

Influence of oxygen content and structural defects on low-temperature mechanical properties of high-temperature superconducting single crystals and ceramics

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The data for the microhardness and fracture toughness of Y-Ba-Cu-O and Bi-based single crystals and ceramics in the temperature range 77–293 K are presented and analysed. Our study reveals that the microhardness of high temperature superconductors is very sensitive to the oxygen stoichiometry, the phase composition, the temperature, and to the microstructural defects such as impurities, intergranular boundaries, and voids. Attention is drawn to the anisotropy of the micromechanical properties and to the features of the fracture in the vicinity of the indentation. The data available on the plasticity of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O from micro- and macrotests are compared.

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1. Introduction

Practical applications of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O superconducting compounds are often limited by their poor mechanical performance, i.e., extremely low ductility and elevated brittleness, especially at low and moderate temperatures. Plasticity and strength of high-temperature superconductors (HTSCs) are adversely affected by numerous defects: voids, surface and bulk microcracks, grain and twin boundaries, phase inhomogeneities, impurities, oxygen nonstoichiometry which result from the synthesis process at high temperature and from subsequent cooling to room temperature and mechanical treatment or loading.

A study of the mechanical properties of such complicated objects, whether they are ceramics (polycrystals) or single crystals, does not appear to be a simple task. Nevertheless, several procedures have been devised for this purposes. It is possible to suppress the intrinsic brittleness of superconducting oxides and reveal clear plastic flow with dislocation generation by deforming at elevated temperatures

[1–5], at room temperature with the application of hydrostatic pressure [6] or by using shock-loading techniques [7]. However, most investigations have been made with the indentation techniques which can be used successfully over a wide range of temperatures [8–12].

The purpose of the present paper is to report new results and consider briefly some previous measurements of microhardness and fracture toughness of single crystals and ceramics of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O compounds in the temperature range 77–293 K. The behavior of the microhardness near the N - S phase transition temperature T_c and the mechanism of microplasticity of HTSCs are of interest to us. We will discuss the dependence of micromechanical properties on temperature, oxygen and impurity concentrations, density, and microstructural and phase inhomogeneities of ceramics, and we will estimate a difficult-to-measure property such as surface energy. Finally, we will compare the available data on the plasticity of these materials obtained from micro- and macrotests.

2. Experimental procedure

The Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O compounds were prepared by high-temperature solid state reaction. Ceramic specimens were prepared first by cold pressing and then by sintering of synthesized powder. Variations in pressure (0.2–5 GPa) and annealing temperature (1073–1233 K) permitted different densities to be attained. The Y-Ba-Cu-O test samples had a density D between 2.1 and 5.85 g/cm³ (0.33–0.92 of the x-ray density, $D_R = 6.38$ g/cm³) and $T_c = 85$ –92 K. Single crystals were grown in alundum or platinum crucibles (below referred to as Y-Al and Y-Pt, respectively) by a spontaneous crystallization technique. The crystals were flat with (001) faces dominating. The concentration of platinum in Y-Pt crystals and aluminum in Y-Al crystals was found to be 0.01 wt.% Pt and 0.25 wt.% Al. The investigation of the influence of the oxygen deficiency on microhardness was carried out on YBa₂Cu₃O_{7- δ} crystals with four concentrations of oxygen: $\delta = 0.1, 0.3, 0.4,$ and 0.9 . The oxygen index in as-grown crystals was varied by further thermal treatment in oxygen or in argon. The microindentations were carried out at room temperature by using a PMT-3 standard diamond tester and at temperatures from 77 to 300 K they were made by using a special tester set described in Ref. 12. Hardness H_V and fracture toughness K_c (the critical stress intensity factor) were calculated by using the relations [9,13]

$$H_V = 1.854(P - P_{th})/(2a)^2,$$

$$K_c = 0.016(E/H_V)^{1/2}(P - P_{th})/c^{3/2},$$

where $2a$ is the impression diagonal; P is the indentation load; P_{th} is the threshold load which does not result in an impression or a crack; E is the elastic constant (along the axes [100] and [010] $E_{11} = E_{22} = 156$ GPa and along the axis [001] $E_{33} = 89$ GPa for Y-Ba-Cu-O at room temperature [14]). The experimental data plotted in the coordinates $(2a)^2 - P$ and $c^{3/2} - P$ are well described by the linear relations giving the load-independent values of H_V and K_c .

