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Effect of Mixed Grinding on Superconductivity YBaCu Composite Oxide

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Effect of mixed grinding with a planetary ball mill of starting materials before heat treatment on the crystal structure and superconducting properties in the YBaCu composite oxide was studied. The size reduction of powders too place in the early stage of grinding, followed by aggregation of the resultant fine particles. The uniformity of the composition in the mixture was improved with grinding, which later decreased in the crystal grain size and well distribution of twin phase in the sintered bodies. The critical current density of the sintered bodies obtained from the mixture ground for 60 minutes showed the maximum value about 150 A/cm^2, while critical temperatures were around 90K and were independent of the grinding time.

Kew words : YBaCu oxide, Mixed grinding, Superconductivity, Degree of mixing

I. Introduction

The discovery of the high critical temperature superconducting YBaCu composite oxide makes it possible to prepare practical superconducting materials at liquid nitrogen temperature (77K).[1,2] A clear understanding of how processing controls the physical properties of superconducting ceramics is not only of basic physical research importance, but also can provide a solid basis for commercial applications. One of the most widely used methods of producing bulk superconducting YBaCu composite oxide is the solid state reaction, with repeated calcination and grinding for uniformity before sintering.[3-5] An alternative way to prepare the uniform mixture of powders is the use of grinding mills. However, little attention has been paid on the effect of mixed grinding on the microstructure and superconducting properties of the YBaCu composite oxide.

The main purpose of the current study is to investigate the effect of mixed grinding of raw powders with a planetary ball mill on the crystal structure and superconductivity of YBaCu composite oxide by means of X-ray diffraction analysis, SEM, TEM, EDX, EELS, and the critical current density of sintered bodies.

II. Experimental Procedure

YBaCu composite oxide were prepared by the solid state reaction method. High quality powders of Y_2O_3 (Japan Yttrium K.K.), $BaCO_3$ (High Purity Chemicals Co., Ltd.), and CuO (Rare Metallic Co., Ltd.) were mixed to meet the $YBa_2Cu_3O_{7-y}$ composition and were ground for different periods of time by a planetary ball mill at the atmospheric condition. The mill has two pots (made of agate, each having 50 cm^3 in volume) with seven agate balls of 16 mm in diameter per pot. Weight of the mixed powder for grinding was 8 g and 4 g was charged into each pot. The actual rotational speed of the mill was kept at 1350 rpm throughout the experiment. Specific surface area of the mixtures was measured by a nitrogen-gas-adsorption method. Mixing state of each component in the mixture was determined by an SEM-EDX spectroscopy. Figure 1 shows the arrangement for measurement of degree of mixing. As shown in Fig. 1, the area and the number measured with EDX were $20 \times 20\ \mu m^2$ and 10, respectively. The distance between measuring parts were 20 μm. The mixtures were heated from room temperature to 1203 K at 10 K/min, calcined at the temperature for 15 hours, cooled down to 723 K at a rate 1 K/min, kept at the temperature for 15 hours, and were cooled down again to room temperature at 1 K/min. The calcined powders were pressed into pellets with 13 mm in diameter and 2 mm in thickness by a pressing device at 58.8 MPa. The pellets were sintered from room temperature to 1223 K with 1 K/min, and kept at the temperature for 15 hours, and followed a cooling schedule similar to that of calcination, except for the cooling rate of 0.5 K/min. Pure oxygen gas was introduced into the furnace to oxygenate the pellets sufficiently during heat treatment. Characteristics of the mixtures, and calcined and sintered bodies were investigated by XRD analysis, SEM and TEM observations, and EDX and EELS analyses. Resistivity-temperature curves and critical transport current of sintered body were obtained using the conventional four-point probe method.

