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Chemical and materials science aspects of the studies of polycrystalline bismuth-based high-temperature superconductors

V S Kravchenko

Contents

I. Introduction 555
II. Characteristic physicochemical properties of bismuth-based high-temperature superconductors and systems forming them 556
III. Correlations of superconducting properties with the chemical composition and crystal structure of bismuth-based superconductors 568
IV. Conclusion 574

Abstract. The chemical and materials science aspects of the studies of bismuth-based materials exhibiting high-temperature superconductivity are considered. The knowledge on their crystal chemical features and chemical composition is generalised. Data on the phase equilibria and regions of thermal stability of bismuth-based superconducting phases are discussed. The effect of the crystal structure, chemical and phase composition on the properties of bismuth-based superconductors is considered. The bibliography includes 501 references.

I. Introduction

The history of bismuth-based high-temperature superconductors (Bi-HTSC) dates back to the discovery in 1987 of superconductivity in the cuprate $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ (phase 2201) with superconducting transition temperature $T_c \approx 20$ K.[1,2] Then more complex Bi-HTSC were discovered, in particular, $Bi_2Sr_2CaCu_2O_{8+\delta}$ (phase 2212, $T_c \approx 90$ K) and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (phase 2223, $T_c \approx 110$ K),[3,4] which are of great practical importance, especially phase 2223 (to facilitate its formation, some bismuth atoms are usually replaced by lead atoms).

From the practical standpoint, bismuth-based HTSC have a number of advantages over other HTSC: unlike, for example, Tl- and Hg-HTSC, they contain no toxic highly volatile elements; unlike Y- and REE-HTSC, they do not prone to degradation, contain no expensive elements and are fairly plastic. The last-mentioned fact is important for the design of extended articles such as tapes or wires from the polycrystalline Bi-HTSC-based composite in a silver shell.[5–11] Several years ago, (Bi,Pb)2223/Ag cables meant for industrial use rather than for laboratory experiments were designed;[12,13] currently, the manufacture of more than kilometre-long tapes presents no considerable difficulty.[14,15] Nevertheless, their wide use is still hampered by a number of economic, technological and engineering reasons.[16,17] The most important are the insufficient current-carrying ability of the tapes and poor reproducibility of properties due to uncontrolled action of various factors affecting the formation and properties of Bi-HTSC.

Currently, the main efforts of researchers and the designers of Bi-HTSC articles are directed at improving their transport properties. Certain progress has already been attained along this line,[18–23] but a key problem related to the sharp decrease in the critical current density (j_c) in Bi-HTSC on increasing the temperature of article operation or external magnetic current strength remains unsolved. For this reason, the use of polycrystalline Bi-HTSC (ceramics and tapes) is most often restricted by the boiling point of liquid hydrogen (20 K),[24,25] although T_c of phase 2223 is above the boiling point of liquid nitrogen (77 K). At best, these articles can operate without loss of superconductivity only to 35 K in a $\sim$1 T field.[14] This is due to the fact that Bi-HTSC ceramics and tapes are polycrystalline structures composed of separate superconducting grains (crystallites) connected by weak Josephson bonds. The current-carrying ability of these materials depends mainly on the properties of these bonds. At grain contacts, conditions for pinning of Josephson vortices may arise[26] and, hence, an increase in j_c is probable. However, more often these contacts are responsible for a sharp decrease in the critical current.[26,27] In fact, the synthesis of Bi-HTSC is inevitably accompanied by the formation of by-products, which are accumulated to higher or lesser degree at the grain boundary. Finally, the 'intergrain' critical current density is much lower than the 'intragrain' one and the performance of Bi-HTSC, for example, (Bi,Pb)2223/Ag tapes, is deteriorated.[6,28,29] In addition, passage of the superconducting current is affected by configuration and mutual orientation of the superconducting grains.[30,31]

Note that even record-breaking j_c values for the tapes are only $\sim$5% of the value typical of thin single-crystalline (Bi,Pb)2223 films.[32,33] The fact that 'intragrain' critical current density of phase (Bi,Pb)2223 is much higher than the 'inter-

V S Kravchenko A V Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrentieva 3, 630090 Novosibirsk, Russian Federation. Fax (7-383) 330 94 89, tel. (7-383) 316 56 39, e-mail: krav@che.nsk.su

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grain' one reflects the theoretical possibility of improving the current characteristics of the polycrystalline material.[34] In solving the problem of enhancing the transport properties in the polycrystalline (Bi,Pb)2223 phase, key aspects include improvement of its real structure (microstructure) towards increasing size of the superconducting grains, improvement of bonding between the grains by decreasing the amount of impurity phases, formation of a texture, decrease in the porosity, syntactic intergrowth of related phases 2201 and 2212, *etc*.[35,36] Yet another possibility for increasing the current-carrying ability is to form microcomposite structures comprising specially introduced nano- or micro heterogeneities, resulting in more pronounced pinning of magnetic vortices.[37]

Unfortunately, the current level of research into formation processes and detailed microstructure of Bi-HTSC does not go beyond the scope of empirical methods. The j_c values of (Bi,Pb)2223/Ag tapes attained to date were obtained by trial-and-error selection of the process conditions,[38] establishing correlations and further development of particular procedures in the conventional series: initial composition → synthesis conditions → chemical and phase composition of the material → crystal and real structure → properties. Due to the complex influence of various chemical and process parameters, it is yet impossible to finely control the Bi-HTSC synthesis and to deliberately choose the optimal conditions for the formation of material with a specified set of superconducting properties. One reason for this is the exceptionally complicated phase diagram of the Bi–(Pb)–Sr–Ca–Cu–O multicomponent system, which comprises not only three superconducting phases, but also a number of phases exhibiting no superconductivity. The proper Bi-HTSC are formed in narrow ranges of conditions and are phases of variable composition. At the temperatures of synthesis, they can melt incongruently, thus forming heterogeneous systems that may contain a melt in addition to solid phases. Most often, these are open systems the quantitative composition of which may vary due to oxygen exchange with the gas environment and to partial loss of volatile components such as Pb. The phase formation may follow different routes; therefore, the features of formation, the microstructure and the superconducting properties of Bi-HTSC are highly sensitive to the conditions of synthesis.

Without considering the chemical properties of Bi-HTSC and associated phases, features of their formation and chemical reactions, one can hardly expect that the design of these materials would be successful. Exceptionally important is the knowledge of phase equilibria and phase ratios in these multicomponent systems, the kinetics and mechanisms of phase formation, *etc*. The scope of current research related to Bi-HTSC is quite extensive and, naturally, this cannot be fully covered in this review. We consider the crystal chemical features and chemical composition of bismuth superconductors, phase equilibria and stability regions of superconducting phases. The superconducting properties of Bi-HTSC depending on their chemical and phase composition and crystal and real structures are also discussed.

II. Characteristic physicochemical properties of bismuth-based high-temperature superconductors and systems forming them

1. Crystal chemical features and microstructure

a. Crystal chemical features

A number of reviews[39–44] consider comprehensively the crystal chemistry of bismuth-based HTSC; therefore, we restrict ourselves to general structural information. These superconductors belong to the homologous series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1-3$; the deviation from the ideal stoichiometry regarding either cations or oxygen is neglected). They have sandwich type layered structures in which perovskite-like blocks with different numbers of Ca and CuO_2 layers occur between doubled BiO layers forming a NaCl type structure (Fig. 1). These structures usually refer to a tetragonal or orthorhombic system. All three phases have almost equal lattice parameters in the *ab* plane and differ only in the parameter *c*.

Bismuth-based HTSC are prone to atom modulation in the crystal lattice. According to a publication,[45] they have composite structures composed of two interpenetrating incommensurate sublattices, namely, sublattices of all atoms except oxygen in BiO layers and oxygen sublattices. The ratio of sublattice parameters depends on the amount of hyperstoichiometric oxygen in bismuth–oxygen layers. In these layers, structural modulation takes place, *i.e*., the Bi–Bi distance between the BiO layers varies with a definite periodicity along the direction [010]. The modulation also occurs in the perovskite blocks, although to a lesser extent.[45] Taking into account the modulation directed along the diagonal of the face of the perovskite tetragonal unit cell (with the parameter of ~0.38 nm), the Bi-HTSC structure is considered as orthorhombic with parame-

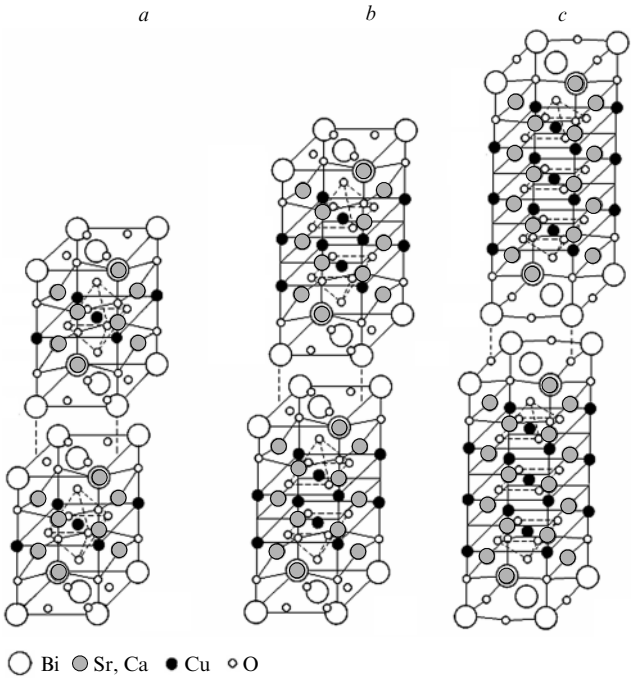


Figure 1. Structural models of the phases $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$: 2201 (*a*), 2212 (*b*), 2223 (*c*).[41]

ters a and b equal to $\sim$0.54 nm.[46] The possible reasons for the appearance of modulations in Bi-HTSC, *e.g.*, the presence of additional oxygen in BiO layers, poor correspondence of the crystal parameters between the perovskite block and BiO layers, *etc.*, were considered.[47]

The replacement of some Bi atoms by Pb gives rise to one more type of modulation in Bi-HTSC, the displacement field being different from that observed for undoped phases.[48] This modulation is associated with ordering of lead atoms in crystal lattices, which occurs as the positional displacement of lead atoms from their mean sites.[48,49] The period of this modulation depends on the lead content.[42] Lead incorporation into Bi-HTSC also affects the crystal lattice parameters. For example, the replacement of bismuth atoms by lead in phase 2212 results in a decrease in the parameters b and c (Fig. 2) [50–52] and, as the lead content increases, the distortion of the tetragonal structure becomes more and more pronounced resulting in transition to the orthorhombic or even monoclinic system.[53] The degree of this modification depends on the oxygen partial pressure in the gas environment.[50]

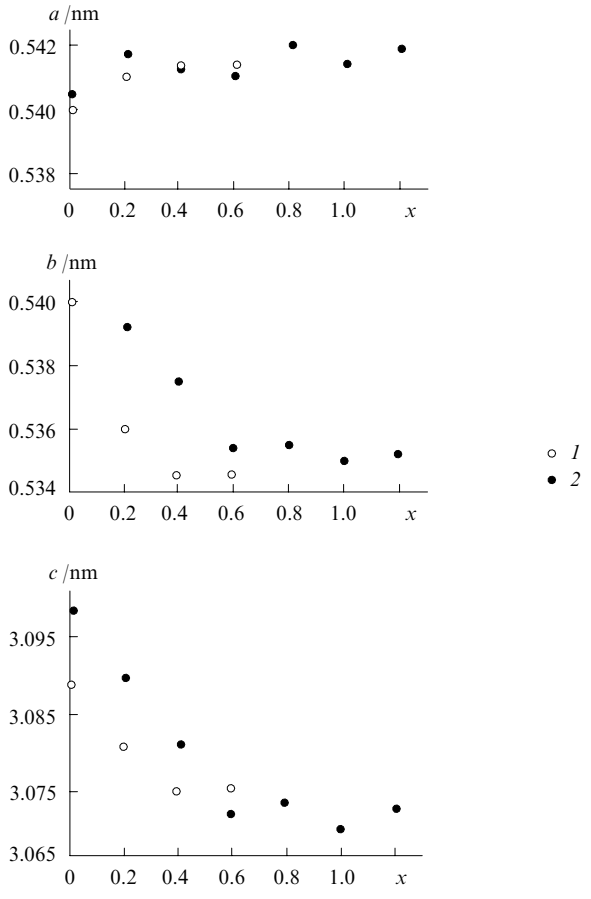


Figure 2. Lattice parameters of $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ *vs.* lead content.[52]
Data from Refs 50 (*1*) and 51 (*2*).

Due to similarity of crystal structures, the Bi-HTSC grains are most often not individual but represent mixed crystallites with hetero-attachments of related phases in the major phase matrix. The major phase that forms heteropolytypes has a basic crystal structure with local structural defects, *e.g.*, stacking faults. Thus microcrystals of phase 2223 may incorporate areas of phases 2201, 2212 and even 2234 [54–58] separated by small-angle or twin boundaries or by twist boundaries.[59]

The compounds the structures of which are also composed of structural fragments of known compounds but have a new strictly ordered crystal lattice should be assigned to a separate group. The structures of these phases include fragments with strictly alternating variable number of CuO_2 layers, which retain the long-range order and have structural characteristics differing from the characteristics of precursors.

Examples of such 'hybrid' phases can be found in publications,[60,61] which describe crystals differing from known phases in the chemical composition, X-ray diffraction patterns and unit cell parameters, which are intermediate between those of phases 2201 and 2212. Depending on the preparation method, these crystals correspond to the formulas $Bi_{4.43}Sr_{3.42}Ca_{1.23}.Cu_3O_z$ or $Bi_{4.24}Sr_{3.75}Ca_{1.06}Cu_3O_z$ (by analogy with the phases 2201, 2212 and 2223, the new phase is designated by 4413). The parameter $c_{4413} \approx (c_{2201} + c_{2212})/2$ equals 2.77 nm. These data suggest that the structure of the obtained crystals is composed of discrete lamellas of phases 2201 and 2212 with the thickness $c_{2201}/2$ and $c_{2212}/2$ grown together along the axis c_{4413} in an ordered fashion.

Yet another intermediate phase (4435) with the parameter c = 3.4 nm was found [62] in early stages of transformation of phase 2212 into 2223 during the production of tapes.

b. Microstructure

The above examples reflect the structural features of Bi-HTSC at the atomic level. Another structural level, *i.e.*, the real structure or microstructure, reflects the material morphology. For polycrystalline superconductors, this is an exceptionally important characteristics. Recall that polycrystalline HTSC, whether this is bulk ceramics or composite tapes, are systems of superconducting grains (crystallites) connected by a three-dimensional network of weak Josephson contacts, which decrease the superconducting current. The nature of weak bonds may be different: impurities of associated phases, disturbance of grain stoichiometry in the boundary regions, stacking faults, edge dislocations and so on. The formation of grain interlayers due to impurity segregation is the simplest and most natural source of weak bonds in Bi-HTSC.

The microstructure covers also defects such as fractures and pores, resulting in the break of continuity of the superconducting material and essential deterioration of its electrophysical properties. Unfortunately, the formation of polycrystalline Bi-HTSC is almost inevitably accompanied by the appearance of pores in the material both in the production of bulk ceramics [63,64] and in the production of tapes,[65–68] although to a lesser extent in the latter case.[69] The pore formation and the decrease in the sample density in Bi-HTSC synthesis is caused by anisotropic growth of crystallites in different crystallographic directions. Due to pronounced difference between the parameters a and b, on the one hand, and the parameter c, on the other hand, the crystallisation rate in the ab plane is $\sim$1000 times as high as that along the c axis.[70] This gives randomly oriented plate-like crystallites, which push one another apart while growing and thus give rise to voids.

The synthesis of phase 2223 can be accompanied by the formation of some liquid phase, which conversely results in the sample compaction and compression. A change in the density caused by a change in the porosity is sometimes called 'retrograde densification'.[71] The degree of porosity depends on the initial composition and synthesis conditions. Thus during the synthesis of (Bi,Pb)2223 ceramics, the increase in temperature to 850 °C is accompanied by a decrease in the density but at

higher temperatures, the density of ceramics increases again.[63] Some increase in the density of this ceramics in the initial period of synthesis ($\sim$1 h) was noted and attributed to the appearance of a liquid phase.[72] Subsequently, the density of samples decreased to a constant value after 50 h of the synthesis. The decrease in the density of the (Bi,Pb)2223 ceramics is approximately proportional to the amount of phase 2223 formed and follows an exponential time dependence, which can be expressed as the following empirical equation:[64]

$$\rho = \rho_t + (\rho_0 - \rho_t)\exp(-\beta\tau),$$

where ρ is the density at time τ, ρ_t is the final density, ρ_0 is the initial density, β is the rate of retrograde densification. For the temperature range of 845–855 °C, the average β value is 0.063 h^{-1}.

