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# Anomalous ferromagnetic behaviour of $Y_2O_3$ and CuO nanoparticles in $YBa_2Cu_3O_y$ superconductor

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**Abstract.** Anomalous ferromagnetic behaviour of the  $Y_2O_3$  and CuO components in  $YBa_2Cu_3O_y$  (Y123) was observed after severe reduction of particle size. The particle size reduction was performed in following way:  $Y_2O_3$ ,  $BaCO_3$  and CuO were ground for different times to reduce the particle size to the nanoscale. It was found that the superconducting phase could not be obtained without heat treatment, but a weak ferromagnetic behaviour of the mixture was observed at liquid and room temperatures. . In order to understand which compound is responsible for this weak ferromagnetism, the  $Y_2O_3$ ,  $BaCO_3$  and CuO powders were separately ground and M-H loops taken at 290K. The results indicated that both  $Y_2O_3$  and CuO powders showed weak ferromagnetism, but  $BaCO_3$  showed anti ferromagnetism. It is thought that energy transfer to the powder particles by grinding results in severe plastic deformation of the particles to produce dislocations, vacancies and atomic disorder. We discuss then the observations in the context of recent studies of the magnetic properties of nanoscale oxide materials.

## 1. Introduction

Most physical and chemical properties of solid matter change when the particle size is decreased to the nanoscale [1]. There are several methods for the production of nano powders; conventional methods for particle size reduction like milling, grinding, jet milling, crushing, and air micronization [2-4]. Advantages of reducing of the particle size in ceramic materials include increased reaction rates during sintering and improvements in both microstructure and properties even of reduced processing temperatures [5].

The aim of this work was to reduce the particle size to the nanoscale of material with a nominal composition of  $YBa_2Cu_3O_y$  using mechanical alloying. We were then interested to characterize the differences in structural and magnetic properties between mixtures of  $Y_2O_3$ ,  $BaCO_3$  and CuO in stoichiometric ratios subjected directly grinding without any heat treatment and powders of pre-calcined  $YBa_2Cu_3O_y$ . The primary aim was to explore the feasibility of preparing nanoscale YBCO powder directly by mechanical alloying of oxide precursors, but we have found it necessary to study the magnetic properties of both kinds of samples in some detail.

## 2. Experimental details

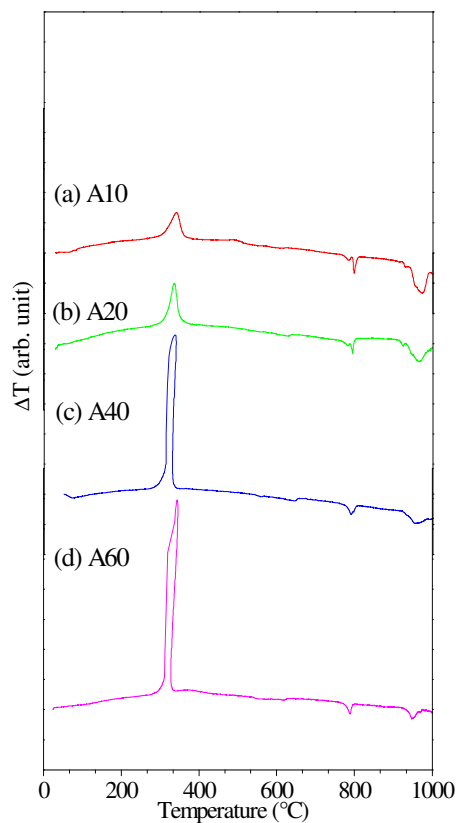
100 grams batches of  $Y_2O_3$  (Aldrich 99.99%),  $BaCO_3$  (Strem Chemicals 99.999%) and CuO (Alfa Aesar 99.0%) powder were mixed together for 1h in a molar ratio 1:2:3 using a mortar machine. The mixture was transferred back to the mortar machine and ground for 10, 20, 40, and 60h in air. These samples will be referred to below as A10, A20, A40 and A60.

