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Microcomposites based on superconducting cuprates

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Abstract. Chemical aspects of the formation of microcomposites based on superconducting cuprates are considered. The materials are composed of a superconducting ceramic matrix and micro- or nanoinclusions of the non-superconducting phase, which are uniformly distributed in the matrix. Requirements on the operating characteristics of the superconducting ceramics are described and routes to high critical current densites are outlined. Phase equilibria in the generic systems are considered. Physical and chemical criteria for the choice of phases that can form non-superconducting inclusions are proposed. Methods of preparation and the microstructures and superconducting properties of the composites based on cuprates $RBa_2Cu_3O_{7-\delta}$ (R is the rare-earth element) and on $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ are considered. The bibliography includes 247 references.

I. Introduction

Progress towards preparation and investigation of functional inorganic materials is closely related to complexity of the chemical composition and structure of systems in different levels of a material's organisation. On the atomic scale, advances are due to the preparation of multicomponent chemical compounds and to passage from simple to more complex crystal structures. For the nano- and micrometre-sized systems, the determining factor is an optimum organisation of domains, crystallites and ensembles of microscopic structural defects. The range of values of the operating parameters can be considerably extended by using multiphase composite materials. Some examples of the efficiency of such materials are provided by fabrication of magnets with high coercive force, intermetallide superconductors with high critical current densities, high-strength and heat-resistant ceramics obtained by eutectic crystallisation, nanocomposites possessing specific optical properties, chemical sensors, *etc*.

Considerable advances in studies on superconductivity have been achieved in the last fifteen years. The discovery of high-temperature superconductivity in oxide ceramics by Bednorz and Müller [1] gave an impetus to expansion of the area of search for novel, chemically complex ceramic superconductors. A number of promising compounds were found, whose superconducting transition temperatures (T_c) much exceeded the boiling temperature of liquid nitrogen. However, the route to practical use of these compounds appeared to be rather long. Severe problems arose due to low efficiency of the magnetic flux pinning, weak intergranular contacts in the polycrystalline materials, brittleness and low mechanical strength of ceramics and the rather narrow range of external conditions for the formation of the superconducting phases.[2–4] These difficulties can be to some extent resolved by carrying out international research collaboration. In particular, considerable progress has been achieved towards fabrication of silver-sheathed tapes and wires based on Bi-containing cuprates,[5,6] $YBa_2Cu_3O_{7-\delta}$ tapes on bitextured metallic substrates,[7] thin epitaxial films of various high-temperature superconductors (HTSC),[8,9] bulk $RBa_2Cu_3O_{7-\delta}$ (R is the rare-earth element) ceramics [10] and $Bi_2Sr_2CaCu_2O_{8+\delta}$ rods.[11] Advances in development of graphotexturing techniques are also encouraging.[12]

In this review we analyse the currently available results of the studies on the synthesis of microcomposites based on superconducting cuprates containing highly dispersed inclusions of different phases. The significant role of such microcomposites in the development of materials science makes research in this field topical.

II. The problem of design of superconducting materials with high critical current densities

The most important operating characteristic of a superconducting material is the critical current density (J_c). Being considered as a function of the temperature and magnetic field, the J_c value characterises the maximum electric current which can flow through the conductor without energy loss.[2] The theoretical limit for the superconducting current density in HTSC is $\sim 10^8$ A cm^{-2}; this value is due to kinetic energy induced unpairing of charge carriers (electron pairs).[10] In real materials, the J_c values are much smaller. This is due to the fact that the critical current density depends on the force and energy of pinning of the

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magnetic vortices present in the superconductor in a nonzero magnetic field and on the intergranular electric contacts in ceramics. Weak pinning in HTSC causes a rapid decrease in the critical current density with increasing magnetic field strength and on raising the temperature. Breakdown of intergranular electric contacts is responsible for the presence of weak Josephson junctions and for the low J_c, which dramatically decreases as the magnetic field increases. Therefore, the design of a material with high J_c requires efficient pinning of magnetic vortices and strong intergranular contacts. Besides, the material should possess a sufficiently high mechanical strength. To this end, the materials are prepared in the form of tapes and wires with a silver alloy core,[5,6] films on single-crystalline oxide and metallic substrates[7–9] and bulk composites.[11,13] Intercrystalline contacts can be improved by forming pure grain boundaries containing no impurity phases and by texturing of ceramics (after, *e.g.*, deposition of epitaxial films or thermomechanical treatment).

The magnetic vortices are pinned to inhomogeneities, such as both point and extended lattice defects and inclusions of alien phases (Fig. 1). Enhancement of pinning can be achieved by forming a material containing micrometre- and nanometre-sized inhomogeneities.

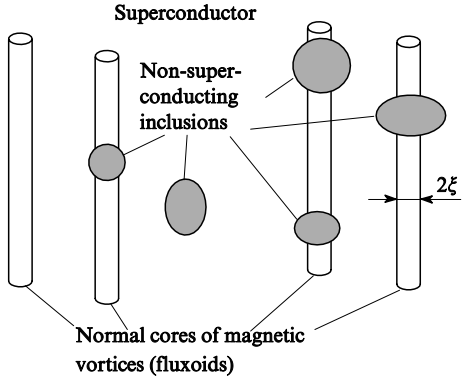


Figure 1. Illustration of pinning of magnetic vortices to non-superconducting inclusions.
The vortex energy decreases if its normal core (with destroyed superconductivity) passes through the non-superconducting inclusion. The vortex is pinned to such inclusions, so that its depinning and displacement require some force (pinning force) to be applied. Depinning and displacement of the vortex are accompanied by loss of energy in the superconductor;
ζ is the coherence length of the Cooper pairs.

According to calculations, the greatest pinning force can be attained if the dielectric inclusions or defects are of the order of the coherence length, ξ, of the Cooper pair[2,14] (in most cases, several nanometres). In addition, the pinning force is expected to increase on increasing the concentration and, correspondingly, the volume fraction of inclusions up to 40 vol.% in the superconductor matrix.[14] At higher concentration of inclusions, J_c decreases due to a marked decrease in the matrix cross-section area. For HTSC, the maximum J_c value due to a finite value of pinning energy is 10^7 A cm^{-2}.

One to several vortices can be pinned to large inclusions.[15] According to calculations, in this case the pinning force is proportional to the total surface area of the inclusion–matrix interface; inclusions of size about 1 μm can provide the critical current densities lying between 10^4 and 10^5 A cm^{-2}.

The pinning centres in a superconducting material can be created using different approaches. The three main methods are as follows:

(1) exposure to accelerated particles and heavy ions, resulting in the appearance of amorphised domains and channels (of size of several nanometres) with destroyed superconductivity;[16–19]

(2) heat treatment and mechanical treatment, which cause an increase in the density of the lattice defects or result in the formation of a fine-grained material with high concentration of grain boundaries (defects);[20–25]

(3) introduction of micro- and nanoinclusions of the alien non-superconducting phases or creation of nanoscale inhomogeneities differing in the chemical composition and properties from the matrix phase.[15,26]

The first method is highly efficient but is mainly applicable to small samples of thickness at most several tens of micrometres. It is often used in studies of the pinning mechanism.[27]

Enhancement of pinning due to heat treatment and mechanical treatment can be exemplified by the formation of a fine-grained material based on Nb_3Sn (Ref. 20) and epitaxial HTSC films less than 1 μm thick. The maximum critical current densities for such films reach nearly 10^5–10^6 A cm^{-2} at 77 K, which can be explained by high concentration of dislocations at small-angle boundaries of submicrometre-sized domains.[21–23] Similar results were also obtained in the experiments on creation of high concentrations of dislocations by mechanical treatment of HTSC.[24,25]

The third method of pinning enhancement is of prime importance for bulk and long samples. It appeared to be rather promising for engineering of metallic superconductors based on Nb–Ti alloy.[14] Using heat treatment and mechanical treatment (drawing), it is possible to prepare materials with controllable sizes of the second phase inclusions (Ti, Nb, Cu, V, Ni). The size of inclusions varies from several to tens of nanometres and the J_c value can be as high as 4.5×10^5 A cm^{-2} at a field of 5 T at $T = 4.2$ K.[14] Melt processing was used to obtain bulk samples of $RBa_2Cu_3O_{7-\delta}$ ceramics containing microinclusions of R_2BaCuO_5 phases (R is the rare-earth element). The critical current densities for such ceramics reach several tens of kiloamperes per square centimetre at 77 K.[15,26] Considerable attention has been given to the formation of inclusions in bismuth-containing cuprates, for which the pinning of magnetic vortices is a challenge.[28,29] Sometimes the critical current density can be increased by creating micro- and nanoinclusions of phases of the generic chemical system (*i.e.*, the system to which a particular superconducting complex oxide belongs) and the phases containing additional chemical elements (dopants). This effect is most pronounced at elevated temperatures (> 20 K).

Thus, materials with high operating parameters should be composites. Taking into account the necessity of structuring the materials at micro- and nanolevels, we will call them microcomposites.

III. Main methods of preparation of microcomposites

Methodologically, the design of microcomposites is based on the principle of complication of the phase composition of the system,[30] according to which the material must be at least a two-phase system, in which the non-superconducting phase is uniformly distributed in the superconducting matrix in the form of micro- or nanoinclusions. These phases should be to the greatest extent chemically inert towards each other, while the entire system should be highly stable towards recrystallisation and segregation of the inclusion phase.

The chemical inertness of the phases in a composite is best achieved when using thermodynamically compatible components, which are in equilibrium at such values of the external parameters (temperature and the partial pressure of oxygen) that correspond to the conditions for the synthesis of the composite or to the operating conditions. Of course, this does not exclude the preparation of microcomposites containing incompatible phases; however, in these instances it is hard to prevent rather intense reactions between the constituents at high synthesis temperatures (850–1000 °C). This was confirmed by numerous observations of reactions between superconductors (and their melts) and the high-melting materials of crucibles and substrates.[31–38] It should

be noted that inertness of different phases is of importance not only for microcomposites of the superconducting matrix – inclusion phase type but also for other types of materials, in which the superconducting phase immediately contacts some alien solid phases. This can be exemplified by substrate grown (deposited) films,[7,9] composite wires of the 'metal-sheathed superconductor' type[5,6] and reinforced superconducting composites.[10,11] The problem of chemical inertness of phases in the composite is closely related to the problem of preparation of the so-called barrier materials, which prevent superconductors from being entered into chemical reactions with the environment during the synthesis and operation of microcomposites.[31,38]

Sometimes, both the non-superconducting and superconducting phases of the microcomposite belong to the same chemical system, while the formation of the former phase is due to a shift of the system's composition from the homogeneity region of the superconducting phase to the two-phase or multiphase region at particular values of external parameters. An alternative strategy involves the chemical complication of the system, *i.e.*, introduction of some extra components (chemical elements) to form the non-superconducting phase along with the components of the generic system. This technique has a greater potential for varying the system's properties and, correspondingly, preparation of a material with the desired microstructure and operating characteristics.

Pinning centres (inclusions) can be created using different approaches (Fig. 2).

