Preparation and reactivity of metal containing monomers
42.* Copolymerization of metal containing monomers as a route for the synthesis of the precursors of high temperature superconducting ceramics

A. D. Pomogailo,[a] V. S. Savost'yanov,[b] G. I. Dzhardimalieva,[a] A. V. Dubovitskii,[a] and A. N. Ponomarev[b]*

[a] *Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 265 5714
[b] *Branch of the Institute of Energetic Problems of Chemical Physics, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation

The preparation of HTSC ceramics based on Y^{III} and Bi^{III} was studied. The polymers were obtained by two methods: by the reaction of preliminarily synthesized polyacrylic acid (PAA) or polyacrylamide (PAAm) with Y^{III}, Ba^{II}, and Cu^{II} nitrates or by copolymerization of metal containing monomers (metal (Y^{II}, Ba^{II}, and Cu^{II}) acrylates or acrylamide complexes of metal (Bi^{III}, Ca^{II}, Sr^{II}, Pb^{II}, and Cu^{II}) nitrates). The copolymerization was carried out in solution, in the solid phase, or using spontaneous polymerization, which has been previously discovered by the authors. The properties of the HTSC ceramics obtained are improved when the products of copolymerization of metal containing monomers are used.

Key words: HTSC ceramic, metal acrylate, acrylamide complex, copolymerization, polyacrylic acid, polyacrylamide, polyacrylamide complex, metal containing monomer.

The traditional methods for preparing batches of high-temperature superconducting (HTSC) ceramics (direct mixing of oxides, carbonates, oxalates, nitrates, and other salts of the corresponding metals) have substantial limitations regarding their reproducibility. This is associated not only with the quality of grinding and stirring of the starting solid components, but also with the complex physicochemical and mechanochemical transformations that occur during the preparation of the samples. As a consequence, heterogeneities at the microscopic level arise, and various phases, including nonconducting phases, are formed, which results in low-quality HTSC ceramics with a smeared superconductor transition (ST).

In recent years some papers dealing with the preparation of HTSC ceramics *via* the preliminary synthesis of polymers have been published. This method makes it possible to approach the solution of the above-mentioned problem. The method involves the use of a polymeric matrix containing metal ions dispersed at a molecular level. For example, one of its versions is the preparation of polymeric complexes of Y^{III}, Ba^{II}, and Cu^{II} nitrates with polymethacrylic acid using polymer-analogous transformations.[1,2] Other techniques for the synthesis of HTSC ceramics *via* the preliminary preparation of a polymer are also possible. For example, it has been suggested that acrylic acid (AA) be polymerized in a mixture with an aqueous solution of Y^{III} nitrate and Ba^{II} and Cu^{II} acetates.[3] However, in these cases, the composition of the resulting metal containing polymer is quite uncertain, which is a drawback of polymer-analogous transformations in macroligand—metal compound systems.[4]

A much more homogeneous distribution of metal ions can be achieved when these ions are introduced into monomer molecules prior to the synthesis of the polymer, and then polymerization is carried out. Copolymerization of the corresponding metal containing monomers should afford a polymeric matrix with a controlled distribution of metal ions.[5] The polymeric chain will certainly be free of functional groups not bound to metal ions.

Therefore, in the present paper we compared two methods for the synthesis of the polymeric precursors of HTSC ceramics: (1) the preparation of metallopolymer complexes through polymer-analogous transformations and (2) copolymerization of metal containing monomers.

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Experimental

Acrylic acid (AA) was purified by distillation under reduced pressure, acrylamide (AAm) was recrystallized from benzene, and the metal nitrates $Y(NO_3)_2 \cdot 6H_2O$, $Ba(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Bi(NO_3)_2 \cdot 5H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, and $Pb(NO_3)_2$ of "pure" or "chemically pure" grades were used as received. Polyacrylic acid (PAA) was synthesized by radical polymerization of AA in the presence of 2 % azoisobutyronitrile, and polyacrylamide (PAAm) was prepared by radical polymerization in acetone through the action of ^{60}Co γ-radiation.

Macromolecular complexes were synthesized by the reaction of PAA or PAAm with a mixture of Y^{III}, Ba^{II}, and Cu^{II} nitrates in a molar ratio of 1 : 2 : 3 in ethanol with an excess of the macroligand ($[COOH] : [MX_n]$ = 6 to 10 : 1, $[CONH_2] : [MX_n]$ = 10 : 1, where MX_n is the metal compound). The complexes were precipitated from the ethanolic solution by diethyl ether, and the unchanged components were washed out.