Solid state phase transformations in the powder samples were studied using a Differential Thermal Analysis (DTA) model NETZSCH1. Structural analyses were carried out in an X-ray

diffractometer (XRD), Rikago Dmax/III, which emits X-rays from a  $\text{CuK}\alpha$  source at a wavelength of 0.154nm. Analysis of the particle size of the powders was monitored by a high resolution JEOL 840F Scanning Electron Microscopy (SEM) working at 5kV, and Energy Dispersive X-ray analyses (EDX) were performed using a JEOL 6300 SEM working at 10kV. The magnetic properties (M-H loops) of samples were determined using a Vibrating Sample Magnetometer (VSM) on the same system.

### 3. Results and Discussion

In order to see any solid state phase transformations in the powders during heating to determine appropriate processing temperatures, DTA measurements were performed for samples series A (Fig. 1). It is clearly seen that an exothermic peak at around 330°C and two endothermic peaks at around 800°C and 970°C were observed for all samples. We believe that the peak at around 330°C corresponds to the strain release temperature for the lattice damage induced during grinding. It can also be seen that for the 10h sample, A10, the peak intensity at 330°C is very low and the peak is very broad, but that this peak becomes sharper and higher gradually for series A samples with increasing grinding time, consistent with the residual strain in the particles increasing with additional grinding. The higher endothermic peaks correspond to the formation of liquid phase and the peritectic temperature of Y123 respectively.



**Figure 1.** DTA curves of samples in series A

It is well known that a substantial energy transfer to powder particles takes place by grinding action. This process results in plastic deformation of the particles which introduces strain and lattice defects. With the continued grinding action the joining of particles develops lamellar structures. Initially, grinding process flattens ductile powders into flaky/ plate-like particles. As the particles are

repeatedly ground, the lamellar structure is continually getting thinner until a steady state is established and the layers cannot become any thinner [6]. An optical photograph of powder A60 is given in Fig.2 which shows a flaky morphology as discussed.

