SOLUBILITY AND DIFFUSION OF CHEMICAL ELEMENTS IN HIGH-TEMPERATURE_SUPERCONDUCTORS

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Abstract

Solubility and diffusion of admixtures of cationic (Ni, In, Sn, Au, Cd, Bi, Ag, Y, Hg) and anionic (S, Se) subsystems in structural-inhomogeneous HTSC-polycrystalline YBa₂Cu₃O₇₋₈ and $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ were studied. Methods of radioactive indicators, X-ray spectral microanalysis, scanning electron microscopy, and electron Auger spectroscopy were used.

We have investigated solubility and diffusion of admixtures of cationic and anionic subsystems in polycrystalline HTSC, $YBa_2Cu_3O_{7-\delta}$ and $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ by the method of radioactive isotopes [1-22]. Two types of diffusion processes were found: the slow and fast one. It was shown that a fast component of diffusion coefficient was due to migration processes of diffusing elements across grain boundaries (surface diffusion) and the slow one was due to a spatial diffusion. It was found a change of diffusion mechanism for Ni, Au, S, Ag in the YBa2Cu3O7-8 material in the temperature range of 573-673K. The above mentioned effect was assigned to generation of oxygen vacancies in Cu-0-planes of the crystal lattice of a superconductor. The nature of temperature dependencies of the slow and fast components of diffusion coefficient allowed to conclude that violation of stoichiometry by oxygen had an influence on both the spatial and the surface diffusion.

Let us discuss experimental results by an example of studies of solubility and diffusion of Ni, In, Sn, Bi, S, Se [1-3, 5-8, 11] and admixtures in HTSC ceramics of YBa₂Cu₃O₇₋₈ and (Pb_xBi₁.

HTSC-ceramics samples were produced by a method of solid-phase synthesis. Production $_{x})_{2}Ca_{2}Sr_{2}Cu_{3}O_{v}$ technology of YBa2Cu3O7-8 ceramics was described in the works [1-3]. This ceramics was a singlephase system having orthorhombic structure, average crystallite size was 5-20 μ m. Granular chemical composition corresponded to the phase 1-2-3. The specimens exposed a transition to a superconducting state at Tc = 92K, a transition width was Tc = 1.5 K.

A density of ceramics was 5,5 g/cm³.

Production technology of $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ was described in the works [1,4]. The mentioned ceramics was a single-phase homogeneous system with a content of 2223 phase not more than 95 %. Transition to the superconducting state was in the range of 116-110K, ceramics density was 4,6 g/cm³. Average granular size was 20-30 µm.

It should be noted that in the intergrain boundary area significant variations in a chemical composition were not found according to the data obtained by means of scanning electron microscope equipped with X-ray spectral microanalyser ICXA-7 33 type JEOL (Japan).

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The ⁶³Ni, ¹¹⁴In ¹¹³Sn, and ²⁰⁷Bi isotopes were used when studying diffusion of nickel, indium and tin by a method of radioactive indicators. A salt of the corresponding metal isotope, $Ni(NO_3)_2$, $Sn(NO_3)_2$, $InCl_3$, $Bi(NO_3)_3$ was applied on a surface of the ceramic specimen from a solution. A thickness of the salt coating was 100 μ m.

³⁵S, ⁷⁵Se isotopes were used for studying a diffusion of sulphur and selenium.

Diffusion profiles were formed in the temperature range of 200-500 °C with a step of 25 °C. Diffusion of sulphur into ceramic samples was carried out from the vapor phase during 20-80 hours, diffusion of selenium was carried out from 6 to 57 hours. Diffusion profiles of Ni, Sn, In and Bi were formed in air for 6-57 hours.

Uniformity of the coating and a diffusion front across a sample area was controlled by a method of layer to layer autoradiography.

It was suggested that a diffusion from a constant source took place in a given case. Diffusion profiles were determined by a method of successive peeling of layers with a step of 3-5 μm to a depth of 150 μm and by measurement of a residual radioactivity. A diffusion coefficient was determined by a linearization method of erfc-function.

A value of Ni, In, Sn concentration near a surface was determined by a reference method and was not in excess of 10¹⁸ cm⁻³

Figure 1 shows diffusion coefficients of Ni, In, Sn versus temperature. D-values given in Fig.1 correspond to the average value of four measurements. Statistical treatment was carried out



Fig. 1. Diffusion coefficients vs. temperature: 1 - Ni, 2 - In, 3 - Sn.

by standard methods. Errors in estimating a diffusion coefficient and activation energy (E_a) were 30 and 10 percent, respectively. For nickel at the temperature of 400 °C (i.e., in the range of a start of oxygen depletion) a fracture is observed that indicates different diffusion mechanisms in the temperature intervals of 200-400 and 400-500 °C:

for the range of 200-400 $^{\circ}\mathrm{C}$ $D = 3.16 \cdot 10^{-10} \exp(-/O.17/kT) \text{ cm}^2/\text{s},$ for the range of 400-500 °C $D = 1.0 \cdot 10^{-2} \exp(-/1.3/kT) \text{ cm}^2/\text{s}.$

Since in ceramic materials of a density below that of a monocrystal, along with a volume diffusion, it appears, possibly, to be an occurrence of grain-boundary and surface diffusion mechanisms, the resulting experimental parameters (D_o and E_a) have an integral character.

