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Nanosuperconductor $YBa_2Cu_3O_y$

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After 60 h grinding, a ground sample of $YBa_2Cu_3O_y$ was turned into agglomerates that were characterized as amorphous materials with a small number of crystals left. After subsequently keeping the agglomerates in air at room temperature for eight months, nanocrystals growing from the agglomerates were observed. These nanocrystals were pine-tree-fibered ceramic materials with a diameter of the order of dozens of nm and length of the order of hundreds of nm. By electron-diffraction analysis, the nanocrystal was determined to have an orthorhombic structure; magnetic measurements demonstrated that it was a nanosuperconductor with a 90-K superconducting phase. The appearance of this nanocrystal gives us an opportunity to fabricate superconductive nanomaterials. On the practical side, the fact that a superconducting nanocrystal of $YBa_2Cu_3O_y$ is in the form of a fiber gives us the potential, by nanocrystal growth, to fabricate a real superconducting wire or fiber without any metal tube to wrap and hold it, like an optical fiber. Another practical potential for the nanosuperconductor in nanotechnologies is to use the nanocrystals in microcircuits as superconducting wires. [S0163-1829(98)07113-6]

I. INTRODUCTION

During the past ten years since the discovery of high-T_c superconductors, research on the superconductivity of ceramic cuprates has developed significantly.[1–4] The superconductor $YBa_2Cu_3O_y$ (YBCO) is promising for applications at liquid-nitrogen temperatures. Bulk YBCO is expected to be applied in power products, such as transmission cables and high-field magnets.[5–8] One difficulty is that the bulk is a polycrystalline ceramic that can hardly be transformed into superconducting wire. Moreover, polycrystals growing at high temperatures, have numerous defects, and polycrystals with a large number of defects hamper studies of both the superconductivity and structure.[5] Thus, an alternative method of growing YBCO crystals would be of significance. By overgrinding the crystals to destroy crystal cells, we find that the crystals renew in the form of nanocrystalline fibers from the overground samples in air at room temperature.

II. EXPERIMENTS AND RESULTS

A polycrystalline YBCO sample was prepared by high-temperature solid-state reaction,[9,10] and had an orthorhombic phase whose superconducting critical transition temperature with zero resistance, T_c, was 91 K. Mechanochemical effects of grinding on ceramic superconductors were observed.[11,12] In this experiment, grinding on the sample was performed with a pestle and agate mortar by hand for 6 h a day and the total grinding time was about 60 h. The sample was ground into agglomerates that were observed with a transmission-electron microscope (TEM) and shown in Fig. 1. According to the weak electron-diffraction pattern (Fig. 2), the agglomerates were characterized as being in an amorphous phase with few surviving crystals. After keeping the agglomerates in air at room temperature for eight months, nanocrystals appearing in the agglomerates were observed with TEM, as shown in Figs. 3(a) and 3(b).

The nanocrystal structure was characterized as having an orthorhombic phase by x-ray-diffraction and electron-diffraction analyses and the electron-diffraction pattern is shown in Fig. 4. The superconductivity of the nanocrystal was determined by ac magnetic susceptibility, which was performed on a magnetometer with $f = 350$ Hz, as shown in Fig. 5. The critical superconducting transition temperature,

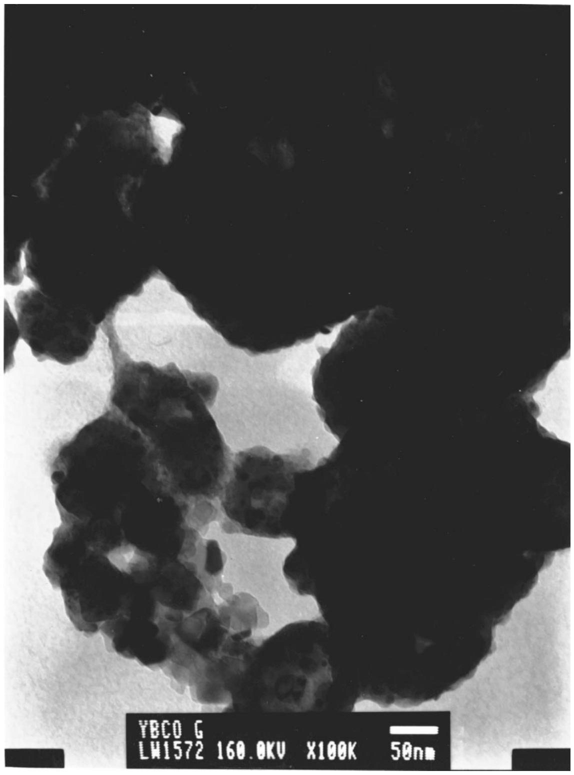

FIG. 1. After 60-h grinding morphology of YBCO is observed on TEM. The 60-h ground sample is in the form of agglomerates that are characterized as an amorphous material by TEM.