Y^{III}, Ba^{II}, and Cu^{II} acrylates were prepared by the previously described procedure.[6] The monomers obtained were mixed in a 1 : 2 : 3 molar ratio, dissolved in the minimum amount of methanol, and dried. Solid mixtures of AAm complexes of metal nitrates were prepared by mixing $Y(NO_3)_2 \cdot 6H_2O$, $Ba(NO_3)_2$, and $Cu(NO_3)_2 \cdot 3H_2O$ (in 1 : 2 : 3 molar ratio) with AAm in an [AAm] : [nitrates] molar ratio of 4 : 1. The mixture was dried at room temperature and evacuated. The monomeric mixtures thus obtained were processed using tools like Bridgman anvils under a pressure of 1 GPa and at room temperature; the angles of rotation of the anvils reached 500°.

Y^{III}, Ba^{II}, and Cu^{II} containing tercopolymers are green materials insoluble in organic solvents. In the case of the copolymer derived from metal acrylates, the molecular weight of PAA after the removal of metal ions from the copolymer was ~40000 Da. As shown by magnetic measurements, the oxidation numbers and the coordination states of the metal ions remained unchanged during polymerization.

To obtain metal containing polymers, *viz.*, the precursors of HTSC ceramics, spontaneous copolymerization of AAm complexes of metal nitrates in concentrated aqueous solutions was carried out.[7] AAm was added to a mixture of Bi^{III}, Pb^{II}, Sr^{II}, Ca^{II}, and Cu^{II} nitrates taken in a molar ratio of 2 : 0.3 : 2 : 2 : 3; the [AAm] : [nitrates] molar ratio was 4 : 1. The mixture was stirred until water appeared in the system, which indicated the formation of AAm complexes. The resulting blend was kept for 48 h at 20 °C. A blue-green-colored glass-like polymer containing water was formed during this storage.

In order to burn out the organic phase, the metal containing copolymers were subjected to thermal treatment in air for 2—10 h at 800 °C. The mixture of metal oxides formed was dispersed in a planetary ball mill and pressed into pellets of 10 mm diameter and 1—2 mm height, and then the main thermal treatment in air for 5 h at 920 °C (in the synthesis of Y^{III} containing ceramics) or for 60 h at 850 °C (in the synthesis of Bi^{III} containing ceramics) was carried out. The samples were cooled at a rate of 50 deg h^{-1}; no additional annealing in oxygen was carried out.

The superconductor properties of the ceramics synthesized were studied by measuring the temperature dependences of the electric resistivity and diamagnetic susceptibility. The resistivity was measured by the standard four-contact method using 956 Hz alternating current; the diamagnetic susceptibility was measured by the inductive method using alternating current with a frequency of approximately 1 kHz.

The mass spectrometric analysis of the gases evolved during the vacuum thermal treatment was carried out at an ionizing potential of 17 V, an accelerating potential of 3 kV, and a rate of heating of 4 deg min^{-1}.

The critical currents in the superconducting ceramics were measured at 77 K by the transformer method. For this purpose, rings of 10 mm diameter and 1 mm^2 cross-sectional area were cut out of the pellets of the ceramic samples under study. The volume densities of the samples were measured by the pycnometric method in the course of the stepwise synthesis with intermediate grinding and pressing of the samples.

The complex thermal study was carried out in air using a C MOM derivatograph (Hungary) at a rate of heating of 5—10 deg min^{-1} in the 20—700 °C temperature range. The calorimetric measurements were carried out using a DSM-3 differential scanning microcalorimeter (the "Biopribor" design office, Pushchino). The X-ray diffraction patterns of the powders obtained after burning-out the organic phase were measured on a DRON-UM-2 diffractometer using Cu(Kα) radiation. The phase identification of the samples of ceramics obtained was carried out using a Siemens X-ray diffractometer with Cu-K_{21} monochromic radiation. The IR spectra of the polymers were recorded on a Perkin-Elmer FI-IR 1720x instrument. The samples were prepared as pellets with KBr.

