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GRAIN SIZE DISTRIBUTION OF THE $YBa_2Cu_3O_{7-x}$ HIGH TEMPERATURE SUPERCONDUCTING COMPOUND

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The grain size distributions of three $YBa_2Cu_3O_{7-x}$ ceramic samples, annealed at 960 °C for different times (t = 7, 70 and 700 hours, respectively), have been investigated. Both the average grain size (r) and that in the longest dimension of the grain (l) have been measured. The ratio l/r (reflecting the deviation from the spherical shape) initially increases with the annealing time (t) but tends to decrease at elevated t. An approximate $t^{1/2}$ increase of l probably reflects a plate-like shape of grains. For all samples the distributions of r and l are fitted best with the log-normal (Gauss) grain size distribution. The correlation between the grain size and critical current distributions is briefly discussed.

1. *Introduction*

The variation of critical currents and their distributions with thickness has been investigated for $YBa_2Cu_3O_{7-x}$ samples with different grain sizes (10 μm and 30 μm) in the temperature range from 78 K to 90 K in the magnetic fields up to 5 mT [1]. The critical current density initially increased in the samples with smaller grains, but later on leveled off on reducing of the thickness of the samples, whereas for the samples with bigger grains, it remained essentially unchanged even after a three-fold reduction in thickness. Since other parameters did not change on reducing the thickness of the samples, the variation of the critical currents are interpreted in terms of the thickness and grain size dependent self-field effects [1].

The critical current distribution functions of the samples were quite similar [1] and could be fitted rather well by the log-normal distribution [2].

In this work, the analysis of the grain size distributions as functions of the thermal pre-experiment treatments is presented. Various approaches to the measurements and analysis are discussed. The histograms are fitted by some of the most common types of the grain size distribution functions. The results are compared to those obtained from the transport property measurements on the same samples [1-3].

2. *Experimental procedures*

2.1. *Preparation of the samples for the measurements*

After the standard preparation procedure of the ceramic HTS [1], the pellets of $YBa_2Cu_3O_{7-x}$ were subjected to different thermal treatments of annealing at 1233 K (960 °C) in the pure oxygen atmosphere:
a) for $t_0 = 7$ hours (sample NOZ 1-I),
b) $t_2 = 70$ hours (NOZ 1-II), and
c) for $t_3 = 700$ hours (NOZ 1-III).

Samples prepared for the electrical measurements in the form of rectangular rods cut out from the pellets [1] were also used for the grain size and the shape analysis. For the metallographic inspection the rods were embedded in the polymerized plastic and polished with a diamond paste with nominal particle sizes from 20 μm to 2 μm. Polished samples were etched for a few seconds (5 to 10 s) in a mild aqueous solution of HCl (3 drops of concentrated HCl in 50 ml of distilled water). The prepared samples were examined in a metallurgical microscope using unpolarized white illumination.

Photographs of the revealed structures were taken along the rods (i.e. along the direction of current in the electrical measurements), and in the cross section perpendicular to that direction. For illustration, a choice of photographs are presented in Figs. 1 to 5. Upper and lower edges of the micrographs are parallel to current direction in the electrical measurements.

