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Formation of high-temperature superconducting phase $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ in functional materials (ceramics and composite tapes)

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Contents

I.	Introduction	473
II.	Stability and crystal structure of the 2223 phase and its homologues	474
III.	Investigations of phase formation and microstructure formation in (Bi,Pb)2223/Ag tapes	478
IV.	The mechanisms and kinetics of formation of the 2223 phase	479
V.	Effect of the phase formation conditions on the transport properties of (Bi,Pb)2223/Ag tapes	484

Abstract. The review is devoted to the kinetics and mechanisms of formation of the superconducting polycrystalline phase $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$. Data on the stability of this phase and its homologues are generalized. Methods of investigation of phase formation and microstructure formation in composite tapes are considered. The results of studies on the evolution of the phase composition during the manufacturing of composite tapes are presented. The crystallization models for the superconducting phase $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$, the kinetics and the limiting stages of crystallization are considered. A possible reaction scheme for the formation of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ is proposed. The effect of phase formation on the transport properties of tapes is briefly discussed. The bibliography includes 416 references.

I. Introduction

The high-temperature superconducting phase of an idealized composition $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ [the (Bi,Pb)2223, or simply 2223] having a transition temperature T_c of about 110 K is one of the most promising systems for various practical applications.[1–4] In the form of bulk ceramics, this phase can potentially be used for production of devices (*e.g.*, current limiters) operating at liquid nitrogen temperature because liquid nitrogen is a relatively cheap and operationally convenient cryogenic agent. However, the main field of application of 2223 is thought to be manufacturing of flexible long items for heavy-current devices. This phase is characterized by sufficient plasticity and greater ability to form an ordered microstructure (texturing)[5,6] compared to other high-temperature superconductors (HTSC) and therefore becomes in high demand for production of long items in the form of tapes or wires for power transmission lines,[7,8] production of accessories for motors,[9] magnetic systems,[10–12] *etc*. At present, the 'powder-in-tube' method[7–22] allows one to manufacture composite tapes [in particular, silver-sheathed 2223 phase (2223/Ag)] a few kilometres long without significant difficulties.[1,23,24] However, such tapes are still of limited use because of some economical, technical and technological factors[25,26] including low current-carrying capability and low reproducibility of the properties owing to uncontrollable action of different factors affecting the formation and properties of the 2223 phase.

The last-mentioned circumstance is due to the fact that the 2223 phase is formed in a complex multicomponent system Bi – Pb – Sr – Ca – Cu – O and this process is accompanied by the formation of its homologues $(Bi,Pb)_2Sr_2Ca.Cu_2O_{8+\delta}$ (2212 phase) and $(Bi,Pb)_2Sr_2CuO_{6+\delta}$ (2201 phase) as well as other phases including $(Ca,Sr)_2PbO_4$, $Pb_3Sr_{2.5}Bi_{0.5}Ca_2CuO_x$ (3321 phase), $(Ca,Sr)CuO_2$, $(Ca,Sr)_2CuO_3$, $(Sr,Ca)_{14}Cu_{24}O_{41}$, (Sr,Ca)O, CuO, *etc*.[27–31] At the synthesis temperatures, some of them may undergo melting and thus form heterogeneous systems comprising solid phases and melts. In the course of synthesis, these systems participate in oxygen exchange with the gas phase. In addition, partial loss of volatile components, *e.g.*, lead can occur at the synthesis temperatures (intense oxygen exchange[32] and some loss of lead[33] occur even through the silver sheath in the synthesis of tapes). In addition, the 2223 phase itself is a variable-composition phase with respect to cations[27,34–39] and oxygen.[40–43]

The multicomponent character of the system and the complicated synthesis of the 2223 phase are responsible for extremely high sensitivity of the properties of this material to complex influence of many process parameters including the elemental and phase compositions of the starting powder mixtures,[44–70] their pre-annealing temperatures,[59,63,68–81] the final synthesis temperature,[14,63,77,82,83] the partial pressure of oxygen,[45,47,75,79,82,84–88] duration of the synthesis,[45,48,59,74,89,90] intermediate mechanical deforma-

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tions,[59,91] the heating[92,93] and cooling regimes,[52,86,94–103] *etc*. Depending on the particular conditions chosen, the process may follow different reaction pathways, which should unavoidably affect the real structure (microstructure) and the superconducting properties of the material.

At present, the efforts of researchers and materials scientists working with 2223 are mainly aimed to improve the transport properties of polycrystalline materials. Some advances have been achieved for the composite tapes based on the 2223 phase,[104–108] but even the record-high critical current densities (j_c) are only $\sim 5\%$ of the values characteristic of thin single-crystalline 2223 films.[109–111] The transport properties of polycrystalline items can also be improved[112] by improving the microstructure of materials and first of all the coupling between superconducting granules. One of the main reasons for the decrease in the transport current is the presence of impurities of side reaction products, which are unavoidably accumulated between the superconducting 2223 granules. In this connection, information on the processes occurring in the synthesis of the 2223 phase, on their mechanisms and on the effects of various reaction products on the superconducting properties of the material becomes of great importance.

Studies on the mechanisms of formation of the 2223 phase began immediately after its discovery and different opinions were reported.[113–120] Since then, more than two decades have passed, but no considerable progress in the field was made and the chemical reactions responsible for the formation of 2223 are still unclear.

Earlier,[121] we have considered the phase states in the system Bi–Pb–Sr–Ca–Cu–O under equilibrium conditions. In this review, we will analyze the available data on the kinetics and mechanisms of formation of 2223 and propose a possible mechanism of this process. But prior to discussing the subject, we have to consider some physicochemical and structural properties of the 2223 phase and related compounds as well as relevant methods of investigation.

II. Stability and crystal structure of the 2223 phase and its homologues

1. Stability of the 2223 phase and its homologues

A traditionally used method of fabrication of HTSC-ceramics involves alternating grinding, pressing and heat treatment of corresponding compositions. When producing long items, additional operations are needed. In fabrication of 2223/Ag tapes, a tube made of silver or silver alloys is filled with a mixture of powdered components and then drawn. A bundle of wires is rolled, annealed and pressed to obtain a multifilament tape 3-mm wide and 200-μm thick (typical sizes). The tape thus obtained is again heat treated at desired temperatures and partial pressures of oxygen and then cooled under specified regimes.

The heat-treatment stages of the fabrication of ceramics and tapes are key to the formation of the 2223 phase and should be thoroughly controlled. The case in point is that 2223 is formed within a limited temperature range which is further narrowed if the goal is to synthesize a phase containing a minimum number of impurity phases. The choice of the optimum temperature depends on the initial elemental composition (nominal composition) and on the partial pressure of oxygen.

A typical stability diagram of 2223 plotted in the 'temperature–partial pressure of oxygen' coordinates is shown in Fig. 1. It is based on the data[122] and information available from other publications. In spite of some differences between the results obtained by different authors (this seems to be first of all due to different content of lead and other elements in the nominal compositions of the 2223 phase), one can determine the stability region of this phase (given in grey). Above the high-temperature boundary of this region, the 2223 phase undergoes peritectic decomposition; the loss of stability under the lower boundary is likely to be due to the chemical metastability of this phase at reduced temperatures.[27]

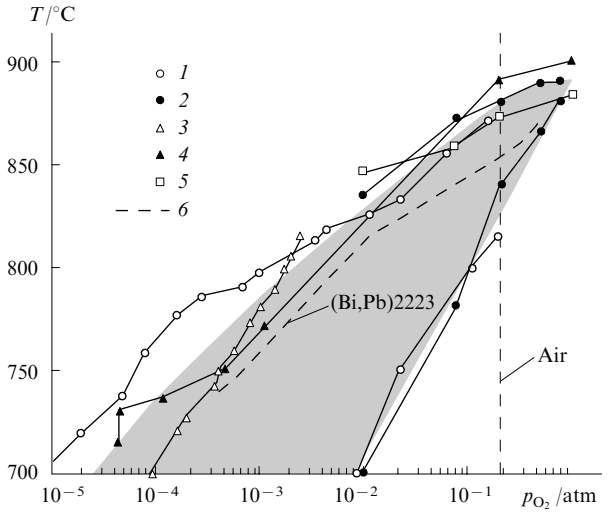


Figure 1. Typical boundaries of formation and stability of the 2223 phase plotted *vs*. temperature and partial pressure of oxygen. Data taken from Refs 123 (*1*), 124 (*2*), 84 and 125 (*3*), 126 (*4*), 127 (*5*) and 128 (*6*).

Within the stability region, 2223 coexists with some accompanying phases; at the same time, there are very narrow regions where the amount of impurity phases in 2223 is minimum. In Fig. 1, this is a dashed line corresponding to the data[128] for the nominal composition $Bi_{1.72}Pb_{0.34}Sr_{1.83}Ca_{1.97}Cu_{3.13}O_z$. For other compositions of the 2223 phase, the line corresponding to optimum temperatures and p_{O_2} may shift to one or another side, but its pattern remains essentially the same.

Interestingly, this line passes more closely to the high-temperature boundary of the stability region of 2223. In the region between this line and the high-temperature boundary of the stability region, the 2223 phase coexists with the 2201 phase and the higher the temperature the higher the content of 2201.[128] At temperatures below the optimum temperature, the 2223 phase coexists, in particular, with 2212 and the lower the temperature the higher the content of the 2212 phase.[128] Transitions from the 2223 to the 2212 and 2201 phases are reversible and very sensitive to temperature variations. From Fig. 1 it also follows that the temperature range corresponding to the stability region of the 2223 phase extends and the optimum synthesis temperature of 2223 decreases as p_{O_2} decreases. Practically, in the case of tapes the 2223 phase is usually synthesized at 820–840 °C

at an oxygen content in the gas phase ranging from 1% to 20 %.[129–131]

The formation of the 2223 phase always involves the 2201 and 2212 phases as intermediate ones. Therefore, in discussing the mechanisms of formation of 2223 it is appropriate to consider some properties of these three phases. The 2223 phase is a variable-composition phase (see Introduction). Deviations of the actual chemical composition from an idealized one are also characteristic of the other two phases. The variable composition affects the superconducting, crystal-chemical and physicochemical properties of the compounds and is an important factor in the formation of the 2223 phase (see below). In our case, the key issues are as follows:

— the 2201 phase may contain not only strontium (as in an idealized case), but also calcium atoms as constituents of the substitution solid solution;

— in the three phases, some bismuth sites may be occupied by lead atoms;

— typical of the three phases is replacement of strontium sites by calcium atoms and *vice versa*; the 2201 and 2212 phases have wide homogeneity regions while the 2223 phase has a narrower homogeneity region corresponding to variation of the calcium content (subscript in the empirical formula) from 1.8 to 2.2 only.[27,29]

The concentrations of cations depend on the synthesis conditions.[27] Figure 2 shows how the content of calcium in the solid solutions $(Bi,Pb)_{2+x}Sr_{4-y}Ca_yCu_3O_{10+\delta}$ can vary with temperature during the synthesis in air. Initially, the homogeneity region extends with temperature and then narrows.[27,37] The *I*–*VI* phase fields are shown near the boundaries of the homogeneity regions. At low calcium content, the 2223 phase is adjacent to solid phases only, whereas at high calcium content, the neighbours include phases containing liquid (L) at temperatures above 840 °C.