Results and Discussion

Synthesis of HTSC ceramics via the precursors obtained by polymer-analogous transformations. The polymer-analogous reactions of macroligands with MX_n were monitored by IR spectroscopy. In addition to the main absorption bands (AB) at 1530 cm^{-1} corresponding to ν(COO$^-$) stretching vibrations, the IR spectra of the products of the reaction of PAA with Y^{III}, Ba^{II}, and Cu^{II} nitrates exhibit a broadened band with a maximum at 440 cm^{-1} corresponding to the M-OOC overall vibrations. In the spectra of the products of the reaction of PAAm

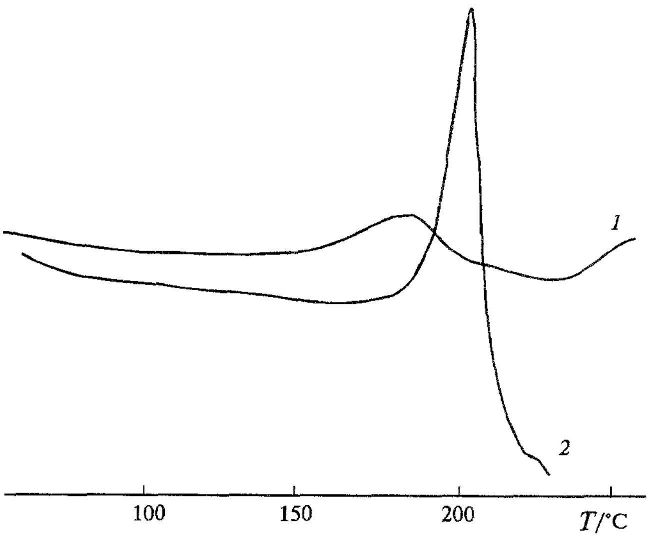

Fig. 1. DSC curves for the products of the reaction of Y^{III}, Ba^{II}, and Cu^{II} nitrates with PAA (*1*) and PAAm (*2*); the rate of scanning was 8 deg min^{-1}.

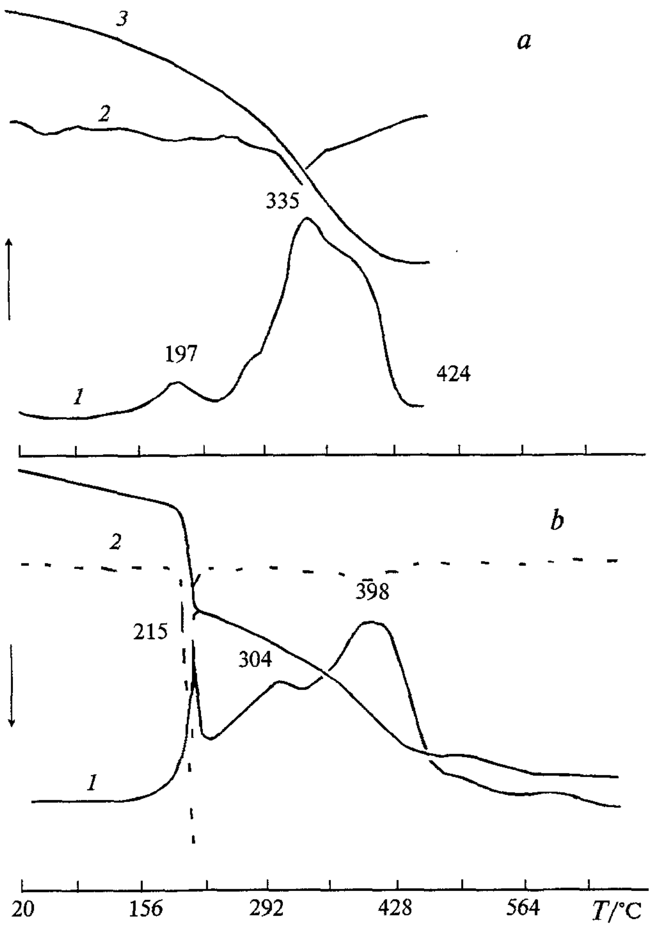

Fig. 2. DTA (*1*), DTGA (*2*), and TGA (*3*) curves of the products of the reaction of Y^{III}, Ba^{II}, and Cu^{II} nitrates with PAA (*a*) and PAAm (*b*).

with the same MX_n, the absorption bands are shifted from 1680 to 1660 cm^{-1} (ν(C=O)) and from 3400 to 3390 cm^{-1} (ν(N—H)). This confirms that the metal ions are coordinated to the macroligand. The shift of these AB is also averaged over the corresponding values for the complexes of all three of the metal ions.