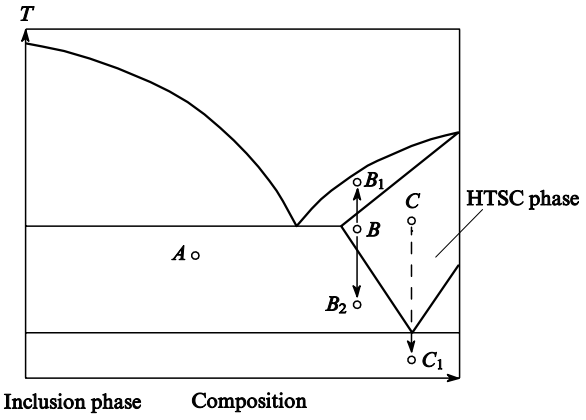


Figure 2. Scheme of the choice of system's composition in the model phase diagram using the first (configurative point *A*) and second (configurative points *B*, *C*) methods of synthesis of microcomposites (see text).

The first method is to choose the chemical composition of the system in the two-phase or multi-phase region of the phase diagram at particular values of external parameters (temperature and partial pressure of oxygen) and to prepare the microcomposite material under these conditions (configurative point *A*).

The second approach involves the synthesis of the starting single-phase material followed by variation of the external parameters in such a way that the figurative point is in the instability region of the superconducting phase. The instability can mean either decomposition of the superconducting phase into non-superconducting phases ($C \rightarrow C_1$) or a change in the composition within the solid solution region without loss of superconductivity ($B \rightarrow B_1, B_2$).

Clearly, the first approach requires the decomposition to be stopped at some intermediate stage to retain the superconducting matrix. In the second case, the process can be carried out up to attainment of the phase equilibrium. A special type of decomposition is provided by separation of the starting superconducting phase into two solid solutions differing in chemical composition and, correspondingly, in the superconducting properties.[39] In this case, structural similarity of the solid solutions allows a spinodal decomposition and formation of very small non-superconducting domains in the material.

Currently, the systems R – Ba – Cu – O and Bi – (Pb) – Sr – Ca – Cu – O are most practically valuable. They have been studied in most detail. Here, we will use them to illustrate some chemical problems concerning the design of superconducting microcomposites (see below).

IV. Phase relations in the existence regions of the superconductors $RBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$

To carry out successful syntheses of ceramic superconducting composites, one should obtain critically important information on the phase relations in the corresponding chemical systems, on the stability regions of the superconducting phases, and on the dependence of the superconducting properties (usually, T_c) on the chemical composition.

The R – Ba – Cu – O systems containing rare-earth elements of small radii (R = Y, Dy, Ho, Er, Tm, Yb) form stoichiometric (with respect to cations) phases $RBa_2Cu_3O_{7-\delta}$ (R123).[39–41] The highest superconducting transition temperatures (90 – 93 K) correspond to some non-stoichiometry with respect to oxygen ($\delta \approx 0 - 0.1$), which is usually achieved by annealing at moderate temperatures in oxygen. The Y123 phase has been studied in most detail. In the subsolidus region of the phase diagram ($\sim$900 °C) in air the Y123 phase is in equilibrium with $BaCuO_2$ (011), CuO and Y_2BaCuO_5 (211) (Fig. 3). Raising the temperature causes the appearance of melt in the $YBa_2Cu_3O_{7-\delta}$ – $BaCuO_2$ – CuO field. At 1010 – 1020 °C, the Y123 phase undergoes incongruent decomposition into Y211 and melt and at temperatures above 1100 – 1200 °C the system consists of Y_2O_3 and melt (Fig. 4).[42] At lower temperatures (below 900 °C and elevated pressure of oxygen), two new superconducting phases, $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14}$, are formed, while the Y123 phase becomes unstable.[40] Studies of systems containing other rare-earth elements of the yttrium subgroup showed that in the subsolidus region the R123 phases exist in the same compositional triangles ($BaCuO_2$ – CuO – R_2BaCuO_5) as the Y123 phase.[39–41]

The rare-earth elements with large ionic radii (La, Nd, Sm, Eu, Gd) form solid solutions of the type $R_{1+x}Ba_{2-x}Cu_3O_z$ (123ss).[39–41,43] Figure 5 presents the isothermal section of the phase diagram of the Nd – Ba – Cu – O system. The solid solution $Nd_{1+x}Ba_{2-x}Cu_3O_z$ ($x \approx 0$), which is characterised by the highest T_c, is in equilibrium with $BaCuO_2$, CuO, $Nd_xBa_{2-x}CuO_3$ and

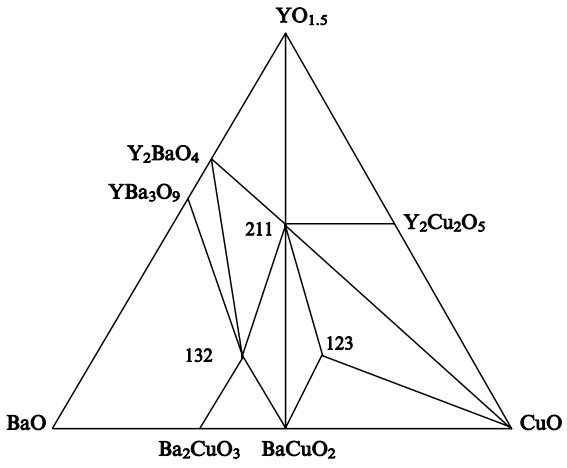


Figure 3. Phase relations in the subsolidus region of the $YO_{1.5}$ – BaO – CuO system in air.[41]

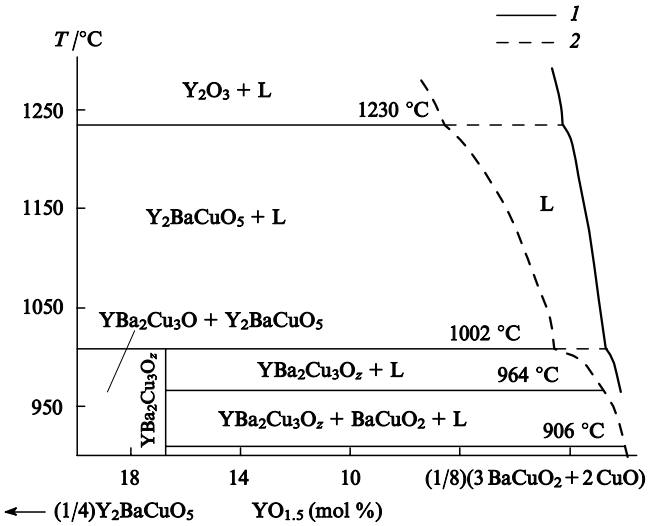


Figure 4. Polythermal section of the phase diagram of the $YO_{1.5}$–BaO–CuO system in air.[42]
Experiment (*1*) and calculations (*2*). Hereafter L stands for melt.

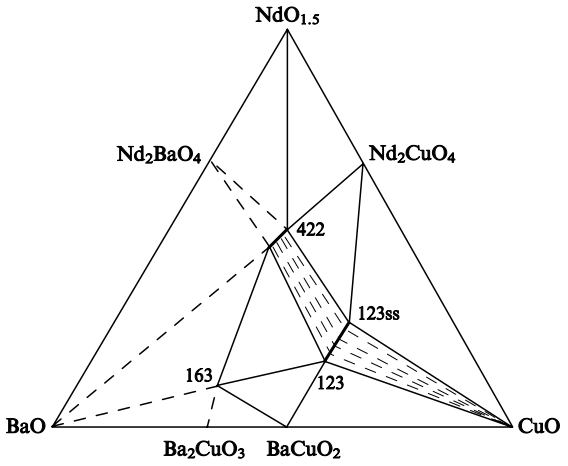


Figure 5. Phase relations in the subsolidus region of the $NdO_{1.5}$–BaO–CuO system in air.[41]

$Nd_{4-2x}Ba_{2+2x}Cu_{2-x}O_{10-2x}$ (422). The last-mentioned phase is compositionally analogous to the Y_2BaCuO_5 phase but has another crystal structure.[44] The polythermal section of the phase diagram of $NdO_{1.5}$–BaO–CuO is shown in Fig. 6. The homogeneity region of the $Nd_{1+x}Ba_{2-x}Cu_3O_z$ phase ($-0.1 < x \leqslant 1$ at 1000 °C) narrows as the temperature decreases; the process can be accompanied by separation of the solid solution.[45–47] In the system with R = Pr the non-superconducting oxide $Pr_{1+x}Ba_{2-x}Cu_3O_z$ ($x \approx 0$) coexists with $BaCuO_2$, CuO and $PrBaO_3$ (Fig. 7). No $RBa_2Cu_3O_z$ compounds are formed in the systems with R = Ce and Tb.[40]

The quinary(sextenary) system Bi(Pb)–Sr–Ca–Cu–O exhibits much more complex phase relations. A considerable body of contradictory data on both the exact phase compositions and the phase fields in this system is available.[40,48] Figure 8 presents the compositional tetrahedron and its section for the quasi-quaternary system Bi_2O_3–SrO–CaO–CuO.[49] It is of importance that the phase diagram exhibits extended regions of solid solutions for both the superconducting phases and the phases coexisting with them and that the superconducting transition temperature is strongly dependent on the cationic composition of the phases and on the oxygen content. The

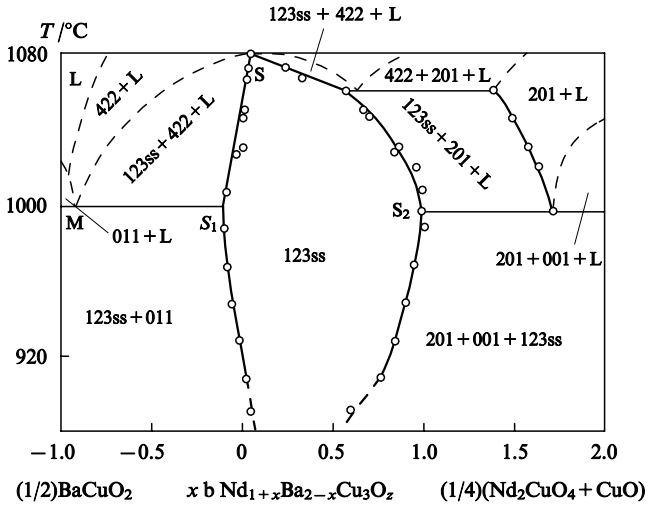


Figure 6. Polythermal section of the phase diagram of the $NdO_{1.5}$–BaO–CuO system in air.[40]

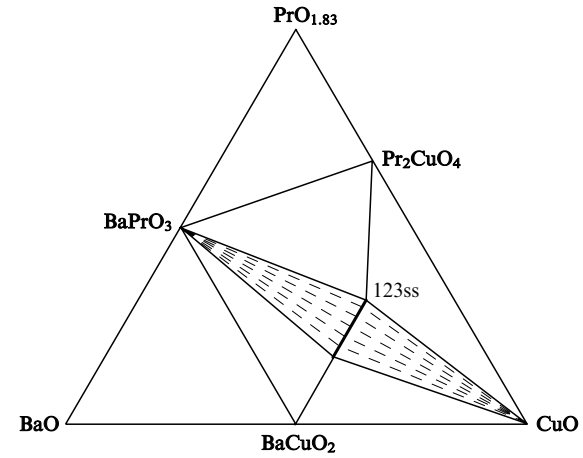


Figure 7. Phase relations in the subsolidus region of the $PrO_{1.83}$–BaO–CuO system in air.[41]

system contains three superconducting phases, namely, $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ (Bi2201 or $\underline{119}x5$, $T_c \approx 20$ K), $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212, $T_c \approx 90$ K) and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223, $T_c \approx 110$ K), which are the first three representatives of the homologous series $Bi_2Sr_2Ca_{n-1}Cu_nO_{6+2n+\delta}$. The second and third homologues are of practical value. In Bi2223, bismuth is, as a rule, partially replaced by lead.[49] The formation of the Bi2223 phase can also be significantly improved upon partial replacement of Bi by V, Nd, Ta (see Ref. 50) or Ga.[51] It is more appropriate to write the formula for the second homologue ($n = 2$) as $Bi_{2+x}Sr_{2-x-y}Ca_{1+y-r}Cu_{2-r}O_{8+\delta}$.[48,49,52–54] This compound is characterised by a relatively broad homogeneity region with respect to the strontium : calcium ratio (Fig. 9), which, according to different authors, can vary from 2.2 : 0.8 to 1.2 : 1.8.[48,55,56] Strontium can be to some extent ($x \leqslant 0.2$) replaced by bismuth, while the content of copper can somewhat decrease due to the formation of stacking faults (sublayers of the first homologue). The third homologue has a narrower homogeneity region with respect to the strontium : calcium ratio (from 1.9 : 2.1 to 2 : 2); the content of bismuth (or bismuth and lead together) can exceed the stoichiometric value by $\sim 20\%$.[49]