It is noteworthy the fact that the temperature range of varying Ni diffusion parameters coincides with a temperature range of generating anion vacancies. This suggests that stoichiometry deviation by oxygen results in replacing a diffusion mechanism. It should be noted in connection with this, that an activation energy in the low temperature interval ($E_a = 0.17 \text{ eV}$) is a characteristic one for an internode mechanism, but in the high temperature range ($E_a=1.3 \text{ eV}$) - for a vacancy mechanism [3]. It should also be noted that $E_a = 1.3$ eV is close to an oxygen activation energy (1.24 eV) in crystals of CaWO₄.

In the temperature dependence of indium and tin diffusion coefficients in the temperature range being studied, features due to a change of a diffusion mechanism are not observed. At the same time, attention is drawn to a sharp difference of temperature dependencies of diffusion coefficients for such similar metals in atomic radii:

for indium (in the range of 200-500 °C)

 $\tilde{D} = 1.1 \cdot 10^{-8} \exp(-/0.26/kT)$,

for tin (in the range of 200-500 °C) $D = 8.0 \cdot 10^{-6} \exp(-/0.58/kT).$

A lack of breaks on In and Sn diffusion coefficients temperature dependencies may indicate that a stoichiometry deviation by oxygen (planar Cu-O) does not influence the respective diffusion flows. If the sharp difference in diffusion coefficient temperature dependencies observed experimentally is due to a difference in an electronic structure of outer electron shells of a difference in charge states of diffusing metals, so it is interesting to gain insight into a mechanism of this phenomenon. It should be noted that a difference in diffusion activation energy variations is symbate to a variation of ionization potential of atoms (In - 5.7864 eV, Sn - 7.344 eV).

In the studied temperature interval the sulphur concentration near the surface area of YBa2Cu3O7.8 (which was determined by standard methods corresponding to maximum solubility) had a little dependence on the temperature and decreased from $7 \cdot 10^{20}$ cm⁻² at 200 °C to $4 \cdot 10^{20}$ cm⁻³ at 500 °C.

Selenium concentration in near surface area of YBa2Cu3O7-8 did not depend on temperature and was $\sim 10^{20}$ cm⁻³ Increase in selenium solubility depending on the temperature was observed in (Pb_xBi_{1-x})₂Ca₂Sr₂Cu₃O_y. Limit of Se solubility was 10¹⁹ cm⁻³ at 200 °C and it was $\sim 10^{20}$ cm⁻³ in the range of 300-500 °C. Solubility of bismuth in the studied HTSC materials was not possible to determine in the limits of the measuring method.

The presence of two types of diffusion flows and corresponding diffusion processes (slow and fast) were determined by analysis of diffusion profiles in $YBa_2Cu_3O_{7.8}$ and (Pb_xBi_{1-x})₂Ca₂Sr₂Cu₃O_y ceramics.

Fig. 2(a) shows the temperature dependence of Ds(I) (slow) and Dq(2) (fast) components of sulphur diffusion coefficient in YBa2Cu3O7-8 ceramics. These data show exponential dependencies and a fracture point at 300 °C area, which indicates the different diffusion mechanisms. It should be noted that this point coincides with oxygen vacancy generation start in Cu-O planes that is probably the reason of change of diffusion mechanism.

It should be noted that similar dependencies of diffusion coefficients on temperature changes were observed in investigation of nickel and gold [4] in 1-2-3 ceramics.

Fig. 3(a) shows Ds and Dq sulphur temperature dependencies for (PbxBi1-x)2Ca2Sr2Cu3Oy

ceramics.

 $Ds = 6.9 \ 10^{-9} exp(-0.31/kT) \ cm^2/sec$ $Dq = 1.6 \ 10^{-8} exp(-0.15/kT) cm^{2}/sec$

When comparing the data on sulphur diffusion in and YBa2Cu3O7-8 $(Pb_{x}Bi_{1-x})_{2}Ca_{2}Sr_{2}Cu_{3}O_{y}$ it is possible to confirm that the threshold effects in bismuth ceramics connected with stoichiometry deviation in oxygen were not appeared. This principal difference of temperature dependencies of sulphur diffusion coefficient is probably connected with this fact.

