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Structural features and mechanism of crystallization of CuO ultrafine particles

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The structural features and mechanism of crystallization of CuO ultrafine particles (200–450 nm) were studied by transmission electron microscopy, as well as by thermal analyses (differential scanning calorimetry, thermogravimetric analysis, etc). The CuO ultrafine particles were not single crystals, but built up of subunits of much smaller size; between two of these subunits low-angle crystal boundaries exist. In the heating procedure, as the temperature increased, CuO ultrafine particles lost their absorbed and inclusive water gradually, the crystalline completeness was improved, and the temperature of crystallization was about 320 °C.

1. Introduction

Recently, substantial progress has been achieved in the development of techniques and in the understanding of the fundamental principles for the production of ultrafine particles. In these materials, the number of atoms on the surfaces was about 50% of the total number, therefore they had many special properties of mechanics, magnetism and thermophysics.

Ultrafine particles of CuO, BaO and Y_2O_3 can be prepared by reproducible methods, and monodispersed sols of CuO, BaO and Y_2O_3 were composed. By depositing the sols on $SrTiO_3$ (1 0 0) single-crystal substrate, and annealing at higher temperature, we could obtain YBCO superconducting thin films of large size and any shape, the thickness of the films being ~200–500 nm.

For its easy preparation, we chose CuO ultrafine particles to study their structural features and mechanism of crystallization; the results were helpful in our film-preparation research.

2. Sample preparation

All chemicals were of purest reagent grade and were used without further purification; the water was distilled twice. After mixing cold solutions of $CuSO_4$ (1.0×10^{-3}M) and NaOH (2.0×10^{-3} M), and heating the mixed solutions at 85°C for > 6 h, we obtained monodispersed sols of CuO. To discontinue the reaction, the systems were quenched in cold water. The resulting dispersions were centrifuged at 8000 r.p.m. for 15 min, the supernatant solutions discarded, and the particles resuspended in doubly distilled water in an ultrasonic bath. This process was repeated five times and the purified precipitates were dried at 50°C.

3. Structure features

Transmission electron microscopy was used to examine the particles at magnifications ranging from × 35000–90000, samples for transmission microscopy were prepared by placing a drop of sol on to a collodion film supported on a 200 mesh copper grid. Electron micrographs of CuO ultrafine particles are shown in Figs 1 and 2. From Fig. 1, it can be seen that the ultrafine particles of CuO were monodispersed, and the single particle was not a single crystal, but built up of subunits of much smaller size. This was also observed in the high-resolution micrograph (Fig. 2), from which the lattice fringe of CuO and the low-angle crystal boundaries could be seen. The electron diffraction pattern differed from that of either crystal or amorphous; it may be explained as the existence of low-angle crystal boundaries. The particle shape was spindle-like, this being related to the anion in the preparation [1, 2].

