Representations about nature of processes occurring in the material at different stages of Bi(Pb)–Sr–Ca–Cu–O ceramic manufacture

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The state of material and processes occurring in material during synthesis of bismuth HTSC ceramic are analyzed in this article. Special attention is given to the mechanism of $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) phase synthesis and processes resulting in its intensification, as well as to the processes responsible for superconducting grain contacts formation. A scheme of structural and phase transformation at sintering is proposed. The known mechanisms of 2223 phase formation are included in the proposed scheme as its stages which can occur with various degree of probability depending on features of concrete technology of bismuth ceramic's synthesis. Numerous experimental results are explained by proposed combination of processes that occur during synthesis of bismuth ceramic.
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1. Introduction

In [1, 2] are shown technological investigations of intensification of Bi(Pb)–Sr–Ca–Cu–O superconducting ceramic, and conclusions about the phase composition and structure of ceramic are made on the basis of material's properties definition. In this work, technology—introduced in [1]—is surveyed through points of view on processes occurring in the material at the time of synthesis. The significance of this study is in the fact that the investigations of spray frozen, freeze drying synthesis of the precursor for bismuth ceramic, as well as introduction of the 2223 phase additive is not described well enough in the literature; and the mechanism of the 2223 phase synthesis is a vexed question and is actively discussed.

Fig. 1 shows a general view of the technological scheme of bismuth ceramic's manufacture used for investigation in [1].

2. Results and discussion

2.1. Spray frozen, freeze drying synthesis of saline product

Basic processes occurring at this stage:

- mixing of metal components of ceramics as water solutions of nitrates;
- dispergation of a solution;

- freezing of the sprayed drips;
- water removal from cryogranules by sublimation.

According to experimental results and data of other contributors (for example, in [3] is given a comprehensive picture of processes that occur in spray frozen and freeze drying synthesis using different salting liquids for a broad spectrum of manufactured materials), presented stage of bismuth HTSC-ceramic's synthesis can be described as follows.

The high level of mixing of components in a diluted solution in a large degree is maintained by the subsequent processes—freezing of dispergated solution with high speed (cryocrystallization) and cryogranules dehumidification by sublimation, which allows to avoid global melting of material.

As is informed by [3], the crystallization of a salting liquid with speed 5–10^4 K/min (this band includes cooling rates achievable in substantial conditions of freezing of a dispergated jet in volume of liquid nitrogen) for the majority of used water solutions results in formation cryogranules containing crystalline (practically pure ice) and glass-like (enriched by salt as contrasted to original composition of salting liquid) phase.

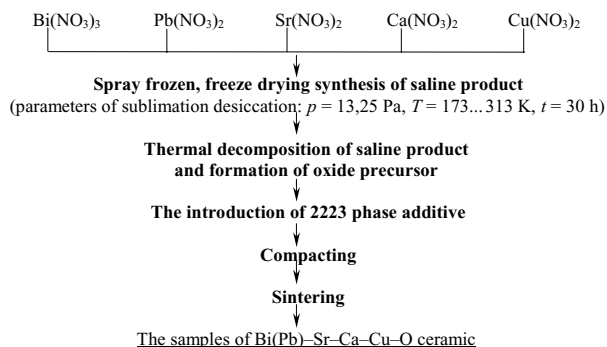Obtained by sublimation of cryogranules, saline powder of the bismuth ceramics precursor represents the

$Bi(NO_3)_3$ $Pb(NO_3)_2$ $Sr(NO_3)_2$ $Ca(NO_3)_2$ $Cu(NO_3)_2$

↓

Spray frozen, freeze drying synthesis of saline product
(parameters of sublimation desiccation: $p = 13,25$ Pa, $T = 173...313$ K, $t = 30$ h)

↓

**Thermal decomposition of saline product
and formation of oxide precursor**

↓

The introduction of 2223 phase additive

↓

Compacting

↓

Sintering

↓

The samples of Bi(Pb)–Sr–Ca–Cu–O ceramic

Figure 1 The generalized technological scheme of manufacture of samples from superconducting Bi(Pb)–Sr–Ca–Cu–O ceramic.

porous granules of light blue color (defined by the copper nitrate), that consist from disperse particles. Main components of saline product granules' microstructure of spray frozen and freeze drying dehydration are crystal grains about 0,1 μm in size (this size, apparently, can vary depending on performance of the solution and condition of the sublimation dehydration), joined among themselves in aggregates. Crystallization stage created strong links that retain separate saline crystals in one. These links aggregate during the subsequent heat treatments in a stationary layer; however granules grinded to the size 30–40 μm at hand-operated grind in a mortar do not require considerable efforts.

The authors of [3] specify two stages of sublimation process. On the incipient stage of sublimational dehydration local rize of the vapour compression results in infringement of saline skeleton's walls integrity and formation of conferred system of pores ensuring driving the vapour back from microareas of sublimation. The terminating stage of sublimational dehydration represents sequential chemical process of crystallohydrates' dehydration. Transformation of one crystallohydrate into another, with smaller water content happens through X-ray amorphous phase. A fracture of crystallohydrate's large crystal grains is produced by considerable diminution of molar volume, and X-ray amorphous particles of obtained crystallohydrate again derivate rather large crystals by relative moving and diffusive accretion of identical crystal planes.

Thus, spray frozen and freeze drying synthesis of a precursor result in formation of saline granules with highly developed interior surface. Processes of formation, fracture and upgrowth of salt-based crystalline structures accompany the elimination of water from cryogranules. However these are not global processes and they do not result in essential modification of saline skeleton's structure (except formation of holes that ensure through steam transmission of granules). Preservation of structure with highly developed interior surface (which is maintained and after stage of hightemperature decomposition) is, apparently, not only connected with relatively low diffusive activity of saline granule's components (temperatures of sublimation are low enough), but also with mentioned

earlier strong inter-crystalline links. Diffusive activity of atoms in saline precursor's granules of bismuth ceramic can be proved by formation of a small amount of visually apparent pores; however it is necessary to understand that the reason for their formation is the pressure of gas and water vapor in decomposed saline product.

Preservation of the initial shape of granules and developed interior surface of saline product proves absence of global melting of material. Non-rational conditions of sublimational dehydration form a long-term present liquid phase, and the exterior of saline product range from slightly melted accrete granules to dried equal layer of the solution.

Most important for the subsequent synthesis of bismuth superconducting ceramic is the fact that the saline product obtained after sublimational dehydration consists of crystalline phases. Thus, homogeneity of this multicomponent system is somewhat disturbed at the first stage of synthesis. The XRD analyze shows that the formed crystal grains are not X-ray amorphous; the product contains crystalline phases of simple and double nitrates of Ca, Sr, Pb of variable composition, crystallohydrate of nitrate Cu, and Bi_2O_3 [1]. Some upgrowth of crystals can occur also as a result of powder heating at the end of sublimational dehydration up to 40°C, which is applied to more complete dehumidification at the completing stage. However homogeneity of the product of spray frozen and freeze drying synthesis is much higher than of products produced by traditional ceramic's synthesis. The product has large extent of homogeneity not only in volume of batch, but in volumes of significantly smaller granules. This fact is specially important for multicomponent system containing small additives that addicted to phase intergrowth, i.e. formation of similar complicated structures such as $Bi_2Sr_2Ca_nCu_{n-1}O_y$, which joint formation can be caused by fluctuations of composition.

2.2. Thermal decomposition of saline product and formation of oxide precursor

During thermal decomposition following steps occur:

- decomposition of nitrates with NO_2 removal;
- removal of residual crystallohydrated water from saline product;
- crystallization of oxide phases.