III. Results and Discussion

1. Ground mixture

Figure 2 shows the variation of specific surface area, S_w, and equivalent specific surface diameter, d, of ground mixtures with grinding time. The equivalent specific surface diameter was calculated from the equation, $d=\Phi/(\rho S_w)$, where, ρ is density, by assuming the specific surface shape factor, Φ, as 6. The specific surface area increased linearly with an increase in grinding time up to 60 minutes. A downward trend is seen over 60 minutes grinding due to aggregation of fine particles, which is again due to the mechanical activation induced by a prolonged grinding.[6] By the change in the specific surface area, the equivalent diameter decreased from 0.39 μm to 0.05 μm after 60 minutes grinding, and was maintained at the same value until 120 minutes grinding. Figure 3 shows SEM photographs of the mixtures ground for 15, 30, 60 and 120 minutes by a planetary ball mill, together with that of the original (unground, 0 minute) mixture, where the shape of particles changed from sticky to flaky or spheroidal with grinding. Particle sizes of the original powder were found to be reduced quickly after only 15 minutes grinding, which was also verified by a steep decrease of equivalent specific surface diameter in Fig. 2. Since then, the particle sizes of the ground products seem to be decreased gradually with an increase in grinding time until 60 minutes grinding. The particle sizes after 120 minutes grinding were observed to be larger, compared with that after 60 minutes grind-

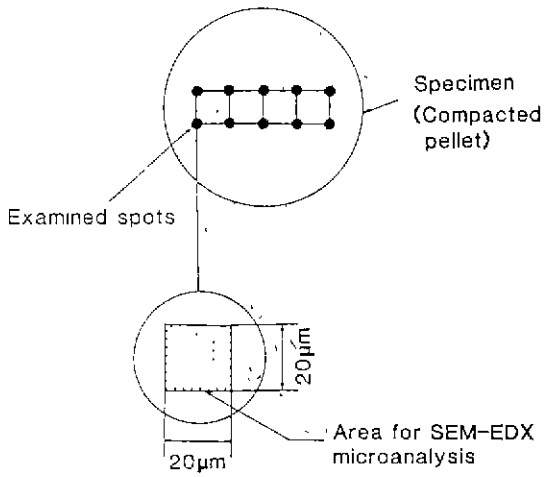

Fig. 1. Arrangement of SEM-EDX measurement for degree of mixing of each component in the mixture.

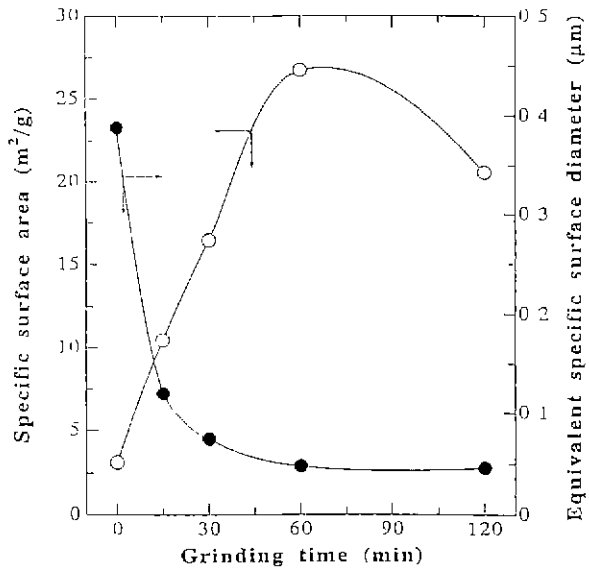

Fig. 2. Variation of specific surface area and equivalent specific surface diameter of ground mixtures with grinding time