3. Results and discussion

3.1. Y-Ba-Cu-O system. Single crystals

Effect of oxygen content on microhardness. The hardness of the Y-Ba-Cu-O system is highly sensitive to oxygen concentration [12,15,16]. The results of our measurements are shown in Fig. 1 for three temperatures. The strongest concentration depend-

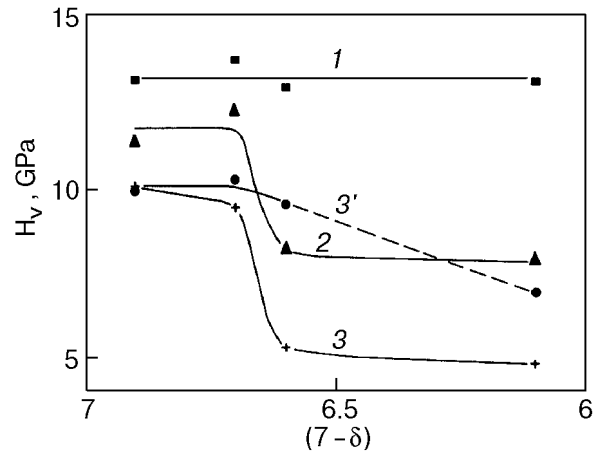


Fig. 1. Effect of oxygen concentration in Y-Ba-Cu-O single crystals on microhardness at temperatures 77 (1), 200 (2), and 293 K (3 and 3'). Curves 1, 2, and 3 correspond to crystals from the series Y-Pt, and curve 3' corresponds to the Y-Al crystals.

ence $H_V(\delta)$ for Y-Pt crystals is observed at room temperature: the hardness changes about 1.5 times in the δ interval from 0.3 to 0.4, i.e., in the range of orthorhombic-1 \rightarrow orthorhombic-2 phase transition, but it is not affected by orthorhombic-tetragonal phase transition ($\delta \approx 0.5$). Thus, the sharp variation of H_V can apparently be associated with the variation in the properties of the lattice within the orthorhombic symmetry due to one-dimensional ordering of oxygen vacancies. The aluminum impurity in Y-Al crystals weakens the softening effect and extends the range of microhardness-oxygen concentration dependence toward higher values of δ .

The strong effect of oxygen stoichiometry on the plasticity of Y-Ba-Cu-O speaks in favor of shear in the BaO/CuO plane, since the main variations upon changing the oxygen index, occur just in the CuO plane.

The available data [17,18] show that the elastic moduli corresponding mainly to shear modes increase monotonically with oxygen concentration. The moduli corresponding to dilatation modes increase up to the values ~ 6.7 of the oxygen index, after which they begin to decrease. Consequently, the considered behavior of $H_V(\delta)$ is due not to the variation of the elastic properties of crystals but to the effect of oxygen concentration and oxygen ordering on the core structure and mobility of dislocations.

The microhardness and fracture toughness of Y-Ba-Cu-O and some rare-earth cuprates Re-Ba-Cu-O (Re: Gd, Ho, Dy, Er, Yb) single crystals studied are shown to vary over wide ranges: at room temperature $H_V = 5$ –10 GPa and $K_c = 0.4$ –1 MPa m^{1/2} [8,9,12,19]. This considerable spread of the meas-

ured values may be attributed to the variations in oxygen concentration which was not controlled.

Mechanical anisotropy of Y-Ba-Cu-O crystals. The hardness of Y-Ba-Cu-O crystals was found to be isotropic within an experimental error. However, the special measurements made on relatively large crystals with well-developed (100) and (001) faces have demonstrated that the hardness ratio of (100) to (001) surfaces is 1.2 for the orthorhombic phase and 1.8 for the tetragonal phase [20].

The length of cracks and the direction of their propagation are very sensitive to indentation crystallography. Cleavage of these layered structures is easier along basal planes [9,14]. That is the reason why the hardness of aligned Y-Ba-Cu-O was found to be strongly anisotropic [21]: preferential cleavage of the basal planes results in much lower hardness for indentation on the (100)/(010) plane than on the (001) plane: 3.8 and 6.7 GPa, respectively.

Notice that the mechanical anisotropy may be affected by the presence of twin boundaries. Hardness was found to be insensitive to a twin structure, which arose during the tetragonal-orthorhombic phase transition; however, the fracture toughness for twinned crystals was different than that for untwinned crystals, according to Ref. 14.

Temperature dependence of microhardness. So far, only few results of an experimental study of the temperature dependence of the microhardness of Y-Ba-Cu-O single crystals have been reported. However, they cover a wide temperature range from the boiling point of liquid nitrogen to almost 1200 K and concern both phases of the Y-Ba-Cu-O compound, i.e., tetragonal and orthorhombic phases. We have summarized the basic data in Fig. 2.

