Samples sintered in the temperature range 1000 – 1450 °C in air, followed by quenching in air.

The composition of phase and the parameters of a lattice were determined by X-ray. The parameter of a lattice was determined with an accuracy of ±0.0001 nm. The loss of mass was with an accuracy of ±0.0002 g. The calculation of the energy of transformation and formation of solid solutions found with an error ±0,01 eV. The relative error in determining the electrical resistivity, the carrier concentration n, mobility was 3 – 5 %.

2.3 The phase transformation in the oxide of indium

In the indium oxide during heating of the samples in X-ray chamber in the temperature range

25 – 1000 °C in air, the construction of the profile lines (211), (222), (400), (622) was found to split them in the temperature range 500 – 550 °C. These lines correspond to the splitting of the phase transformation from the ordered phase of the disordered type C^1. This transition is of the first kind and is reversible by cooling the samples from temperatures not above 1000 °C. The temperature of 550 °C is the critical point for a continuous function y = f(a) in which this function has a break of the first kind. There is a transformation in the phase of the type C^1. The new phase is disordered with respect to the original one. The parameter of lattice of the phase type C^1, determined by extrapolation of the direct parameters of lattice when heated to the point at room temperature (exclude thermal expansion), has a value of $a_{C^1} = 1.0115$ nm ± 0.0001 nm.

2.4 Mathematical calculation of energies of the phase transformation, the formation of solid solutions in the $In_2O_3 – TiO_2$

The energy of the solid solution on the basis of the disordered phase of C^1 can be estimated by the Boltzmann equation with different states of the system with the probability of the formula [8]:

$$P[A(T)] = Ao \exp(-u/kT) \tag{2}$$

where Ao – the overall frequency of lattice vibrations starting positions, A – the function of the physical parameters of the system depending on the temperature (violation of the order of anion vacancies in the structure of type C). For the two states of a solid at temperatures T_1; T_2, the relative probability of finding the energy states of solids can be determined

$$\frac{P[A(T_1)]}{P[A(T_2)]} = \frac{\exp(-\frac{\phi}{kT_1})}{\exp(-\frac{\phi}{kT_2})} \tag{3}$$

where: φ – the energy state of a solid; k - Boltzmann constant current, T °K – temperature solid state. The energy of the solid solution based on indium oxide is determined by the formula:

$$\phi = \frac{T_1 T_2}{T_2 - T_1} k \ln \frac{V_1}{V_2} \qquad (4)$$

where V_1, V_2 - the volumes elementary cells of the solid solution of indium oxide at different temperatures. At high temperatures, 1000 – 1450 °C changes the chemical composition of indium oxide and titanium on the content of oxygen.

In the structure of the indium oxide appear more anionic vacancies. Its vacancies are change of physical properties of samples on based of the indium oxide: the parameters of lattice, the electric resistance of sample, weight decrease of samples, changed color from yellow to black.

The excess charge of anionic vacancy is compensated by the formation of centers of color. The recovery of indium oxide with the formation centers of color of samples is next formula:

$$InO_{1,5} \rightarrow InO_{1,5-0,5x}\upsilon[F]_{0,5x} + 0,25xO_2 \uparrow \qquad (5)$$

where x – deviation from stoichiometry, v [F] - color centers are formed by the reaction of:

$$In^{2+} + v(O) \rightarrow In^{3+} + v[F] \qquad (6)$$

On the determinate values of the radius of the cations of titanium and indium, can be to assume that in this system can be form solid solutions bounded: solid solution subtraction - substitution - introduction, solid solution subtraction – substitution. The formation of solid solutions based on indium oxide made according to the following scheme: at 1100 °C appear a composition In_2TiO_5-orthorhombic modification, which with increasing annealing temperature is reacted with a base – disordered phase C^1 to form a limited solid solutions. At 1300, 1450 °C there is a loss of the samples for all compositions (Fig. 1).

On the curves appear of a peak for samples with concentrations of 2 mol. % TiO_2, which is incremented at1450 °C. The presence and increase of the peak in the temperature dependence of the loss of the mass of the samples can be explained by the following rule. In the structure of indium oxide have additional anion vacancies in the structural positions and positions Frenkel and the presence of small additions of cations of the titanium with of different valences in the structure, which cause disturbances in the vibrations of the atoms, which leads to a local deformation complex interactions of the atoms in the lattice.