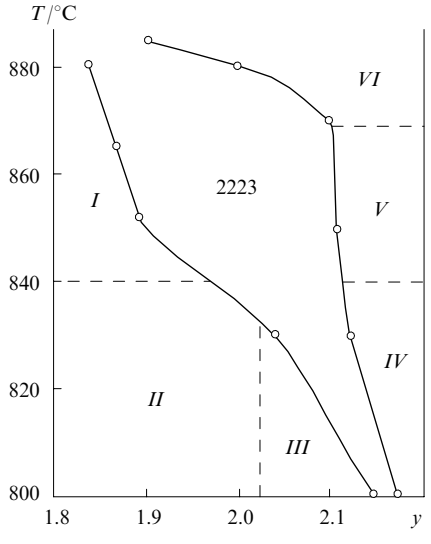


Figure 2. Typical boundaries of calcium content in $(Bi,Pb)_{2+x}Sr_{4-y}$. $.Ca_yCu_3O_{10+\delta}$ solid solutions plotted *vs.* temperature.[28] $2223 + 2212 + Ca_2CuO_3 + Sr_{14}Cu_{24}O_{41}$ (*I*), $2223 + 2212 + CuO + (Pb,Bi)_4(Sr,Ca)_5CuO_x + Ca_2CuO_3$ (*II*), $2223 + 2212 + CuO + Ca_2PbO_4 + Ca_2CuO_3$ (*III*), $2223 + CuO + Ca_2PbO_4 + Ca_2CuO_3$ (*IV*), $2223 + CuO + Ca_2CuO_3 + L$ (*V*) and $2223 + Ca_2CuO_3 + Sr_{14}Cu_{24}O_{41} + L$ (*VI*).

Seemingly, such a pattern of the phase diagram does not exclude the possibility of formation of the 2223 phase both with and without participation of the liquid depending on the synthesis conditions.

The 2201 solid solutions differ from the compound $Bi_2Sr_2CuO_6$ with idealized stoichiometry in many parameters and properties. This compound is a semiconductor.[132,133] Bismuth-rich, strontium-deficient solid solutions $Bi_{2.2+x}Sr_{1.8-x}CuO_z$ exhibit the properties of superconductors.[132] Structurally, they are somewhat different from $Bi_2Sr_2CuO_6$ and are therefore often treated as an individual phase called the Raveau phase.[133] Calcium-containing Raveau phases have the formula $Bi_{2.2+x}Sr_{1.8-x-y}Ca_yCu_{1\pm w}O_z$ $(0 < x < 0.5)$.[134] In some cases, they are denoted as 11905 $(Bi_{11-x}Sr_{9+x}Cu_5O_z)$. We will use a conventional notation '2201' followed by 'solid solutions'.

The physicochemical properties of the 2201 phase and solid solutions based on it have been much less studied than those of the 2212 and 2223 phases. At 850 °C in air, a 2201 substitution solid solution with strontium sites occupied by calcium atoms exists until a Sr : Ca ratio of about 1.5 : 0.5 and is in equilibrium with the 2212 phase except the compositions with very low calcium content (Sr : Ca < 1.9 : 0.1).[135] At high calcium concentrations (Sr : Ca < 1.5 : 0.5), the 2201 phase undergoes melting at 850 °C and the 2212 and 2223 phases are in equilibrium with the melt.[135]

A study[136] of phase equilibria in a pseudobinary system $Bi_2Sr_2CuO_6$–$(Ca,Sr)CuO_2$ revealed that heating causes polymorphous transformations of the 2201 phase and oxygen release near the melting point; however, melting of the 2201 phase occurs without decomposition. An investigation[137] of the regularities of phase formation in the system Bi—Pb–Sr–Ca–Cu–O and in its subsystems showed that doping with calcium leads to a decrease in the melting point of 2201 and to its stabilization before melting.

A considerable reduction of the melting points of calcium-containing 2201 solid solutions with an increase in the calcium content was reported (see Fig. 3).[138] It follows that as the calcium content increases, the melting points of these solid solutions in air decrease from 910 °C for

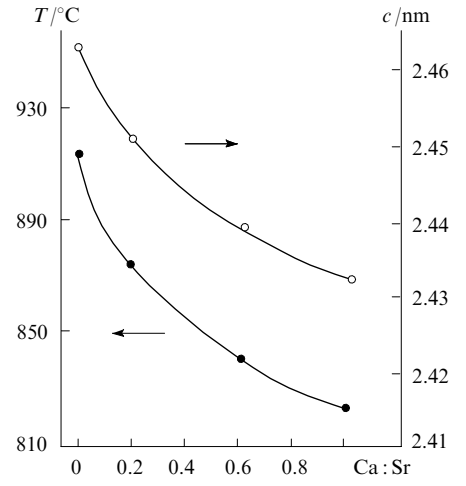


Figure 3. Melting points and lattice constant (*c*) plotted *vs.* Ca : Sr ratio in 2201 solid solutions.[138]

$Bi_2Sr_2CuO_{6+\delta}$ to 820 °C for a composition in which 50% of strontium atoms are replaced by calcium atoms. Unfortunately, no methods used for sample preparation and determination of melting points were reported and the structural characterization of the samples involved only measurements of the lattice constant *c*.

Information on the stability of 2212 is of particular importance for understanding of the formation mechanisms of 2223 because the former phase is an immediate presursor of the 2223 phase and participates in its formation. The 2212 phase undergoes incongruent melting;[123, 126, 139–147] the melting point and the phase compositions in the region between the liquidus and solidus surfaces depend on the partial pressure of oxygen and on the cation composition of the compound. Melting and peritectic decomposition of the 2212 phase are accompanied by the evolution of oxygen,[141, 143] which is first of all due to the 'release' of superstoichiometric oxygen.

Figure 4 presents the high-temperature stability boundaries of the 2212 phase containing (i) no lead and (ii) the limiting amount of lead, plotted in the 'partial pressure of oxygen – temperature' coordinates. The plots were constructed using published data. In the regions above these boundaries, the 2212 phase decomposes. Namely, solid-phase decomposition occurs in region *A* at reduced temperatures and partial pressures of oxygen, while the decomposition in the region *B* is accompanied by incongruent melting. At the same p_{O_2} value, the Pb-containing phase undergoes melting at a lower temperature than the lead-free phase. As the lead content increases, the melting point of the 2212 phase monotonically decreases.[144, 147–149]

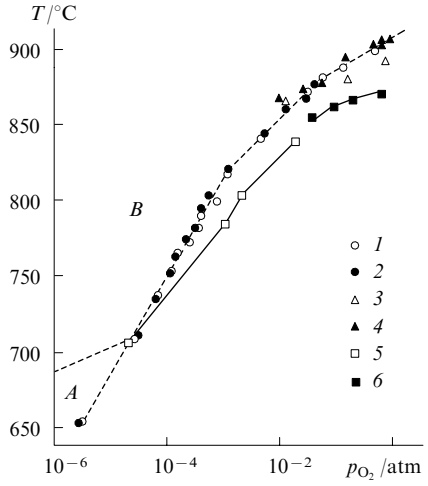


Figure 4. High-temperature stability boundaries of lead-free 2212 phase (dashed line) and 2212 phase with the limiting content of lead (solid line) plotted *vs*. temperature and partial pressure of oxygen. Data taken from Refs 123 (*1*), 139 (*2*), 141 (*3*), 143 (*4*), 146 (*5*) and 147 (*6*).

Reduction of the melting point of the 2212 solid solutions is also observed on partial replacement of strontium atoms by calcium atoms.[144, 149–153] The effect is particluarly pronounced on joint action of lead and calcium atoms.[144, 149, 152] As an illustration, Fig. 5 shows a decrease in the incongruent melting points of the solid solutions

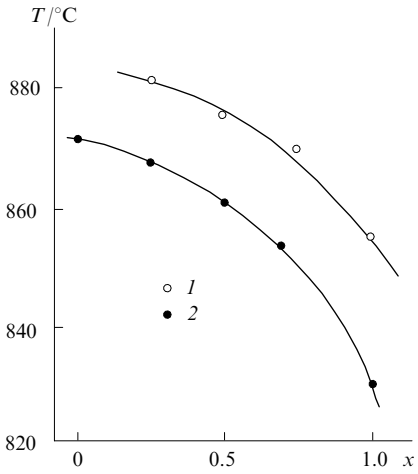


Figure 5. Incongruent melting points of $Bi_2Sr_{2-x}Ca_{1+x}Cu_2O_{8+\delta}$ (*1*)[150] and $Bi_{1.8}Pb_{0.4}Sr_{2-x}Ca_{1+x}Cu_2O_z$ (*2*)[152] solid solutions in air plotted *vs*. calcium content.

$Bi_2Sr_{2-x}Ca_{1+x}Cu_2O_{8+\delta}$ and $Bi_{1.8}Pb_{0.4}Sr_{2-x}Ca_{1+x}Cu_2O_z$ with an increase in the calcium content. Note that $Bi_{1.8}Pb_{0.4}Sr_{2-x}Ca_{1+x}Cu_2O_z$ is the nominal composition. The samples studied[152] represented a 2212 monophase containing trace amounts of Ca_2PbO_4 at $x \leqslant 0.5$ and small impurities of Ca_2PbO_4 and 2201 at $x = 0.75$ and 1.0.