Diffusive difficulties don't preclude the decomposition stage. Gaseous products of reaction from finely dispersed particles drive back through rather large pores derived in cryogranules at dehumidification during sublimation. The highly developed interior surface that represents interphase boundary is an energy favourable place for nucleating of new phases. The application of high speed heating does not allow to take place diffusion processes occurring up to the moment of decomposition, and results in "hightemperature phases" formation required for the subsequent synthesis. Besides, at high speeds of heating

prompt removal of gaseous products of reaction is required.

At small duration of this stage (30 min) the material undergoes considerable changes. In the powder decomposed at 650–750°C there are phases of 2201, CuO, SrCu$_2$O$_3$, (Ca, Sr)$_2$PbO$_4$ and also small amount of 2212 phase. During decomposition at temperature range 750–850°C, composition of the product includes predominantly the 2212 phase (at decomposition points 800–850°C this phase dominates in composition of oxide precursor), as well as CuO, Ca$_2$CuO$_3$, (Ca, Sr)$_2$PbO$_4$ [1]. High reactivity of components immediately after decomposition of nitrates and their high diffusive activity at high temperature promote formation of complex oxides.

At optimum regimes of decomposition (control of temperature and height of powder layer) formed conglomerates derived the shape of saline product conglomerates. For further processing the powder was grinded and was filtered through a deck with mesh size 63 μm. The microscopic analyze demonstrates that size of the base fraction of oxide precursor powder is 30–40 μm. In spite of the fact that it consists of disperse grains with size less 1 μm (which does not much more exceed the size of particles in cryogranules), further diminution of decomposed powder's particles requires considerable intensification of grinding process. Probably intensive chemical reactions and diffusion processes, and also presence of some liquid phase (as DTA [1] shows, partial melting of saline product starts at 730°C) result in formation of contact necks between disperse particles despite of small duration of the stage.

In [3] are presented the legitimacies of different factors influence the performances of phases formed at thermal decomposition of saline product of spray frozen and freeze drying synthesis:

- at moderate heating temperatures the process of formation of new phase grains dominates; and at higher temperatures main process is grains upgrowth;
- low removal speed of gaseous products' decomposition from reaction zone promotes sequential growth of nuclei of new phase (formed crystalline mass represents practically nonintegrated particles), and high speed promotes parallel upgrowth (accreting particles form uniform crystalline structure intercrossed by dislocations);
- the speed of oxygen exchange between condensed and gas phases at moderate heating temperatures is neglectfully small, however as temperature rise, speed of oxidation-reduction reactions increases and probably disturbs oxygen homogeneity of material.

The authors of [3] consider that during transportation of gaseous products of reaction true interdiffusive inhibiting is practically missing and is connected to a small size of crystal grains of saline skeleton. Granules interdiffusive inhibiting, connected with transport of gaseous products from surface of separate crystal grains to geometric boundary of saline granule, as well as truly outwardly diffusive inhibiting can render essential influence on processes occurring during thermal decomposition.

However in the case of bismuth system, large granules of saline product (about 1–3 mm) pierced by visually apparent pores were manufactured. Probably these factors are the reason of practically absent outward diffusion and granules interdiffusive inhibiting. The color of the decomposed powder supports this conclusion. Usually color varies from light blue to black at first minutes of decomposition stage. If a thin layer (about 1 sm) of filling is used, color of the product of decomposition is uniform on all volume. Considerable difference in colour of oxide precursor decomposed at different temperatures—from black at 800–850°C up to light brown at 600°C—is observed. Further lowering of decomposition point results in obtaining even lighter colour of products. This is connected to increase of quantity of not decomposed salts. Blue colour of saline product is explained by presence of Cu^{2+} ion, hydrated by water molecules. Intensity of coloring varies depending on H$_2$O quantity. Darkening of the powder happens during transition of copper ions (and other elements) from salt to oxide.

Thus oxide precursor of bismuth hightemperature superconducting ceramic obtained after decomposition of saline product represents friable granules that combine mechanically strong agglomerates (30–40 mμ size). These agglomerates consist of dispersible particles of oxide phases and the phase composition of which depends on decomposition point.

2.3. Introduction of the 2223 phase additive

At the stage of the 2223 phase additive's introduction with the purpose of intensification of this phase synthesis [1], its particle are uniformly distributed in powder volume (that confirmed by recurrence of results of the specially conducted experiments) at mechanical mixing due to proximity of densities of mixed components (basically, the 2212 in precursor dominates, and the 2223 phase has 95% of the additive contents).

In [1] 0–100% (mass.) of the 2223 phase additive from powder, obtained at grinding of sintered samples, was introduced. Powder of the additive with size of mean fraction 30–40 μm (coarse additive) and 3–10 μm (fine additive) were used. Since properties of the sintered ceramics essentially differ [1] with various quantities and sizes of particles of the additive, it was necessary to study distribution of additive's particles in volume of samples in more in detail.

Mean distance between the additive's particles in compact material λ approximately can be calculated with known formula:

$$\lambda = \frac{2d}{3V}(1 - V),$$

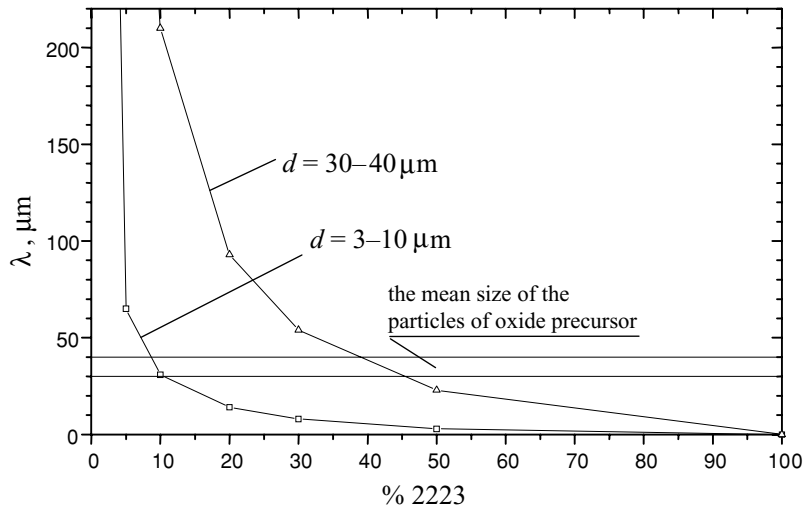where d is size of particles of the additive, V–its volumetric content.

Figure 2 Calculated distance between particles of the additive of 2223 phase depending on their quantity and size.

Using mean size of additive's particles d_{mean}, mean distance between these particles in compact material was calculated depending on its quantity (Fig. 2). Due to porosity of pressed material, substantial value of λ should be a little more that, but that cannot considerably affect relative distribution of particles of oxide precursor and additives.

The analyze demonstrates that at addition of 5–10% of the 2223 phase and uniform mixing, the additive's particles separates at least one particle of oxide precursor and the probability of immediate contact of the additive's particles is not great. With addition of more than 10% of fine powdered additive and more than 40% of coarse-grained additive (let's term critical ($C_{\mathrm{crit.}}^{2223}$) the relevant concentration of the additive of 2223 phase) mean distance between additive's particles is less than a medium size particle of oxide precursor (shape is approximately equiaxial; size of the basic fraction is 30–40 μm). Thus, probability of contact of the additive's particles among themselves considerably increases and continues to raise with increase of quantity of the 2223 phase powder in the precursor. The distribution of additive's particles of different size and quantity is shown on Fig. 3.

It is possible to add that the powder of coarse-grained additive—used in experiments described in [1]—is not monodispersive; some part of it was finer (but not coarse), than the size of the base fraction which used in calculation. Therefore $C_{\mathrm{crit.}}^{2223}$ value in some arias of ceramic can appear below theoretical.