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Fig. 2. Temperature dependencies of S, Se, Bi diffusion coefficients in $YBa_2Cu_3O_{7-\delta}$ ceramics a - S, $1 - D_s$, $2 - D_q$; b - Se, $1 - D_s$, $2 - D_q$; c - Bi.



Fig. 3. Temperature dependencies of S, Se, Bi diffusion coefficients in $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ ceramics a - S, $1 - D_s$, $2 - D_q$; b - Se; c - Bi.

Fig. 2(b) shows two components of selenium diffusion coefficient in $YBa_2Cu_3O_{7-\delta}$ ceramics:

for slow component: $Ds = 2.8 \ 10^{-8} exp(-0.28/kT) \ cm^2/sec.$ for fast component: $Dq = 3.0 \ 10^{-6} exp(-0.26/kT) cm^2/sec.m$

Temperature dependencies of selenium diffusion coefficient in $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ ceramics are: $D = 6.9 \ 10^{-7} \exp(-0.24/kT) \ cm^2/sec.$

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Fig. 3(b) shows that there are no effects connected with the presence of different flows in $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$. Therefore, the principal temperature dependence was observed in the mentioned materials

Table 1

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Diffusion parameters in compound $YBa_2Cu_3O_{7-\delta}$

Ele- ment	Iso- tope	Compound	Com- ponent	Do (cm ² /sec)	Ea (eV)	Temperature range (K)	Refere- nces
Ni	⁶³ Ni After U	Ni(NO ₃)2 JS treatment	fast	3.16*10 ⁻¹⁰ 1.0*10 ⁻² 2.7*10 ⁻⁹ 4.0*10 ⁻⁹	0.17 1.3 0.16 0.33	470 - 570 570 - 770 470 - 770 470 - 770	[1-3] [1-3] [1-3] [1-3]
In Sn Au	¹¹⁴ MIn ¹¹³ Sn ¹⁹⁵ Au	InCl ₃ Sn(NO ₃) ₂ AuNO ₃	slow slow fast fast	1.1*10 ⁻⁸ 8.0*10 ⁻⁶ 2.8*10 ⁻¹¹ 6.6 1.9*10 ⁻⁹ 1.9*10 ⁻² 1.0*10 ⁻⁸	0.26 0.58 0.072 1.62 0.13 1.08 0.41	470 - 770 470 - 770 570 - 670 670 - 770 570 - 670 670 - 770 470 - 770	[1-3] [1-3] [4] [4] [4] [4] [4] [11]
Bi Ag	²⁰⁷ Bi ¹¹⁰ Ag	B1(NO3)3 AgNO3	slow slow fast fast	3.16*10 ⁻⁹ 2.51*10 ⁻⁸ 4.4*10 ⁻⁶ 2.9*10 ⁻¹¹ 2.8*10 ⁻⁷	0.12 0.23 0.3 2.6 0.32	470 -670 670 -770 470 -670 670 -770 470 - 770	[22] [22] [22] [22] [14]
Cd	¹²⁵ MC d	$Cd(NO_3)_2$	slow fast	$4.5*10^{-5}$	0.26	470 - 770 470 - 570	[14] [11]
S	³⁵ S	vapor	slow slow fast fast	2.0*10 ⁻⁸ 5.0*10 ⁻⁷ 4.6*10 ⁻⁶	0.37 0.32 0.42	570 - 770 470 - 570 570 - 770	[11] [11] [11]
Se	75 S	vapor	slow fast.	2 8*10 ⁻⁸ 3 0*10 ⁻⁶	0.28 0.26	470 - 770 470 - 770	[11] [11]
Y	e 58 Y	YCl ₃	slow fast.	1.25*10 ⁻⁸ 1.9*10 ¹⁴	0.22 3.23	470 -670 670 -770	[22] [22]

It also should be noted that in $YBa_2Cu_3O_{7-\delta}$ ceramics the generated oxygen vacancies had no influence on selenium diffusion in the corresponding temperature range.

Let us consider the reasons of appearance of two components of the diffusion coefficient According to the general consideration and the data it should be noted that besides the volume diffusion, the intergrain boundary (surface) diffusion may appear in the ceramic materials, which density is lower than monocrystal one is. Hence, it is possible to suppose that the fast component of diffusion coefficient (for sulphur and selenium) is connected with migration through intergrain boundary and porous surfaces. The slow component of diffusion coefficient is connected with

This suggests that in case of sulphur diffusion, the stoichiometric deviation by oxygen in volume diffusion. Cu-O plane of YBa₂Cu₃O_{7-δ} has essential influence on the volume and surface diffusion (Fig. 2a).

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Try oxygen in (Fig. 2a).

