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Influence of the heat treatment on the structure of $SmBa_2Cu_3O_{7-x}$

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In this paper we present the results of our study of different heat treatment regimes on the structure of $SmBa_2Cu_3O_{7-x}$ samples. We have shown that using a light microscope it is possible, in polarized light, to distinguish between a tetragonal and an orthorhombic phase and to study their morphology. The independence of the thickness of orthorhombic phase twins on the transition temperature was quantitatively determined, this may be connected with a constant oxygen content in the $SmBa_2Cu_3O_{7-x}$ phase during tetragonal to orthorhombic transition.

1. Introduction

Most of the rare earth elements form with barium and copper a perovskite phase of the $YBa_2Cu_3O_{7-x}$ type, appearing in two structural modifications, tetragonal and orthorhombic [1–8]. The tetragonal phase is not superconducting, whereas the orthorhombic phase shows superconducting properties, with a transition temperature into the superconducting state depending on the oxygen content [5, 9]. The transition temperature from the high-temperature tetragonal phase into an orthorhombic phase depends on the oxygen partial pressure in the annealing atmosphere and it is ~ 700° C for a pure oxygen atmosphere [5]. It was shown by electron microscopy [9, 10] and X-ray studies [11], that this phase transition is accompanied by the twinning of the orthorhombic phase along the (1 1 0) plane. The observed twins were from 10 nm up to more than 100 nm thick [12]. By quenching it is possible to obtain samples showing tetragonal or orthorhombic structure at room temperature [8]. Above 1000° C, the decomposition of the $YBa_2Cu_3O_{7-x}$ phase was observed also in 100% oxygen [13].

2. Experimental procedure

Samples weighing 1.2 g and of $SmBa_2Cu_3O_{7-x}$ nominal composition were prepared from dried Sm_2O_3, $BaCO_3$ and CuO powders more than 99.9% pure. Powders were mixed, ground and pressed at a pressure of 10 MPa into pellets 10 mm in diameter, then annealed for 2 h at 950° C in air and then for 16 h at 1000° C in O_2, followed by slow cooling to room temperature. Samples so prepared had a transition temperature, T_c of 90 K and served as the initial experimental material. The samples were placed into a platinum boat inside a horizontal tube furnace in an argon and oxygen atmosphere. The quenching was realized by pulling out the boat containing the sample from the furnace and submerging it into a liquid nitrogen bath. Sample transfer took no more than 1 sec. All heat treatment regimes are described in Table I.

Sample structure was studied by a Neophot 21 light microscope and by a Tesla BS 300 scanning electron microscope. X-ray phase analysis was performed on a HZG/4A universal diffractometer using Co*Kα* radiation, and its results are shown in Table I.

3. Experimental results

The technology used for the preparation of $SmBa_2Cu_3O_{7-x}$ superconducting samples produced the orthorhombic structure containing plate-like grains with dimensions of approximately 4 μm × 20 μm × 40 μm (Fig. 1) and strongly twinned (Figs 2 and 3). Within one grain the twins with a maximum of two orientations may be found. Twins form packs

TABLE I The regimes of heat treatments of samples

Sample No.	Heating rate ($°C\,min^{-1}$)	Heat treatment	Cooling	Phase composition
3	10	800° C/Ar	10° C/min	T
3a	10	800° C/Ar + 350° C/O_2	O_2 stream	T
3b	10	800° C/Ar + 400° C/O_2	O_2 stream	T + O
3c	10	800° C/Ar + 450° C/O_2	O_2 stream	O
3d	10	800° C/Ar + 500° C/O_2	O_2 stream	O
4	10	900° C/2 h/O_2	Quenched/N_2	T
4a	10	900° C/2 h/O_2 decrease to 750° C/4 h/O_2	Quenched/N_2	T + O
4b	10	900° C/2 h/O_2 decrease to 700° C/4 h/O_2	Quenched/N_2	O
4c	10	900° C/2 h/O_2 decrease to 650° C/4 h/O_2	Quenched/N_2	O
4d	10	900° C/2 h/O_2 decrease to 600° C/4 h/O_2	Quenched/N_2	O

Notes: T is the tetragonal phase; O is the orthorhombic phase.