2.4. Compacting
Densification of compacting samples includes following processes:

- dense stacking of powder in the direction of moving of particles;
- fracture of the least strong particles.

Considerable strain of powder's particles is less probable. As it is known, during static pressing complete fracture of conglomerates usually does not occur. Generally, the precursor of bismuth superconducting ceramic mouldes and allows yielding compacting without introduction of plastifier. However powders decomposed below 800°C have high hardness and it is hard to press from its samples free of defects (laminations, chipping). Difference of phase composition of powders (at the decomposition point below 800°C content of the 2212 phase in pressed powder is insignificant) determined plasticity, size and morphology of powder's particles (the relatively coarse particles of the 2212 phase have the plate shape) define this effect.

2.5. Sintering
Processes at ceramic sintering stage:

- formation of contact necks (mechanical contacts) between particles and contraction (classic sintering at the presence of liquid phase);
- formation and upgrowth of the 2223 phase grains (including chemical and diffusion processes which are not concerning classic sintering);
- formation of quality contacts between superconducting grains ("superconducting contacts").

It is possible, probably, to say that the second process immerses the first one. During first hours of sintering, one can still observe the process of contraction (for example, see Figs. 9 and 11a). Then there is upgrowth of samples connected with phase formation; quantity of this upgrowth essentially depends on technology factors (primarily, from parameters defining phase composition of oxide precursor). Problems of formation of the 2223 phase and formation of superconducting contacts between grains are two self-maintained enough subjects, and discussion in the literature is far from being exhausted yet.
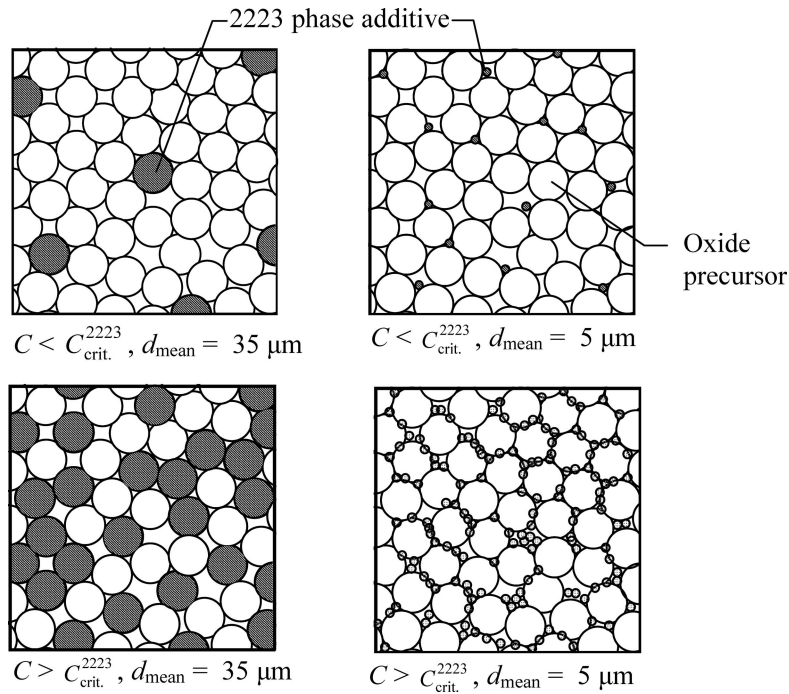
Figure 3 The scheme of distribution of particles of 2223 phase additive among oxide precursor's particles.

2.5.1. Formation of the 2223 phase

Great number of publications is dedicated to the mechanism of formation of the 2223 phase. It is possible to define two basic directions: one part of the authors considers that the 2223 phase is formed by an intercalation of padding layers (Ca) and (CuO$_2$) in a lattice of the 2212 phase, other (more numerous) group of authors prefers mechanism guessing of fracture of the 2212 phase's lattice that dissolves in liquid (or melting), nucleation of the 2223 phase and its upgrowth. For the benefit of the intercalation mechanism, for example, stand such experimental facts as existence of the 4435 phase—an intermediate between the 2212 and the 2223 phases [4]; preservation of direction of 2212 phase's texture in 2223 phase's strip [5]. For the benefit of upgrowth of the 2223 phase from nucleuses stand kinetic legitimacies of process [6], influence of the 2223 phase's additives on speed of the process [1, 7, 8], and also increase of the 2223 phase's quantity if intermediate crushing of a product during a sintering used [8].

As is known, for example [9], the diffusion processes during heating happen rather quick. If transformation of the 2223 phase onto the 2212 phase happens at premelting temperatures, it is possible to suspect, that diffusion of ions of Ca, Cu and O is quite probable because: (1) the volumetric lattice of 2212 phase is dilated; (2) the mobility of atoms in its junctions is great; (3) the literature tells us about presence of essential quantity of vacancies in lattices of superconducting phases.

Presence of the liquid phase ensures delivery of components to the surface of a growing grain of 2223 phase. Results of some investigators evidence high speed of fill-ing of all layers in the 2212 phase with atoms of Ca, Cu and O after the reaction of initialization on the surface of a grain. Among structural defects apparent in bismuth ceramics, the "unfinished" layers in which the 2212 phase transforms into the 2223 phase have not being discovered (though it can evidence and to absence of an intercalation generally). Thus, quick weep of intercalation mechanism is quite probable and it can be limited by initialization act on the grain surface.

The change of material's morphology—observed through submicroscopy—during synthesis of the 2223 phase from a precursor with preferred content of the 2212 phase and considerable upgrowth of material's grains even at sintering stages, on which—from the XRD data—there is already a small quantity increase of the 2223 phase in material (see, for example, Figs. 7a and 8), might occur due to the fact that upgrowth of grains of the 2223 phase happens at the expense of precipitation of liquid phase's components. Gradual and fission improvment of a state of boundaries of the 2223 grains in a Fig. 7b (in relation of the 2212 to the 2223 change) confirm that. This fact is ambiguous and can be treated also in benefit of the intercalation mechanism. But the essential changes of ceramic's morphology during sintering (i.e. during the 2212 to the 2223 phase composition of ceramic transition) benefit nevertheless possibility of the 2223 phase's grains upgrowth at the expense of inflow of elements from the liquid phase. Besides it is complicated to present the mechanism during which there can be an acceleration of the 2223 phase's synthesis at the introduction of the additive to this phase [1] in case of extremely intercalation mechanism of synthesis (Fig. 4).
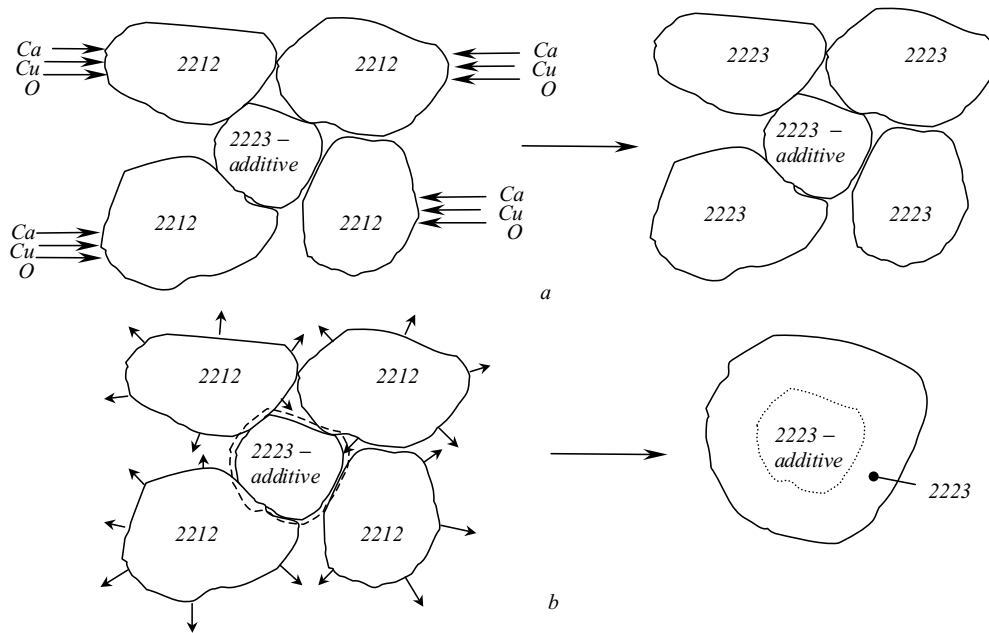
Figure 4 The role of the additive of the 2223 phase at synthesis of this phase on mechanisms "intercalation" (a) and "nucleation and grains growth" (b).

