

The Influence of Organic Binders on the Formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ Thick Film Coatings

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X-ray diffraction, microscopic, and thermogravimetric analyses were used to study the influence of organic binders on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ thick film coating formation. It was shown by the example of 1,3-butylene glycol, terpineol, tetraethylene glycol, ethylene glycol, and glycerine that during the film synthesis the organic binder can react with the superconducting phase causing its degradation. The degree of degradation depends on heat treatment conditions of samples and the reducing power of an organic substance chosen to serve as the binding element. A transformation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ orthorhombic modification into the tetragonal one is possible at $T = 300^\circ\text{C}$ in air under the influence of strong reductants, such as tetraethylene glycol, ethylene glycol, and glycerine. In a He atmosphere at $T = 450^\circ\text{C}$ this compound completely decomposes into Y_2O_3 , BaCO_3 , and metallic Cu. When heated with 1,3-butylene glycol and terpineol in air, $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ powders do not change considerably, while in the mixture with tetraethylene glycol and glycerine they decompose completely into metallic Bi and Cu and Ca and Sr carbonates at $T = 300^\circ\text{C}$. A similar effect is produced on $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ by 1,3-butylene glycol and terpineol when heated in an inert atmosphere. It was determined that ethylene glycol and glycerine rather actively interact with the powder-like $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ even at room temperatures. © 1993 Academic Press, Inc.

1. Introduction

One of the frequently used techniques for obtaining thick films of Y- and Bi-containing high-temperature superconductors is the screen-printing method, which consists in the application of a paste made of a finely dispersed superconducting powder and a liquid binder, on the surface and subsequent heat treatment (1). Widely available organic substances, such as ethanol, ethylene glycol, glycerine, toluol, high-molecular alcohols, amines, and various liquid composites, are used as the binding component. That is why the high-temperature superconducting thick films technology based on the screen-printing method and similar techniques (painting, spraying) necessarily includes a stage of preliminary heat-treatment at relatively low temperatures (200–600°C) to remove the organic component of the paste

and to densify the superconducting layer, as well as to orient, if possible, grains on the substrate surface. The coatings obtained are heat-treated, as a rule, in an oxidizing atmosphere; the interaction between the powder and the binder is assumed to be absent. The thick film coatings are also given a heat-treatment in an argon or helium atmosphere to improve their quality and service characteristics. At the same time there are some indirect data showing that the interaction of the superconducting material with the binder is probable enough and can be the cause of its degradation. For example, the study of vapor-phase (300–450°C) oxidation reactions of organic substances by using the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder as a catalyst testifies that some of them reduce Cu in the catalyst to Cu_2O (2). It has been also reported about the decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ accompanied by the formation of

BaCO₃ after it has contacted with organic polymers at 300–650°C (3). We therefore thought it interesting to obtain a more detailed information on the mechanism and nature of the influence the organic substances used as a binder or plastifier in thick film coating synthesis exert on superconducting cuprates. In the present paper we publish the results of our investigations of the interaction between the YBa₂Cu₃O_{7-δ} and Bi_{2-x}Pb_xCa₂Sr₂Cu₃O_y powders and 1,3-butylene glycol and glycerine heated in air and He atmospheres. We have also studied the influence of these organic substances on some other Cu oxide compounds, in particular, Y₂Cu₂O₅, Y₂BaCuO₅, BaCuO₂, and CuO.

2. Experimental Techniques

The YBa₂Cu₃O_{7-δ} powder obtained by the solid state reaction method from Y₂O₃, CuO, and BaO₂ (4) was used. According to X-ray investigations, the synthesized sample did not contain any impurities and had an orthorhombic structure with the following parameters: $a = 3.818 \pm 0.003 \text{ \AA}$, $b = 3.885 \pm 0.003 \text{ \AA}$, $c = 11.656 \pm 0.006 \text{ \AA}$. The chemical analysis data show that the value of δ characterizing the oxygen content in YBa₂Cu₃O_{7-δ} was 0.12 ± 0.02 . It was established by electrical resistivity measurements that its transition in the superconducting state occurs at 92 K.