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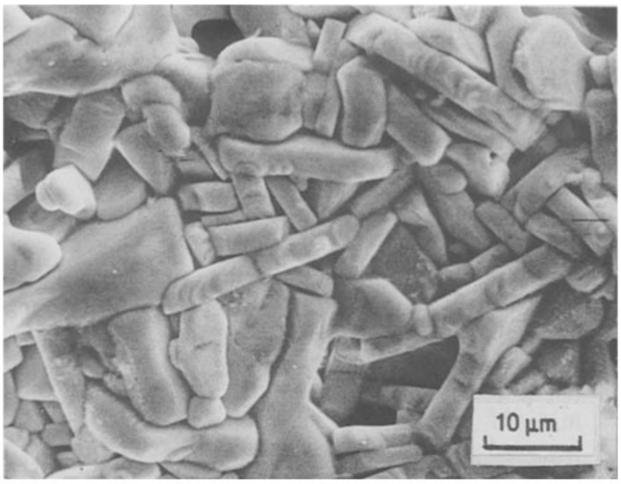

Figure 1 SEM image showing the surface of $SmBa_2Cu_3O_{7-x}$ sample.

which may be seen under a polarized light and at suitable grain orientation as regions with two different brightnesses (Fig. 4).

Samples with a tetragonal phase do not show twins in grains (Fig. 5).

The coexistence of both orthorhombic and tetragonal phase was revealed in samples annealed at 350–500° C. The twinned orthorhombic phase propagated from the surface into the sample middle (Fig. 6). At 350° C the orthorhombic phase was found only sporadically and even at 500° C the tetragonal phase was not transformed into an orthorhombic one.

Samples 4 to 4d (saturated by oxygen at 600–750° C) contain only the twinned orthorhombic phase, with the observed decrease in the (light) contrast between the twins with increasing saturation temperature (Fig. 7).

The influence of the heat treatment on the twin thickness was characterized by the mean distance between the coherent boundaries $\bar{d}$, as measured on the cut. It may be seen from the dependence shown in Fig. 8, that $\bar{d}$ is practically independent of the temperature of annealing in oxygen.

In grains of the sample in the initial state, in which at least two packs with clearly visible twins could be found, the distance between twins in packs as well as the angle between twin orientations were measured.

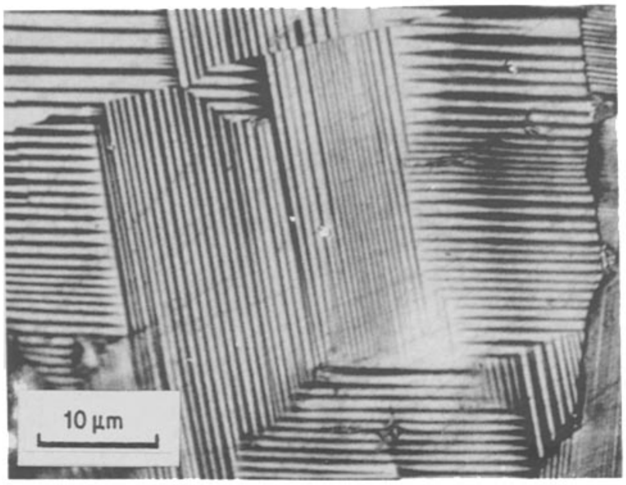

Figure 3 Interaction of the twin crystallites on the noncoherent pack boundaries. $SmBa_2Cu_3O_{7-x}$ in the initial state. (Polarized light).

Considering that the orthorhombic phase forms twin along the (1 1 0) plane [9–11] and assuming a constant twin thickness in the packs, the relation between d_1, d_2, α, s, α_1, α_2 may be described by the following set of equations:

$$\cos\alpha = \sin\alpha_1 \sin\alpha_2 \qquad (1)$$

$$\frac{d_1}{d_2} = \frac{\cos\alpha_2}{\cos\alpha_1} \qquad (2)$$

$$s = d_1 \cos\alpha_1 = d_2 \cos\alpha_2 \qquad (3)$$

where d_1 and d_2 are the distances between coherent boundaries in the two packs within one grain on the cut, α is the angle formed by the two twin orientations in one grain on the cut, s is the real twin thickness, and α_1 and α_2 are the angle deviations of the [0 0 1] plane in orthorhombic structure from the cut plane. From the measured values the mean thickness for the sample in initial state was calculated as $\bar{s} = 133 \pm 33.6$ nm.

