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Highly Textured Bismuth-Containing High-Temperature Superconductor Ceramics Obtained by Uniaxial Pressing in Liquid Medium: Fabrication and Properties

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Abstract—A new method of fabricating textured ceramics with a composition of $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ is described, according to which the initial low-density ceramics is subjected to uniaxial pressing in a liquid medium followed by drying and annealing. Analysis of the X-ray diffraction and scanning electron microscopy data show evidence for a high degree of texture in high-temperature superconductor ceramics fabricated using the proposed method. The results of magnetic measurements indicate that the obtained material possesses anisotropy of the magnetic moment for the magnetic field **H** oriented parallel and perpendicular to the direction of uniaxial pressing. The textured ceramics also show high diamagnetic response for **H** parallel to the *c* axis of grains, which makes these ceramics promising materials for practical applications.

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There are several methods for the fabrication of textured high-temperature superconductor (HTSC) ceramics [1–6]. In particular, texture can be created by mechanical deformation using the so-called sinter-forging process [1–3]. According to this two-stage method, a material of the preset initial composition is synthesized and pressed (by uniaxial compression) in the first stage. In the second stage, the intermediate products are wrapped in a silver foil and subjected to additional uniaxial compression for a long time (several hundred hours) at a high temperature (830–860°C) and a preset compression rate. Without pressing at high-temperature in the second stage, the degree of texture is insufficiently high even upon multiply repeated separate pressing–annealing cycles [6]. This circumstance is related to the fact that cold pressing involves a high probability of grain fracture, which results in increased disorder. It was pointed out [1] that hydrostatic pressure could increase the forging ability of a processed material. However, the creation of a hydrostatic compression condition within the framework of sinter-forging method is problematic [1].

This Letter describes a relatively simple method that does not involve the stage of pressing at high-temperature, which nevertheless allows a dense, highly textured bismuth-containing HTSC ceramics to be fabricated.

The final textured ceramics was obtained proceeding from a preliminarily synthesized porous ceramics with a composition of $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ [7, 8]. This initial material consists of grains separated by microscopic pores. The grains are platelike, with a thickness of ~1 μm and linear dimensions from several units to several tens of microns. The initial porous samples with a density of 1.55 g/cm^3 had the form of disks with a diameter of 30 mm and a thickness of 7–12 mm. These disks were impregnated with ethyl alcohol and pressed in the axial direction at room temperature and a pressure of up to 250 MPa. Then, the residual ethyl alcohol was evaporated by heating the disks in a thermal box at $T = 70$°C for 5 h. The pressing led to a significant decrease in the dimensions of disks, whereby the thickness was reduced to 2–3 mm at a diameter of 30 mm (mold diameter). Finally, the pressed disks were annealed for 50 h at $T = 825$–845°C. The density of obtained ceramics was $\rho = 5.29 \pm 0.01$ g/cm^3, which amounts to 89% of the theoretical value (5.95 g/cm^3). Thus, a single pressing–annealing cycle provides HTSC ceramic disks, which are characterized by a high degree of texture and a large diamagnetic response.

Figure 1 shows the typical scanning electron microscopy (SEM) micrographs of a textured sample of $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics fabricated using the process described above. The micrographs show regions of (a) the fracture surface of a disk broken in the direction of pressing and (b, c) the flat faces of the disk.