The formation of pores in the synthesis of phase (Bi,Pb)2223 results, on the one hand, in deterioration of the transport properties and the mechanical strength of the material and, on the other hand, in retardation of the formation process of phase 2223 due to increasing limitation of diffusion. In order to decrease the porosity, the phases are subjected to intermediate cold or hot moulding, rolling, *etc*.

Yet another characteristics of Bi-HTSC microstructure is the orientation of crystallites relative to one another. Their mutual orientation affects considerably the critical current density through the crystallite boundary.[73] Therefore, the problem of producing a material with a perfect texture (predominant spatial orientation of crystallites in a particular crystallographic direction), which enhances the microstructure homogeneity, occupies a special place in the Bi-HTSC technology. The texture formation is facilitated by a layered structure of Bi-HTSC, especially during processing operations such as moulding, drawing, *etc*.[74,75] If the crystallites in ceramics (without using hot moulding) are randomly oriented, then during drawing of tapes the formation of textured microstructure is much easier. The texture formation processes in the Bi-HTSC tapes were considered in detail (Refs 7, 36, 68, 74–109).

2. Chemical composition of bismuth-based superconductors

a. General

Bismuth-based superconductors are phases of variable composition, their real chemical composition most often differs from the composition reflected by the idealised formula. The difference includes several issues: phase 2201 may contain not only Sr atoms (as in the ideal case), but also Ca atoms in a solid substitutional solution;[110,111] the contents of Sr and Ca are variable in all three superconducting phases;[110,112,113] the Bi atoms replace some of the alkaline earth metal sites;[95,96,110] Cu can partially substitute Sr and Ca, and also Bi;[114] all Bi-HTSC solid solutions tend to contain some excess of Bi atoms and a deficiency of Sr atoms or the sum (Sr + Ca) with respect to stoichiometric formulas.[115–117] The content of cations depends appreciably on the conditions of synthesis.[70,118] In addition, the content of oxygen is also variable and copper may be highly deficient. The contents of Bi, Sr and Ca atoms are usually interrelated; the sum of Bi, Sr and Ca atoms in the formula units is equal to three for phase 2201, five for phase 2212 and six for phase 2223. In view of the foregoing, the general chemical formula of these compounds can be represented as $Bi_{2+x+z}Sr_{2-x-y}Ca_{n-1-z+y}Cu_{n-y}O_{4+2n+\delta}$.[70]

Typically, alkaline earth elements in these phases substitute each other. The homogeneity regions are rather broad for phases 2201 and 2212 and more narrow for phase 2223.[70,119–126]

b. Phase 2201

Strictly speaking, compound with the ideal stoichiometry $Bi_2Sr_2CuO_6$ is not a superconductor but a semiconductor.[127,128] Solid solutions $Bi_{2+x}Sr_{2-x}CuO_z$ with excess bismuth and deficient strontium are superconducting in the composition range $0.1 \leqslant x \leqslant 0.13$,[115,129] although their composition can vary in the range $0.1 \leqslant x \leqslant 0.5$.[127] These solid solutions differ somewhat in the structure from the compound with ideal stoichiometry; therefore, they are often considered as a separate phase called Raveau phase,[128] which is also designated by 11905 ($Bi_{11-x}Sr_{9+x}Cu_5O_z$). We will adhere to the usual designation 2201 for both the stoichiometric compound and solid solutions, specifying the cases where this is necessary.

The substitutional solid solution with calcium atoms replacing strontium atoms in phase 2201 at 850 °C exists up to the ratio Sr : Ca $\approx$ 1.5 : 0.5 and occurs in equilibrium with phase 2212, except for the compositions with very low calcium contents (Sr : Ca > 1.9 : 0.1).[121] In the concentration range with a high calcium content (Sr : Ca < 1.5 : 0.5), phase 2201 melts at this temperature and phases 2212 and 2223 exist in equilibrium with the melt.[121]

c. Phase 2212

Among all Bi-HTSC, the chemical composition of phase 2212 is best studied.[111,130–142] The sizes of the homogeneity regions of solid solutions 2212 and the fields of the neighbouring phases depend on temperature.[70] Figure 3 shows the delineated homogeneity region of the solid solutions $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\delta}$ at 850 °C. (Unless otherwise stated, these data were obtained in air, the letter L means liquid). It is noteworthy that the composition $Bi_2Sr_2CaCu_2O_8$ does not fall into the

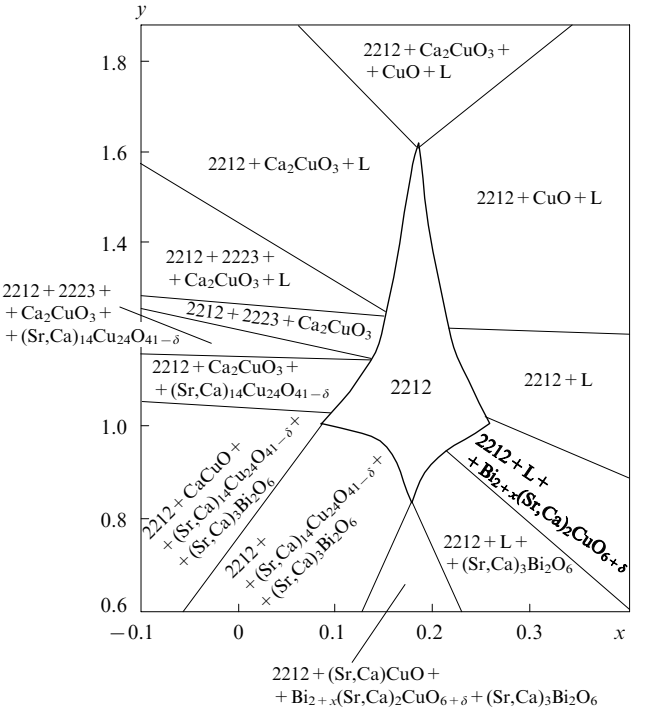


Figure 3. Regions of existence of the solid solutions $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\delta}$ and adjoining phase regions at 850 °C.[70]

homogeneity region of phase 2212 at 850 °C. This is consistent with the fact that the synthesis of samples with the ideal initial composition $Bi_2Sr_2CaCu_2O_8$ normally gives the secondary phases Ca_2CuO_3, $Sr_{14-x}Ca_xCu_{24}O_{41}$ and $Bi_2Sr_{3-x}Ca_xO_6$.[116, 121, 126, 130, 133–143] However, this does not mean that the ordered phase $Bi_2Sr_2CaCu_2O_{8+\delta}$ cannot in principle be synthesised. As shown previously,[134] this phase can be prepared by long-term annealing at a temperature close to the melting point (at 860 °C for 5 days).

The 'solubility' of lead in phase 2212 depends on the temperature and oxygen partial pressure in the gas phase. As p_{O_2} decreases, the limiting content of lead in the phases (Bi,Pb)2212 and (Bi,Pb)2223 markedly increases.[144] The highest content of lead in (Bi,Pb)2212 is found at 850°C;[125, 145, 146] for the compositions $Bi_{2-x}Pb_xSr_2CaCu_2O_z$ synthesised in air x reaches 0.4,[51, 53, 147, 148] while in argon $x = 0.6$.[51] Both above and below 850 °C, the content of lead in (Bi,Pb)2212 decreases.

Phase 2212 is characterised by oxygen nonstoichiometry. The oxygen content varies from 8.0 to 8.34 depending on p_{O_2} and heat treatment.[138, 149–155] This results in variation of superconducting properties.

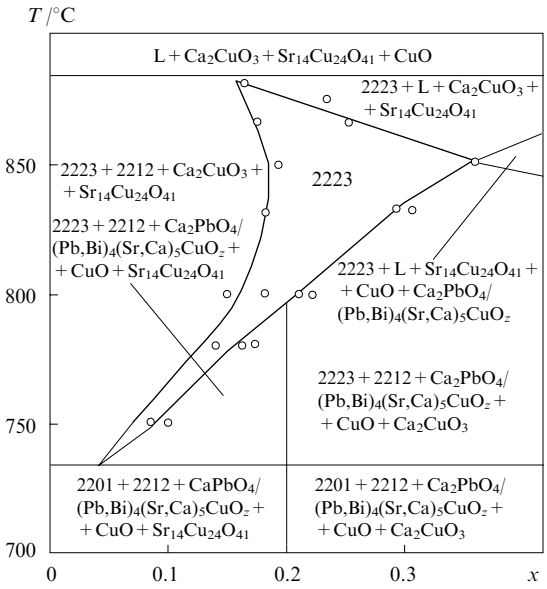


Figure 4. Approximate boundaries of lead content in the solid solutions $Bi_{2.27-x}Pb_xSr_{2-y}Ca_{2+y}Cu_3O_{10+\delta}$ at different temperatures.[70]

d. Phase 2223

Unlike phase 2212, phase 2223 has a narrower range of Sr and Ca contents, the Sr : Ca ratio varying from 1.9 : 2.1 to 1.8 : 2.2 (for lead-free system).[70, 124–126, 156] Published data about the bismuth content are contradictory: the formula indices vary from 2 (Ref. 156) to ~2.5 (Ref. 124).

When some of the bismuth atoms have been replaced by lead, the sum (Bi + Pb) is taken into account when considering the stoichiometry.[157] In single phase samples, this sum is usually greater than in the samples with ideal composition,[158–162] although some publications (see, for example, Ref. 163) present the ideal composition of the monophase. The degree of lead substitution for bismuth in phase 2223 appreciably depends on temperature.[125, 126, 164–166] Figure 4 shows the schematic view of the concentration field of Pb contents in $Bi_{2.27-x}Pb_xSr_{2-y}Ca_{2+y}Cu_3O_{10+\delta}$ at different temperatures. The highest lead content is observed at 850 °C, while both above and below this temperature its content decreases as in the case of (Bi,Pb)2212.

The cross-section of the single-phase region of (Bi,Pb)2223 at 850 °C as function of the bismuth and lead contents is presented in Fig. 5, which also shows three-, four- and five-phase regions surrounding this phase. At 850 °C, the homogeneity region of $(Bi,Pb)_{2+x}Sr_yCa_{4-y}Cu_3O_{10+\delta}$ occurs in the ranges $0.18 \leqslant x \leqslant 0.27$ and $1.87 \leqslant y \leqslant 2.1$.[164] It was

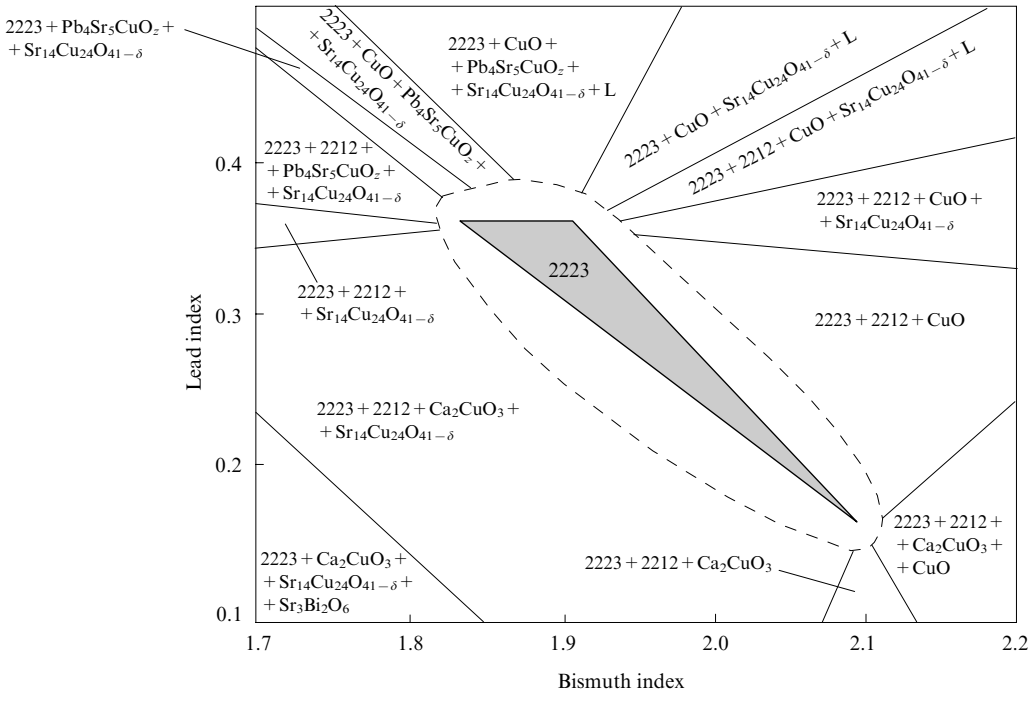


Figure 5. Schematic cross-section of the homogeneity region of the phase (Bi,Pb)2223 at 850 °C depending on the content of bismuth and lead in the initial nominal compositions and adjoining phase regions.[126] The region shown by the dashed line around the phase (Bi,Pb)2223 is not studied.

reported [159] that the single-phase composition has the formula $Bi_{1.68}Pb_{0.32}Sr_{1.75}Ca_yCu_zO_{10+\delta}$, where $1.75 < y < 1.85$ and $2.65 < z < 2.85$, while in another publication,[131] the monophase obtained at 860 °C was described by the formula $[(Bi,Pb)_xCu_{1-x}]_{5+y}(Sr_zCa_{1-z})_{4-y}O_{10+\delta}$, where $0.38 < x < 0.46$, $0 < y < 0.13$, $0.44 < z < 0.54$, Pb : Bi = 0.1.

The variations of the strontium and calcium contents depending on temperature for (Bi,Pb)2223 solid solutions described as $(Bi,Pb)_{2+x}Sr_{4-y}Ca_yCu_3O_{10+\delta}$ are reflected in Fig. 6. The range of variations of Sr : Ca ratio in (Bi,Pb)2223 following temperature rise first increases and then at higher temperatures somewhat decreases.[70, 164, 167] It was found that phase (Bi,Pb)2223 adjoins only solid phases on the side of lower calcium contents, while on the calcium-rich side, it adjoins phases that incorporate a liquid above 840 °C. Thus, it cannot be ruled out that depending on the synthesis conditions, the formation of phase 2223 may involve or not involve a liquid phase.

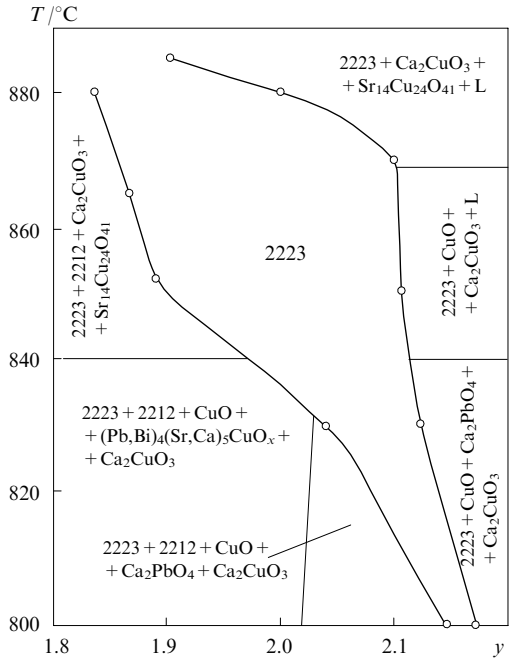


Figure 6. Approximate boundaries of strontium and calcium contents in the solid solutions $(Bi,Pb)_{2+x}Sr_{4-y}Ca_yCu_3O_{10+\delta}$ depending on temperature.[125]

It is noteworthy that the above-described results refer to the case of a constant oxygen partial pressure (synthesis in air). When this parameter changes, the chemical composition of the phases can change. First of all, this is true for the content of oxygen itself in phase 2223, which varies [168] from 10.0 to 10.2.

3. Phase equilibria

Phase diagrams represent the first principle of material science research, especially for complex multicomponent systems such as Bi–Sr–Ca–Cu–O, Bi–Pb–Sr–Ca–Cu–O, Ag–Bi–Pb–Sr–Ca–Cu–O, *etc*. Using phase diagrams, one can predict the variation in the phase composition and chemical stability of compounds under the action of various process parameters: temperature, overall pressure and partial pressures of gas components and upon the introduction of other components into the system, *etc*.