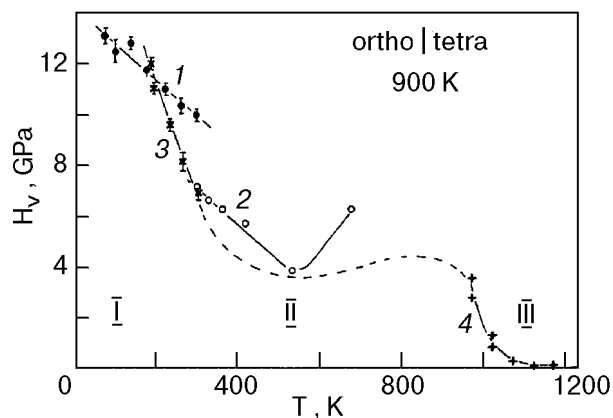


Fig. 2. Microhardness of Y-Ba-Cu-O single crystals as a function of temperature: the orthorhombic phase, $\delta = 0.1$ (1) [12]; the orthorhombic phase, as-grown (2) (Ref. 20); the tetragonal phase, $\delta = 0.9$ (3) (Ref. 12); the tetragonal phase (4) (Ref. 10).

Notice a linear increase in the hardness of the orthorhombic phase (Fig. 2, curve 1) with decreasing temperature, without any anomalies near $T_c \approx 93$ K [12]. The data obtained for softer crystals and at a higher temperature [22] (Fig. 2, curve 2) show a similar temperature dependence. The increase of H_V at $T > 550$ K can be attributed to the changes in oxygen stoichiometry. Samples with the tetragonal structure exhibit lower hardness at room temperature, which increase rapidly, with decreasing temperature, and a sharp transition from ductile behavior to brittle fracture at about 200 K Ref. 12 (Fig. 2, curve 3). Analogous H_V and their low-temperature dependences of normal brittle semiconductors (e.g., Si, Ge) and Y-Ba-Cu-O single crystals can indicate that in region I the similar thermally activated dislocation mechanisms control plastic deformation produced by indentation [12]. It may be suggested that strong covalent bonds (in the first case) and ionic bonds (in the second case) create high Peierls barriers, which constrain the dislocation mobility in these crystals.

The high-temperature deformation processes in the tetragonal phase (region III, Fig. 2, curve 4; Ref. 10) are obviously diffusion assisted. In the intermediate region II the mixed dislocation-diffusion mechanisms are expected to control plastic flow (see, for example, Refs. 5 and 23 and the bibliography cited there).

Fracture toughness and surface energy. Measurements of the temperature dependence of the fracture toughness have been carried out with two series of Y-Ba-Cu-O single crystals: Y-Al and Y-Pt [24]. They are characterized by the same oxygen index $\delta \approx 0.3-0.4$ and the same critical temperature $T_c \approx 60$ K. For Y-Pt crystals, a decrease of H_V and K_c with increasing temperature arises from thermally activated dislocation glide. This provides evidence for a quasi-brittle type of fracture. In contrast, a weak rise of K_c of Y-Al crystals from 3.4 $\text{MPa}\cdot\text{m}^{1/2}$ (at 77 K) to 3.5 $\text{MPa}\cdot\text{m}^{1/2}$ (at 292 K) (and a weak drop of H_V from 9.3 GPa (at 77 K) to 8.5 GPa (at 292 K) with increasing temperature may point to an ideally brittle mode of fracture, without allowance for the glide dislocations or with their slight participation. In this situation, the calculated values of K_c are determined essentially by the material constants. Using the Griffith-Orowan relation $K^2 = 2\gamma E / (1 - \nu^2)$, where ν is the Poisson ratio, we could estimate the surface energy γ of two surfaces (100)/(010) and (001). The (001) face indentation gives an average K_c of about 0.35 $\text{MPa}\cdot\text{m}^{1/2}$ and hence $\gamma_{100/010} \approx 360$ erg/cm². An indentation of (100)/(010)

face showed a large anisotropy in crack length for crack directions perpendicular to and parallel to the basal plane (cf. Refs. 14–16, and 19): $K_c \approx 0.7 \text{ MPa}\cdot\text{m}^{1/2}$ and $\gamma_{100/010} \approx 1400 \text{ erg}/\text{cm}^2$ in the first case and $K_c \approx 0.2 \text{ MPa}\cdot\text{m}^{1/2}$ and $\gamma_{001} \approx 160 \text{ erg}/\text{cm}^2$ in the second case.

