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Electron microscopic investigation of high-temperature oxide superconductors*

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Abstract. Electron microscopic investigations have been carried out on superconducting $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$ and related oxides. All these orthorhombic oxides exhibit twin domains. Based on high resolution electron microscopy, it is shown that there is no significant change in the structure across the twins. Oxides of the $La_{2-x}Sr_x(Ba_x)CuO_4$ system do not show twins, but exhibit other types of defects. Twins appear to be characteristic of only the orthorhombic 123 structures.

Keywords. Electron microscopy; twins; oxide superconductors.

1. Introduction

Two series of high temperature oxide superconductors have been intensively investigated in the last few months. These are the 123 oxides of the type $LnBa_2Cu_3O_{7-\delta}$, (Ln = Y or rare earth) with T_c 90 ± 5 K and $La_{2-x}Sr_x(Ba_x)CuO_4$ of the K_2NiF_4 structure with $T_c \sim 30 \pm 10$ K (Nelson *et al* 1987; Rao 1987, 1988a, b). All these oxides possess orthorhombic structures in the superconducting phase. In the case of $YBa_2Cu_3O_{7-\delta}$, the orthorhombic structure extends up to $\delta \sim 0{\cdot}6$. Electron microscopy has been employed to investigate defects as well as twins in $YBa_2Cu_3O_{7-\delta}$ (Rao 1987; Rao *et al* 1988; Raveau *et al* 1987; Subbanna *et al* 1987). It has been shown that twins in the superconducting $YBa_2Cu_3O_{7-\delta}$ are related to the orthorhombic structure, which in turn depends on the presence of Cu-O chains along the *b*-axis (Rao 1988a). In the present study, detailed electron microscopic investigations have been carried out on several 123 oxides to understand the nature of twins. In addition, oxides of the $La_{2-x}Sr_x(Ba_x)CuO_4$ system have been investigated by electron microscopy.

2. Experimental

Samples of $YBa_2Cu_3O_{7-\delta}$ and other 123 oxides as well as $La_{2-x}Sr_x(Ba_x)CuO_4$ were prepared by the ceramic route starting with the appropriate mixtures of the component metal oxides or/and carbonates. Repeated grinding and pelletizing were carried out to ensure formation of the desired oxide. For varying the oxygen stoichiometry of $YBa_2Cu_3O_7$, the samples were heat-treated in an appropriate (O_2/N_2) atmosphere. Samples of $La_{2-x}Sr_x(Ba_x)CuO_4$ were prepared at 1200 K in air.

X-ray powder diffraction patterns were recorded (Philips PW 1140) using CuK_α radiation to establish the structure of the oxides. Resistivity was measured using the four-probe d.c. method. Electron microscopic investigations were carried out in a

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JEOL JEM 200CX and Philips EM 301 (for in situ low temperature work) electron microscopes. The samples for the microscopic examination were prepared by dispersing finely ground powders on holey carbon grids.

3. Results and discussion

In figure 1a, we show the bright-field image of a sample of superconducting $YBa_2Cu_3O_7$ ($T_c \sim 90$ K) recorded at room temperature, the sample for microscopic examination being prepared (by dispersing the powder in acetone) at room temperature. The image clearly shows twin domains of ~ 200 Å width. Cooling the sample in the microscope down to 77 K, produced no change in the twin density or in the width of the domain. Polycrystalline $YBa_2Cu_3O_7$ dropped into liquid nitrogen for preparing samples for microscopic examination, however, showed a large number of 90° twins (figure 1b). The average width of these twin domains was considerably smaller (~ 90 Å). The estimated width of the twins, obtained by the simple empirical rule, $S = (ab/a\text{-}b)$, where a and b are unit cell parameters of the orthorhombic phase (Pande *et al* 1987), works out to be ~ 250 Å. Pande *et al* reported variable twin widths ranging from 150 Å to 4000 Å. The small twin domains shown in figure 1b do not conform to the simple rule of Pande *et al.* In spite of the small width and high twin density, the T_c of this sample (zero-resistance) of $YBa_2Cu_3O_7$ remained around 92 K.