Joint action of lead and calcium atoms may cause interesting variations of the chemical composition of the 2212 phase. Below the melting point of 2212, its decomposition and oxygen exchange with the gas phase are characterized by slow kinetics.[154] Therefore, on rapid heating in air (2 deg min^{-1}), the 'pure' (Bi,Pb)2212 phase almost does not decompose until 880 °C and undergoes melting at this temperature.[15, 155–157] However, in a mixture with Ca_2CuO_3 and CuO it readily loses lead at the same heating rate and undergoes transformation to Bi2212 and a lead-containing 3321 phase is formed; this occurs at relatively low temperatures (above 400 °C). Above 835 °C, the 3321 phase decomposes and the (Bi,Pb)2212 phase, Ca_2CuO_3 and CuO are formed again. Subsequent heating and long-term storage gives the (Bi,Pb)2223 phase. Reformation of the lead-containing 2212 phase immediately preceding the formation of (Bi,Pb)2223 is an important step in the chain of chemical reactions. This is accompanied by enrichment of the 2212 phase with not only superstoichiometric lead, but also superstoichiometric calcium (in the lead-free system, with calcium only).[36] Enrichment of the intermediate 2212 phase with lead and calcium facilitates the formation of the 2223 phase owing to lower stability and lower melting points of the 2212 solid solutions compared to the 2212 phase with idealized stoichiometry.

The technology used for fabrication of tapes should take into account the effect of silver atoms. In the solid state, silver does not react with the 2212 and 2223 phases and no solid solutions are formed.[158–160] However, local formation of a liquid phase at temperatures somewhat lower than the temperature of the bulk system occurs at the interface between the starting mixture and the silver sheath.[46, 161] This is probably due to the existence of a low-temperature eutectic in the system Ag – Bi – Sr – Ca – Cu – O.[162, 163]

2. Structural features of the 2223 phase

The 2223 phase and its homologues (phases 2212 and 2201) have sandwich-type layered structures. BiO double layers and SrO layers form a NaCl-type structure. Perovskite-like blocks with different numbers of calcium ions and CuO_2 layers are arranged between the BiO double layers.[164] Therefore, these three phases, although have almost equal size of the basis planes *ab*, differ in lattice constant *c* ($c \approx 2.4, 3.1$ and 3.7 nm for 2201, 2212 and 2223, respectively). The 2201 phase with idealized stoichiometry crystallizes in the monoclinic system, whereas 2212 and 2223 crystallize in the orthorhombic system. A characteristic feature of these phases is modulation of atomic positions in the crystal lattices because the perovskite-like block and the NaCl-type block are incommensurate. Asymmetry of the coordination environment of Bi atoms causes a cooperative displacement of all atoms in the BiO layer, while a periodic change in its coordination environment from four to three leads to rotation of the coordination polyhedra of Bi atoms and restoration of cationic positions in this layer.[165] Transformation of the BiO layer leads to insertion of extra oxygen atoms ($\sim$1 atom per five unit cells) into particular positions. As a result of modulation-induced displacements of bismuth atoms, the Bi—Bi separation between BiO planes varies periodically. Such a structure influences the character of formation of bismuth-containing cuprates, being to a great extent responsible for their physical properties. Very weak coupling between the BiO layers favours the formation of granules comprising thin plates and is the reason for low conductivity along the *c* axis (see below).

Owing to structural similarity between these phases, their granules often represent mixed crystals with intergrowths of related phases in the main-phase matrix having the basic crystal structure with local stacking faults. For instance, microcrystals of the 2223 phase may contain inclusions of the 2201, 2212 and even 2234 phases[166,167] separated by small-angle, twin or twist boundaries.[168]

Hybrid phases comprising structural fragments of known phases and having new ordered crystal lattices were synthesized. These phases include fragments with rigorously alternating variable number of CuO_2 layers, are characterized by long-range order and their structural parameters differ from those of corresponding prototypes. An example of a hybrid phase is provided by microcrystals of the $Bi_4Sr_4CaCu_3O_z$ phase (4413) which occupies an intermediate position between the 2201 and 2212 phases with respect to the chemical composition, X-ray diffraction patterns and unit cell parameters.[169–172] Interestingly, the 4413 phase can be formed during the synthesis of 2223/Ag composite provided an intermediate peritectic decomposition of the 2212 phase; this was confirmed by high-temperature X-ray diffraction studies.[173] Yet another intermediate phase, $Bi_4Sr_4Ca_3Cu_5O_z$ (4435), represents a combination of regularly alternating fragments of the 2212 and 2223 phases; it was discovered by high-resolution electron microscopy (HREM) in a study[174] of the early stages of the transition 2212 $\rightarrow$ 2223 during the fabrication of tapes.

The synthesis of ceramics and tapes is almost always accompanied by the formation of discrete 2212 intergrowths in the 2223 crystal lattice.[167,175,176] This feature, as well as the discovery of fragments of the intermediate phase 4435 adjacent to fragments of the 2212 and 2223 phases in the crystal lattice, are the main arguments in favour of the hypothesis that the 2223 crystalline phase is formed through intercalation of extra layers comprising calcium atoms and CuO_2 into 2212.[174]

These examples characterize the structure of the 2223 phase and its homologues on the atomic level. One can also investigate their microstructure which characterizes the structure and morphological features of the materials. This is a very important characteristic of polycrystalline superconductors because the quality of the microstructure immediately affects the transport current that can flow through the superconductor. The case in point is that polycrystalline HTSC in the form of ceramics or tapes represent systems of superconducting granules (crystallites) interlinked into a three-dimensional network of weak Josephson junctions that reduce the superconducting current. Weak couplings can be due to different reasons, *e.g.*, impurities of accompanying phases, violation of grain stoichiometry in the near-boundary regions, structural defects (*e.g.*, stacking faults, edge dislocations), *etc*. Defects causing discontinuity of a material, *e.g.*, cracks and pores, significantly deteriorate its electrophysical properties.

Yet another reason for deterioration of the current-carrying capability is high anisotropy of the physical properties along different crystallographic axes. Owing to specific features of their crystal structures, for the 2223 phase and its analogues this anisotropy is even more pronounced than for the well-known lanthanum- and yttrium-containing HTSC. The conductivity of bismuth-based HTSC in the *ab* plane is a few orders of magnitude higher than along the *c* axis;[177,178] *i.e.*, the superconductivity is essentially two-dimensional, and almost all current flows in the *ab* plane. Therefore, the material with randomly oriented superconducting crystallites exhibits poor transport properties.[179] The homogeneity of a polycrystalline material and its current-carrying capability can be improved by alignment of crystallites in some way, *i.e.*, by texturing.

Texturing is favoured by the layered structure of bismuth-based HTSC, especially when using pressing, rolling, *etc*.[180,181] Ceramics (no hot pressing) is characterized by mainly random orientations of crystallites, but rolling of tapes significantly facilitates texturing of the microstructure.[182] This results in the formation of ordered plate-like crystals whose *c* axis is perpendicular to the rolling direction.[183] But this is not the only factor. In the early stages of synthesis, the silver sheath promotes the formation of a textured layer of the 2212 phase[183,184] a few micrometres thick.[93,161,185] This layer is basic to the formation of oriented granules of the 2223 phase.[183] A feature of the formation and growth of the 2223 granules is inheritance of the texturing direction of the preceding intermediate 2212 phase.[186–188] This is yet another factor which affects the formation of texture in tapes and 'operates' in the ceramic core during the synthesis of 2223. As the duration of the synthesis and the amount of the 2223 phase increases, the degree of texturing of 2223 gradually increases.[186,188] This was called 'reaction induced texturing'.[186] Thus, texturing and the mechanisms of formation of the 2223 phase are closely interrelated. Studies on texturing in tapes have been well documented (see, *e.g.*, Refs 189–202).

III. Investigations of phase formation and microstructure formation in (Bi,Pb)2223/Ag tapes

1. Instrumental methods of investigation

Consider methods of investigation of the regularities of phase formation and microstructure formation during the fabrication of 2223/Ag tapes. The phase and chemical compositions of the tapes are often characterized by X-ray diffraction (XRD) analysis and energy dispersive X-ray spectroscopy (EDS). Transformations of the microstructure are studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The most informative methods include neutron diffraction and high-energy synchrotron X-ray diffraction. They provide a unique possibility to investigate the phase transformations and evolution of the microstructure in tapes in the course of synthesis.

Each of these methods has specific scope and limitations and is characterized by its own length scale. Synchrotron X-ray diffraction and neutron diffraction allow one to analyze surface areas of the order of $1-2$ mm^2 and to study the phase formation and texturing throughout the thickness of the tapes rather than a thin near-surface layer. Combining SEM and EDS gives information on the local composition of the 2223 phase and secondary phases on a length scale of the order of a few micrometres.[192] TEM allows granules, their thickness and angle boundaries to be studied on the submicrometre level.[203] HREM is used to study various objects on the atomic level and provides information on grain boundaries, intergrowth, *etc*.[134, 204]

In many studies (see, *e.g*., Refs 205 and 206) the formation of the 2223 phase was investigated *ex situ* at room temperature after annealing of heat treated samples at a certain reaction stage. This approach gives valuable information, but has the following significant drawback: the phase composition of a cooled sample can change in the course of annealing and thus be different from the actual composition at the heat treatment temperatures.

High-temperature diffractometers enable *in situ* monitoring of the process during the synthesis of the 2223 phase. The authors of some studies (see, *e.g*., Refs 87, 207–209) used conventional low-energy CuK_α radiation. The initial samples represented thin layers of powdered precursors on silver substrates arranged in sampling boats on heated holders.

Next, synchrotron radiation was used because the silver sheath is transparent to this kind of radiation. The first attempt to use X-ray diffraction with a source of synchrotron radiation was reported in an *ex situ* study[210] of tapes. Soon, high-temperature *in situ* studies of tapes by synchrotron X-ray diffraction were reported.[211, 212] Nearly 25-keV synchrotron radiation allowed one to conduct nondestructive analysis of the evolution of the phase composition and texture of tapes and was more recently employed by other researchers.[213–215] Great potential of synchrotron X-ray diffraction using higher-energy (80–100 keV) source of synchrotron radiation was demonstrated.[33, 95, 193, 216–218] The advantages of synchrotron radiation include fast measurements, high-resolution diffraction patterns, sufficiently high intensity of the primary and diffracted ray and variable radiation wavelength.[219] This allows one to monitor the process under study and to additionally control the penetrating power of X-ray radiation by varying the radiation wavelength.[219]

An original method employing X-ray diffraction called 3D XRD microscopy[220] deserves attention. Micro-focused X-ray radiation from a source of synchrotron radiation (80 keV) passes through a rotatable sample using a focusing system. Unlike the available X-ray diffraction techniques, which give averaged parameters of systems under study, the new method allows one to detect individual granules (to 0.3 μm^3 in volume) and to monitor their behaviour in time. An *in situ* study[220] of the formation, growth and disappearance of granules in the course of the synthesis of (Bi,Pb)2223/Ag tapes at nearly 840 °C showed that the transition of 2212 to 2223 is a dynamic process, *viz*., individual granules of the 2212 and 2223 phases are formed in different periods of time, dissociate and again recrystallize during the synthesis of the 2223 phase. The average lifetimes of such granules (time interval from their formation until dissolution) are about 1 h. This interesting result indicates an oscillatory character of the process.

