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# Surface morphology of $PrBa_2Cu_3O_{7-\delta}$ single crystals after the long-lasting high-temperature reduction

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**Abstract:** The results of the detailed *scanning electron microscopy* study of $PrBa_2Cu_3O_{7-\delta}$ single crystals after the long-lasting high-temperature post-growth treatment are reported. The presence of the unstable decomposition products on the crystal surface indicates that the onset of superconductivity must be related to the structural transformations in the bulk (approximately 20% of the total volume of the examined crystals). The time-dependent character of the superconductivity in the Pr-123 crystals could be attributed to the migration of defects in the Pr-Ba sublattice from the bulk toward the surface.

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## 1 Introduction

The $PrBa_2Cu_3O_{7-\delta}$ (Pr-123) compound is probably still the most controversial member of the well known (rare-earth)-123 family of high-temperature superconductors. It is known that this material, as well as its isostructural homologues, exhibits orthorhombic structure when oxygenated but a great number of authors regarded it as neither metallic nor superconducting [1–9]. On the other hand, there is the reported evidence that superconductivity could generally exist in this system [10–18] but in the case of bulk crystals the synthesis should be carried out in the oxygen-reduced conditions [11–13, 15].

Some interesting models, such as magnetic pair breaking, hole filling, carrier localization, Pr4$f$–O2$p$ hybridization, have been proposed to explain the phenomena. Recently it

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has been argued that Pr at the Ba site ($\mathrm{Pr}_{Ba}$) and not the rare-earth site ($\mathrm{Pr}_{Pr}$) destroys the superconductivity by the large magnetic moment of Pr since the superconducting carriers were first proposed to occupy the vicinity of the chains [18] but more recently have been located in the BaO layers [19]. The *ab initio* calculations of Pr123 with $\mathrm{Pr}_{Ba}$ seem to support this point of view [20]. Despite the great number of papers published on this controversial subject, there is no common agreement concerning the structural and physical properties of Pr123 and it still waits for coherent theoretical description.

The discovery of superconductivity in $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ single crystals, introduced to this system by applying the *post-growth* high-temperature annealing in argon atmosphere (reduction), quick cooling and typical for this class of compounds oxidation process [15], has become a natural motivation for further careful structural investigation of this material [16]. The observed scatter of crital temperatures $T_c$ related to particular conditions of reduction [15] shows the extremely strong correlation between structural and superconducting properties of Pr-123 crystals. The thermodynamical imbalance caused by high-temperature annealing could lead to partial decomposition of crystal surface followed by some rearrangement of atoms in the bulk. The *energy dispersive x-ray* (EDX) investigations performed on the cross-sections of the superconducting Pr-123 crystals [16] indicate that the reduction at high temperatures could minimize the excess of Pr (always present in the bulk samples of this compound [21]) in the surface layer and make this regions almost *perfectly stoichiometric,* i.e. with nominal molar composition Pr : Ba : Cu = 1 : 2 : 3. However, it was not quite clear if the decomposition products appearing on the surface during the high-temperature treatment are stable and could affect the superconductivity in this system.

This *scanning electron microscopy* study (SEM) has been undertaken as the continuation of previous research [15,16]. The aim of this paper is to present the results of surface morphology study of the $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ single crystals after the *prolonged* post-growth thermal treatment and comment on the obtained experimental data in the context of the superconductivity in this system.

## 2 Experimental

The $\mathrm{PrBa_2Cu_3O_{7-\delta}}$ crystals were obtained by the self-flux method well described in [22, 23]. The as-grown single crystals with the size up to $4 \times 6 \times 0.2\,mm^3$ were annealed in the argon and oxygen atmosphere in different thermal conditions, that is, reduced for 1–2 hours at 900–1000°C in Ar, cooled to the room-temperature and oxygenated for 72 hours at 350°C.

The apparatus used in this study was PHILIPS XL30 Scanning Electron Microscope.