Ceramics

Indentation technique is very useful in estimating the density and homogeneity of samples because of the possibility of accurately locating the impressions on the surface and through the sensitivity of microhardness to the presence of structural and other defects. This is particularly evident in measurements on ceramics.

The influence of microstructure inhomogeneities on the hardness of Y-Ba-Cu-O ceramics is reflected very distinctly in histograms and in average values of hardness [19]. The hardness in the vicinity of grain boundaries is smaller and its dispersion is higher than they both measured within grains. The role of intergrain material in the formation of the ductility of ceramics can be demonstrated best of all by the example of fine-grain ceramics with the grain size $d \approx 5 \mu\text{m}$. Its average hardness was found to be smaller by a factor of 3 as compared with that of ceramics of about the same density with $d \approx 40 \mu\text{m}$, which indicates the determining influence of grain boundaries on the impression formation.

The temperature dependences of the microhardness of ceramics with an average grain size $d \approx 5 \mu\text{m}$ and different densities $D/D_R = 0.73, 0.91,$ and 0.98 are plotted in Fig. 3 [25]. Figures 3,a and 3,b show the data of H_V measurements at an indenter load $P_1 = 0.15 \text{ N}$ and $P_2 = 2 \text{ N}$, respectively. At the P_1 load an impression area was very nearly equal to the grain area, whereas at the P_2 load it far exceeded the grain area. The measured values of H_V at P_2 characterize the hardness of given ceramics on average, as a whole, and then they are less than H_V values obtained at indentation with smaller load P_1 . The smaller the load on the indenter, the closer are the measured values to the hardness of the grains. From Fig. 3 we see that the hardness is near-linear with temperature without any detectable features in the range from 77 to 293 K for all samples examined, but, what is more important in this context, it depends strongly on density.

Recently [19] we studied the dependence of the hardness on the density of Y-Ba-Cu-O ceramics in the interval of $D/D_R = 0.33\text{--}0.92$ at room temperature and deduced from the experiments that the hardness increases exponentially with increasing

density (see also Ref. 26), as is usually observed for many structural ceramics:

$$H_V = H_{V0} \exp[-n(1 - D/D_R)].$$

This equation adequately describes the data in Fig. 3 at all temperatures (the plots for two fixed temperatures, 77 and 293 K, are presented in the insets in Figs. 3,a, and 3,b). The H_{V0} value de-

