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High-resolution transmission electron microscopic (HRTEM) studies of $Tl_2Ba_2CuO_{6\pm x}$

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Abstract

High resolution transmission electron microscopy (HRTEM) and diffraction techniques were used to characterize $Tl_2Ba_2CuO_6$ specimens prepared using a variety of new synthetic paths. Thus the degree of crystalline perfection, at atomic resolution, of the tetragonal phase, which usually has a superconducting transition in the range 0-90K, could be characterized and compared with that of the orthorhombic phase.

Excellent quality $Tl_2Ba_2CuO_6$ crystals, with Tc = 92K, were obtained under high pressure of argon to minimize Tl-loss. In the best quality material there were no extended defects. The application of computer-simulation and image-matching techniques allowed the CuO_2 layers of the structure to be located on the HRTEM images. High-Tc materials showed typically perfect order for the CuO_2 and adjacent Ba-O sheets : for non-superconducting orthorhombic crystals fluctuations of image intensity and contrast for the CuO_2 sheets were observed. It is suggested that such fluctuations, associated with variations of Tl occupancy, including vacancies and/or Cu substituting for Tl, are responsible for the variability of Tc exhibited by this cuprate material.

1. Introduction

$Tl_2Ba_2CuO_6$ (so called "2201") is one of the more puzzling members of the cuprate family of superconductors. Different samples of this compound may have Tc ranging from 0 to 90K whilst they appear virtually isostructural according to X-Ray and neutron powder diffraction analyses [1,2]. It is reported that 2201 crystals may be tetragonal or orthorhombic; some authors report only tetragonal crystals are superconducting [1,2]. There has been considerable inconclusive discussion in the literature concerning the role of Tl-vacancies, Cu substitution for Tl, and oxygen stoichiometry, as well as valence fluctuations in determining the detailed characteristics of the superconducting transition : see for example [3,4].

The purposes of the present work were firstly to characterize, up to atomic resolution, the structural features of $Tl_2Ba_2CuO_6$ phases prepared by different synthetic routes and thereby guide improvements in preparation techniques. Secondly, one attempts to answer the question what is the basis for the great variability of Tc(0-90K) exhibited by the tetragonal phase of this material.

2. Experimental

Orthorhombic and tetragonal specimens of "$Tl_2Ba_2CuO_6$" were supplied

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by J.L. Jorda (Physico-Chimie Minérale II, Lyon) and C. Opagiste (CENG, Grenoble)[5,6]. All had been characterized previously by metallographic examination, X-Ray powder diffraction, microprobe analysis, plasma emission spectroscopy and magnetic susceptibility measurements. Further details are available in refs [5,6].

Electron microscopic observations were made using a JEOL-200CX instrument operating at 200 kV. The objective lens pole pieces allowed interpretable atomic resolution of 0.23nm to be achieved for very thin crystals (say ≤ 10nm), prepared by crushing.

3. Results

(a) Transmission electron microscopy Samples heated under oxygen flow at 630°C for 24h, followed by 20mn at 840°C, exhibited mean grain size of up to 0.5μm, but many areas showed poorly crystallized regions on the scale of 50-100nm. They contained a high density of defects, such as dislocations, twin lamellae and minor phases such as 1223 and thallium oxide; Tl_2O3, Tl_2CuO_5 was indicated by XRD but was not identified by electron diffraction. Some amorphous and poorly crystalline material also occurred.

Further annealing of this starting material under high pressure (100 bar of oxygen or argon) at about 900°C led to relatively large crystals (20-50μm in length) for both orthorhombic (under oxygen) and tetragonal (under argon) phases. Small flakes of poorly crystalline Tl_2O_3 or Tl_2CuO_5 were found (rarely) attached to the surface of the tetragonal phase. These most probably formed between 2201 crystallites. The degree of crystalline perfection of these high pressure preparations was stunning, compared to the material obtained at 1atm.

(b) Electron diffraction. Figures 1 a,b compare [100] zone diffraction patterns for the 1 atm and 100 bar preparations of the orthorhombic phase respectively. Note the relatively sharp spots obtained for the 100 bar preparation, indicative of the higher degree of crystalline order. There is apparently a small decrease in the ratio c/a for the ordered sample, with virtually no change in the a parameter. Furthermore the 100 bar preparation showed a pronounced superstructure (enlargement Fig. 1(b)) with well-resolved spots along <015> directions and periodicity of approx. 1.64 nm (cf Hewat et al [7]). Close inspection of Fig.1(a) (see enlargement) shows very diffuse spots having approximately the same geometry, which may be considered as of the same nature as Fig. 1(b) but the superstructure ordering must be short-range rather than long-range. Hewat et al [7] proposed this super-structure may be due to Tl and oxygen vacancies. Consideration of the more recent structural studies of Shimakawa et al [1] and Kolecnikov et al [3] suggest that ordering of Cu substituted for Tl sites may be involved.