Taking in consideration references and experimental data (Table I), it is possible to suspect the following sequential scheme of formation of 2223 phase at the stage of sintering of samples:

- fine grains of 2212 phase at temperatures close to melting point of this phase are dilating volumetric;
- there is diffusion of ions of calcium, copper and oxygen in some, most favourable grains of 2212 phase, there is a stabilization of these grains due to formation of the 2223 phase, other grains of 2212 phase start gradually dilut or melt;
- the grains of the 2212 phase with padding layers (Ca) and (CuO$_2$) become nucleuses of the 2223 phase, which grows at the expense of components coming from the liquid phase;
- there is docking of growing grains of the 2223 phase and under pressure of growing crystals material is dilates;

- during decay of the 2223 phase's grains upgrowth quality electromagnetic contacts between it's grains are forming (presumably uncontaminated contacts with small quantity of defects and minimum breadth between grains of interlayer with disturbed atomic-crystalline structure).

Schematically possible mechanism of formation and upgrowth of 2223 phase's grains is shown in Fig. 5. Depending on exact technological conditions different stages of presented scheme can occur with different intensity and that causes inconsistency of the experimental facts. With presence of great many grains of the 2212 phase which are capable to becoming nucleuses of 2223 phase, or at inhibiting of upgrowth of the 2223 phase's grains owing to highly dense stacking of the 2212 phase's grains and their large size, the process can be looked at as a two stage process: stage of intercalation and following stage of coordination of boundaries of adjacent grains. Probably

TABLE I Grounding of the scheme of 2223 phase formation

| Basic considered mechanisms of the 2223 phase formation	
Formation and growth of the 2223 phase nucleuses	Intercalation of padding atoms in a lattice of the 2212 phase
Influence of additive of the 2223 phase on formation rate of this phase (see Fig. 4)	Existence of the phase 4435 (intermediate between 2212 and 2223) [4]
Affirming of this mechanism by thermodynamic calculations [6]	Preservation of texture's direction during formation of the 2223 phase from the 2212 [5]
The factors evidencing to high probability of embodying of the mechanism (indirect factors)	
Growth of grains with minor change of quantity of 2223 phase	High speed of diffusion at sintering temperature near to melting point of the 2212
	The absence of difference in formation rate of the 2223 phase from oxide precursor with average fraction size 3–10 and 30–40 μm [1]
	Absence of evidence about the existence of colonies of layers of 2223 phase passing on some distance from a surface of grains into 2212 phase
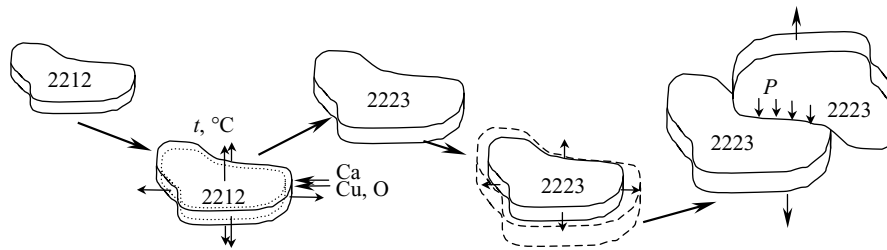
Figure 5 The step-by-step scheme of processes occurring during formation of the 2223 phase.

this case was also observed by the authors of [10] to explain preservation of the texture's direction of the 2212 phase during formation of the 2223 phase in rolled strips from bismuth ceramic. They studied formation of the 2223 phase's grains in vacuities derived during melting of the 2212 phase's grains. The authors did not present a clear explanation in what the vacuities can be formed if melting 2212 phase and dissolution of other components required for formation of the 2223 phase.

Generally, depending on which of the different stages of the presented scheme of the 2223 phase's formation prevail, the speed of synthesis and microstructure of formed phase can essentially differ. For example, if the precursor with large particles of the 2212 phase is used, the mechanism of intercalation predominates. This process is specially rapid in the beginning, then braked in accordance to lower concentrations of diffusing elements in liquid. If composition of the precursor differs from the stoichiometry of the 2223 phase, the quantity of nucleuses of 2223 phase diminish, the stage of upgrowth of grains predominates. Based on the data presented in [4], existence of the 4435 phase can evidence about substantial mechanism that requires minimum energy consumption—intercalation of calcium and copper's atoms in the lattice of the 2212 phase (probably, at the incipient state of formation of nucleuses of 2223 phase). Also there are no warrants to refute participation of the mechanism of the 2212 phase's disproportionation during nucleating of the 2223 phase (which is also connected to diffusion of ions of Ca, Cu and O, though it differ from conventional intercalation), the authors of [11] indicated, that the presented mechanism is only the step in a more complicated scheme. In the literature this mechanism is refuted because of just little amount of the 2201 phase present during formation of the 2223 phase from the 2212 phase. However the 2201 phase can be disintegrated, and products of its decay may became a source of grains upgrowth of the 2223 phase.

The authors of [8] consider, that the 2223 phase originates on a fractionally elted surface of the 2212 phase's grains and grows at the expense of component inflow from a melt. These authors demonstrate, that 5% addition of the 2223 phase's additive accelerate formation of this phase. They also recommend to applying intermediate grinding during material's sintering "to unblock" 2212 phase that is isolated by 2223 phase. The authors also think that intrusion of complementary layers of atoms in the lattice of

2212 phase is not derived. Probably intercalation does not go all the way down the 2212 phase's grains in case of a coarse-grained precursor, however such experimental data was not used in the literature (probably, in case of a "surface" intercalation on of the microstructure's image which has been created by applying of high-resolution submicroscopy, the colonies of the 2223 phase layers were transformed at some distance from grains's surface in the 2212 phase layers). Probably, if significant amount of 2223 phase formed intermediate grinding during sintering promotes more complete interaction of melted or dissolved grains of 2212 phase delivers components for upgrowth of grains of 2223 phase, with other phases containing calcium and copper. However, intermediate grinding entails increase of sintering time, since the contacts of superconducting grains formed immediately after docking of grains are disturbed. According to experimental data [1], such formation of contacts of superconducting grains is optimal.

2.5.2. Formation of contacts between superconducting grains

As it is known [12–15], in customary polycrystals the boundaries of grains can be coherent, half-coherent, special, large-angles with different degrees of order and energy depending on orientation and some other parameters. But, as investigations demonstrate, lattice disordering is maintained usually only on one (maximum a few) parameter of a lattice cell. Looking at the basic reasons of low conductance of polycrystalline body in contrast to a single crystal, it is possible to conclude that dissipation of electrons energy occurs on structural defects and impurities, concentration of which on boundaries of grains is usually very high (quantity of these irregularities usually determines the degree of efficiency of boundary). It is interesting to note that the contaminating of a single crystal by the same quantity of impurities does not result in noticeable lowering of conductance [14].

