Order-disorder transitions and metastable phases produced by mechanical deformations in the $YBa_2Cu_3O_{7-x}$ superconducting system

F. Lavallée, M. Simoneau, and G. L'Espérance

Ecole Polytechnique, Département de Métallurgie et de Génie des Matériaux, Montréal, Québec, Canada H3C 3A7

R. Schulz

Hydro-Québec Research Institute, 1800 montée Ste-Julie, Varennes, Québec, Canada J3X 1S1

High-energy mechanical deformations have been used to induce order-disorder transitions in the $YBa_2Cu_3O_{7-x}$ orthorhombic structure and to synthesize metastable phases. During the milling process, a disorder is produced on the oxygen sublattice and on the Y- and Ba-cationic sites. A metastable simple cubic $(Y_{0.33}Ba_{0.67})CuO_{3-y}$ structure is formed. This cubic phase can also be synthesized by mechanical alloying a mixture of the elemental oxides. Discussions on the mechanism of formation, the thermal stability of the metastable structure, and the superconducting properties are presented.

Several methods have been used in the past few years to synthesize the $YBa_2Cu_3O_{7-x}$ (1:2:3) superconducting phase. Among them are the standard sintering technique, the melt-growth processes, coevaporation or sputtering, and many others. In most of these techniques, a thermally activated process is responsible for the diffusion of the chemical species and the crystal growth.

None of the above techniques use mechanical energy to assist or convey the chemical reaction. Recently, however, shock-wave-induced chemical synthesis of the 1:2:3-related compounds was reported.[1] The shock wave was applied to a mixture of the elemental oxides and the product was identified as the orthorhombic or the tetragonal phase together with some unidentified second phases. In a shock-wave compaction experiment conducted on $YBa_2Cu_3O_{7-x}$ (1:2:3) powders, Wier et al.[2] found an increase in the flux pinning energy after shock compaction. Among the pinning sites proposed to explain the superconducting properties of the consolidated solid, Murr et al.[3] proposed a configurational disorder on the cationic or the oxygen sites. The same type of defects has also been proposed to explain the increase in J_c observed in bulk-irradiated 1:2:3 superconductors.[4,5]

Mechanical alloying, also a high-energy collision process, is a simple and well-recognized method to synthesize metastable phases such as amorphous,[6] nanocrystalline,[7] quasicrystalline,[8] or stable intermetallic compounds.[9] In most cases, the final state of the system has a higher configurational disorder than the initial state. Thus, the process of milling has the potential of introducing atomic disorder which may be helpful for improving the pinning properties of superconductors.

Two types of powder have been subjected to high-energy ball milling. The first contained a mixture of Y_2O_3, BaO_2, and CuO in the ratio [Y]:[Ba]:[Cu] = 1:2:3 and the second one was a presynthesized $YBa_2Cu_3O_{7-x}$ (1:2:3) powder. The elemental oxides had a purity of 99% or better and the size of the particles ranged from 1 μm (Y_2O_3) to 175 μM (BaO_2). The powders, along with the three steel balls having diameters of 1.43, 1.11, and 0.95 cm, were introduced in a steel container and sealed under argon. For the oxide mixture, a ball to powder weight ratio of 6 was kept constant throughout the milling process. For the 1:2:3 powder, the starting ball to powder weight ratio was 5 and sampling was done at regular intervals for analysis. As a result, the weight ratio increased towards 6 at the end of the experiment. The milling was performed in a SPEX 8000 Mixer Mill.

The x-ray measurements were taken on a Siemens D-500 diffractometer with Cu $K\alpha$ radiation. The sample holder was covered with a thin foil of Kapton to avoid reaction with the atmosphere. Analytical transmission electron microscopy was carried out on a Jeol 2000 FX equipped with an ultrathin windowed energy dispersive x-ray (EDX) detector for chemical analysis. High-resolution TEM was performed on a Hitachi H-9000 NAR. The oxygen content was measured by carbothermal reduction on a LECO TC-136 apparatus. Trace analysis of the contaminants was carried out on a Jarell-Ash ICAP 9000 atomic emission spectrometer. Thermal analysis was done using a Perkin-Elmer differential scanning calorimeter.