(c) High resolution transmission electron microscopy. Figures 2(a,b) compare typical HRTEM images of orthorhombic and tetragonal preparations respectively. The degree of crystalline order and perfection was quite remarkable, compared with earlier preparations at 1 atm. Virtually no extended defects such as intergrowth of adjacent phases, dislocations or twin boundaries could be found. Small traces of amorphous or poorly crystalline materials were found, only rarely, apparently attached to the surface of tetragonal phase crystals. Presumably this was originally intergranular.

Perhaps not surprisingly there were no gross differences between the structure images of the two phases, since the atomic coordinates and site occupancies are not significantly different. Computer simulations of the HRTEM images were achieved for both phases without difficulty using published crystallographic data [1,3]. Simulated images are inset in Figures 2 (a,b). Comparison of images simulated for various (Tl/Cu) site occupancies on the Tl sites, including vacant sites, showed no remarkable differences if the total

occupancy was unity ; however the 10% Tl-vacancy simulations were marginally different from Tl + Cu = 1.0, but only for very specific specimen thicknesses and objective lens defoci. We do not consider the difference between Tl vacancy and Tl/Cu substitution may be determined absolutely at the present stage of analysis.

The computer simulations did allow the CuO_2 sheets to be identified as indicated by arrows in Figs. 2(a,b). Furthermore careful inspection of the two sets of images, for the optimum defocus condition (≅ 45 nm) leaves the qualitative impression that, if there is any significant difference between the images of the two phases, it concerns only the perfection of individual CuO_2 sheets, and perhaps the adjacent BaO layers. A structural drawing is given for convenience as Figure 2(c). Fluctuations of intensity and image detail occur more frequently for the orthorhombic phase (Fig. 2(a)) than for the tetragonal phase (Fig. 2(b)).

4. Discussion

One may conclude that the presence of varying densities of small defects in the CuO_2 sheets, such as copper and/or oxygen vacancies, would certainly lead to variable Tc. Further attempts to resolve this issue are proceeding. HRTEM and electron diffraction may be expected to play a direct role in this study since it has the capability to reveal local fluctuations in short-range ordering within the CuO_2 sheets. HRTEM images for the [110] tetragonal zone axis may reveal the structural origin of the superstructure spots shown in Figs. 2(a,b).

On thinking about the crystal chemistry of this phase we propose the following. Assume that it is necessary to replace some Tl by Cu ions and/or Tl vacancies in order to induce the superconducting phase transition [1,3,5]. Further assume that the Tl-O layer cannot form without ≈ 5% Tl replaced by Cu ; this may be required in order to reduce the mean Tl-O intralayer bond length so that the Tl-O layers remain coherent with the adjacent Ba-O and Cu-O layers. Now assume one may prepare a phase with stoichiometry $(Tl_{1.90}, Cu_{0.10})$ $Ba_2Cu_{0.90}$ $O_{6\pm x}$, where 10% of the Cu sites are vacant on the CuO_2 sheets. This may be characteristic of the orthorhombic phase, which would certainly not have a superconducting phase transition due to imperfection of the CuO_2 sheets. Further assume one may then prepare a phase with stoichiometry $(Tl_{1.90}, Cu_{0.10})$ $Ba_2Cu_{1.0}O_{6\pm x}$, having fully ordered and occupied CuO_2 sheets. This may be expected to correspond to the tetragonal phase, which has a superconducting Tc of 92K and reduced Tl/Cu ratio. Note that the precise oxygen stoichiometry will depend on the valence of both Tl and Cu ; both are expected to exhibit variable valency, dependent on temperature and partial pressure of oxygen during preparation.

Clearly it is necessary to produce systematically a set of specimens with carefully controlled Tl/Cu ratios and site occupancies as well as controlled oxygen stoichiometry. Then perhaps the puzzling variations of Tc exhibited by "$Tl_2Ba_2CuO_6$" may be better understood.