In addition to X-ray diffraction techniques, neutron diffraction methods[26, 196, 221–226] including *in situ* high-temperature neutron diffraction[221, 223, 224] were developed to study the formation of 2223/Ag tapes. Neutron diffraction is more sensitive to light elements (Ca, Cu and O) than X-ray diffraction. The intensities of the neutron diffraction peaks are proportional to the content of each phase. This allows reflections from all phases to be involved in the analysis[223, 224] and enables exact quantification of phases and simultaneous monitoring of the evolution of up to seven phases, which is of importance in studies of such a complex system, as Bi–Pb–Sr–Ca–Cu–O. Neutron diffraction also makes it possible to evaluate the overall content of crystalline phases and to monitor the dynamics of their formation during the synthesis. Nonmonotonic dynamics of formation of crystalline phases in the synthesis of 2223/Ag tapes[223, 224] suggests that the process is accompanied by partial melting and recrystallization.

The regularities of formation of the 2223 phase and the dynamics of changes in its microstructure can also be studied by electron microscopy methods which allow one to investigate the morphology and structure of samples, obtain information on the distribution of different phases and on the local interactions between them in the sample. A method for visualization of the pattern of microstructure transformations in tapes during the synthesis of 2223 was developed; however, this required partial removal of the Ag sheath.[227] *In situ* observations of changes in the surface morphology, formation and propagation of the liquid phase, *etc*. were carried out by SEM.

Most often, electron microscopy studies are performed using samples cooled after completion of a certain reaction stage. The influence of synthesis at different temperatures and partial pressures of oxygen on the composition and microstructure of tapes was studied using a combination of SEM and EDS.[192, 228–230] Such a combination was also used (see, *e.g*., Refs 231–234) to investigate the formation and composition of phases and their temporal evolution. Particular attention was paid to the formation, evolution and composition of liquid phase. It was established that the liquid phase is enriched with lead and calcium atoms[134, 233] whose content depends on the region in which the liquid is confined in the solid matrix.[134] The total amount of liquid initially increases and then gradually decreases.[231, 233] The liquid is formed until the appearance of the 2223 phase, and

there is some induction period preceding the formation of 2223.[235]

Individual granules were studied by high-resolution TEM (HRTEM) [134, 204, 235] which makes it possible to investigate the structural parameters, morphology and size of the 2223 granules, as well as the angle boundaries, *etc*.[166, 176, 203, 236] In particular, it was shown that the interface between the 2212 phase and the annealed liquid is covered by a thin layer of the 2201 phase formed from the liquid.[134]

Summing up this Section, note that the phase and structural transformations occurring during the synthesis of 2223 can be best understood only using all methods mentioned above. At the same time, even the most informative methods of investigation, such as synchrotron X-ray diffraction and *in situ* neutron diffraction still cannot provide the whole picture of the reaction.

2. Evolution of the phase composition

Determination of kinetic parameters and explanation for the mechanisms of formation of the 2223 phase require information on the qualitative and quantitative changes in the reactant compositions during the synthesis. Consider the regularities of the evolution of the phase composition in the synthesis of 2223 taking into account the fact that particular types of alkaline-earth cuprates [$(Sr,Ca)CuO_2$, $(Sr,Ca)_2CuO_3$, $(Sr,Ca)_{14}Cu_{24}O_{41}$] and the phase ratios depend on the initial reactant ratios, partial pressure of oxygen, *etc*.[33, 134, 233, 234]

Changes in the relative content of the 2212, 2223, $(Ca,Sr)_2PbO_4$ and $(Ca,Sr)_2CuO_3$ phases during the synthesis of 2223/Ag tapes determined from synchrotron X-ray diffraction data [216] obtained *in situ* are shown in Fig. 6. The authors reported that heating causes the reflections from $(Ca,Sr)_2PbO_4$ to weaken and eventually disappear at 820 ± 5 °C. An earlier EDS analysis [237] revealed that the formation of the 2223 phase is preceded by enrichment of the 2212 phase with lead and calcium [decomposition products of, *e.g.*, $(Ca,Sr)_2PbO_4$ phase]. This is a possible explanation for the decrease in the content of the $(Ca,Sr)_2PbO_4$ phase (see Fig. 6). The cuprate $(Ca,Sr)_2CuO_3$ is detected just at similar temperatures. The appearance of the cuprate was associated [216] with partial peritectic decomposition of 2212 to a liquid and $(Ca,Sr)_2CuO_3$. The concentration of $(Ca,Sr)_2CuO_3$ rapidly increases, reaches a maximum value at the temperature of the onset of formation of the 2223 phase and then slowly decreases. The concentration of 2212 also decreases. The regularities of the evolution of these phases suggest the involvement of 2212 and alkaline-earth cuprates in the formation of the 2223 phase.

However, the role of the liquid phase remains unclear. The evolution of this phase can be monitored by SEM, which allows one to evaluate the surface areas occupied by different phases including the liquid phase from the colour contrast in the electron micrographs. Changes in the amount of the 2212, 2223 and liquid phases assessed [231] using the electron micrographs of the samples annealed from 840 °C in different stages of the synthesis are shown in Fig. 7. Two time intervals can be distinguished. In the first period (0 – 10 h), the content of the 2223 and liquid phase rapidly increases while that of 2212 rapidly decreases. In the second period (10 – 50 h), the changes observed are more smooth. The content of the liquid phase increases in the first period, reaches a maximum value and then gradually decreases. The amount of the liquid phase was found [231] to be much smaller than one could expect based on the content of the decomposed 2212 phase; this suggests that the liquid phase is consumed and participates along with 2212 and alkaline-earth cuprates in the formation of the 2223 phase.

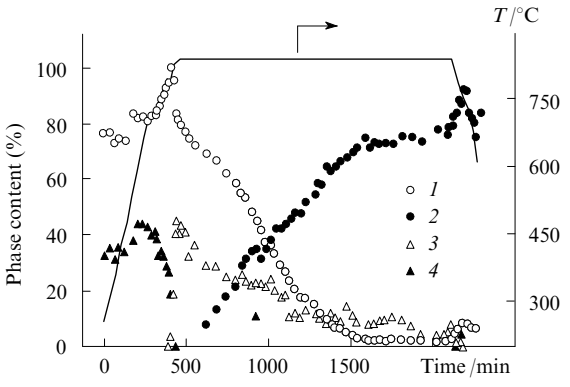


Figure 6. Relative content of phases plotted *vs*. duration of synthesis of 2223/Ag tapes.[216]
Nominal chemical composition is $Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.2}O_{10+\delta}$, synthesis in air at 835 °C. The phases: 2212 (*1*), 2223 (*2*), $(Ca,Sr)_2CuO_3$ (*3*) and $(Ca,Sr)_2PbO_4$ (*4*); the solid line illustrates temperature variation with time.

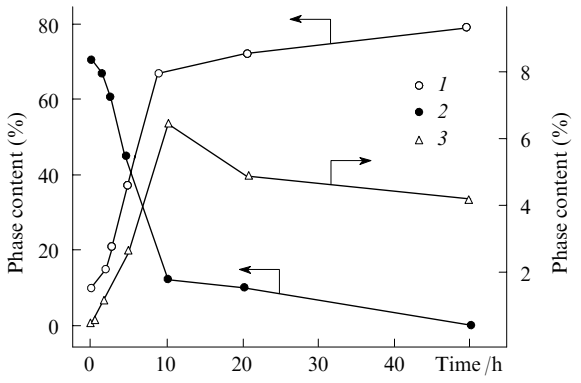


Figure 7. Volume fractions of the phases 2223 (*1*), 2212 (*2*) and annealed liquid phase (*3*) plotted *vs*. duration of synthesis at 840 °C in mixture (8.5% O_2 + 91.5% N_2).[231]

IV. The mechanisms and kinetics of formation of the 2223 phase

1. Models for formation of the 2223 phase

Various models have been proposed to describe the formation mechanism of the 2223 phase. A few examples on the subject are provided by the models considered in a review,[238] *viz*., disproportionation of 2212 phase; dissolution – precipitation; liquid drop migration; peritectic transformation; cation diffusion and intercalation; liquid-assisted synthesis; and Lewis acid – base equilibrium. This list is far from being completed.

Such a variety of models is due to:

— multidimensional character and high complication of the phase diagram of the system Bi – Pb – Sr – Ca – Cu – O;

— possibility for the same experimental facts to be interpreted from different standpoints;

— difficulties in monitoring the evolution of the phase composition during the synthesis and, which is most important, uncertainty in the composition of the liquid phase accompanying the formation of 2223.

Of course, different models for the formation of the 2223 phase lead to different conclusions that should not be absolutized and treated as undeniable truth. At the same time, they describe different aspects of a complex phenomenon and thus may complement rather than exclude one another; in this sense, all of them are reasonable. These models can be grouped as follows:

1. The 2223 phase is formed along with 2201 as a result of disproportionation of another related superconducting phase 2212.[113, 114, 239 – 244]

2. The 2223 phase is formed due to transformation of 2212 crystals to 2223 by intercalation of extra layers comprising Ca atoms and CuO_2 into the structure of the 2212 phase.[115, 174, 211, 212, 245 – 252]

3. Most researchers (Refs 36, 69, 116 – 120, 204, 223 – 225, 237, 253 – 289) believe that 2223 is synthesized involving the liquid phase which is formed in small amounts on heat treatment. Corresponding models differ in details, but common to them is the decisive role of the microquantities of the liquid phase.

4. Conclusions drawn by some authors (see Refs 17, 216, 231, 276, 282, 283, 290 – 327) about the formation mechanisms of crystalline 2223 were based on analysis of the kinetics of formation of 2223 and comparison of the results of data processing with theoretical models. Such a comparison allows one, in particular, to propose a macromechanism including the rate-limiting stages for the overall process (diffusion of reactants, surface nucleation and growth of crystallites, *etc*.).