In case of a porous powder body the degree of efficiency of interparticle contacts can be defined by physical-mechanical characteristics of material response to this performance. The projection method estimates quality of contacts based on a share of diffusive contacts, which can be detected by a pit-like morphology of facets of a fracture. Generally, formation of metallic bindings between contacting particles not necessarily require diffusive

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transport of mass, and at low temperatures can be carried out by any of the thermally labilized dislocation processes. For example, formation of interparticle contacts in copper compacted samples can be described as follows. During preliminary plastic strain during compacting interparticle contacts are shaped; later the contacts are healed (weld together) during low-temperature (up to 0.55 t_{melt}) sintering of contacting surface segments almost without diffusion (there are interparticle contacts with very small share of diffusive connections). At temperature equal to 0.55–0.75 t_{melt} diffusion processes start to play essential role, however this ensures transportation of diffusive mass within limits of contacts created by pressing (general square of contacts is not incremented, but share of diffusive connections arises). Only with applying higher temperatures formation of perfect contact in limits of geometry given by compacting finishes and further processes of diffusive upgrowth of contact neck's sizes explicate [16].

In powder metal bodies the conductance of system is restricted primarily by square of interparticle contacts, and it is necessary to ensure presence of diffusive connections between particles, whereas a rather large square of contacts can be taken by lack of adhesions. The contacts of particles in models describing flow of current in powder bodies studied primarily because of their heightened vacancionity. Presence of oxide films and contaminatings on the surface of particles caused transition resistance that impacts the resistance of powder metal body, however these factors are eliminated on an incipient state of sintering.

It is necessary to note, that unlike polycrystalline materials, and even majority of materials obtained by method of the powder metallurgy, the customary not textured bismuth HTSC ceramics cannot be considered as combination of crystal grains, which contact mostly of free surface. The other essential difference of bismuth system is very strong anisotropy of properties in different crystallographic directions, bound with considerable difference of lattice cell parameters a (b) and c. Grains of the 2212 and the 2223 phases of bismuth ceramics have the plate-like shape with large sizes along the ab plane (predominantly just in this plane the superconducting current flows). Therefore if used not textured ceramics with random arrangement of grains of superconducting phases, the square of their contacts is restricted enough, the orientation of adjacent grains is far from optimal, the superconducting connections between many grains is carried out only due to tunneling effect (weak Josephson links). Caused the analog to "transition" resistance in ceramic superconductors it is possible to consider nonsuperconducting phases, is foregone generated in these multicomponent systems and are concentrating on boundaries of grains, however, unlike interlayers of impurity in powder metal bodies, removing of these components during sintering is complicated.

Thus, along with strong anisotropy of properties of superconducting grains, their brightly expressed flat mor-

phology which caused (at lack of the actions of the texturing factors) unordered–honeycombed structure of material, and also with complexity of crystalline structure and multicomponentity of composition of bismuth system, performance of grains on contacts (very important because of superconducting properties), it is impossible to approach this material with stands of others, more studied materials produced by method of the powder metallurgy (at broad comprehension of essence of this technology).

At stage when the grains of the 2223 phase are already formed and have contacts, further upgrowth stops for the reason of grains calling inside a sample with strong pulling stresses. The termination of upgrowth of grains of 2223 phase (and substantially—limiting content of the 2223 phase in bismuth ceramic) can be connected not only to lower of concentration of some components in local volumes, but also to resistance of material to mentioned above pulling stresses. That is the most probable process with parallel influence of these two factors. The stage starts with formation of compounded contacts between grains, which should supply their collateral participation in processes connected to superconductivity.

The process of formation of "superconducting" contacts can include turn with slipping of adjacent grains, and also (by itself or together with the first mechanism) their additional structural constructing. The first occurrence can be caused by combination of following factors:

1. pressures of crystallization of the 2223 phase;
2. flat morphology of grains that ensures nonequilibrium of mechanical actions on them;
3. realization of the process at premelting temperatures and presence of some liquid phase;
4. considerable lowering of surface energy during "accretion" of flat surfaces of adjacent grains (texturization).

As is known from XRD analysis, surface of sintered samples has some texture, whereas in volume this appearance practically is not observed. The microscopic investigations also do not let us to say about presence of texture in volume of samples manufactured by the customary compacting method with subsequent sintering (for example, see Fig. 6). Parallel stacking of grains in local volumes of such samples occurs with not much greater probability than oriented "under angle"; global texturization of the sample does not happen. Thus, it is impossible to speak about essential influence of the turn with slipping mechanism on apparent improving of the superconducting properties during sintering of samples with already formed grains of the 2223 phase. Apparently, this mechanism will be actuated during hot pressing of samples, when strongly textured samples are gained.

The mechanism of additional structural constructing, probably, prevails during formation of superconducting contacts in material. Allowing long time of this process (tens of hours) [2] made it possible to conclude that in case of bismuth ceramic diffusive transport of mass
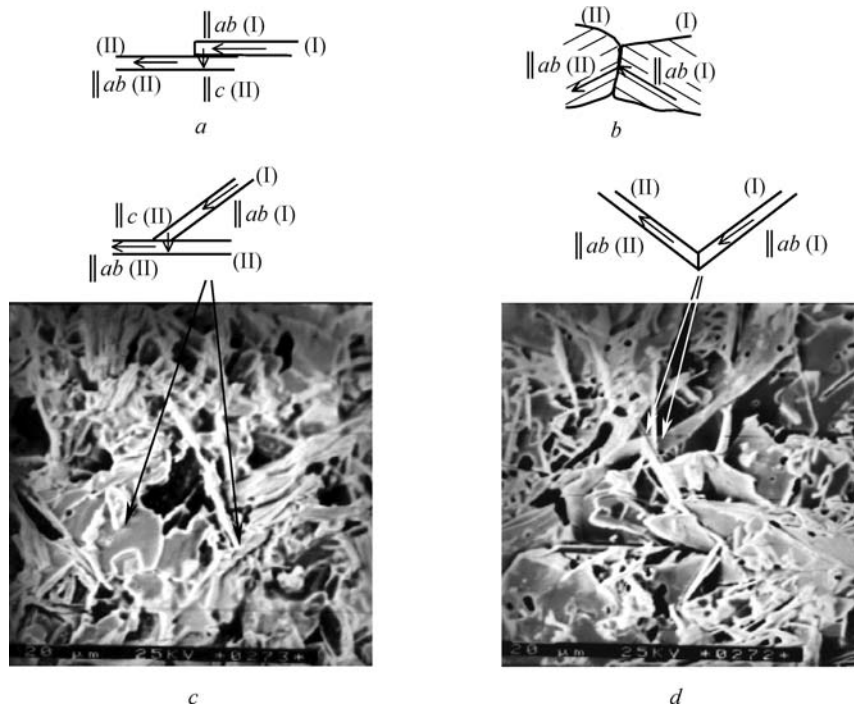
Figure 6 Variants of an arrangement of contacting grains and directions of superconducting current flow in them.

(complicated by multicomonent composition) instead of dislocation process plays a leading role. Doubtlessly, dissolution of dispersible inclusions of impurity particles in the saturated by vacancies lattice of the 2223 phase also occurs during sintering (certainly, complete disappearance of impurity phases does not happen and flow of this process depends on conditions of the sintering). This process was observed in [17]: in samples compacted at low pressures and increasing mass during sintering at 8%, the superconducting properties after 150 h of sintering were much worse than in samples pressed at higher pressure and stable mass. Addition of 100 h of sintering improves properties in all samples, but most interesting is that properties of all samples steel practically identical. Collecting all data about the samples, the authors explained this process as formation and subsequent dissolution in superconducting grains of dispersible (X-ray amorphous) impurities of phases generated in elements by filling diffusion in volume of the samples pressed at low pressures (in spite of the fact that the element composition of filling did not differ from the contetts of the samples).