$YBa_2Cu_3O_{6.7}$, which is also orthorhombic and superconducting with ($T_c \sim 60$ K) (Rao 1988a), shows twins (figure 2a) similar to $YBa_2Cu_3O_7$. Although the T_c is lower,

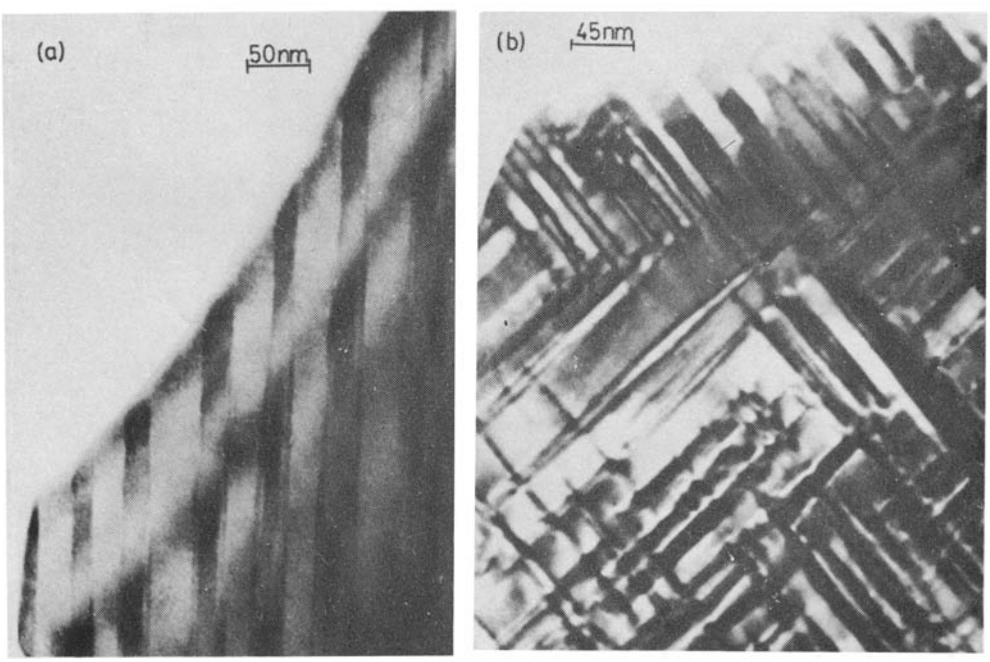

Figure 1. Bright-field images of (**a**) twins in $YBa_2Cu_3O_7$ and (**b**) 90° twins in $YBa_2Cu_3O_7$ (LN_2 preparation).

