JOURNAL OF SOLID STATE CHEMISTRY 69, 189–195 (1987)

Order–Disorder in $YBa_2Cu_3O_7$

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Communicated by J. M. Honig, April 29, 1987

We summarize here results of a fairly detailed study by high-resolution electron microscopy and electron diffraction of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$. Data from the perfect structure for (100), (110), and (001) zones indicate that the material has an oxygen-deficient perovskite structure as previously reported from X-ray and neutron diffraction studies. In some cases planar defects along (001) directions were observed. A more important observation is the existence of a phase with disorder of the Y and Ba ion positions and of an additional amorphous phase. The perfectly ordered (defect-free) phase grows from the disordered material, and the planar defects are probably due to mechanical deformation during preparation of the material. These defects probably are not related to the superconducting properties, as recently suggested. The conclusions are consistent with the commonly encountered problems in the preparation of superconductors in high yields. © 1987 Academic Press, Inc.

There is currently substantial interest in the new set of high-temperature superconductors. The primary material at present is $YBa_2Cu_3O_{7-\delta}$ (*1, 2*) which from X-ray (*3*) and neutron (*4*) diffraction data has been reported to have an oxygen-deficient perovskite structure. The synthesis of this superconductor from the carbonates is straightforward, but the yield is quite small and the material requires an oxygen anneal to improve on the superconducting percentage which, in most cases, is quite small (~20–50 vol%). This suggests that most such materials contain extraneous phases along with the true superconductor.

Recently two groups have reported by high-resolution electron microscopy images of $YBa_2Cu_3O_{7-\delta}$. Work at IBM (*5*) confirmed the presence of a material which from images along one zone axis appeared to be a perovskite with reported twinning on (110) planes. Workers at AT&T and Arizona State University (*6*) have reported the presence of defects in this material (again apparently from images along one zone axis) which they linked to the superconducting properties. At the same time we have been examining in detail superconductors synthesized at Northwestern University (*7, 8*). We summarize here our results which indicate a completely different situation, more consistent with the commonly encountered problems in producing high yields of the superconductor.

0022-4596/87 $3.00

Specimens were prepared as described elsewhere (*7, 8*) and then crushed and sprinkled onto holey carbon films and examined in a Hitachi H-9000 electron microscope operating at 300 kV. In addition to small quantities of $BaCuO_2$, the major component of the specimens was the $YBa_2Cu_3O_{7-\delta}$ compound as separately confirmed by X-ray studies. Images and diffraction patterns of the perfect $YBa_2Cu_3O_{7-\delta}$ along three of the primary zone axes (100), (110), and (001) shown in Fig. 1 confirm the perovskite structure. While the majority of regions of the crystal are perfect, some showed evidence of a fairly high concentration of planar defects on (001) planes (see Fig. 2). In addition we also found large regions which showed the classic high background intensity (without Kikuchi lines) and broadened diffraction spots of a disordered material (*9*) (see Figs. 3 and 4). The basic unit cell of this phase is simple cubic with a lattice parameter of ~3.8 Å. (The diffraction spot positions are close enough to those of the ordered phase that this phase would probably not be detected in X-ray diffraction experiments except as broadened peaks unless a careful measurement was made of the short range order parameter.) On closer examination it became apparent that perfectly ordered *defect-free* perovskite was growing from the disordered phase which had exactly the lattice parameter, image contrast, and orientation relative to the ordered material that would be expected from simple disorder of the Y and Ba atom positions. We also observed an amorphous phase (see Fig. 4) at the surface of the disordered regions. The amorphous regions grew (slowly) in the electron beam; some regions of partial order were also observed to degrade with time, both effects occurring primarily at or very near to the surface. (The initial specimens did not have extensive surface contamination due to a mild ~100°C baking before examination and these effects occurred only in the absence of any residual carbonaceous contamination layers.) The electron beam tends to produce some oxygen point defects in the bulk and to cause oxygen desorption from the surface (electron stimulated desorption (*10, 11*)); thus, a clear link has been established between oxygen point defects, the oxygen content of the material, and the ordering of the heavy metal ions.