With the point of view of the superconducting properties it is very important that after joining of grains, the width of disordered layer has appeared comparable with length of coherency of electron pairs—only such contacts allow superconducting grains to be "connected". In HTSC-materials, as it is known, length of coherency is very insignificant (for example, in direction of c axis it is comparable with distance between CuO_2 planes [18]); therefore maximum coordination of contacting grains is especially important. Additional structural constructing of superconducting grains forms maximum quantity of interatomic connections, lowers of quantity of vacancies

in contact zone, and also coordination of joined layers (probably, as a result of minor slipping of grains).

Two models of the current flow to different kind of boundaries are described in the literature [19]. The "brick wall" model assumes that rotary boundaries play basic role—they are perpendicular to axis c and have maximum contact surface of two grains (that is basic current between adjacent grains flows in direction of c axis). The model of "railway arrows" allows current to flow through large-angles boundary, parallel c axis (the current flows along ab plane); in this case sufficient quantity of intercrystalin connections have to exist. Both models can feature current flow through textured along c axis material (for example–in a wire, strips). Diagrammatically they are shown in Fig. 6a and b.

A few of variants of relative orientation of grains can occur in case of volumetric (and more often not textured) ceramics. For parallel oriented along c axis, the possibility of grains joining "under angle" is added:

(a) ajoining the ridge of the first grain to plane of the second one (in this case superconducting current flowing along ab plane of the first grain can pass in the second grain only in direction of c axis, or on the contrary)—Fig. 6c;
(b) coupling of two ridges of grains (with current flow along ab planes of two grains arranged "under angle")—Fig. 6d.

Point contact of grains does not disagree with practical point of view (though in substantial ceramics any of the described above variants of grains joins can contain combination of contact points).
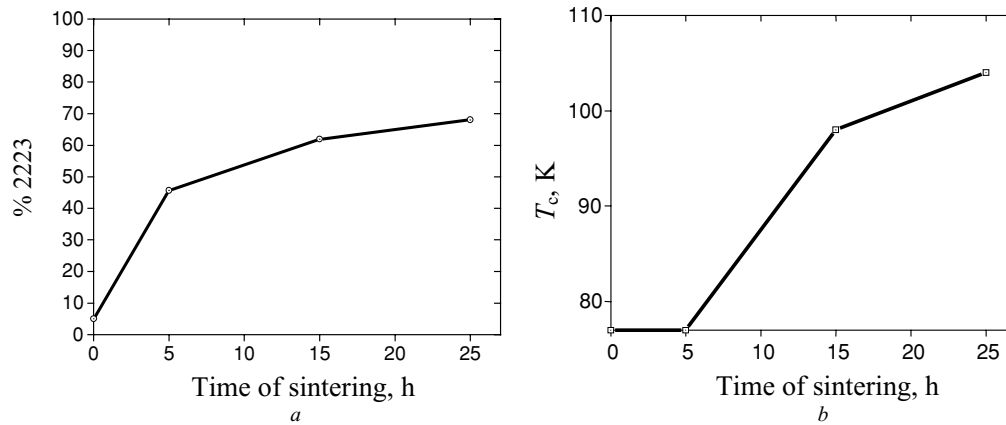
Figure 7 Dynamic of relation of the content of superconducting phases (2223/(2223+2212)) (a), and critical temperature from AC susceptibility (b) of bismuth ceramic change during a sintering.

Thus, an important factor in connection with strong anisotropy of properties is relative orientation of lattices of bordering grains—a barrier is necessary for the flow of superconducting current along unusual to its direction of c axis. At presented stage of research it is complicately to define the contribution of any model to current flow and to describe them quantitatively. At any rate, for superconducting current to flow through boundary, both the elements and the phase composition of the boundary should be "pure" enough and structurally perfect enough (with minimum quantity of vacancies and maximum lattice ordering) to not introduce insuperable "barrier" for tunneling of electron pairs possessing particular, comparable to parameters of lattice cell, length of coherency.

It is possible to conclude that in case of bismuth ceramics carrying superconducting current, important role is played by degree of boundary's perfection (forming a compact polycrystalline body) in restricted areas of grain contacts (as in other materials manufactured by the method of powder metallurgy). However requirements to boundaries that ensure flow of superconducting current for electronic pairs are higher than for boundaries of grains of metal materials, in which electrons do the job.

Thus, at this point it is hard to offer reliable structural parameter, which would allow to uniquely identify what the "quality superconducting contact" is. It depends on:

- relative orientation of bordering superconducting grains;
- degrees of structural perfection of joining grains contact area and its phase and element purity (the combination of these parameters should ensure minimum breadth of interlayer with dislocated atom-crystalline structure between grains, smaller lengths of coherency of electronic pairs);
- general square of structurally joined contacts

Different versions of contacts influence structure-sensitive superconducting properties (SSP) of material can be observed. The most natural method of comparative quantitative assessment of quality of contacts between superconducting grains is the integrated performance that permit to take into account combined effect of the numbered factors.

2.6. Connection of technology factors to the properties of bismuth ceramic

Let's try to explain some experimental results presented in [1 and 2], using enunciated above representations about processes occurring at synthesis of bismuth superconducting ceramics.

1. In about 50% of the 2223 phase with 5% addition of the 2223 phase nucleuses are derived through 5 h of sintering, and temperature of superconducting transition is jumpily increased at interval of sintering times 5–15 h (Fig. 7).