Figure 1 shows the x-ray diffraction patterns of the powder mixture after various milling times. The $BaO_2(\blacktriangledown)$ and CuO ($\blacksquare$) react rapidly. During the first 10 h of milling, the x-ray peaks associated with these oxides become very large, the intensities decreased, and a broad halo located around 29° is formed. The peaks of Y_2O_3 ($\bullet$) remain almost unaffected. Only a slight increase in the width of the x-ray lines is observable, indicating a reduction in the Y_2O_3 crystal size. There is no significant shift of the peak positions during this period of time. After 10 h, only the broad halo and the Y_2O_3 peaks are practically visible. A detailed study[10] using x-ray diffraction and high-resolution TEM has revealed that

the broad halo in this specimen, as well as in mixtures of BaO_2 and CuO in a [Ba]:[Cu]=2:3 proportion milled for an equivalent amount of time, is in fact a mixture of amorphous phase and nanocrystalline $BaCuO_2$. Some $BaCuO_{2.5}$ has also been detected.[10] The amount of yttrium in solution in these phases is small.

Also, after this period of time, a small peak (∇) located around 32.5° appears. Upon further milling, its intensity increases and six other lines become visible. They all coincide with the most intense reflections of $YBa_2Cu_3O_{7-x}$ (1:2:3) but several lines belonging to the 1:2:3 orthorhombic structure are missing. The absence of these reflections, which should have been detectable if the structure was orthorhombic, suggests that this additional phase may be a disordered state associated with the 1:2:3 structure. The growth of this phase coincides with a reduction in the x-ray intensity of the Y_2O_3 and quasi-amorphous Ba-Cu-O phases. The additional crystalline structure is thus formed by a reaction between the Ba-Cu-O quasiamorphous phase and the Y_2O_3 crystallites.

Figure 2(a) shows a TEM lattice image of the new crystalline phase taken on the 65 h milled specimen. None of the lattice fringes have spacings larger than 0.4 nm. This is consistent with the x-ray diffraction patterns in which no reflections were observed below 22°. The largest d spacing calculated from the diffraction patterns is 0.387

nm. Typical electron diffraction patterns of the amorphous and the disordered crystalline structures are shown in Figs. 2(b) and (c), respectively.

The EDX chemical analysis of the disordered phase is shown in Table I together with the measured concentration of an orthorhombic 1:2:3 standard. The results indicate that this phase has a cationic ratio identical to the $YBa_2Cu_3O_{7-x}$ (1:2:3) superconducting structure. During the first hour of milling, the oxygen content of the powder mixture, measured by the LECO detector, decreases from 19.7 to 18.2 wt.%. After this period of time, the average oxygen content does not change significantly. The iron contamination from the milling tools is about 0.48 wt.% after 65 h.

The x-ray diffraction patterns obtained by milling the 1:2:3 orthorhombic structure are shown in Fig. 3. After less than an hour of milling (not shown), the structure cannot be identified as orthorhombic or tetragonal because of peak broadening. An order-disorder transition on the oxygen sublattice may therefore occur during this initial period of time. This mechanically induced ortho-rhombic to tetragonal transition which is associated with the loss of superconductivity will be discussed in more detail elsewhere.[11] After 20 h of milling, the structure is identical to the one obtained after milling $YBa_2Cu_3O_{7-x}$ the oxide mixture for 65 h [Fig. 1(b)]. High-resolution
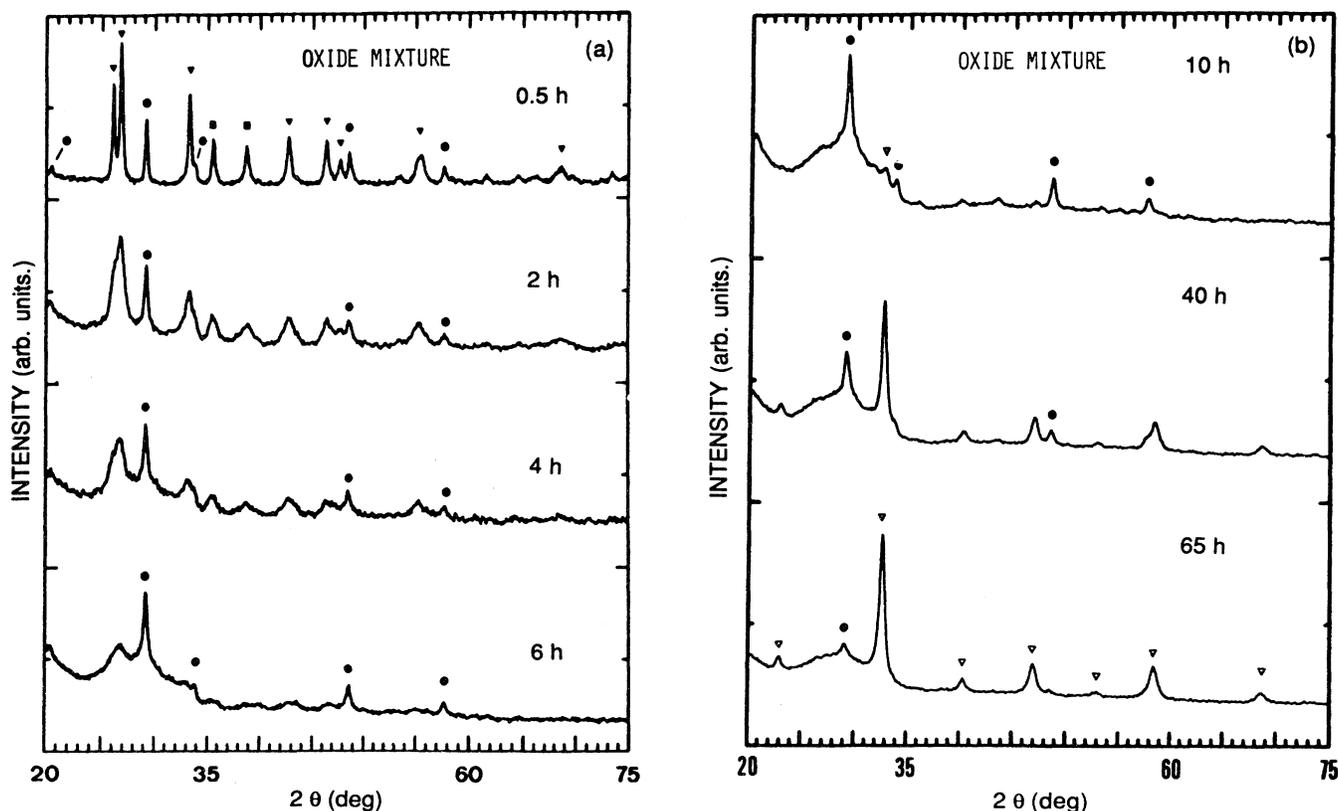