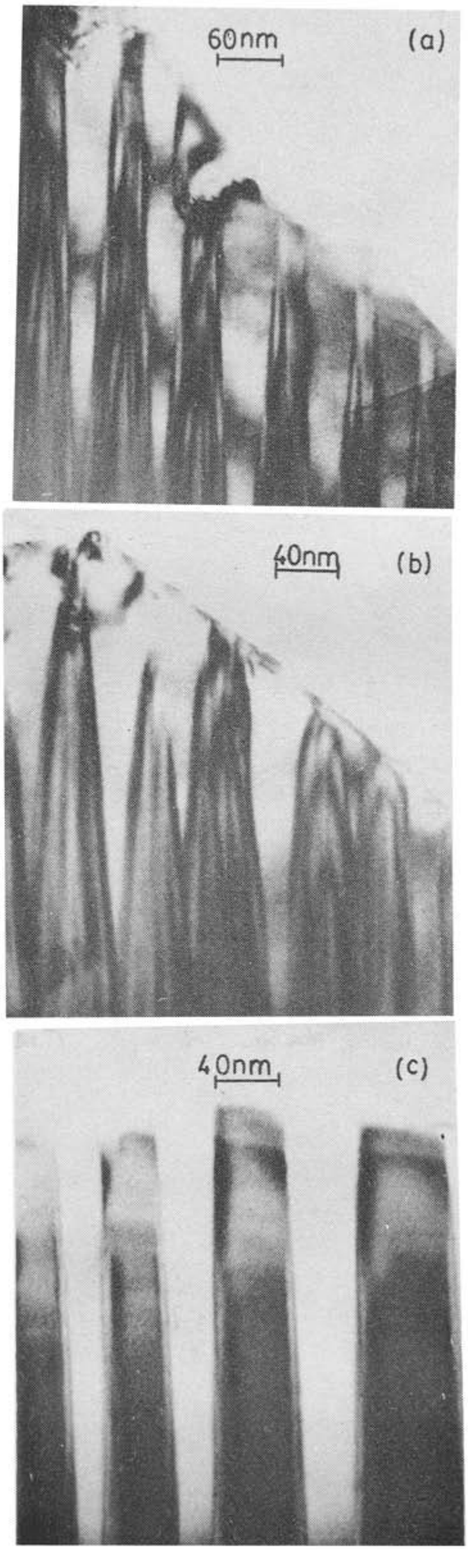

Figure 2. Bright-field images of **(a)** twins in $YBa_2Cu_3O_{6\cdot7}$ **(b)** twins in $NdBa_2Cu_3O_7$ and **(c)** twins in $Lu_{0\cdot75}Y_{0\cdot25}Ba_2Cu_3O_7$.