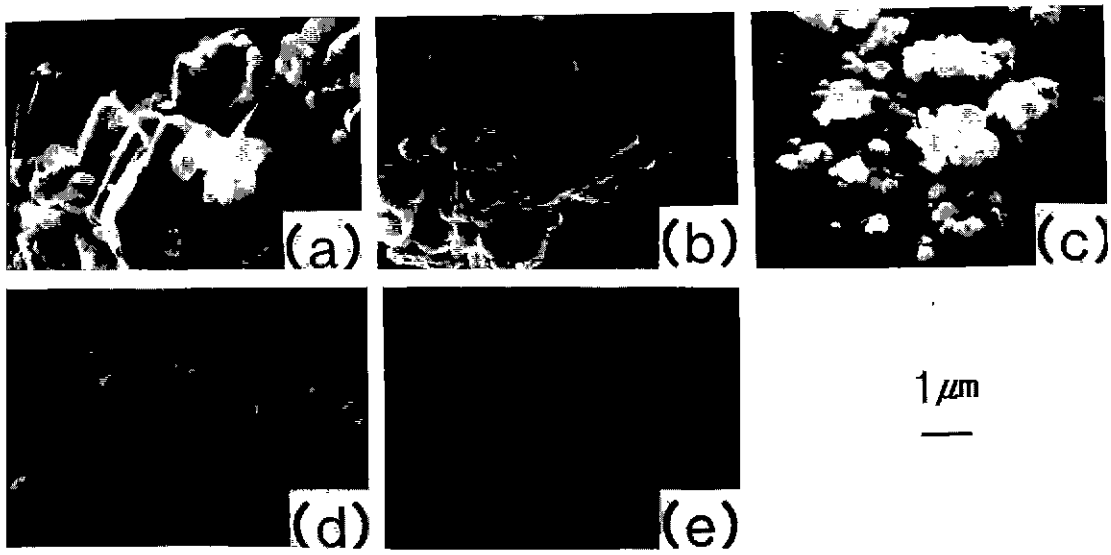

Fig. 3. SEM photographs of the ground mixtures.
(a) original (unground, 0 minute), (b) 15 minutes, (c) 30 minutes, (d) 60 minutes, (e) 120 minutes.

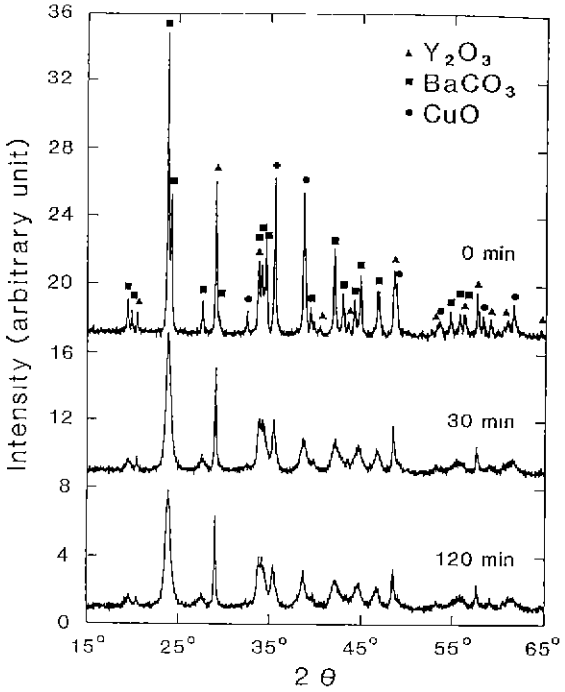

Fig. 4. X-ray diffraction patterns of the mixtures ground for different periods of time.

ing. This agglomeration phenomenon is consistent with the reduced specific surface area in Fig. 3. It was not possible to determine which particles of the three components of starting material were ground selectively during milling.

Figure 4 shows X-ray diffraction patterns of the mixtures ground for different periods of time. A decrease in the intensity of diffraction peaks is clearly observed with the progress of grinding. This change indicates the disrupted structure and size reduction of the mixture, although the structure of each component did not change into fully amorphous state even in the mixture ground for 120 minutes.

Figure 5 shows average contents of Y, Ba and Cu elements in the mixtures determined by EDX spectroscopy as a function of grinding time. Coefficients of variation of each element content measured during the grinding are shown in Fig. 6. Though the average contents of each element of the original mixture were quite deviated from each stoichiometric value, shown by the dashed lines in Fig. 5, they approached to the dashed lines after only 15 minutes grinding. Then, each average content was found to come closer to the dashed lines with an increase in grinding time. Final determination of the composition in the chosen points were: Y; 16+0.6%, Ba; 32+1%, Cu; 48+2%. The absolute values are of relevance to the stoichiometric composition. The coefficients of variation for these components during grinding were remarkably small, while the values for the original mixture were in higher stage between 0.12 and 0.24. This result confirms that well mixed powders can be prepared by relatively short