FIG. 1. X-ray diffraction patterns of a mixture of ($\bullet$) Y_2O_3, ($\blacktriangledown$) BaO_2, and ($\blacksquare$) CuO in the ratio [Y]:[Ba]:[Cu]=1:2:3 as a function of milling time; (∇) $(Y_{0.33}Ba_{0.66})CuO_{3-y}$ metastable cubic perovskite structure.
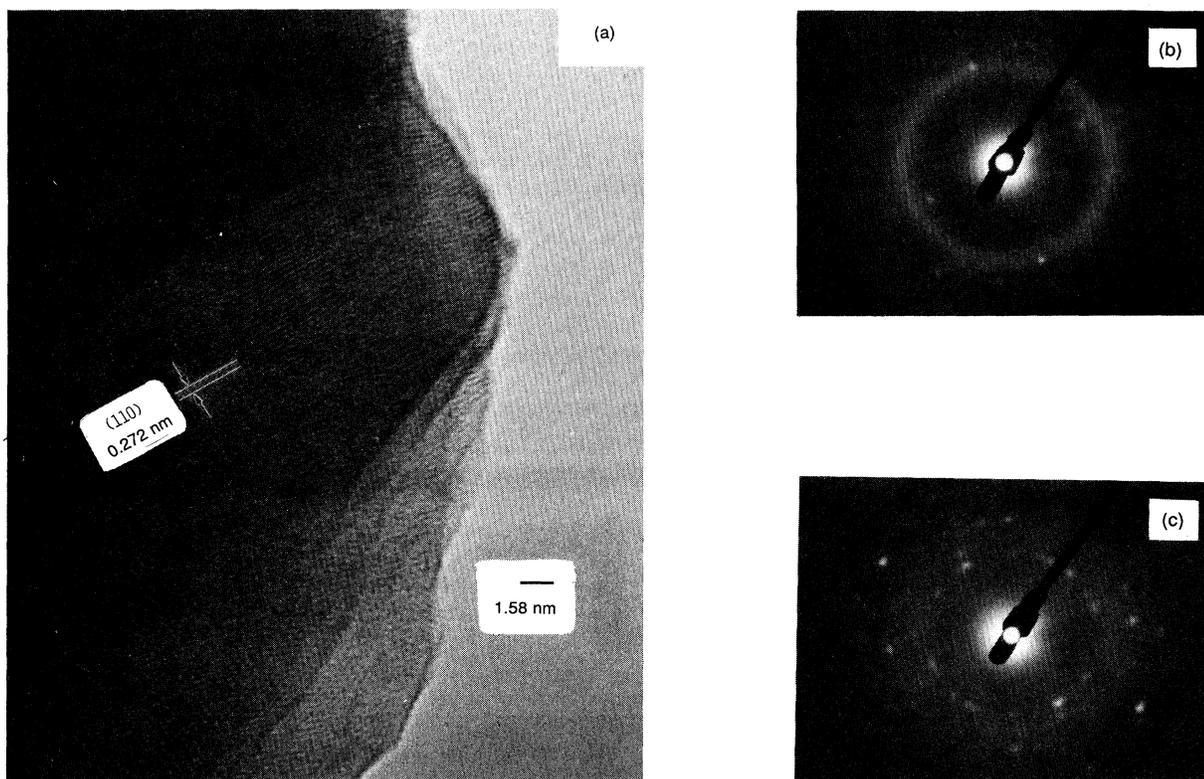
FIG. 2. (a) High-resolution TEM micrograph of the metastable crystalline structure taken on the oxide mixture milled for 65 h. Typical diffraction patterns of (b) the amorphous phase and (c) the disordered crystalline structure.
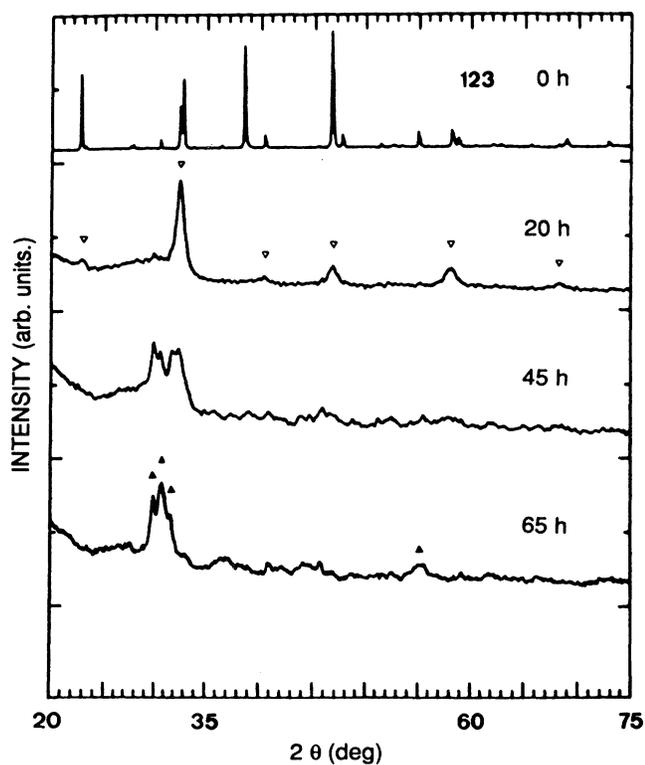