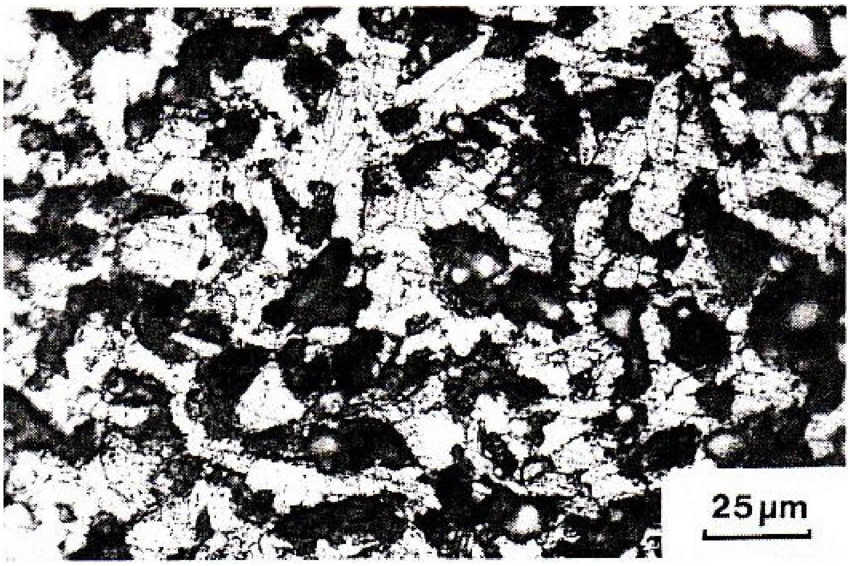

Fig. 1. Optical micrograph of the $YBa_2Cu_3O_{7-x}$ *ceramic, sample NOZ 1-I (aged for 7 hours at 960 °C), polished with diamond paste and etched for 5 seconds in a mild solution of HCl in distilled water.*

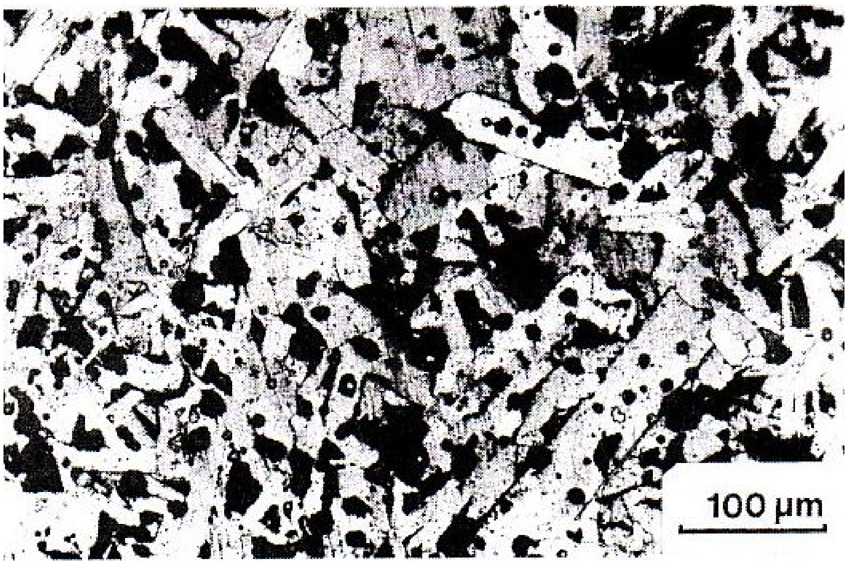

Fig. 2. Optical micrograph of the $YBa_2Cu_3O_{7-x}$ *ceramic, sample NOZ 1-II (aged for 70 hours at 960 °C), polished with diamond paste and etched for 5 seconds in a mild solution of HCl in distilled water.*

Fig. 3. Optical micrograph of the $YBa_2Cu_3O_{7-x}$ *ceramic, sample NOZ 1-III (aged for 700 hours at 960 °C), polished with diamond paste and etched for 5 seconds in a mild solution of HCl in distilled water.*