It can be seen from the complex diagrams considered above (see Figs 3–6) that the phase compositions occurring in equilibrium with Bi-HTSC are highly sensitive to the change in independent parameters. Hence, as noted in a review,[169] it is necessary to take into account the limitations imposed on the system and decreasing the number of degrees of freedom. Thus additional introduction of silver changes the equilibrium phase composition.[170] A simplified consideration of the production of tapes (without considering the effect of the silver shell) may lead to faulty conclusions.

Usually, in analysis of these systems, only the regions of stability of superconducting phases and the most important pseudobinary polythermal or pseudoternary isothermal cross-sections are considered or thermodynamic analysis is carried out by computer software. Examples of these diagrams can be found in reference books [171, 172] and reviews.[70, 125] In this Section when considering the phase equilibria, we will mainly discuss new results that were not included in the reference books.

The phase relations in the Bi_2O_3–SrO–CaO–CuO system were studied at different temperatures covering the subsolidus, oversolidus regions and the liquidus surface.[116, 120–123, 131, 133, 137, 143, 173–182] In some studie, consideration took into account the effect of system components such as lead [126, 164–166, 183–190] and silver [170, 176, 191–194] and the joint influence of these metals.[125, 195, 196] The most comprehensive investigations of these systems were carried out by Majewski and co-workers from the Max Planck Institute (Germany) [120–126, 135, 138, 153, 155, 164–167, 170] and researchers of the National Institute of Standards and Technology (USA).[176, 189–191, 196–199]

The attention is focused on the investigations of the existence regions of the superconducting phases 2212 and 2223 and the regions of phases equilibrated with them. These are various strontium and calcium cuprates and bismuthates, CuO, the mixed oxide (Ca,Sr)O and a liquid phase. Thus in the Bi_2O_3–SrO–CaO–CuO system, 10 phases that form 16 four-phase bulk regions may occur in equilibrium with phase 2212 in the subsolidus region.[176, 189]

The phase composition becomes more complicated if lead is introduced additionally into the system. Below we present the five-phase compositions in which the phase (Bi,Pb)2223 in the subsolidus region occurs in equilibrium with other phases at a reduced oxygen partial pressure in the gas medium (7.5 vol.% O_2 + 92.5 vol.% Ar) and a temperature of 810–820 °C.[189, 191]

Entry	Five-phase equilibrium
1	$2223 + 2212 + (Ca,Sr)_2PbO_4 + (Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z +$ $+ Bi_2(Sr,Ca)_4O_z$
2	$2223 + 2212 + (Sr,Ca)_{14}Cu_{24}O_{41} + (Ca,Sr)_2PbO_4 +$ $+ (Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z$
3	$2223 + 2212 + Ca_xSr_{1-x}CuO_2 + Bi_2(Sr,Ca)_4O_z +$ $+ (Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z$
4	$2223 + 2212 + (Ca,Sr)_2PbO_4 + Bi_2(Sr,Ca)_4O_z + CaO$
5	$2223 + 2212 + Bi_2(Sr,Ca)_4O_z + Ca_xSr_{1-x}CuO_2 +$ $+ (Pb,Bi)_3(Sr,Ca)_5CuO_z$
6	$2223 + 2212 + (Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z +$ $+ Ca_xSr_{1-x}CuO_2 + CuO$
7	$2223 + 2212 + (Ca,Sr)_2CuO_3 + (Ca,Sr)_2PbO_4 + CuO$
8	$2223 + 2212 + (Sr,Ca)_{14}Cu_{24}O_{41} +$ $+ (Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z + CuO$

Entry	Five-phase equilibrium
9	2223 + 2212 + $(Ca,Sr)_2CuO_3$ + $(Sr,Ca)_{14}Cu_{24}O_{41}$ + CuO
10	2223 + 2212 + $(Ca,Sr)_2PbO_4$ + $Ca_xSr_{1-x}CuO_2$ + + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$
11	2223 + 2212 + $(Sr,Ca)_{14}Cu_{24}O_{41}$ + $(Ca,Sr)_2CuO_3$ + + $(Ca,Sr)_2PbO_4$
12	2223 + 2212 + $Ca_xSr_{1-x}CuO_2$ + $Sr_xCa_{1-x}CuO_2$ + CuO
13	2223 + 2212 + $(Ca,Sr)_2PbO_4$ + CuO + $Ca_xSr_{1-x}CuO_2$
14	2223 + 2212 + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$ + CaO + $(Ca,Sr)_2PbO_4$
15	2223 + 2212 + $Ca_xSr_{1-x}CuO_2$ + $Sr_xCa_{1-x}CuO_2$ + + $Bi_2(Sr,Ca)_4O_z$
16	2223 + 2212 + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$ + CaO + + $Bi_2(Sr,Ca)_4O_z$
17	2223 + $Sr_xCa_{1-x}CuO_2$ + $Bi_2(Sr,Ca)_4O_z$ + $Ca_xSr_{1-x}CuO_2$ + + $(Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z$
18	2223 + $Sr_xCa_{1-x}CuO_2$ + $Bi_2(Sr,Ca)_4O_z$ + + $(Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z$ + $(Sr,Ca)_{14}Cu_{24}O_{41}$
19	2223 + $(Ca,Sr)_2PbO_4$ + $Sr_xCa_{1-x}CuO_2$ + CuO + + $Ca_xSr_{1-x}CuO_2$
20	2223 + $Sr_xCa_{1-x}CuO_2$ + $(Sr,Ca)_{14}Cu_{24}O_{41}$ + + $(Bi,Pb)_{2.2}Sr_{1.8-x}Ca_xCuO_z$ + CuO
21	2223 + $Sr_xCa_{1-x}CuO_2$ + CaO + $Ca_xSr_{1-x}CuO_2$ + + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$
22	2223 + $(Ca,Sr)_2PbO_4$ + CuO + $(Ca,Sr)_2CuO_3$ + + $(Sr,Ca)_{14}Cu_{24}O_{41}$
23	2223 + $(Ca,Sr)_2PbO_4$ + CuO + $Sr_xCa_{1-x}CuO_2$ + + $(Sr,Ca)_{14}Cu_{24}O_{41}$
24	2223 + $Bi_2(Sr,Ca)_4O_z$ + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$ + CaO + + $Ca_xSr_{1-x}CuO_2$
25	2223 + $(Ca,Sr)_2PbO_4$ + CaO + $Sr_xCa_{1-x}CuO_2$ + + $Bi_2(Sr,Ca)_4O_z$
26	2223 + $(Ca,Sr)_2PbO_4$ + $Bi_2(Sr,Ca)_4O_z$ + $(Sr,Ca)_{14}Cu_{24}O_{41}$ + + $Sr_xCa_{1-x}CuO_2$
27	2223 + $(Ca,Sr)_2PbO_4$ + $Sr_xCa_{1-x}CuO_2$ + + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$ + $Ca_xSr_{1-x}CuO_2$
28	2223 + $(Ca,Sr)_2PbO_4$ + ô + $Sr_xCa_{1-x}CuO_2$ + + $(Pb,Bi)_3(Sr,Ca)_5CuO_z$
29	2223 + $Sr_xCa_{1-x}CuO_2$ + CaO + $Bi_2(Sr,Ca)_4O_z$ + + $Ca_xSr_{1-x}CuO_2$

It was found experimentally[189, 191] that the number of possible mutually correlated five-phase equilibrium compositions in the subsolidus space alone increases to 29. With allowance for the existence of oversolidus regions and for the fact that, apart from five-phase equilibria, there are two-, three- and four-phase ones, the maximum number of the possible regions surrounding phase 2223 increases theoretically to 56.[166] Actually, their number is apparently somewhat lower. The minimum number is 37 (Ref. 166).

It can be seen that in more than half of cases (16 out of 29), phase 2212 exists in equilibrium together with phase 2223 in the subsolidus volume. In half of these cases (8 out of 16), $(Ca,Sr)_2PbO_4$ occurs in equilibrium together with two superconducting phases. Nine volumes contain the 2223 + CuO pair of phases, and nine other, the 2223 + $(Sr,Ca)_{14}Cu_{24}O_{41}$ pair. In four cases, $(Ca,Sr)_2CuO_3$ is detected together with phase 2223.

Here it is pertinent to make some remarks about the phase $(Pb,Bi)_3(Sr,Ca)_5CuO_z$. It was first detected in the Bi–Pb–Sr–Ca–Cu–O system and studied it detail by Dou *et al.*[200] This phase was found to play a certain role in the processes of formation of phases (Bi,Pb)2212 and (Bi,Pb)2223.[201] However, there is no common opinion about the exact composition of this phase. Some publications[70, 125, 145, 146] describe the composition as $(Pb,Bi)_4$. $(Ca,Sr)_5CuO_z$ (the phase is designated as 451 rather than 351). Another work[199] gives the composition of $Pb_2Bi_{0.8}Sr_{3.3}Ca_{2.6}CuO_z$. Some authors (see, *e.g.*, Refs 20, 52, 144, 202–205) believe that the composition of this phase is $(Pb,Bi)_3Sr_2Ca_2CuO_z$ and designate it as 3221, while some other authors[206, 207] describe the phase as $Pb_3Bi_{0.5}Sr_{2.5}Ca_2CuO_z$ and use the designation 3321. This difference is apparently due to the fact that this phase has variable composition, the element ratio being dependent on the formation conditions. Since there is no generally accepted designation for the considered phase, we used the designations taken from the studies cited, bearing in mind that this is the different notation for the same phase.

The above data concerning the five-phase equilibrium can be graphically presented as hypervolumes in a 5D space (at a specified oxygen partial pressure and a constant overall pressure). The technique of generation and examples of such images on a plane have been reported.[191] However, these are quite complicated for the perception and practical use. Nevertheless, this approach allows one to narrow down the possible combinations of the initial compositions and may be quite useful in the future for optimisation of synthetic procedures.

The simulation can be considerably simplified by decreasing the number of independent parameters (naturally, with the loss of some information). For a 2D display it is most reasonable to specify the temperature and the Bi : Pb ratio and to use pseudoternary diagrams.

Consider a reported method.[126, 164] The researchers studied samples characterised by constant ratios: Bi : Pb = 1.8 : 0.4 and [SrO + CaO + $(Bi,Pb)_2O_3$] : CuO = 63 : 37. These compositions are located in the cross-section of the concentration tetrahedron of the pseudoquaternary $(Bi,Pb)_2O_3$–SrO–CaO–CuO system shown in Fig. 7 where regions corresponding to different phase equilibria are marked off.

The real chemical compositions of phases 2201 and 2212 determined by X-ray spectroscopic microanalysis with energy dispersion are as follows:

2201: in regions *i* and *j* the composition is $(Bi,Pb)_{2.3}Sr_{1.3}Ca_{0.4}CuO_{6+\delta}$, the ratio Bi : Pb ≈ 4.5 : 1;

2212: the composition regarding Ca and Sr changes substantially on going from one region to another: for equilibrium with phase 2223 (regions *d*, *h*, *m*, *n*), the Sr : Ca ratio is ≈ 2 : 1; for equilibrium with $Sr_{14}Cu_{24}O_{41}$, the Sr : Ca ratio varies from 1.5 : 1 (region *o*) to 2.15 : 0.85 (region *l*); the ratio Bi : Pb ≈ 7.5 : 1 is almost always constant; the content of (Bi + Pb) varies from 2.05 (region *c*) to 2.25 (region *i*); for equilibrium with phase 2223, the (Bi + Pb) content is intermediate.

Phase 2223 has narrow composition ranges, and in the diagram this is a point corresponding to the composition $(Bi,Pb)_2Sr_2Ca_2Cu_3O_z$. On this scale, this simplification is quite justified, although this results in a loss of some regions adjoining phase 2223 of variable composition. A number of four- and three-phase regions surrounding the solid solution 2223 are shown in Fig. 5.

Analysis of this phase diagram has shown that with the invariants chosen, phase (Bi,Pb)2223 can be equilibrated with solid phases (regions *d*, *e*, *m*, *n*) and with liquid-containing phases (regions *f* and *h*). It is important that even minor variations of the composition (or temperature) may result in different phase compositions and different contents of phase 2223. It can be seen in the diagram that regions involving phase 2223 (*d*, *e*, *f*, *h*, *n*, *m*) are depleted in bismuth and are located closer to the $(SrO)_{63}(CuO)_{37}$–$(CaO)_{63}(CuO)_{37}$ side, while regions covering phases 2212 and 2201 (*i*, *j*, *k*, *l*, *m*, *n*, *o*, *r*) are closer to the $(SrO)_{63}(CuO)_{37}$–$[(Bi,Pb)_2O_3]_{63}(CuO)_{37}$ side.

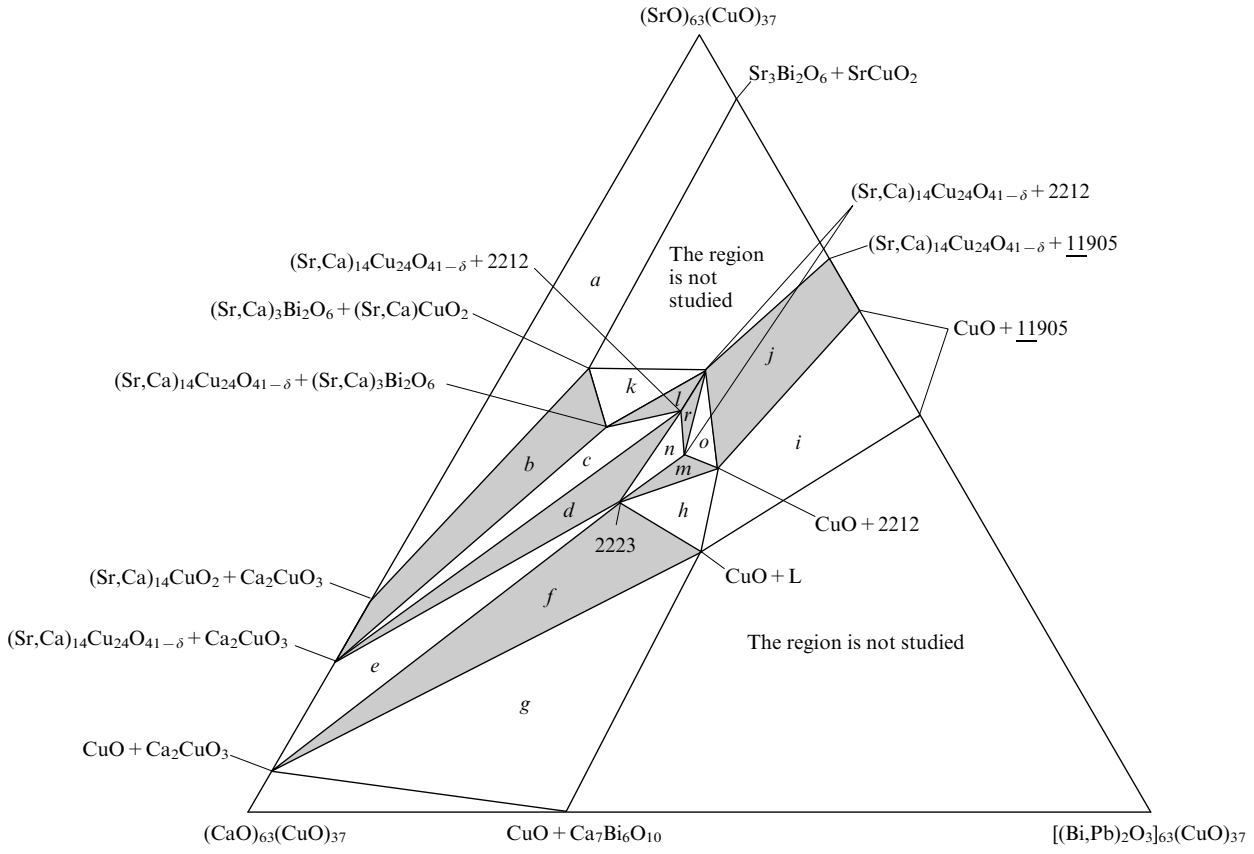


Figure 7. Cross-section of the concentration tetrahedron of the pseudoquaternary system $(Bi,Pb)_2O_3-SrO-CaO-CuO$ at constant ratios $[SrO + CaO + (Bi,Pb)_2O_3] : CuO = 63 : 37$ and $Bi : Pb = 1.8 : 0.4$ and a temperature of 850 °C.[126]

The effect of temperature on the phase composition has been studied.[177, 185, 208–210] This was done using the polythermal cross-sections of pseudobinary systems, $Bi_2Sr_2CuO_6-CaCuO_2$ (see Refs 177, 208–210) and $(Bi,Pb)_2Sr_2CuO_6-CaCuO_2$.[183–185] These systems were chosen as most informative for analysis of the behaviour of superconducting phases, because in this case all superconducting phases are located in one line of compositions of more complex pseudoternary systems. Figure 8 shows the phase diagram corresponding to a polythermal cross-section along the $Bi_2Sr_2CuO_6-CaCuO_2$ line.[177] In can be seen that in the region between compositions 2201 and 2212, with an increase in the $CaCuO_2$ content, the liquidus and solidus lines have different slopes. In the region of 2212–2223, phase 2212 is split into 2201 + $(Sr,Ca)CuO_2$ + L in a rather narrow temperature range (887–894 °C), while at higher temperatures, into $(Sr,Ca)CuO_2$ + L.