The burning-out of the organic phase from the metal containing polymers obtained occurred rather readily. According to the data of differential scanning calorimetry (DSC) (Fig. 1), the greatest heat evolution during the heating of the precursors of Y^{III} ceramics occurred in the 140—200 °C region for the PAA-based systems and in the 170—220 °C region for the PAAm-based systems. Thermal decomposition of the macro-complexes probably begins with the abstraction of water molecules. The DTA curve of the product of the reaction of PAA with Y^{III}, Ba^{II}, and Cu^{II} nitrates (Fig. 2, *a*) exhibits exoeffects at 197 and 335 °C; the first section corresponds to the loss of 25 % of the mass of the sample, and in the second section, the loss of mass is 70 %. In the case of PAAm complex, 32.4 % of the mass of the sample is lost in the first section, *viz.*, below 212 °C; at 361 °C, the loss of mass is 50 %. The overall loss of the mass of the macromolecular PAAm complex in the 20—575 °C temperature range reaches 71.4 %. One may believe that decomposition of the ligand in these systems is completed below 450 °C.

The resulting mixture of metal oxides (X-ray phase analysis), after the corresponding thermal treatment, dispersion, and pressing, possesses superconducting properties (Fig. 3). However, the temperatures of the superconductor transition (ST), T_C, are low (62 and 92 K for Y^{III} ceramics obtained using PAA and PAAm as macroligands, respectively), and the ST is smeared.

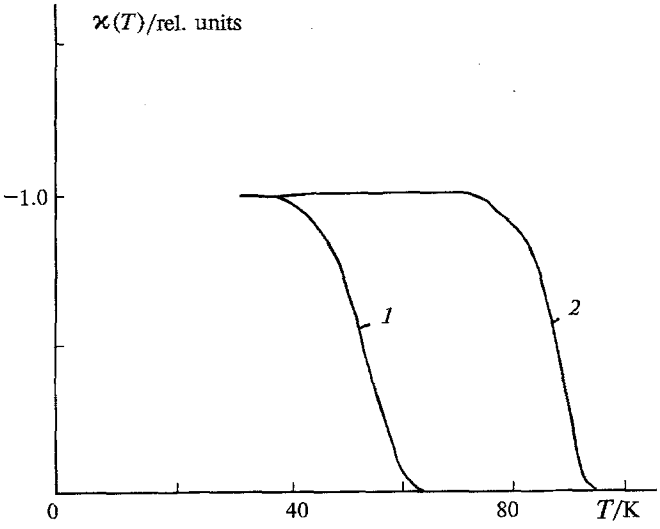

Fig. 3. Temperature dependences of the magnetic susceptibility of HTSC ceramics prepared from the products of the reaction of Y^{III}, Ba^{II}, and Cu^{II} nitrates with PAA (*1*) and PAAm (*2*).

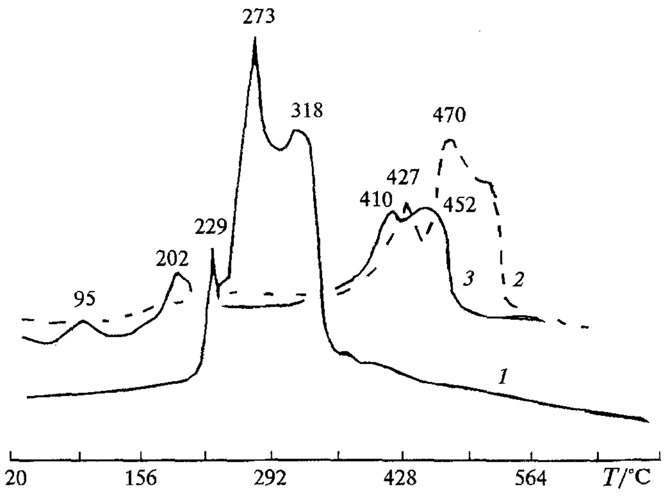

Fig. 4. DTA data for a mixture of Y^{III}, Ba^{II}, and Cu^{II} acrylates (*1*), the copolymer of Y^{III}, Ba^{II}, and Cu^{II} acrylates (*2*), and the product of spontaneous polymerization of AAm complexes of Bi^{III}, Ca^{II}, Sr^{II}, Pb^{II}, and Cu^{II} nitrates (*3*).

