

The suitability of various substrates for $\text{YBa}_2\text{Cu}_3\text{O}_y$ thin film formation: thermodynamic and structural considerations

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Abstract

Thermodynamic simulation of chemical interactions and lattice period misfits of the 123 phase with various substrate (contact) materials was carried out by computer. The following types of contact were distinguished: nonreactive (Ag, Pd, Pt, Au, SrTiO_3 , MgO, MgAl_2O_4 , Ba_2SiO_4 , CuO, Y_2BaCuO_5 , BaCuO_2 , BaF_2 , HfO_2 , ZrO_2 , TiO_2 , CaF_2 , Nb_2O_5), partially destroying (Y_2O_3 , Ag_2O , SrSiO_3 , Al_2O_3 , Cu, C, V_2O_3 , WO_2) and totally destroying (Si, W, V, Ti, Zr, Hf, Fe, Nb, Sn, In, Ga, SiC, SiO_2 , GdN) the 123 phase.

INTRODUCTION

In an earlier paper [1] there were presented and discussed the results of thermodynamic simulation (TS) of the chemical interaction of $\text{YBa}_2\text{Cu}_3\text{O}_y$ (123- O_y) SC-phase in an inert gas environment (Ar) with Ti, Zr, Hf, Nb, Fe, W, V, Si, Cu, Pd, Pt, Ag, Sn, In, Ga, CuO, Y_2O_3 , ZrO_2 , HfO_2 , MgO, Al_2O_3 , TiO_2 , SiO_2 , WO_2 , SrSiO_3 , GdN, BaCuO_2 , Y_2BaCuO_5 , MgAl_2O_4 , BaF_2 , CaF_2 , Ba_2SiO_4 , Nb_2O_5 , SiC, C, Ag_2O and CdN at 100–1500 K and normal pressure. The initial systems had the following composition: 1 mol of 123 phase + 1 mol of substance + 1 mol of Ar. In addition to the materials of ref. 1, the results of TS of 123 phase interaction with Au and SrTiO_3 in an Ar environment were used.

The initial 123 phase was considered as an ideal solution $0.85\text{YBa}_2\text{Cu}_3\text{O}_7 + 0.15\text{YBa}_2\text{Cu}_3\text{O}_6$ (mole fractions), equivalent to the composition of $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$. The basis of the choice of phase model, the essence of the TS method, the thermodynamic functions of the com-

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ponents of studied systems and sources of data about them were given in ref. 1–3.

THERMODYNAMICS AND CRYSTAL CHEMISTRY OF CONTACTS

In this work we have carried out the analysis of crystal structures of contacting phases on the boundary of the system “123 phase–substrate (contact) material” with the aim of their comparison to establish the character and possibility of conjugation of structures in this system.

We tried to find a connection between the correspondence of the parameters of 123 phase crystal lattices and the contacting material with the character of their chemical interaction in an inert gas environment.

Formation of a film is a phase transition of primary origin; from a three-dimensional vapour (or liquid) phase on the substrate surface form and grow embryos of the condensed phase.

Experimental data show the existence of a large number of ordered structures on the film–substrate boundary; depending on the energetic and crystallogometric parameters, phase diagrams for quasi-two-dimensional systems can be rather complicated. The main reason for this variability is the superposition of the complex periodic field of the substrate on the interaction of the film’s atoms with each other [4].

To analyse transformations in thin films (or, better, in the transition layer) one must take into consideration two main features of these systems: their characteristic dimensional effects (i.e. elasticity properties) and the influence of the substrate itself (meaning its energetic and crystallogometric parameters). In the present paper the elastic properties of the film–substrate system are not considered.

Two-dimensional structures on the film–substrate boundary can be divided into two main classes [4].

- (1) Coordinated structures, where the relation of periods of the film and substrate lattices is expressed by an integer (simple coordinated structures) or by a broken rational number (cone structures). In the first case all atoms of the film occupy energetically equivalent positions on the substrate surface, in the second only some atoms are in equivalent positions.
- (2) Uncoordinated structures with irrational relationship of the film and substrate periods. In this case only a more or less extensive order can be established in the film.

It is obvious that if the energy of interaction between the atoms of the film is less than the energy of their interaction with the substrate, i.e. the potential well is deep enough, coordinated structures are formed. In the opposite case a shallow potential well cannot rigidly localize the film atoms, so leading to the formation of uncoordinated structures [4].