In these areas the oxygen can be easily moved to the surface and evaporates, in these solid solutions is ionic conductivity, accompanied by the formation of local areas with broken electronic conductivity. The peak of the loss of weight for samples with a concentration of 2 – 5 mol.% TiO_2 in the solution decreases, but remains substantially different depending from the temperature of annealing. Such a pattern can be explained by the appearance of another type of solid solution in which there are cations of different valences of titanium in the structural positions of indium oxide and oxygen associated with them. Mobility of these complexes reduced and they have electronic conductivity. The loss of mass for samples of 1:1 increased.

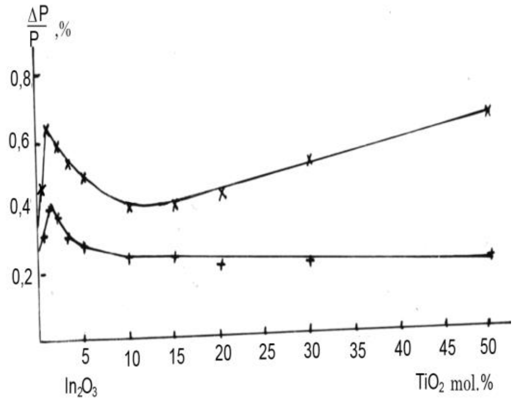

Fig. 1 – The loss of weight of sample in the system In_2O_3 – TiO_2 depending on the annealing temperature in air 1300° C, x – 1450 °C

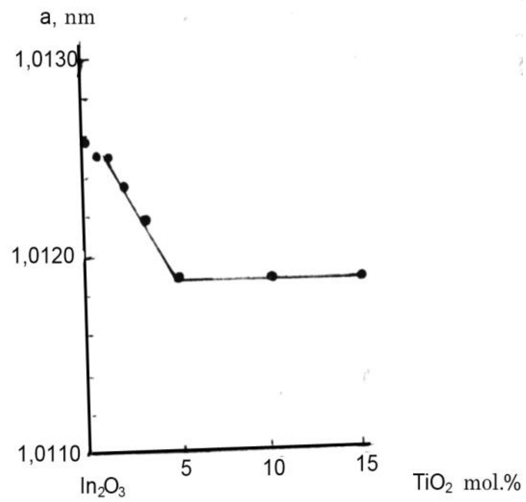

Fig. 2 – The dependence of the parameter of unit cell of solid solutions in the In_2O_3 – TiO_2 after annealing at 1450 °C

Fig. 2 held unit cell parameters of a solid solution obtained after annealing at 1450 °C. On the dependence of parameter of lattice have different slopes: for compositions (0 – 2 mol.% TiO_2) in the solution, there is one slope and to compositions (2 – 5 mol.% TiO_2), the other slope of the parameter of lattice, which indicates a different mechanism of formation of the solid solution oxide indium.

According to our data, we can assume that at 1300, 1450 °C in samples of (0 – 2 mol.% TiO_2 + 100 98 mol.% In_2O_{3-x}) is formed: solid solution (subtraction – substitution – inculcation), and for samples of (2 – 5 mol.% TiO_2 + 98 – 95 mol.% In_2O_{3-x}) – subtraction – substitution.

The probability of formation of such solutions is determined by the geometric probability of the first type W = 0.11; for 2 type W = 0.14. The energy of formation of solid solutions for a determined formula (4) is respectively 1.72 eV and 0.98 eV .

The solid solution of subtraction – substitution – inculcation of a mathematical model can be

$$(1-y)InO_{1,5-0,5x}\upsilon[F]_{0,5x}+yTiO_2\rightarrow(In^{3+}_{1-y}\upsilon[F]_{0,5x}Ti^{4+}_{y-u}[Ti^{3+}]\upsilon(k)_u)O_{1,5-0,5x-0,5y} \quad (7)$$

where u-cation concentration Ti^{4+}, Ti^{3+} – embedded in the non-structural position $\upsilon(k)_u$ – Frenkel defects.