4. Discussion

It is an advantage to use a polarized light source for the structural studies of the samples 1, 2 and 3, since it enables the differentiation between a tetragonal and an orthorhombic structure. The light contrast makes it possible to see the twin crystallites, to characterize

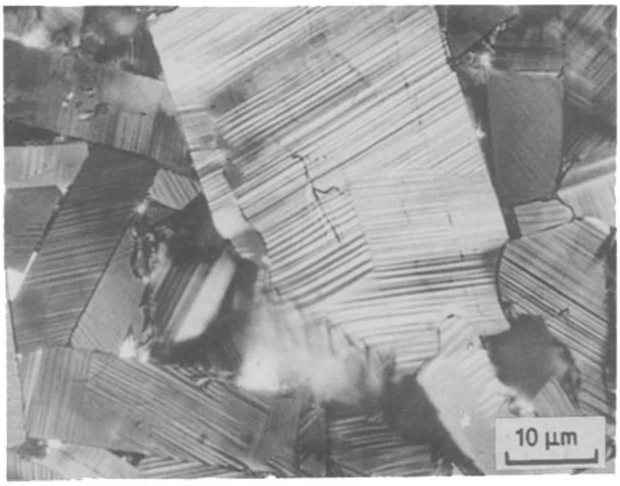

Figure 2 Twins in grains of the $SmBa_2Cu_3O_{7-x}$ phase, visible in the polarized light.

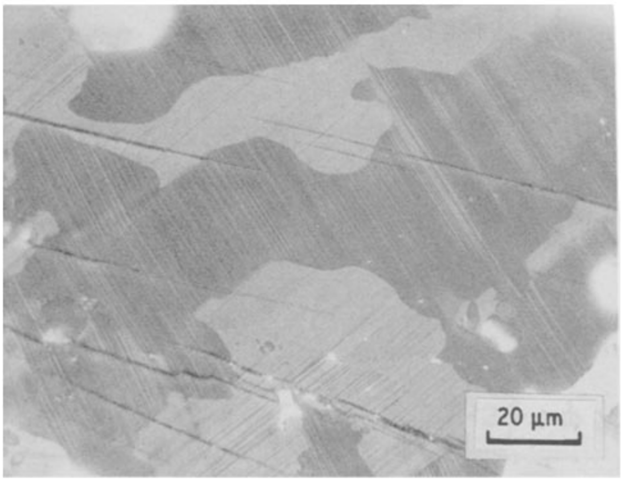

Figure 4 Twin packs in one grain, made visible by the polarized light and separated by noncoherent boundaries.

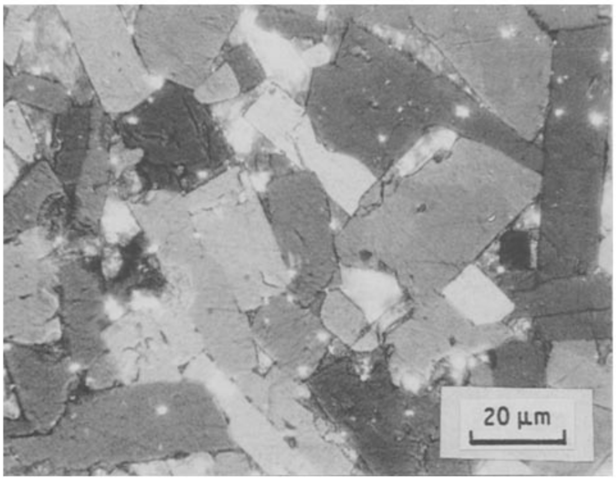

Figure 5 Structure of the sample No. 3 with tetragonal $SmBa_2Cu_3O_{7-x}$ phase. (Polarized light.)