In particular, during studies of epitaxial growth of films, one should

take into consideration that film growth is realized more easily if the difference in parameters of the two lattices is no more than 10% [5]. In this case there are no marked distortions of the film lattice, which favourably influences its properties. Thus, close reliable contact between phases is established. We consider the initial ideal to be defect-free structures of surfaces of the film–substrate system. If the difference between parameters is more than 10%, distortion of the film lattice occurs in the transition layer between the film and the substrate, which leads to an accumulation of structure defects, appearance of dislocations and to probable chemical interaction at a definite temperature with the appearance of new phases.

The systematic study and analysis of the crystal structures' states and the character of interaction on the boundary between two phases, one of which is $\text{YBa}_2\text{Cu}_3\text{O}_y$, were carried out at room temperature. Comparison of results of studies of chemical interaction of the 123 phase with the substrate material [1] and the data of Table 1 allow us to distinguish several groups of substances. Because of a lack of experimental data on heat expansion for some phase–substrate pairs at present, it is difficult to carry out an analysis of behaviour of the system “123 film–substrate material” beginning from the temperature of film preparation to the temperature of its future application.

The first group consists of substances chemically inert to the 123 phase. During contact with them $\text{YBa}_2\text{Cu}_3\text{O}_y$ retains its superconducting properties ($y > 6.5$ – 6.65 [6]) in a definite temperature range, which agrees with the experimental data surveyed in ref. 1. Such materials are Ag, Pt, Pd, Au, BaCuO_2 , MgO , Y_2BaCuO_5 , MgAl_2O_4 , SrTiO_3 and Ba_2SiO_4 . They are characterized by a crystal lattice (cubic) with parameters coordinating with those of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ lattice in limits not exceeding 10% (simple coordinated structures). Exceptions are Y_2BaCuO_5 and Ba_2SiO_4 , which have an orthorhombic crystal lattice with parameters a_0 , b_0 , c_0 correlated with the analogous parameters of the 123 phase, as shown in Table 2.

In general form, for these phases we can write

$$\frac{a_0}{a_{0123}} \approx 2 \quad \frac{b_0}{b_{0123}} \approx 3 \quad \frac{c_0}{c_{0123}} \approx 0.5$$

These relations meet the permissible level of deviations within 10%.

However, doubt is aroused by the fact that, for a group of substances (CuO , BaF_2 , HfO_2 , ZrO_2 , TiO_2 , CaF_2 , Nb_2O_5) for which, according to ref. 1, no chemical interaction with the 123 phase was found, there is no good coordination (within 10%) of the crystal lattices of the contacting phases (Table 1). These chemically inert phases (according to ref. 1) have, as a rule, a more complicated crystal lattice than the cubic one. In ref. 1, some phases were not taken into account during calculations for systems with their participation owing to the absence of thermodynamic properties. For

TABLE 1
 Characteristics of interaction and structures of contacting phases. Structural data taken from refs. 7–11

Substance	Fraction of SC phase in the mixture of phases	γ	Impurity phases according to ref. 1	Crystal structure of substrate			Deviation of periods from lattice periods of SC phase (%)	δ (%)	
				Syngony	Lattice parameters (Å)				
				<i>a</i>	<i>b</i>	<i>c</i>			
YBa ₂ Cu ₃ O _y	–	6.65		Orthorhombic ^a	3.842	3.914	11.742		
<i>Substances inert to 123 phase according to calculations</i>									
Ag	0.5	6.85	$\approx 10^{-6}$, BaCuO ₂ + CuO	Cubic	4.086	–	–	<i>a</i> – <i>a</i> + 6.35 <i>a</i> – <i>b</i> – 4.39 3 <i>a</i> – <i>c</i> + 4.4 <i>a</i> – <i>a</i> + 1.25 <i>b</i> – <i>a</i> – 0.61 3 <i>a</i> – <i>c</i> – 0.6 <i>a</i> – <i>a</i> + 2.11 <i>a</i> – <i>b</i> + 0.24 3 <i>a</i> – <i>c</i> 0	<10 Simple structure <10 ³ Simple structure <10 Simple structure <10 Simple structure <10 Simple structure <10 Simple structure <10 Simple structure <10 Simple structure
Pd				Cubic	3.89	–	–		
Pt				Cubic	3.9233	–	–		
Au				Cubic	4.0781	–	–		
SrTiO ₃				Cubic	3.9051	–	–		
MgO				Cubic	4.208	–	–		

TABLE 1 (continued)