The presented phase diagrams reflect the phase equilibrium in air, but a change in the oxygen concentration in the gas phase may change appreciably the outcome. Thus study of compositions equilibrated with (Bi,Pb)2223 has shown that a decrease in the oxygen partial pressure entails not only an increase in the lead content in phases 2212 and 2223, but also a gradual decrease in the amount of Pb-containing phases, Ca_2PbO_4 and $Pb_4(Sr,Ca)_5CuO_z$, and eventually depletion of these phases may result in a decrease in the overall number of equilibrated phases.[144]

Note that the dependence of the form of phase diagrams on the oxygen partial pressure is typical of all HTSC systems.[169] Unfortunately, considerations of the equilibria in such systems do not always pay adequate attention to the oxygen exchange

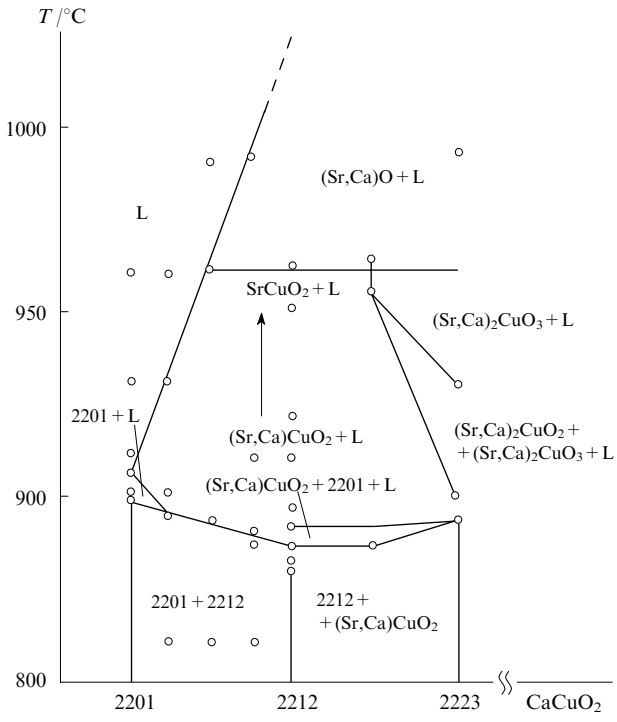


Figure 8. Phase diagram of the pseudobinary system $Bi_2Sr_2CuO_6-CaCuO_2$ in air.[177]

of condensed phases with the gas environment. During the Bi-HTSC phase formation, active oxygen exchange with the gas phase caused by the fact that the system elements (Bi, Cu and Pb) exhibit variable oxidation states may result in the phase formation conditions being not strictly equilibrium in the case of uncontrolled oxygen exchange.[210] The peritectic melting of phase 2212 is also accompanied by oxygen evolution.[210, 211] In this case, for obtaining unambiguous results it is necessary to strictly specify and control the oxygen partial pressure in the gas medium, as the compositions of phases that may be in equilibrium with phase 2212 at the peritectic decomposition point and the temperatures corresponding to this decomposition would necessarily depend on p_{O_2}.[169]

Since Bi-HTSC phase formation occurs in open thermodynamic systems, it is also necessary to take into account high volatility of some components (Pb, Bi or their oxides). It was shown [212] that at high temperatures the loss of mass of samples 2212 and 2223 is due to not only their decomposition with oxygen evolution, but also to evaporation of other elements. The loss of lead is especially pronounced both in the synthesis of phase (Bi,Pb)2223 in air [213, 214] and in its synthesis in a silver shell.[215]

To prevent the loss of volatile elements, it is necessary to create high external pressure. (This problem is even more topical for Tl–Ba–Ca–Cu–O and Hg–Ba–Ca–Cu–O systems containing highly volatile Tl and Hg.) It was found [216] that decomposition – recrystallisation of (Bi,Pb)2223 becomes reversible at high pressures but conditions for formation of a closed thermodynamic system that prevent uncontrolled loss of lead at high temperatures are attained only at overall pressure of > 100 atm.

In the production of (Bi,Pb)2212/Ag and (Bi,Pb)2223/Ag tapes, it is important to know the effect of silver on the phase composition. In the solid state, silver does not react with phases 2212 and 2223 and does not form solid solutions with them.[217–219] However, it was noted that at the interface between the initial blend and the silver shell, local formation of a liquid phase takes place at temperatures lower than the temperature of the main bulk,[83, 220–224] which is evidently due to the existence of low-temperature eutectics in the Ag–Bi–Sr–Ca–Cu–O system.[170, 193, 195]

No state diagrams of the Ag–2223 and Ag–(Bi,Pb)2223 systems have been reported as yet, but phase diagrams for a less complicated Ag–2212 system constructed using experimental data [170] and calculation data [193, 195] obtained by the so-called CALPHAD (CALculation of PHAse Diagram) method are known.[225] These diagrams reflect the change in the phase ratios upon the addition of silver and indicate that the Ag–2212 system has eutectics the temperatures of which were shown [195] to substantially depend on the oxygen partial pressure. Evidently, when developing the production process for tapes, one should take into account the effects of both the silver shell and the oxygen partial pressure, while simplified consideration may result in a failure.

4. Temperature regions of formation and stability of phases 2223 and 2212

The problem of increasing the stability of phases 2212 and 2223, which is important for development of their production process, has been discussed in many papers (Refs 187, 193, 194, 216, 221–223, 226–246). The conditions of formation and stability of some Bi-HTSC were presented above. We will consider this issue in more detail from the standpoint of thermal stability of phases 2223 and 2212 depending on process variables, specifically, the gas environment, lead and silver additives and overall pressure. We will also discuss decomposition of phases 2223 and 2212.

a. Phase 2223

The thermal stability of Bi-HTSC is appreciably affected by the partial pressure of oxygen.[214, 226, 227, 238–240, 243–248] The upper limits of the thermal stability of phases 2223 and (Bi,Pb)2223 depending on p_{O_2} are shown in Fig. 9. Above these boundaries in region *A*, solid-phase decomposition takes place, while in region *B* decomposition is accompanied by incongruent melting (the dashed line separating these regions is drawn approximately). It can be seen that the stability of the phases decreases with a decrease in p_{O_2} and that the most pronounced difference between the stabilities of 2223 and (Bi,Pb)2223 is observed in the subsolidus region *A*: (Bi,Pb)2223 is much more stable than 2223. Meanwhile, the effect of lead in oversolidus region *B* is insignificant.

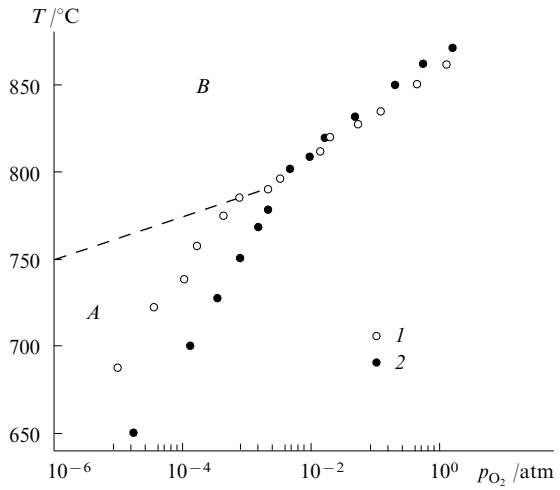


Figure 9. Positions of high-temperature stability limits of phases 2223 and (Bi,Pb)2223 described as $Bi_{2.1}Sr_{1.9}Ca_{2.0}Cu_{3.0}O_z$ (*1*) $Bi_{1.8}Pb_{0.3}Sr_2Ca_2.Cu_3O_z$ (*2*) depending on temperature and oxygen partial pressure (plotted using the data of Ref. 226).

Even in early studies dealing with the conditions of formation of phase 2223, it was noted that a decrease in the oxygen partial pressure leads to a noticeable decrease in the temperature of appearance of the liquid phase [168, 249–252] and that the temperature region in which the formation of 2223 is possible extends.[249, 251] This is properly illustrated in Fig. 10, which shows the phase stability diagram for (Bi,Pb)2223 *vs.* temperature and oxygen partial pressure (the diagram is based on the reported data [241] taking into account some information we found in other published sources). Some discrepancy of the results obtained by different authors is probably caused by different contents of lead and other elements in the nominal compositions (Bi,Pb)2223. Another cause for different results is the use of crucibles made of different materials (Al_2O_3, MgO) which differ in the reactivity towards (Bi,Pb)2223.[241] Despite some inconsistency of the data, it is possible to distinguish a 'stability corridor' for (Bi,Pb)2223 shown as the white region in Fig. 10. Above the corridor boundary, (Bi,Pb)2223 completely decomposes as a result of peritectic decomposition, while in the subsolidus region the loss of stability is apparently related to the chemical metastability of this phase at reduced temperatures.[70]

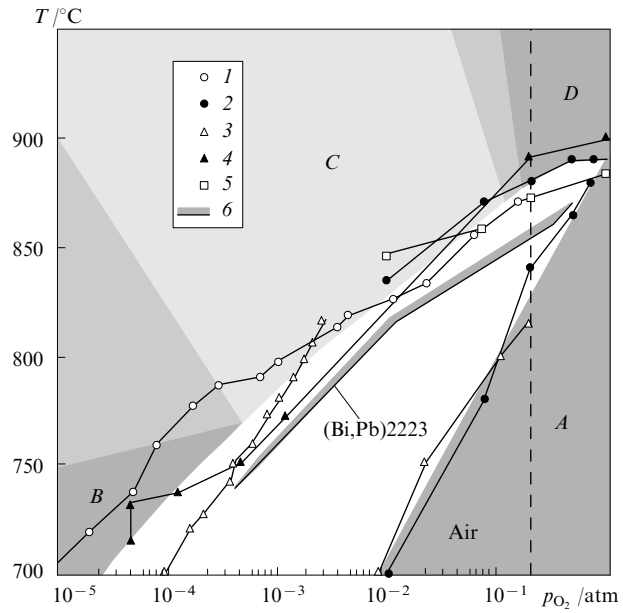


Figure 10. Positions of the stability regions of the phase (Bi,Pb)2223 depending on the temperature and oxygen partial pressure.
Data from the publications [226] (*1*),[214] (*2*),[237, 239] (*3*),[238] (*4*),[216] (*5*),[240] (*6*).

Within the 'stability corridor', one can distinguish a very narrow region in which (Bi,Pb)2223 is formed with minimum amount of impurities. In the diagram, this is shown by a shadow line which reflects data from Ref. 240 for $Bi_{1.79}Pb_{0.34}Sr_{1.83}Ca_{1.97}Cu_{3.13}O_z$. The syntheses with variation of the temperature and oxygen partial pressure along this line gave an almost pure phase (even the best samples contained only traces of Ca_2PbO_4 and CuO). For other compositions of (Bi,Pb)2223, the line of optimal T and p_{O_2} is somewhat shifted to either side but the pattern remains generally the same.

Typically, this line is located closer to the high-temperature stability limit of (Bi,Pb)2223 above which the phase entirely decomposes. In the intermediate region between this line and the high-temperature stability limit, phase 2223 coexists with 2201 (apart from Ca_2PbO_4 and CuO), and the higher the temperature, the greater the amount of phase 2201 formed.[240] At temperatures below the optimal one, phase 2223 coexists with phase 2212, and the farther the temperature from the optimal one, the greater the amount of phase 2212.[240] The transitions from phase 2223 to phases 2212 and 2201 are reversible but the simultaneous presence of phases 2201, 2212 and 2223 was observed in only one case.[240] This implies that, depending on the conditions, the process is substantially shifted in either direction, the course of the process being highly sensitive to temperature.

Several regions differing in the decomposition products of (Bi,Pb)2223 can be distinguished in the diagram. Regions *A* and *B* correspond to solid-phase decomposition, regions *C* and *D* reflect decomposition with incongruent melting (the boundaries between regions *B*, *C* and *D* were drawn arbitrarily). According to a number of publications,[214, 233, 253, 254] in region *A* decomposition of phase (Bi,Pb)2223 is accompanied by the formation of Ca_2PbO_4, while according to another publication,[255] this phase decomposes to give $Pb_3Bi_{0.5}Sr_{2.5}Ca_2.CuO_z$ (3221). While analysing these results, researchers [241] concluded that the formation of phase 3221 is more probable. This is formed in air at temperatures < 830 °C (Ref. 255) upon partial decomposition of (Bi,Pb)2223; decomposition is reversible: at 850 °C, phase (Bi,Pb)2223 is formed again. Decomposition of (Bi,Pb)2223 is rather slow and even after annealing for 120 h, (Bi,Pb)2223 remains the predominant phase.[214] The amount of the decomposed phase increases as the distance from the stability region increases.[233, 255]

In region *B*, the solid-phase decomposition follows a different mechanism. In this case, parallel and consecutive reactions take place.[226] The overall reaction can be written as follows:

$$\text{(Bi,Pb)2223} \longrightarrow \text{(Bi,Pb)}_2\text{Sr}_2\text{CaO}_z + \text{CaO} + \text{Cu}_2\text{O} + \text{O}_2 .$$

The intermediate Bi-containing products include (Bi,Pb)2212 and (Bi,Pb)2201, and the final product is (Bi,Pb)2210. The lead liberated upon decomposition of (Bi,Pb)2223 is completely incorporated into these bismuth-based products. In the absence of lead, decomposition in this region follows the reaction [226]

$$2223 \longrightarrow 2212 + Ca_2CuO_3 + Cu_2O + O_2 .$$

In the oversolidus regions *C* for $2 \times 10^{-4} < p_{O_2} < 0.2$ atm, decomposition of (Bi,Pb)2223 is accompanied by the formation of a liquid phase and $(Ca,Sr)_2CuO_3$

$$\text{(Bi,Pb)2223} \longrightarrow \text{L} + (\text{Ca,Sr})_2\text{CuO}_3 + \text{O}_2 ,$$

while in region *D* ($p_{O_2} > 0.2$ atm and $T > 850$ °C), (Ca,Sr)CuO_2 is formed in addition to the liquid phase and $(Ca,Sr)_2CuO_3$.[226] The composition of the liquid phase determined after crystallisation corresponds to the ratio Bi : Sr : Ca : Cu = 2.0 : 1.63 : 0.31 : 1.20, very close to a similar ratio in solid solution 2201. The formation of 2201 upon high-temperature decomposition of (Bi,Pb)2223 was also noted in other studies.[214, 227, 240, 241]

Data on the effect of silver on the thermal stability of (Bi,Pb)2223 are ambiguous.[222–224, 226, 235, 240, 241] The researchers,[226] who investigated the stability of (Bi,Pb)2223 in the presence of silver over a fairly broad ranges of temperature (650–885 °C) and oxygen partial pressure (10^{-5}–1.0 atm), state that silver has a minor effect on the thermal stability of (Bi,Pb)2223. However, it was found that the addition of silver to (Bi,Pb)2223, as in the case of phase 2212, markedly decreases the incongruent melting point (by 10 °C [240] or even by 30 °C [125]).

Detailed investigation of the effect of silver on (Bi,Pb)2223 was reported.[241, 256] The thermal stability of (Bi,Pb)2223 in contact with silver was studied in the temperature range of 830–905 °C in air and in a 95% Ar + 5% O_2 mixture. A study of the chemical and microstructural transformations taking place near the interface with silver has shown that during heat treatment for 2 h in region *A* (at 830°C in air) and in the stability region of (Bi,Pb)2223 (at 845–865 °C in air), processes limited to the interface between (Bi,Pb)2223 and Ag take place. Near the higher temperature limit of stability, the sample slightly decomposes but at the contact site with silver, (Bi,Pb)2223 melts with complete decomposition. At high temperatures in regions *C* and *D*, (Bi,Pb)2223 decomposes in less than 2 h according to the reaction [241]

$$\text{(Bi,Pb)2223} \longrightarrow$$
$$\longrightarrow \text{L (2201, rich in Ca + Ag)} + (\text{Ca,Sr})_2\text{CuO}_3 + (\text{Ca,Sr})\text{CuO}_2 .$$

Silver dissolves in the liquid phase and diffuses through it, thus ensuring further incongruent melting in the near-boundary region.