In air, the phase of the second homologue is stable from $\sim$600 °C to the melting temperature (850–885 °C depending on the composition).[48,57–63] The highest melting temperature refers to a composition similar to the stoichiometric composition

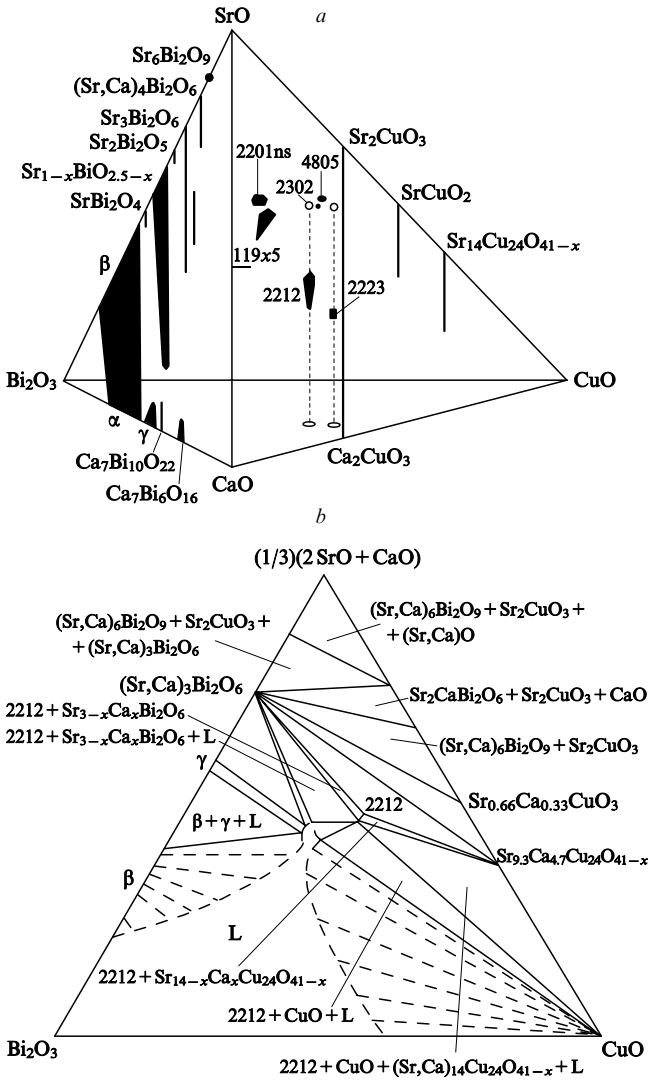


Figure 8. Phase relations in the Bi_2O_3 – SrO – CaO – CuO system in air at 850 °C.[49]
Compounds in the quaternary system (*a*) and the section of the compositional tetrahedron by the plane passing through the (1/3)(2 SrO + CaO) – Bi_2O_3 – CuO points (*b*). The phases in the ternary and quaternary systems are denoted using their cationic compositions (Bi : Si : Ca : Cu).

Bi2212. Melting and crystallisation processes play a significant role in the preparation of both bulk samples of HTSC (Ref. 64) and sheathed wires (tapes) possessing high critical current densities.[65] The melting diagram along the Bi2201 – Bi2223 compositional line is schematically shown in Fig. 10.

A great body of information on melting of the Bi2212 phase is available (see, *e.g.*, Refs 48, 59, 63, 66–71). Often, the results obtained by different authors were essentially different. The most plausible order of processes is as follows. In air, Bi2212 undergoes peritectic decomposition into two oxides, $(Sr,Ca)_{4-y}Bi_2O_z$ and $(Sr,Ca)CuO_2$, and melt.[66, 72, 73] This is accompanied by release of oxygen, which corresponds to reduction of the oxygen content.[63] Storage of the melt over a period of 1 h at a temperature which only slightly exceeds the melting temperature leads to crystallisation of yet another phase, Bi2201.[67] Further increase in the temperature in the range 900 – 1000 °C causes disappearance of the bismuth-containing phases and the following sequence of transformation of the cuprate phase [66, 68, 72]

$$(Sr,Ca)CuO_2 \longrightarrow (Ca,Sr)_2CuO_3 \longrightarrow CaO.$$

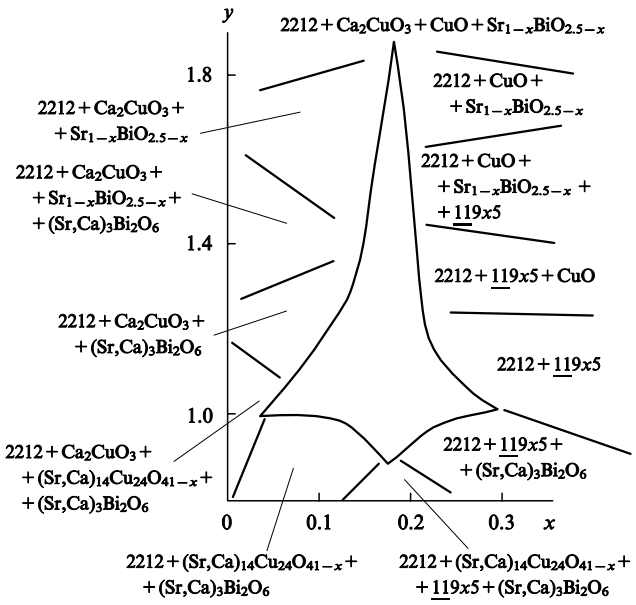


Figure 9. Homogeneity region of the Bi2212 phase for the $Bi_xSr_{3-y}Ca_yCu_2O_{8+\delta}$ composition in air at 800 °C.[49]

At temperatures above 1100 °C the system consists of a melt only.[66, 72]

The Bi2223 phase exists in the narrower temperature interval (840 – 890 °C). Doping with lead shifts this temperature range towards lower temperatures.[49, 52, 74] The extent of bismuth replacement by lead depends on the partial pressure of oxygen and can reach 30% for Bi2212 and 15% – 18% for Bi2223.[48, 49, 52] In air, the (Bi,Pb)2223 phase doped with lead oxide melts incongruently at temperatures above 870 °C to give strontium – calcium cuprates of different compositions (the melting temperature reducing as the pressure of oxygen decreases).[52, 75, 76]

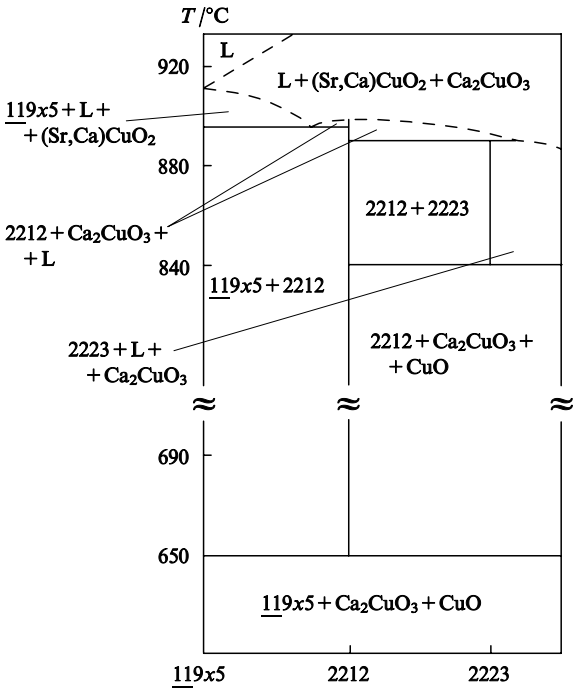


Figure 10. Polythermal section of the phase diagram of the Bi_2O_3 – SrO – CaO – CuO system along the Bi2201 – Bi2223 line.[49]

Cooling of the melt causes crystallisation of the second homologue as the major product. This significantly hampers the use of the melt technique in obtaining the third homologue, which is of the greatest interest.

In the temperature range 800–870 °C in air, the Bi2212 phase can be in equilibrium wuth CaO, CuO, $(Sr,Ca)_{14}Cu_{24}O_{41}$, $Bi_{2.2}(Sr,Ca)_{1.8}CuO_{6+\delta}$, $(Sr,Ca)_{1-\delta}BiO_z$, $(Ca,Sr)_2CuO_3$, $(Sr,Ca)_{4-y}Bi_2O_z$, $Bi_4(Sr,Ca)_8Cu_5O_z$, $Bi_2Sr_2CuO_6$, Bi2223 and melt.[49,52,77–81] Other phases in this system were also found. These are $(Sr,Ca)_3Bi_2O_6$,[49] $Sr_9Bi_{11}O_{25.5}$,[77] $Ca_{0.86}Sr_{0.14}CuO_2$,[80] $(Sr,Ca)CuO_2$ and $(Sr,Ca)_6Bi_2O_{11}$,[81] which probably also coexist with the Bi2212 phase under particular conditions. Studies of the lead-doped system revealed[82,83] that at 810–820 °C and $p_{O_2} = 0.075$ the (Bi,Pb)2223 phase is in equilibrium with CaO, CuO, (Bi,Pb)2212, $(Sr,Ca)_{14}Cu_{24}O_{41}$, $(Ca,Sr)_2CuO_3$, $(Bi,Pb)_{2.2}(Sr,Ca)_{1.8}CuO_{6+\delta}$, $(Bi,Pb)_2Sr_2CuO_{6-\delta}$, $(Sr,Ca)_{4-y}$. $.Bi_2O_z$, $(Sr,Ca)CuO_2$, $Ca_{0.86}Sr_{0.14}CuO_2$, $(Ca,Sr)_2PbO_4$ and $(Pb,Bi)_3Sr_2Ca_2CuO_z$.

Thus, the generic (with respect to the superconducting phases) chemical systems contain a large number of thermodynamically compatible phases, which can be used as inclusions in the superconducting composites.