As investigations have shown, Meissner effect in samples from superconducting grains with lack of quality contacts (coherence in different grains of processes connected to superconductivity) and with identical parameters of measurement makes only small share diamagnetic effect that takes place in "linked" superconducting ceramics (based on available data—10–20% [1, 20]). Synthesis of the 2223 phase is not restricted to intercalation of padding ions in the lattice of the 2212 phase; formation of contacts between its grains requires a long process (upgrowth of grains, formation of low defect and, whenever possible, compounded boundary between them during crystallization pressure of the 2223 phase and global expansion of material), and the diamagnetic effect even owing to a great many of the 2223 phase grains will be very weak up to the moment of "closing of fractures" of isolated grains. Fig. 8 shows that during sintering up to 25 h microstructure of the sample image gradually shows plate grains, characteristic for superconducting phases. Apparently, it characterizes dynamic of upgrowth of the 2223 phase grains at the expense of disperse grains of the 2212 phase and nonsuperconducting phases, which are generated in conditions of sintering at the presence
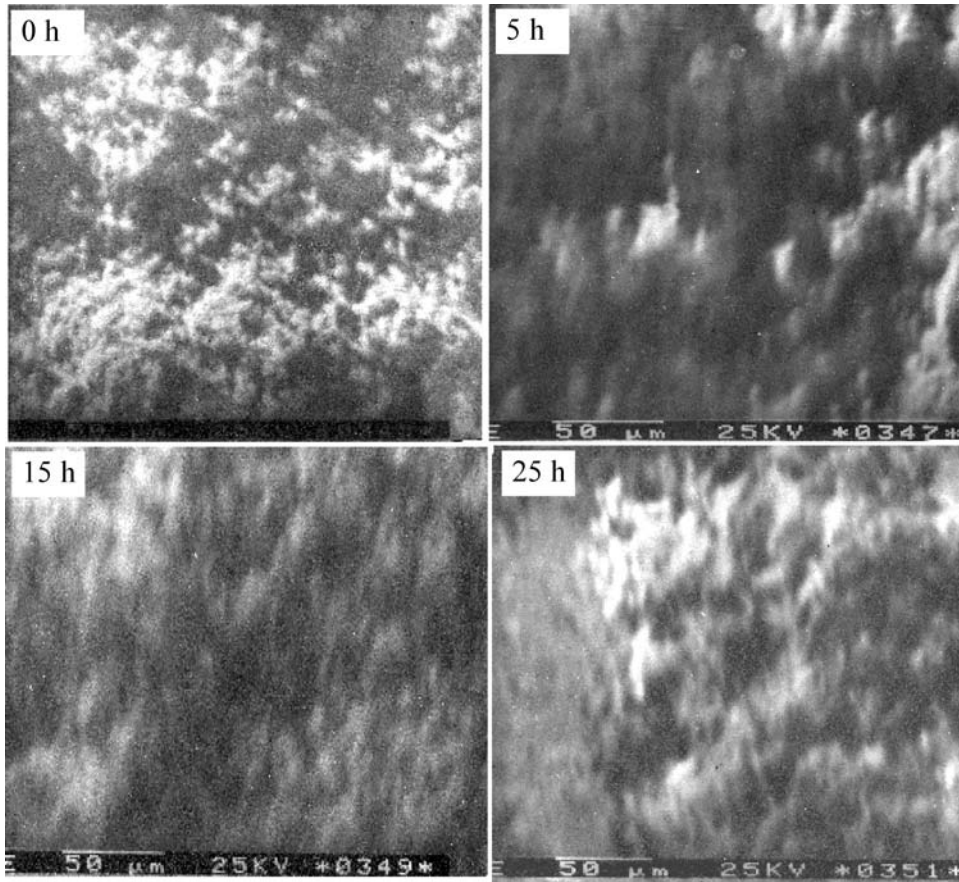
Figure 8 Change of microstructure of samples during a sintering.

of liquid phase environment around of growing grains of 2223 phase.

One more affirming that after 5 h of sintering there are no contacts between grains of the generated 2223 phase is the contraction at this stage (increase of sample's density). Whis 15 h of sintering, density of products is reduced and that can be connected to joining of growing grains (Fig. 9).

2. With increase of quantity of the 2223 phase additive up to 20% and more there is no acceleration of formation of this phase, and temperature of superconducting transition from dependence χ'–T is reduced [1]. Immediate contact of particles of the additive among themselves contributes to volumetric SSP. These properties are determined by the performances and volume of superconducting grains (at temperature above 100 K—only of grains of the 2223 phase), which were generated during sintering or annealing ($2223_{samp.}$) and brought in as the additive ($2223_{addit.}$), as well as matrix, environmental these grains (defect boundaries of grains of the 2223 phase (GB), inclusions of the 2212, 2201 phases (PhI) and nonsuperconducting phases, pores (P)) (Fig. 10):

$$SSP = f(2223_{samp.}; 2223_{addit.}; GB_{samp.}; GB_{addit.}; PhI; P).$$

"Linked" $2223_{samp.}$ and $2223_{addit.}$ ensure the basic volume of SSP, and $GB_{samp.}$, $GB_{addit.}$, PhI and P should
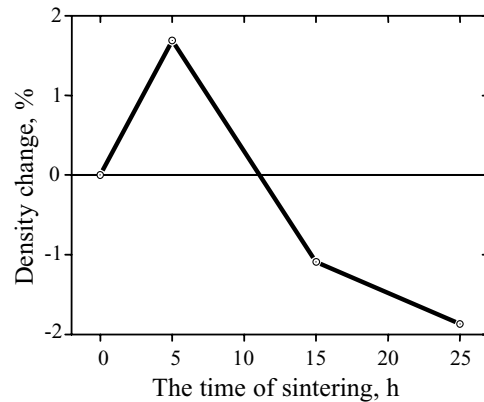

Figure 9 Dependence of density change of samples from sintering time.

minimally hinder among themselves on contact of grains of the 2223 phase.

The aggravation of SSP (lowering temperature of superconducting transition based on results of measuring temperature dependence of magnetic susceptibility) with addition of the 2223 phase's additive, more of $C_{crit.}^{2223}$, can occur because $2223_{addit.}$ or contacts of $GB_{addit.}$ (that more probable because the best samples were used for manufacture of the additive). After grinding a sample from the 2223 phase and repeated compacting not less 75 h arerequired for reduction of contacts between superconduct-
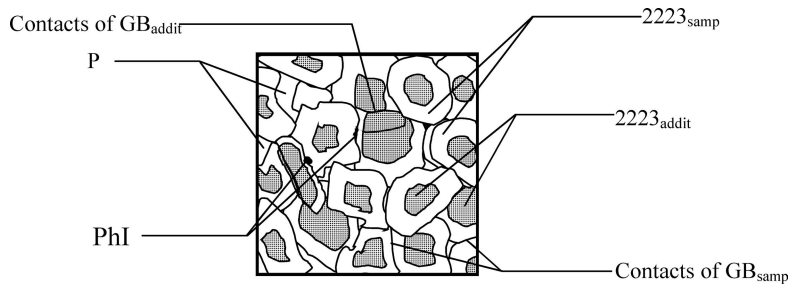
3517

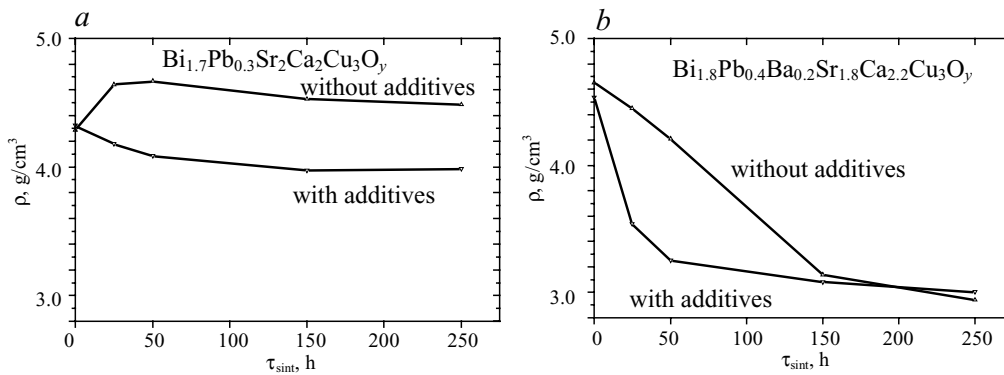*Figure 10* Schematic representation of structural components of bismuth ceramics.

Figure 11 Density change of samples of compositions $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ and $Bi_{1.8}Pb_{0.4}Ba_{0.2}Sr_{1.8}Ca_{2.2}Cu_3O_y$ (with and without 2223 phase additives) during sintering.

ing grains from results of measuring dependence $\chi'-T$ [2]. The assumption is, that between contacting grains of the additive the electromagnetic contacts linking 2223_{addit} are shaped much slower than between 2223_{samp}.

3. The nucleuses promote acceleration of the 2223 phase, formed only from a precursor with high content of the 2212 phase (with identical chemical composition of material) [1]. It is highly probable, that the formation of the 2223 phase from the 2212 phase requires smaller energy consumption than from other oxide phases. During intercalation mechanism the reason for it can be structural proximity of phases, during formation and upgrowth of nucleuses—greatest proximity to chemical composition possible in this system. Probably additional chemical reactions that occurr during the 2212 phase formation in the precursor result in fracture of nucleuses of the 2223 phase added in material.