Bi_{2-x}Pb_xCa₂Sr₂Cu₃O_y ($x = 0.3$ and 0.5) was synthesized by the solid state reaction method from Bi₂O₃, PbO, CuO, and Ca and Sr carbonates. The mixture of these reagents was thoroughly ground with ethanol in an agate mortar, dried, pressed into pellets, and preliminarily annealed at 700°C for 12 hr. After that the samples were ground again, pressed into pellets, and annealed in air, the temperature being gradually increased from 800°C up to 850°C ($x = 0.5$) and 855°C ($x = 0.3$). The total time of annealing at maximal temperatures was 60 hr. The annealing temperature was controlled with accuracy $\pm 0.5^\circ\text{C}$. The presence and concen-

tration of the 2223-type phase was determined by X-ray phase analysis and electrical resistivity measurements. The synthesized samples contained mainly the 2223-type phase and a small quantity of the Cu₂PbO₄ impurity. At 290 K, the ceramic samples had electrical resistivity $2.1 \cdot 10^{-3}$ ($x = 0.3$) and $2.4 \cdot 10^{-3}$ Ohm · cm ($x = 0.5$) and $T_C = 110$ K. The Y₂Cu₂O₅, Y₂BaCuO₅, and BaCuO₂ compounds were obtained from Y₂O₃, CuO, and BaO₂ in air at 930°C. According to the X-ray phase analysis data, all the samples were monophase. The pastes were prepared by mixing the powders, the grain size of which was not more than 5 μm, with organic liquid until a gel-like mass was formed. In order to perform X-ray analysis of the heat treatment products, the pastes were painted on ceramic beryllium oxide substrates in the form of 200 μm thick layers and heated in a tube furnace with a controllable gaseous atmosphere. After each heating cycle the internal surface of the furnace was washed with ethanol to remove binder thermolysis products. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) of the pastes with the ratio between hard and liquid components 5:1 were carried out in platinum crucibles by Q-1500 D derivatograph, the heating rate in air being 10 degrees/min. The phase analysis was carried out in CuKα radiation by means of X-ray diffractometer DRON-3 and polarizing microscope POLAM C2112 making use of the optical immersion control technique.

3. Results and Discussion

3.1. The YBa₂Cu₃O_{7-δ} System and Other Ternary Cuprates

The data obtained show that YBa₂Cu₃O_{7-δ} rather actively reacts with all the above-mentioned organic substances. The character and degree of reagents transformation depend on the heat-treatment conditions and reducing power of the binder.

Figure 1 gives X-ray patterns of the initial YBa₂Cu₃O_{7-δ} sample and that annealed with

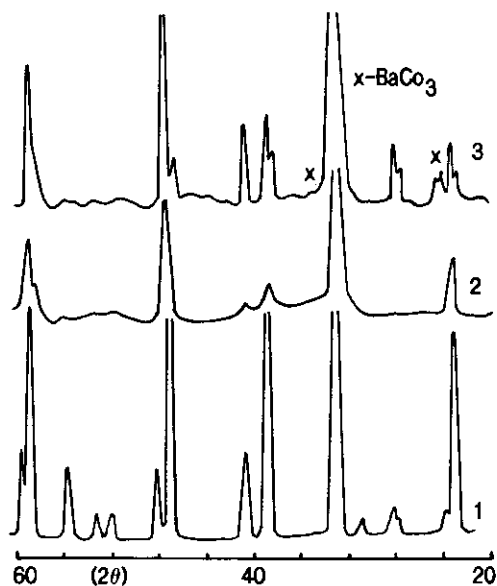


FIG. 1. X-ray patterns of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ orthorhombic modification (1) and of the same sample annealed in air in contact with tetraethylene glycol at 270°C (2) and 300°C (3) for 30 min.