## 3 Results and discussion

The typical SEM images of the reduced surface of the Pr-123 single crystal are presented in Fig. 1. It was found that even the short-lasting exposure to the oxygen-deficient

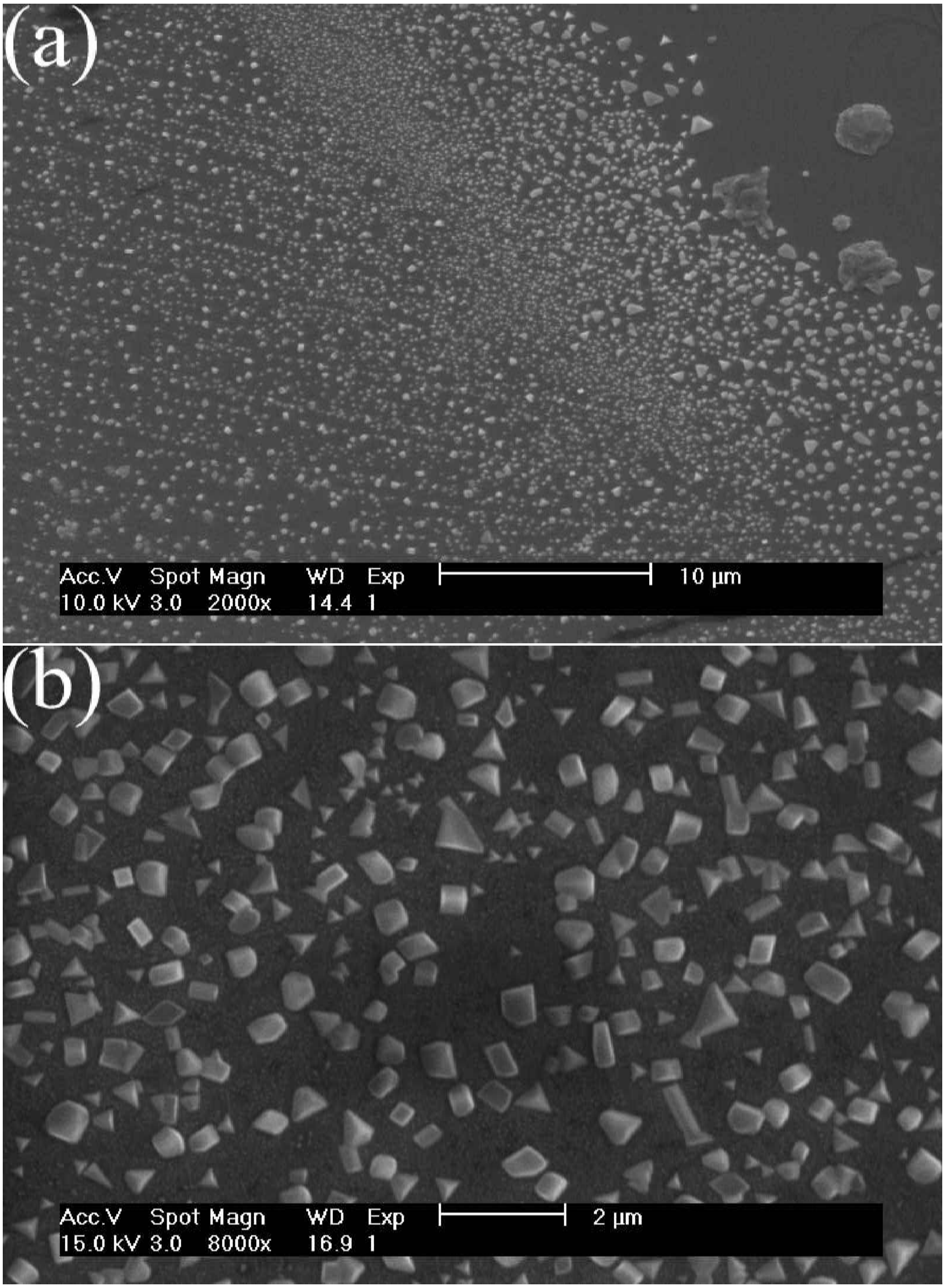

**Fig. 1** The SEM images of Pr-123 single crystal after reduction in Ar at 950°C for 1 hour. Magnitudes: a) 4000× and b) 8000×. The regions covered by randomly distributed crystallites coexist with the 'clean' regions — see the upper right corner of the picture a).