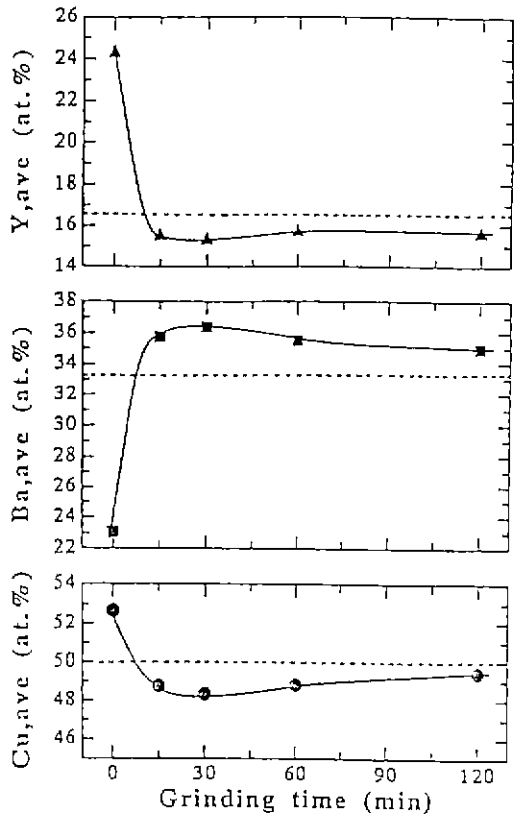

Fig. 5. Average contents of Y, Ba and Cu elements in the mixtures as a function of grinding time

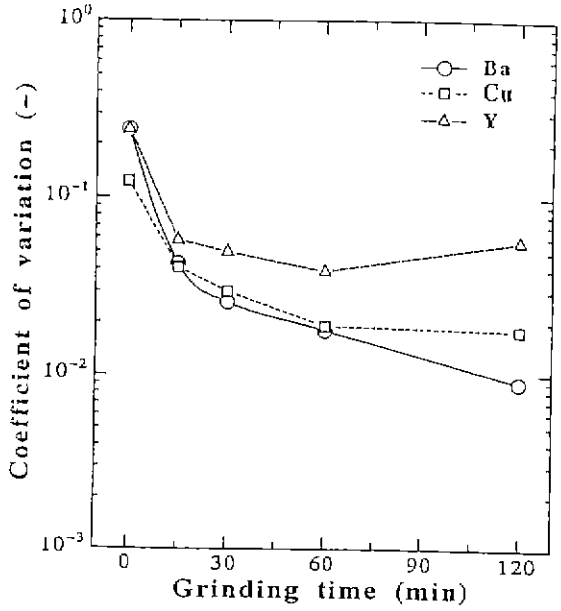

Fig. 6. Coefficients of variation of the each element in the mixtures as a function of grinding time.

grinding periods of time by a planetary ball mill.

2. Calcined powder and sintered body

It is reported that promotion of the decomposition of $BaCO_3$ resulted in the main source of undesirable phases

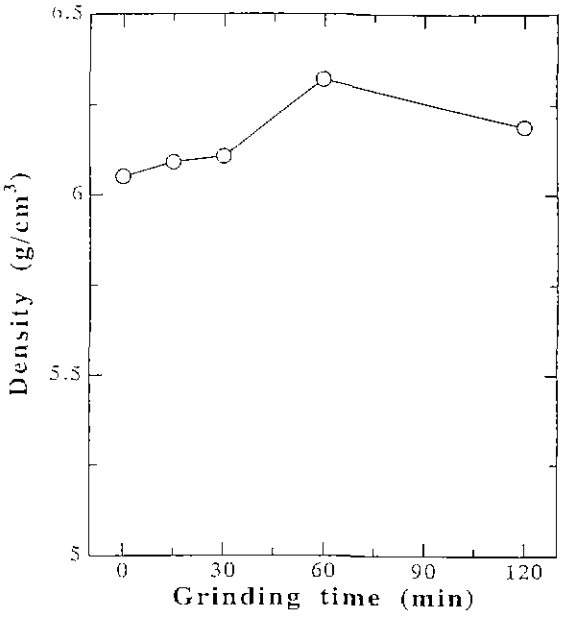

Fig. 7. Density of sintered bodies obtained from the ground mixtures as a function of grinding time.