FIG. 3. X-ray diffraction patterns of the $YBa_2Cu_3O_{7-x}$ powder after various milling times: (∇) $(Y_{0.33}Ba_{0.66})CuO_{3-y}$ cubic structure and ($\blacktriangle$) Y_2BaCuO_5.

TEM reveals a similar microstructure in both cases.[11] Further milling produces the equilibrium Y_2BaCuO_5 ($\blacktriangle$) (Fig. 3).

The crystalline phase obtained after milling $YBa_2Cu_3O_{7-x}$ for 20 h or the oxide mixture for 65 h has a chemical composition identical to 1:2:3 and its structure is also closely related to the 1:2:3 structure [Fig. 4(a)]. We expect, however, a much higher degree of
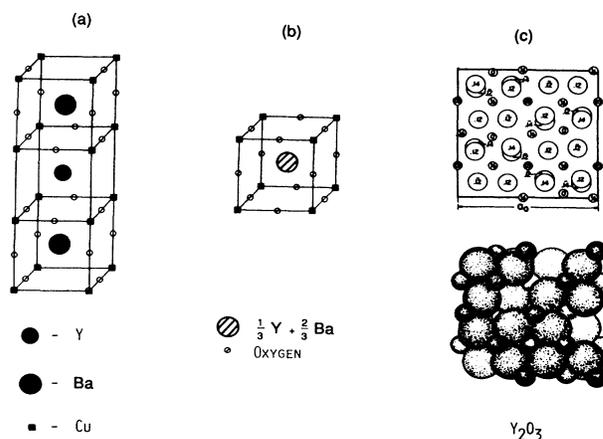

FIG. 4. (a) Atomic structure of the $YBa_2Cu_3O_7$ (1:2:3) orthorhombic phase, (b) atomic structure of the metastable cubic $(Y_{0.33}Ba_{0.67})CuO_3$ perovskite, and (c) atomic structure of bcc Y_2O_3.