These low characteristics may be due to the formation of immobilized complexes of various compositions, to the complex character of the distribution of the metal ions both throughout a chain and among the chains, to the formation of homo- and heteronuclear clusters, to the incomplete phase formation, *etc.*

Synthesis of HTSC ceramics via the products of polymerization of metal containing monomers. The decomposition of the copolymer of Y^{III}, Ba^{II}, and Cu^{II} acrylates differed substantially from that of the products of polymer-analogous transformations of PAA and nitrates of these metals. In fact, practically no thermal effects were observed up to 427 °C (Fig. 4). Decomposition of the copolymer occurs mostly between 367 and 520 °C; the loss of mass is 45.9 %. The DTA curve of the product of spontaneous polymerization of the AAm complexes of Bi^{III}, Ca^{II}, Sr^{II}, Pb^{II}, and Cu^{II} nitrates exhibits exoeffects at 95, 202, 410, and 452 °C. The loss of mass at 193 °C is 15 %, and at 356 °C, it is 50 %. In the 350—470 °C range the polymeric complex completely decomposes.

The properties of HTSC ceramics prepared from the ternary copolymer of Y^{III}, Ba^{II}, and Cu^{II} acrylates can be followed by looking at Fig. 5. An analysis of the $R(T)$ dependence shows that at $T < T_C$ these ceramics behave as a metal, though the T_C values are not so high as those of single crystals or better specimens of Y^{III} ceramics. However, one should bear in mind that the quality of the normal state of a polycrystalline specimen is to a greater extent associated with the quality of inter-grain contacts than with the quality of the structure of grains themselves. The superconductor transition is rather sharp; the 0.1—0.9 interval in the decrease in the resistivity occurs over a temperature range of no more than 2—3 K. A zero electric resistance of the sample is already achieved at 87 K, which is close to the corresponding value for the best specimens of HTSC ceramics prepared under conditions of thorough oxygen annealing. The character of the $\chi(T)$ dependence (see Fig. 5) also indicates that the transition is sharp and only one superconductor phase is present. The complete volume of the diamagnetically shielded phase evaluated using a lead reference can be as high as 100 %.

The use of polymeric precursors for the synthesis of Bi^{III} containing HTSC is of even greater interest. The reproducible synthesis of superconducting bismuth cuprates $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4-\delta}$ (n = 1 to 3) (often doped with lead) with high T_C values (110 K) is known to be a complicated problem.[8] As a rule, the resulting specimens contain an admixture of a phase with T_C = 85 K. This is due to the nonhomogeneity of the ceramics at the microscopic level and the successive transition of phases, 2201 → 2212 → 2223. However, in all of the cases where the ceramics were synthesized from the products of the spontaneous polymerization of AAm complexes of metal nitrates, single-phase materials with T_C = 110 K were obtained. Their properties are presented in Fig. 6, which shows the temperature dependences of the resistivity and the magnetic shielding signal. A 100 % shielding and narrow transitions to the superconducting state

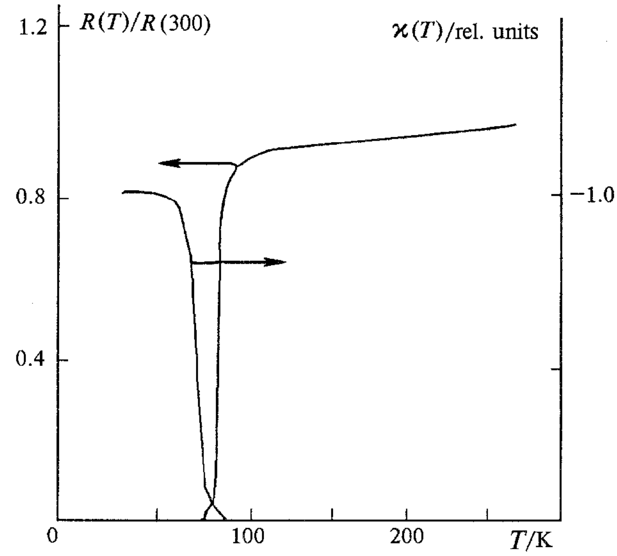

Fig. 5. Temperature dependences of the resistivity and the magnetic susceptibility of HTSC ceramics prepared from the copolymer of Y^{III}, Ba^{II}, and Cu^{II} acrylates.