The first studies of the stability of (Bi,Pb)2223 at high isostatic pressure were carried out by Kawahara *et al.*[257] It was

found that at a temperature of 850 °C, oxygen partial pressure of 0.08 bar and overall pressure of 0.4 kbar, phase (Bi,Pb)2223 does not decompose and retains superconductivity. However, at very high pressures (54 kbar), this phase decomposes to give an unknown phase and modified phase 2223 (with a greater lattice parameter *c*). The superconductivity disappears but after the standard annealing of samples under atmospheric pressure, superconductivity is restored. This is indicative of reversibility of decomposition–crystallisation processes on passing from high to low pressures.

A more detailed investigation of the effect of high pressure on the stability of (Bi,Pb)2223 has been reported.[216] The resulting patterns of variation of the decomposition temperature of (Bi,Pb)2223 *vs.* pressure are presented in Fig. 11. It can be seen that this temperature depends on not only p_{O_2} but also on P_{tot} and the temperature range exceeds 45 °C over the pressure variation limits studied.

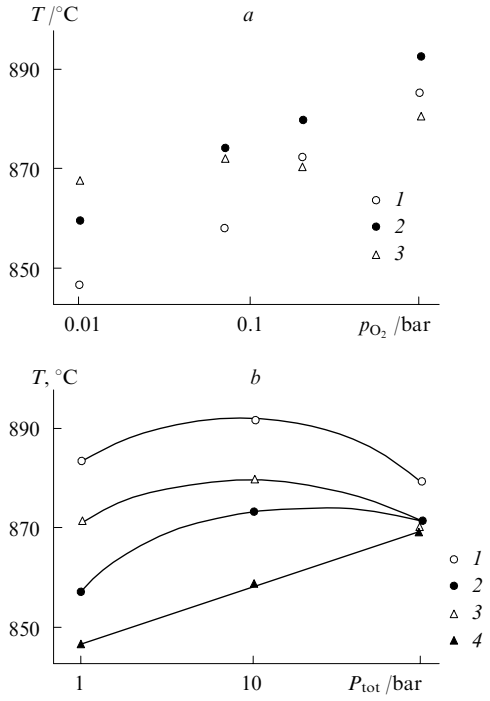


Figure 11. Decomposition temperature of the phase (Bi,Pb)2223 *vs.* oxygen partial pressure (*a*) and total pressure of the gas environment (*b*).[216]
(*a*): P_{tot} = 1 (*1*), 10 (*2*), 100 (*3*) bar;
(*b*): p_{O_2} = 0.01 (*1*), 0.07 (*2*), 0.2 (*3*), 1 (*4*) bar.

The pattern of dependences is noteworthy. At $p_{O_2} > 0.01$ bar, the dependences of decomposition temperature on P_{tot} have maxima at about P_{tot} = 10 bar. This interesting fact can be attributed to noticeable evaporation of lead during annealing of (Bi,Pb)2223,[164, 212–215, 258] resulting in a change in the composition. The change depends appreciably on the isostatic pressure.[216] The limiting content of lead in (Bi,Pb)2223 depends on p_{O_2} (Ref. 144) and on temperature (Refs 70, 125, 126, 164–166). The region of lead contents in (Bi,Pb)2223 as a function of temperature (see Fig. 4) has the shape of a deformed triangle beyond which this phase starts to decompose. The decrease in the limiting content of lead in the phase (Bi,Pb)2223 at temperatures of > 850 °C results in an increase in its decomposition temperature. Under the action of pressure, evaporation is retarded, and the higher the pressure the larger amount of lead remains in the sample and the lower the rate of increase in the decomposition temperature. At some stage of pressure gain, the decomposition temperature may start to decrease (this was actually observed [216]).

b. Phase 2212

The research into the thermal stability of phase 2212 is of interest for at least two reasons: this is important for targeted synthesis of this particular phase and also for the understanding of the formation mechanisms of phase 2223, because the formation of the latter is always preceded by phase 2212 as an intermediate.[259–261]

The stability of phase 2212 at different temperatures is the subject of a number of publications;[221, 238, 262–266] that for phase (Bi,Pb)2212 was also reported.[51, 204, 267, 268] A number of studies consider melting processes of phase 2212 (Refs 154, 167, 177, 226, 228, 265) and phase (Bi,Pb)2212.[147, 244, 268] It was found that phase 2212 melts incongruently, the melting temperature and phase composition between the liquidus and solidus surfaces being dependent on the oxygen partial pressure and the cationic composition of the compound. Melting and peritectic decomposition of phase 2212 are accompanied by oxygen evolution.[228]

Figure 12 shows the high-temperature limits of thermal stability of 2212 and (Bi,Pb)2212 as functions of p_{O_2} plotted on the basis of published data. The dashed line is an averaged result for 2212,[154, 226, 228, 238] while the continuous lines show the experimental data [244, 268] for (Bi,Pb)2212 with a limiting Pb content. In the regions above these curves, the phases decompose; at low temperatures and oxygen partial pressures (region *A*) solid-phase decomposition takes place, while in region *B* decomposition is accompanied by incongruent melting. It can be seen that phases become less stable with a decrease in p_{O_2}, while at equal p_{O_2} the peritectic decomposition of (Bi,Pb)2212 takes place at lower temperatures than decomposition of 2212. As the lead content in phase (Bi,Pb)2212 increases, its melting point decreases monotonically.[147, 148, 268]

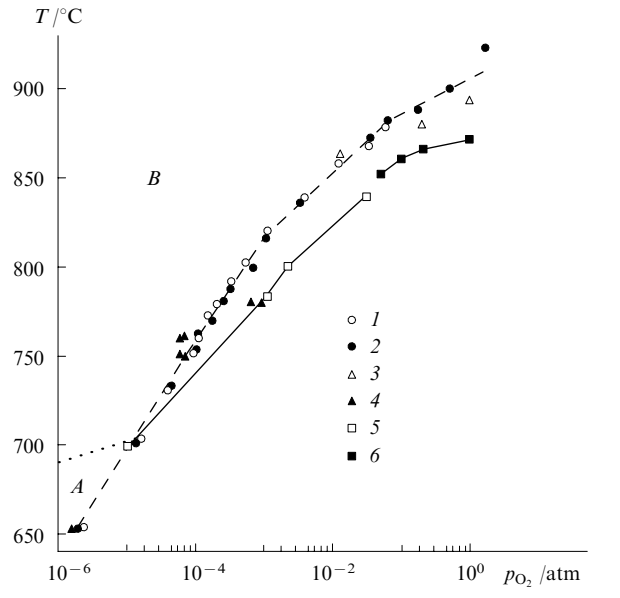


Figure 12. Positions of high-temperature stability limits of phases 2212 (dashed line) and (Bi,Pb)2212 (solid line) *vs.* oxygen partial pressure.
Plotted using data from publications: Ref. 154 (*1*), Ref. 226 (*2*), Ref. 228 (*3*), Ref. 238 (*4*), Ref. 244 (*5*), Ref. 268 (*6*).

The melting points of $Bi_{2-x}Pb_xSr_2CaCu_2O_z$ samples at different p_{O_2} are summarised in Table 1.[147, 268]

Table 1. Melting points (°C) of the samples described as $Bi_{2-x}Pb_xSr_2Ca.Cu_2O_{8+\delta}$ depending on the Pb content at different partial pressures of oxygen (atm).[268]

x	p_{O_2} = 0.05	p_{O_2} = 0.1	p_{O_2} = 0.21 [a]	p_{O_2} = 1.0
0.0	861	869	876 (874)	880
0.1	–	–	– (873)	–
0.2	858	863	870 (870)	872
0.3	–	–	– (868)	–
0.4	856	862	869 (866)	871

[a] The values in parentheses are data from Ref. 147.

A decrease in the melting point is also observed in solid solutions $Bi_2Sr_{2-x}Ca_xCu_2O_z$ upon partial replacement of strontium atoms by calcium [269–272] and upon replacement of calcium atoms by strontium in $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_z$.[147] The effect is even more pronounced when the two above factors, that is, introduction of lead and mutual replacement of calcium and strontium, act simultaneously.[147]

Different products of melting of phase 2212 were described in the literature. For example, it was reported that melting of 2212 in air, in addition to the melt, gives the following phases: (Sr,Ca)CuO_2 + (Sr,Ca)$_4Bi_2O_7$ (Refs 263, 264, 273–275), (Sr,Ca)CuO_2,[221, 265, 266] (Sr,Ca)$_{14}Cu_{24}O_{41}$,[276] (Sr,Ca)CuO_2 + + (Sr,Ca)$_2CuO_3$,[262, 277, 278] (Sr,Ca)CuO_2 + 2201 [177, 210] and 2201.[116, 279] The discrepancies are due to a number of reasons. It was noted [147] that one reason is that the samples may contain secondary phases that pass to the melt. Yet another reason is a change in the product composition at different decomposition temperatures. This is illustrated in Table 2, which presents the decomposition products of phase 2212 formed upon temperature increase at different oxygen partial pressures.[263] It can be seen that changes in the temperature and p_{O_2} result in noticeable changes in the phase compositions of decomposition products. Thus as the temperature increases in air, the bismuth-based phase gradually disappears, while the cuprate phases gradually undergo the following changes:[265]

(Sr,Ca)CuO_2 ⟶ (Sr,Ca)$_2CuO_3$ ⟶ CaO.

At low partial pressure of oxygen, $Bi_2(Sr,Ca)_3O_6$ is formed instead of $Bi_9(Sr,Ca)_{16}O_z$. In an oxygen atmosphere, the peritectic decomposition is accompanied by the formation of a more copper-rich cuprate $(Sr,Ca)_{14}Cu_{24}O_{41}$ instead of (Sr,Ca)CuO_2 and (Sr,Ca)$_2CuO_3$.

Although melting of phase 2212 in air has been studied most comprehensively, the nature of the first peritectic reaction taking place here is not known exactly. In a study [147] dealing with melting of phase 2212 and its solid solutions with different contents of lead and calcium (primary attention was paid to the phase purity of the initial material), no bismuth-based phase $Bi_9(Sr,Ca)_{16}O_z$ was found. Powder X-ray diffraction analysis of quenched melts showed the presence of phase 2201 and (Sr,Ca)CuO_2 in all samples and additional phases $(Sr,Ca)_{14}Cu_{21}O_{41}$ and (Ca,Sr)$_2CuO_3$, which replace each other as the calcium content in the initial phase 2212 changes and are not detected simultaneously. On the basis of the research, it was concluded that 2201 crystallises from the liquid phase on cooling, and (Sr,Ca)CuO_2 is formed upon decomposition of 2212 and is an equilibrium phase coexisting with the liquid. In the researchers' opinion, (Ca,Sr)$_2CuO_3$ and $(Sr,Ca)_{14}Cu_{21}O_{41}$ are not equilibrium products of the first peritectic decomposition of phase 2212 but crystallise together with 2201 from the cooled melt. As the temperature increases, the situation changes. First, traces of (Ca,Sr)$_2CuO_3$ appear at 900 °C together with (Sr,Ca)CuO_2,[262, 278] and at higher temperatures (Ca,Sr)$_2CuO_3$ completely replaces (Sr,Ca)CuO_2.

Table 2. Sequence of formation of decomposition products of 2212 following temperature rise at different partial pressures of oxygen.[263]

p_{O_2} /atm	T /°C	Phase composition [a]
0.01		2212
	850	(Sr,Ca)CuO_2 + (Sr,Ca)$_2CuO_3$ + $Bi_2(Sr,Ca)_3O_z$ + L
	860	(Sr,Ca)CuO_2 + (Sr,Ca)$_2CuO_3$ + $Bi_2(Sr,Ca)_3O_z$ + + (Sr,Ca)O + L
	880	(Sr,Ca)$_2CuO_3$ + $Bi_2(Sr,Ca)_3O_x$ + (Sr,Ca)O + L
	891	$Bi_2(Sr,Ca)_3O_z$ + (Sr,Ca)O + L
	920	(Sr,Ca)O + L
0.21		2212
	890	(Sr,Ca)CuO_2 + $Bi_9(Sr,Ca)_{16}O_z$ + L
	900	(Sr,Ca)CuO_2 + (Sr,Ca)$_2CuO_3$ + $Bi_9(Sr,Ca)_{16}O_z$ + L
	925	(Sr,Ca)CuO_2 + (Sr,Ca)$_2CuO_3$ + L
	937	(Sr,Ca)$_2CuO_3$ + (Sr,Ca)O + L
	965	(Sr,Ca)O + L
1.0		2212
	902	$(Sr,Ca)_{14}Cu_{24}O_{41}$ + $Bi_9(Sr,Ca)_{16}O_z$ + L
	942	$(Sr,Ca)_{14}Cu_{24}O_{41}$ + (Sr,Ca)$_2CuO_3$ + + $Bi_9(Sr,Ca)_{16}O_z$ + L
	943	$(Sr,Ca)_{14}Cu_{24}O_{41}$ + (Sr,Ca)$_2CuO_3$ + + (Sr,Ca)CuO_2 + $Bi_9(Sr,Ca)_{16}O_z$ + L
	944	(Sr,Ca)CuO_2 + (Sr,Ca)$_2CuO_3$ + $Bi_9(Sr,Ca)_{16}O_z$ + L
	963	(Sr,Ca)$_2CuO_3$ + $Bi_9(Sr,Ca)_{16}O_z$ + L
	966	(Sr,Ca)$_2CuO_3$ + (Sr,Ca)O + L

[a] The phase $Bi_9(Sr,Ca)_{16}O_z$ (Refs 173, 280) presented in the Table is often considered as a monoclinic phase with a somewhat different composition: $Bi_2(Sr,Ca)_4O_7$ (Refs 264, 281); however, it was shown [282] that this is the same phase.

The effect of p_{O_2} on the products of peritectic decomposition of (Bi,Pb)2212 has been less studied than that for 2212. However, it is known that at $p_{O_2} > 0.55$ atm, melting of (Bi,Pb)2212 gives rise to solid lead-containing products such as (Sr,Ca)$_2PbO_4$,[268] the stability of which decreases with a decrease in the oxygen partial pressure. At $p_{O_2} < 0.55$ atm and temperatures of 750–840 °C, no lead-containing solid phases are formed, the decomposition process being described by the reaction [244]

(Bi,Pb)2212 ⟶ L + (Sr,Ca)CuO_2 + CaO + O_2.

The effect of silver on peritectic melting of phase 2212 has been investigated using 2212/Ag [221, 226, 228, 264, 265, 267, 283–287] and (Bi,Pb)2212/Ag samples.[244, 268, 288] Figure 13 shows the calculated limits of thermal stability of phase 2212 in the absence and in the presence of silver depending on p_{O_2}.[195] Together with the calculated curves, this Figure shows some experimental results, which are in reasonably good agreement with the results of calculations. Attention is attracted by the fact that with an increase in p_{O_2}, the difference between the melting point of pure phase 2212 and the melting point of 2212/Ag samples increases. One more specific feature is the presence of maxima in the curves at p_{O_2} values close to the partial pressure of atmospheric oxygen.

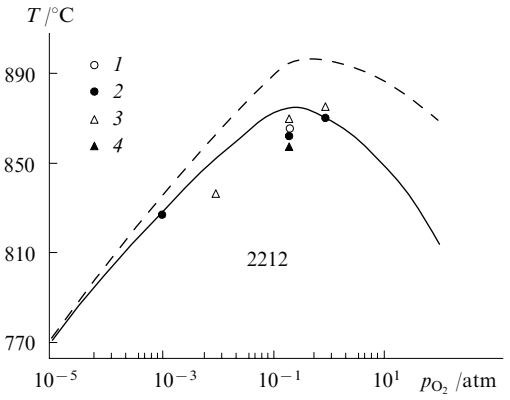


Figure 13. Calculated thermal stability limits of 2212 in the absence (dashed curve) and in the presence of silver (solid curve) *vs*. oxygen partial pressure.[195]
The dots are data of publications Ref. 170 (*1*), Ref. 228 (*2*), Ref. 263 (*3*), Ref. 284 (*4*).