4. In the precursor with a low content of the 2212 phase and clear of nucleuses of the 2223 phase, this phase derived a little faster than in the precursor with a high content of the 2212 phase [1]. Probably, the 2212 phase that is derived right before the synthesis of the 2223 phase (during the adjustment of their synthesis in one technological operation) has greater "activity". One of the reasons for it can be size optimization of the 2212 phase's grains, which are precursors to synthesis of the 2223 phase, or any kind of activity of the fresh derived phase. With considerably higher speeds of the 2212 phase formation as opposed to the 2223 phase, it is possible to justified the precursor with low content of 2212 phase obtaining at the

stage of decomposition (if the additive of 2223 phase for intensification of synthesis was not used—see item 3).

5. A considerable increase in volume is observed during sintering of samples of compositions distinguished from the composition of the 2223 phase, but samples of compositions close to composition of the 2223 phase "grow" weakly [1]. Samples with various ratios of chemical elements in composition have various phase composition. At formation of 2223 phase from such compositions the relation differs of the contributions of different stages of the 2223 phase's synthesis, for example the relation of processes of "nucleation" and "grains growth" of the 2223 phase's grains. In compositions that are close to a stoichiometry of the 2223 phase, formation of a great many fine grains of the 2223 phase is observed, apparently; in distinguished compositions–the upgrowth of a relatively small amount of nucleuses of the 2223 phase occurs and upgrowth of samples is more probable (Fig. 11).

This observation is confirmed by the analysis of structure of samples with different compositions (Fig. 12). The size of aggregates in samples of composition $Bi_{1.8}Pb_{0.4}Ba_{0.2}Sr_{1.8}Ca_{2.2}Cu_3O_y$ (much differed from stoichiometry of the 2223 phase) noticeably exceeds the size of aggregate in composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ (close to a stoichiometry of 2223 phase).

6. The quantity of the 2223 phase in relation to the 2212 phase in samples of composition is close to stoichiometry of the 2223 phase is about 70%. A few factors—increase of square of reactionary surface during upgrowth of the
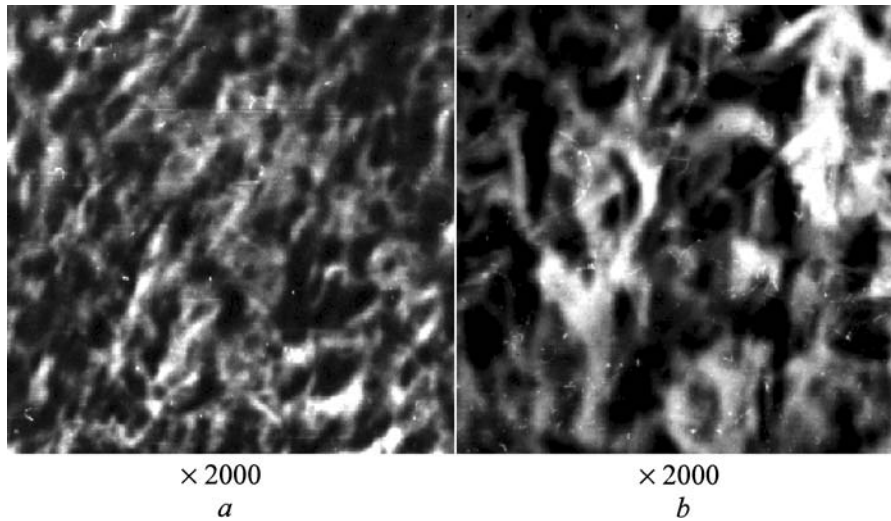
$\times 2000$
a

$\times 2000$
b

Figure 12 Microstructure of samples $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ (a) and $Bi_{1.8}Pb_{0.4}Ba_{0.2}Sr_{1.8}Ca_{2.2}Cu_3O_y$ (b) compositions with additives of the 2223 phase.

2223 phase's grains, gradual lowering of Ca and Cu concentration in liquid, isolation of some segments of volume by "accretion" of the 2223 phase's grains—can create barrier to formation of the 2223 phase's grains. Intermediate grinding of samples during sintering and correct selection of material's composition can promote an increase of saturation limit. However both these factors promote aggravation of contact conditions of superconducting grains, and also essential increase in sintering time necessary for reaching material's optimum performances.

3. Conclusions

1. During manufacture of bismuth hightemperature superconducting ceramics the starting components (individual oxides or salts) are transformed to form a composite multicomponent structure. Based on surveyed work cycle, the parameters of the initial stages (synthesis of saline precursor) should ensure optimal element composition, homogeneity of component's distribution, gas permeability of the product. The parameters of the thermal decomposition stage correspond to obtaining of oxide precursor of particular phase composition. Concerning addition of nucleuses of 2223 phase and compacting of preforms, the parameters of these stages has direct influence the state of contacts between grains. The quality of material of superconducting properties is shaped in basic at the stage of sintering.

2. The superconducting properties of material are determined by two basic performances—phase composition and structure of material. It is possible to distinguish other the factors, like contribution of superconducting grains (defined by their phase purity, atomic-crystalline perfection and grain structure) and contribution of boundaries of these grains (depending on their phase and on elements purity, relative orientation and degree of structural coordination of docked crystal lattices, general square of the structurally docked contacts). Thus, the requirements to contacts of superconducting grains are less strict than the requirements to boundaries (contacts) between grains

in compact polycrystalline or powder material. That is determined by strong anisotropy of properties of high-temperature superconductors, plate morphology majority of it's grains, features of superconducting current flow (restrictions, bound with length of coherency of Cooper pairs) as opposed to a current flow in metal bodies.

3. The formation of grains of the 2223 phase happens in two stages: the nucleating of the 2223 phase (in absence of the additive of 2223 phase in oxide precursor, nucleating can occur by an intercalation of padding ions in the lattice of 2212 phase); upgrowth of nucleuses at the expense of elements inflow from the liquid phase, in which grains of the 2212 phase that were not becoming nucleuses of 2223 phase (in conditions of "competition" of processes of nucleating and upgrowth it possible at the expense of fluctuations of phase's composition or other factors), and other phases included in composition of oxide precursor (primarily, containing Ca and Cu) are diluted. Depending on parameters of technological process, any of these two stages can predominate. For example, when material's composition is close to that of the 2223 phase, the formation of a great many of nucleuses of this phase is observed and as the result of that, the structure of the sintered ceramic contains more dispersible grains than that of compositions retrieved by stoichiometry of the 2223 phase, in which upgrowth of grains predominates. Probably the technological differences played their role in the literature's disagreement on two basic mechanisms of the 2223 phase's formation—"intercalation" and "nucleation and grains growth".

4. Because the formation of contacts between grains of the 2223 phase can occur only after their upgrowth is terminated, this process biased that time of last stage of sintering and contact necks' formation between grains of oxide precursor (similar to sintering of particles in powder materials that do not undergo chemical and structural transformations during sintering) practically have no value (except for technological conditions, when the role of intercalation during formation of the 2223 phase

is dominating). Thus, possible starting point of super-conducting contact's formation of the 2223 phase happens at the time of saturation of the 2223 phase formation and termination of "upgrowth" of samples due to intracrystalline pressure. The requirements to the structural coherence and purity of boundary between super-conducting grains are rather high, additional structural constructing of crystal lattice of adjacent grains does not occur because of the complexity of the 2223 phase's structure, therefore process of formation of quality super-conducting contacts is rather long-lived. During single-pass sequential realization of compacting and sintering the mechanism of turn with slipping is capable to speed up formation and to improve quality of contacts between superconducting grains, but is implemented only on the surface of the samples. Apparently, presence of some grain contacts and random stacking of grains obstruct its weeping despite of series of the contributing factors.

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