These approaches are equally admissible, but all of them are one-sided with respect to the complex phenomenon in question. Indeed, the models bring to the forefront either chemical transformations (disproportionation reaction), or structural changes (intercalation of extra layers into the crystal lattice), or phenomenology of the reaction (nucleation and growth from the liquid phase) and its macrokinetics (limiting stage). This is due to not only the standpoints of different authors, but first of all to 'multilayered' character of the process. Strictly speaking, in considering the mechanisms of the synthesis of 2223 one should keep in mind that the formation of this phase is a multistage process involving phenomena of different nature, namely, crystallization, diffusion of reactants and chemical reactions. A comprehensive description of the synthesis requires consideraton of the mechanisms of all these phenomena. It was reported [15, 225, 288] that the formation mechanisms of the 2223 phase for different versions of synthesis (in bulk samples or tapes, with or without lead, in air or at lowered partial pressures of oxygen) differ insignificantly, only the kinetics and stability regions of phases are changed.[47, 281]

2. Mechanisms of formation of crystalline 2223

The formation of the 2223 phase includes the stage in which the crystal lattices of the starting compounds break down and the crystal lattice of the 2223 phase is formed. The mechanism of transformation of the starting compounds to crystalline 2223 is key to research in this field. It remains unknown as yet. Nevertheless, despite the variety of initial conditions and synthesis conditions, researchers agree that the formation of 2223 involves an intermediate 2212 phase. This was confirmed by many observations. Therefore, understanding the formation mechanisms of 2223 requires knowledge of how does the transformation $2212 \rightarrow 2223$ occur. Formally, one should only intercalate the 2212 structure with extra layers comprising Ca atoms and CuO_2.

In most cases, the formation of the 2223 phase is preceded by the appearance of an intermediate liquid phase, which accompanies and accelerates the synthesis of 2223.

These facts underlie two main models for the formation mechanisms of crystalline 2223 phase, namely, the mechanism of intercalation of extra layers and the dissolution – crystallization mechanism, or, in a broader sense, the nucleation and growth mechanism.[328] Each of the two models has its substantiation and it is hard to say which of them is more correct.

The intercalation model is based on the observation by HREM of individual, sometimes incompleted monolayers of the 2223 phase in the 2212 matrix.[246] These layers even can form rather highly ordered intermediate structures (4435 phase).[174] It is assumed that the formation of such structures is due to intercalation of layers comprising Ca atoms and CuO_2 through one-dimensional diffusion of calcium and cooper atoms along edge dislocations.[248, 249, 329] Researchers did observe such dislocations, but their number is limited. This suggests that intercalation is a fast process.[204, 246, 301, 306] The intercalation model is popular.[174, 210 – 212, 245 – 252, 275, 329, 330]

The model based on the dissolution – crystallization mechanism assumes the presence of a liquid phase that precedes the formation of the 2223 phase. Numerous arguments in favour of this mechanism were reported. For instance, drops migrating across the surface of 2212 or 2223 granules with the formation of terrace epitaxial layers of the 2223 phase were observed.[267] Thorough studies of changes in the surface morphology of particular regions on the surface of ceramics and the evolution of their chemical composition during the synthesis of 2223 showed [237] that the content of lead and calcium in the 2212 phase, which gradually decomposes with the formation of some amount of a liquid phase, increases, and the 2223 granules grow near the decreasing 2212 granules. Taking these facts into account, it was concluded that the formation of the 2223 phase proceeds by the dissolution – crystallization mechanism. A convincing proof of correctness of this model was obtained by high-temperature neutron diffraction in an *in situ* study of the formation of 2223 in tapes.[223, 224] It was established that immediately prior to the appearance of 2223 the overall content of crystalline phases somewhat decreases and then increases, which suggests the occurrence of melting and recrystallization. This mechanism was confirmed by the results obtained in many studies (see, *e.g*., Refs 70, 217, 218, 331, 332).

Some researchers (see Refs 212, 301, 307, 317, 318, 333 – 337) believe that both mechanisms are in operation and, depending on the reaction conditions, can either compete with each other or one of them can dominate. Most likely, both mechanisms can operate in the early

stages of synthesis. It is believed [212] that if there is no liquid or its amount is very small, the intercalation mechanism is in operation, and that an increase in the content of the liquid phase causes the dissolution–crystallization (nucleation and growth) mechanism to operate.

However, it should be noted that intergrowths of 2212 and 2223 can form not only through intercalation with layers comprising calcium atoms and CuO_2 into the crystal lattice of 2212, but also due to the formation of the 2212 monolayers in the 2223 phase in the early stages of the growth from the liquid phase. This was shown by *in situ* observation [338] synthesis of (Bi,Pb)2223/Ag tapes and the evolution of anisotropic strain in the crystal lattices of 2212 and 2223 by high-temperature synchrotron X-ray diffraction technique. It was found that strain produced by defects is higher in the 2223 rather than 2212 crystallites. In the course of synthesis, this strain decreases for 2223 and remains almost unchanged for 2212. Would intercalation occur in the 2212 phase, the strain should increase owing to an increase in the defectiveness of 2212. Since this is not the case, it was concluded that, actually, the 2212 intergrowths are formed in 2223 during the nucleation and growth of the 2223 phase rather than 2223 intergrowths in the 2212 phase. Thus, the main argument in favour of the intercalation mechanism becomes less convincing. Probably, under the synthesis regimes used (usually, the process proceeds involving a liquid) crystalline 2223 is mainly formed by the dissolution–crystallization (nucleation and growth) mechanism. This model is the most popular at present.[232]

3. The kinetics and the limiting stage of formation of the 2223 phase (macromechanism)

Many researchers who analyzed the kinetics of formation of the 2223 phase suggested that this process proceeds by the nucleation and growth mechanism. Among various models for the description of the kinetics of reactions in heterogeneous systems,[339–342] most authors (see Refs 231, 290–321) chose the Avrami model [343] because it best fits their experimental data. This model describes the nucleation and growth of a new phase for isothermal crystallization and phase transformations in alloys. Note that the Avrami model gives an essentially simplified idea of real processes.[344, 345] It was mentioned [231] that the Avrami equation was derived for simple solid-phase reactions, whereas the process under study includes a series of reactions and, in particular, a reaction involving a liquid phase. Therefore, information obtained from the kinetic data should be treated qualitative rather than quantitative.

The Avrami equation has the form

$$V(t) = 1 - \exp(-kt^n),$$

where V is the mole fraction of the new phase formed over the period of time t; k is the rate constant for the process under the given conditions; and n is a factor which is sometimes interpreted as the reaction order.

It is believed that the numerical value of the parameter n is determined by the nature and peculiar features of the transformations under study. Namely, the n value allows one to evaluate the geometry ('dimensonality') of the front of growth of nuclei and crystallites, on the limiting stages of the process, *etc*. To this end, the numerical values of n determined from the $\ln[-\ln(1-V)] - \ln t$ plots are compared with the theoretical n values corresponding to different types of the limiting stages of the process and of the geometries of the nucleation and growth.

Having analyzed the kinetics of formation of the 2223 phase, most researchrs (see Refs 45, 291–298, 306, 311, 313, 325) arrived at the conclusion that in this process one deals with two-dimensional diffsion-controlled growth of crystallites.

At the same time, there is a large scatter of n values from 0.2 (Refs 305 and 316) to 2.28 (Ref. 311). It should be noted that the n values, all other things being equal, depend on the methods of synthesis,[307, 309] reaction temperature,[276, 291, 299, 301, 304, 305, 314] nominal chemical compositions,[299] preliminary heat treatment of precursors,[317] lead content,[327] *etc*.

The n values vary with the synthesis conditions as well as in different periods of time under identical synthesis conditions. Variation with time of the rate of formation of the 2223 phase and the parameter n seems to be a consequence of the evolution of macromechanisms as a result of, *e.g*., changes in the 'dimensionality' of the growth of crystallites or a change in the limiting stage during the process. This was ignored in some publications (see, *e.g*., Refs 276, 292, 293, 297) whose authors obtained an averaged result. Clearly seen changes in the reaction order during the formation of the 2223 phase were reported (Refs 290, 299, 306, 307, 310, 313).

During the synthesis, the parameter n initially takes a small value, then significantly increases and, finally, decreases again. The initial stage corresponding to the induction period whose duration depends on the temperature and on the partial pressure of oxygen [74, 229, 235, 292, 313, 346, 347] involves nucleation of the 2223 phase. Here, one has $n = 0.3–0.4$.[317] Next, the process accelerates and the parameter n takes values in the range from 1 to 2 according to different data.[299, 306, 313, 317] This stage involves diffusion-controlled two-dimensional growth of nuclei. Then, the n value decreases on the average to 0.5.[313, 314] This fact, as well as the slower formation of the 2223 phase was associated [299, 306, 313, 314] with retardation of the two-dimensional growth as the growing plate-like granules collide with one another and thicken with slower nucleation.

A feasible case involves analysis of the kinetics of the process in the mixed (or transient) regime.[299] Here, the experimental n values can to some extent vary depending on the contributions of the factors controlling the overall process.

Yet another kinetic parameter is the apparent activation energy of the formation of the 2223 phase.[291–293, 297, 299, 305, 314, 348, 349] It is related to the rate constant for the process k (determined from the expressions listed above) by the Arrhenius equation

$$k = k_0 \exp\left(\frac{E}{RT}\right),$$

where k_0 is the pre-exponent, E is the activation energy, R is the universal gas constant and T is absolute temperature.

For such a complex process as the formation of the 2223 phase, E depends on many parameters, being the apparent activation energy. Depending on the experimental conditions, it varies over a wide range from 460 (Ref. 292) to 2900 kJ mol^{-1} (Ref. 297), and its numerical values are interesting only for comparison. In this relation, quite

significant are the E values at different temperatures.[292, 293, 297, 305, 314] At lower temperatures (no melting), the apparent activation energy is high and lies in the range 1500–2900 kJ mol^{-1} according to different authors.[292, 293, 297, 305] It is believed [101, 102] that in this case the rate of the overall process is controlled by the solid-state reactions. At higher temperatures, in the presence of liquid phase, the apparent activation energy considerably decreases and lies between 460 and 1000 kJ mol^{-1} (Refs 292, 293, 297, 305). This gives grounds to assume a gradual transition from the kinetic regime to the diffusion-controlled one. At the same time, it was reported [292, 297] that even when melting occurs, the apparent activation energies are too high to characterize the pure diffusion-controlled regime. Probably, the process proceeds in a mixed regime and includes series of chemical reactions and diffusion stages.[292] High thermal sensitivity of the kinetics of the process can be explained by rather high apparent activation energies of the formation of the 2223 phase.[297]

The results of a study of the effect of various factors on the apparent activation energy of formation of the 2223 phase [349] show why the scatter of data obtained by different authors is so large. It was found that the initial conditions are of crucial importance. Also, it was established that:

— variation of the nominal chemical composition even in narrow limits leads to a significant change in the activation energy;

— the parameter E depends on the average precursor grain size;

— slower heating, longer annealing time and higher precursor annealing temperatures cause the E values to decrease.