V. Microcomposites based on $RBa_2Cu_3O_{7-\delta}$

The first method of preparation of composites can be well illustrated by taking the system $RBa_2Cu_3O_{7-\delta}$–R_2BaCuO_5 as an example. Microcomposites are synthesised by crystallising the superconducting phase from a peritectic melt[10,39] containing micrometre-sized particles of the R_2BaCuO_5 phase, which is partially consumed for the formation of the R123 phase in the reaction

$$\text{melt} + R_2BaCuO_5 \longrightarrow RBa_2Cu_3O_{7-\delta},$$

while the remaining fraction of R_2BaCuO_5 forms inclusions in the superconducting matrix. Depending on the synthetic procedure and composition of the starting materials, the average size of the inclusion particles can vary from several fractions of a micrometre to tens of micrometres. The smallest inclusions are prepared by melting a mixture of $RBa_2Cu_3O_{7-\delta}$ with highly dispersed R_2BaCuO_5 and subsequent crystallisation of the melt.[84,85] The R_2BaCuO_5 particles can be trapped with ease by the growing $RBa_2Cu_3O_{7-\delta}$ crystals, which leads to a uniform distribution of these particles in the material. However, sometimes (in the case of, *e.g.*, doping with platinum) the distribution of Y_2BaCuO_5 particles over the volume of the Y123 crystal is nonuniform, which is described and explained using the pushing–trapping model.[86–89]

Coarse-grained, textured composite samples obtained by the melt processing technique and containing 0.1–0.4 mole of R_2BaCuO_5 per mole of $RBa_2Cu_3O_{7-\delta}$ are characterised by the critical current densities of the order of 10^4–10^5 A cm^{-2} at 77 K.[10,15,90–93] Studies of the dependence of the pinning force (F_p) on the magnetic field (B)

$$F_p(B,T) = J_c(B,T)\,B$$

revealed a dominant role of the magnetic flux pinning by inclusions (or inclusion–matrix interface).[94–96] However, the role of R_2BaCuO_5 is not restricted to the pinning effect, namely, the presence of the second phase favours a complete peritectic crystallisation of the superconducting phase.

Introduction of (micro)additives into the R–Ba–Cu–O system can lead to a further increase in J_c. In most cases, this approach results in R123–R_2BaCuO_5–alien phase composites. The efficiency of pinning can be due to the effects of both inclusion phases. Often, it is assumed that this parameter is mainly due to the dopant effect on the size of inclusions of the main non-superconducting phase R_2BaCuO_5. Doping with Pt(PtO_2), CeO_2 and SnO_2 (usually, of the order of a per cent) can cause a substantial increase in the degree of dispersion of the R_2BaCuO_5 phase.[97–108] Introduction of platinum leads to a decrease in the energy of the R_2BaCuO_5–liquid interface, thus facilitating nucleation and slowing down the growth of the R_2BaCuO_5 phase. The effect of the cerium and tin oxides is explained by heterogeneous nucleation of R_2BaCuO_5 on microinclusions of products of the reactions of these additives with the melt.[98]

The platinum-doped system contains the following accompanying (and, possibly, thermodynamically compatible with Y123) phases: $Ba_4CuPt_2O_9$, $Y_2Ba_3Cu_2PtO_{10}$ and $Y_2Ba_2CuPtO_8$, which are more likely treated as undesired inclusions.[100,109,110] Introduction of extra impurity (alumina) causes the formation of large (tens of micrometres in size) $Ba_3YAl_2PtO_{9-\delta}$ inclusions.[111] The addition of SnO_2 results in $BaSnO_3$,[112] $YBa_2SnO_{5.5}$ (see Ref. 113) and $YBa_3Sn_{2-x}Cu_xO_{9-\delta}$.[101,114] The cubic double perovskite $YBa_2SnO_{5.5}$ phase seems to be the most stable and introduction of platinum or cerium into the system causes the formation of solid solutions $Y_2Ba_5(Sn_{3-y-x}Cu_yPt_x)_3O_z$ (see Ref. 115) and $Ba_2(Y_{2/3-x}Cu_x)\cdot(Ce,Sn)_{4/3}O_{6-\delta}$.[101] Tin and platinum are insoluble in Y123, whereas cerium occupies some sites in the Y123 lattice.[101]

Particular emphasis should be placed on the doping of the Y123 system with oxides of ^{235}U.[116–118] In these cases, submicrometre-sized inclusions of the compositions $Ba(U_{0.6}Y_{0.4})O_3$ or $Ba_2Y(U_{0.6}Pt_{0.4})O_8$ (in the presence of platinum) are formed in the superconductor crystallites and the corresponding J_c values somewhat increase. Neutron irradiation causes fission of ^{235}U nuclei and the appearance of numerous tracks in the superconductor matrix, which leads to a subsequent manyfold increase in J_c due to the pinning of magnetic vortices to the new defects. This technique was used for preparation of a bulk material characterised by a record J_c value ($\approx 3\times10^5$ A cm^{-2} at 77 K).[117]

Reactions of ceria, zirconia and hafnia with R123 result in stable phases ($BaCeO_3$, $BaZrO_3$ and $BaHfO_3$, respectively).[101,112,119–121] In the case of melt growth of the superconducting phase, particles of these phases are pushed by the growing R123 crystal and segregated in the intercrystalline space, thus impeding the flow of the superconducting current between crystallites. These phases are inert and can therefore be used as barrier materials for crucibles, substrates and coatings in the synthesis of superconductors.[122–124]

The estimates of thermodynamic parameters[123] indicated that the Y123 phase cannot be treated as being in equilibrium in the mixtures with TiO_2, ZrO_2, HfO_2 and CeO_2. This disequilibrium manifests itself in the chemical reaction, which proceeds on heat treatment of the mixture of the corresponding dioxide and Y123 and results in Y211, CuO and compounds of the starting dioxide with (mainly) barium oxide.

Among all metals, only silver is thermodynamically compatible with R123. In the presence of silver the melt crystallisation temperature of Y123 reduces down to 970 °C, while the overall process is described by a monoteutic-peritectic reaction

$$\text{Y211} + \text{L1} \longrightarrow \text{Y123} + \text{L2},$$

where L1 is the BaO- and CuO-rich liquid and L2 is the Ag-rich liquid.[125] Crystallisation from oxide melt is accompanied by trapping of silver in the form of spherical or disk-like particles.[125–128] The introduction of silver improves the mechanical strength of and precludes crack formation in the ceramics.

The second method of preparation of microcomposites is based on the decomposition of a solid solution in the R–Ba–Cu–O system. It can be exemplified by the synthesis of $Nd_{1+x}Ba_{2-x}Cu_3O_z$ ceramics.[39,129–133] Under particular heat treatment conditions (hypothetically, at a rather low temperature), a solid solution ($x \approx 0$) is separated into two solid phases. One phase is characterised by a high extent of replacement of neodymium by barium and low T_c while the other phase is characterised by a lower extent of replacement and higher T_c (>90 K). The first phase forms nanometre-sized inclusions in the matrix of the second phase. A feature of such superconductors is the so-called peak effect (J_c first increases with an increase in the magnetic field and then decreases).[134] This effect is associated with

magnetic field induced destruction of superconductivity in nanodomains, which makes these domains efficient pinning centres at intermediate magnetic fields. The peak effect was also observed in $YBa_2Cu_3O_{7-\delta}$ ($\delta > 0$);[134, 135] however, it was treated as a consequence of phase separation accompanied by the appearance of nanodomains enriched with and depleted of oxygen and, correspondingly, characterised by different superconducting transition temperatures.

The dependence of the pinning force in $Nd_{1+x}Ba_{2-x}Cu_3O_z$ on the reduced magnetic field B/B_{ir} (B_{ir} is the irreversibility field induction) passes through a maximum at $B/B_{ir} = 0.4-0.5$, which indicates pinning of magnetic vortices to small regions with weakened superconductivity.[95, 96, 136] For the composites $RBa_2Cu_3O_{7-\delta}-R_2BaCuO_5$ (R = Y, Yb; see Ref. 94), the maximum value of the B/B_{ir} ratio is nearly halved and corresponds to dominant pinning at the interface between the superconducting matrix and inclusions of the second phase. As to the $Nd_{1+x}Ba_{2-x}Cu_3O_z-Nd_4Ba_2Cu_2O_{10}$ composite, both interface pinning and pinning to small regions with weakened superconductivity are possible.[137]

Simultaneous introduction of several rare-earth elements into yttrium lattice sites is thought to have considerable promise. The $J_c(B)$ plots constructed for the superconductors $(Nd,Eu,Gd)Ba_2Cu_3O_{7-\delta}$ and $(Nd,Sm,Gd)Ba_2Cu_3O_{7-\delta}$ exhibit a pronounced peak effect, so that the maximum critical current density reaches a value of 10^5 A cm^{-2} at a magnetic field of about 2 T at 77 K.[138, 139] It was established that the superconductor crystallites are characterised by fluctuations of the composition (variation of the rare-earth element : barium ratio) in the regions from several to tens of nanometres in diameter. The smaller the 'fluctuation' domain size, the more pronounced the peak effect in the materials. Besides, the character of the inclusion phase, R_2BaCuO_5, also changes. Melting of $(Nd,Sm,Gd)Ba_2Cu_3O_{7-\delta}$ is accompanied by redistribution of the rare-earth elements between the solid and liquid phases in such a way that the composition of the newly formed solid phase approaches Gd_2BaCuO_5. In the course of subsequent crystallisation the second phase of the composite $(Nd,Sm,Gd)_2BaCuO_5$ first of all reacts with the melt. As a result, the end product contains a large number of small Gd_2BaCuO_5 inclusions, which are much smaller than the grain size of the second phase. Such a dispersion of the second phase causes an increase in the critical current density at zero magnetic field.

More than a twofold increase in J_c at 77 K was found in the large-domain composites $YBa_2Cu_3O_{7-\delta}-Y_2BaCuO_5$ doped with microscopic amounts (hundredth fractions of a per cent) of zinc oxide.[140–142] It is assumed that the zinc ions replace copper in the crystal lattice and create nanoscale domains with destroyed superconductivity, which act as efficient pinning centres. This is indirectly confirmed by the shift of the maximum in the field dependence $F_p(B/B_{ir})$ from $B/B_{ir} = 0.31$ to 0.41 after relevant doping.

VI. Microcomposites based on phases of the Bi–(Pb)–Sr–Ca–Cu–O system

The system Bi–(Pb)–Sr–Ca–Cu–O is characterised by equilibrium between the superconducting phases and a large number of other phases and by extended regions of solid solutions for the superconducting phases. This allows a wider use of both methods of synthesis of composites (see Section III).

Cooling of a peritectic melt permits preparation of Bi(Pb)2212–Ca_2CuO_3 (10 mol.%–15 mol.%) composites with the Ca_2CuO_3 inclusions (of size of several micrometres) uniformly distributed in the Bi(Pb)2212 phase. These composites exhibit an increased (by several times) critical current density at $T \geqslant 20$ K.[143, 144] Magnetooptical studies revealed pinning of magnetic vortices to the Ca_2CuO_3 particles.[145] A considerable increase in J_c within grains of sintered Bi2223–Ca_2CuO_3 ceramics was also reported.[146] Single crystals of Bi2212 containing inclusions of CuO (elongated particles 1 μm in diameter and 3–4 μm long) were obtained by melt–solution crystallisation from KCl.[147]

Majewski *et al.*[148–150] reported detailed phase diagram studies concerning the possibility of partial decomposition of the solid solution. If a solid solution of a particular composition is heat treated at a lower or, *vice versa*, a higher temperature, it loses homogeneity and submicrometre-sized inclusions of products are formed in the matrix of the starting compound. This approach was used for the synthesis of ceramic Bi2212 samples containing inclusions of the Bi2201, $Sr_3Bi_2O_6$, $Sr_{14}Cu_{24}O_{41}$ and Ca_2CuO_3 phases (see Refs 148 and 149) and of Bi2223 samples containing inclusions of the Bi2212, Ca_2CuO_3 and $(Sr,Ca)CuO_2$ phases.[150] A scheme illustrating the trajectory of the figurative point in the phase diagram during heat treatment is shown in Fig. 11. The J_c value inside of the grains of the samples heat treated for a restricted time increases by three to six times at 30 K. Prolonged annealing causes coarsening of the inclusions and a decrease in the critical current density. It was shown[151] that annealing of Bi2212 at 550 °C results in precipitation of smaller particles of size 0.02 to 0.1 μm and in greater nonuniformity of the distribution of the components in ceramics.

