

Mechanochemical effects of grinding on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor

J. Baszyński

Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznań, Poland

Abstract

The effects of mechanical grinding on the powder of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor (so-called „high T_c superconductor”) were examined. The decrease of the grain size of the powders with the increase of the grinding time is accompanied by the decrease of the orthorhombicity of the unit cells and a decrease of T_c . According to the XRD results the degradation of crystallinity and chemical stoichiometricity are the effects of mechanical grinding.

1. Introduction

The 90K $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ orthorhombic superconductor represents a potential material for various applications but as for the polycrystalline bulk materials many problems have to be solved before its application. In addition, ceramic materials must be formed and sintered before application. For some practical applications, these HTS-oxides need to be fabricated into sheets or wires. During the process, the powders are often subjected by mechanical grinding to achieve the desired grain size. Fine homogeneous powders are required to obtain dense, uniformly sintered bodies. The densely sintered body probably has good properties as a superconductor.

In this paper, the mechanochemical effects of the grinding process on fine powders of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor were evaluated. Grinding caused degradation of the crystallinity of the „high T_c 123-phase” and the phase became unstable through the accumulation of elastic strains, elongation of the b -axis and contraction of a -axis, induced during the tetragonal to orthorhombic transition.

2. Experimental

Ceramic of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [1] were pulverized in an agate balls-mill, balls diameter 6 mm, using ethanol as wetting agent. The grinding time was varied from 10 min. to 110 hours. The rotating speed of the shaft was kept at about 100 r.p.m.

The changes of the structural parameters of the grain of each of the ground powders were monitored by X-ray powder diffraction analysis using $\text{CuK}\alpha$ and $\text{CoK}\alpha$ radiations. The superconductivity of each ground powder was tested by an AC inductive method (1.2 MHz).

3. Results and discussion

Figure 1 shows X-ray diffraction patterns for various grinding times in ethanol of a ceramic sample. As the grinding time increases up to 40h the intensities of the X-ray lines weaken significantly and their widths increase. The intensities of the X-ray lines of an impurity phase of BaCO_3 become relatively strong.

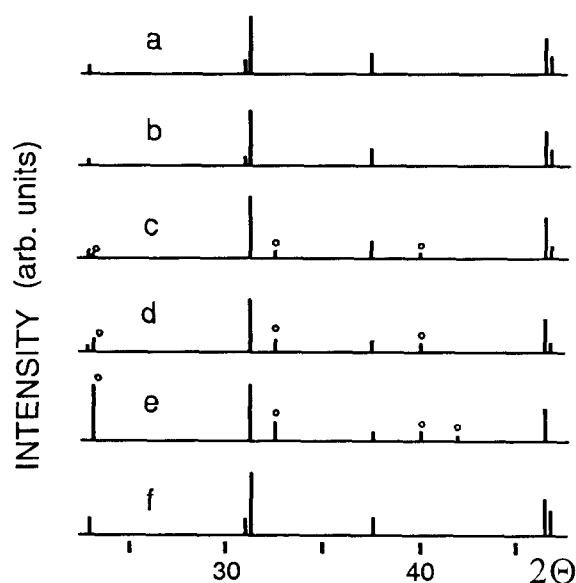


Figure 1. X-ray diffraction patterns of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor, main peaks of the 123-phase, ground powders for each grinding time (t): *a* – ceramic sample; *b* – $t = 20$ h, *c* – $t = 40$ h, *d* – $t = 64$ h, *e* – $t = 110$ h, and *f* – sample were annealed at 930°C for 6h in oxygen atmosphere after grinding for 110h. *o* – marked the impurity phase – BaCO_3 .

The width of each crystalline peak shows appreciable broadening because the ground powders were degraded with increased grinding time. This degradation includes not only the effect on the change of the superconductive crystal structure but also the effect of the decomposition of the 123-phase – decreasing of the barium content. This experimental result of an extraction of Ba, well corresponds to the calculation of potential energies of an ions in 123-phase in Wedepohl's model [2]. The potential energy of cation $1h\text{-Ba}_2$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is smaller than the corresponding energies for other cations in this compound. It should be emphasized that this conclusion is based upon a fully ionic model.

The increase of a relative volume of the BaCO_3 with decreasing grain size is the result of the chemical reaction in air atmosphere of the Ba with CO_2 . The X-ray data (impurity phase of BaCO_3) points on a creation of the Ba-defects in unit cells – this is a chemical effect of grinding. It was also shown that in the degraded sample, the ground powders and the impurity phase of BaCO_3 , can be easily transformed to the initial state by heat treatment – annealing at 930°C at oxygen atmosphere (Fig. 1f) and a slowly cooling to RT.

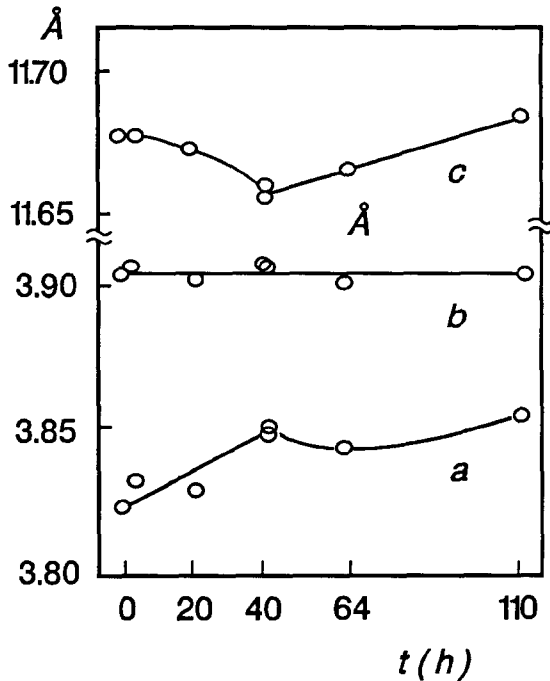


Figure 2. Lattice parameters 123-phase: a -axis, b -axis and c -axis vs grinding time t .