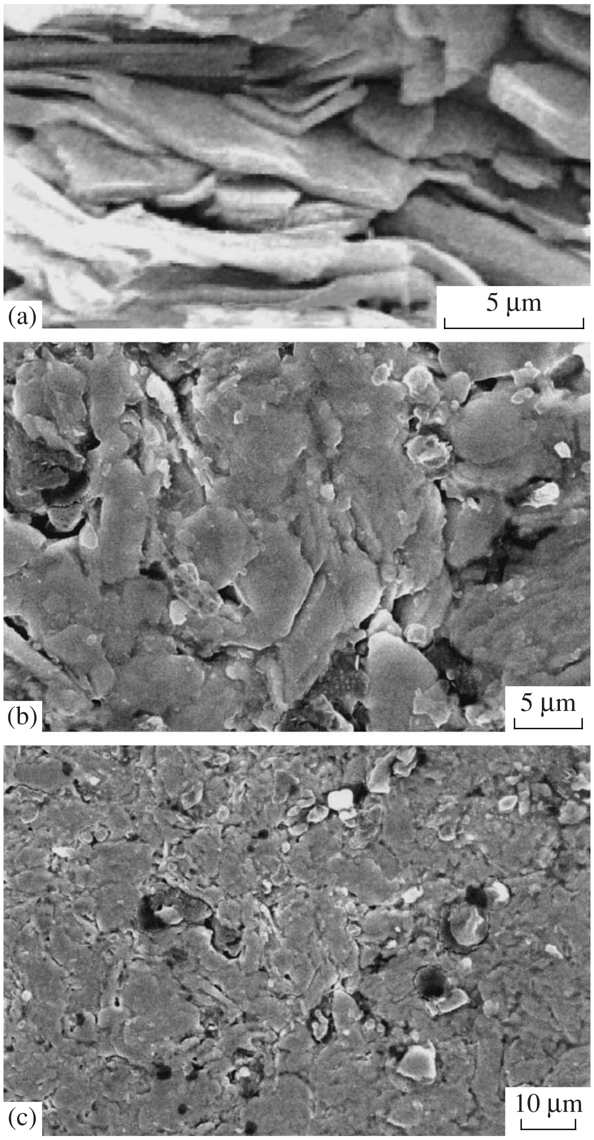

Fig. 1. Typical SEM micrographs of textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics fabricated using the proposed method: (a) the fracture surface of a disk broken in the direction of pressing; (b, c) flat faces of a disk.

As can be seen, the sample exhibits qualitatively different microstructures in mutually perpendicular directions. The plates are mostly perpendicular to the axis of pressing (Fig. 1a) and exhibit clear intergranular boundaries in this direction. The platelike grains have a thickness of about ~1 μm, which is the same as that in the initial porous HTSC ceramics. The *c* axis of grains is perpendicular to the surface of plates. The SEM micrographs of the surface of pressed disks (Figs. 1b, 1c) also confirm that the plates (i.e., their *ab* planes) are parallel to the disk plane. Figure 1b reveals inhomogeneities, which represent the cleavage planes of grains. Clear boundaries usually correspond to a cluster consisting of several jointed grains (Fig. 1c).

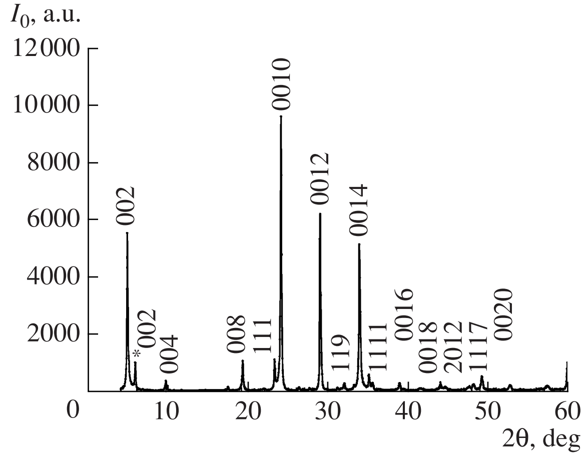

Fig. 2. Typical Debye powder X-ray diffraction pattern of textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics fabricated using the proposed method.

Figure 2 shows the typical Debye powder X-ray diffraction pattern of textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics, where the reflections mostly correspond to the Bi2223 structure. An analysis of Fig. 2 shows that the fraction of a low-temperature Bi2212 phase in dense ceramics is below 5%, similar to that in the initial porous material [7].