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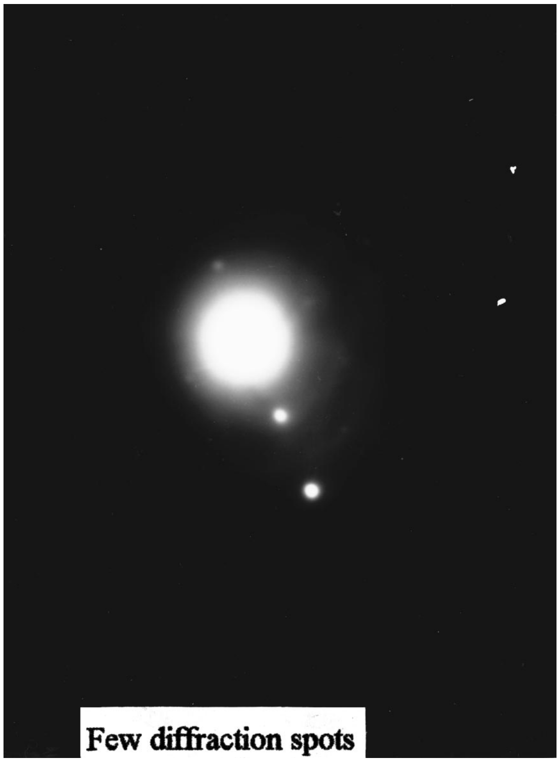

FIG. 2. Most of the agglomerates are in an amorphous phase without electron-diffraction patterns, and only a small amount of it is showing weak electron-diffraction pattern that is caused by a small number of surviving crystals.

T_c, of the nanocrystal was determined as having a value of 88 K.

III. DISCUSSION

Nanocrystal growth may also be considered as a solid-state reaction, although the reaction generally occurs at high temperature. How can the nanocrystal grow at room temperature? In our view, there are three reasons as follows. First, in our case the atoms of Y, Ba, and Cu, even oxygen, are evenly mixed and well distributed. Thus, the atoms are not required to diffuse long distances and combine with each other into crystal cells. Second, the surviving crystal cells, and/or parts of the destroyed cells if they exist, are ideal crystal nuclei to grow crystal. Finally, the agglomerate, as a result of pulverizing the sample consists of extremely superfine particles with required stoichiometry and large active surfaces, which are favorable for crystal growth.

We also found nanocrystals in a sample ground for only 36 h, although only a few were found in TEM view fields. Therefore, the long grinding time is not a required condition for nanocrystal growth. We suppose that superfine, pulverous, and active particles with nuclei is required for this growth.

The next interesting problem is the speed of the growth. In Fig. 3 we also find some broken nanocrystals and the growth always continues from the breaking sections. Every broken nanocrystal consists of two parts, an original part and a continued one. We note that the growth of the continued one is faster than that of the original one. The former dimension is 600–800 nm in length, and the latter is 100–200 nm.

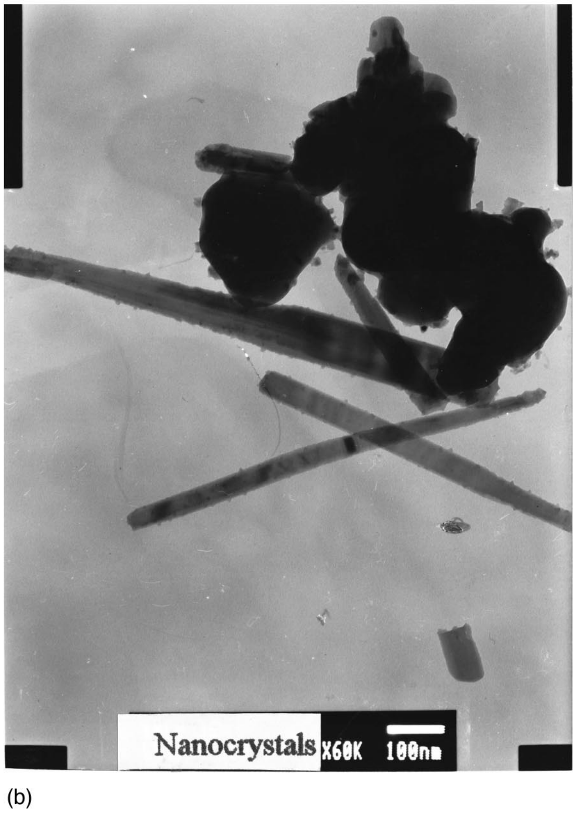

FIG. 3. Photographs (a) and (b) show the nanocrystals together with agglomerates in the view fields on TEM. Due to grinding some are broken, and some broken ones continue to grow from the breaking sections. The existence of continuing growth demonstrates a strong tendency of the nanocrystals to grow in the surroundings of amorphous agglomerates at room temperature.