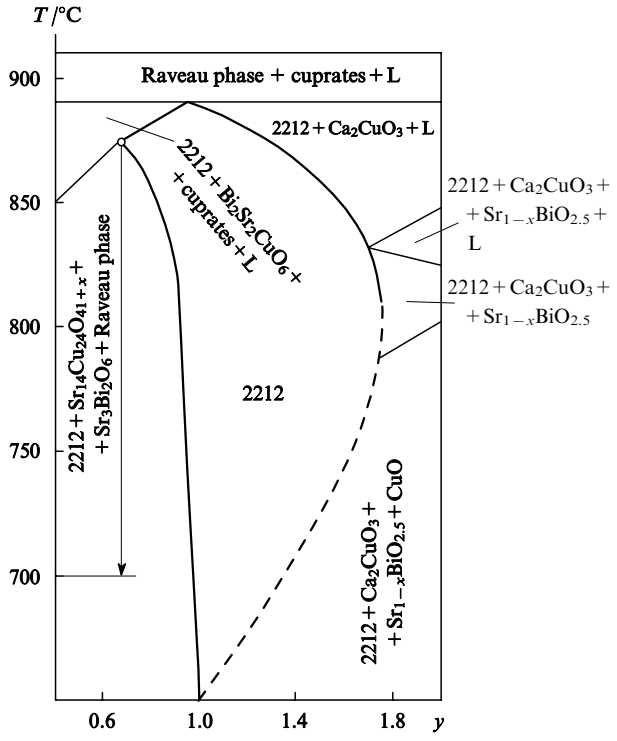


Figure 11. Section of the phase diagram of the Bi–Sr–Ca–Cu–O system along the $Bi_{2.18}Sr_{3-y}Ca_yCu_2O_{8+\delta}$ composition.[149]
Shown are the homogeneity regions of the Bi2212 (2212) phase and the trajectory of the figurative point of the system upon heat treatment (phase-forming annealing at 875 °C–low-temperature annealing at 700 °C).

Separation of the solid solution was found and studied in detail taking $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ ($x > 0.4$) samples as examples.[152, 153] Melt processed single crystals and coarse-grained ceramics exhibited the formation of submicrometre-sized domains (in the form of stripes or closed regions), which were both depleted of and rich with lead. Such samples are characterised by increased irreversibility fields and J_c.

A study on the decomposition of Bi2212 solid solutions characterised by partial replacement of calcium or strontium by rare-earth elements *via* annealing at a reduced temperature has been reported.[154] Precipitation of the second phases was observed

only for the early rare-earth elements (R = La, Pr, Nd). The Bi2212 phase with R = Pr decomposed much faster than other phases. This was associated with the fact that the starting phase contained praseodymium in the Pr^{3+} state, while annealing in air caused its oxidation to Pr^{4+} with a smaller ionic radius and subsequent destabilisation of the Bi2212 phase.

VII. Microcomposites based on phases of the Bi – (Pb) – Sr – Ca – Cu – A – O system

The best way of preparing superconducting materials with good intergranular contacts is to use melt techniques. However, under these conditions the generic second phases form rather large inclusions (of size greater than 1 μm). The reason is that in the melt all components of the system are present in comparable amounts. To improve the efficiency of pinning, one should make the inclusions smaller. This can be achieved by introducing some alien phases containing an extra component A into the system.

Multicomponent systems are extremely complex objects. Because of this, 'engineering' methods of doping of the generic system often fail. In most cases the introduction of some high-melting oxide additives is accompanied by partial decomposition of the superconducting phase and by the formation of the accompanying complex oxide phases.[28]

The authors of this review believe that a consistent method for solving the problem of design of microcomposites based on superconducting cuprates must include:

— searching for new components, which do not destroy the superconductivity in the matrix material;

— establishment of phases which contain the new components and are chemically inert towards the superconductor; and

— elaboration of methods for synthesis of materials containing fine-grained, uniformly distributed inclusions of the above-mentioned phases.

The superconducting phase, which acts as the matrix, must be characterised by a rather high T_c value. The optimum compositions and the heat treatment regimes of such phases have been reported.[48,49] In the search for various dopants it can appear that the simplest way is to retain the composition of the generic system because of the minimum solubility of the new component in the superconducting phase. As mentioned above, the chemical inertness of the system is best achieved if its components are thermodynamically compatible, *i.e.*, if the impurity and the matrix superconducting phase are in equilibrium at least at such values of the external parameters (temperature and the partial pressure of oxygen) that correspond to the conditions for the synthesis of the composite. Therefore, determination of the compositions of the equilibrium phases is of prime importance. The next stage involves preparation of the composite containing inclusions of the equilibrium phases. Here, one should take into account the effects related to the interface interactions, such as agglomeration and recrystallisation of the particles of the inclusion phase and their effect on the nucleation and growth of crystallites of the superconducting matrix. Besides, in the text below we will show that the presence of the equilibrium phase can change the phase relations in the system in the region above the solidus and, correspondingly, the crystallisation mechanism of the matrix phase.

The thermodynamic compatibility of silver with the superconducting phases in the Bi – (Pb) – Sr – Ca – Cu – O and Y – Ba – Cu – O systems has been established reliably.[63,155–158] This is of crucial importance for fabrication of flexible sheathed HTSC wires and tapes.[5,158] The solubility of silver in the solid phases Bi2212 and (Bi,Pb)2223 is at most 1% while its solubility in the corresponding oxide melts is nearly 5%, which leads to reduction of the melting temperature of the superconducting ceramics by 20 – 30 °C.[82,157,159] It was found that the peritectic melt contains the same phases as the melt containing no silver (see Section IV). Because of doping, the melting temperature of metallic silver in the composite decreases by ~ 10 °C. Gold also seems to be compatible with the above-mentioned phases.[6,160–163] Metallic platinum slowly reacts with the melts of the ceramic matrix and forms complex oxide phases containing alkaline-earth elements and copper along with platinum.[163,164]

The compositions and properties of the microcomposites based on the superconducting Bi2212 matrix are listed in Table 1.

Apparently, MgO is the only individual oxide which possesses a sufficient chemical inertness towards the superconducting phases. Nevertheless, it was shown[165,166] that the Bi2212 phase is in equilibrium with the solid solution $Mg_{1-x}Cu_xO$ ($x \approx 0.1$). Pure fine-grained magnesia causes decomposition of the superconductor phase due to partial removal of copper, while coarse-grained MgO does not readily react with either the solid Bi2212 phase or its melt. The solubility of MgO in Bi2212 is at most 1 at.%, so the T_c value of the superconducting matrix remains virtually unchanged.

The introduction of other chemical elements into the Bi – (Pb) – Sr – Ca – Cu – O system results in the formation of complex oxides. Alumina, gallium sesquioxide and oxides of rare-earth elements form two compatible phases with the oxides of the generic system each,[164,168–172] while oxides of the other elements listed in Table 1 form one compatible phase each.[28,72,167,172,173,176–182]

In spite of a wide variety of chemical compositions of the Bi2212-compatible complex oxides, some general trends were revealed. At the phase equilibrium, the components of the coexisting phases have the same chemical potentials. To a first approximation the oxide systems can be characterised by the chemical potential of the common component (O^{2-} anion), which reflects the acid – base properties of the system (reduced potential corresponds to an acid medium while increased potential corresponds to a basic medium).[183] The compatible phase must be stable in a range of chemical potentials of the O^{2-} anion which overlaps with the chemical potential range corresponding to the stability of the superconducting phase. Thus, the strongest acid oxides will form compounds with the stronger basic oxides of the generic system in order to increase the chemical potential of O^{2-} to a value corresponding to the lower boundary of the stability of the Bi2212 phase. Analogously, the basic oxides will form compounds with the stronger acid oxides. Clearly, the interaction between the strongest acid oxides and the strongest basic oxides is most energetically favourable. One should also take into account that the acidity of the oxide increases with increasing oxidation state and decreasing ionic radius of the element.

Analysis of general trends of changes in the compositions of complex oxides (see Table 1) suggests that the oxides characterised by high oxidation state of the corresponding element ($\geqslant +4$) and, hence, by relatively high acidity usually form compounds with strontium oxide, which is the strongest basic oxide in the generic system. Reduction of the acidity of the extra oxides formed by the triply charged cations leads to the formation of calcium, bismuth and copper oxide constituents of the non-superconducting complex oxide along with strontium oxide. In the case of rare-earth elements with the largest ionic radii, the composition of the complex oxide cannot include strontium oxide (see Table 1), which is consistent with the lowest acidities of the oxides of rare-earth elements. From the standpoint of the acidity criterion, MgO is compatible with the Bi2212 phase. Barium oxide (the strongest basic oxide) forms a compound with bismuth oxide (the strongest acid oxide in the generic system).

Sometimes, the Bi2212 phase contains a minor amount of dopant (less than 1 at.% with respect to all cations), which allows the rather high superconducting transition temperature of the composite to be retained (see Table 1). Small amounts of gallium sesquioxide and titania can be dissolved in the solid phase of the superconductor, which reduces T_c by several degrees. The values listed (~ 2 at.%) correspond to the lower bounds of the solubilities of these oxides in the Bi2212 phase, which is in equilibrium with the non-superconducting oxide phase. It is assumed that titanium occupies sites in the copper sublattice[184] while gallium can replace both copper and bismuth.[164,171,185,186] It is also

Table 1. Compositions and properties of microcomposites with the Bi2212 superconducting matrix.