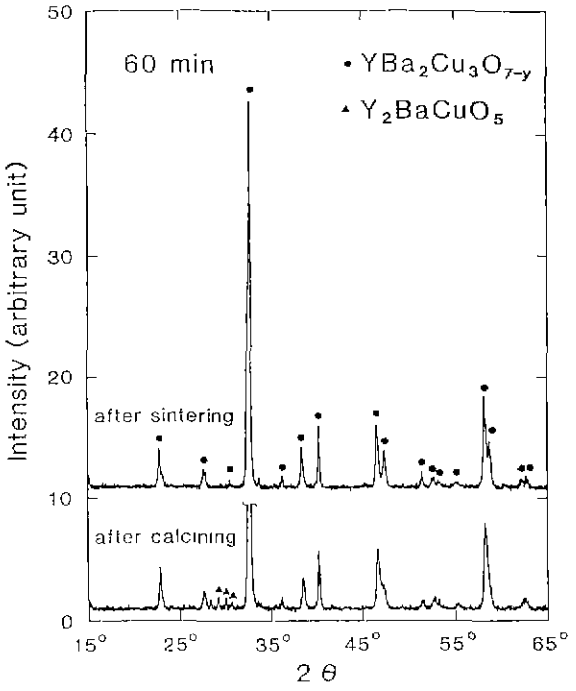

Fig. 8. X-ray diffraction patterns of the calcined powder and sintered body obtained from the mixture ground for 60 minutes.

appearing in YBaCu composite oxide superconductor in the case of improper heat treatment[7] and that the oxygen content of $YBa_2Cu_3O_{7-y}$ is less than 7 (i.e., 0<y) at the normal sintering temperature(over 1173 K).[8] By low temperature oxygen annealing at 673 K~823 K, the value increases to the ideal value of 7,[9] accompanying the transformation from tetragonal to orthorhombic phase. The total reaction in the sintering process is given by the following equation:[10]

$$Y_2O_3 + 4BaCO_3 + 6CuO \rightarrow 2YBa_2Cu_3O_{6.5} + 4CO_2.$$

Therefore, high temperature heat treatment sufficient to decompose $BaCO_3$ is strongly required. Also, further oxidation treatment at lower temperature is quite important for increasing the oxygen content to obtain a stoichiometry close to $YBa_2Cu_3O_7$.

Densification of formed body is an important step, which controls mechanical properties as well as its electrical, magnetic, or superconducting properties. Figure 7 shows the density of sintered bodies obtained from the ground mixtures as a function of grinding time. The densities increased gradually of increasing grinding time up to 60 minutes. The highest density is 6.32 g/cm^3 for 60 minutes ground sample. This corresponds to 99% of the theoretical value, 6.374 g/cm^3, of $YBa_2Cu_3O_7$ ceramics.[2] The density decreased at larger grinding time, due to the agglomeration.

Figure 8 shows a comparison of the X-ray diffraction patterns of the calcined powder and sintered body obtained from the mixture ground for 60 minutes. It is clearly observed that only the superconducting phase of $YBa_2Cu_3O_{7-y}$ was detected in the sintered body, while a secondary phase (Y_2BaCuO_5) appeared in the calcined powder. This feature seems almost independent of the grinding time. Actually X-ray diffractometry does not necessarily provide a correct judgment if a sample contains a relatively small amount of a secondary phase. In the present case, inclusions and grain boundary segregations could not be detected and the samples might be assumed to be phase pure. Therefore, microscopic method plays an important role in detecting the segregations and inclusions in the microstructures of a sintered body, because the microstructure and produced phases of this material have been found very sensitive to both temperature and atmosphere during sintering.[11]