These results indicate that there are a number of classical order–disorder phase transformations between an amorphous state, a disordered arrangement of the Y and Ba atoms, and the fully ordered material, in which the ordering quite possibly depends on the oxygen defect concentration. This is completely consistent with the established problems in preparing high yields of the superconductor and oxygen-deficient mixed oxides in general (*12*). As regards the highly defective regions, it should be remembered that synthesis of these superconductors involves calcination followed by at least one grinding and annealing cycle of the material and that the standard preparation of specimens for high-resolution electron microscopy involves grinding of the material before placement on support films. These steps involve mechanical deformation which can be expected to introduce planar slip defects of various types in the specimens. As stated, completely defect-free regions grow from the disordered phase; this fact strongly indicates that the planar defects result from mechanical deformation during preparation of the material and very probably are not directly associated with the superconducting properties. Indeed, the defects in Fig. 2, (110) zone, are shear planes, exactly as expected. (We cannot completely rule out incomplete ordering with domain structure, although the growth observation tends to make this a less likely interpretation.)

A more detailed description of this work will be published elsewhere.

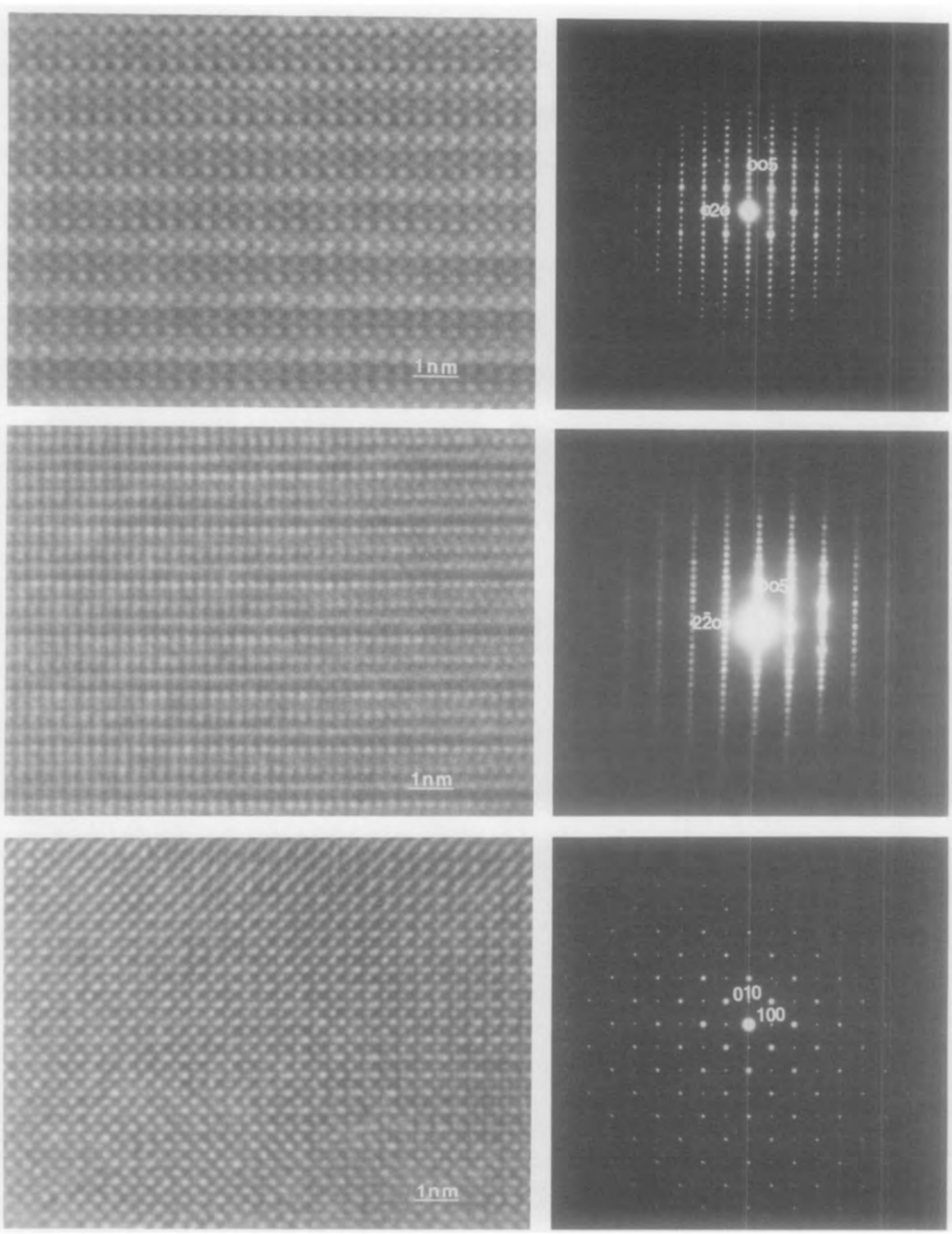

FIG. 1. High-resolution images (left) and diffraction patterns (right) from, in order downward, the (100), (110), and (001) zones of the perfectly ordered perovskite. In all images the positions of the metal atoms appear black, the oxygen atom locations not being apparent, as confirmed by detailed image simulation calculations which are not included here for brevity.

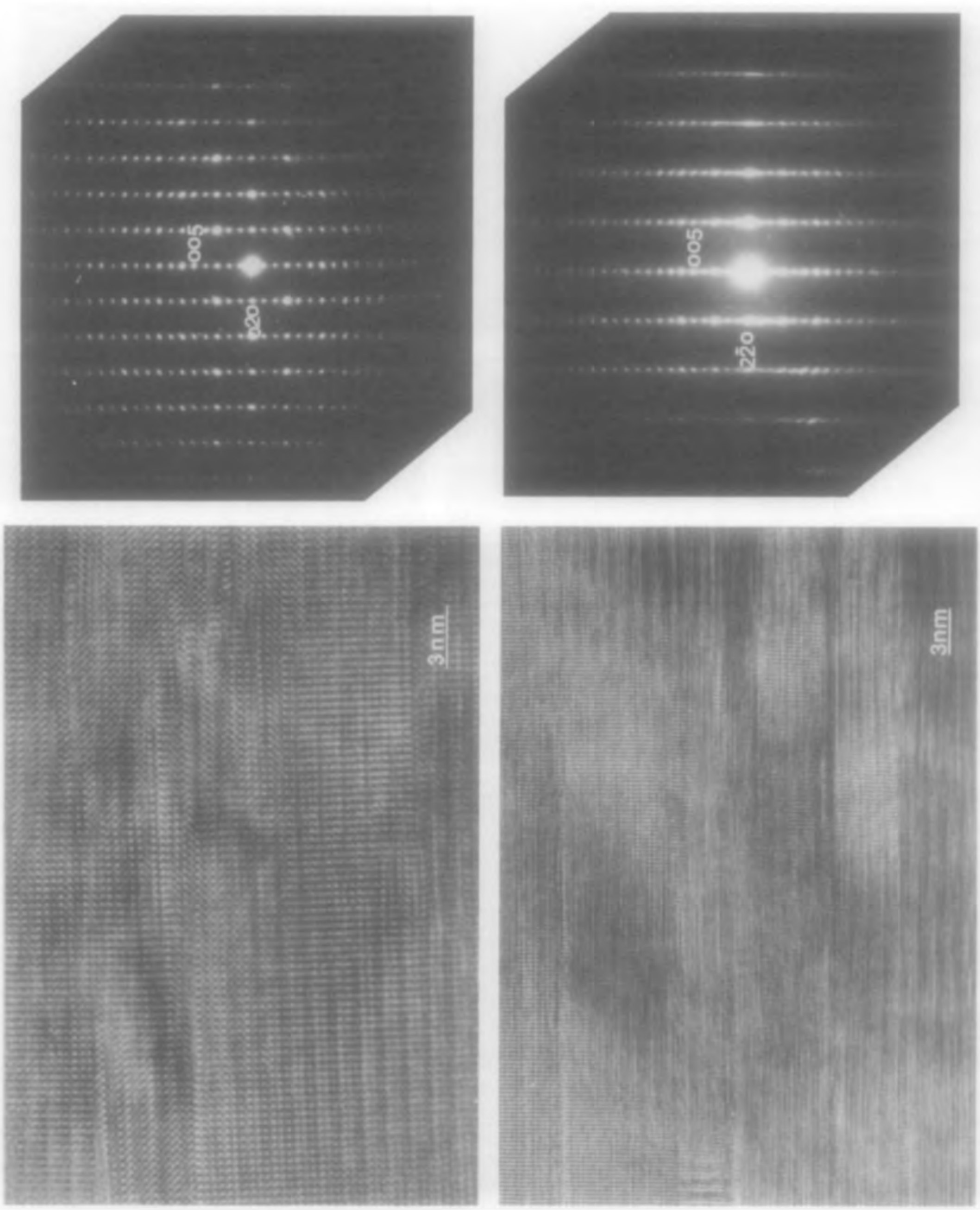

FIG. 2. Planar defects viewed along (100), top, and (110), bottom, directions with diffraction patterns on the right. The defects, as described in the text, are believed to be due to mechanical deformation.