In the synthesis of Bi-HTSC, strontium and calcium carbonates are often used as the starting compounds. These compounds have high thermodynamic stability and their incomplete decomposition may cause undesirable contamination of the material with carbon during preliminary annealing or synthesis. This fact should be taken into account, especially in the production of tapes. In the latter case, incompletely decomposed carbonates or minor amounts of CO_2 captured from air would inevitably produce impurities: the silver shell is oxygen-permeable and CO_2-impermeable. The presence of residual carbon affects the melting temperature of Bi-HTSC. All other factors being the same, the temperature of the onset of melting proved to be 10–15 °C lower for (Bi,Pb)2223/Ag samples highly doped with carbon (0.6 mass %) than for carbon-free samples.[289] The peritectic melting temperature of 2212/Ag and the amount of liquid formed depend on not only the amount of introduced silver but also on the carbon content. In order to distinguish between the silver and carbon effects on the decrease in the melting temperature of phase 2212, a special study was carried out,[273] which showed that in the presence of carbon, the melting point of phase 2212 decreases to a considerably lesser extent than in the presence of silver. The effect of carbon increases, while that of silver, conversely, decreases with a decrease in the oxygen partial pressure.

It has been shown [290] that the partial pressure of CO_2 has an appreciable influence on the stability of phase 2212 and phase ratios in the $Bi_2O_3-SrO-CaO-CuO$ system. Even minor amounts of CO_2 may induce decomposition of 2212 to give a liquid phase, CuO and $(Sr,Ca)CO_3$. When the CO_2 partial pressure is above 10^{-2} atm, phase 2212 cannot be synthesised (even with associated phases) at any temperature. It is clear that in the production of tapes from precursors containing residual carbonates, local regions with increased CO_2 concentration may arise, and these may be responsible for undesired reactions and impair the material homogeneity and this, in turn, would deteriorate the HTSC characteristics. Thus it was shown that decline of the transport properties of Bi-HTSC depends on the amount of admixed carbon.[291–296]

Phase 2212, like 2223, has a low-temperature stability limit. On long-term annealing in air at 790 ± 5 °C, phase 2212 decomposes to give $Bi_2Sr_2CuO_{6+\delta}$ and $Bi_2(Sr,Ca)O_4$.[238] Similar decomposition products were found [297] after annealing of single crystals of 2212 at 400–750 °C.

The plase (Bi,Pb)2212 shows a somewhat different annealing behaviour. During annealing in air (~700 °C), this phase loses lead giving rise to $Pb_3Bi_{0.5}Sr_{2.5}Ca_2CuO_z$ (3221).[50,267] The process is reversible: after annealing at ~860 °C, the initial composition of (Bi,Pb)2212 is fully restored.[267] The formation of phase 3221 and the reverse process, the formation of phase (Bi,Pb)2212, are accompanied by considerable changes in the sample weight.[298] This is associated with oxygen absorption and subsequent loss during the chemical transformations of lead compounds following increase in temperature. The fact is that phase 3221, as well as Ca_2PbO_4, contains lead in an oxidation state of about +4 (Ref. 255), while (Bi,Pb)2212, of about +2 (Ref. 299). The change in the lead oxidation state in chemical processes naturally results in a change in the oxygen content in the system.

During peritectic melting of phase 2212, oxygen exchange with the gas environment is fast,[228,300] but before melting, decomposition and oxygen exchange follow retarded kinetics.[267] Therefore, as shown by Flükiger and co-workers,[7,51,52,204] on fast heating in air (2 K min^{-1}), the 'pure' phase (Bi,Pb)2212 barely decomposes below 880 °C where it starts to melt. However, when blended with Ca_2CuO_3 and CuO, lead from (Bi,Pb)2212 passes to phase 3221, and this takes place even in the region of relatively low temperatures (> 400 °C) at the same heating rate. Above 835 °C, phase 3221 starts to decompose to give again (Bi,Pb)2212, Ca_2CuO_3 and CuO,[7,51,52,204] from which phase (Bi,Pb)2223 is formed on further increase in temperature over a long residence time. The repeated formation of phase (Bi,Pb)2212 directly prior to the formation of (Bi,Pb)2223 is an important intermediate link. In a series of studies, Grivel *et al.*[119,156,259,260] have shown that phase 2212 is enriched not only in lead but also in calcium (in a lead-free system, only in calcium) above the stoichiometric amount. This transformation of phase 2212 (confirmed also in other publications [99,206,215]) can be regarded as a preparatory stage facilitating the subsequent formation of phase 2223 due to lower stability and melting point of the solid solution of phase 2212 compared to the stoichiometric phase 2212.[147,167,259,301]

Now we compare the effect of lead on the thermal stability of phases 2223 and 2212 at different p_{O_2}. On introduction of lead into phase 2223, the stability limit of the phase moves towards higher temperatures into the subsolidus region, and the stability limit of this phase in the oversolidus region changes little [226] (see Fig. 9). For phase 2212, conversely, the difference between the temperature limits of stability is manifested in the oversolidus region (see Fig. 12). The stability limit of (Bi,Pb)2212 shifts to lower temperatures compared with the stability limit of 2212.[226] Thus, on variation of the temperature and p_{O_2}, the effects of lead on the stability limits of phases 2223 and 2212 are substantially different. Apparently, this is of prime importance for the formation of 2223, which includes decomposition of intermediate phase 2212. The introduction of lead increases the stability of phase 2223 and facilitates its formation due to easier peritectic decomposition of phase (Bi,Pb)2212 compared to 2212. The peritectic decomposition of (Bi,Pb)2212 becomes even easier when lead and calcium are introduced simultaneously,[147,167] as is the case in the synthesis of (Bi,Pb)2223.[259,301]

III. Correlations of superconducting properties with the chemical composition and crystal structure of bismuth-based superconductors

1. Real structure and transport current

The real structure (or microstructure) of the material has direct influence on the transport current, which can flow through a superconductor. For free flow of the superconducting current, the thickness of grain interlayers arising due to segregation of impurities and due to other inhomogeneities should not exceed the so-called coherence length (ξ), which is almost an order of magnitude lower for some oxide HTSC than for low-temperature superconductors.[302] In chemical systems with three structurally related phases and a set of other associated phases, it is exceptionally difficult to avoid the presence of impurities; therefore, thickness of grain interlayers in an HTSC material is most often much larger than the coherence length. This is one of the reasons for the sharp decrease in the critical current density at grain boundaries.

One more reason for deterioration of the current-carrying ability is high anisotropy of physical properties in different crystallographic directions, which is even more pronounced for Bi-HTSC due to their specific crystal structure than for known lanthanum and yttrium HTSC.[303] In Bi-HTSC, the electrical conductivity in the *ab* plane is several orders of magnitude higher than that along direction *c*,[304, 305] *i.e.*, the conductivity is essentially two-dimensional, the current mainly flowing in the *ab* plane. It is believed that the CuO_2 layers arranged in this plane are responsible for superconductivity.

The coherence lengths of Bi-HTSC found by different methods are summarised in Table 3. The results poorly correlate with one another. This is caused, on the one hand, by the different compositions of the samples, and on the other hand, by fundamental difficulties of determination of this type of characteristics. However, in this case, the order of magnitude is important. Analysis of the presented data revealed the anisotropy of the coherence length in the *ab* plane and along the *c* axis. Other fundamental physical characteristics, *e.g.*, the lower and higher critical fields and the depth of field penetration, are also clearly anisotropic.[313] The superconducting grains are disoriented relative to one another, and this factor also contributes to violation of the material homogeneity and deteriorates its transport properties.[314] The critical current density through interfaces considerably depends on the mutual spatial arrangement of the crystallites forming them.

Table 3. Coherence lengths of bismuth HTSC.

$\xi_{ab}(0)$ /nm	$\xi_c(0)$ /nm	Coherence length anisotropy	Ref.
Phase 2212			
4.2	0.1	42	303
3.5	0.13	27	306
3.2	0.06	53	307
3.1	0.4	8	308
2.7	0.045	60	309
2.7	0.18	15	310
0.9	0.05	18	311
Phase 2223			
3.3	0.18	18	306
2.0	0.03	67	73
2.9	0.093	31	312

However, the question of the current paths through the interfaces has not been ultimately solved.[315] A number of models describing the possible ways of current flow through grain boundaries have been proposed. These are the so-called 'disordered bond',[316] 'brick wall' [317, 318] and 'railroad point' models.[30, 319, 320] Each model reflects the possible pattern of grain orientation with respect to one another and the bonds thus established.

According to the simplest mechanism of current flow, the arrangement (packing) of plate-like crystallites is considered to resemble a brickwork. In this case, all crystallites are oriented along the *c* axis but disoriented in the *ab* plane; therefore, twist boundaries are formed. This version is typical of single crystals or separate elements of a polycrystalline material. According to the 'brick wall' model, weak bonds are formed by twist boundaries.

Detailed consideration of the microstructure of (Bi,Pb)2223/Ag tapes with high critical current density has shown that small-angle boundaries between lamellas (sets of accreted plate crystallites) serve as the main interfaces. This fact underlies the 'railroad point' model which postulates the possibility of current flow also through small-angle interfaces. It is assumed that this micromechanism describes most adequately the current flow in textured (Bi,Pb)2223/Ag tapes.[52]

In non-textured ceramics where the superconducting grains are randomly oriented, high-angle boundaries and impurity interlayers and mechanical discontinuities in the samples play an important role in restriction of the transport current.

Extensive knowledge of the effect of interfaces on the critical current density has been accumulated to date (see reviews [316, 321]). It was found that deterioration of the current-carrying ability of the material at twist boundaries may be due to local variations of the chemical composition at (or near) the boundaries.[322] However, the appearance of twist boundaries is not always accompanied by changes in the composition. Bismuth-based HTSC with high-quality twist boundaries through which the superconducting current passed in the same way as in the single crystals forming them were produced.[323–325]

The deterioration of the current characteristics at small-angle edge boundaries may be caused by a local change in the composition at interfaces and stresses caused by edge dislocations. The critical current density follows a sharp exponential dependence on the interface inclination angle, which is manifested as a sharp decrease in j_c even at small disorientation angle.[326] This sensitivity of the current characteristics to the interface orientation or to the degree of a texturing may be responsible for the spatial variation of the critical current in tapes. In particular, it was found that the highest superconducting current flows in a thin layer of the superconductor near the silver shell.[327]

Conversely, the transport current density through high-angle boundaries between the crystallites depends little on the disorientation angle,[326] but it is however two to three orders of magnitude lower than that within the crystallite. This ratio is observed for non-textured ceramics.

Note that the question of mechanism (or mechanisms) of current suppression by interfaces is still debated.[326] Nevertheless, the use of accumulated knowledge promoted considerable progress as regards attainment of high critical current densities, in particular, in (Bi,Pb)2223/Ag tapes.

2. Impurities and magnetic flux pinning

The grain structure of polycrystalline Bi-HTSC has a dual effect on the critical transport current: on the one hand, weak intergrain bonds restrict j_c and, on the other hand, together with crystal structure defects of the superconductor, they may create conditions for pinning of magnetic vortices and increase in j_c.[328, 329] Bismuth-based HTSC have pinning centres with relatively low energy, which are capable of keeping magnetic vortices only at very low temperatures. At temperatures above 20–30 K, the superconducting behaviour of the material is destroyed by the thermally activated magnetic flux: as the temperature increases, the critical current density rapidly decreases, and simultaneously it sharply drops due to an increase in the magnetic field intensity (at 20 K the j_c value decreases by approximately two orders of magnitude even in a 2 T field [6]). Thus, the problem of enhancement of the transport properties of Bi-HTSC is related, at least, to solution of the problems of improving the material microstructure and bonds between the grains and increasing the energy of magnetic flux pinning and the number of pinning centres. Now we consider these problems from the standpoint of possible positive effect of impurities on the Bi-HTSC behaviour.

The positive role of impurities present in Bi-HTSC may be as follows:

— impurities, especially low-melting ones, may promote the formation of Bi-HTSC phases and extend the range of conditions where the superconductor is formed;[330, 331]

— dopants may promote stabilisation of Bi-HTSC and increase the Bi-HTSC content in the composite material with the respective decrease in the amount of secondary phases;[332]

— impurities may improve the material microstructure, thus promoting texturing, increase in the grain size and improve the intergrain bonds;[333]

— impurities may serve as effective centres of magnetic flux pinning;[37, 334]

— impurities may improve the mechanical characteristics of the material.[334]

It follows from the foregoing that specially designed composite Bi-HTSC should possess the best functional characteristics. An important task in the synthesis of such HTSC is the search for dopants and conditions for their addition to improve the superconducting properties of the major component. These may be dopants that either do not interact with the superconducting phase [335] or form compatible phases (equilibrated with the superconductor phase); the replacement of the superconductor cations by the dopant cations should be as minor as possible.[334]

The microstructure was improved by using dopants that promoted phase formation, enlargement of superconducting grains and enhancement of intergrain contacts. An example is the effect of lead on the synthesis of phase 2223.[336, 337] In the formation of (Bi,Pb)2223 microstructure, a useful role is played by a slight excess of calcium and copper.[213, 338–340] Admixtures of strontium sulfate,[314] boron-containing phases,[330, 341–344] silicon carbide [345] and vanadium oxide [346] are also favourable. Some researchers noted a positive effect of addition of magnesium oxide to the superconducting matrix on the microstructure: the addition of a minor amount of finely dispersed MgO as whiskers (thread-like crystals) to the 2212 (see Refs 347–349) and (Bi,Pb)2223 ceramics [333, 350] and to 2212/Ag [332] and (Bi,Pb)2223/Ag [351, 352] tapes increased the critical current density by improving the intergrain bonds,[349–351] decreasing the phase inclusions [332, 349, 352] and more pronounced texturing.[333, 347–349, 353–357] It was also noted that the addition of MgO whiskers to (Bi,Pb)2223 improved the mechanical properties of the composite.[358] It was reported [332, 351, 353] that the addition of MgO not only improved the material microstructure but also enhanced the magnetic flux pinning. The same effect may be exerted by other dopants, for example, SiC.[345]

The problem of increasing the efficiency of magnetic flux pinning for Bi-HTSC is the most topical.[359, 360] This problem has been addressed by various methods: by forming pinning centres by inclusion of secondary phases formed in the Bi–(Pb)–Sr–Ca–Cu–O system,[146, 200, 253, 328, 361–379] by introduction of additional elements,[345, 380–399] or by means of defects formed upon irradiation,[400–413] thermal or mechanical treatment.[74, 414–416] Various structure inhomogeneities may serve as pinning centres. Apart from admixture particles, the pinning centres can be formed by stacking faults,[417] dislocations,[415, 417] oxygen vacancies,[418] atom substitutions,[380, 419] columnar defects arising upon irradiation with heavy metal ions [400, 409] and other crystal structure defects.

One of most efficient methods for the creation of pinning centres is to form columnar defects with a diameter of 10–20 nm and a length of 1–10 μm by irradiating the sample with heavy ions.[411] However, it is clear that irradiation is a fairly complicated and expensive process, not very practical for extended articles. In addition, irradiation results in a minor penetration depth of ions and the defects thus formed have low thermal stability.[420] This considerably restricts the applicability of this method.

The works on formation of pinning centres by introducing dopants into superconductors are most extensive. Lots of dopants that either modify the chemical composition of superconducting phases or produce inclusions of impurity phases compatible with the superconductor have been tested. In some cases, encouraging results were obtained. For example, a many-fold increase in the j_c value upon increase in the pinning efficiency has been attained in the bulk 2212 ceramics as a composition with highly dispersed (Sr,Ca)SnO_3,[395, 399] (Sr,Ca)In_2O_4 [396] or Mg(Cu)O,[274, 386] in 2212/Ag tapes with submicrometre inclusions of $SrZrO_3$,[390] in single crystals of 2212 with microinclusions of MgO,[387, 388] and in (Bi,Pb)2223/Ag tapes with MgO nanoparticle inclusions.[351, 353, 384, 385] Note that MgO is the most popular dopant used to improve the current characteristics of Bi-HTSC. The above examples can be supplemented by an increase in the efficiency of pinning upon the introduction of MgO nanowhiskers into textured 2212 ceramics [383] and 2212 films.[382] It was considered until recently that magnesium oxide is chemically inert with respect to Bi-HTSC. However, it was shown [274] that only coarsely crystalline MgO is inert, while finely dispersed MgO actively reacts with Bi-HTSC to give the solid solution $Mg_{1-x}Cu_xO$ ($x \sim 0.1$). Apparently, it is expedient to use this compound as a precursor for the synthesis of compositions.