tetraethylene glycol in the form of thick film coatings at 270 and 300°C for 30 min in air. As is seen, under these conditions $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transforms from the rhombic modification into the tetragonal one under the influence of tetraethylene glycol. This transformation is the result of decreased oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which is observed already at $T = 250^\circ\text{C}$. The elementary cell parameters of the tetragonal phase change together with the heat-treatment temperature: $a = 3.847$, $c = 11.670 \text{ \AA}$ at 270°C; $a = 3.850$, $c = 11.820 \text{ \AA}$ at 300°C. The character of the parameters changes showing that oxygen deficiency increases as the temperature of annealing rises. At $T = 270^\circ\text{C}$ barium carbonate crystals appear in the samples in the form of small colorless grains and aggregations with random extinction. After having been heated to 900°C, BaCO_3 grains form twins with the refraction parameters ($N_g = 1.677$, $N_p = 1.529$) corresponding to the data (5). $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ undergoes analogous transformations when

contacting under similar conditions with ethylene glycol and glycerine, which are somewhat more active than tetraethylene glycol.

Figure 2 presents a thermogram of the paste made of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder and ethylene glycol. Exothermic effects at 220 and 372°C on the DTA curve are due to the interaction of the components, which leads to catalytic oxidation of ethylene glycol and reduction of Cu. The increase of the sample mass observed at 250 and 500°C is connected, apparently, with Cu oxidation by oxygen contained in the air. The endothermic effect at 810°C is caused by a polymorphous transformation in BaCO_3 . Though Y_2O_3 and CuO are not found in the product by the X-ray method, the appearance of BaCO_3 indicates that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ partially decomposes in the process of interaction with the organic binder. The transformation of BaO into BaCO_3 occurs due to its interaction with one of the binder oxidation products. This is proved by the following investigation results of the transformations of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in contact with organic substances in a He atmosphere.

The processes considered are much more intensive in a He atmosphere. Indications

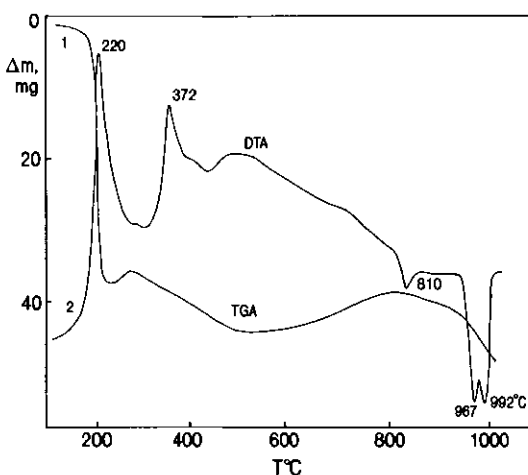
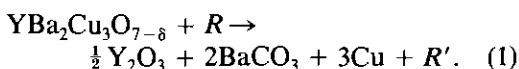


FIG. 2. The TGA (1) and DTA (2) curves of the paste made of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and tetraethylene glycol taken in the ratio 1 : 10.

of orthorhombic-to-tetragonal transformation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and those of BaCO_3 formation are revealed after the sample annealing at about 200°C . Above 450°C , $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ decomposes completely forming Y_2O_3 , BaCO_3 , and metallic Cu, which gives a reddish shade to the films. The films obtained by annealing the pastes containing 1,3-butylene glycol, terpineol, tetraethylene glycol, ethylene glycol, and glycerine at 930°C for 10 min, acquired a red color and metallic conductivity. The process of the superconducting phase transformation under these conditions can be roughly represented as follows, the chemical behavior analysis of organic substances (*R*) in oxidation reactions being not taken into account:



It is interesting to study the influence of organic binders on simple and complex Cu oxides. It was established in this investigation that in the series of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, Y_2BaCuO_5 , $\text{Y}_2\text{Cu}_2\text{O}_5$, BaCuO_2 , and CuO compounds, CuO reacts with them least actively. After having been annealed in the mixture with tetraethylene glycol at 500°C in a He atmosphere, CuO only partially transforms into Cu_2O , while the other substances decompose completely forming metallic Cu. The analysis results of the products of interaction between Cu oxide compounds and tetraethylene glycol exposed to 930°C for 10 min are given in the Table I.