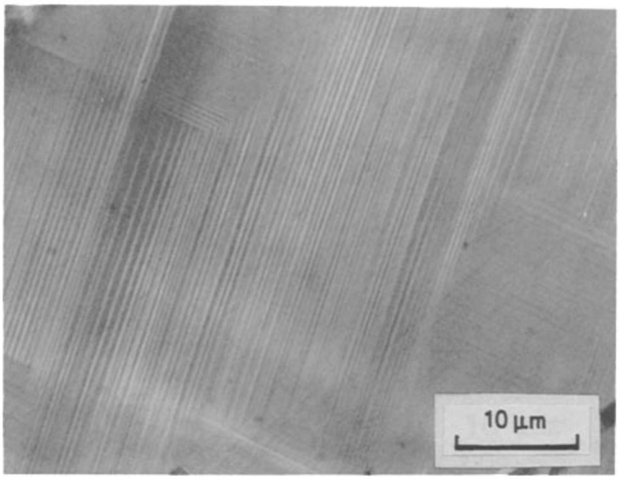

Figure 7 Lower contrast between twins of the $SmBa_2Cu_3O_{7-x}$ phase in the sample annealed at 650° C for 4 h. (Polarized light.)

their morphology and to determine their dimensions. As was shown in [11], twinning during the transformation of the tetragonal phase into an orthorhombic one produces crystallites showing four orientations (Fig. 9). Orientations I and II form one pack and orientations III and IV form another one within one grain. Such a configuration of the orthorhombic phase crystallites makes it possible, at suitable grain orientation in the polarized light, to see the noncoherent twin boundaries forming the pack boundaries (Fig. 4).

The saturation of the tetragonal phase by oxygen and its transition is realized through oxygen diffusion into open pores, and this is connected with the growth of the orthorhombic phase beginning at grain boundaries and with the presence of the tetragonal phase in the middle of grains.

Isothermal annealing at 600–750° C in O_2 leads to the formation of a homogeneous structure of the orthorhombic phase with oxygen content corresponding to the equilibrium oxygen concentration. The lower contrast between twins may be connected with this lower oxygen content resulting in a lower difference (*b–a*) of the orthorhombic lattice. The presence of an orthorhombic phase in samples quenched from 750° C was observed also in [5] and it may be probably connected with the transformation of the tetragonal phase during quenching.

Formation of twins during tetragonal to orthorhombic transition is in [9] connected with dilatation changes. Twinning along (1 1 0) planes compensates for these dilatation changes (contraction in the *a* direction and dilatation in the *b* direction), considering the fact that the observed twinned structure may form only when the transition is not accompanied by a loss of coherence on the tetragonal–orthorhombic phase boundary, the atomic planes of the newly forming orthorhombic phase may shift by a maximum of one lattice parameter per thickness of the forming element of the orthorhombic phase. (Loss of coherence would lead to the morphology of uniaxial grains). Using this assumption we can determine the maximum twin thickness in the first approximation as [9]:

$$s = \frac{ba}{b-a}$$

To estimate s it is necessary to take the lattice parameters of the orthorhombic phase corresponding

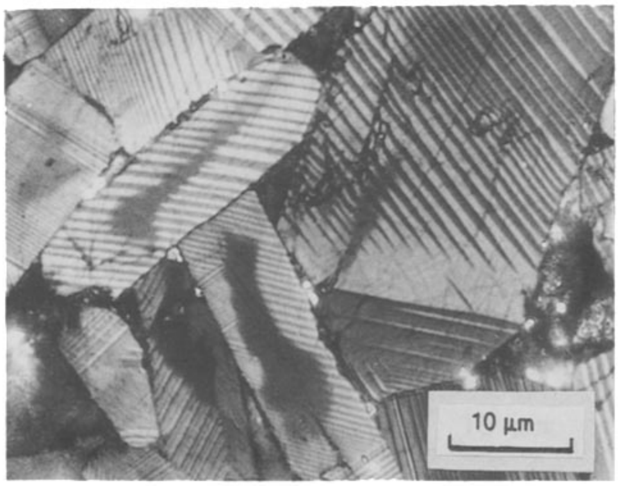

Figure 6 Mixture of the tetragonal and orthorhombic $SmBa_2Cu_3O_{7-x}$ phase in the sample saturated by O_2 with heating rate 10° C min^{-1} to 450° C.