An attractive idea is to introduce artificial nanosized structures such as carbon nanotubes into the superconductor. A successful attempt of introducing carbon nanotubes into 2212 ceramics has been reported;[397] the composite thus obtained had an intragrain critical current density an order of magnitude higher than the pure sample. Unfortunately, at high temperatures, carbon reacts in an oxidative environment and preparation of this composite requires special conditions.

Widely used is doping of superconducting phases by additional chemical elements. This may occur as both replacement of atoms in the superconducting phase and the formation of impurity phases. The partial replacement of bismuth atoms by lead is best studied. In this case, taking into account pinning, of interest is the result of lead doping of 2212 crystals.[329] It was

found that phase (Bi,Pb)2212 with a high lead content is separated into two solid solutions to give a structure with plate-like domains with sizes of 10 to 50 nm. This nanocomposite has an enhanced j_c value. Studies of the effect of other doping elements the reaction products of which are compatible with phases 2212 and 2223 have been surveyed.[37, 334]

Natural impurities that are present in higher or lower amounts in Bi-HTSC as associated secondary phases can also serve as pinning centres. Some publications reported a positive role of small amounts of Ca_2CuO_3 or $(Ca,Sr)_2CuO_3$ in a superconducting matrix. Their presence increases j_c in lead-free bulk ceramics, 2223 (Ref. 361) and 2212,[362, 363] in lead-containing 2223 ceramics,[364, 365] and in wires and tapes.[366–371] A positive effect of CuO inclusions in 2212 films[379] and nanosized Ca_2PbO_4 precipitates in (Bi,Pb)2223/Ag tapes [357] has been reported.

The contents of secondary phases can be regulated by specifying the initial composition or by controlling the partial decomposition of Bi-HTSC by slight change in the conditions, for example, by temperature variation. The development of the last-mentioned approach, which allows one to design nanosized or submicrometre precipitates of impurity phases is the subject of a number of publications.[146, 253, 372–376] This is based on the use of equilibrium phase diagram to select the conditions of synthesis of a superconducting phase and its transformation into a multiphase composite. Usually, this is accomplished by deliberate partial decomposition of a superconductor by means of annealing at temperatures beyond the region of existence of the single-phase state. The annealing temperatures can be both above and below the temperature of synthesis of the conductor. The concentrations of admixtures and other defects can be controlled by varying the annealing temperature and time. The possibility of formation of pinning centres in this way was demonstrated for phases 2212,[373–375] (Bi,Pb)2212 [146, 376] and (Bi,Pb)2223.[372] A good example of implementation of this approach is phase 2212. This phase tends to exhibit considerable temperature dependences of the limiting contents of calcium, strontium, bismuth and lead. Going beyond the temperature limits of existence of single-phase 2212 induces separation of various secondary phases. For different directions of transition to the annealing temperature (above or below the synthesis temperature), the chemical composition of the superconducting phase and the nature of impurity phases change in different ways. However, irrespective of the direction of this transition, the transport properties were improved in all cases.[376] However, it should be noted that the formation of impurity precipitates upon low-temperature (below the temperature of thermodynamic stability of 2212) annealing is not always successful: substantial kinetic difficulties hampering the processes may arise.

The highest pinning efficiency can be attained if the impurity inclusions or defects are comparable with the coherence length of this superconductor.[421, 422] For Bi-HTSC, this length is < 10 nm (see Table 3). However, it was noted that the characteristic length of impurity precipitates associated with the three-dimensional pinning centres reaches several hundreds of nanometers.[376] Large inclusions can capture one or several vortices.[423] In this case, the interfaces between the impurity and the superconductor are apparently responsible for pinning.[332] The specific surface area of precipitates might also play the crucial role.[375] The highest pinning efficiency is achieved in the case of optimal ratio of the dimensions and concentration of precipitates. Simultaneously, the intragrain critical current density increases by a large factor; this indicates once again that defects are localised inside the grains. As regards the nature of defects, they may be a result of both impurity precipitates and disturbance of the crystal lattice of superconductor during decomposition.[375]

One should borne in mind the complex nature of the impurity effect. It was noted above that impurities may improve the transport properties of a superconductor not only by increasing the pinning efficiency but also by improving the material microstructure. In some cases, both factors act simultaneously.[332, 345, 349, 351, 353] We have shown [338, 339] that upon introduction of a slight excess of calcium and copper during the synthesis of (Bi,Pb)2223 ceramics the resulting increase in the superconducting and electrophysical properties would be caused by not merely the presence of Ca_2CuO_3 as such, but also by the formation of a microstructure with large grains. There exists an optimal composition (in our case, $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_{2.8}Cu_{3.4}O_z$) with the best set of superconducting and electrical properties: the highest T_c, j_c, current carrier mobility and the lowest specific electric and magnetic resistance. These samples have higher density and greater dimensions of superconducting grains than dopant-free samples. This provides grounds for believing that in this case the tightest contact between the superconductor grains is provided and an extensive network of superconducting contacts with enhanced current-carrying ability is formed. It cannot also be ruled out that the introduction of calcium and copper may also give rise to effective pinning centres under particular conditions. For samples described as $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_{2.8}Cu_{3.4}O_z$, the pinning energy proved to be such that the superconducting transport current was retained even in a 0.8 T field at 77 K.

3. The effect of chemical composition and crystal structure on the temperature of superconducting transition

Bismuth-based HTSC are typical phases of variable composition the properties of which depend on their cationic and anionic composition. In particular, these and other metal oxide HTSC tend to be non-stoiochiometric as regards oxygen; probably, this is fairly important for determination of T_c (especially for phase 2212). Therefore, to identify the nature of the superconducting state, it is necessary to elucidate the regularities of the effects of oxygen content and the chemical composition as a whole on the superconductivity parameters. This accounts for the steady interest in the investigations of the effect of chemical composition on the properties of Bi-HTSC.[424]

Most likely, excess oxygen is accumulated in $(BiO)_2$ layers,[47, 425–427] as indicated by the data from neutron diffraction,[111, 428] high-resolution electron microscopy,[47] raster tunnelling microscopy [426] and Raman spectroscopy.[429] The amount of inserted hyperstoichiometric oxygen depends on the temperature and oxygen partial pressure in the gas phase, the range of its contents in Bi-HTSC being rather narrow compared, for example, with that for $YBa_2Cu_3O_{6+\delta}$ [recall that the oxygen content above the stoichiometry does not exceed 0.34 for 2212 (Refs 138, 150–155, 430–434) and (Bi,Pb)2223 [435, 436]].

Despite the rather narrow range of variation of the oxygen content in Bi-HTSC, their superconducting properties are fairly sensitive to oxidation conditions. The effect of heat procedures is illustrated by Fig. 14, which shows dependences of T_c of bismuth-based superconductors on the annealing temperature in air.[437, 438] One can see that the effect is quite pronounced.

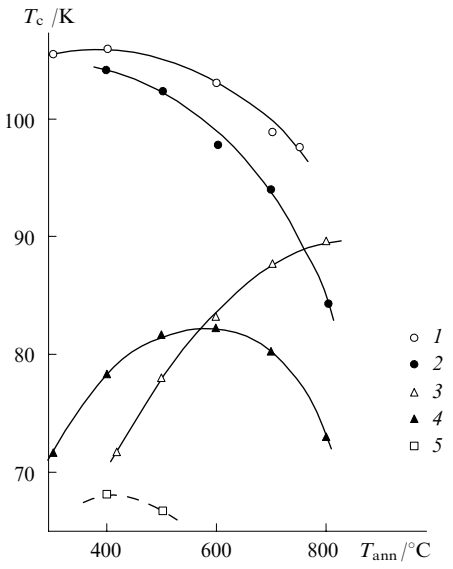


Figure 14. Superconducting transition temperature *vs.* temperature of annealing in air followed by quenching into liquid nitrogen for $Bi_{1.8}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ (*1*), $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (*2*), $Bi_2Sr_2Ca.Cu_2O_{8+\delta}$ (*3*), $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ (*4*), $Bi_2SrCaCuO_{6+\delta}$ (*5*).[437,438]

As for other p-type metal oxide HTSC, the content of hyperstoichiometric oxygen has an effect on the hole (charge carrier) concentration.[438–441] Presumably, the superconductivity in Bi-HTSC is due to the dynamic transfer of holes from $(BiO)_2$ layers to CuO_2 or of electrons in the opposite direction. Thus, $(BiO)_2$ layers function as hole donors in the system.[47,442] The oxidation state of bismuth thus decreases and correspondingly the formal oxidation state of copper increases according to the redox reaction [427,443,444]

$$Bi^{(3+\alpha)+} + Cu^{2+} \rightleftharpoons Bi^{(3+\alpha)-\delta} + Cu^{2+\delta}.$$

In this connection we would like to note the following. It was found[445] by thermogravimetric analysis and different titration procedures that phase 2212 contains two forms of hyperstoichiometric oxygen differing in the bond energy with cations and in the ease of removal from the sample. It was also found[149,168] that an increase in the content of hyperstoichiometric oxygen in phases 2212 and 2223 results in a change in the thermodynamic characteristics and, hence, properties. Finally, it was shown[446] that with an increase in the oxygen content in 2212, the bismuth oxidation state unexpectedly decreases (together with a decrease in the modulation period in $(BiO)_2$ layers and an increase in the planar O–Cu–O bond lengths in CuO_2 layers). There are also opposite observations indicating an increase in the oxidation state of bismuth in phase 2212 upon an increase in the oxygen content.[427,443] In any case, a change in the oxidation states of bismuth and copper atoms reflects charge redistribution between the $(BiO)_2$ layer and the CuO_2 layer responsible for superconductivity.

No consensus about the real charge distribution between copper and oxygen in a CuO_2 layer has been reached to date. Holes may be located at the copper atom sites as Cu^{3+}, at oxygen atom sites as O^-, or at the Cu–O bonds as the $[Cu-O]^+$ complex.[447] The last-mentioned version is commonly accepted and has been experimentally supported.[445] Holes can be redistributed under the action of various factors. Thus below T_c the number of holes increases in the oxygen 2p orbitals and correspondingly decreases in the copper 3d orbitals.[448,449]

In order to elucidate the superconductivity mechanism of oxide cuprates, it is important to find the relationship between the superconductivity parameters and concentration of current carriers. It was found that the highest critical temperature ($T_{c\,max}$) is achieved at the optimal value of hole concentration. The pattern of these dependences is reflected in the diagram presented in Fig. 15, which shows how the relative $T_c/T_{c\,max}$ value varies depending on the number of holes per copper atom for the homologous series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$.[438] The experimental points applied on the curve were obtained for the samples described as $Bi_{1.9}Pb_{0.2}Sr_2Ca_{0.9}Cu_2O_{8+\delta}$ annealed in air at different temperatures ranging from 300 to 800 °C. The same Figure shows the calculated ranges of variation of the density of holes formed under these conditions in phases 2201, 2212 and 2223.

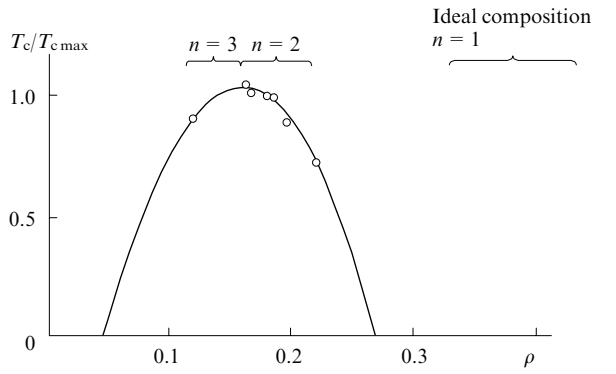


Figure 15. Plot of $T_c/T_{c\,max}$ *vs.* hole density (ρ) for bismuth cuprates $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$.[438]

Note that analysis of numerous experimental data revealed certain versatility of the relationship between $T_c/T_{c\,max}$ ratios and hole concentrations for many p-type cuprate HTSC.[450] Despite the fact that each particular compound has its own maximum T_c value, the variation of the normalised $T_c/T_{c\,max}$ value *vs.* hole concentration often obeys a versatile dependence the plot of which is a parabola[438] or a curve with a smooth maximum and steep slopes on both sides of the maximum.[450] Hence, to reach the highest T_c value it is necessary to ensure the optimal content of holes for the given superconductor; otherwise, the deficiency or excess of holes would deteriorate the superconductivity parameters.

The hole concentration is usually controlled by replacement of the cations [451–461] or annealing of samples at definite temperatures and partial pressures of oxygen (Refs 437, 440, 441, 443, 458, 462–472) or by creation of cation vacancies.[473] In all cases, the oxygen content in the samples changes. However, one should borne in mind the following: upon a change in the cationic composition, the oxygen content changes due to the change in the cation valence (or due to vacancies) and upon annealing, the oxygen content changes due to structural implementation of oxygen non-stoichiometry caused by oxidation [even in ordered phases like $Bi_2Sr_2Ca.Cu_2O_8$ (Ref. 474)]. This affects the superconductivity parameters in different ways.

The effect of oxygen non-stoichiometry on the superconducting properties of Bi-HTSC has been studied for phase

(Bi,Pb)2223 [168, 438, 472, 475] and, especially extensively, for phase 2212.[149–152, 430, 432, 437, 438, 440, 463–471, 476] Many publications note a clear-cut correlation between the content of hyperstoichiometric oxygen (the factor affecting the concentration of current carriers) and the temperature of superconducting transition (Refs 437, 438, 440, 447, 458, 462, 465, 471, 475, 477–479). In some cases, the dependences of T_c on the oxygen content had maxima (Fig. 16). The curves shown in this Figure comply with the concept stating that there exists an optimal concentration of charge carriers defined by the hyperstoichiometric oxygen. The pattern of curves is determined by the cationic composition of phase 2212 and the positions of maxima, by both the oxygen and cationic compositions.

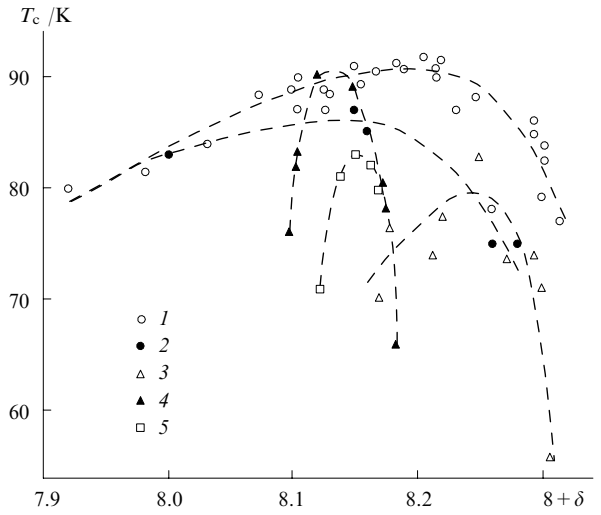


Figure 16. Superconducting transition temperature *vs.* oxygen content in phases 2212 with different composition.
Composition: (*1*) $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Ref. 432), (*2*) $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Ref. 479), (*3*) $Bi_2Sr_{1.88}CaCu_{2.14}O_{8+\delta}$ (Ref. 149), (*4*) $Bi_2Sr_{1.75}Ca_{1.25}.Cu_2O_{8+\delta}$ (Ref. 474), (*5*) $Bi_2Sr_{1.2}Ca_{1.8}Cu_2O_{8+\delta}$ (Ref. 150).