atmosphere led to creation of groups of regular-shaped crystallites with the average size of 0.5 $\mu m$ randomly distributed on the smooth and flat crystal surface typical for the as-grown crystals. This effect was observed in the full range of 900–1000°C of the applied temperatures and there was no significant differences in the surface morphology after annealing for up to 1 hour at the various temperatures from this range. The longer reduction time, however, had a distinct impact on the surface structure since after 2 hours

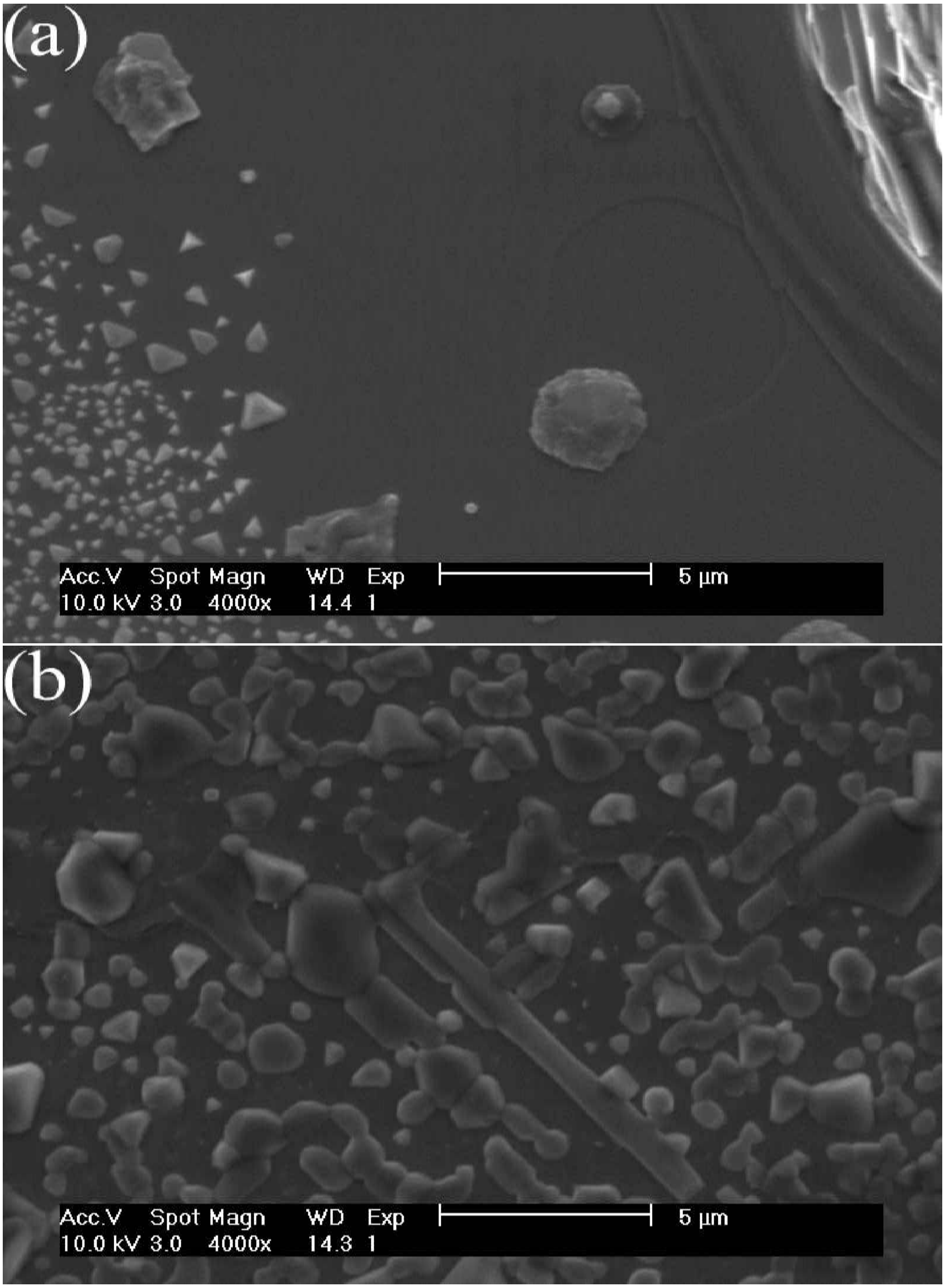

**Fig. 2** The surface of the two pieces of the same Pr-123 crystal reduced in Ar at 950°C for a) 1 h and b) 2 h. The crystallites visible on the picture a) start melting when the reduction process is longer than two hours — picture b). Note the characteristic fragmented paths of melted material.

the crystallites started getting melted forming some kind of fragmented paths on the crystal surface. The morphological changes during the prolonged high-temperature annealing in oxygen-deficient conditions