TEM-INVESTIGATIONS ON PHASES OF CERAMIC SAMPLES OF THE Tl-Ca-Ba-Cu-O SYSTEM

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Abstract

Tl-Ca-Ba-Cu-O high-T_c ceramic superconducting samples of nominal composition 1111 were investigated by SAED and HRTEM. The identified crystalline components are 2223, 2122, 1223 and $BaCuO_2$. Different formations in the real crystal lattice (small-angle boundary, anti-phase boundary) have been observed. The interstratified phases appearing in different host matrices were studied in detail.

Introduction

The transmission electron microscopy (TEM) is an ideal tool to study the quantitative phase compositions, the intergranular connections and the properties of the crystalline structure of polycrystalline materials. In the recent years the TEM has been applied in the studies of high-T_c ceramic superconductors too [1].

The crystallographic parameters of the phases of the Tl-Ca-Ba-Cu-O system have been determined by Beyers [2]. Up to now the phases with compositions of 1021, 1122, 1223, 2021, 2122 and 2223 have been identified by their symmetries and lattice parameters.

The aim of the recent work is the quantitative identification of the phases of samples having the 1111 nominal composition and the characterization of the real crystal structure of these phases. Among the methods of the TEM first of all the selected area electron diffraction (SAED) and the high resolution transmission electron microscopy (HRTEM) have been applied.

* Dedicated to Professor János Giber on the occasion of his Sixtieth Birthday

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Sample

The sample has the nominal composition of $TlCaBaCuO_{4.5}$. The main steps of the heat treatment process were the following [3, 4]. The ground and mixed starting compounds were first annealed at 450 °C in air for 30 min and then cooled with a slow rate of 15 °C/min to room temperature. After the second heating stage, at 900 °C in air for 10 min the material had a quick cooling of 1000 °C/min to liquid nitrogen temperature. Following another grinding and mixing procedure it was pressed at 10 MPa into pellets of 15 mm diameter and 4 mm in thickness, and sintered at 900 °C in air for 3 min after heating up in 5 min. Finally the samples were cooled down to room temperature with a slow rate of 2 °C/min.

Methods

The TEM investigations were carried out by a JEOL-JEM 100 CX type equipment using 100 kV accelerating voltage.

Crystal grains with thickness of well transilluminable were prepared by grinding under alcohol. The alcoholic suspension of the sample was deposited onto a copper microgrid covered by a holey carbon supporting film. The grains covering the holes can be studied without the disturbing background.

The grains chosen for investigations have been oriented by a tilt-rotating side-entry ($\pm 60°$; $\pm 360°$) goniometer. The high-T_c superconductive phases were oriented in the [100], the barium cuprate crystals in the [100], [110] and [111] projection. SAED patterns were made on the chosen areas with minimum diameters of 0.3 μm. The evaluation has been carried out on magnified photographs.

The HRTEM micrographs were made by axial illumination using an objective aperture of 5.4 $Å^{-1}$. The details of the structure were resolved down to the limit imposed by the objective blende.

Results

The sample consists of superconductive phases and barium cuprate. The SAED patterns (Figs 1, 2) and the HRTEM micrographs (Fig. 3) of the $BaCuO_2$ hints at an ideal monocrystalline structure.

The gross of the superconductive phases is 2223 (Fig. 4). Beside the phases 2122 (Fig. 5) and 1223 (Fig. 6) can also be identified. The diffuse scattering along the axis 'c^*' with intensity different for different grains hints at randomly distributed interstratifications.