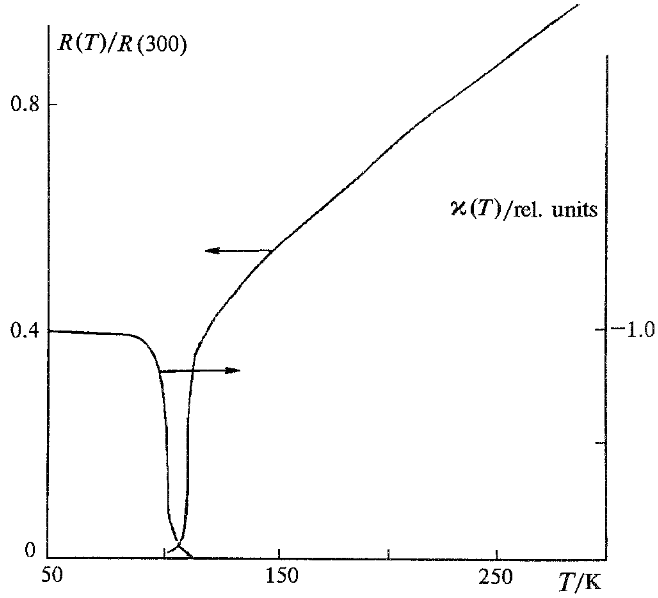

Fig. 6. Temperature dependences of the resistivity and the magnetic susceptibility of HTSC ceramics prepared from the product of spontaneous polymerization of AAm complexes of Bi^{III}, Ca^{II}, Sr^{II}, Pb^{II}, and Cu^{II} nitrates.

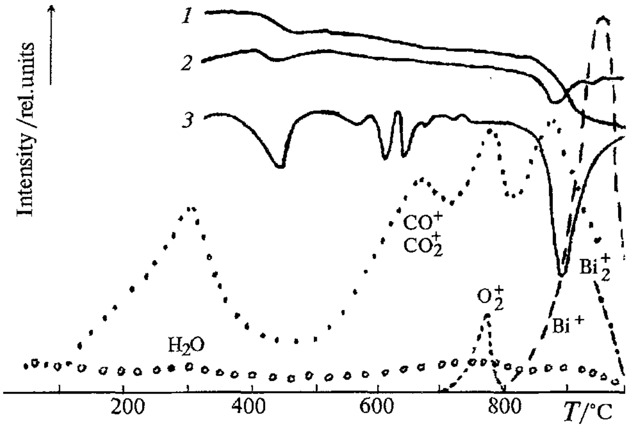

Fig. 7. Results of thermal analysis of specimens of the 2223 composition: *1*, TGA, *2*, DTA, *3*, DTGA curves. The rate of variation of the temperature was 4 deg min^{-1}; the curve for $CO^+ + CO_2^+$ is drawn on a 50 times enlarged scale.

regarding both conductivity and susceptibility are achieved. The rather large drop of the resistivity in the normal metallic state (it decreases by a factor of more than two as the temperature decreases from the ambient temperature to the beginning of the transition) is also noteworthy. The electric conductivity of the specimens at ambient temperature was as high as 800—1000 Ω^{-1} cm^{-1}. According to X-ray diffraction analysis, the compounds obtained crystallize in the pseudotetragonal system with $a = b = 5.410$ (2) Å, $c = 37.124$ (3) Å.

The temperature behavior of the precursors of bismuth containing superconducting ceramics is rather interesting. The maximum rates of the loss of mass are achieved at 420 and 870 °C. In their pure states all of the oxides that constitute the ceramics are rather stable. To find out what is evolved from the ceramics we carried out a mass spectrometric analysis of the gases liberated from bismuth containing ceramics of the composition 2223 during vacuum thermal treatment. The results of this experiment are presented in Fig. 7 together with the data of thermal analysis. A small peak of the evolution of oxygen, which is detected as O_2^+ ions, is observed in the 700—800 °C range, and a large peak corresponding to the evolution of bismuth as Bi^+ and Bi_2^+ ions occurs in the 800—1000 °C range. The maximum rate of loss of mass determined by DTG virtually coincides with the maximum rate of the evolution of Bi. The main losses of the mass of the ceramics at high temperatures are associated in a certain manner with bismuth. This result is quite unexpected; however, based of the data of X-ray photoelectron spectroscopy, Chanrachood *et al.*[9] previously suggested that ceramics contain bismuth in an oxidation state lower than +3. In addition to the main gas evolution peaks corresponding to O_2^+, Bi^+, and Bi_2^+, minor amounts of other ions, OH^+, H_2O^+, CO^+, N_2^+, NO_2^+, and CO_2^+, are detected over the whole temperature range. Thus, the ceramics formed contain only traces of residual carbon.