As is known, the ratio of the intensities of reflections $\Sigma(00l)$ and $\Sigma(hkl)$ increases depending on the extent of preferred *c* axis orientation. This ratio can be used for evaluating the degree of texture [4, 5, 9]. We selected the following reflections of Bi2223 crystal for this quantitative analysis: (002), (004), (008), (00$\underline{10}$), (00$\underline{14}$), (00$\underline{16}$), (00$\underline{20}$) and (115), (119), (11$\underline{15}$), (11$\underline{17}$), (11$\underline{19}$). The degree of texture was defined as [4, 5, 9]

$$P = \Sigma I(00l)/[\Sigma I(hkl)],$$

where $I(hkl)$ is the intensity of the (hkl) reflection, $\Sigma I(hkl)$ is the sum of intensities of all selected peaks, and $\Sigma I(00l)$ is the sum of reflections of the ($00l$) type. It was found that the textured ceramics obtained using the proposed method has $P = 0.97 \pm 0.01$. Such a high P value (the maximum possible degree of texture is $P = 1$) is characteristic of highly textured ceramics [4, 5].

Figure 3 presents the temperature dependence of the electric resistivity $\rho(T)$ of textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics fabricated using the proposed method. The transport current was passed in the *ab* planes of grains. The temperature of the onset of the superconducting transition is ~113 K, and the temperature at which the sample resistance vanishes is ~106 K (see the inset to Fig. 3). At $T > T_C$, the $\rho(T)$ curve exhibits a "metallic" character.

Figure 4 shows the typical hysteresis loops of the magnetization $M(H)$ of the textured HTSC ceramics. A cubic sample for these measurements was cut from

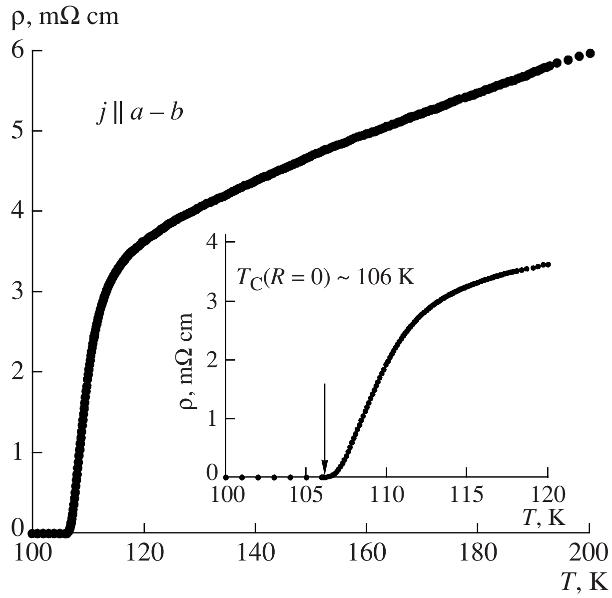

Fig. 3. The temperature dependence of electric resistivity $\rho(T)$ of textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics fabricated using the proposed method. The inset shows the behavior of $\rho(T)$ in the vicinity of the superconducting transition on a larger scale.

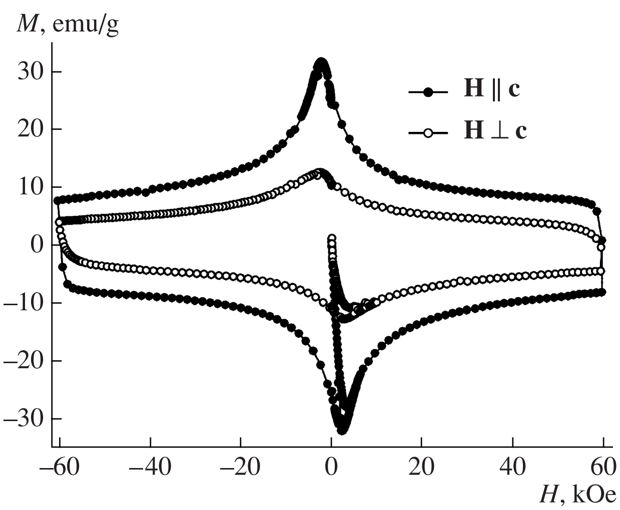

Fig. 4. The typical hysteresis loops of the magnetization $M(H)$ of textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ ceramics measured at $T = 4.2$ K for two variants of orientation of the applied magnetic field relative to the crystallographic axes of grains.