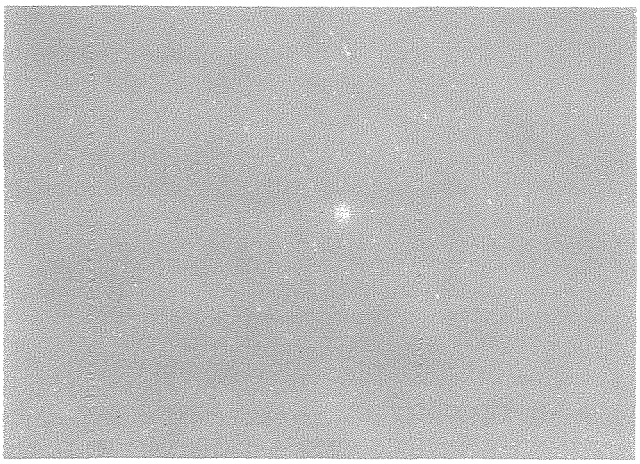

Fig. 1. [100] SAED pattern of $BaCuO_2$

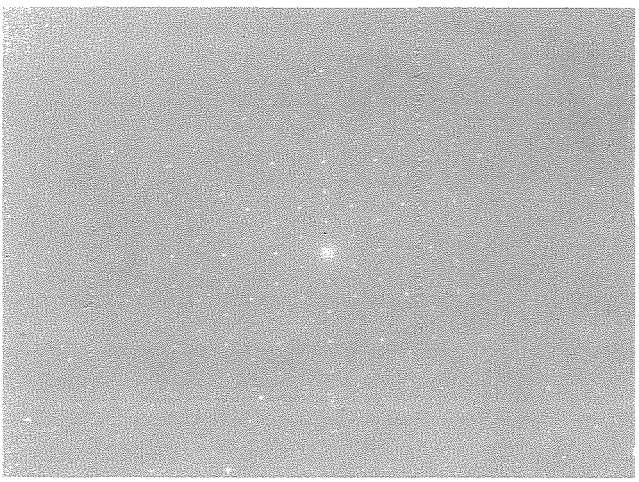

Fig. 2. [111] SAED pattern of $BaCuO_2$

A small angle grain boundary — a rather frequent formation in the sample — is shown in HRTEM micrograph of small magnification (Fig. 7). The contrast of the elementary layers of the interstratified phases is different than that of the host matrix with a composition and structure of 2223. On the two sides of the grain boundary there are elementary layers of 2122 and 1223 structures respectively (Fig. 8).

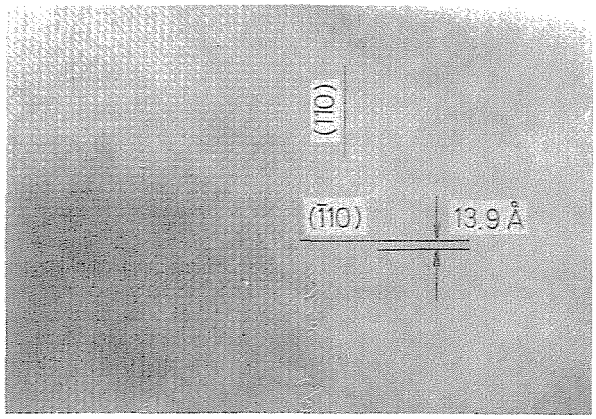

Fig. 3. [100] HRTEM micrograph of $BaCuO_2$

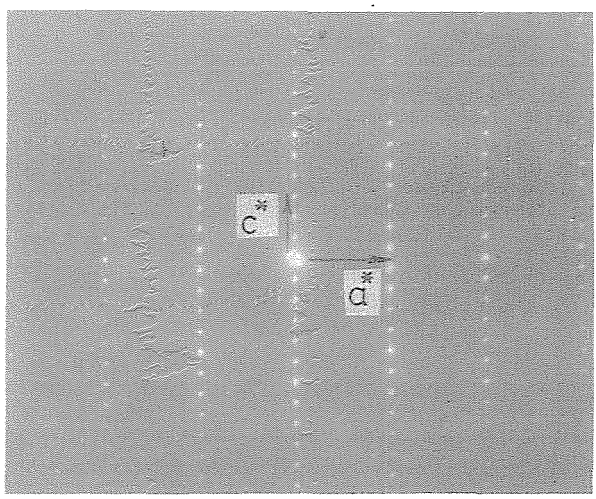

Fig. 4. [100] SAED pattern of 2223 phase

In Fig. 9 randomly distributed interstratifications can be seen in a matrix of structure 1223. The interstratifications give a dark contrast compared to the contrast of the (001) lattice planes of the matrix. Regarding that the HRTEM image represents the projection of the charge density distribution in the sample, the dark bands can be identified as Tl—Tl layers characteristic to the phases 2021, 2122 and 2223. This supposition is justified by the fact that the distance between the neighbouring dark bands is equal to the $d(002)$ value of the phase of 2122 structure ($= 14.7$ Å).