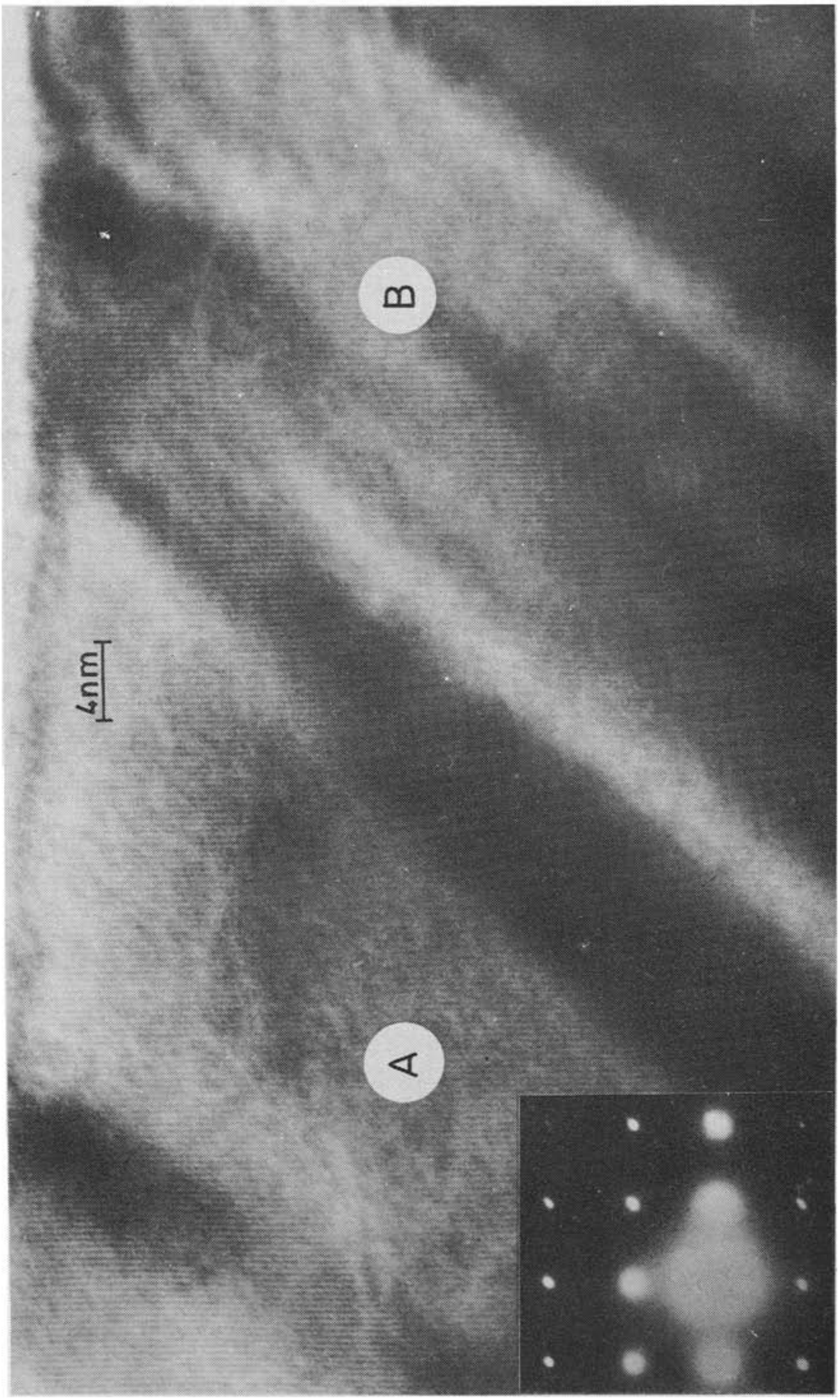

Figure 3. Lattice image of twins in $YBa_2Cu_3O_7$ (selected area diffraction pattern is shown in the inset).

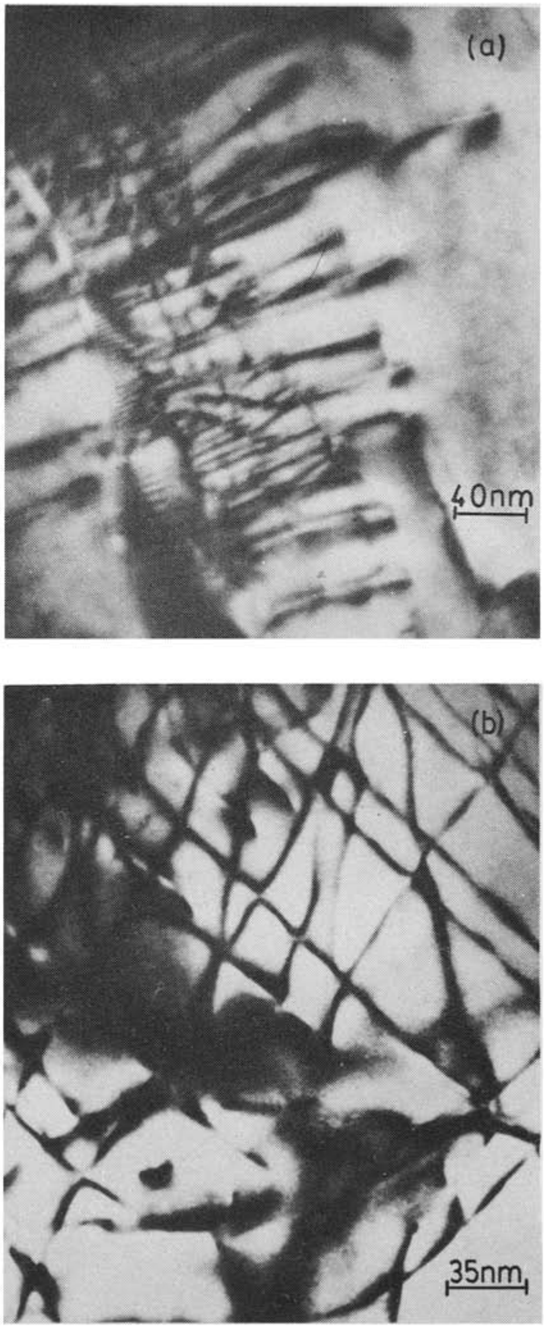

Figure 4. Bright-field images of dislocations in (**a**) $La_{1\cdot8}Sr_{0\cdot2}CuO_4$ and (**b**) $La_{1\cdot85}B_{0\cdot15}CuO_4$ (note samples quenched to 77 K from room temperature).