TABLE I. EDX chemical analysis (thin regions) of the metastable cubic phase and a standard 1:2:3 orthorhombic structure.

	Y_L	Ba_L	Cu_K
	Intensity ratio (%)		
1:2:3 standard	66.0±3	100	46.5±3
Metastable cubic phase	65.6±3	100	44.6±3

chemical and topological disorder. A disorder on the cationic or oxygen sites has been proposed to explain the superconducting properties of shock-wave compacted 1:2:3 compound.[3] A similar explanation has been proposed in the case of $GdBa_2Cu_3O_{7-x}$ (1:2:3) thin films irradiated with x rays[12] and $YBa_2Cu_3O_{7-x}$ (1:2:3) irradiated by He^+, O^+,[4] or neutrons.[5] Thermal-induced disorder on the Ba^{2+} and Y^{3+} sites has also been reported.[13] These results suggest, as a natural choice for the model of this crystalline phase, a simple structure with complete disorder on the Y and Ba sites as well as a complete disorder on the oxygen sites. The structure, shown in Fig. 4(b), is a simple cubic perovskite $(Y_{0.33}Ba_{0.67})CuO_{3-y}$ with a lattice parameter of 0.386 nm. The calculated d spacings and relative intensities of the various hkl reflections are shown in Table II for $y = 0$ and $y = 1$. The best results are obtained for the oxygen-deficient perovskite. The agreement between the observed and calculated d spacings is very good.

During the mechanical alloying of the oxide mixture, the formation of the metastable simple cubic structure occurs, most likely, by a nucleation and growth mechanism. In ductile systems, the milling usually produces a lamellar microstructure formed by the juxtaposition of the elemental components.[14] The phases produced by the process, whether amorphous or crystalline, usually form by heterogeneous nucleation at the interface between these components.[15] Since, as mentioned before, the disordered crystalline phase is formed by a reaction between the Y_2O_3 crystallites and the quasiamorphous Ba-Cu-O phase, the former particles may act as heterogeneous nucleation sites for the reaction. Y_2O_3 has a very large unit cell. Its structure is bcc and the lattice parameter is 1.06 nm [Fig. 4(c)]. Although quite different from the metastable perovskite or the orthorhombic 1:2:3, these structures all have one crystallographic plane in

common [Figs. 4(a) and 4(c)]. Indeed the (002) plane of the tetragonal 1:2:3 structure forms a two-dimensional yttrium square lattice with a parameter of 0.3866 nm; the (040) plane of the Y_2O_3 structure [shown in Fig. 4(c)] also forms an yttrium square lattice with a parameter of about 0.375 nm and so does the (002) plane of the metastable pervoskite structure ($a = 0.386$ nm) without taking into account the oxygen atoms. The lattice mismatch is about 3% and therefore the (002)/(040) interface is almost coherent. It is also interesting to note that the local chemical composition of the regions on each side of the yttrium (002) plane in the 1:2:3 tetragonal structure is $BaCuO_x$, and so is the case of the quasiamorphous phase which reacts with the Y_2O_3 crystallites. In such a model, the formation of the metastable perovskite structure is limited by the total surface area of Y_2O_3 and therefore the rate of formation increases by lowering the size of the Y_2O_3 particles.

The mechanism of formation of the metastable cubic phase is simpler in the case of the milling of the 1:2:3 powder. The repeated collisions produce a large amount of structural defects such as grain boundaries, dislocations, and vacancies on the oxygen and cationic sites. As a result, atomic diffusion proceeds until a completely random state is achieved. The transformation is similar to an order-disorder transition.

The metastable cubic structure is not superconducting since a complete disorder on the oxygen sublattice (orthorhombic to tetragonal transition) in the 1:2:3 structure is sufficient to destroy superconductivity.[11] Disorder between Ba and Y is known to suppress T_c as shown in $Y_{1+x}Ba_{2-x}Cu_3O_{7-y}$.[16] Matijasevic et al. have also discussed, recently, the effects of cation disorder on the superconducting properties of the Y-Ba-Cu-O compound.[17]

Partial or complete recovery of the configurational order is possible by heat treatment. The recrystallization and ordering temperatures associated with the oxygen and cationic sites are still unknown for this metastable system. Nevertheless it should be possible to restore superconductivity while still maintaining a level of disorder. Indeed, the increase in flux pinning energy observed in shock-wave compacted 1:2:3 powders was attributed to a configurational disorder of the Y, Ba, or oxygen sites.[3] Irradiation-induced disorder in 1:2:3 thin films has also been reported to increase the critical current density.[5]

TABLE II. Experimental and calculated d spacings and relative x-ray intensities of the metastable $(Y_{0.33}Ba_{0.67})CuO_{3-y}$ cubic structure.