Figure 9 shows TEM micrographs of sintered bodies from the original and ground mixtures with EDX analysis for their local parts: (a) 0 minute, (b) 15 minutes grinding, (c) 60 minutes grinding. The TEM-EDX analysis revealed that the grain with twin marked by C in Fig. 9 (c) consists of the single phase of $YBa_2Cu_3O_{7-y}$, while the areas marked A and B in Figs. 9 (a) and (b) respectively consist of phases with chemical compositions other than $YBa_2Cu_3O_{7-y}$. These results suggest that grinding of starting materials for a certain period of time is necessary to obtain a sintered body containing superconducting phase. It was found that the twin was well distributed in sintered bodies obtained from the ground mixtures. This means that phase transformation from tetragonal to orthorhombic occurred during the sintering process.

3. Superconductivity of sintered body

The variation of critical current density, J_c, can be at-

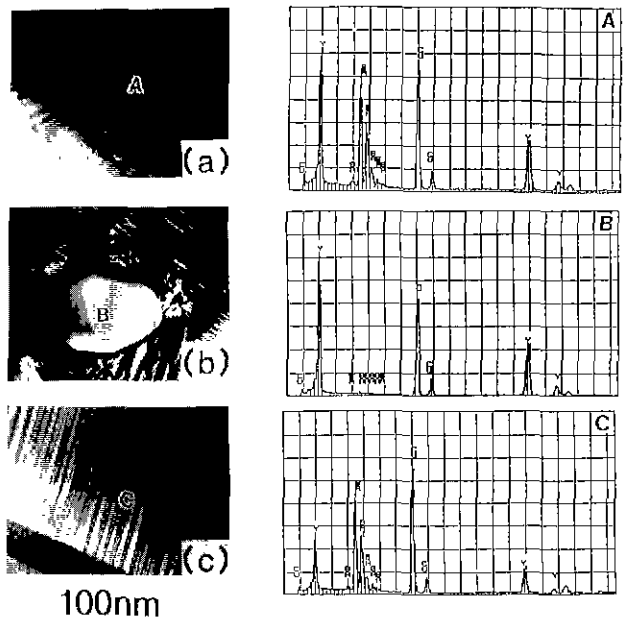

Fig. 9. TEM micrographs and microanalysis by TEM-EDX of composition of sintered bodies from ground mixtures.
(a) 0 minute. (b) 15 minutes, (c) 60 minutes.

tributed to many kinds of resistive grain linkage such as porosity, crack, and chemical inhomogeneity. Many efforts to increase the value of J_c of sintered bodies have been focused on the homogeneity of oxide powder, and the density and grain alignment of a sintered body and the impurities therein.[12,13] It is important to prepare starting powders with homogeneous composition in order to induce a sharp transformation into the superconductive state. Mixed grinding of the powders using an energy intensive planetary ball mill improves the homogeneity in terms of the composition of starting materials.

Figure 10 shows the critical temperature and the critical current density of sintered bodies obtained from mixtures as a function of grinding time. The critical temperature, T_c, is independent of grinding time and is around 90 K, which is comparable with the results appearing in the references.[14,15] This means that grinding of raw materials does not have an appreciable effect on T_c, suggesting that the oxygen content of sintered bodies for each sample is almost the same.[16]

EELS (electron energy loss spectroscopy) analysis was performed to confirm the oxygen content of the sintered body. A peak at around 528 eV at oxygen K-edge was suggested to be very sensitive to the oxygen content of hole content.[17] Figure 11 shows an example of electron energy loss spectra in the energy range 500~568 eV for the sintered bodies from the original and 60 minutes ground mixtures. The sharp peak at around 528 eV corresponds to the hole state, and the peak height is almost independent of grinding time. This result is consistent with the observed critical temperatures in Fig. 10.