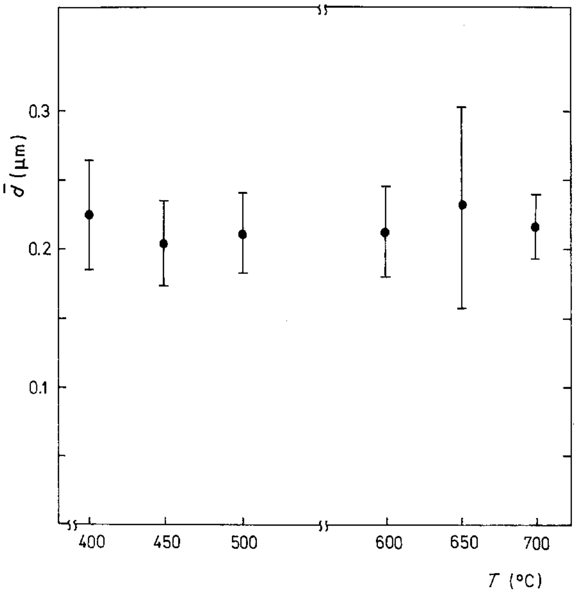

Figure 8 The dependence of the mean distance between coherent boundaries $\bar{d}$ on the temperature of annealing in oxygen.

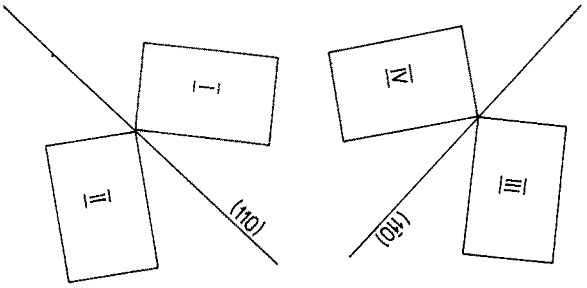

Figure 9 The orientations of the orthorhombic crystallites formed by twinning at tetragonal to orthorhombic transition [11].

to the oxygen content during transition, i.e. the parameters obtained by *in situ* measurements at a temperature as near to the transition temperature as possible. Using the parameters from [5] we obtained $s \doteq 140$ nm. This value is in a good agreement with $\bar{s}$ obtained for the sample in its initial state.

Considering the connection between the difference (b–a) (which is a primary factor in determining the twin density) and the oxygen content in the 1:2:3 phase, the obtained independence of $\bar{d}$ on the conditions of the saturation process may be formulated so, that the tetragonal to orthorhombic transition takes place at the same oxygen concentration, independent of the transition temperature.

The effects of the mutual interactions between twins near the noncoherent twin boundaries are in connection with the dilatation changes during tetragonal to orthorhombic transition. The alternating orientation of crystallites within one pack compensates in fact for the arising dilatations (crystallites are in an angle of 90° to each other). A random contact of crystallites at pack boundaries results in such a modification of their thickness near noncoherent boundaries that the resulting dilatation is kept down to a minimum.

5. Conclusions

By an optical microscopy and using polarized light it is possible to distinguish the tetragonal and the orthorhombic $SmBa_2Cu_3O_{7-x}$ phase.

Transition of the tetragonal phase takes place at temperatures of 350–500° C heterogeneously from pore and grain surfaces. The thickness of the orthorhombic phase twins does not depend on the transition temperature, which also means that the transition is temperature independent at the same oxygen content in the $SmBa_2Cu_3O_{7-x}$ phase.

The obtained mean twin thickness $\bar{s} = 133 \pm 33$ nm is in a good agreement with the value determined under the assumption of the lattice coherence of the tetragonal and the orthorhombic phase at the transition.

The observed modification of the twin thickness near the noncoherent boundaries is connected to the compensation of dilatation stresses originating during transition at noncoherent boundaries.

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