Interestingly, competing reactions of formation of non-superconducting alkaline-earth cuprates are characterized by lower apparent activation energies [74, 324] and, therefore, the accompanying non-superconducting phases are formed more readily than 2223.

4. Reaction mechanism of formation of the 2223 phase

Perhaps, the most debatable issues are which chemical reactions, and in which order, result in the formation of the 2223 phase, as well as how the intermediate liquid phase favours the formation of the 2223 phase (the nature of this liquid phase still remains unclear).

A general regularity of the reaction process consists in the formation of all three superconducting phases; they are formed with an increase in temperature in the order

$$2201 \longrightarrow 2212 \longrightarrow 2223.$$

These phases almost always coexist during the synthesis of 2223 (see Refs 128, 266, 273, 306, 325, 350, 351) in larger or smaller amounts. Remind that the process results in not only superconducting, but also non-superconducting secondary phases, such as $(Ca,Sr)_2PbO_4$, $Pb_3Sr_{2.5}Bi_{0.5}Ca_2.CuO_x$ (3321), $(Ca,Sr)CuO_2$, $(Ca,Sr)_2CuO_3$, $(Sr,Ca)_{14}Cu_{24}O_{41}$, (Sr,Ca)O, CuO, *etc*. Their amounts depend on the initial conditions and on the synthesis conditions.[74, 215, 328] Of course, the variety of compounds formed in the synthesis of 2223 implies the occurrence of a number of competitive and successive reactions.

Numerous attempts to establish the formation mechanism of the 2223 phase have been undertaken and different opinions were reported. Now we will consider a number of reaction schemes. It was assumed [113] that the lead-free 2223 phase is formed along with the 2201 phase through disproportionation of the 2212 phase. A more detailed scheme was proposed for the process with participation of lead.[114] It is believed that in this case the 2201 phase formed as a result of disproportionation of 2212 phase reacts with the Pb–Ca–Cu–O melt to give a new melt Pb–Bi–Sr–Ca–Cu–O from which the 2212 phase is formed and then again undergoes disproportionation. The appearance of the 2223 phase was observed [352] at a temperature close to the melting point of the 2212 phase of composition $Bi_2Sr_{1.5}.Ca_{1.5}Cu_2O_{8+\delta}$, which seems to undergo a peritectic decomposition to a liquid and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$. A more complex reaction scheme [272] assumes that Ca_2PbO_4 undergoes incongruent melting on heating with release of CaO; the liquid reacts with CuO, CaO and 2212 to give a liquid of a new composition from which the 2201 phase precipitates and then reacts with Ca^{2+} and Cu^{2+} ions present in the liquid solution to afford the 2223 phase. Note that an argument against this reaction scheme consists in that calcium plumbate is stable to temperatures that much exceed the temperature at which the 2223 phase is synthesized,[237] whereas the decomposition of Ca_2PbO_4 may be a consequence of its high reactivity. Indeed, it was shown that Ca_2PbO_4 readily reacts with the 2201 phase at 825 °C to give a liquid, which seems to interact with 2212 to form the 2223 phase.[270]

Subsequent intensive investigatons of the evolution of the phase composition and the chemical composition of the phases revealed a number of important details of the overall process. In a series of studies, Grivel *et al*.[36, 237, 277, 288, 308] showed that the formation of 2223 is preceded by the interactions between Pb-containing secondary compounds with the 2212 phase, which lead to enrichment of 2212 with lead and calcium (only calcium for the lead-free system). A simplified description of such interactions is as follows:

$$Ca_2PbO_4 + Bi_2Sr_2CaCu_2O_8 \longrightarrow \longrightarrow Bi_{2-x}Pb_xSr_{2-y}Ca_{1+y}Cu_2O_8 + CaO, \quad (1)$$

$$CaO + CuO \longrightarrow \text{alkaline-earth cuprates.} \quad (2)$$

This transformation of the 2212 phase was confirmed by other studies.[33, 216, 223] It represents a kind of 'preparatory stage' facilitating subsequent formation of the 2223 phase owing to lower stability and incongruent melting point of the (Bi,Pb)2212 phase compared to the Bi2212 phase of idealized stoichiometry [44, 144, 277, 353] (see Figs 4 and 5).

According to a scheme [36, 237] supported by the results of other studies,[216, 218, 233, 328] the next step is partial decomposition of the (Bi,Pb)2212 phase to a liquid phase and alkaline-earth cuprates whose chemical compositions depend on the process conditions.[144, 218] In the final step, alkaline-earth cuprates are again dissolved in the liquid phase enriched with lead and bismuth and, as the composition of the liquid becomes equal to the corresponding stoichiometry, nucleation and growth of the 2223 phase begins.

However, this scheme gives no answer to the main queston, *viz*., what is the reaction pathway for the final step of the interacton between the liquid and cuprates, *i.e*., it is unclear which reaction (or reactions) is responsible for the formation of the 2223 phase.

This is not surprising because details of the process, such as the composition of the liquid and the changes in its composition during the synthesis, are left out of consider-

ation even when modern methods of *in situ* investigations using synchrotron radiation are involved. In addition, the formation of the 2223 phase may be accompanied by the appearance of different types of liquids.[78, 354] In locally inhomogeneous mixtures, transient liquids of different compositions are formed. The case of slow kinetics of formation of the solid phase is characterized by the appearance of a metastable liquid phase with a lower melting point and different composition compared to the equilibrium liquid phase prior to the formation of the solid phase. In addition, the chemical composition of liquids is determined from the composition of the solidified melt; here, one should take account of the errors due to possible changes in the composition in the course of cooling. The aforesaid indicates that the liquid introduces the largest uncertainty among the reactants participating in the formation of the 2223 phase. This significantly complicates elucidation of the reaction mechanism; nevertheless, we will try to solve the problem based on analysis of available publications.

To construct a correct scheme of possible reactions of formation of the 2223 phase with participation of liquid phase, we will take into account the following experimental results obtained in different studies.

1. The results of quantification of the chemical composition of liquids after annealing of the samples obtained in the synthesis of 2223 show a large scatter. According to different authors,[28, 44, 233, 235, 286, 292, 344] the elemental composition of the solidified liquids are described as $Bi_aPb_bSr_cCa_dCuO_n$ ($a = 1.3-2.7$, $b = 0.4-1.7$, $c = 0.5-2.0$, $d = 0.4-2.3$). It was also reported[246, 313, 355] that on cooling of samples the liquid crystallizes as a 2201 phase in which a large proportion of strontium atoms is replaced by calcium atoms. The compositions of the annealed liquids are close to those of modifications of the 2201 phase, namely, the lead- and calcium-containing Raveau phases of general formula $(Bi,Pb)_{2.2+x}Sr_{1.8-x-y}Ca_yCu_{1\pm w}O_z$ ($0 < x < 0.5$).[134] Incongruent melting of Bi2212, (Bi,Pb)2212 and (Bi,Pb)2223 samples produces liquids whose compositions are intermediate between those of 2201 and 2212; they crystallize as the 2201 phase.[123, 144] Compositionally, these liquids are very close to 2201 solid solutions[123] that form a liquid phase coexisting in equilibrium with 2212 and 2223 in the system Bi–Sr–Ca–Cu–O.[135] We believe this gives grounds to consider the calcium-enriched 2201 phase as the main component of solution in the melt constituting the liquid phase.

2. The formation of liquid phase in the synthesis of 2223 was detected[44] in two temperature intervals. In the lower-temperature region, the appearance of a liquid is a result of the interaction between Ca_2PbO_4 and $Bi_2Sr_2CuO_6$ resulting in Ca-containing 2201 solid solutions (Refs 33, 270) and their subsequent melting. In the higher-temperature region, the appearance of a liquid follows partial incongruent melting of 2212 (Refs 44, 144–147).

3. The melting points of the 2201 and 2212 solid solutions depend on the content of lead and calcium in the systems and considerably decrease at high concentrations of these elements (especially if the solid solutions contain the limiting amounts of both elements[144]). A key issue to our consideration is the decrease in the melting point with an increase in the calcium content in the solid solutions $(Bi,Pb)_2Sr_{2-x}Ca_{1+x}Cu_2O_{8+\delta}$ (Refs 144, 150–153) and $(Bi,Pb)_2Sr_{2-x}Ca_xCuO_{6+\delta}$ (Refs 137 and 138). According to Ref. 138, the melting point of 2201 phase in air decreases from 910 °C for $Bi_2Sr_2CuO_{6+\delta}$ to 820 °C for $Bi_2SrCaCuO_{6+\delta}$ (see Fig. 3).

4. As mentioned above, the formation of the 2223 phase is preceded by enrichment of intermediate 2212 phase with lead and calcium. Accordng to EDS analysis, the Ca : Sr ratio in 2212 immediately prior to the formation of 2223 may be as high as 0.7–0.8,[134, 233] much exceeding a value of 0.5 corresponding to the 2212 phase with idealized stoichiometry. For the liquid phase, this ratio is even higher; taking into account inhomogeneous character of the mixture, it depends on the spatial region where the liquid is confined.[134, 233] For the 2223 phase, usually one has Ca : Sr $\leqslant$ 1; this is close to the idealized value.[270, 356]

As the formation of 2223 proceeds, the average amount of calcium in 2212 gradually decreases;[33, 134, 216] possible reasons are as follows:

— too short lifetimes of calcium-enriched 2212 granules;

— reactions result in new 2212 granules with lower content of calcium owing to 'consumption' of this element for building the 2223 phase.

The amount of calcium in the cuprates $(Ca,Sr)_2CuO_3$ and $(Ca,Sr)_{14}Cu_{24}O_{41}$ decreases simultaneously (especially in the latter system; this may indicate either a faster diffsion of calcium from the cuprate or a faster dissolution of $(Ca,Sr)_{14}Cu_{24}O_{41}$ granules with higher calcium content[134]).