a tablet and had the dimensions ~1.6 × 1.6 × 1.6 mm, with one face coinciding with the disk plane. The measurements were performed for two variants of orientation of the magnetic field relative to the direction of predominant grain orientation (texture) in the sample: **H || c** and **H ⊥ c**. The obtained textured material exhibits anisotropic magnetic properties: the diamagnetic response in the case of **H || c** is 2.6 times that for **H ⊥ c** and about two times as large as the response of a reference polycrystalline sample of bismuth ceramics of the same composition.

Thus, the SEM and X-ray diffraction data indicate that the obtained dense ceramics possess a texture in which the platelike grains are oriented with their *ab* planes parallel to the disk faces. We believe that there are two factors favoring the enhancement of texture in the ceramics fabricated using the proposed method: (i) use of low-density porous ceramics as the initial material and (ii) impregnation of this high-porosity precursor with a liquid. We have used ethyl alcohol, which readily penetrates into pores because (for a density amounting to 26% of the theoretical limit) almost all pores are open. The presence of a nearly incompressible liquid creates conditions analogous to hydrostatic pressure for the grains, which favors their uniform compaction in the entire depth of a disk. The presence of a large number of pores provides enough room for the rotation of platelike grains, whereby their planes are aligned parallel to the disk plane, and decreases the probability of brain breakage.

Using the values of diamagnetic response and characteristic dimensions of grains in various directions, it is possible to evaluate the density of critical intragranular current in the *ab* plane (J_C^{ab}) and along the *c* axis (J_C^c). According to the Bean model of a homogeneous superconductor, the anisotropy of the critical intragranular current (J_C^{ab}/J_C^c) is the same as the anisotropy of the diamagnetic response. As is known, the latter parameter in Bi2223 superconductors reaches 50 and above [10]. In order to explain the observed discrepancy (Fig. 4), it is necessary to take into account the orientation and dimensions of grains. A simple approach to this evaluation consists in using an average grain size instead of sample dimensions in the Bean model [11]. According to this, $J_C = 30\Delta M(0)/d$, where J_C [A/cm^2] is the critical current density in the plane perpendicular to the field, ΔM(0 [emu/cm^3] is the width of the magnetization hysteresis loop in a zero field, and d [cm] is the average crystal size in the direction parallel to the external field. The fact that the critical current is proportional to the $\Delta M(0)/d$ ratio also follows from the model of magnetization of a granular superconductor with allowance for the grain size distribution [12].

According to the SEM data (Fig. 1a), the thickness of grains in the *c* axis direction is $d \sim 1$ μm. The corresponding intragranular current density in the *ab* plane is $J_C^{ab} \sim 9 \times 10^7$ A/cm^2. This estimate is probably somewhat overstated owing to the simplified approach [11]. In order to evaluate the critical current along the *c* axis, it is necessary to know the characteristic grain size in the *ab* plane. Using Figs. 1b and 1c, the lateral linear size of platelike grains separated by clear boundaries can be estimated as $d \sim 20$–30 μm. With this value, we obtain the intragranular current density along the *c* axis as $J_C^c \sim 1.3–1.9 \times 10^6$ A/cm^2. Then, the parameter of anisotropy determined as J_C^{ab}/J_C^c amounts to ~50–70 in agreement with the known data [10]. These estimates also confirm that the obtained material possesses a high degree of texture.

In conclusion, a relatively simple technology of Bi-containing textured HTSCs is developed, which is based on the uniaxial pressing of an initial, low-density highly porous precursor in a liquid medium. Using this method, it is possible to obtain highly textured ceramics with a high diamagnetic response for **H || c**, which makes these ceramics promising materials for superconducting suspensions, bearings, and levitation devices.

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