are shown in Fig. 2. The surfaces of the as-grown Pr-123 crystals and the ‘background surface’ of the reduced crystals were compared and carefully analysed but no dissimilarity in the morphology was distinguished. It is noteworthy

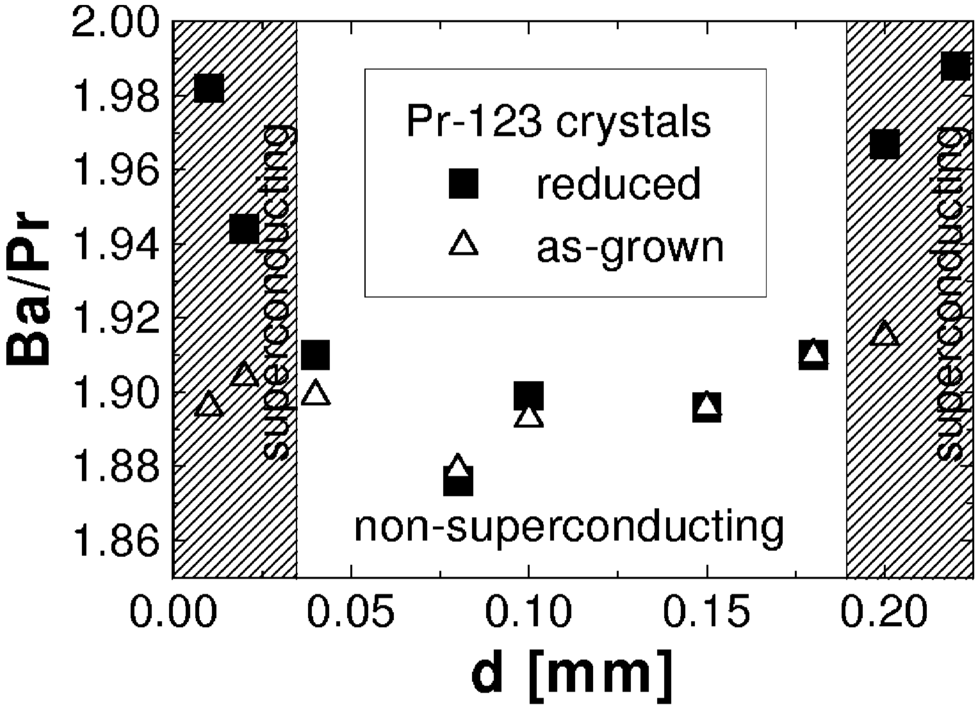

**Fig. 3** The influence of the high-temperature reduction process on the Ba/Pr ratio from the EDX analysis of the cross-section of Pr-123 crystal with the size of $3.2 \times 2.1 \times 0.25\,\mathrm{mm}^3$ (solid squares). Note that after the thermal treatment praseodymium and barium stoichiometry of the surface layers with approximately 25 $\mu$m of thickness is almost nominal (Pr : Ba : Cu = 1 : 2 : 3) and should be regarded as potentially superconducting. In the bulk of the same crystal the Pr on Ba-site substitution could be as high as in the as-grown one (non-superconducting) with the comparable size (open triangles). Presented data have been taken from [16].

that the oxidation processes did not introduce any observable changes in the structure of either the crystallites or crystal surface.