The other organic compounds studied exert a similar influence on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 930°C in an inert atmosphere.

DTA and TGA methods were used to investigate the processes occurring when the reaction products (*I*), obtained as a result of interaction of ethylene glycol and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 930°C in an He atmosphere for 30 min, are heated in air. As is seen in Fig. 3, two exothermic effects (at 310 and 480°C) correspond to Cu oxidation, which begins at about 200°C . On the TGA curve

TABLE I

DECOMPOSITION OF Cu OXIDE COMPOUNDS UNDER THE INFLUENCE OF TETRAETHYLENE GLYCOL AT 930°C IN AN He ATMOSPHERE FOR 10 min

Composition	Identified reaction products
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	Y_2O_3 , BaCO_3 , Cu
Y_2BaCuO_5	Y_2O_3 , BaCO_3 , Cu
$\text{Y}_2\text{Cu}_2\text{O}_5$	Y_2O_3 , Cu
BaCuO_2	BaCO_3 , Cu
CuO	CuO , Cu_2O , Cu

there can be observed three stages of oxygen absorption from air: in temperature ranges $200\text{--}400$, $400\text{--}810$, $810\text{--}870^\circ\text{C}$, and a stage where the formed oxides interact with BaCO_3 with CO_2 isolation (above 870°C). It is characteristic that in the film coating formation from products of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ decomposition by ethylene glycol in a He atmosphere, one cannot get rid of BaCO_3 in subsequent annealing in air at 980°C even for 24 hr.

3.2. The $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ System.

The degradation of the powder-like $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ is more considerable

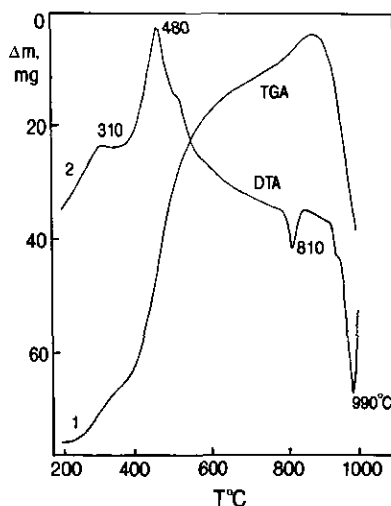


FIG. 3. The TGA (1) and DTA (2) curves of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ reduced by tetraethylene glycol at 930°C in a He atmosphere.

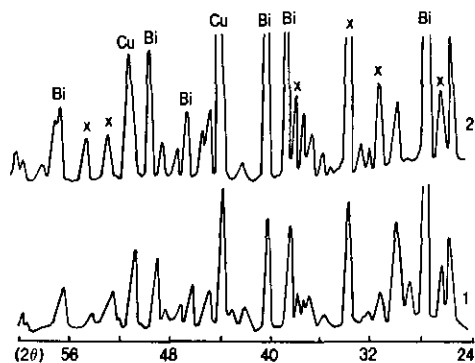


FIG. 4. X-ray patterns of $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ heated in the mixture with tetraethylene glycol in air up to 330°C (1) and in a He atmosphere up to 800°C (2). (x), unidentified phase.

under the influence of organic binders. This can be seen from the analysis of the products of their interaction heated in air. For example, when glycerine-, ethylene glycol-, and tetraethylene glycol-based pastes are heated in air, the superconducting phase decomposes completely forming elementary Bi and Cu, as well as Ca and Sr carbonates and their solid solutions. As is seen from the X-ray patterns presented in Fig. 4, the heating of the $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ + ethylene glycol paste in air and an He atmosphere up to 300°C gives almost similar results. However, further increase of temperature in air, as distinct from the He atmosphere, leads to the oxidation of Bi and Cu formed in reactions with ethylene glycol and, when the temperature reaches 550°C , Cu oxides, Bi_2O_3 , Ca, and Sr carbonates are found in the sample. The peaks in Fig. 4 marked with crosses belong to an unidentified phase, which is likely to contain Pb. X-ray patterns of the powders heated under similar conditions in a mixture with tetraethylene glycol and glycerine do not differ from those in Fig. 4.