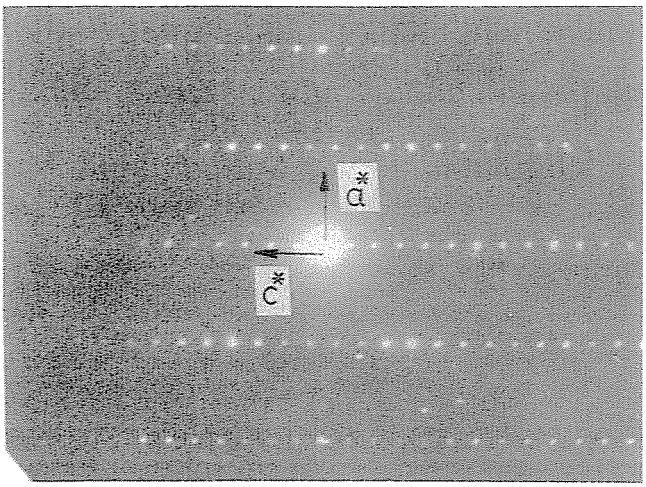

Fig. 5. [100] SAED pattern of 2122 phase

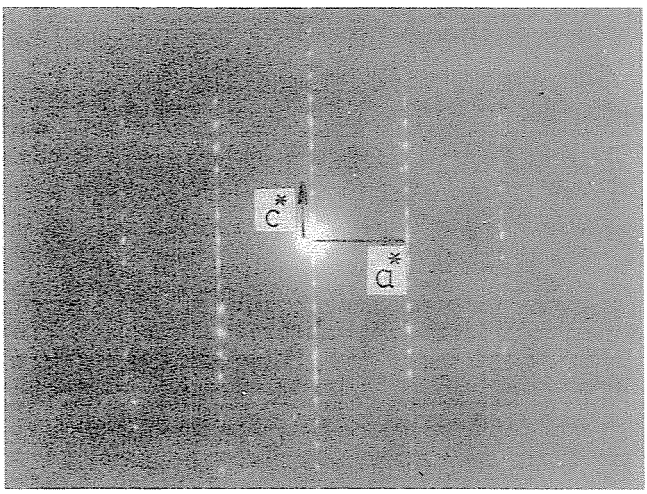

Fig. 6. [100] SAED pattern of 1223 phase

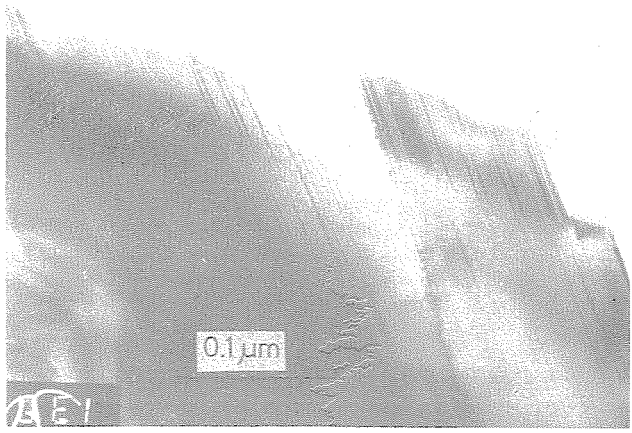

Fig. 7. HRTEM micrograph of a small angle grain boundary

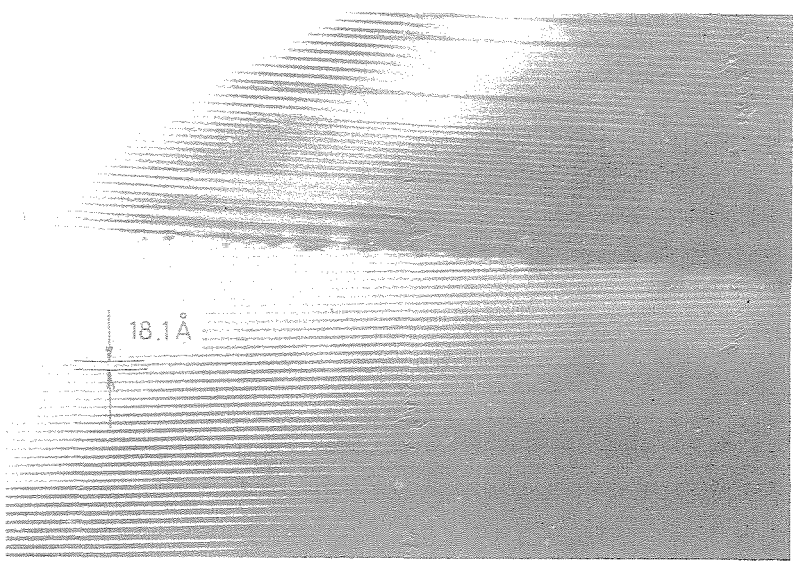

Fig. 8. Interstratified phases of type 1223 and 2122 in the matrix of type 2223 (Enlarged area of low angle grain boundary shown by Fig. 7)

In Fig. 10 the HRTEM micrograph of a crystal of 2122 structure is shown. The interstratifications are of type 1122 and 1021 ending within the crystal. An antiphase-boundary (APB) like connection can be observed almost perpendicularly to these endings. These boundaries are practically absent of mechanical strains. They can be interpreted by the structure model presented in Fig. 6 of the report by Van Tandeloo et al. [5].