5. In the synthesis of 2223, the appearance of liquid phase is mainly due to incongruent melting of 2212.[231] However, the volume of the liquid phase is much smaller than could be expected taking into account the proportion of the 2212 phase that decomposed after a particular period of time.[231] This indicates that the liquid is consumed in the formation of the 2223 phase, being a reactant rather than a medium necessary to dissolve calcium and copper and to transfer them to the precipitation zone.

6. According to SEM observations of the microstructure, the 2223 phase is mainly formed at the liquid/2212 interface and the reaction propagates toward the liquid.[231] HREM studies showed that the regions of the 2212 and 2223 phases in the annealed samples are separated by a thin layer of the 2201 phase.[241]

7. In the case of incongruent melting of 2212, the equilibrium product of the first peritectic reaction is cuprate $(Sr,Ca)CuO_2$; under nonequilibrium conditions, either $(Sr,Ca)_2CuO_3$ or $(Sr,Ca)_{14}Cu_{24}O_{41}$ are formed in addition.[144] These cuprates are also present among reaction products in the synthesis of the 2223 phase.[74, 216, 220, 223, 357] It was reported[233] that they are formed and decompose in the formation of 2223 simultaneously. The same processes (formation and decomposition) are also characteristic of the 2212 phase. An *in situ* 3D XRD-microscopy (see Section III.1) study[220] of the behaviour of microgranules in the synthesis of 2223 showed that the transformation of 2212 to 2223 is a dynamic process involving the formation, decomposition and re-formation of individual microgranules of the 2212 phase during the synthesis of 2223. This is also confirmed by the results of a study[358] on the formation of 2223 where not only the decomposition of 2212, but also clear indications of its local formation near the alkaline-earth cuprates were observed. The decomposition and formation of the 2212 phase and a similar behaviour of alkaline-earth cuprates may be a consequence of reversibility of the reactions and/or a result of several competing

reactions and indicates an oscillatory (cyclic) character of the process.

8. *In situ* studies of the evolution of the phase composition during the synthesis of 2223/Ag tapes by synchrotron X-ray diffraction showed that as the content of the 2223 phase increases the amount of the 2212 phase decreases and the content of cuprates decreases to almost the same extent. This indicates that 2212 and cuprates are the main participants of the reactions of formation of 2223.[216] However, the overall process is more complex than simple reaction of 2212 with cuprates (see, *e.g.*, Ref. 359). Based on the results of synchrotron X-ray diffraction of the evolution of the phase composition on temperature cycling, it was concluded [218, 315] that the formation of 2223 involves at least two types of processes:

— fast reversible reaction between 2212 on the one hand and the liquid and alkaline-earth cuprate on the other hand;

— slow reaction of formation of 2223; reactants for this process are delivered from 2212, the liquid and alkaline-earth cuprates.

This conclusion was confirmed by the results of analysis of peritectic decomposition of calcium-enriched crystals of 2212.[360, 361] *In situ* observations with a high-temperature optical microscope showed that incongruent melting is accompanied by the appearance of $(Sr,Ca)CuO_2$ whiskers (fast reaction) followed by slow formation of 2223 crystals.[360, 361]

The aforesaid allows one to propose the following simplified scheme of the final stages of the process. The formation of the 2223 phase is preceded by the formation of lead- and calcium-enriched 2201 and 2212 solid solutions in type-(1) reactions. The liquid is formed, first, due to melting of the calcium- and lead-rich 2201 solid solutions [135, 138, 270] and, second, as a result of peritectic decomposition of 2212 to a liquid and alkaline-earth cuprates.[36, 44, 144, 237] Taking into account the fact that the latter process is fast and reversible,[218, 315] having restricted ourselves (for simplicity) to one cuprate phase $(Sr,Ca)CuO_2$ and assuming that the liquid represents a melt of the calcium-enriched 2201 phase, the decomposition of 2212 can be described by the following equation:

$$(Bi,Pb)_2Sr_{2-x}Ca_{1+x}Cu_2O_8\ (\text{solid}) \rightleftharpoons \quad (3)$$
$$\rightleftharpoons (Bi,Pb)_2Sr_{2-2x}Ca_{2x}CuO_6\ (\text{liquid}) + Sr_xCa_{1-x}CuO_2\ (\text{solid}).$$

Since this reaction is reversible and the equilibrium can be shifted towards the formation of 2212 under corresponding conditions, we will re-write the equation of this reaction in the reverse order for the sake of convenience

$$(Bi,Pb)_2Sr_{2-2x}Ca_{2x}CuO_6\ (\text{liquid}) + Sr_xCa_{1-x}CuO_2\ (\text{solid}) \rightleftharpoons \quad (3a)$$
$$\rightleftharpoons (Bi,Pb)_2Sr_{2-x}Ca_{1+x}Cu_2O_8\ (\text{solid}).$$

Yet another possible route of peritectic decomposition of the calcium-rich 2212 phase is the decomposition to a liquid and the 2223 phase, as was observed experimentally.[352] Assuming that in this case the composition of the liquid phase is the same as above, the peritectic reaction can be written in the form:

$$2\,(Bi,Pb)_2Sr_{2-x}Ca_{1+x}Cu_2O_8\ (\text{solid}) \rightleftharpoons \quad (4)$$
$$\rightleftharpoons (Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}\ (\text{solid}) + (Bi,Pb)_2Sr_{2-2x}Ca_{2x}CuO_6\ (\text{liquid}).$$

It seems likely that it is this reaction that eventually results in the 2223 phase (this is at least the most probable reaction).

Reaction (4) is a joint reaction. It is much slower than reaction (3), being rate-limiting.[218, 315, 360, 361] The overall brutto process involves reactions (3a) and (4) and can be described as follows:

$$(Bi,Pb)_2Sr_{2-x}Ca_{1+x}Cu_2O_8 + Sr_xCa_{1-x}CuO_2 \longrightarrow \quad (5)$$
$$\longrightarrow (Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}.$$

It cannot be ruled out that the disproportionation reaction can also occur in the liquid phase as a result of disproportionation of the 2212 phase dissolved in melt solution. In any case, one deals with continuous cyclic changes in the composition of the liquid. Additional liquid formed in the disproportionation of 2212 is used to dissolve a new portion of cuprates and favours transfer of calcium and copper ions to the precipitation zone. A simplified scheme of formation of the 2223 phase is as follows:

$$2201\ (\text{liquid}) + (Ca,Sr)\text{-cuprates}\ (\text{solid}) \longrightarrow 2212\ (\text{solid}) \longrightarrow \quad (6)$$
$$\longrightarrow 2223\ (\text{solid}) + 2201\ (\text{liquid}).$$

And cycle after cycle.

In this case, the driving force of the process is the chemical potential difference between calcium and copper ions at cuprate/liquid interfaces. The liquid will remain in a quasi-equilibrium (or metastable) state until cessation of mass transfer. Consumption of reactants due to, in particular, gradual depletion of the sources of calcium and copper will cause the process to slow down and eventually stop at the moment when calcium and copper ions in the cuprates and in the liquid will have equal chemical potentials and the system will be in equilibrium.

To simplify the description of the real process of formation of the 2223 phase, we assumed that the liquid represents a melt of the 2201 phase which is probably a component of a melt solution. In addition, only the cuprate $(Sr,Ca)CuO_2$ was taken into account, although $(Sr,Ca)_2CuO_3$ and $(Sr,Ca)_{14}Cu_{24}O_{41}$ can also participate in the process. Nevertheless, this model of the reaction process is useful because it treats the liquid not only as a medium for delivery of components to the reaction zone where new portions of 2223 are formed, but also as active reactant which is continuously consumed and renewed. This scheme of the mechanism of formation of the 2223 phase was reported elsewhere.[362]

V. Effect of the phase formation conditions on the transport properties of (Bi,Pb)2223/Ag tapes

The superconducting 2223 phase in the form of tapes is considered as one of the most promising HTSC for industrial applications.[226] However, there is a number of serious engineering problems concerning the establishment of conditions for fabrication of a material with well-reproducible properties including first of all a high current-carrying capability.

Information on the phase equilibria in the system Bi – Pb – Sr – Ca – Cu – O at different temperatures and partial pressures of oxygen (see a review [121]) is very useful for the primary choice of the synthesis conditions of 2223. However, data on the equilibrium states of the existing

phases are insufficient. One should have information on the evolution of phases during the fabrication of the material based on 2223 because peculiarities of phase formation in different steps of production process determine the microstructure and superconducting properties of the final product. The scope of problems concerning the influence of fabrication conditions on the functional properties of materials is wide. We want to show how can the reaction kinetics and specific features of phase formation affect the transport properties of composite tapes in different process stages.

Any operation related to the synthesis of 2223, from preliminary procedures to cooling of the final material, can strongly affect the superconducting properties of items. Fabrication of 2223/Ag tapes showed that the kinetics of formation of the 2223 phase, as well as the microstructure and transport properties of tapes depend strongly on the methods for and quality of preparation of precursors.[62–65, 69, 80, 88, 212, 314, 347, 363–369] A reason is that different methods for preparation of precursors (solid-state synthesis,[67, 301, 370] sol–gel technique,[371, 372] aerosol pyrolysis,[89, 373] spray drying,[374] cryochemical technology,[375, 376] chemical codeposition from solution,[377, 378] *etc.*) lead to different sets and spatial arrangement of phases. In addition to the possibility for precursors to have different phase compositions, they may exhibit different reactivities depending on the prehistory. The particle size and distribution in a precursor have a pronounced effect on its reactivity, the rate of formation and microstructure of the 2223 phase and, eventually, on the properties of tapes.[51, 65, 347, 379–385]

Experience has shown that the use of fine-grained rather than coarse-grained powder mixture can improve the transport properties, *viz.*, the more fine-grained the precursor the higher its reactivity owing to the more developed surface, larger surface area of contacts between components and shorter diffusion pathways. A differential thermal analysis study [383] showed that the smaller the particle size in the starting mixture for the synthesis of 2223 the lower the temperatures of the onset of partial melting. At first glance, these conditions are more appropriate for the formation of the 2223 phase. But the situation is not so simple as it seems. The particle size of the precursor affects not only the 2223 phase, but also the formation and distribution of secondary phases and, therefore, the quality of intergranular bonds in the superconductor, which determine the transport current.[65] It was established that when using too fine-grained precursor powder, the formation of 2223 slows down and numerous accompanying phases are formed [383] and reduce the transport current. It is believed that this behaviour of the too fine-grained mixture can be due to the loss of crystallinity (amorphization) of the intermediate phases, *e.g.*, 2212, which play an important role in the formation of 2223.[381, 383] Yet another reason is that the formation of secondary phases requires a lower activation energy [74, 324] and these phases, being kinetically more preferable in the early stage of synthesis, probably form large particles which preclude the formation of the 2223 phase.[367]

Detailed studies [383] of the effect of the particle size of a precursor prepared by sol–gel technique and ground over different periods of time on the evolution of the phase composition, microstructure and the transport properties of 2223/Ag tapes showed that, first, there is a range of optimum particles size, which is most appropriate for the formation of the 2223 phase with the lowest amount of impurity phases and the best transport properties. Second, as the precursor grain size decreases, the optimum temperature for the fabrication of tapes decreases. Figure 8 presents the plots of the critical current density *vs.* temperature of synthesis of tapes fabricated from powders with different average particle size (l) of precursors [different grinding time (t)]. As can be seen, the critical current density j_c depends strongly on both the particle size and the temperature of synthesis. The highest current-carrying capability was obtained for the samples fabricated from powders with an average particle size of 3–4 μm at 831 °C. These samples are also characterized by the lowest content of impurity phases and by the greatest stability of j_c against degradation in a magnetic field. If the precursor particle size was less than 2.5 μm, the current-carrying capability of tapes decreased drastically [383] (see Fig. 8).