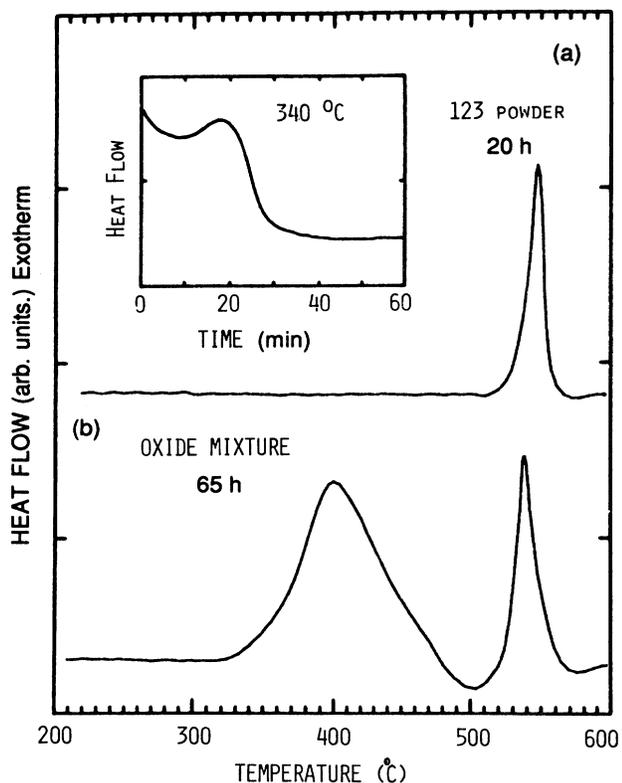| hkl	d_{meas} (nm)	d_{calc} (nm)	I_{meas} (%)	I_{calc} $y=0$	I_{calc} $y=1$
100	0.387	0.386	9.2	4.3	5.7
110	0.273	0.273	100	100	100
111	0.224	0.223	8.0	12.9	8.4
200	0.193	0.193	25.2	35.7	29.2
210	0.173	0.173	4.0	2.3	2.8
211	0.158	0.158	34.7	41.5	41.0
220	0.137	0.137	7.7	22.5	18.7

FIG. 5. Differential scanning calorimetry of (a) $YBa_2Cu_3O_{7-x}$ powder milled for 20 h and (b) the oxide mixture milled for 65 h. The inset shows the isothermal DSC trace measured at 340 °C on the milled oxide mixture.
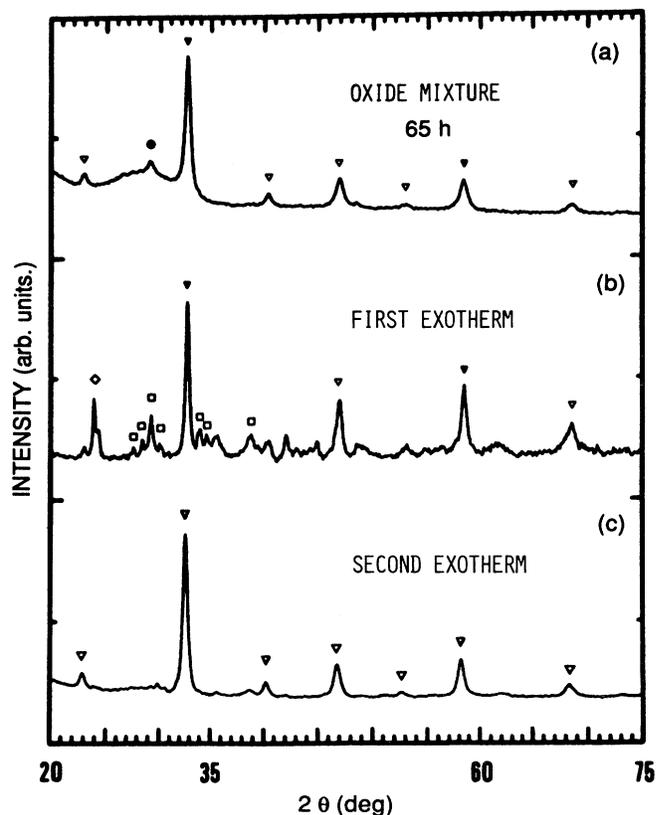

FIG. 6. X-ray diffraction scans of (a) the oxide mixture milled for 65 h, (b) the same sample annealed after the first exotherm, and (c) sample b annealed after the second exotherm.