Dependence (u) of the temperature T and the composition (y) of the solid solution is defined by a minimum free energy

$$\Delta\Phi(x,y,u)=[0,5\phi_{v(O)}-0,5\phi_{v(F)}+A-0,25F](x)+\phi_{subs}(y-u)-\phi_{incul.}(u)-T\Delta S(x,y,u) \quad (8)$$

where $\phi_{subs.}(y-u)$ – the free energy of the substitution of cations In^{3+} on Ti^{4+};Ti^{3+}, $\phi_{incul}(u)$ – the free energy of the inculcation cations Ti^{4+}, Ti^{3+} in the non-structural position of the indium oxide lattice; $T\Delta S$ (x, y, u) – the entropy of the solid solution – subtraction – substitution – inculcation.

The solid solution type subtraction - substitution for the samples of composition (2 – 5mol.% TiO2) in a solution of indium oxide can be present mathematical model (9):

$$(1-y)InO_{1,5-9,5x}\upsilon[F]_{0,5x}+yTiO_2\rightarrow(In^{3+}_{1-y}\upsilon[F]_{0,5x}[Ti^{3+},Ti^{4+}_y])O_{1,5-0,5x-0,5y}+0,25xO_2\uparrow \quad (9)$$

where y – the addition of TiO_2.

The change in free energy of formation of solid solution type subtraction - substitution on the basis of non-stoichiometry type C[1] indium oxide (2 – 5 mol.% – TiO_2) is determined by the addition of titanium dioxide

$$\Delta\Phi(x,y)=[0,5\phi_{\upsilon(O)}-0,5\phi_{\upsilon(F)}+A-0,25F](x)+\phi_{subs}(y)-T\Delta S(x,y), \quad (10)$$

where $\phi_{\upsilon(O)}$ – the free energy of formation of anionic vacancies, $\phi_{v(F)}$ – free energy of formation of color centers; A – the energy of the electron affinity of the anion; F – transition energy of oxygen in the gas environment; $\phi_{subs.}(y)$ – is of free energy substitution of cations In^{3+} on Ti^{4+},Ti^{3+}, ΔS (x, y) – is of entropy change of formation of solid solution.

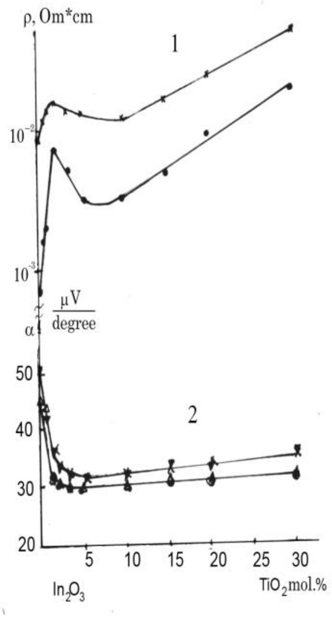

Fig. 3 – 1) Changes in electrical resistance of the samples, and 2) the coefficient of thermal EMF of samples based on indium oxide with the addition of titanium oxide: ▲ – after annealing at 1300 °C, ● – after annealing 1450° C

The formation of solid solutions: subtraction – substitution – inculcation, subtraction - substitution in this system proved change of electrical resistance of the samples, thermal EMF, carrier concentration and mobility. The temperature dependences electric resistance of the sample and thermal EMF of solid solutions on the basic indium oxide with the addition of titanium oxide is on (Fig. 3).

Similar containers observed patterns of the mechanisms of formation of solid solutions in the system.

The energy of free carriers charge of the conductivity of the samples with additives to 2 mol.% TiO_2 in the solution is φ = 2.20 eV, and the thermal EMF decreases harsh.

Samples with additives 2 – 5 mol.% TiO_2 have the energy of free carriers charge is reduced to φ = 0.93 eV, and the thermal EMF decreases slightly. In the two-phase region of the solid solution (solid solution subtraction – substitution and a connection

In Ti_2O_{5-x}) is the energy of the conduction of free carriers increases to φ = 1.77 eV. In_2TiO_5-orthorhombic modification compound remains after annealing at 1450 °C with the electrical resistance of composition 1:1 ρ = 2.8 10^{-1} Om cm; n = 1,2 1019 cm^{-3}; μ = 5 cm^2/V s.