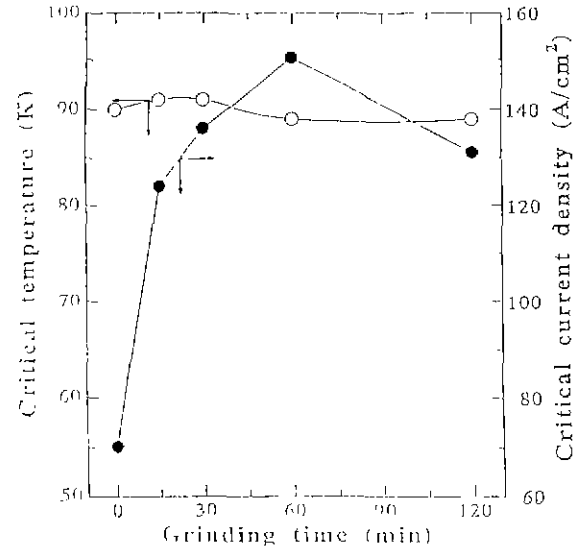

Fig. 10. Critical temperature and critical current density of sintered bodies obtained from mixtures as a function of grinding time.

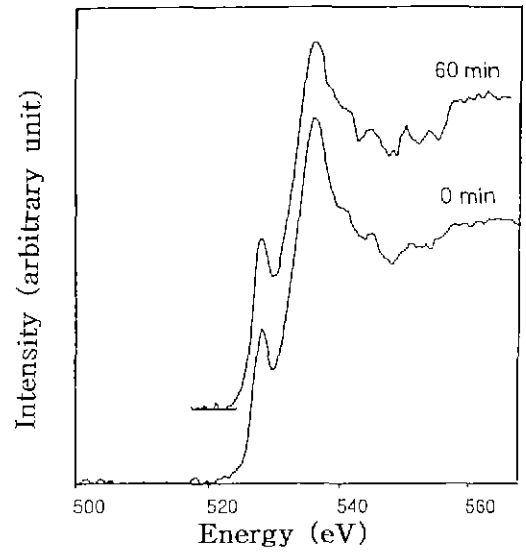

Fig. 11. Fine structures of oxygen K-edge spectra observed at room temperature in sintered bodies obtained mixtures.

The sintered body from the original mixture had a low bulk density, resulting in poor contact at grain boundaries compared with that of ground mixtures. The sintered body from the original mixture showed a relatively low value of J_c, 55 A/cm² (Fig. 10). The critical current density of the sintered bodies showed a strong dependence on the grinding time, and the value at 60 minutes grinding showed the maximum value of about 150 A/cm². The density at a longer grinding time was higher than that from the original one (Fig. 7). The higher density then leads to a better contacts at the grain boundaries and concomitantly an improvement in J_c. The present experimental data clearly demonstrate that improvement of J_c cannot be attained without sufficient mixing of

starting materials. Furthermore, a large number of grain boundaries in sintered bodies obtained from the mixture ground for 120 minutes may lead to a lower critical current density, arising from the restriction of oxygen diffusion in grain during calcination by the formation of dense aggregation of particles. It is known that variations in particle morphology and size distribution markedly affect sintering behavior. Smaller particle size is necessary to obtain sintered bodies with high density. Such an alternative way to the high temperature sintering for densification is important to obtain high J_c values necessary for wide applications of high-T_c materials.

IV. Concluding Remarks

From the present work, the following concluding remarks could be made;

(1) Size reduction of the mixture of Y_2O_3, $BaCO_3$, and CuO predominates in the mixed grinding by a planetary ball mill. The resultant fine particles of ground products were found to aggregate subsequently with increase in grinding time.

(2) Mixed grinding can lead to a homogeneous mixture forming the orthorhombic phase of $YBa_2Cu_3O_{7-y}$ (y is close to 0) with small amount of additional phase.

(3) X-ray diffraction analysis revealed structural changes with slight disruption in the ground mixture, although the structure did not change into a fully amorphous state within 120 minutes grinding.

(4) The critical current density of the sintered bodies depended heavily on the grinding time of mixture, while the critical temperatures were almost independent. The critical current density showed a maximum value of about 150 A/cm^2 in the case of 60 minutes grinding.

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