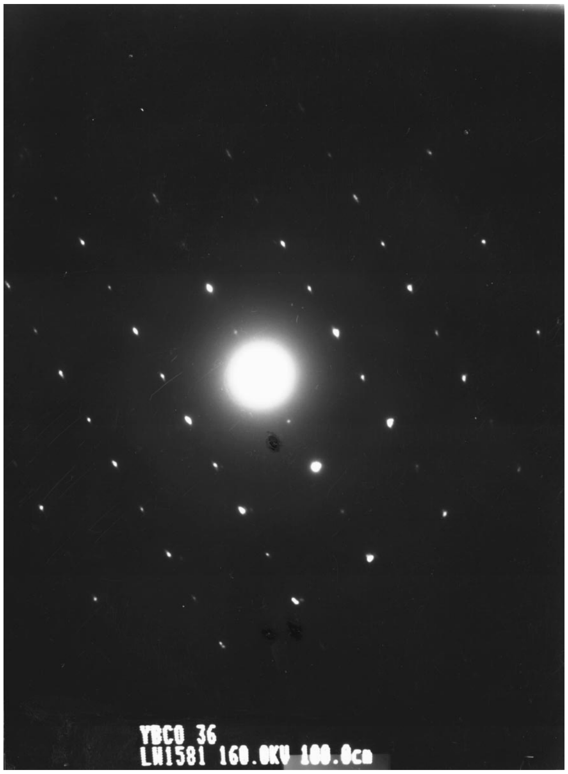

FIG. 4. A photograph of an electron-diffraction pattern of the nanocrystals. Electron-diffraction analysis shows that the structure of the nanocrystals is an orthorhombic phase. Since periodic weaker spots appear in the pattern, there is a superlattice structure in the nanocrystals.

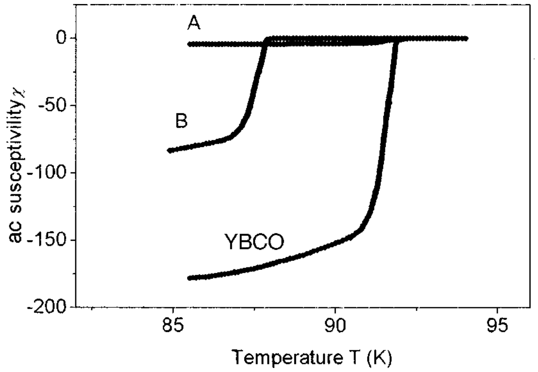

FIG. 5. Superconductivities are determined by a measurement of ac magnetic susceptibility on a magnetometer with $f = 350$ Hz. ac susceptibility of 60-h ground YBCO is plotted in curve A. Eight months later, nanocrystals appear and the measurement of ac susceptibility is performed again, as shown in curve B. T_c of the nanocrystals is 88 K, determined from curve B. As a comparison, ac susceptibility of YBCO is also shown in the figure.

The grinding lasted about two weeks. In other words, during the first two weeks of growth, the nanocrystal length did not exceed 100–200 nm.

The morphology of the grown nanocrystals is a pine-tree-fibered ceramic crystal whose diameters are from 25 to 90 nm and lengths from 200 to 900 nm. For many nanocrystals, their L/D ratios are about 20, which is the same ratio as the maximum of strength a configuration has.

Figure 4 shows an electron-diffraction pattern of the nanocrystals, similar to that of YBCO.[13] Those periodic weaker diffraction spots in the pattern reveal a superlattice structure existing in the nanocrystals. A close examination of this pattern shows that the diffraction is close to [114] zone, and the weak superlattice spots occur along (110) reciprocal lattice vectors. The $\frac{1}{2}(110)$-type superlattice reflection require the periodicity of the (110) atomic cell by doubling the unit cell along the a and b axes. Fortunately, the superlattice does not affect its superconductivity, and a nanosuperconductor like YBCO has a superconductivity with a 90 K phase. It is believed that the superlattice is the result of oxygen vacancy appearing at some special site in the crystal cells, and we will discuss this problem in detail soon.

To summarize, we find that the nanosuperconductor of YBCO can freely grow in air at room temperature from the amorphous agglomerates with the stoichiometry of $YBa_2Cu_3O_y$. Furthermore, the grown nanosuperconductor in the form of nanocrystals has orthorhombic structure and 90 K phase superconductivity, similar to one growing at high temperatures. It is believed that the nanocrystals growing at low temperatures have a smaller quantity of crystal defects than those growing at high temperatures. It is advantageous to approach the intrinsic properties of the superconductor YBaCuO regarding structure and superconductivity with the nanocrystals.

On the other hand, the fact that YBCO nanocrystals are in the form of fiber gives us the potential: by nanocrystal growth to fabricate a real superconducting wire or fiber without any metal tube to wrap and hold it, like an optical fiber. Another practical potential for the nanosuperconductor in nanotechnologies is to use the nanocrystal in microcircuits as superconducting wires.

ACKNOWLEDGMENT

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