the twin population is not altered. We have studied bright-field images of $NdBa_2Cu_3O_7$ and $Lu_{0\cdot75}Y_{0\cdot25}Ba_2Cu_3O_7$ both of which are orthorhombic and superconducting (T_c $\sim$80 K). These oxides also show twins (figures 2b and 2c). The only samples of the

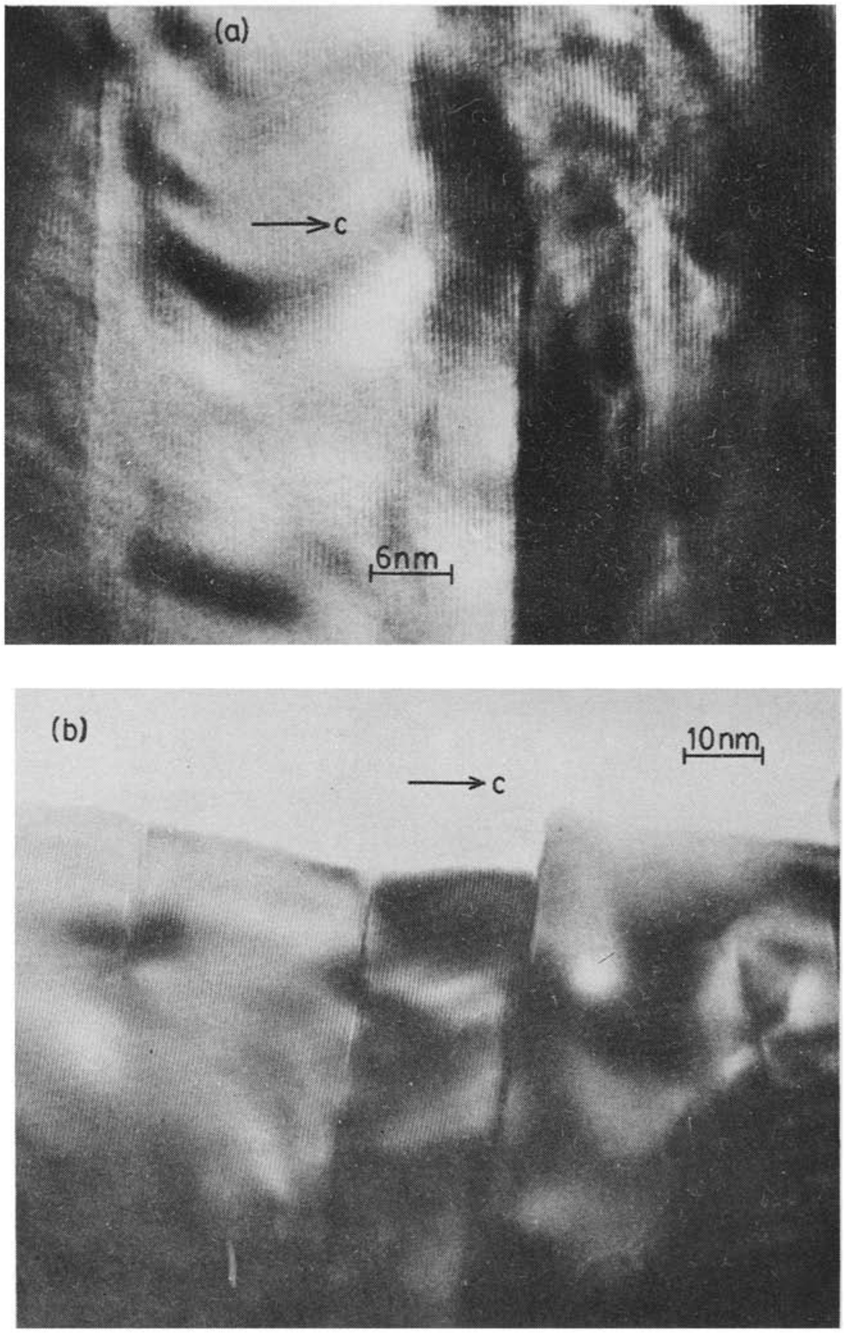

Figure 5. Lattice image of fine domains along *c*-axis in (**a**) $La_{1.8}Sr_{0.2}CuO_4$ and (**b**) $La_{1.85}Ba_{0.15}CuO_4$.

123 oxides without twins are the ones with high oxygen-deficiency (e.g. $YBa_2Cu_3O_6$) and the structure is tetragonal.

The twins in $YBa_2Cu_3O_7$ show interesting changes in contrast across the twin domains. Thus within the ~ 200 Å domains, we often see darker bands of ~ 90 Å width. It was of interest to find out whether this was due to a change in structure and/or stoichiometry of the sample across the twin domains or due to dynamical effects in the microscope. It was also of interest to examine any structural change across the twin boundary. For this purpose, we have studied the high-resolution images of the twin domains of the 123 oxides. In figure 3, we show a typical HREM image of the twin boundary of $YBa_2Cu_3O_7$. It is seen that the lattice fringes run across the boundary continuously without any change in contrast, except for a small tilt at the twin interface. There is a subtle change in the lattice fringe spacings from one twin domain to another (twin domain A and B in figure 3), indicating switching of the *a* and the *b*-axes across the boundary. Since most of the crystals studied were wedge-shaped, dynamical diffraction conditions possibly play an important role in the contrast observed across the twin boundary.

