Microhardness of the compounds La$_2$CuO$_4$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ at temperatures from 81 to 292 K

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The microhardness of La$_2$CuO$_4$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ crystals is measured in the temperature range 81–292 K, and the influence of various factors on it is investigated. The thermal activation parameters of the plastic deformation process in the vicinity of the indenter impression are estimated. The change of the phase state of the compound La$_{1.85}$Sr$_{0.15}$CuO$_4$ at the temperature $T_0$ = 180 K and the appearance of domain (twin) boundaries formed in the ferroelastic tetra-ortho transition are not seen in the temperature dependence of the microhardness. The results of the study are compared with previously published results for YBa$_2$Cu$_3$O$_7$ crystals.

1. EXPERIMENTAL PROCEDURE

Single crystals of LCO and LSCO were grown by the method described in Refs. 20 and 21. The As-grown LCO crystals were in the shape of oblique-angled prisms with approximate dimensions $4 \times 4 \times 2$ mm and habit planes (001) and (111), or they were grown as wafers of thickness $\sim 1.5$ mm with dimensions $\sim 6 \times 4$ mm in the (001) basal plane. Only the habit plane (110) was clearly defined in the LSCO crystals. The LSCO crystals entered the superconducting state at $T_c \approx 25$ K.

The indentation procedure was the same as that described in Ref. 4. The Vickers microhardness was determined from the equation

$$H_V = 1.854P/(2a)^2,$$

where $2a$ is the length of the diagonal of the indenter impression. The load $P$ on the indenter varied in the interval 0.05–1 N. At least ten indentations were made on the sample surface at each temperature. The average values of $H_V$ are given here; the error of their determination was at most 1–2%. The temperature dependence of the microhardness was measured on one sample. The defect structure of the as-grown and indented samples was investigated by means of a metallographic microscope in normal and polarized light. The linear dimensions of the indentations were measured with a PMT-3 hardness-gauging microscope.

2. RESULTS AND DISCUSSION

2.1. Domain structure of LCO crystals and its rearrangement under the influence of mechanical stresses

The as-grown LCO crystals have a domain structure which, viewed in polarized light in the (001) plane, appears as a system of alternating light and dark bands (domains) of
width \( \sim 5-20 \mu m \) parallel to the \((100)\) direction. The coloration of the domains can reverse itself when the position of the analyzer is changed. Occasionally two systems of domains with mutually perpendicular boundaries can be observed.

The as-grown polydomain structure is transformed under the application of a concentrated force (Fig. 1). The direction of motion of the domain boundaries leading to growth of the light or dark domains is determined by the sign of the stresses present near the indenter impression (see the diagram in Fig. 3 of Ref. 2). As a result, the dark domains broaden and absorb the light bands in the first and third quadrants. The opposite effect is observed in the other two quadrants: broadening of the light bands and their absorption of the dark bands. This local conversion to a single-domain state encompasses a small region in the vicinity of the indentation, as seen in Fig. 1.

The transformation of the domain structure takes place within a time of the order of a minute, showing that the boundaries in LCO must be highly mobile even at room temperature. We note that the domain boundaries in YBCO crystals have a much lower mobility: The boundaries of the narrow domain shift at room temperature for a whole day, and loading up to 350–420 K is required to stimulate motion of the boundaries of the wide domains. The motion of the domain (twin) boundaries in YBCO is monitored by the diffusive motion of oxygen atoms and in LCO by the reorientation of the \( \text{CuO}_6 \) octahedra. The higher mobility of the twin boundaries in LCO implies that the activation energy associated with reorientation of the \( \text{CuO}_6 \) octahedra is lower than the activation energy of oxygen diffusion, approximately 1 eV, in YBCO.

The presence of domains in LCO crystals and their structural transformation under mechanical stresses lead to the classification of these crystals as ferroelastics. The change in the point group \( 4/mmm \) to \( mmm \) in the TO structural phase transition corresponds to one of the 52 types of pure ferroelastic transitions.

The number of such domains partitioning the crystal in transition to the ferroelastic state is determined by the ratio of the order of the point groups of the as-grown and ferroelastic phases, and the geometry of the domain structure formed in the ferroelastic phase transition can be predicted from the condition of minimum elastic energy of the sample. In the \( 4/mmm \rightarrow mmm \) transition four orientation states are possible in the ferroelastic phase. Two systems of domains can be distinguished here. The domains belonging to one system are in twin positions relative to each other, and the boundary between them has on the (001) plane a direction close to \((100)\) (Ref. 33); the domain boundaries associated with different systems are mutually perpendicular. Our experimental observations of the number, shape, and relative positioning of the domains in LCO fit the above pattern.

It has been shown that the twin boundaries in YBCO create fairly strong barriers to the motion of slip dislocations. However, we have not detected any appreciable variation in the microhardness during the TO transition, which results in the formation of domain structure, either in LSCO crystals as the temperature is lowered or in YBCO crystals as the oxygen concentration is varied. The value of the microhardness is also identical for twinned and untwinned YBCO crystals. Consequently, the twin (domain) structure of high-\( T_c \) superconducting oxides obviously has little influence on the resistance to plastic deformation in indentation.

We now consider the influence of other factors on the micromechanical characteristics of the crystals: the indenter load, the anisotropy of the crystal, doping, temperature, and the TO phase transition.

### 2.2. Influence of the load

For LCO crystals at room temperature we have obtained detailed plots of the length of the indentation diagonal and the length of a radial crack as functions of the indenter load. The linearity of the relation between the quantities \((2a)\) and \( P \), indicating constancy of the high-\( T_c \), is preserved for loads \( P \leq 0.50 \) N. At \( P \geq 0.70 \) N we observe a deviation from linearity toward higher indentation diameters, most likely attributable to the accompanying crack formation. This influence of the load on the microhardness of LCO and LSCO crystals has been observed previously. The threshold load above which a visible indentation is left on the crystal surface is close to zero, whereas the threshold for the YBCO crystals investigated in Ref. 3 is approximately 0.01–0.02 N.

The dependence of the length \( l \) of the radial crack on the load is well described by the relation \( l^{3/2} \sim P \) over the entire load range. The critical stress intensity coefficient (fracture toughness), calculated from the equation,

\[
K_{1c} = 0.1P/l^{3/2},
\]

is found to be equal to 0.96 MPa/m\(^{1/2}\). This value is close to one obtained earlier for YBCO (Refs. 1, 3, and 5) and is several times higher than for bismuth-containing high-\( T_c \) superconductors.

### 2.3. Microhardness anisotropy

The microhardness of an LCO crystal was measured on the two habit planes \((001)\) and \(\{111\}\) with two positions of the indenter diagonal: aligned with the \((100)\) direction and at