Substance	Fraction of SC phase in the mixture of phases	γ	Impurity phases according to ref. 1	Crystal structure of substrate			δ (%)
				Syngony	Lattice parameters (Å)		
				a	b	c	
ZrO ₂				5.07	-	-	+31.96 >10
TiO ₂				4.172	-	-	-13.6 <10
CaF ₂				5.462	-	-	+8.6 +6.6 -6.95 <10
				21.34	3.816	19.47	+1.6 -7.4 <10
				3.607	-	3.925	$a/6 - a$ $b - b$ -2.5 -2.5 <10
Nb ₂ O ₅	0.5	6.85		6.19	3.65	3.94	$a - a$ $a - b$ -7.84 +0.3 +5.5 <10'
<i>Substances totally destroying the 123 phase (at the assumed ratio of initial phases)</i>							
Si	0	-	Cu, Cu ₂ O, Ba ₂ SiO ₄ , BaSiO ₃ , Y ₂ BaCuO ₅	5.4282	-	-	+41.29 +38.7 -7.5 38.7
				6.636	-	-	$a/2$ $a/2 - b$ -13.6 -15.23 +13.1 13.05

W	0	-	Cu, Y ₂ BaCuO ₅ , BaO, WO ₂ , WO ₃	Cubic	3.1652	-	-	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 3 <i>a</i> - <i>c</i>	-17.6 -19.1 -19.1	17.62
V	0	-	Cu, BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, V ₂ O ₃	Cubic	3.0282	-	-	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 3 <i>a</i> - <i>c</i>	-21.16 -22.6 -14.1	14.1
Ti	0	-	Cu, BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, TiO ₂	Ti- Hexagonal	2.95	-	4.6843	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 2 <i>c</i> - <i>c</i>	-23.2 -24.6 -20.2	20.2
Ti	0	-	Cu, BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, TiO ₂	Ti Cubic	3.287	-	-	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 3 <i>a</i> - <i>c</i>	-14.45 -16 -16	14.45
Zr	0	-	Cu, BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, ZrO ₂	Hexagonal	3.2317	-	5.1476	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 2 <i>c</i> - <i>c</i>	-15.9 -17.43 -12.3	12.3
Hf	0	-	BaCuO ₂ , Cu, Y ₂ BaCuO ₅ , BaO, HfO ₂	1135 K Cubic Hexagonal	3.609	-	-	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 3 <i>c</i> - <i>c</i> <i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 2 <i>c</i> - <i>c</i>	-6.06 -7.9 -7.8 -16.8 -18.4 -13.95	<10 14
				>2050 K Cubic	3.615	-	-	<i>a</i> - <i>a</i> <i>a</i> - <i>b</i> 3 <i>a</i> - <i>c</i>	-5.9 -7.64 -7.62	<10

TABLE 1 (continued)

Substance	Fraction of SC phase in the mixture of phases	γ	Impurity phases according to ref. 1	Crystal structure of substrate			δ (%)		
				Syngony	Lattice parameters (Å)				
				<i>a</i>	<i>b</i>	<i>c</i>			
Fe	0	-	Cu ₃ , BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, Fe ₂ O ₃ , Fe ₃ O ₄	Cubic	2.8665	-	23.4	<i>a</i> - <i>a</i>	-23.4
								<i>a</i> - <i>b</i>	-26.8
								4 <i>a</i> - <i>c</i>	-2.33
				Cubic	3.6467	-	<10	<i>a</i> - <i>a</i>	-5.03
				1189 K				<i>a</i> - <i>b</i>	-6.83
								3 <i>a</i> - <i>c</i>	-6.8
Nb	0	-	Cu, BaCuO ₂ , BaO, Y ₂ BaCuO ₅ , Nb ₂ O ₅	Cubic	3.3002	-	12.44	<i>a</i> - <i>a</i>	-14.1
								<i>a</i> - <i>b</i>	-15.7
								4 <i>a</i> - <i>c</i>	-12.4
Sn	0	-	Cu, BaCuO ₂ , BaO, Y ₂ BaCuO ₅ , SnO	Cubic	6.5043	-	10.8	<i>a</i> /2	-15.3
								<i>a</i> /2 - <i>b</i>	-16.9
								2 <i>a</i> - <i>c</i>	10.8
								<i>a</i> /2 - <i>a</i>	-24.1
In	0	-	Cu, BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, In ₂ O ₃	Tetragonal	5.8312	-	15.7	<i>a</i> - <i>a</i>	+19.74
								<i>a</i> - <i>b</i>	+16.2
								2 <i>a</i> - <i>c</i>	-21.67
								2 <i>c</i> - <i>c</i>	-15.7
Ga	0	-	Cu, BaCuO ₂ , Y ₂ BaCuO ₅ , BaO, Ga ₂ O ₃	297 K	4.5258	4.5185	15.4	<i>a</i> - <i>a</i>	+17.9
								<i>b</i> - <i>b</i>	+15.4
								<i>c</i> - <i>c</i>	-34.8