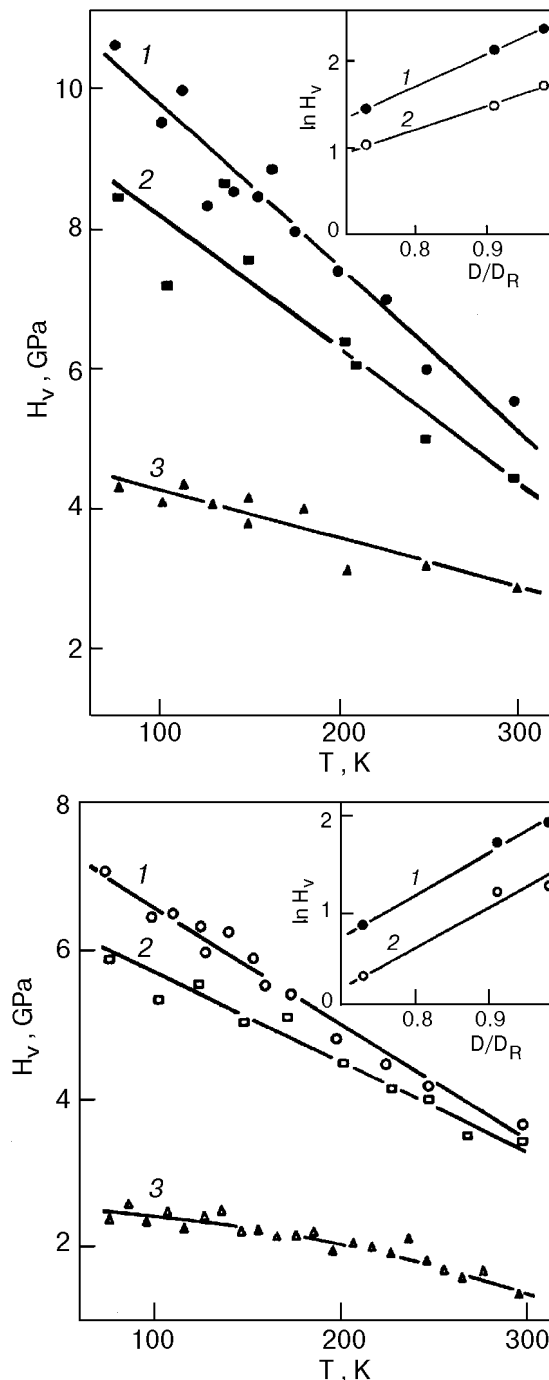


Fig. 3. Microhardness of Y-Ba-Cu-O ceramics as a function of temperature, at the loads on the indenter $P_1 = 0.15 \text{ N}$ (a) and $P_2 = 2 \text{ N}$ (b). Relative density $D/D_R = 0.98$ (1), 0.91 (2), and 0.73 (3). The insets show D/D_R dependences of $\ln H_V$ at two temperatures 77 (1) and 293 K (2).

creases with increasing temperature from 8.1 to 4.6 GPa at $P_2 = 2$ N and from 11.6 to 5.7 GPa at $P_1 = 0.15$ N. The factor n in the exponent is equal to 4.6 at a load of 2 N independently of temperature. At a load of 0.15 N the n value increases from 2.6 at 293 K to 3.6 at 77 K. An increase in the value of n with decreasing temperature and an increase in the load is likely due to the crack formation along the grain boundaries. These microcracks enhance the dependence of hardness on density, which in the initial ceramics is determined by the intrinsic voids.

The maximum hardnesses of grains in ceramic samples and single crystals of the same oxygen concentration are in good agreement in the whole temperature range from 77 to 293 K.

3.2. Bi-Sr-Ca-Cu-O system

The Bi-containing HTSC ceramics and crystals exhibited highly nonuniform micromechanical properties [27]. The hardness of single crystals at room temperature was found to have three typical values: 0.5, 1.1, and 3.1 GPa. The data observed are close to those measured individually on two types of ceramic crystallites with different optical reflective capacities: 0.43 GPa and 1.08 GPa for «dark» crystallites and 3.8 GPa for «bright» crystallites. These values are considerably lower than the microhardness of a Y-Ba-Cu-O system.

Nonuniform mechanical properties of a Bi-Sr-Ca-Cu-O system apparently are attributable to their multiphase nature. Preparation of single-phase crystals of this system is seriously hindered by different causes. As was demonstrated, nearly single phase material (2212) can be obtained only by thoroughly controlling the processing parameters: the oxygen pressure, the maximum sintering temperature, the

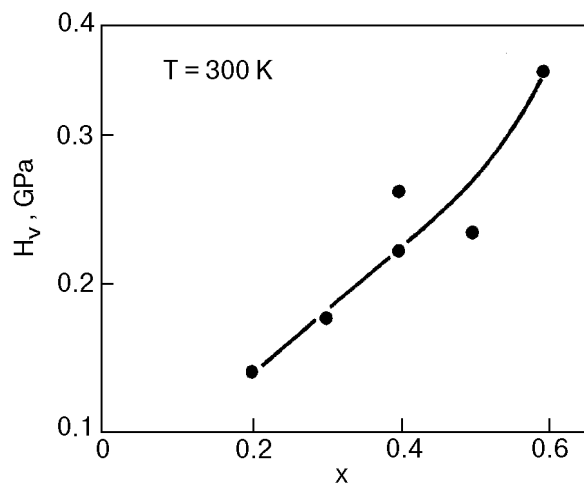


Fig. 4. Microhardness of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramics as a function of Pb dopant concentration at room temperature.

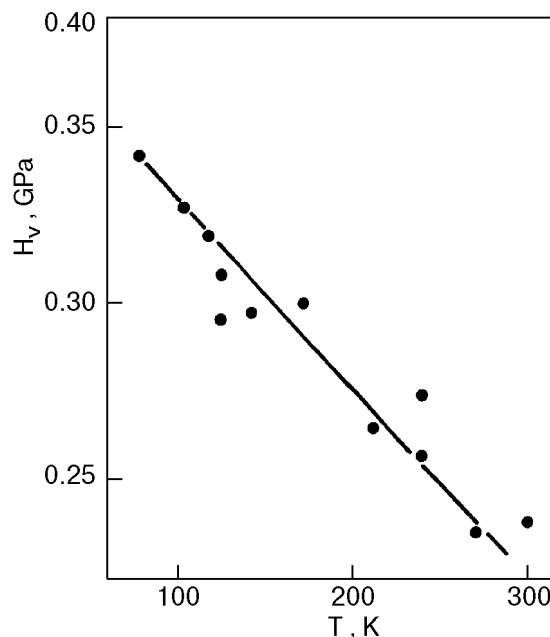


Fig. 5. Microhardness of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramics as a function of temperature for $x = 0.4$.

annealing time, and the cation stoichiometry [28]. The high quality (2223) phase samples were also prepared [29,30].