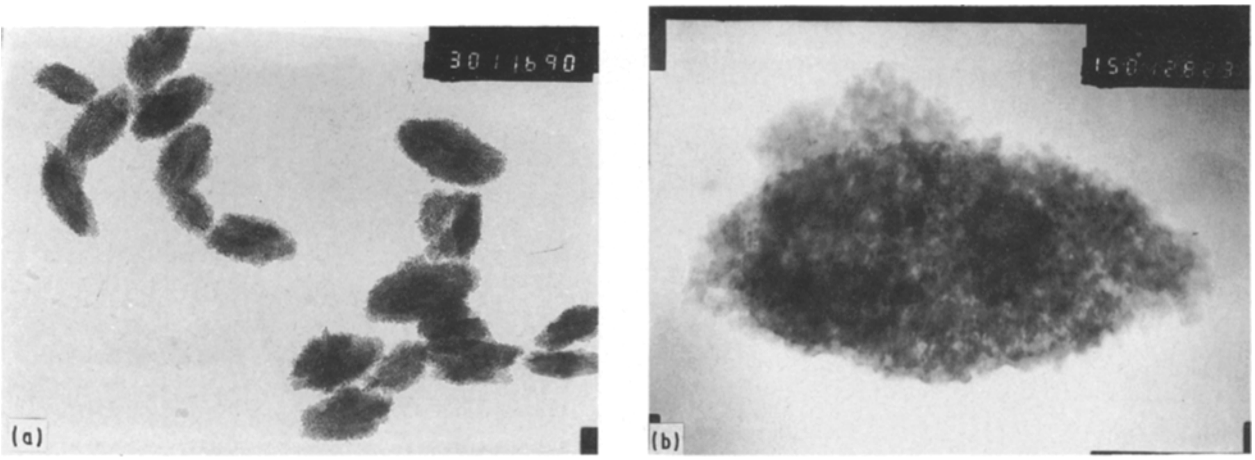
4. Crystallization mechanism

The mechanism of crystallization of CuO ultrafine particles was studied using differential scanning calorimetry (DSC) with an aluminium crucible and by thermogravimetric analysis (TGA) with a platinum crucible in air; the heating rate was 10 °C min^{-1}, and the results are shown in Fig. 3.

During the heating procedure from room temperature to 600 °C, about 10% weight loss occurs, the weight loss before 500 °C being responsible for the absorbed and inclusive water loss [3].

The endothermal effect in the DSC curve at 120 °C was due to facial absorbed water loss. The exothermal effect at about 320 °C was caused by the crystallization of sample, i.e. the crystalline completeness improved. The plateau in the exothermal curve was caused by the sample losing its inclusive water during crystallization, and this was the endothermal effect.

The CuO sols was prepared by a procedure similar to that described by Matijevic for chromium hydroxide [4]. In the ageing process, the basic copper (II) sulphate species are formed until the solution reaches



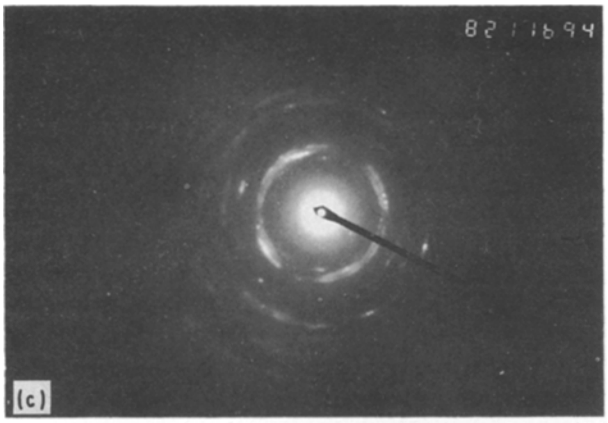


Figure 1 Electron micrographs of CuO sols obtained by ageing a mixed solution of NaOH (2.0×10^{-3} M) and $CuSO_4$ (1.0×10^{-3} M) at 85 °C for 6 h. (The modal diameter of the particles, D_H = 380 nm.)

(a) High-magnification electron micrograph of CuO sols (× 30 000). (b) Low-magnification electron micrograph (× 15 000). (c) The electron diffraction pattern of one single particle (× 82 000).

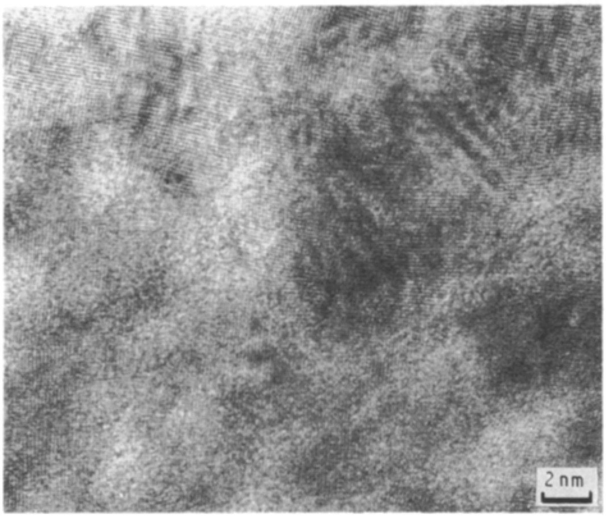


Figure 2 High-resolution TEM image showing lattice fringes of CuO ultrafine particles.