Another significant characteristic of ceramics is the critical current density (I_{cr}). According to our tentative data, it depends only slightly on the method of preparation. We found that the volume density (specific gravity, ρ) of the ceramics synthesized is lower than that of the starting pressed oxide batch. It is likely that during sintering of the batch, vacancies are formed in it that increase its volume. Probably there is a relationship between the number of vacancies and the critical current density in a superconductor, *i.e.*, between the specific gravity of the ceramics and the critical current density. We found this relationship in a certain interval of the volume density of the superconductor ceramics: ρ/g cm^{-3} 2.4, 3.0, 3.6, 4.2, 4.7; I_{cr}/A cm^{-3} 9.0, 20, 90, 130, 240.

Grinding is known to create new dislocations, which are drains of vacancies. The optimal conditions for sintering in the final step of the process should ensure that the branched network of dislocations, *viz.*, drains of vacancies, be preserved until all of the pores are welded.[10] The theoretical density of the 2223 bismuth ceramics is ~6.5 g cm^{-3}. Therefore, one may hope that bismuth ceramics with sufficiently great critical currents will be obtained.

It should be emphasized that copolymerization of metal containing monomers is a necessary condition for the synthesis of high-quality HTSC ceramics. The experiments on thermal treatment of nonpolymerized mixtures of monomers resulted in the formation of HTSC samples with low T_C and smeared transitions.

Thus, one may believe that copolymerization of metal containing monomers is one of the efficient routes for synthesis of high-quality HTSC ceramics. It is significant that thermal decomposition of the polymeric precursors yields highly dispersed mixtures of metal oxides. This makes it possible to rather easily obtain single-phase HTSC ceramics with T_C = 110 K. This approach is also of interest because it allows one to prepare superconducting specimens such as plates, rods, rings, *etc.*

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References

1. J. C. W. Chien, B. M. Gong, J. M. Madsen, and R. B. Hallock, *Phys. Rev.*, 1988, **38B**, 11853.
2. J. C. W. Chien, B. M. Gong, X. Mu, and Y. Yang, *J. Polym. Sci.: Polym. Chem. Ed.*, 1990, **29**, 1993.
3. I. Valente, C. Sanchez, M. Henry, and J. Livage, *Ind. Ceram.*, 1989, 1193.

4. A. D. Pomogailo, *Polimernye immobilizovannye metallokompleksnye katalizatory* [*Polymeric Immobilized Metal-Complex Catalysts*], Nauka, Moscow, 1988, 303 pp. (in Russian).
5. A. D. Pomogailo and V. S. Savost'yanov, *Metallsoderzhashchie monomery i polimery na ikh osnove* [*Metal containing Monomers and Polymers Based on Them*], Khimiya, Moscow, 1988, 384 pp. (in Russian).
6. G. I. Dzhardimalieva, A. D. Pomogailo, V. I. Ponomarev, L. O. Atovmyan, Yu. M. Shul'ga, and A. G. Starikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1525 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1346 (Engl. Transl.)].
7. V. S. Savost'yanov, V. N. Vasilets, O. V. Ermakov, E. A. Sokolov, A. D. Pomogailo, D. A. Kritskaya, and A. N. Ponomarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, 2073 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1992, **40**, 1615 (Engl. Transl.)].
8. A. V. Dubovitskii, E. F. Makarov, M. K. Makova, V. A. Merzhanov, and V. N. Topnikov, *Sverkhprovodimost': fizika, khimiya, tekhnika* [*Superconductivity: Chemistry, Physics, Engineering*], 1991, **4**, 1024 (in Russian).
9. M. R. Chanrachood, S. R. Sinkaz, I. S. Mulla, and S. Badzinazayanan, *Material Lett.*, 1989, **8**, 349.
10. Ya. E. Geguzin, *Fizika spekaniya* [*Physics of Sintering*], Nauka, Moscow, 1984, 312 pp. (in Russian).

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