Figure 5 presents a thermogram of the paste containing 80 mass% of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ and 20 mass% of ethylene glycol, which was recorded immediately after its preparation. The DTA and TGA curves show that the oxidation-reduction process

of the interaction between the paste components in air is accompanied by exothermic effects with maxima at 50, 242, and 398°C and the mass decrease. If we take into account that ethylene glycol boils at 197.6°C and does not decompose (6), the observed three-stage decrease of the sample mass cannot be explained by its evaporation. At $T = 400^\circ\text{C}$ the sample mass increases again due to Bi and Cu oxidation by oxygen contained in the air. The oxygen absorption process is completed at about 600°C . At $T = 600^\circ\text{C}$ the mass decreases again, but this time mainly as a result of decomposition of carbonates reacting with Bi and Cu oxides. The endothermal effects at 730, 805, 860, 900, and 960°C correspond to these reactions and the products melting.

A sloping transition of the DTA curve in a maximum at 50°C can be explained by the fact that the interaction of ethylene glycol with the hard component of the paste begins at a lower temperature. Indeed, after the paste has been held at 22°C for 2 hr there appear bluish prismatic crystals of a phase with an unidentified composition. They have high refraction ($N_p = 1.785$) and low double refraction values. An X-ray pattern of the product obtained by such treatment is given in Fig. 6. Being heated up to $T = 50^\circ\text{C}$, the crystals are dissolved in ethylene glycol and the mass formed hardens in the form of glass. In water, the glass hydrolyzes

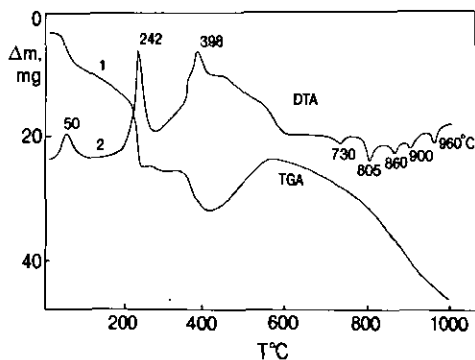


FIG. 5. The TGA (1) and DTA (2) curves of the paste containing 80 mass% of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ and 20 mass% of ethylene glycol.

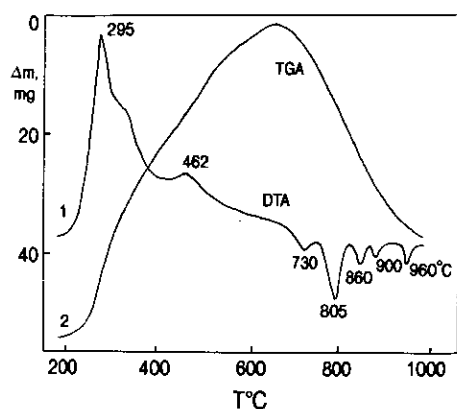


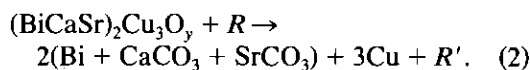
FIG. 6. The DTA (1) and TGA (2) curves of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ preliminarily affected by 1,3-butylene glycol when heated up to 800°C in a He atmosphere.

easily and transforms into a blue X-ray-amorphous mass. A similar transformation is also characteristic of the glycerine-based paste, but in this case the process is slower, probably, due to high viscosity of glycerine. Three exothermal effects with maxima at 68, 235, and 397°C correspond to the interaction of the paste components. At $T = 100^\circ\text{C}$ the paste acquires a reddish shade, which becomes more intense as the temperature rises further. The analysis of a cooled sample by microscopy shows that the sample is a blue glass with inserted very tiny grains of a black opaque phase, which is considered to be elementary copper according to the X-ray phase analysis data. Tetraethylene glycol is not very active at room temperature and, apparently, that is why the DTA curve of the paste based on it has only two pronounced peaks with maxima at 243 and 395°C . It should be pointed out that on the DTA curves of glycerine- and tetraethylene glycol-based pastes there were also observed endothermic peaks with minima at 730, 805, 860, 900, and 960°C .