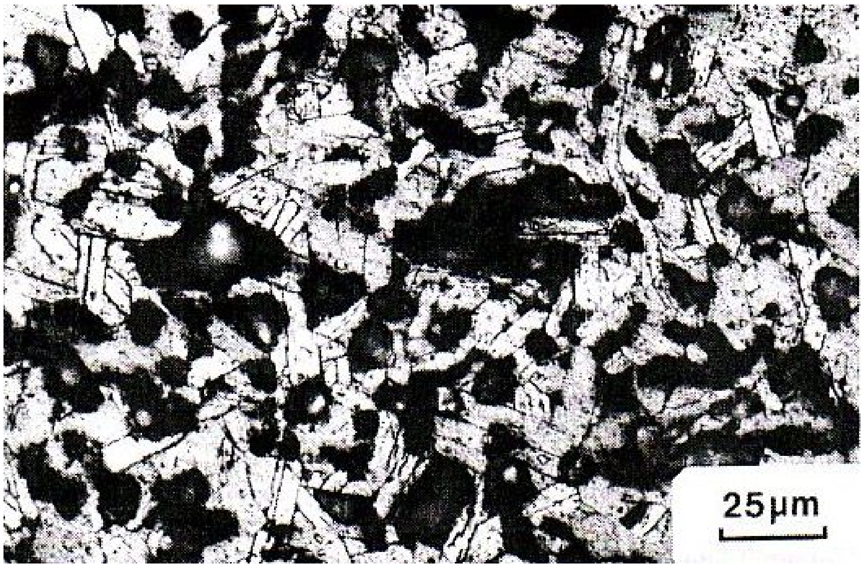

Fig. 4. Optical micrograph of the sample NOZ 1-I, etching time doubled (10 s).

Fig. 5. Optical micrograph of NOZ 1-III, etching time 10 seconds.

We should note that dark irregular areas on all photographs represent dimples in the polished area left out from the porosity of the $YBa_2Cu_3O_{7-x}$ and caused by crushing the crystals by hard diamond particles.

Figs. 4 and 5 illustrate the effects of preparation of the samples on details on the surfaces, as seen in metallographic investigations. E.g., changing the etching time from 5 to 10 seconds revealed grain boundaries more clearly, but increased the number and the size of etch pits inside the grains.

Inspection of all photographs, from Fig. 1 to Fig. 5, shows that the grains are predominantly elongated and occasionally rounded. This may be explained by the fact that the easy-growth directions in this compound lies in the (001) planes, i.e. in the Cu-O planes. The crystals appear as "needles" if the [001] direction is closely parallel to the sample surface, or as irregular "plates" if the [001] direction is nearly perpendicular to the surface of the investigated sample. Note that the "needle like" appearance of grains is dominant.

2.2. Principles of the measurements, analysis and calculations

Dimensions of the crystallites were measured in two different ways, with the aim to obtain information about the volume of crystallites in the course of the aging process and their dimensions along the conducting Cu-O planes. The linear-intercept method (measurements of grain sizes parallel to the current flow in electrical measurements) was applied in the first case (we shall call it the "sphere approximation"), and randomly oriented lines across the grains but along their long axis (we shall call it the "plate" or "needle" approximation), in the second case. These two sets of measurements give us the information of what we shall call the "elipticity" (e). It is defined as the ratio of average of the long axis of the grains (l) and the "radius of the sphere" (r), that is the average of grain sizes as measured by the line-intercept method: $e = l/r$. The "elipticity" (e) we measured and calculated as the function of the annealing time, is telling us about the possible preferred growth of grains along the conductive (001) Cu-O planes.

The samples were also investigated in two cross sections, parallel to the direction of the current measurements and in the cross section perpendicular to it. The aim was to obtain information about the possible existence of texture. In each case linear dimensions of over four hundred grains have been measured from the same area of the sample.