TABLE 1 (continued)

Substance	Fraction of SC phase in the mixture of phases	y	Impurity phases according to ref. 1	Crystal structure of substrate			Deviation of periods from lattice periods of SC phase (%)	δ (%)	
				Syngony	Lattice parameters (Å)				
				a	b	c			
SrSiO ₃	2.2×10^{-2}	7.0	CuO, Ba ₂ SiO ₄ , Y ₂ BaCuO ₅ , Sr ₃ SiO ₅	High pressure orthorhombic	8.492	10.913	36.25	$a/2 - a$ +10.6 $b/2 - b$ +39.4 $b - c$ - 7.04	≈ 10
				Hexagonal	7.127	-	10.115	$a/2 - a$ - 7.2 $1/2 - b$ - 8.9 $c - c$ - 13.8 $a - a$ +23.9 $a - b$ +21.6 $c - c$ +10.7 $a - a$ +46.9 $a - b$ 14.1	10 on two axes
Al ₂ O ₃	0.2	7.0	Y ₂ BaCuO ₅ , BaCuO ₂ , BaAl ₂ O ₄	Trigonal	4.758	-	12.991	$c/2 - c$ - 3.53 $a/2 - a$ + 0.26 $a/2 - b$ - 1.6 $2a - c$ +34.6	> 10.7
				Hexagonal	5.64	-	22.65	$a - a$ +46.9 $a - b$ 14.1 $c/2 - c$ - 3.53 $a/2 - a$ + 0.26 $a/2 - b$ - 1.6 $2a - c$ +34.6	< 10
Substances partially destroying phase ($y = \delta$)									
Cu	0.3	6.0	Cu ₂ O, CuO, BaCuO ₂	Cubic	3.6148	-	-	$a - a$ - 5.9 $a - b$ - 1.9 $3a - c$ - 7.6	< 10

V ₂ O ₃	0.26	6.0	Y ₂ BaCuO ₅ , V ₂ O ₄ , BaCuO ₂ , Cu	Trigonal	4.933	–	13.94	<i>a</i> – <i>a</i> <i>a</i> – <i>b</i> <i>c</i> – <i>c</i>	+28.5 +26.03 +18.7	18.7
WO ₂	0.26	6.0	Y ₂ BaCuO ₅ , Cu, BaCuO ₂ , WO ₃	Monoclinic	5.56	4.884	5.546	<i>a</i> – <i>a</i> 2 <i>a</i> – 3 <i>a</i> <i>b</i> – <i>b</i> 2 <i>c</i> – <i>c</i>	+44.8 + 7 +24.8 – 5.5	24.8 on two axes
C	0.1	6.0	Cu, BaCO ₃ , Y ₂ BaCuO ₅ , Cu ₂ O	Hexagonal (graph- ite) Cubic (diamond)	2.4612	–	6.7078	<i>a</i> – <i>a</i> <i>a</i> – <i>b</i> 2 <i>c</i> – <i>c</i> <i>a</i> – <i>a</i> <i>a</i> – <i>a</i> 3 <i>a</i> – <i>c</i>	– 35.9 – 37.1 +14.3 – 7.11 – 8.87 – 8.9	14.27 <10

^a I.N. Dubrovind, personal communication.

TABLE 2

Substrate material	Ba ₂ SiO ₄		Y ₂ BaCuO ₅	
	Ratio of crystal lattice parameters of substrate material and 123 phase	Deviation from the rational number (%)	Ratio of crystal lattice parameters of substrate material and 123 phase	Deviation from the rational number (%)
$\frac{a_0}{a_{0123ph}}$	1.93 (≈ 2)	-3.5	1.85 (≈ 2)	-7.5
$\frac{b_0}{b_{0123ph}}$	2.6 (≈ 3)	-13	3.11 (≈ 3)	+4
$\frac{c_0}{c_{0123ph}}$	0.482 (≈ 0.5)	-3.6	0.494 (≈ 0.5)	-1

example, for BaF₂ and CaF₂ YOF was not considered; for HfO₂, BaHfO₃ and Ba₂HfO₄; for ZrO₂, BaZrO₃ and Ba₃Zr₂O₇; and for TiO₂, BaTiO₃. The structural characteristics of these phases are given in Table 3. We can suppose that, with due regard to all these phases in the corresponding systems, which (as is seen from Table 3), form coordinated structures with the 123 phase, chemical interaction will take place in another way, different from that found in ref. 1.