The data of X-ray phase and microscopic analyses show that, when heated in air, 1,3-butylene glycol and terpineol do not produce any noticeable effect on $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$. At the same time in an inert atmo-

sphere they behave as rather strong reductants and destroy the material of the superconducting phase reducing Bi and Cu to metals. Figure 7 presents DTA and TGA curves of the 2223-phase with $x = 0.3$, which was preliminarily affected by 1,3-butylene glycol while heated up to 800°C in a He atmosphere. The exothermic effect on the DTA curve with a maximum at 295°C associated with a sharp increase of the sample mass is caused by the oxidation of metallic Bi. The process of Cu oxidation completes at 650°C .

The presence of the peaks on the DTA curve with minima at 730, 805, 860, 900, and 960°C (Figs. 5 and 7) indicates that the decomposition of $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ under the influence of various organic substances occurs in accordance with a common mechanism with the same products being formed. If one does not analyze the chemical behavior of organic substances (R) in oxidation reactions and the role of Pb in them, the transformation process of Bi-containing high-temperature superconductors heated in contact with the binder can be represented in the following way:



The formation of CaCO_3 and SrCO_3 both in air and an inert atmosphere shows that this process is the result of the interaction be-

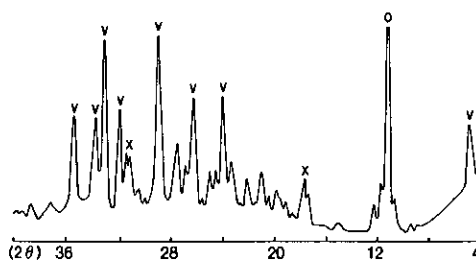


FIG. 7. The X-ray pattern of the paste with the composition $\text{Bi}_{1.7}\text{Pb}_{0.5}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ + ethylene glycol held at room temperature for 12 hr. The curve of the 2223-type phase, which did not react, and that of Ca_2PbO_4 are marked by (V) and (X), respectively. (O), unidentified phase.

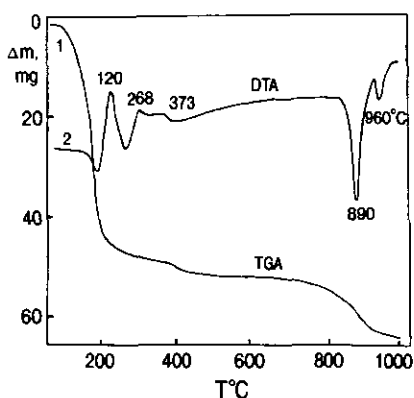


Fig. 8. The TGA (1) and DTA (2) curves of the paste containing 80 mass% of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$, and 20 mass% of 1,3-butylene glycol.

tween the products of R oxidation (possibly, carboxylic acids) and oxides of these elements appeared due to the superconducting phase decomposition. SrCO_3 formed at low temperatures does not disappear even after prolonged annealing at 850°C . As the temperature rises, initially very small SrCO_3 crystals become larger and acquire a prismatic form. The measured refraction parameters of the crystals are close to the reference data: $N_g = 1.669$, $N_m = 1.667$, $N_p = 1.520$ (5). In order to completely decompose SrCO_3 and obtain the 2223-type phase, a thorough grinding is needed, which is possible only for a bulk sample, but not for films.