The existence of the crystallites, previously identified as $PrBaO_3$ and $BaCuO_2$ [15,16], on the crystal surface of Pr-123 could be explained by the decomposition process to to the same extent as that taking place during synthesis in oxygen-deficient atmosphere [13, 21]. One should remember that in both cases the thermodynamical conditions are comparable because of the same range of temperatures and low partial oxygen pressure. The difference between the synthesis and the post-growth thermal treatment lies only in the *scale* of structural changes. As a result of the decomposition of Pr-123 single crystals the Ba/Pr ratio increases in the bulk what means that occupancy of Pr ions on the Ba sites should be minimized.

In the light of the above-mentioned experimental facts, two regions should be considered in the context of the superconductivity introduced to the Pr-123 single crystals: (i) the 0.5 $\mu m$ layer of crystallites *on* the flat crystal surface and (ii) the close-to-nominal-composition layer with approximately 25 $\mu m$ of thickness (estimated from [16] — see Fig. 3) *under* the visible crystal surface. The observed instability of decomposition products during the long-lasting annealing (note that exactly the same treatment was used in the previous work) allow you to exclude the hypothesis that the thin layer of crystallites could be the source of the inhomogeneous superconductivity. Therefore the root of the superconductivity must rather lay *under* the flat 'background surface' of $PrBa_2Cu_3O_{7-\delta}$ single crystals. The estimated from Fig. 3 volume of structurally-improved fraction of Pr-123 (i.e. with low level of Ba-site Pr) is about 20% of the total volume of examined crystal what seems to be consistent with the reported magnetic *ac* susceptibility and resistivity measurements showing that superconducting phase was in minority [15].

Lastly, we will comment on the time-dependent character of the diamagnetism of Pr-123 crystals, initially attributed to internal stresses induced by the quick cooling of the reduced crystals [15]. Although this interpretation seems to be still valid, another mechanism should be also considered: the successive *migration of defects* in Pr-Ba sublattice from the bulk of Pr-123 crystal toward the surface regions leading to suppression of the inhomogeneous superconductivity after a few weeks. The observed higher efficiency of the low-temperature oxidation, subsequently leading to higher $T_c$, supports this point of view because the annealing at higher temperatures should provide better conditions for the migration of defects responsible for $Pr_{Ba}$ substitutional disorder.

## Summary

The scanning electron microscopy (SEM) analysis of $PrBa_2Cu_3O_{7-\delta}$ single crystals after the long-lasting reduction was performed. All the observations, namely: (i) creation of thin layer (0.5 $\mu m$) of randomly distributed on the flat surface crystallites, (ii) their low resistance for the long-lasting annealing used to introduce superconductivity [15] and, finally, (iii) simultaneous minimization of Pr excess in the surface layers with approximately 25 $\mu m$ of thickness (about 20% of the total crystal volume), support the concept that the minimization of Pr on the Ba sites could restore the superconductivity in this system. Moreover, the following hypothesis could be put forward. The reported unstable character of superconductivity in Pr-123 crystals could be also attributed to the *migration of defects in the Pr-Ba sublattice* from the bulk toward the surface.

The further experimental and computational work on the point defects in Pr-123 material is still necessary. Especially the *scanning tunneling microscopy* and *atomic force microscopy* (STM-AFM) techniques could be useful since they should give the absolute height and shape of the crystallites which information might be useful in case of comparison of the time and/or temperature of the reduction process.

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