Fig. 2 shows the lattice constants a , b and c as a function of grinding time, determined by least squares fitting: 001 are used for c , and higher-angle diffractions hkl for a

and b . This figure shows that the lattice constants b are not affected by grinding time (t), but c decreases and a increases for t up to 40h. For $t > 40\text{h}$ a and c increases gradually.

Fig. 3 shows the orthorhombicity 123-phase, $2(b-a)/(b+a)$, and unit cell volume – V as a function of grinding time.

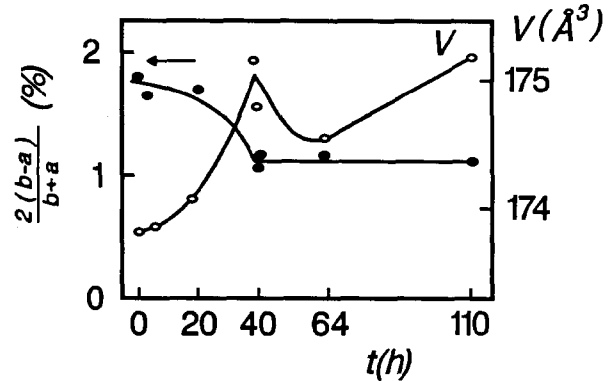


Figure 3. Orthorhombicity 123-phase $2(b-a)/(b+a)$ and unit cell volume – V vs grinding time t .

It is well known that T_c decreases with increase of the oxygen deficiency until superconductivity finally disappears, and also that the oxygen deficiency appears only in the $\text{Cu}(1)\text{-O}$ linear chain [3].

A review of published lattice parameters of well characterized samples has shown that the oxygen content of the 123-phase is related to the c axis by a linear relation e.g. $7 - \delta = 76.40 - 5.95 \cdot c$ [4].

According to this relation and above experimental results for c vs. $t < 40\text{h}$ we conclude the increase of oxygen in 123-phase resulting from a grinding effect. From the fact that only the occupancy of the $1b\text{-O}(1)$ and $1e\text{-O}(2)$ oxygen atoms was varied and increased a vs. $t < 40\text{h}$, we suppose that an absorbed oxygen atom enters into $1e\text{-O}(2)$ site of the orthorhombic unit cell of YBCO . This variation of oxygen site occupancies n up to 0.1 is quantitatively consistent with structural data (a -axis, unit-cell volume and n versus δ) reported by Jorgensen et al. [5]. If all $1e\text{-O}(2)$ sites are occupied, this is a hypothetical situation, the crystal symmetry should change to the tetragonal i. e., a -axis increases up to b -axis (the latter does not change during the grinding processes). This transformation is different from the one observed for the classical orthorhombic/tetragonal phase change of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

The observed change in lattice symmetry is different from this obtained by the quenching procedure in which the decreasing of the oxygen content is accompanied by the decreasing of b -axis and increasing of a -axis.

Conclusions obtained from the above experimental results are as follows:

First, the orthorhombic crystal structure of YBCO is partially modified by the grinding; i.e., decrease of the orthorhombicity $2(b-a)/(b+a)$ and decrease of c to $t = 40\text{h}$. According to the relation between c and oxygen content [4] in this grinding time oxygen content σ in 123-phase increase from $\sigma = 6.95$ up to $\sigma = 7.05$.

Second, for $t > 40\text{h}$ long-range order of the linear chain structure of Cu(1) – O is not affected because the orthorhombic structure of YBCO is essentially kept unchanged independent of t .

Third, T_c are changed with the change of orthorhombicity according to the results obtained by M. Sarikaya et al. [6].

The change in lattice symmetry obtained by grinding method is different from this for the atom substitution and reveals a strong dependence of orthorhombicity and c -axis on grinding time but does not indicate any change of b -axis.

References

- [1] Commercial sample of Y-123 made in Poisk Coop., Moscow, USSR.
- [2] E. Iguchi and Y. Yonezawa, *J. Phys. Chem. Solids*, **51** (1990) 313.
- [3] K. Yukino, T. Sato, S. Ooba, F. P. Okamura and A. Ono, *Jpn. J. Appl. Phys.*, **26** (1987) L867. M. O. Eatough, D. S. Ginley, B. Morosin and E. L. Venturini, *Appl. Phys. Lett.*, **51** (1987) 367.
- [4] R. Flukiger, T. Muller, T. Wolf, I. Apfelstedt, E. Seibt, H. Kupfer and W. Schauer *Physica C* **153-155** (1988) 1574
- [5] J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus and W. K. Kwok *Phys. Rev.* **B41** (1990) 1863.
- [6] M. Sarikaya and E. A. Stern, *Phys. Rev.* **B37** (1988) 9373