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Abstract

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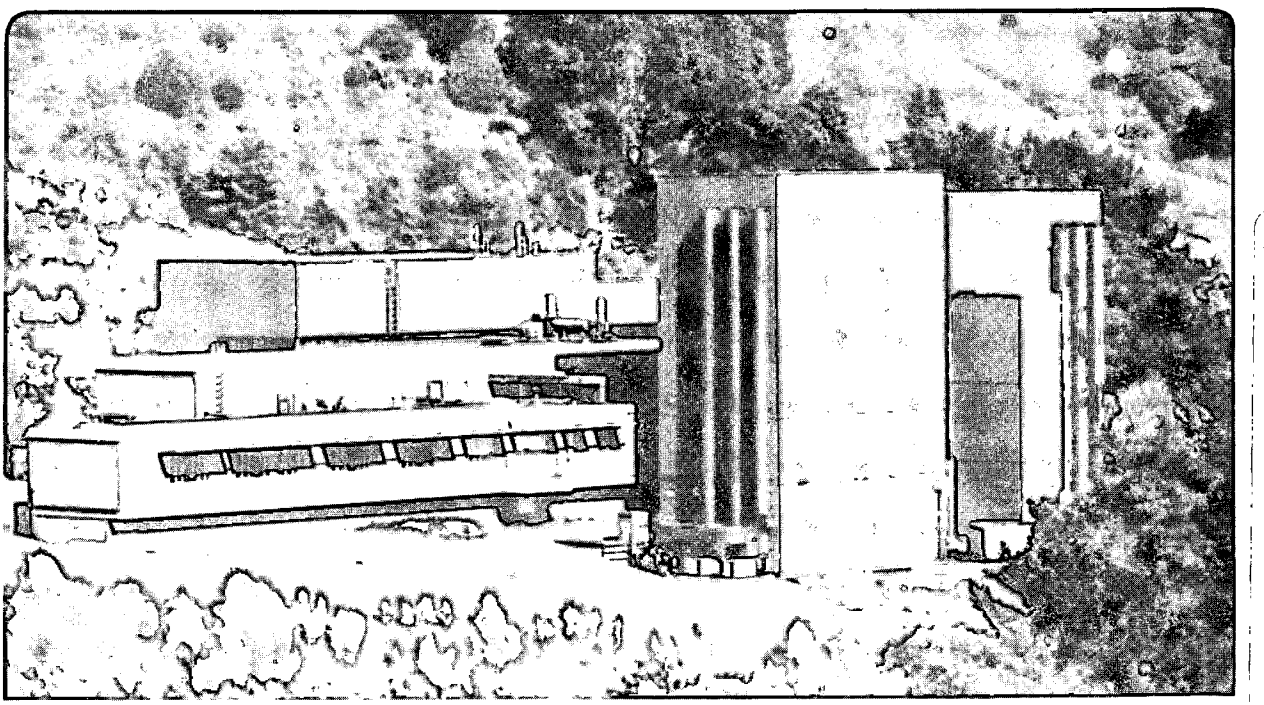

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DISCLAIMER

PREPARATION OF BiCaSrCuO SPECIMENS FOR HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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Transmission electron microscopy, in particular high-resolution TEM, is proving to be a valuable tool in the continuing effort to characterize and understand the "high-T_c" superconducting oxides. Since specimen quality is of critical importance in high-resolution studies, care must be taken to choose the most appropriate specimen preparation technique for the material under study. The BiCaSrCuO material investigated here was in the form of small, sintered pellets with a porous microstructure which consists of small, randomly oriented, poorly connected, plate-like grains (see Figure 1). We have found that this morphology can significantly effect the production of suitable TEM specimens.

The simplest and most rapid specimen preparation method employed consists of crushing a small amount of the starting material to a fine powder in an agate mortar and suspending the powder in pure ethanol or propanol.[1] An eye dropper or syringe is then used to transfer 4-6 drops of the suspension onto a holey carbon film supported on a mesh grid, thus effectively dispersing the powder across the grid. A strong tendency for the crystal to cleave along (001) planes, due to the weak bonding between BiO layers, results in flake-like particles which exhibit a preferred [001] orientation on the grid. A high-resolution image of a specimen prepared using this method is shown in Figure 2. We have observed that some specimens produced in this manner are unstable under a 200kV beam (with LaB_6 filament), with heavy damage occurring within the time that a through-focus series of micrographs can be exposed. It is also important to note that since separation along grain boundaries occurs during crushing, this method is not an appropriate choice for imaging grain boundary structures.

A related, but often superior, method of specimen preparation for the superconducting oxides involves mounting small, but still "macroscopic" particles on an oval grid with an electrically conducting adhesive (we have had excellent results with *EPO-TEK™ H20E* silver epoxy from Epoxy Technology, Inc.), so that thin edges of the material are exposed.[2] The particles to be used are produced by either very coarsely crushing the material or by using a sharp blade to cleave flakes from the starting pellet. This configuration has the advantage of larger continuous material mass and greater thermal contact with the supporting grid, and hence improved stability of the specimen under the electron beam. Because of the natural cleavage of the material, the thin regions of these specimens are again often found in the microscope to be near the [001] zone axis.

Obtaining maximum information from high-resolution TEM studies of superconducting oxides depends upon the ability to directly image the c-plane stacking, thus requiring a sufficiently thin specimen which has the [001] direction perpendicular to the incident electron beam. In this respect the methods described above are unfortunately limiting. Therefore, other specimen preparation techniques which do not depend upon the natural cleavage of the material have been explored, and these provide access to a wider range of crystallographic orientations.

One promising method of this type is non-reactive milling with Ar^- ions. Specimens are first polished using standard metallographic techniques until a thickness of less than 300μm is reached. The specimen is then mounted on a suitable oval or circular TEM grid (again using a durable conductive adhesive), since the superconducting oxides are generally too fragile to be self-supporting. After thinning to approximately 20-50μm by dimple grinding using 1μm diamond paste diluted in kerosene, the specimen is ion milled at liquid nitrogen temperature until perforation occurs. Due to the microstructure of the materials used in this study, ion milling induces significant mechanical damage. As shown in Figure 3, the porosity and poorly connected grain structure result in a thin edge containing numerous holes and large amorphous regions. Various ion beam parameters have been used on these specimens, so far without an appreciable improvement in specimen quality.

In contrast, specimens prepared from a pellet which had undergone hot isostatic pressing after the initial sintering were found to have almost no damage after ion milling. We attribute the improvement to a less porous, larger-grained microstructure (see Figure 4) produced by the additional processing. Other workers have also reported successful ion milling of the Bi-based superconductors.[3,4] Finally, it should be pointed out that ultramicrotomy[5] and chemical methods (jet polishing, etc.) of specimen preparation also offer access to a full range of crystallographic orientations, although both of these methods can produce artifacts which may affect a TEM investigation.[6]

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FIG. 1. -- Scanning electron image of porous microstructure in sintered pellet of BiCaSrCuO.
FIG. 2. -- High Resolution TEM image from crushed specimen, showing (001) cleavage.
FIG. 3. -- TEM image of ion milling damage in porous material.
FIG. 4. -- Scanning electron image of sintered BiCaSrCuO pellet with additional processing.

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