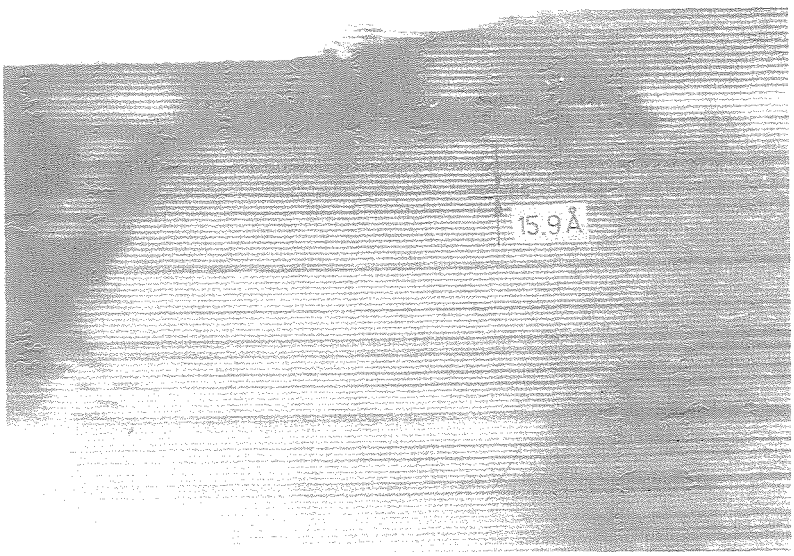

Fig. 9. Interstratification in a matrix of type 1223

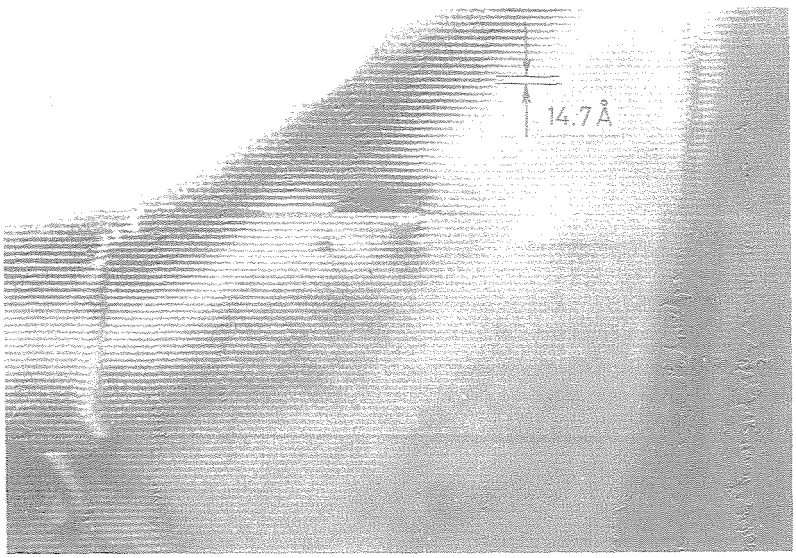

Fig. 10. Interstratification in a matrix of type 2122 and APB

In Fig. 11 it is shown a HRTEM micrograph of a 2223 crystal containing interstratifications and APB-like boundaries in a high density. The interstratification consists of the elementary layers of phase 2122. In the vicinity of

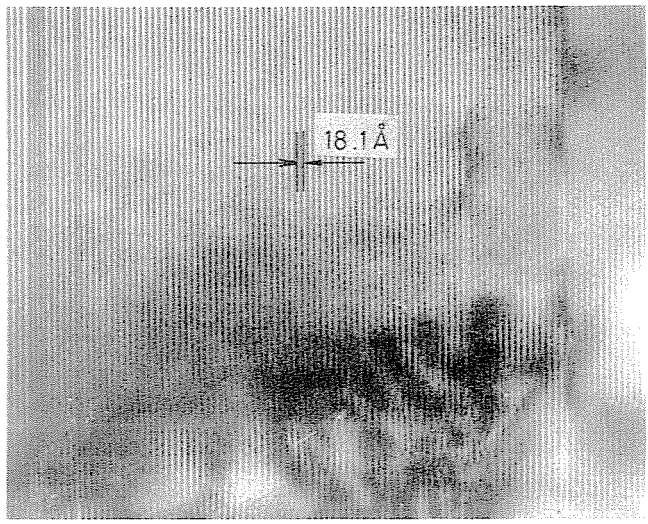

Fig. 11. Interstratification in a (0.17 0 1) modulated matrix of type 2223

the APB-like boundaries a more or less periodic modulation of the structural units of (002) has been observed along the [100] axis. The periodicity and direction of this modulation can be identified by the superlattice of indices (0.17 0 1) mentioned by Beyers [2].

References

1. MITCHELL, T. E.: J. of Electron Microscopy Technique, *8*, 339, 1988.
2. BEYERS, R. et al.: Appl. Phys. Lett. *53*, 432, 1988.
3. KIRSCHNER, I. et al.: "Advances in Superconductivity", 807., Springer-Verlag, Tokyo, 1988.
4. LAIHO, R. et al.: J. of Microscopy *152*, 407, 1988.
5. VAN TANDELOO, AMELINCKX, S.: J. of Electron Microscopy Technique, *8*, 285, 1988.

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