3. *Results and discusssion*

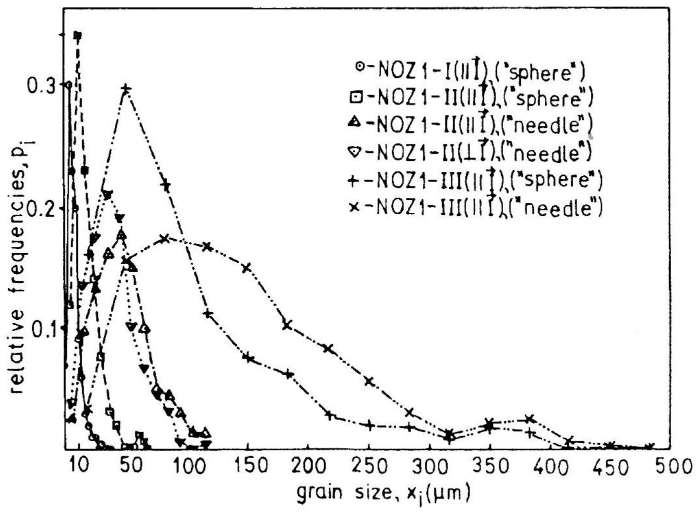

Fig. 6. Plots of grain size distributions in the "sphere" and "needle" approximation of the samples NOZ 1-I,II and III.

Results of the measurements are presented in Fig. 6. From the plots (the frequencies of histograms are connected with lines and dots in an attempt to distinguish the data for different samples) the following conclusions can be made:

a) The volumes of crystals grow during the annealing process. (Plots for NOZ 1-I (⊙), NOZ 1-II (⊓) and NOZ 1-III (+), in the "sphere" representation.)

b) There exists, a slightly, preferred orientation of crystals in the plane paralell to the current measurements (△) relative to the plane perpendicular to that direction (▽), as revealed from a slight translation of the related plots.

c) The plots for the "needles" are considerably broader than those for the "spheres", that is, the distribution of the long axes of the crystals is much wider then that of their average radii. This shows a clearly preferred crystallographically determined grain growth in selected crystallographic directions (and planes).

d) The plots in the "needle" approximation show a shift to larger values in relation to the plots in the "sphere" approximation. This allows defining and calculation of the "elipticity" of grains (e).

e) All plots show a "hump" at their tails. The humps are particularly pronounced in the samples annealed for a longer time. This may be explained by an anomalous grain growth in the annealing process. However, such "anomalous" grains, for example in the NOZ 1-III samples, may serve as secondary crystallization nuclei.

The results of the standard statistical analysis of the experimental data are given in Table 1. It has to be noted that the average sizes of crystals and standard deviations were calculated on the basis of log-normal (Gauss) distribution function.

TABLE 1.

Results of grain-size analysis of $YBa_2Cu_3O_{7-x}$ *ceramic samples.*

Sample	$t(h)/T(^\circ C)$	Diameter of the "sphere" $r(\mu m)$	Growth ratio (r/r_0)	Anneling time ratio (t/t_0)
NOZ 1-I	7/960	8±3	1	1
NOZ 1-II	70/960	16±4	2	10
NOZ 1-III	700/960	87±9	11	100
Sample	$t(h)/T(^\circ C)$	"Needle" l (μm)	Growth ratio (l/l_0)	"Elipticity" $(e = l/r)$
NOZ 1-I	7/960	14±4	1	1.8
NOZ 1-II	70/960	47±7	3.4	3
NOZ 1-III	700/960	143±12	10	1.6

The results in Table 1. show that when the annealing time was increased from 7 to 700 hours, the linear dimensions of the crystals increased by a factor of about ten, and the sizes are approximately proportional to the square root of the annealing time (r/r_0 and $l/l_0 \sim (t/t_0)^{1/2}$). We note that the square root law is better obeyed for the long dimension of the grains. This was be expected since for the plate-like grain, with the growth rate of the thickness considerably lower than that for the other two dimensions, the volume increases in proportion with the surface area (l^2). Therefore the volumes of the grains seem to increase linearly with the annealing time for the explored time periods.