Dopant A	A-Containing phase compatible with Bi2212			Grain size of A-containing phase in composite /μm	Content of A in Bi2212 (at.%) (with respect to all cations)	T_c /K	R [a]	Ref.
	composition	crystal system	structure type					
Mg	$Mg_{1-x}Cu_xO$, $x = 0.08-0.15$	cubic	NaCl	0.3–1.0	< 1	93	0.021	72, 165, 166
Ba	$(Ba,Sr,Ca)BiO_3$	"	perovskite	submicrometre region	<2	–	–	167
Al	$Sr_{3-x}Ca_xAl_2O_6$, $x = 1$,[162] 1.3 (see Ref. 169)	"	$Sr_3Al_2O_6$	2–3	< 0.5	90	0.037	162, 164, 168, 169
	$BiSr_{1.5}Ca_{0.5}Al_2O_6$	tetragonal	–	3	–	90	0.016	168–170
Ga	$Bi_{0.2}SrCa_{0.8}Ga_2O_z$	orthorhombic	–	~ 10	2 [b]	84	0.004	171
	$Bi_{1.7}Sr_{2.3}Ca_{0.6}Cu_{1.6}Ga_{0.4}O_z$	tetragonal	$Bi_4Sr_8Cu_5O_z$	~10	–	–	–	171
In	$Sr_{1-x}Ca_xIn_2O_4$, $x = 0.5-0.6$	orthorhombic	$CaFe_2O_4$	1 × 5 [c]	< 0.7	91	0.038	172
Sc	$Sr_{1.9}Ca_{0.1}ScBiO_6$	cubic	double perovskite	0.3	< 0.7	89	–	173
Lu	Sr_2LuBiO_6	monoclinic	the same	1–5 [d]	5 [e]	77	–	174, 175
	$(Ca,Lu)_{1-x}CuO_2$, $x \approx 0.2$	orthorhombic	$Ca_{0.828}CuO_2$	1–5	5	77	–	174, 175
Yb	Sr_2YbBiO_6	monoclinic	double perovskite	1–5	6.3 [e]	57	–	174, 175
	$(Ca,Yb)_{1-x}CuO_2$, $x \approx 0.2$	orthorhombic	$Ca_{0.828}CuO_2$	1–5	4.1 [b]	87	–	174, 175
Tm	Sr_2TmBiO_6	monoclinic	double perovskite	1–5	8 [e]	52	–	174, 175
	$(Ca,Tm)_{1-x}CuO_2$, $x \approx 0.2$	orthorhombic	$Ca_{0.828}CuO_2$	1–5	8 [e]	52	–	174, 175
Ti	$SrTiO_3$	cubic	perovskite	0.2	~2 [b]	76	–	176
Zr	$SrZrO_3$	orthorhombic	"	0.2	< 0.7	93	0.092 [f]	177–179
Hf	$SrHfO_3$	cubic	"	0.2	< 0.7	93	–	28, 178
Sn	$Sr_{1-x}Ca_xSnO_3$, $x = 0.1-0.15$	"	"	0.3	< 0.5	92	0.074	180
Sb	$Bi_4Sr_4Ca_2SbO_x$	monoclinic	–	–	0	87	–	181
S	$SrSO_4$	orthorhombic	–	> 1	< 0.7	91	–	182

[a] $R = \frac{J_c(60\,\mathrm{K}, 10\,\mathrm{mT})}{J_c(5\,\mathrm{K}, 1\,\mathrm{T})}$. This parameter characterises the average pinning energy of magnetic vortices.[28] For most composites, the R values increase (by up to hundreds per cent) compared to those of single-phase superconductors ($R = 0.01$ for bulk samples of the pure Bi2212 phase; $R = 0.03$ for silver-sheathed tapes).[28] [b] Corresponds to the lower bound of the solubility in equilibrium with the A-containing phase. [c] Rod-like grains. [d] For Bi2212–Sr_2LnBiO_6 composites. [e] Average values for the equilibrium with Sr_2LnBiO_6. [f] For silver-sheathed tape.

known that rare-earth elements can partially or completely replace calcium in Bi2212.[187–189] Under particular conditions the equilibrium with the complex oxides containing the late rare-earth elements permits the content of the rare-earth elements in the Bi2212 phase to be limited, thus retaining the high T_c values (*e.g.*, 87 K for the Bi2212 – Sr_2YbBiO_6 composite).[174]

Figure 12 presents the plots of the critical current density *vs.* the magnetic field induction for the single-phase Bi2212 sample and the Bi2212 – $SrZrO_3$ composite in the form of silver-sheathed tapes.[179] At low temperature (5 K), the J_c values for both samples are comparable. It is assumed[91] that under these conditions the critical current is governed by the pinning to a large number of small defects (*e.g.*, atomic vacancies) with low pinning energies. Raising the temperature to 60 K causes a dramatic decrease in the efficiency of such pinning centres. At this temperature, the composite is characterised by higher J_c compared to the single-phase Bi2212 sample, the difference being increased with increasing magnetic field induction. Apparently, this indicates that inclusions of the second phase create new high-energy pinning centres, which can efficiently operate at a temperature of nearly 60 K.

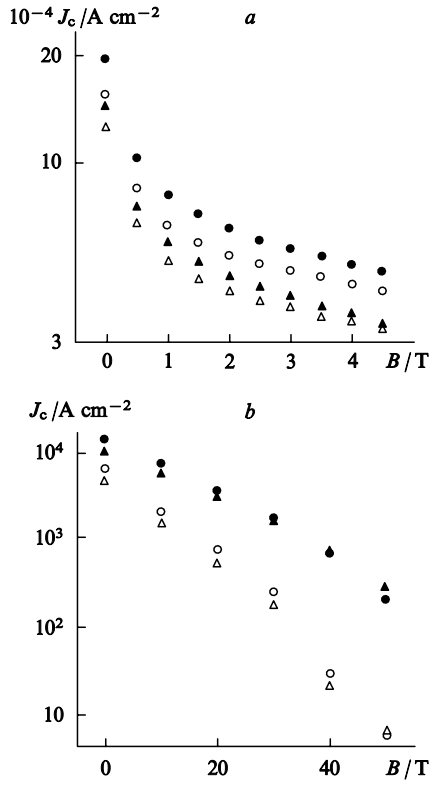


Figure 12. Critical current density *vs.* magnetic field induction for the superconducting silver-sheathed tapes based on pure Bi2212 phase (open circles and open triangles, two samples) and on the Bi2212 phase containing submicrometre-sized inclusions of $SrZrO_3$ (full circles and full triangles, two samples) at 5 (*a*) and 60 K (*b*).[179]

Most studies on the superconducting composites were carried out using MgO as the inclusion phase. Magnesia was introduced into the Bi2212 samples in the form of micro- and nanoparticles[165, 166, 190–193] and aligned whiskers several micrometres[11, 194, 195] or nanometres[196] in diameter. Usually, MgO particles are uniformly distributed in both polycrystalline ceramics (Fig. 13) and Bi2212 single crystals.[72, 164, 166, 193] The size of inclusions depends on the preparation procedure and on the dispersion of the starting powder; however, melt processing is accompanied by recrystallisation of the inclusion phase, so that the MgO inclusions in the composite were of submicrometre size

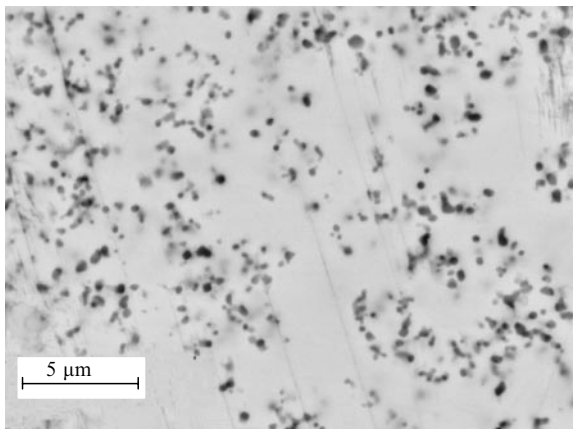


Figure 13. Electron microscopy (BSE) micrograph of Bi2212 – MgO composite.
The grey background is the Bi2212 matrix and the dark objects are $Mg_{1-x}Cu_xO$ inclusions.

even when nanocrystalline ($\sim$ 10 nm) powder was used. The samples exhibited an increase in J_c, which was most pronounced at elevated temperatures and at high magnetic fields and reached one or two orders of magnitude. For instance, a thick Bi2212 film with perpendicularly aligned MgO whiskers 20 nm in diameter was characterised by a critical current density of $\sim 10^4$ A cm^{-2} at a magnetic field of 0.5 T at 60 K.[196] Introduction of larger (micrometre-sized) MgO whiskers causes significant improvement of the strength of bulk composite samples and favours their texturing.[11, 194, 195]

Doping with alumina is often used to modify the properties of the generic superconducting system. In this connection, the effect of Al_2O_3 on the superconducting transition temperatures of Bi2212 and (Bi,Pb)2223,[197–199] on the ability of the phases in the generic system to undergo glass transitions,[200, 201] on the microstructure of molten Bi2212,[197] on the mechanical properties of a (Bi,Pb)2223-based composite (see Ref. 198) and on the pinning force of the magnetic vortices in Bi2212 (see Refs 202 and 203) was studied. Considerable interest in alumina is due to the remarkable positive effect of this compound on the formation and growth of Bi2212 whiskers.[170, 200, 204–207] A mechanism of formation of whiskers involving a phase of the Bi – Sr – Ca – Al – O system as a specific kind of microcrucible was proposed.[204, 205, 207]

Bi2212-based composites with inclusions of compatible Al-containing oxides have been studied in detail.[164, 168, 169, 208] It was found that the $BiSr_{1.5}Ca_{0.5}Al_2O_z$ phase is nearly completely segregated in the intercrystalline space of the Bi2212 phase, so that the intergranular electric contacts are broken. At the same time, $Sr_{1.7}Ca_{1.3}Al_2O_6$ mainly forms inclusions inside of the Bi2212 crystallites and, hence, the superconducting current can flow throughout the whole volume of the sample (Fig. 14). In the presence of $BiSr_{1.5}Ca_{0.5}Al_2O_z$ the melting temperature of Bi2212 reduces down to 860 °C and the process is described by the following peritectic reaction

$$\text{Bi2212} + BiSr_{1.5}Ca_{0.5}Al_2O_z \rightleftharpoons Sr_{1.7}Ca_{1.3}Al_2O_6 + \text{melt}.$$

A Bi2212 – $Sr_{1.7}Ca_{1.3}Al_2O_6$ composite with substantially (by nearly an order of magnitude) reduced size of inclusions (down to 0.3 μm) was obtained from a glassy precursor (Fig. 14 *c*).[208] However, in this case the aluminate grains are partially aggregated in the space between lamellae of the superconducting phase.

If the composite is prepared by a melt technique, particles of the impurity phase (usually, this is the solid phase in the peritectic melt) are either trapped by the growing Bi2212 crystal or pushed by it depending on the energy ratio at the melt – superconducting phase – impurity phase interfaces. If pushing of particles of the impurity phase is energetically favourable, there is a critical growth rate of the crystal, v_c (if the crystal growth rate exceeds

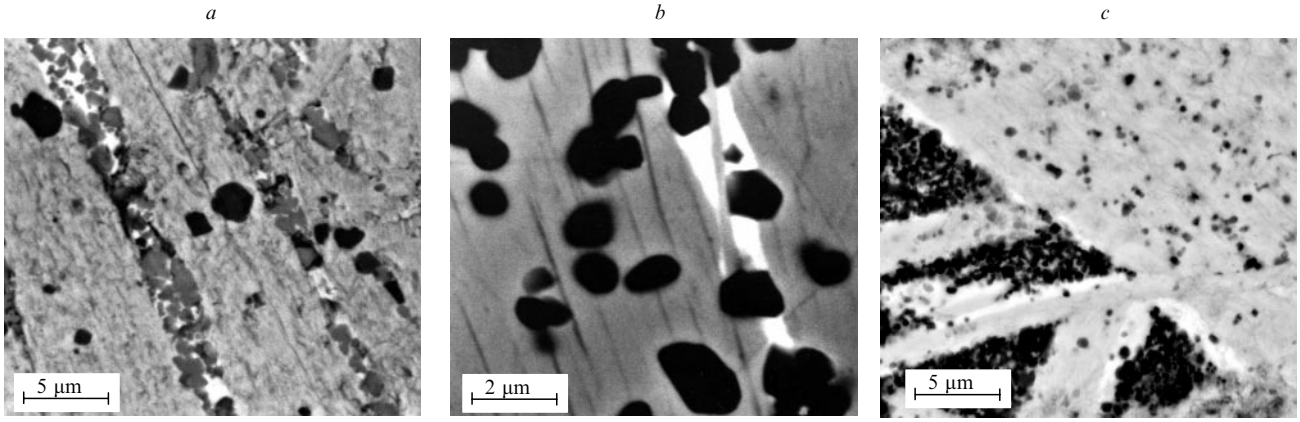


Figure 14. Electron microscopy (BSE) micrographs of Bi2212-based composites with inclusions of Al-containing oxides.
Compositions: Bi2212 + 0.5 $BiSr_{1.5}Ca_{0.5}Al_2O_z$ (*a*), Bi2212 + 0.2 $Sr_{1.7}Ca_{1.3}Al_2O_6$ (*b*) and Bi2212 + 0.2 $Sr_{1.7}Ca_{1.3}Al_2O_6$ (*c*) (prepared from oxide glass). The grey background is the Bi2212 matrix, the light-grey equiaxial objects are the $BiSr_{1.5}Ca_{0.5}Al_2O_z$ grains and the black equiaxial objects are the $Sr_{1.7}Ca_{1.3}Al_2O_6$ grains.