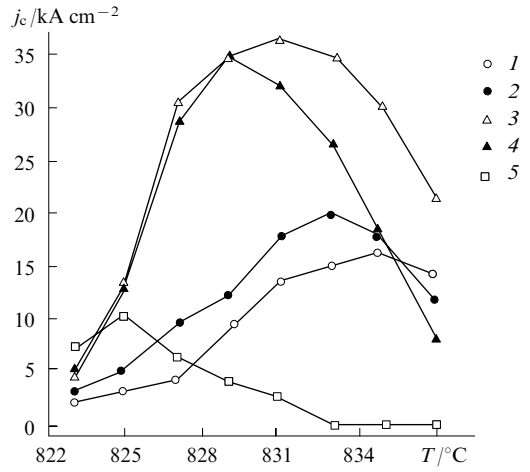


Figure 8. Critical current density of tapes of nominal composition $Bi_{1.8}Pb_{0.4}Sr_2Ca_{2.2}Cu_{3.1}O_z$ plotted *vs.* temperature of synthesis in air over a period of 200 h for samples with different average size of precursor particles.[383]

Curve	*1*	*2*	*3*	*4*	*5*
l/μm	6.5	5.1	3.2	2.5	1.8
t/h	0.25	0.5	1.0	2.0	4.0

Most probably, particular numerical values of these parameters will depend on methods of preparation of precursors and on the synthesis conditions, but general regularities of their changes will be the same. The results of studies [380, 382] confirmed the existence of an optimum particle size for precursors for the preparation of tapes with the highest current-carrying capability. Correlations between the optimum temperature of synthesis and the particle size were also confirmed.[381, 382] Poor standardization of preliminary procedures can be a reason for poor reproducibility of the properties of 2223/Ag tapes; therefore, relevant (including granulometric) control of precursors is required.

The heat treatment steps are of paramount importance for fabrication of tapes. This concerns not only the final, but also the primary (preliminary) heat treatment stage in which the 2212 phase is mainly transformed to the 2223 phase.[44] A study [324] of the evolution of phases in this stage revealed a significant spatial variation of the microstructure and phase composition due to noticeable inhomogeneity of the reaction kinetics and preferred formation of the 2223 phase near Ag. Depending on the primary heat treatment

conditions, the number and type of non-superconducting compounds vary over a wide range.[229] After this stage, the tapes contain to 20% of non-superconducting phases one to a few micrometres in size.[230] These phases are characterized by higher hardness compared to 2223; this causes breakdown of 2223 granules under subsequent rolling and cleavage of bonds between them.[386] A large proportion of defects thus produced remains unhealed after subsequent heat treatment and deteriorates the properties of tapes.[229] Thus, the first heat treatment is a very important step which to a great extent determines the final properties of tapes. Therefore, one should minimize the content and particle size of impurity phases by thoroughly choosing the conditions for primary annealing or by conducting this step under conditions that vary in a specified manner.

Main non-superconducting impurities present in tapes after primary heat treatment include $(Ca,Sr)_2CuO_3$, $(Ca,Sr)_{14}Cu_{24}O_{41}$ and CuO.[229] The amount of impurities and their ratios depend on the composition of precursors, annealing temperature, partial pressure of oxygen and duration of heat treatment. Systematic studies of the effect of the partial pressure of oxygen and the annealing temperature on the kinetics of formation of the 2223 phase, on the content and size of impurities and on the microstructure of 2223 granules revealed the following:

— The highest rate of formation of the 2223 phase, the lowest total amount of impurity phases and the smallest particle size of the impurity phases are attained at (7.5% O_2 + inert gas) and 825 °C;[47]

— the best structural ordering of the 2223 granules and the lowest content of $(Ca,Sr)_2CuO_3$ and CuO are observed at (21% O_2 + inert gas) and 835 °C;[47, 74, 268, 293]

— the lowest content of $(Ca,Sr)_{14}Cu_{24}O_{41}$ is formed at (4.0% O_2 + inert gas) and 815 °C.[74]

Taking into account these results, a procedure for primary heat treatment was proposed[230] and conducted successively at oxygen contents and temperatures specified above under continuous annealing conditions. The made it possible to significantly reduce the content and size of impurity particles compared to simple annealing and, as a consequence, to improve the critical current density by 20 %.[228, 230]

The final cooling is an important technological step and the corresponding conditions have strong effect on the transport properties of a material. The cooling regime specifies the final set of impurity phases whose content, type, as well as the degree of structural ordering of granules, quality of interconnection between them and the pinning energy determine the current-carrying capability of finished items. Experience shows that making use of a slow cooling,[52, 94, 96, 102, 387, 388] so-called stepwise (at different temperatures) sintering[75, 289, 389–397] or low-temperature annealing[108, 398–406] rather than conventional spontaneous cooling allows the critical current density to be improved by 150%–200%.[398] These techniques differ insignificantly. They are necessary to provide the corresponding temperature and sufficiently long time to convert poisoning impurities to more admissible compounds.

The most abundant impurities deteriorating the superconducting properties of finished tapes include inclusions of the 2212,[108, 210, 400, 401, 407] 2201,[101, 387–396, 408, 409] and 3321 phases[410, 411] (for more details on 3321, see Ref. 121). Among them, the key role in limitation of the intergranular current is played by the 2201 phase.[101, 396] Small amounts of this phase accompany the formation of the 2223 phase.[214, 223] The content of 2201 increases with the temperature of synthesis.[256, 289] But the main source of this phase is the liquid always present between superconducting granules after completion of the synthesis of 2223. The content of the liquid is rather high and may exceed 9% by mass.[402, 403] Rapid cooling causes small pools of the liquid to transform to amorphous aggregates[250, 412–414] or crystallize in the form of 2201.[75, 214, 217, 246, 289, 313, 355, 392] The amorphous phase is an insulator, while the 2201 phase of stoichiometric composition is a semiconductor.[409] These phases segregated on the boundaries of 2223 granules block the current or form weak Josephson junctions which significantly reduce j_c. The situation can be improved by transformation of the 2201 phase to other compounds using particular cooling regimes.[101, 289, 387–396]

Studies on the composition of phases formed under different regimes of cooling revealed two temperature intervals corresponding to different products of reactions of transformation of the liquid phase.[289, 402] The main result of annealing at temperatures above 790 °C is the transformation of the 2201 phase to 2212 (Refs 223, 224, 387–389, 391, 393, 394). Annealing at temperatures below 790 °C is aimed to form the 3321 phase and to reduce the content of 2212.[400, 401, 405, 406] It is noteworthy that not only j_c, but also T_c increases under prolonged (100–1000 h) low-temperature (< 790 °C) annealing because changes in the phase composition are accompanied by modification of the 2223 phase, *viz*., the content of lead decreases, the lattice constant c increases and the concentrations of oxygen and charge carriers in this phase are optimized, thus leading to an increase in T_c.[415, 416] The influence of the chemical composition and crystal structure of bismuth-based HTSC on T_c and other parameters has been considered in detail in a review.[121]

However, it should be noted that information on the chemical reactions occurring on cooling of tapes is contradictory even for the same temperature interval. It was reported[387, 391, 393, 394]) that at annealing temperatures above 790 °C, the decrease in the content of 2201 is accompanied by an increase in the content of 2212 and a decrease in the content of 2223. Probably, in such cases the comproportionation reaction [reaction (4), reverse reaction] manifests itself; as a result, 2201 (from liquid) and 2223 are transformed to 2212. Other competing reactions can also dominate. For instance, *in situ* observations of the evolution of the phase composition under slow cooling conditions showed[223, 224] that in the early stage of cooling, at rather high temperatures (above 820 °C), the content of 2223 still increased (this probably indicated incompleteness of the formation of this phase), but further cooling had no effect on the amount of this phase. The content of 2212 increased while the amounts of 2201 and cuprates decreased from the very beginning of cooling. These observations can probably be explained by domination of the interaction between the liquid phase and cuprates [reaction (3a)]. Under slow cooling, the content of 2223 can also vary in another manner, *viz*., increase and then decrease with temperature, as was observed experimentally[95, 216, 217, 388] (see cooling in Fig. 6); this indicates a change in type of the reaction.

These differences are probably due to different compositions of reactants that were formed prior to cooling, because the reaction kinetics and their contributions to the overall process depend not only on temperature, but also on

the reactant concentrations. It was experimentally established that the phase transformations and the efficiency of low-temperature annealing depend on the chemical composition of the starting mixture,[398] on the partial pressure of oxygen,[406] on the duration of the main synthesis[399] and, undoubtedly, on the duration of annealing.[401,405] This again demonstrates the need for well-defined control of a large number of process parameters.

At present, researchers continue the search for conditions for maximum improvement of the superconducting properties of (Bi,Pb)2223/Ag tapes.[416] Clearly, one can hardly climb to success ignoring the chemical properties, specific features of formation and chemical reactions of the 2223 phase with the accompanying compounds. A path to success passes through investigations and understanding of the mechanisms of processes constituting a complex process of fabrication of items from materials based on the 2223 phase.

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