Thus, the possibility of conjugation of the 123 phase lattices with substrate (contact) material at the same time is the sign of chemically inert contacting phases. As stated, in the calculations reported in [1], owing to the lack of thermodynamic functions, some possible components of the

TABLE 3

Substrate material	Structural characteristics of some substances				
	Phases not considered in ref. 1	Type of structure	<i>a</i>	<i>b</i>	<i>c</i>
BaF ₂ , CaF ₂	YOF	Tetragonal	3.91	3.91	5.431
	BaHfO ₃	Cubic	<i>a</i> ₁ = 4.171 <i>a</i> ₂ = 8.333		
HfO ₂	Ba ₂ HfO ₄	Tetragonal	4.161	-	-
	BaZrO ₃	Cubic	4.193		
ZrO ₂	Ba ₃ Zr ₂ O ₇	Tetragonal	4.188	4.188	21.72
TiO ₂	BaTiO ₃	Tetragonal	4.0055	4.0055	4.0163

film–substrate system were not taken into account. Their introduction will increase the validity of the calculations.

In practice, for a group of materials having parameters of their crystal lattices differing from the 123 phase parameters by >10%, we observe total (for Si, W, GdN, SiO₂ and SiC) or partial (Cu, V₂O₃, WO₂, C and Ag₂O) [1] destruction of the 123 phase as a result of chemical interaction. Partial destruction of the superconducting phase, accompanied by degradation of the superconducting properties of the residual phase, manifests itself on contact with Hf, Ti, Zr, Nb, Fe, V, Sn, and Ga (Table 1).

Crystal lattices of the products of interaction for the variant of total destruction also do not conjugate with the lattice of the 123 phase (Table 1). For the variant of partial destruction, as a result, chemical interaction results in the formation of one or several phases with lattices which can conjugate with that of the 123 phase. The ratio of the phases involved allows the phase having the highest concentration to conjugate with the 123 phase. Thus, as a criterion of the possibility of chemical interaction of crystal substances in an inert environment, we can use the evidence of non-conjugation of crystal lattice parameters of contacting phases.

When the parameters of lattices are different (by >10%), chemical interaction proceeds as far as the total destruction of the 123 phase structure if, as a result of interaction substances with conjugated structure are not formed in a sufficient amount to prevent the contact of substances with non-conjugated structure.

The test of this hypothesis in practice is difficult enough, as real surfaces of crystals concentrate a huge number of structural defects, which leads to a considerable energetic effect of non-correspondence between the surface structure and the phase volume. Besides, the composition of the surface layer can noticeably differ from the volumetric composition because of adsorption, chemisorption or formation of an energetic binary layer.

During the analysis of the simulation results [1] we singled out a group of substances (Y₂O₃, SrSiO₃, Al₂O₃, Ag₂O) which can increase the oxygen content in the 123 phase (i.e. improve its superconducting properties). This phenomenon can have the following explanation; because the structures forming during 123 phase interaction with these substances are uncoordinated, chemical interaction, with the formation of intermediate phases, generates active oxygen, which fills oxygen vacancies in the 123 phase, thus improving its superconducting properties. Products of interaction contain a sufficient amount of phases that can conjugate by virtue of their structural parameters with the 123 phase (called “inert”) to cause a blockade of further interaction. Such phases are Y₂BaCuO₅ for Y₂O₃; Ba₂SiO₄ and Y₂BaCuO₅ for SrSiO₃; Y₂BaCuO₅ and BaCuO₂ for Al₂O₃; Ag for Ag₂O. Probably this group of substances can be considered as additional sources of oxygen, which has been experimentally proved for Ag₂O [11].

For a more thorough study of the problem touched upon in this paper, we are planning future improvement of the 123 phase model to take into account in the calculations all reduced Gibbs energies of all possible components in the corresponding systems, the elasticity properties of contacting materials, in particular thermal strains, and the conditions of preparation and maintenance of materials containing the “123 phase–substrate” system.

CONCLUSIONS

We have compared the parameters of crystal lattices of 123 phase and a number of substances used as substrates (contacts) at moderate temperatures (100–300 K) and normal pressure. Our supposition is that, for substrates with coordinated crystal structures, chemical interaction with 123 phase is unlikely.

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