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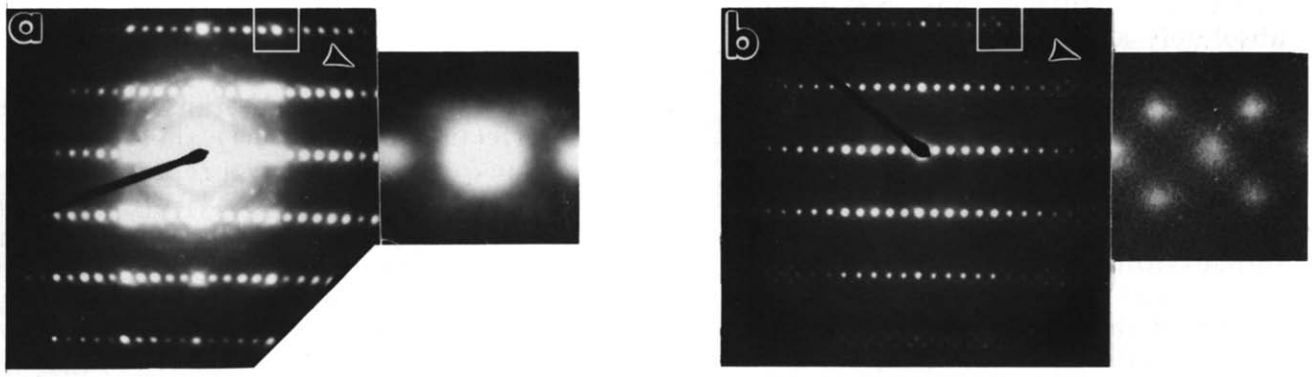

Figure 1. Electron diffraction patterns (with enlargements showing superstructure spots) obtained in the [100] zone from the 1atm (a) and 100 bars (b) preparations of the orthorhombic phase

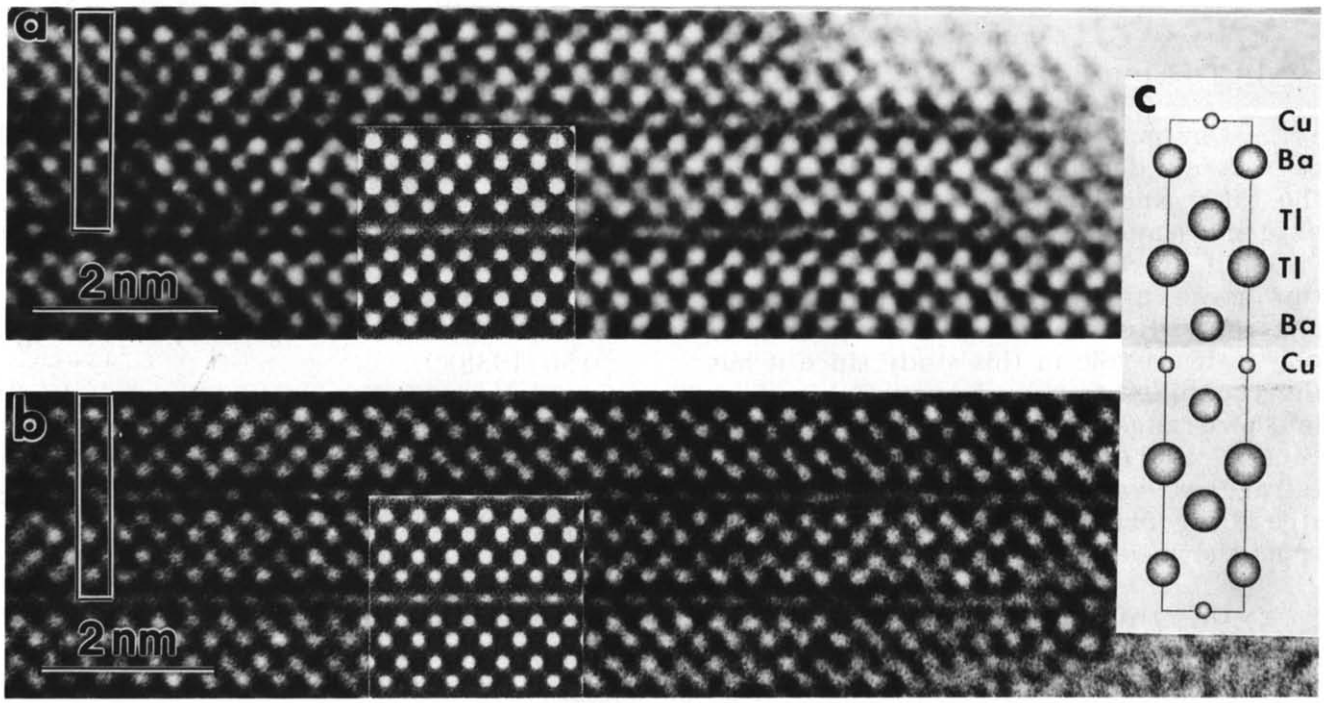

Figure 2. HRTEM images of the orthorhombic (a) and tetragonal (b) 100 bar preparations. Insets are simulated images (parameters being : aberration coefficient C_S = 0.85, defocus spread 10nm, beam semi-convergence 1.0 mrad, objective lens defocus -45nm, specimen thickness 2.3nm). The projected unit cells are outlined.