In the samples of indium oxide with additives of up to 2 mol. % TiO_2 in increase in the concentration of carriers charge and their mobility decreases sharply as a function of annealing temperature. These data confirm the presence of the solid solution type, subtraction – substitution – inculcation with of the ion-conducting. The addition 2 - 5 mol. % TiO_2 in indium oxide lead to the formation of the solid solution type subtraction - substitution, where concentration of the carrier charge varies slightly depending on the annealing temperature and the mobility remains practically constant, which depends on the annealing temperature. Such a solution has electronic conductivity. A connection In_2TiO_{5-x} with a mixture of a solid solution of the type subtraction - of substitution leads to a decrease in the concentration of the carriers of charge and their mobility. The probability of formation of a solid solution-type subtraction replacement for the introduction of samples of indium oxide with addition of up to 2 mol. % TiO_2 in solution can be determined according to the charge carrier mobility of formula:

$$W = \frac{\mu kT}{Zed^2} \quad (11)$$

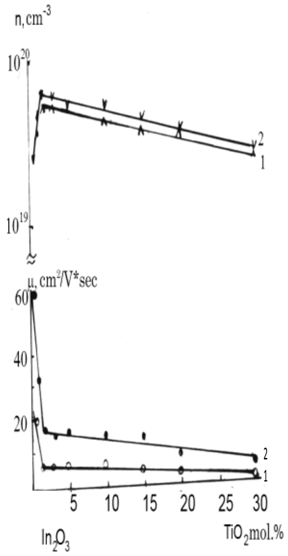

Fig. 4 – 1) Changes in the concentration of free carriers charge and their mobility in branch based on indium oxide with the addition of titanium oxide: 1 – after annealing at 1300 °C, 2 – after annealing at1450 °C

where μ – the mobility of the charge carriers , Ze – a charge carrier , k – Boltzmann constant , d – the distance between the lattice sites.

The probability of solid solution subtraction - substitution – inculcation with ironically conductive solution W = 0.11; and the probability of solid solution subtraction - substitution electronic conductivity W = 0.14.

These findings are consistent with calculations based on geometric probability (Fig. 2 and Fig. 3), indicating on regular basis and calculation mechanisms for the formation of limited solid solutions in the system based on the type C[1] with the addition of titanium dioxide.

3. SUMMARY

1. The formation of solid solutions based on indium oxide with the addition of titanium dioxide flows through a complex scheme: at 1100 °C forms a compound In_2TiO_{5-x} rhombic modification. At 1300, 1450 °C there is a loss of the samples for all compositions. Curves at a peak for the samples with concentrations of 2 mol.% TiO_2, which increases at 1450 °C, in this concentration increases: the electrical resistivity, concentration carrier; decrease: the lattice parameter and the mobility of the carriers charge, change the color of the samples. In this concentration of the solid solution based on indium oxide solid solution exists subtraction – substitution – inculcation with of an ion-conducting of the carriers charge

2. If increasing additives titanium dioxide at 2 – 5 mol.% TiO_2 in the solid solution based on indium oxide decreases: the loss of the mass of samples, the parameter of lattice, electrical resistivity, the concentration of carrier decreases slightly in depending on the annealing temperature, the mobility of carriers charge does not change in this concentration range, but much depends on the annealing temperature. In this area, the concentrations of the solid solution type subtraction - substitution.

3. Defined: the formation energy of these solutions, the conductivity type of carriers charge, energy conduction carriers.

4. The structure and physical properties of the compound In_2TiO_{5-x} were formed.

REFERENCES

1. Z.S. Volchenkova, V.M. Nedopeki, Izvestiya of USSR Academy of Sciences Inorganic materials **11** No. 8. 1412 (1975)
2. L.V. Morozova, P.A. Tihonov, V.B. Glushkova, Izvestiya of USSR Academy of Sciences Inorganic materials **27**, No. 2, 291 (1991).
3. V.A. Gritsenko, K.A. Nasyrov, D.V. Gritsenko, etc., FTP **39** No. 6,748 (2005).
4. V.Ya. Shevchenko, S. Barinov, Technical Keramika. (Moscow: Nauka: 1993).
5. A.U. Solovieva, J. nano - electronic fiz. **2** № 3,103 (2010).
6. A.E. Solovieva, J. nano - electronic fiz. **3** № 4,114 (2011).
7. G.V. Samsonov, Physico-chemical properties of oxides.(Moscow: Metallurgy: 1978).
8. H.F. Worth, P. Thomson, Physics of solid body. (Moscow: Mir: 1969)

   V.S. Postnikov, Physics and chemistry of solid state (Moscow: metallurgy: 1978).

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