"Elipticity", $e = l/r$, ranging from 1.6 to 3 in the early stage of the anneal (7h/960 °C - 70h/960 °C), rises to approximately twice of its initial value, and decreases to its starting value (and somewhat lower) on prolonged annealing (700h/960 °C). This may be tentatively explained as follows. In the first stage of the anneal (7h/960 °C) crystals are elongated as the "easy" axis of recrystallization advances at the expense of "slow" directions (The "easy" axes are in (001), i.e. Cu-O planes.). In the second stage (70h/960 °C) of this type of recrystallization, bigger grains consume its surrounding until they reach each other making a "net" of elongated crystals. This "touching" inhibits further growth in the easy-grow direction, so the bigger grains must consume smaller ones by the side-way growth. That lowers the "elipticity" from $e = 3$ to approximately the starting value of 1.8. So, this may be the end of growing (big) crystals in this type of thermal treatment.

In addition to this analysis of the results of the experiments, some important conclusions can be deduced. Table 1. shows that the average crystallization rates can be calculated for the time intervals given by the experiment. The results can be separated into two groups:

a) The average grain "radius" growth rate ("sphere" approximation): $(\Delta r/\Delta t)_{I-II} = 8/63 = 0.127$ μm/hour; $(\Delta r/\Delta t)_{II-III} = 71/630 = 0.113$ μm/hour; and $(\Delta r/\Delta t)_{I-III} = 0.114$ μm/hour. This shows that the rate of increasing of the "radius", and so of the volume, of the crystals is approximately constant.

b) The average growth rate of the long axis of the crystals ("needle" approx.): $(\Delta l/\Delta t)_{I-II} = 33/63 = 0.524$ μm/hour; $(\Delta l/\Delta t)_{II-III} = 0.1524$ μm/hour, and (of minor importance):$(\Delta l/\Delta t)_{I-III} = 129/693 = 0.186$ μm/hour. These numbers support our earlier discussion on the "elipticity" behaviour.

The experimental data were fitted by theoretical distributions. Various distributions were tried: the Poisson distribution, the log-normal (Gauss) and the Γ(Gamma) distribution.

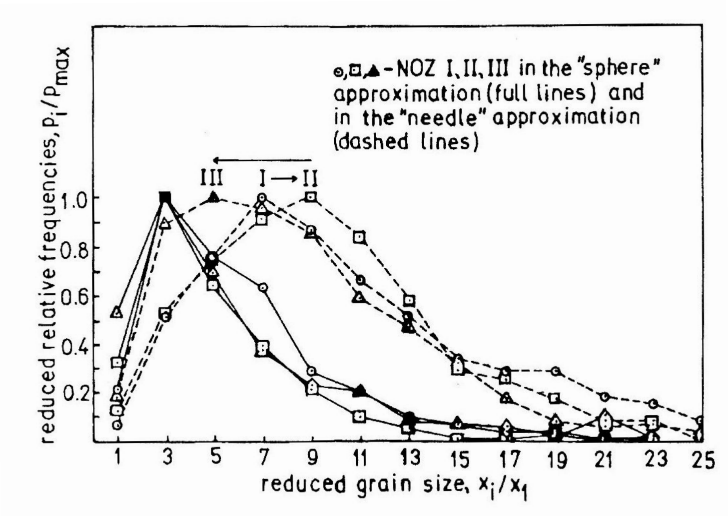

Fig. 7. Plots of data for the NOZ 1-I,II and III samples in reduced coordinates.

Fig. 7. shows the collected data for all investigated samples in the reduced (normalized) coordinates: x_i/x_1 (sizes of grains reduced to the first class) and p_i/p_{max} (frequencies normalized to the maximal frequency). Full lines are connecting points in the plots for NOZ 1-I ($\odot$), NOZ 1-II ($\sqcap$), and NOZ 1-III ($\triangle$) samples obtained in the "sphere" approach, and the dashed lines for the same samples in the "needle" approach. Main features of the histograms are as follows:

1. Plots obtained in the "sphere" approach are quite narrow (most of the grains have radii in first ten classes), showing a normal grain volume growth.