When comparing the data obtained in the present work on sulphur diffusion with the data on nickel diffusion in and gold diffusion [4] in $YBa_2Cu_3O_{7-\delta}$ ceramics, it should be noted the next peculiarities:

1) a change in S diffusion mechanism occurs at 300 °C, when in case of Ni and Au diffusion this point is at 400 °C.

2) Activation energy of fast and slow processes in the temperature intervals before and after a change of a diffusion mechanism of S is different slightly (0.1 eV), but at the same time this value is 1.1 eV for Ni, $\sim 0.85 \text{ eV}$ for Au and accordingly $\sim 1.5 \text{ eV}$ for fast and slow processes.

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	Parameters of diffusion in comp	ound (Bi1-xPbx)2Ca2Sr2Cu3Ov
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Ele-	Iso-	Compound	Com-	Do	Ea	Temperature	Refere-
men	tope		ponent	(cm ² /sec)	(eV)	range (K)	nces
Ni	⁶³ Ni	Ni(NO ₃) ₂	fast	3 6*10.7	0.25	470 - 770	[1.5]
		(slow.	3.5*10 ⁻⁸	0.47	470 - 770	[1,5]
In	¹¹⁴ MIn	InCl ₃	fast	8.0*10 ⁻⁷	0.27	470 - 770	[1,5]
			slow.	8.0*10 ⁻⁹	0.16	470 - 770	[1,5]
Sn	¹¹³ Sn	$Sn(NO_3)_2$	fast.	4.0*10-6	0.3	470 - 770	[1,5]
	105		slow.	2.3*10-5	0.57	470 - 770	[1,5]
Au	¹⁹⁵ Au	AuNO ₃		5.0*10 ⁻⁹	0.3	470 - 770	[4]
Bi	²⁰⁷ Bi	$Bi(NO_3)_3$		4.3*10 ⁻⁸	0.44	470 - 770	[11]
Ag	¹¹⁰ Ag	AgNO ₃	slow.	$1.3*10^{-9}$	0.13	470 - 770	[22]
	126.4		fast.	2.5*10-7	0.056	470 - 770	[22]
Cd	¹²⁵ C	$Cd (NO_3)_2$	slow.	1.3*10-6	0.31	470 - 770	[14]
~	35 -		fast.	7.6*10°	0.28	470 - 770	[14]
S	³³ S	vapor	slow.	6.9*10 ⁻⁹	0.31	470 - 770	[11]
~	75 a		fast.	1.6*10*	0.15	470 - 770	[11]
Se	Se	vapor		6.9*10*/	0.24	470 - 770	[11]

This phenomenon may be connected with the fact that sulphur is the nearest oxygen analogue and is the most sensitive element to the structural changes in anionic sublattice of HTSC.

Fig. 2(b) shows that the stoichiometric deviation by oxygen in Cu-O planes has no an essential influence neither volume nor surface diffusion of selenium. In case of selenium diffusion in $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$, the surface diffusion mechanism is probably dominating (Fig. 3, b).

It is characteristic that on the coordinate dependencies of bismuth concentration in the studied ceramics, one position was only observed (Fig. 2, c and Fig. 3, c). Experimental curves confirm exponential character of temperature dependencies of diffusion coefficient and have no any peculiarity in the area of oxygen vacancy generation.

For YBa₂Cu₃O₇₋₈ ceramics:

 $D = 1.0 \ 10^{-8} \ \exp(-0.41/kT) \ cm^2/sec$

For $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_{y;1}$

 $D = 4.3 \ 10^{-8} \exp(-0.44/kT) \ cm^2/sec.$

Because Do and Ea bismuth diffusion parameters slightly depend on type of HTSC ceramics, we suppose that the defining factor stipulating mechanism of realization is a polycrystalline structure of studied materials. Temperature dependence of diffusion coefficient observed during the test, may be connected with bismuth migration through the intergrain boundaries and pore surfaces of YBa₂Cu₃O₇₋₈ and (Pb_xBi_{1-x})₂Ca₂Sr₂Cu₃O_y ceramics.

A higher D value for $(Pb_xBi_{1,x})_2Ca_2Sr_2Cu_3O_y$ ceramics (porosity W ~ 30 %) in comparison with YBa₂Cu₃O_{7- δ} ceramics (W ~ 14 %) at the same temperature (Fig. 2, c and 3, c) and relatively low values of activation energy of diffusion processes (0.44 eV and 0.41 eV, respectively) with high values of atomic mass and atomic radius of bismuth approve the last assumption.

Parameters of diffusion of chemical elements in HTSC ceramics in YBa2Cu3O7-8 and $(Pb_xBi_{1-x})_2Ca_2Sr_2Cu_3O_y$ are given in Tables 1 and 2.

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