υ_c, the particles are not displaced) and the extent of trapping by the matrix phase dramatically increases [86, 88, 89]

$$\upsilon_c \sim \frac{\Delta\sigma}{\eta r},$$

$$\Delta\sigma = \sigma_1 - \sigma_2 - \sigma_3,$$

where σ_1, σ_2, σ_3 are the energies of the particle – crystal, particle – melt and crystal – melt interfaces per unit of surface area, respectively; η is the melt viscosity and r is the particle radius.

The critical growth rate of the crystal increases with decreasing particle size. This provides an explanation for the fact that small $Sr_{1.7}Ca_{1.3}Al_2O_6$ particles are aggregated much more than large particles.

It was reported that the lattice parameter of $Sr_{1.7}Ca_{1.3}Al_2O_6$ is in good agreement with the interatomic distances in the CuO_2 layers of the matrix Bi2212 phase.[168] This means that $Sr_{1.7}Ca_{1.3}Al_2O_6$ can appear to be a promising substrate material for the preparation of epitaxial superconducting films. A study of the dielectric properties of this aluminate, aimed at using it in HTSC-containing composites, was carried out.[209]

Gallium sesquioxide additives were also used to obtain superconducting ceramics.[171, 186] The composite prepared by solid-phase synthesis exhibited a higher J_c value compared to the single-phase sample.[186] The melt processed material contains large inclusions of gallate $Bi_{0.2}SrCa_{0.8}Ga_2O_z$ (crystallite size of the order of tens of micrometres) and is characterised by reduced T_c and J_c due to insertion of gallium ions into the crystal lattice of the superconductor.[171] Melting of Bi2212 in the presence of the equilibrium gallate can be described by the reversible reaction

$$\text{Bi2212} + Bi_{0.2}SrCa_{0.8}Ga_2O_z \rightleftharpoons (Sr,Ca)_3Ga_2O_6 + \text{melt},$$

which is similar to the peritectic reaction involving the aluminate phase (see above). In both cases at temperatures above the melting temperature the systems contain no solid phases (cuprates and bismuthate of the rare-earth element) typical of the pure Bi2212 melt. Contacts with many other compatible oxides do not violate the nature of peritectic decomposition of the Bi2212 phase.[28]

Bi2212-based composites containing inclusions of perovskite phases $Sr(Ca)AO_3$ (A = Ti, Zr, Hf, Sn) have been reported.[176–179, 210] These composites are prepared using a melt technique and crystalline inclusions thus formed are much less prone to recrystallisation compared to MgO and Al-containing phases. Because of this, the size of inclusions is relatively small ($\sim 0.1-0.3$ μm). As a rule, a considerable fraction of the second phase is inside of the Bi2212 lamellae in the form of submicrometre-sized inclusions while the space between large lamellae is filled with relatively small aggregates of $SrAO_3$ grains, so that some intercrystalline contacts are retained (Fig. 15). Compared to the single-phase material, these composites (except for Ti-containing ones) are characterised by enhanced pinning of magnetic vortices and increased critical current density (by nearly an order

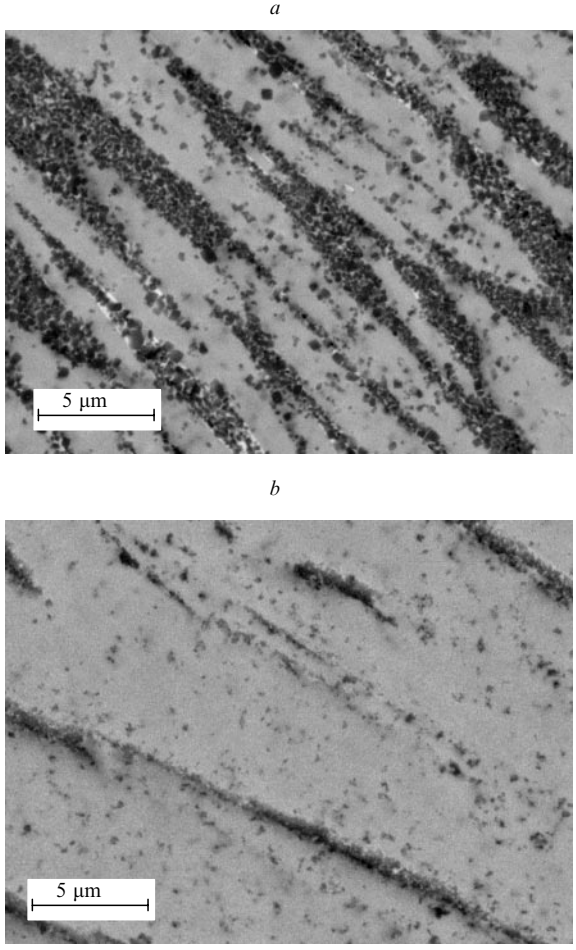


Figure 15. Electron microscopy (BSE) micrographs of composites Bi2212 + 1.6 $SrSnO_3$ (*a*) and Bi2212 + 0.5 $SrZrO_3$ (*b*).
The grey background is the Bi2212 matrix and the dark objects are submicrometre-sized grains of $Sr_{1-x}Ca_xSnO_3$ (*a*) and $SrZrO_3$ (*b*).

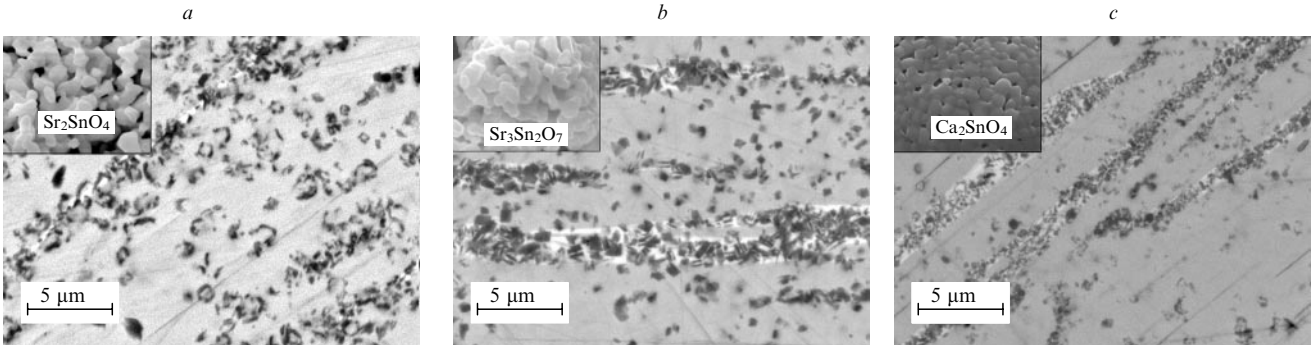


Figure 16. Electron microscopy (BSE) micrographs of Bi2212 – $Sr_{1-x}Ca_xSnO_3$ composites prepared by reactions of molten Bi – Sr – Ca – Cu – O system with Sr_2SnO_4 (*a*), $Sr_3Sn_2O_7$ (*b*) and Ca_2SnO_4 (*c*).
The grey background is the Bi2212 matrix and the dark objects are $Sr_{1-x}Ca_xSnO_3$ inclusions of various shapes. The insets present micrographs of the starting powders of the corresponding tin-containing oxides.

of magnitude at 30 – 60 K). For instance, at 60 K silver-sheathed tapes of Bi2212 – $SrZrO_3$ composite and pure Bi2212 phase are characterised by $J_c = 1.4 \times 10^4$ and 6×10^3 A cm^{-2}, respectively (see Ref. 178).

It should be noted that the use of precursors of various chemical nature eventually leads to the formation of the same type of Bi2212 – perovskite phase composites. In this connection a remarkable example is provided by the preparation of composites from a mixture of nonequilibrium substances *via* a chemical reaction between them.[211–214] This approach allows modification of the shape and size of inclusions. An intense reaction proceeds between the solid phase containing the component A and the molten oxide precursor of the Bi – Sr – Ca – Cu – O system. For instance, micrometre-sized Sr_2SnO_4 grains are transformed into hollow perforated shells of equilibrium (Sr,Ca)SnO_3; $Sr_3Sn_2O_7$ is transformed into corroded (Sr,Ca)SnO_3 particles, while nearly 1 μm Ca_2SnO_4 grains are dispersed into much smaller (Sr,Ca)SnO_3 particles (Fig. 16).[211,212] When heated above 1000 °C in the Bi2212 melt, strontium stannate $SrSnO_3$ is transformed into the $(Sr,Ca)_3Sn_2O_7$ phase, which forms aggregates composed of mutually perpendicular plates located at positions of the grains of the starting stannate (Fig. 17). Cooling of the system is accompanied by the reverse process, *i.e.*, transformation into metastannate, which forms complex-shaped particles.[213] Similar particles are also formed as a result of transformations of Sr_2TiO_4 and $Sr_3Ti_2O_7$ into $SrTiO_3$ and of $Sr_3Zr_2O_7$ into $SrZrO_3$.[214] It is assumed that complex-shaped particles formed during melt processing of a composite are less prone to agglomeration.[211]

The inclusion phases mentioned above have isotropic crystal lattices and, as a rule, form equiaxial grains. The crystal lattice of indium-containing oxide $Sr_{1-x}Ca_xIn_2O_4$ has one-dimensional In – O_2 – In chains with strong bonds. This compound forms uniaxial particles in the composite matrix. Figure 18 presents the micrographs of Bi2212 – $Sr_{1-x}Ca_xIn_2O_4$ composites. Synthesis from nitrate solutions gives the composite containing elongated indate particles of size 1×5 μm, which are partially agglomerated in-between the Bi2212 lamellae.[172] Synthesis from a glassy oxide causes the formation of more anisotropic indate particles, which are much less agglomerated.[215] One can expect that an anisotropic particle placed at a large angle with respect to the front of the growing crystal will be more readily trapped by the crystal compared to an equiaxial particle. A possible consequence is a much more uniform phase distribution in the composite.

The Bi2223 superconductor is less stable than Bi2212 (see Ref. 49) and is formed much more slowly. Namely, a complete solid-phase transformation of the precursor requires tens (hundreds) of hours; the Bi2223 phase cannot be crystallised immediately from melt. A vast majority of experiments were carried out using a lead-doped (Bi,Pb)2223 matrix instead of Bi2223, because phase formation in the former system proceeds much faster and to a greater extent as compared to the undoped system.