More than a twofold increase in the flux pinning energy has been measured in $Gd_1Ba_2Cu_3O_{7-x}$ thin films following x-ray irradiation.[12] The annealed metastable powder has therefore a strong potential for flux pinning.

Figure 5(a) shows the DSC trace of the $YBa_2Cu_3O_{7-x}$ powder milled for 20 h. The heating rate is 20° C/min. A single exotherm with onset at about 510 °C and peak temperature at 547 °C is observed. In the case of the powder mixture milled for 65 h, two exotherms are measured [Fig. 5(b)]. The one with an onset at 505 °C and maximum at 539 °C is similar to the one shown previously. The other has an onset temperature at about 330 °C and a maximum at 400 °C. Figure 6 shows the x-ray scans of the oxide mixture milled for 65 h after each exotherm. The first step is associated with the crystallization or recrystallization of the quasiamorphous Ba-Cu-O phase into $BaCuO_2$ (□) and a crystalline phase which could be associated with $BaCuO_{2.5}$ (◇)[18] [Fig. 6(b)]. The inset in Fig. 6 shows the isothermal trace measured on

the milled powder mixture at 340 °C. The peak on a monotonically decreasing signal indicates a mixed process of nucleation and growth in an amorphous phase and grain growth of a nanocrystalline microstructure.[19] The second exotherm at 540 °C is associated with the growth or the recrystallization of the metastable cubic perovskite structure [Fig. 6(c)]. There is no indication of ordering of the Y and Ba sites.

In summary, a metastable cubic perovskite structure $(Y_{0.33}Ba_{0.66})CuO_{3-y}$ has been synthesized by high-energy mechanical deformations. This phase is derived from the 1:2:3 structure by a complete disorder of the Y, Ba, and oxygen sites. It can be formed by mechanical alloying the elemental oxides or by grinding the orthorhombic 1:2:3 structure. The recrystallization or grain-growth temperature of the metastable cubic structure is about 540 °C. The disorder of the Y and Ba sites is stable up to 600 °C. The annealed powder is expected to exhibit strong flux pinning properties.

[1]B. Morosin, R. A. Graham, E. L. Venturini, D. S. Ginley, and W. F. Hammetter, in *Shock Waves in Condensed Matter 1987*, edited by S. C. Schmidt and N. C. Holmes (Elsevier Science, B. V., 1988), p. 439.

[2]S. S. T. Weir, W. J. Nellis, M. J. Kramer, C. L. Seaman, E. A. Early, and M. B. Maple, Appl. Phys. Lett. 56, 2042 (1990).

[3]L. E. Murr, C. S. Niou, S. Jin, T. H. Tiefel, A. C. W. P. James, R. C. Sherwood, and T. Sieggrist, Appl. Phys. Lett. 55, 1575

(1989).

[4]J. D. Jorgenson, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, Phys. Rev. B 36, 5731 (1987).

[5]J. W. Lee, H. S. Lessure, D. E. Laughlin, M. E. McHenry, S. G. Sankar, J. O. Willis, J. R. Cost, and M. P. Maley, Appl. Phys. Lett. 57, 2150 (1990).

[6]C. C. Koch, O. B. Cavin, C. G. McKamey, and J. O. Scarbrough, Appl. Phys. Lett. 43, 1017 (1983).

[7]E. Hellstern, H. J. Fecht, Z. Fu, and W. L. Johnson, J. Appl. Phys. 65, 305 (1989).

[8]J. Eckert, L. Schultz, and K. Urban, Appl. Phys. Lett. 55, 117 (1989).

[9]J. Eckert, L. Schultz, E. Hellstern, and K. Urban, J. Appl. Phys. 64, 3224 (1988).

[10]F. Lavallée, Master's thesis, Ecole Polytechnique de Montréal, Montreal, 1991.

[11]M. Simoneau, F. Lavallée, G. L'Espérance, M. Trudeau, and R. Schulz, Proceedings of the European Workshop on Ordering and Disordering (Grenoble, 1991) Elsevier (to be published).

[12]S. Kohiki, S. Hatta, K. Setsune, K. Wasa, Y. Higashi, S. Fukushima, and Y. Gohshi, Appl. Phys. Lett. 56, 298 (1990).

[13]T. Kajitani, K. Oh-ishi, M. Kikuchi, Y. Syono and M. Hirabayashi, Jpn. J. Appl. Phys. 26, L1144 (1987).