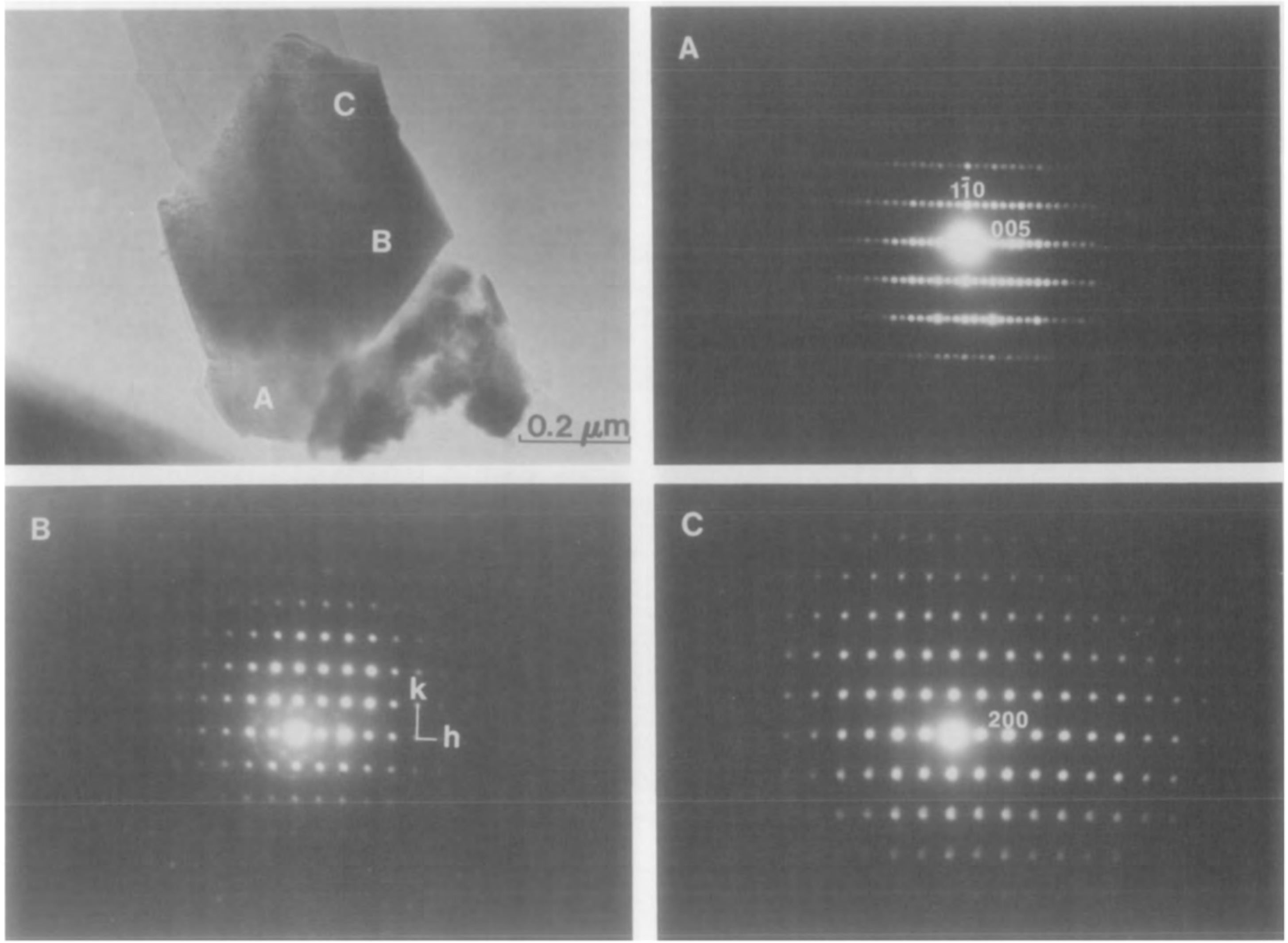

FIG. 3. Micrographs of a grain which showed the perfect perovskite growing from the disordered material: top left, a view at reduced magnification of the total particle; top right, diffraction pattern of ordered region, (110) zone; below, diffraction patterns from two areas of the disordered material (the degree of disorder is slightly different in the two). The markings A, B, C indicate the regions used for the diffraction patterns.