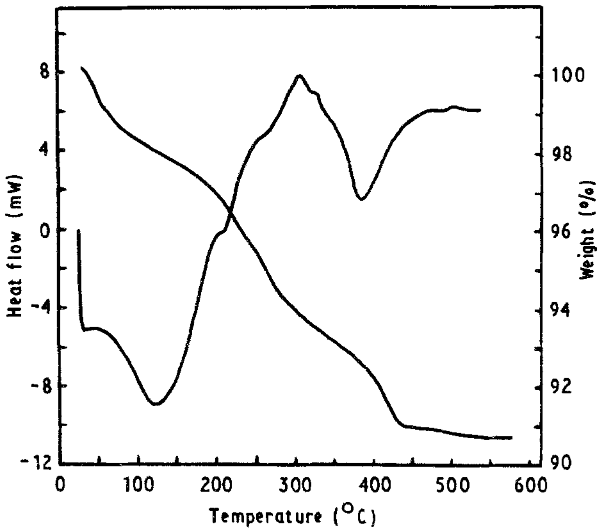


Figure 3 (a) DSC curve and (b) TGA curve for CuO ultrafine particles (320 nm).

its critical limiting supersaturation. At this point the rate of self-nucleation becomes appreciable and the sudden formation of nuclei relieves the supersaturation. From this time on the basic copper sulphate species, formed by ageing, diffuse to the existing nuclei, which grow uniformly to produce sols with a narrow size distribution. It is evident that water molecules were easily bound to the sol particles in the process.

Four series of CuO ultrafine particles, after heating at 120, 300, 350 and 400 °C for 12 h, respectively, and quenching in air, were examined by transmission electron microscopy. From the electron diffraction patterns (Fig. 4), it was shown that when the annealing temperature was higher, the crystalline completeness became better, and the peak temperature of crystallization was about 350 °C; therefore, we can conclude that within the limits of accuracy of our measurement, the crystallization temperatures from the two different methods are in agreement.

5. The correlation between the crystalline completeness of CuO ultrafine particles and the superconductivity of YBCO films

We can deposit sols of CuO, BaO and Y_2O_3 on $SrTiO_3$ to form YBCO films. Some parameters in our film preparation work are listed in Table I. From the parameters, it is shown that films A, B, C and D do not behave as superconductors; X-ray diffraction results