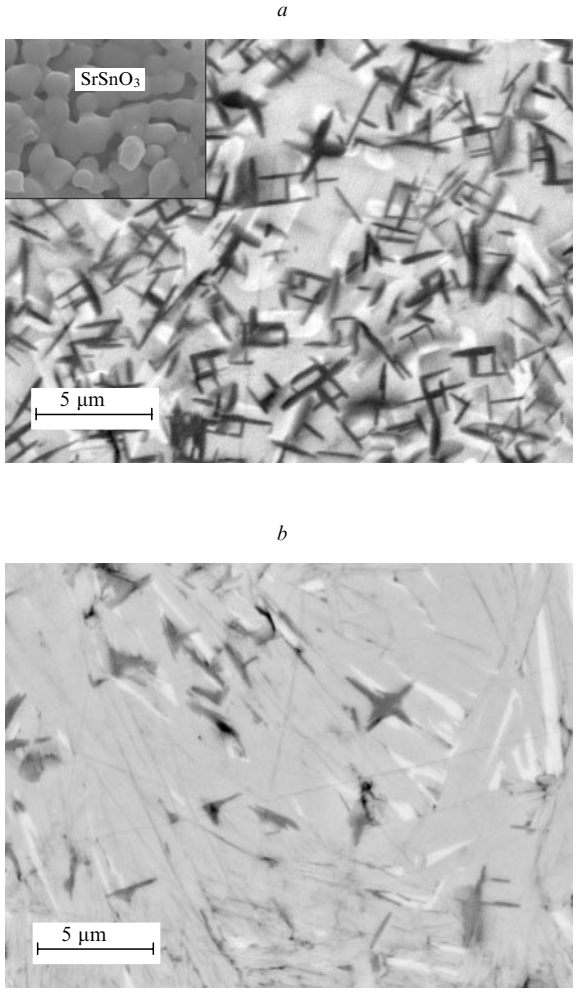


Figure 17. Electron microscopy (BSE) micrographs.
Sample prepared by melting of a mixture of Bi2212 and $SrSnO_3$ followed by annealing; the grey background is the Bi2212 matrix (solidified melt) and the black aggregates are scaly crystals of $(Sr,Ca)_3Sn_2O_7$ (inset: starting $SrSnO_3$ powder) (*a*); Bi2212 – $Sr_{1-x}Ca_xSnO_3$ composite prepared by heat treatment of the sample: the grey background is the Bi2212 matrix and the dark-grey and white objects are the $Sr_{1-x}Ca_xSnO_3$ and Bi2201 inclusions of irregular shapes (*b*).

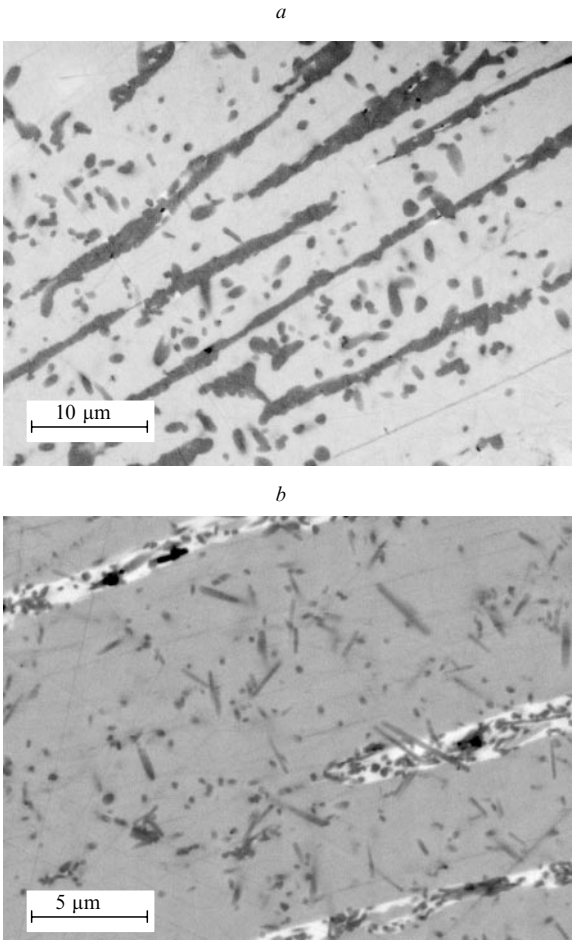


Figure 18. Electron microscopy (BSE) micrographs of $Bi2212-Sr_{1-x}Ca_xIn_2O_4$ composite prepared from nitrate precursor (*a*) and oxide glass (*b*).

Table 2 lists the data on the microcomposites containing different inclusion phases, which are thermodynamically compatible with (Bi,Pb)2223. The content of the impurity element in the matrix phase of the composite is at most 1 at.% and T_c varies in the narrow range from 106 to 110 K. A number of Bi2212-compatible phases (see Table 1) are also compatible with (Bi,Pb)2223. However, some phases including $(Sr,Ca)_3Al_2O_6$ and complex oxides of gallium react with the superconductor.[164, 219]

At present, methods for preparation of (Bi,Pb)2223-based composite materials include only solid-phase synthesis. The impurity components strongly affect the rate of (Bi,Pb)2223 phase formation. The slowest reaction resulting in the (Bi,Pb)2223 phase proceeds between (Bi,Pb)2212, calcium cuprate and copper oxide.[49] Taking the reaction of the oxide precursor of (Bi,Pb)2223 with $Sr_{1-x}Ca_xZrO_3$ as an example, it was shown that during heat treatment the finely dispersed strontium zirconate absorbs the Pb-rich liquid, which is present in the system in small amounts and serves as an important factor of the phase transformation. The absorption slows down the formation of the (Bi,Pb)2223 phase.[224] Acceleration of phase formation observed in the reactions with other additives is associated with the appearance of an additional amount of the liquid phase, which favours diffusion of the components.[224, 225, 229, 230]

Introduction of submicrometre-sized $SrZrO_3$ particles into (Bi,Pb)2223 ceramics causes an increase in the current flowing within grains.[176] At the same time, the $Ca_2B_2O_5$ additive has little effect on J_c,[218] while the addition of $BiSr_{1.5}Ca_{0.5}Al_2O_z$ and vanadium-containing oxide (see Table 2) leads to reduction of J_c, especially at nonzero magnetic fields.[219, 225]

Table 2. Composition and properties of microcomposites with the (Bi,Pb)2223 superconducting matrix.

Dopant A	A-Containing phase compatible with (Bi,Pb)2223	Effect of dopant on phase formation of (Bi,Pb)2223	T_c /K	Ref.
Mg	$Mg_{1-x}Cu_xO$, $x \approx 0.1$	no effect	109	216
B	$(Ca_{1-x}Sr_x)_2B_2O_5$, $x = 0.3-0.4$	acceleration	110	217, 218
Al	$BiSr_{1.5}Ca_{0.5}Al_2O_z$	"	108	219
In	$Ca_{0.9}Sr_{0.7}Pb_{0.4}In_2O_z$	"	109	164
	$Ca_{1-x}Pb_xIn_2O_4$	–	–	220
Sn	$Sr_{1-x}Ca_xSnO_3$	slowing down	110	28
	Ca_2SnO_4	"	–	221
Ti	$SrTiO_3$	"	106–107	57, 222, 223
Zr	$Sr_{1-x}Ca_xZrO_3$, $x \approx 0.1$	"	110	224
V	$Sr_{2.7-2.9}Ca_{0.3-0.2}\cdot Cu_{0.3-0.6}V_2O_z$ (see note [a])	acceleration	104–106	225
	$Sr_3V_2O_6$	"	–	57
Cr	$Bi_4Sr_8Ca_2Cr_3O_y$	–	109	57
Mn	$SrCa_5Cu_2Mn_2O_y$	–	104–107	57
	$Sr_4Ca_2Cu_{1.5}Mn_{2.5}O_y$	–	104–107	57
S	$SrSO_4$	acceleration	110	28
U	$(Sr,Ca)_3UO_6$	–	–	227, 228

[a] Isostructural to $Sr_5(VO_4)_3CuO$.[226]

Considerable enhancement of magnetic flux pinning was observed upon introduction of MgO in the form of micro- and nanoparticles or nanowhiskers into the (Bi,Pb)2223 ceramics and silver-sheathed tapes.[75, 231–234] Tapes containing additives of highly dispersed Ca_2PbO_4 were also prepared.[235] Of special note is the doping of superconducting cuprates with uranium prior to neutron irradiation in order to create a high concentration of defects (tracks) as a result of nuclear fission of ^{235}U.[227, 228] The interaction of U_3O_8 with the (Bi,Pb)2223 phase is mainly reduced to the reactions with the calcium and strontium oxides. The superconductor phase is in equilibrium with the solid solution $(Sr,Ca)_3UO_6$ containing nearly equal amounts of strontium and calcium.

It is noteworthy that doping of both bulk (Bi,Pb)2223 ceramics[236–240] and silver-sheathed wires with some microcomponents[24, 230, 241, 242] causes significant changes in the grain microstructure and the material's texture and finally results in an increase in the critical current density. It was shown[237] that introduction of nanodispersed TaC (0.1%) is followed by a twofold increase in J_c in the sintered ceramics; a further increase in the TaC content leads to reduction of the critical current density. Analogous changes in J_c were observed upon doping with microamounts of NbC (see Ref. 236) and HfN (see Ref. 238). It was assumed that the effect of these dopants is due to the changes in the content and composition of the intermediate liquid phase and to the formation of impurity phases. It was found[241] that (Bi,Pb)2223 tapes sheathed with the silver alloy doped with Ti, Zr or Hf exhibit higher J_c and that their microstructures are characterised by the larger size of the (Bi,Pb)2223 lamellae. This effect seems to be associated with the diffusion of micro amounts of dopants from the sheath to the superconducting core of the tape.

Investigations on the preparation of composites based on other high-temperature superconducting cuprates are on the initial stage yet. The introduction of nanoparticles of high-melting oxides into the $TlBa_2Ca_2Cu_3O_z$ matrix (see Ref. 243) leads to the

formation of inclusions of reaction products (particle size 30 to 100 nm). The product of the reaction with Al_2O_3 was identified as $BaAl_2O_4$. Phase formation of the superconductor $(Tl,Bi)Ba_2Ca_2Cu_3O_z$ in the system containing micrometre-sized $LaAlO_3$ particles was studied.[244]

Partial replacement of barium by strontium and of mercury by lead in the superconducting phase $HgBa_2Ca_2Cu_3O_{8+\delta}$ accompanied by a sharp increase in the irreversibility field at temperatures above 77 K was reported (see Refs 245 and 246). Initially, this effect was associated with a decrease in the anisotropy of the superconducting state due to lattice compression along the *c* axis.[245] A more recent study[247] of the material revealed wave-like fluctuations of the Hg and Pb content with a period of tens of nanometres and pinning of magnetic vortices in the regions with weakened superconductivity [similar to the Nd123 and (Bi,Pb)2212 phases] was assumed.

* * *

Material presented in this review illustrates the importance of taking into account the chemical properties of components in the design of superconducting microcomposites based on cuprate superconductors. Considerable advances can be achieved only by carrying out basic research on the multicomponent oxide systems, formation of the matrix and inclusion phases and on peculiar features of physicochemical interactions between these phases during the composite formation, which is to a great extent governed by the interface energy.

Further progress in the field of design of superconducting microcomposites is related to thorough choice of additives and conditions for the preparation of microcomposites for each particular generic system in order to retain high superconductivity parameters of the matrix phase, reduction and stabilisation of inclusion size at nanolevel and control of the inclusion shape and distribution in the superconductor matrix. On this basis, the potentialities of the chemical complication of the systems under study are still far from being exhausted. It seems not improbable that multiphase materials containing several additives rather than a single extra component will exhibit optimum operating characteristics.

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