The relationship between the oxygen non-stoichiometry and the superconducting properties has also been noted for phase (Bi,Pb)2223,[168, 438] although it is less pronounced than for phase 2212. As an example, Fig. 17 shows the temperatures of the onset and the end of superconducting transition and the oxidation states of bismuth and copper atoms *vs.* the oxygen content in $Bi_{1.74}Pb_{0.27}Sr_{1.86}Ca_{2.09}Cu_{3.04}O_z$. It can be seen that as the oxygen content increases to $z = 10$, T_c grows and for $10 < z < 10.15$, T_c does not change. It can be seen that the major contribution to the change in T_c is made by the change in the bismuth oxidation state. However, for phase (Bi,Pb)2223, too, there is an optimum content of oxygen above and below which T_c somewhat decreases.[472]

Thus, it is obvious that the content of hyperstoichiometric oxygen in Bi-HTSC affects their superconducting properties. However, numerous facts indicate that, unlike other cuprate superconductors, in the case of Bi-HTSC, the hyperstoichiometric oxygen is not the crucial factor responsible for superconductivity. Indeed, by looking at Fig. 16, one can see that the superconductivity in phase 2212 is also retained in the samples with a perfect cation and oxygen stoichiometry (*i.e.*, in $Bi_2Sr_2.CaCu_2O_8$). This means that the concentration of hyperstoichiometric oxygen is not the only parameter affecting the superconductivity of phase 2212 (and probably its homologues) and that even the ideally stoichiometric Bi-HTSC

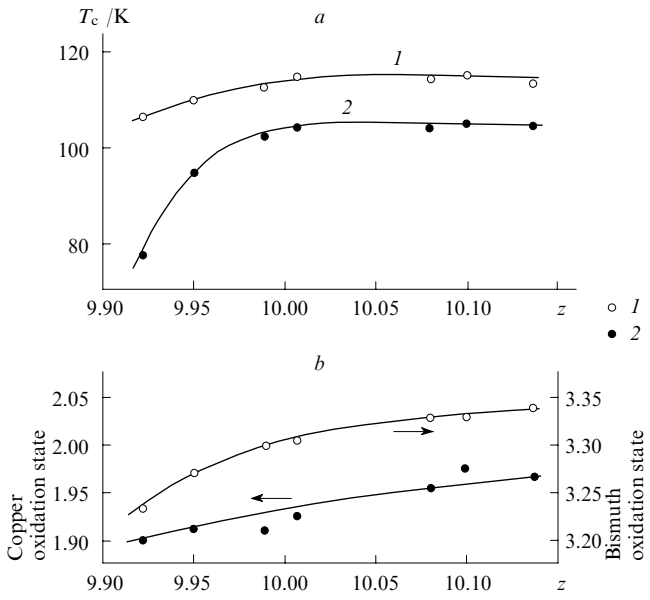


Figure 17. Temperatures of the onset (*1*) and end (*2*) of superconducting transition (*a*) and averaged oxidation states of bismuth and copper atoms (*b*) *vs.* oxygen content in $Bi_{1.74}Pb_{0.27}Sr_{1.86}Ca_{2.09}Cu_{3.04}O_z$.[168]

phases have 'inherent' current carriers that are not directly related to excess oxygen or a change in the cationic composition.[427, 444, 479, 480] In this case, the hole concentration in the CuO_2 layer is determined by 'self-sustained' charge redistribution from $(BiO)_2$ layers, which are the so-called 'hole reservoirs'.[427, 444] The role of this reservoir is most pronounced at low contents of hyperstoichiometric oxygen.[447, 479] Oxygen starts to play the crucial role only as its content in the superconductor increases.

It has been shown[447] that the dependence between the oxygen content and the hole concentration is not linear. It can be seen in Fig. 18 how the hole concentration in phase 2212 described as $Bi_{2.15}Sr_{1.48}Ca_{1.37}Cu_2O_{8.075+\delta}$ varies with an increase in the hyperstoichiometric oxygen content. When

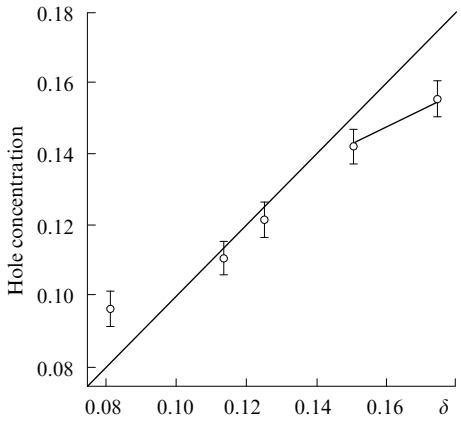


Figure 18. Hole concentration *vs.* content of hyperstoichiometric oxygen in $Bi_{2.15}Sr_{1.48}Ca_{1.37}.Cu_2O_{8.075+\delta}$.[447]
The diagonal line corresponds to the formation of two holes by every excessive oxygen atom per copper atom. The segment connecting two upper dots corresponds to the formation of one hole per copper atom by every excessive oxygen atom.

this content is low, the hole concentration is higher than that determined only by excess oxygen; at an average content, the hole concentration is determined almost completely by excess oxygen (every excessive oxygen atom lends two holes), and at higher content, every excessive oxygen atom lends only one hole. Thus, the number of potential charge carriers is determined by the amount of hyperstoichiometric oxygen. However, this number is also affected by other parameters. In particular, the total number of real holes, *i.e.*, the holes existing in the delocalised state, depends on the local structural order, first of all, on the local structure near the copper cation.[481] A change in the local order entails a shift of redox equilibria and affects the hole localisation–delocalisation process.[482]

The introduction of hyperstoichiometric oxygen into Bi-HTSC leads to noticeable changes in structural characteristics, in particular, in the lattice parameters, especially c.[152, 437, 479] It was found[479] for phase 2212 that with an increase in the content of oxygen, parameter c first increases, then sharply decreases, and T_c changes in parallel. The decrease in the parameter c with an increase in the oxygen content is apparently due to the enhanced electrostatic interaction between bismuth and oxygen.[70] Apparently, due to the high covalence of Bi — O bonds, the $Bi_2O_{2+\delta}$ layers are compressed, and a slight increase in the oxygen content causes a decrease in the parameter c.[483] Simultaneously, the distance between the copper cation and the apical oxygen atom decreases[484] and the equatorial Cu—O bond lengths increase,[446] which entails redistribution of holes between the $(BiO)_2$ and CuO_2 layers.[483, 485] and a change in T_c.

A correlation between c and T_c for phase 2212 was also noted in other works.[437, 438, 483] However, it is unlikely that a change in the parameter c is crucial for T_c and that they are related by an unambiguous dependence. Indeed, whereas in the solid solutions 2223 and 2212, as the strontium atoms are being replaced by calcium atoms, T_c decreases simultaneously with the parameter c,[131, 133, 136, 138, 143, 153, 155, 439] but with an increase in the bismuth content in $Bi_{2+x}Sr_2CaCu_2O_{8+\delta}$, the parameter c increases, while T_c decreases (Fig. 19).[70, 138, 153] Probably, in these examples, the cationic composition affecting the local structural order is the key factor affecting T_c.

Cation substitution causes noticeable local changes in the structure. Thus the substitution of calcium for strontium in phase 2212 results in a decrease in the distance between the copper cation and the apical oxygen atom [$r(Cu-O_{ap})$].[481] Owing to this structural rearrangement, even samples with the same oxygen contents but with different Sr : Ca ratios differ appreciably in the properties as a result of different $r(Cu-O_{ap})$ and, hence, different numbers of holes introduced in a CuO_2 layer. Thus the properties of composition-ordered phase 2212, which differs from the solid solution with excess calcium by a longer $Cu-O_{ap}$ bond, are more sensitive to the change in the oxygen content.[481]

Analysis of the experimental data for phase 2212 has shown that the oxygen content (Fig. 20) increases with an increase in the calcium and bismuth contents and decreases with an increase in the strontium content.[138, 153] The increase in the content of oxygen following an increase in the content of trivalent bismuth with respect to the content of divalent strontium and calcium is quite natural. However, the effect of mutual replacement of likely charged strontium and calcium cations on the oxygen content may seem unexpected. Meanwhile, examples of a change in the content of oxygen upon replacement of likely charged atoms are known: the content of oxygen in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ decreases upon replacement of barium atoms by strontium having smaller ionic radius.[486] In this case, an important role belongs to the structural factor. Apparently, in the series of solid solutions 2212, too, changes that require structural counterbalancing take place. On replacement of strontium ions by calcium, the additional oxygen is apparently built into $(BiO)_2$ layers for counterbalancing the increasing discrepancy between the parameters of these layers and the perovskite-like Sr—Ca—Cu—O block; simultaneously, the $(BiO)_2$ layers are additionally modulated.

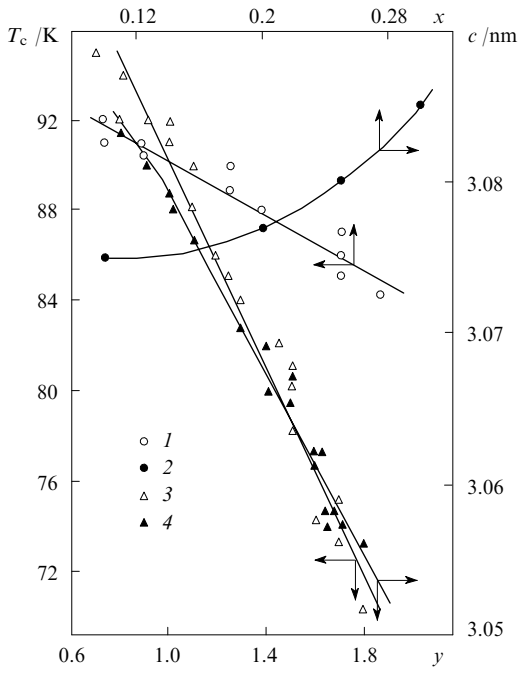


Figure 19. Critical temperature of superconducting transition (*1*, *3*) and lattice parameter c (*2*, *4*) *vs.* bismuth content (*1*, *2*) in $Bi_{2+x}Sr_2CaCu_2O_{8+\delta}$ and *vs.* calcium content (*3*, *4*) in $Bi_{2.18}Sr_{3-y}Ca_yCu_2O_{8+\delta}$. Plotted using data of Ref. 70.

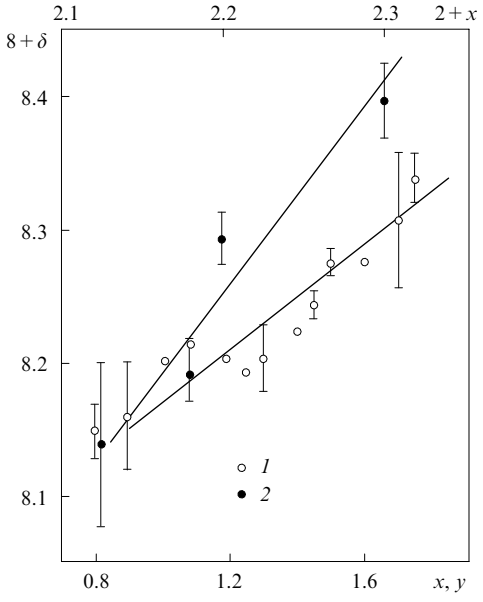


Figure 20. Oxygen index in $Bi_{2.18}Sr_{3-y}Ca_yCu_2O_{8+\delta}$ *vs.* calcium content (*1*) and in $Bi_{2+x}Sr_2CaCu_2O_{8+\delta}$ *vs.* bismuth content (*2*).[70]

The properties of solid solutions are sensitive even to low-temperature annealing where the oxygen non-stoichiometry almost does not change but structural ordering with delocalisation of some of the current carriers takes place.[487] Structural rearrangement on annealing resulting in a change in T_c without noticeable change in the amount of hyperstoichiometric oxygen has also been noted previously.[488,489] However, the most amazing result concerning the effect of annealing was obtained by Wu *et al.*,[467] who have found that single crystals of 2212 with $T_c = 70-83$ K annealed at 450–550 °C in air, nitrogen or oxygen had equally high T_c value of ~86 K irrespective of the annealing time or the atmosphere. In this case, the crucial role is played by structural ordering, oxygen ordering being apparently the key factor.[470] It was shown[490] that annealing of samples of bismuth-based superconductors 2201, 2212 and 2223 induces a structural phase transition in which the oxygen sublattice rearranges from the low-temperature ($T_{ann} < 400$ K) to high-temperature ($T_{ann} > 500$ K) state, which is accompanied by a change in the concentration of delocalised holes. As a result, the T_c value of hole-overdoped samples 2201 and 2212 increases, while that for optimally doped sample 2223 remains invariable. Thus, samples with equal contents of oxygen but with different thermal prehistory can have different T_c.

To conclude this Section, consider the effect of partial replacement of bismuth atoms by lead in Bi-HTSC. A specific feature of this replacement is introduction of a third element with variable valence into the system. This may affect the establishing of redox equilibria and charge distribution. Information on the charge states of lead in Bi-HTSC accumulated to date is not very extensive. It was reported [491] that Pb^{4+} is present in addition to Pb^{2+}, although the latter predominates.[52,153] It is also known that Pb^{2+} replaces Bi^{3+} (Refs 52, 153) and Pb^{4+} replaces Ca^{2+} (Refs 492–494). The appearance of an additional hole donor is possible.[495] Indeed, it was shown by Raman vibrational spectroscopy that upon replacement of bismuth atoms by lead the concentration of holes in the CuO_2 layer increases.[496]

It is noteworthy that replacement of Bi^{3+} by Pb^{2+} may decrease the amount of oxygen in $(BiO)_2$ layers, as indicated, for example, by the increase in the modulation period with an increase in the lead content.[497] The decrease in the overall content of oxygen (oxygen index) takes place against relative invariability of the oxygen non-stoichiometry, as was found for $Bi_{2-x}Pb_xSr_2CaK_{0.1}Cu_2O_z$ with $x < 0.2$.[482] However, for $x > 0.2$, the oxygen index remains constant, while the amount of hyperstoichiometric oxygen somewhat increases; this apparently indicates that the hyperstoichiometric oxygen enters the structural sites in the oxygen sublattice that have become vacant as a result of heterovalent substitution.[482] Thus, in lead-substituted Bi-HTSC, the number of holes may be determined by the amount of hyperstoichiometric oxygen and the amount of Pb^{2+} that has replaced Bi^{3+} (Ref. 497).

In addition, the introduction of lead has a pronounced effect on the crystal lattice parameters. The replacement of bismuth ions in phase 2212 by lead results in a decrease in the parameters b and c (see Fig. 2), and transition from the tetragonal to orthorhombic structure [50,52,204] and even to monoclinic structure (in the case of sample annealing at very low partial pressures of oxygen) becomes more and more pronounced.[53,489]

It is of interest that the content of lead in phase (Bi,Pb)2223 has little influence on the superconducting transition temperature,[168,497] while for (Bi,Pb)2212 this temperature markedly increases in the presence of lead.[110,482,496,497] The 'positive' influence of lead on phase 2212 was attributed to optimisation of the content of hyperstoichiometric oxygen [498] or to phase rearrangement.[499] It is also believed that an increase in T_c may be due to either changes in the electronic states caused by relaxation of structural modulations or a change in the hole concentration upon replacement of bismuth atoms by lead, which is not fully counterbalanced by the change in the oxygen content.[500] In any case, worthy of note is the fact that in (Bi,Pb)2212 samples, T_c increases considerably (to 96 K) as the oxygen content is reduced to nearly stoichiometric.[482] In addition, the sample with highest T_c contains the optimum amount of lead.[482,489] It was also found that (Bi,Pb)2212 samples with monoclinic structure annealed in an inert atmosphere have high T_c values.[489] These facts attest to high significance of the structural changes affecting the formation of local order, *i.e.*, a factor determining the concentration of real current carriers. Presumably,[482] due to the difference between the valence states of bismuth and lead atoms, in this case, a considerable number of holes is retained even when the oxygen index decreases to 8.0, and simultaneously, the appearance of vacancies in the oxygen sublattice creates conditions for oxygen ordering among the structural sites. This apparently accounts for the increase in T_c after thermal treatment at reduced partial pressure of oxygen.

IV. Conclusion

Currently, of all known HTSC, those of (Bi,Pb)2223 and 2212 types manufactured as extended articles are regarded as most promising for industrial application.[501] However, extensive use of these materials is held up by insufficient current-carrying ability of articles and low reproducibility of their characteristics as a result of uncontrolled action of various factors on the formation and properties of these superconductors.

The superconductivity parameters of bismuth-based HTSC materials attained to date result from perfection of particular procedures by empirical selection of process conditions. Targeted selection of the optimal conditions of synthesis, flexible control of processes and appropriate control of their characteristics requires knowledge of the chemical properties of Bi-HTSC and associated phases, trends of phase formation and chemical interactions, in order to design the material with specified chemical and phase composition. To go beyond the empirical search, one needs information on phase equilibria and phase ratios in these multicomponent systems, the stability regions of superconducting phases, *etc.*

It is important to understand the laws of influence of the chemical and phase compositions on the superconducting properties of Bi-HTSC. The examples considered in the review show a complex influence of some factors on the superconducting properties of Bi-HTSC. The elucidation of the relationship between the chemical composition and structure, on the one hand, and properties, on the other hand, remains the key problem in the studies of mechanisms of high-temperature superconductivity.

In view of good prospects of using Bi-HTSC, in particular, Bi-HTSC/Ag tapes, further studies of their formation processes are required. Apart from solution of practical problems, these studies would undoubtedly contribute to development of the views on chemical interactions in complex oxide systems, high-temperature phase transformations, the kinetics and mechanisms of solid-state reactions and so on.

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