2. Plots showing the grain size distribution as measured along their long axis (the

"needle" approximation) are broader, showing larger dispersion of the "needle" sizes. They are also shifted to the right, showing the "elipticity" (see Table 1.). At the same time the shift of maxima of the three plots shows how the "elipticity" of grains increases and then decreases in the growth process.

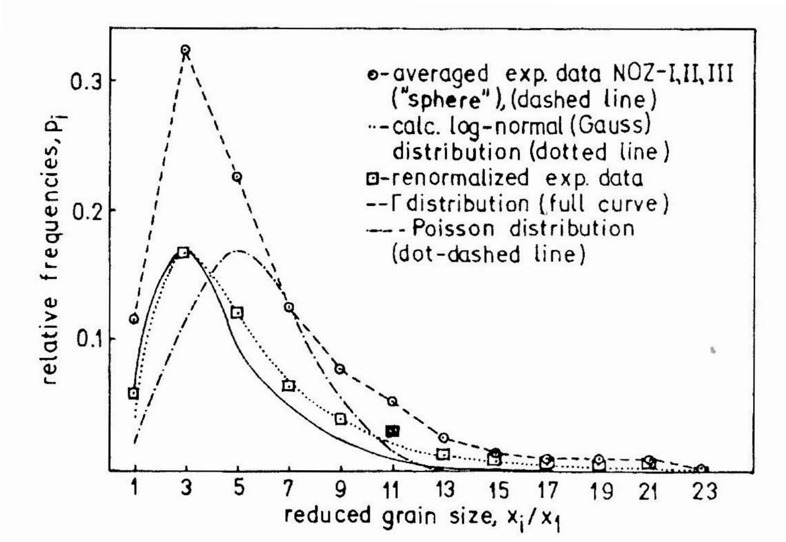

Fig. 8. Fitting of the theoretical distributions to the averaged plots of the NOZ 1-I,II and III samples ("sphere").

The plots for the "sphere" approximation in Fig. 7. show a common behaviour. They were chosen for the demonstration of fitting of some of the theoretical distributions (Fig. 8.). Averaged frequencies are connected with the broken line. Theoretical frequencies were calculated for the Poisson distribution function (dash-dot line), gamma (Γ) distribution function (full line) and the log-normal (Gauss) distribution function (dotted line), using standard expressions [4]. The log-normal (Gauss) distribution function fits best to the experimental data. The experimental data were renormalized in order to minimize the summ of squares of differences between experimental and the theoretical frequencies (χ^2 test). The test resulted in $\chi^2 = 0.02$, substantially lower than 0.05, the limiting value of means that the hypothesis is acceptable and that the distribution of grain sizes in our samples is the log-normal (Gauss) distribution. Test of goodnes of fit was also made by linearization of experimental frequencies assuming the log-normal (Gauss) distribution. A straight line can be drawn between the experimental points using the least-squares method, as seen in Fig. 9. This line fits the experimental data well. That was also checked by the linear regression calculation, which gives the correlation coefficient $r = -0.95$. Finally it has to be pointed out that the same type of distribution (log-normal) holds for the grains measured in the "sphere" and in the "needle" approximation.