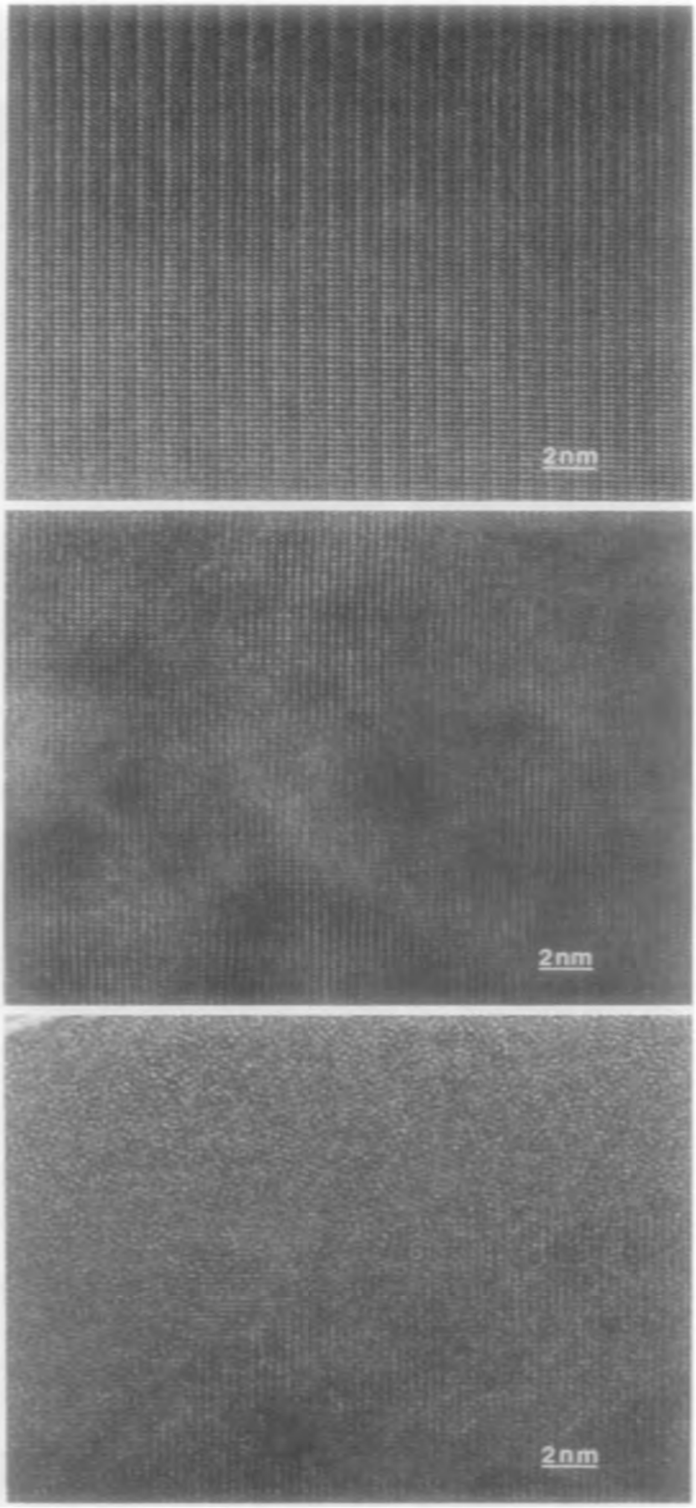

FIG. 4. High-resolution images along a (110) direction showing from top to bottom ordered, disordered, and amorphous regions.

Acknowledgment

This work was supported by the Materials Research Center, Northwestern University (Grant Number DMR 8520280).

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