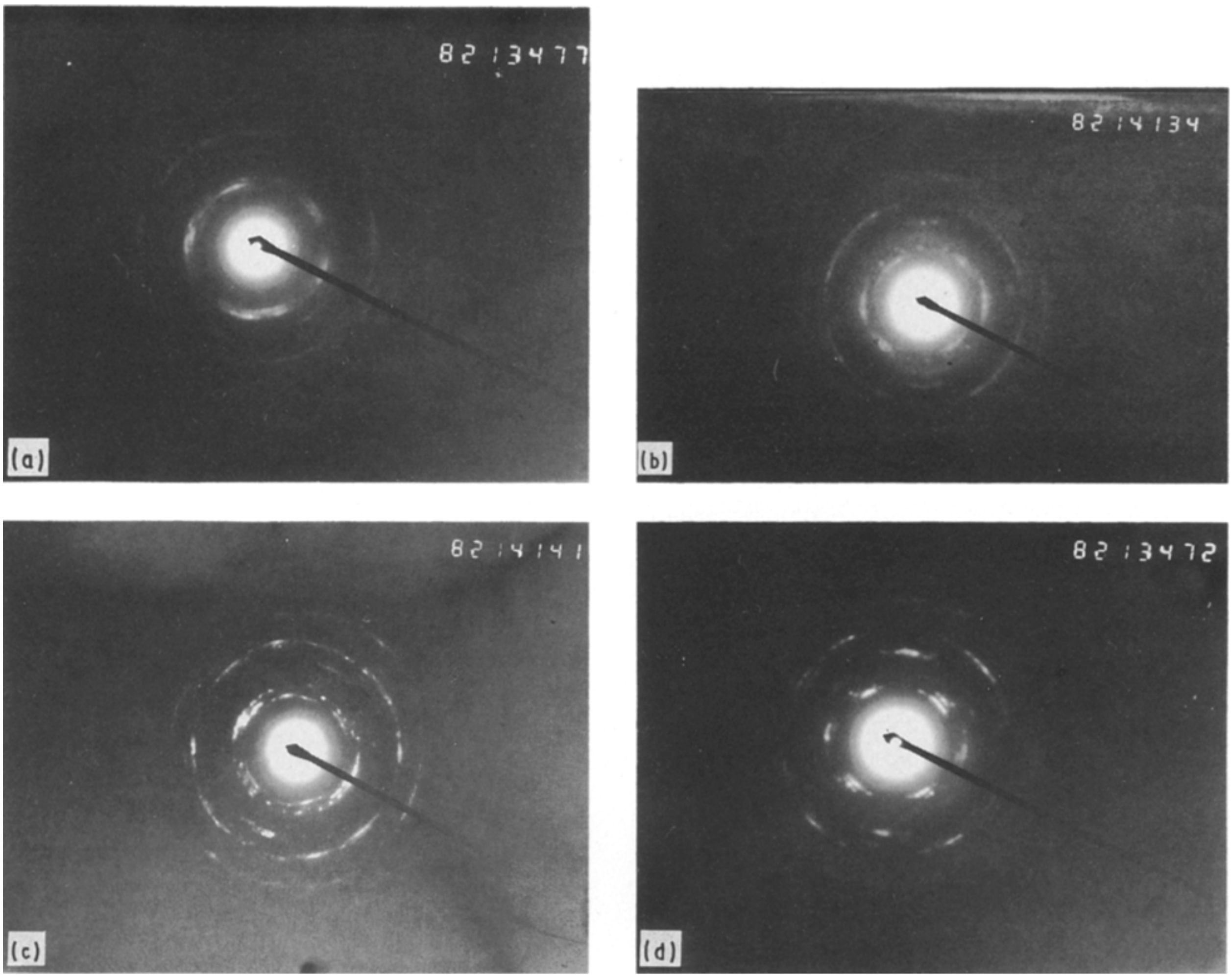


Figure 4 The electron diffraction patterns for CuO ultrafine particles aged at different temperatures for 12 hours (× 80 000). (a) 120 °C, (b) 300 °C, (c) 350 °C, (d) 400 °C.

TABLE I Experimental parameters for YBCO film preparation by the colloidal method

No.	Substrate temperature (°C)	Deposition time (h)	T_{on} (K)
A	700–300	2	No superconducting phase
B	–	2	–
C	–	2.5	–
D	–	2.5	–
7046	200–120	2.5	100(T_{CO} 85 K)
7064	–	0.5	90
9271	–	–	83
9272	–	–	85
12062	–	–	85
12182	–	–	83

show that these four films had no superconducting phase. For the others, the onset temperatures were relatively higher at between 83 and 100 K. This was because for films A, B, C and D, the temperature of the substrate was higher than 320 °C, and the deposition time was relatively longer; this results in the crystalline completeness of CuO, but has disadvantages for the solid reaction of Y_2O_3, BaO and CuO; then the formation of superconducting-phase for YBCO film was difficult when annealing at higher temperature. For the others, the substrate temperature was only 200–120 °C, the deposition time only 30 min, and the crystalline completeness of CuO was nearly unchanged. Therefore, when annealing at higher temperature, the formation of the superconducting phase was easier.

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