We have examined the possible occurrence of twins in the $La_{2-x}Sr_x(Ba_x)CuO_4$ system as well as in La_2CuO_4. $La_{2-x}Sr_x(Ba_x)CuO_4$ is tetragonal at room temperature and becomes orthorhombic on cooling to 180 K (Day *et al* 1987). Samples of $La_{1\cdot 8}Sr_{0\cdot 2}CuO_4$ and $La_{1\cdot 85}Ba_{0\cdot 15}CuO_4$ show no evidence of twins in the bright-field images at room temperature. On slowly cooling the samples to liquid-nitrogen temperature in the microscope stage no twins developed although the structure becomes orthorhombic. Whether twins will occur at liquid helium temperatures is not clear. Samples of these oxides quenched to liquid nitrogen temperature from room temperature (or higher temperature) showed evidence for high dislocation density (figure 4a, b), but showed no twins.

La_2CuO_4 is orthorhombic at room temperature, but it does not show twins in the bright-field images. According to the empirical rule of Pande *et al* we should see twins of ~ 1500 Å width. We see extensive domain patterns along the *c*-axis in the $La_{2-x}Sr_x(Ba_x)CuO_4$ system (figure 5a, b) as well as in La_2CuO_4. These features may arise from faults in the stacking of Cu-O layers along the *c*-axis.

The absence of twins in the oxides of K_2NiF_4 structure such as La_2CuO_4 and $La_{2-x}Sr_x(Ba_x)CuO_4$ is interesting. It seems that the orthorhombic structure is not sufficient for observing twins. It is to be noted that orthorhombic structure of the oxides of K_2NiF_4 structure is related to the monoclinic distortion of the tetragonal structure. In 123 oxides such as $YBa_2Cu_3O_7$, however, the orthorhombic structure is determined by the presence of Cu-O chains along the *b*-axis. It is this feature which may play an important role in the formation of twins in 123 oxides.

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