Addition of Pb dopant to the Bi-Sr-Ca-Cu-O system stabilizes the 2223 phase and therefore hardens the $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramics [31]. Figure 4 shows the microhardness plotted as a function of Pb dopant concentration. Measurements were performed at room temperature by using six samples with different values of x but approximately the same density D/D_R , between 0.6 and 0.7. The microhardness increases almost 2.5 times with increasing x from 0.2 to 0.6. Near-linear rise of H_V with x is probably caused by solid-solution hardening. A deflection of $H_V(x)$ from the linear dependence at $x = 0.6$ may result from Ca_2PbO_4 particle formation, which leads to additional precipitate hardening.

The microhardness of the $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramics increases with decreasing temperature and, as with the Y-Ba-Cu-O system, has no anomalies in the range $T_c = 105\text{--}110$ K. Figure 5 shows the H_V values and their changes in the temperature interval from 77 to 293 K for a sample with $x = 0.4$.

Microhardness measurements with the Knoop indenter carried out on the (001) face of 2223 crystals showed polar hardness anisotropy between $H_{\min} = 0.9$ GPa and $H_{\max} = 1.33$ GPa for azimuth 45° [the short diagonal of the indenter was parallel to the (100) face] and 0° (or 90°), respectively [32]. The corresponding data for 2212 crystals [33] are $H_{\min} = 0.8$ GPa and $H_{\max} = 2.5$ GPa. Attention was drawn to a correlation between the H_{\max} and

T_c values for HTSC materials [32,34,35]: the higher the H_{\max} the lower T_c (in particular, for the 2212 phase $T_c = 85$ K and for the 2223 phase $T_c = 100$ – 110 K). This correlation seems to support the notion that superconductors with higher T_c values have a more friable crystal structure.

The other feature of the Bi-Sr-Ca-Cu-O crystals is considerable lateral cracking or crushing as a result of indentation. As a result, well-developed radial cracks were rarely visible. An estimation of fracture toughness showed values as low as 0.11 MPa·m^{1/2} (Ref. 27) and 0.22 MPa·m^{1/2} (Ref. 36). Lateral cracking causes the formation of surface relief in the form of a «roof». The residual strain of this blister is estimated to be no less than 1%.

4. Comparison of micro- and macrocharacteristics

Some data on the plasticity of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O compounds obtained in micro- and macrotests can be compared. In the temperature range where the material is normally brittle, the empirical ratio of microhardness to yield stress is found to be about 3 (Ref. 37). In accordance with the available data for Y-Ba-Cu-O ceramics, the maximum $H_V = 4.3$ GPa (Ref. 19) and $\sigma_y = 1.25$ GPa (Ref. 6,) hence $H_V/\sigma_y = 3.2$. It is of interest to compare the microhardness and the strength of the single crystals. At 77 K, $H_V = 13.2$ GPa (Ref. 12), and the strength $\sigma_T = 3.1$ – 5.4 GPa, as measured at the same temperature in a field-ion microscope [38,39], therefore, $H_V/\sigma_T = 4.3$ – 2.6 . We note that the σ_T values are close to the theoretical strength of a perfect crystal: $\sigma_T/E_{33} = 1/16$ – $1/30$. A similar value of $\sigma_T \cong 4.3 \pm 0.7$ GPa at 78 K was found for LuBa₂Cu₃O_{7- δ} single crystals of diameter 74–245 nm in Ref. 40.

There are data on hardness of Bi-Sr-Ca-Cu-O (2212) crystals [27, 41], and tensile strength and elastic modulus of whiskers [42] at room temperature: the maximum $H_V = 3.1$ GPa (Ref. 27) and $H_V = 6.2$ GPa (Ref. 41), $\sigma_c = 0.94$ GPa and $E = 92$ GPa (Ref. 42); therefore, $H_V/\sigma_c = 3.3$ – 6.6 and $\sigma_c/E = 1/100$. In this case it is clear that, first, the yield point was not reached because of the brittle fracture of whiskers and, secondly, σ_c is less than σ_T because of the large cross section of whiskers more than $50 \mu\text{m}^2$.

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