The study of chemical reactions in Bi-based pastes heated in inert and oxidizing atmospheres shows that among the chosen organic substances 1,3-butylene glycol is the least active reductant, which, as has been pointed out earlier, does not cause any changes in the $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ powder in air. The DTA and TGA curves (Fig. 8) of the paste containing 1,3-butylene glycol do not differ considerably from those presented in Fig. 5. Endothermic effects at 890 and 960°C on the DTA curve correspond to the points of incongruent melting of the pure superconducting phase. The decrease of the sample mass observed on the TGA curve at 500°C corresponds to the content

of 1,3-butylene glycol in the paste before heating. Therefore, no carbonization of the hard component of the paste occurs under the influence of 1,3-butylene glycol, though an insignificant reduction of Bi and Cu in it is possible, which is not distinguished by the phase analysis methods used in the experiment. The DTA curve of the terpeneol-based paste is characterized by three weak exothermic effects with peak maxima at 120 , 268 , and 393°C . A slight increase of the mass in the range 400 – 500°C , which does not affect the location of the points of incongruent melting of the powder material (890 and 960°C) is likely to be connected with a partial reduction of Bi and Cu when no noticeable amount of Ca and Sr carbonates is formed. The TGA analysis data, in particular, the value of the sample mass decrease (Δm , mass%) down to the minimum point on the TGA curve (Fig. 5), allow one to approximately evaluate the reducing power of an organic substance. The value of Δm calculated from the TGA curves for 1,3-butylene glycol, terpeneol, tetraethylene glycol, glycerine, and ethylene glycol are 100 , 97 , 92 , 79 , and 73 mass%, respectively. Consequently, the closer the value of Δm is to 100% , the lower the interaction of the paste components. Another criterion for evaluating the reducing power of organic binders can be the value of subsequent increase of the sample mass (Fig. 5) caused by Bi and Cu oxidation by oxygen contained in the air at higher temperatures.

4. Conclusions

Thus, the data obtained in this work show that in the formation of thick film superconducting coatings the powder-like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ can interact with an organic binder. The degree of degradation of the superconducting phase is determined by the film heat-treatment conditions and reducing power of the organic substance serving as the binder. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the process occurring in air at 200 – 300°C is limited to the transformation

of the orthorhombic modification into the tetragonal one and the formation of a small amount of BaCO_3 . A more complicated mechanism is observed in an inert atmosphere leading to the decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ into its initial components: Y_2O_3 , BaCO_3 , and metallic Cu. The $\text{Bi}_{2-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ powders are influenced by ethylene glycol and glycerine already at room temperatures, though the mechanism of this interaction is not yet quite clear. When heated in air and an He atmosphere, these organic substances, as well as tetraethylene glycol, destroy the superconducting phase forming Ca and Sr carbonates and metallic Bi and Cu. 1,3-butylene glycol and terpineol, which are almost inactive in air, react rather intensively with Y- and Bi-containing superconducting cuprates causing their degradation. In this connection it is necessary to note that heat-treatment in an Ar or He atmosphere often used to improve the quality of coatings should be carried out only after complete removal of the binder.

The presence of traces of even a relatively weak organic reductant can result in rather considerable changes in the coating composition.

References

1. G. P. SHVEIKIN, V. A. GUBANOV, A. A. FOTIEV, G. V. BAZUEV AND A. A. YEVDOKIMOV, "The Electronic Structure and Physico-Chemical Properties of High-Temperature Superconductors," 239 pp., Moscow, Nauka (1990).
2. J. C. OTAMIRI, S. L. T. ANDERSSON, AND A. ANDERSSON, *Appl. Catal.* **85**(1), 159 (1990).
3. A. V. STRATONOV, L. A. SOKOLOVA, A. V. KLIMENKO, *et al.* *SFKhT Sverkhprovodimost Fiz. Khim. Tekhn.* **9**(9), 2086 (1990).
4. M. LESKELA, C. H. MUELL, T. K. TRUMAN, AND P. H. HOLLOWAY, *Mater. Res. Bull.* **23**(10), 1469 (1988).
5. A. N. VINCHELL, AND G. VINCHELL, "Optical Properties of Artificial Minerals," 526 pp., Mir, Moscow (1967).
6. I. L. KNUNYANTS (Editor-in-Chief), "Chemical Encyclopedia," p. 718, Sovetskaya Entsiklopedia, Moscow (1983).