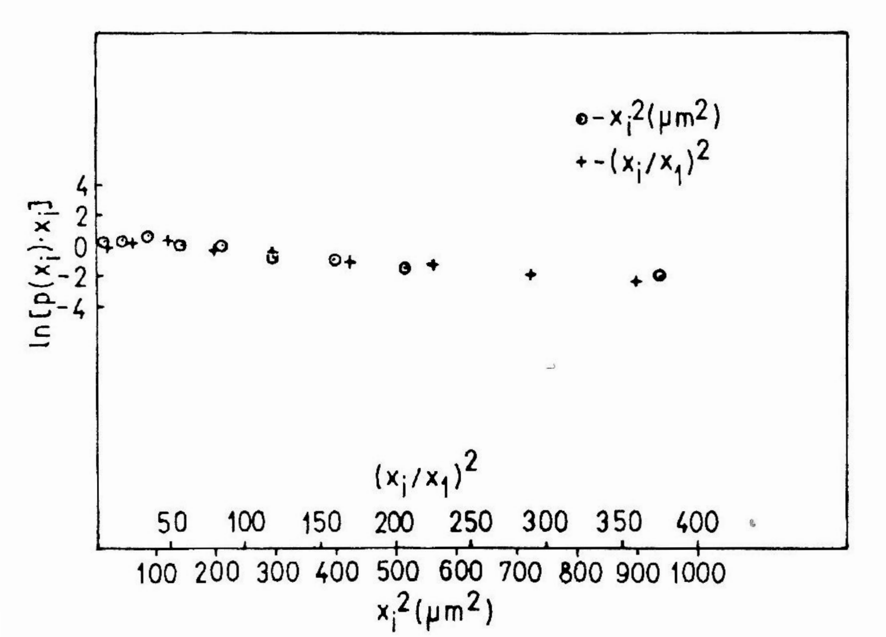

Fig. 9. Check of the goodness of fit of the log-normal (Gauss) distribution data of the samples NOZ 1-I,II and III in the "sphere" approximation.

4. Conclusions

The investigation of the grain sizes in the $YBa_2Cu_3O_{7-x}$ ceramic annealed in an oxygen atmosphere at 960 °C for varying times (up to 700 hours) shows that the grains grow according to an approximate "$t^{1/2}$ law" (see data in Table 1). This can be explained in terms of the plate-like shape of the grains and unequal growth rates for two crystallographic directions, [100] and [001], respectively. Our data indicate that the initial rate of the grain growth along its lenght, $(\Delta l/\Delta t)_{I-II}$, is about four times larger than the average one, $(\Delta r/\Delta t)_{I-II}$.

The rate of grain growth along its length varies with time, being slowed-down in later stages of the anneal by the long axis "collision" effect, as calculated in the "needle" approach. The grain growth rate calculated in the "sphere" approximation is nearly constant. The pronounced needle-like appearance of the grains in the later stages of annealing indicates that the crystallographic c-direction is mostly in the plane of the surface of the sample and thus in the plane of the current flow in the studies of the transport properties. This probably explains the fact that prolonged annealing of the samples did not cause any improvement of the critical current densities [1-3]. Indeed, large improvement in the critical current density has only been obtained for the bulk samples with densely packed plate-like grains having c-axis perpendicular to the current direction [5].

The distribution of grain sizes fit best the log-normal (Gauss) distribution function. Fit of the gamma distribution is reasonable and Poisson diverges too much. Therefore, the grain size distributions of the investigated samples seem to obey the same statistic as the distributions of their critical currents [1-3] deduced from the $V-I$ characteristics [6]. This is consistent with the fact that critical current densities in ceramic HTS samples are limited by the quality of the inter-grain boundaries [7], indicating that this parameter has the same distribution as the grain size.

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ANALIZA RASPODJELE VELIČINE ZRNA VISOKOTEMPERATURNOG SUPRAVODLJIVOG SPOJA $YBa_2Cu_3O_{7-x}$

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Istraživane su raspodjele veličine zrna (kristalita) u uzorcima $YBa_2Cu_3O_{7-x}$ keramike koji su bili dozrijevani na 960 °C 7 sati, 70 sati i 700 sati. Mjerena je prosječna veličina zrna (r) i njihova najveća dužina (l). Omjer l/r, koji odražava odstupanje zrna od sferičnosti, u početku raste s vremenom dozrijevanja (t), te opada za duža vremena. Približna $t^{1/2}$ proporcionalnost s l po svoj prilici odražava plošni oblik zrna. U svim ispitivanim uzorcima raspodjele za r i l najbolje opisuje log-normalna (Gaussova) distribucija. Povezanost raspodjele veličine zrna i raspodjele kritičnih struja za iste uzorke ukratko je diskutirana.