[14]E. Hellstern and L. Schultz, J. Appl. Phys. 63, 1408 (1988).

[15]U. Koster, R. Pries, G. Bewernick, B. Schuhmacher, and M. Blank-Bewersdorff, J. Phys. (Paris) Colloq. Suppl. 51, C4-121 (1990).

[16]Z. Iqbal, F. Reidinger, A. Bose, N. Cipolinni, H. Eckhardt, B. L. Ramakrishna, and E. W. Ong, in Proceedings of the 1987 MRS Fall Meeting, Symposium on High Temperature Superconductors, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller, MRS Symposia Proceedings No. 99 (Materials Research Society, Pittsburgh, 1987), p. 907.

[17]V. Matijasevic, P. Rosenthal, K. Shinohara, A. F. Marshall, R. H. Hammond, and M. R. Beasley, J. Mater. Res. (to be published).

[18]M. Arjomand and D. J. Machin, J. Chem. Soc. Dalton Trans. 1061 (1975).

[19]L. L. C. Chen and F. Spaepen, J. Appl. Phys. 69, 679 (1991).
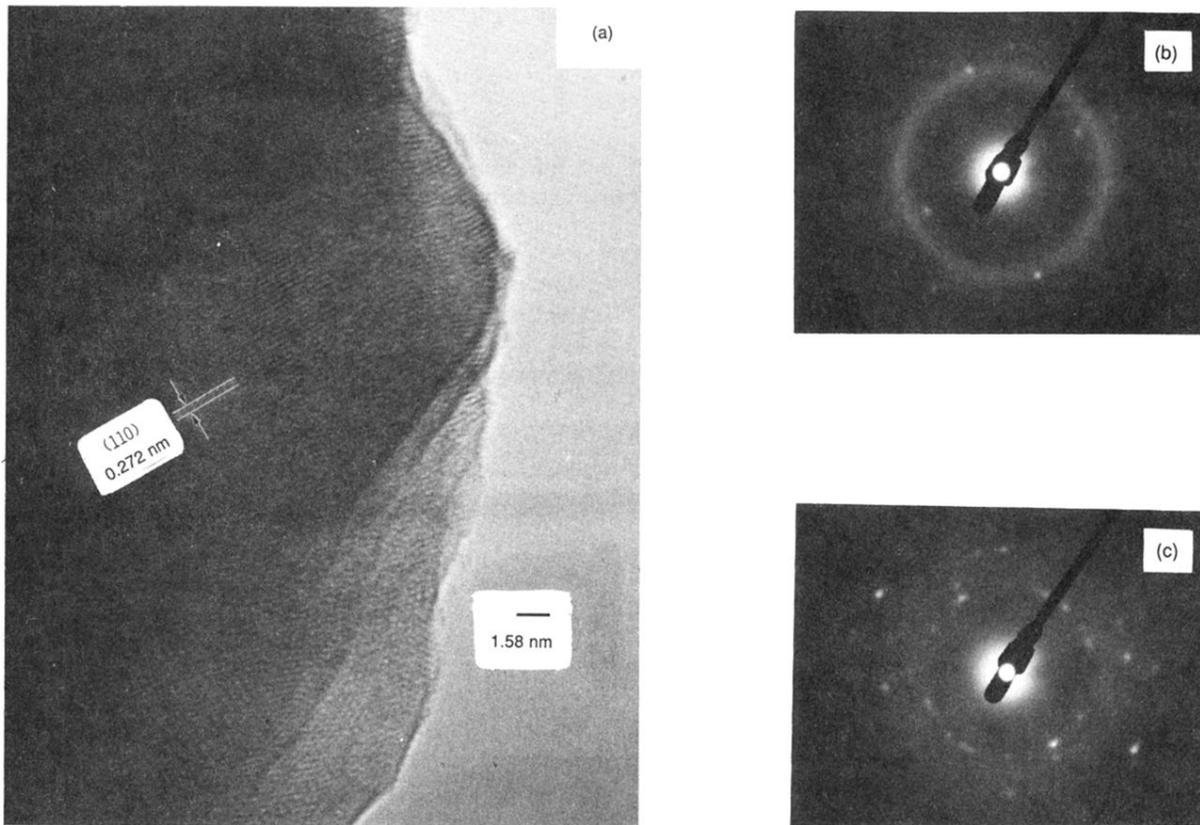
FIG. 2. (a) High-resolution TEM micrograph of the metastable crystalline structure taken on the oxide mixture milled for 65 h. Typical diffraction patterns of (b) the amorphous phase and (c) the disordered crystalline structure.