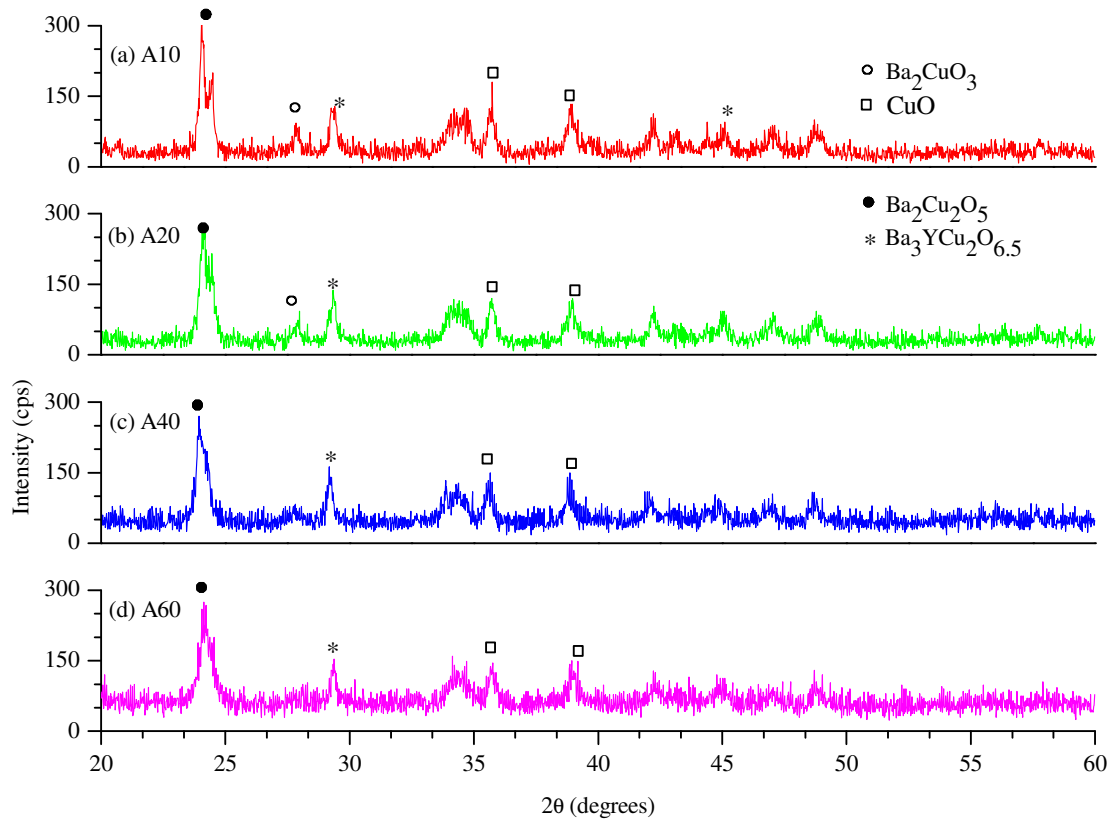


**Figure 2.** Shows an optical photograph of sample A60.

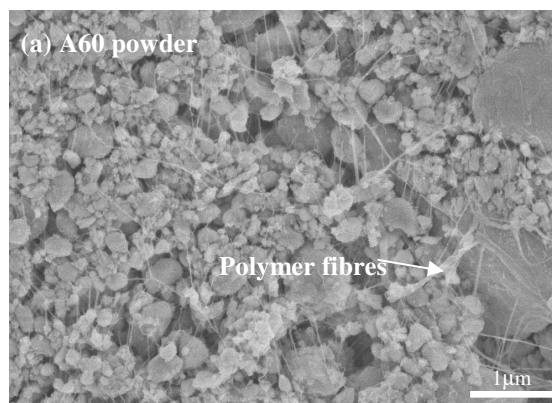
The XRD patterns of samples from series A, which are as-ground without any heat treatment, are given in Fig.3. These profiles indicate no formation of the superconducting high- $T_c$  phase by grinding a mixture of  $Y_2O_3$ ,  $BaCO_3$  and  $CuO$ . The peaks shown in Fig.3 were indexed to  $CuO$ ,  $Ba_2CuO_3$ ,  $Ba_2Cu_2O_5$ ,  $Ba_3YCu_2O_{6.5}$  and a few unknown phases. As a result, we can conclude that the mortar grinder used in this work reduced the particle size, but an appropriate condition could not be found to form the high- $T_c$  phase by direct mechanical alloying.

An SEM/EDX analysis was performed to obtain information on the particle size and determination of the second phases present in the samples. Fig.4 shows SEM images of powder samples of A60. The image of A60 indicates an average particle size much less than  $1\mu m$ , but some thin fibres between the particles are shown in same image. In addition, EDX analysis indicated four different phases are formed in sample A60 during the grinding process. These phases are Y-rich, Cu-rich and two different compositions of Y, Ba and Cu oxides. No evidence of Y123 was found.

At first, we attempted to check the superconducting properties of all these samples by a simple method using the repulsive Meissner effect which allows the suspension of a superconductor above a permanent magnet. We found that samples from series A which were not subjected to any heat treatment, except as a result of grinding, showed no Meissner effect even after 60h grinding. In contrast, all samples, especially samples after long grinding times, showed a weak attractive behaviour to the magnet both after cooling liquid nitrogen temperature and also, more surprisingly, at room temperature there is still a strong attraction between the samples and the magnet. These preliminary results suggested that all the A samples showed ferromagnetic rather than diamagnetic properties.



**Figure 3.** Shows XRD spectrums of samples series A, which were ground for 10, 20, 40 and 60h in air without any heat treatment.



**Figure 4.** Shows SEM images of powder samples of A60.

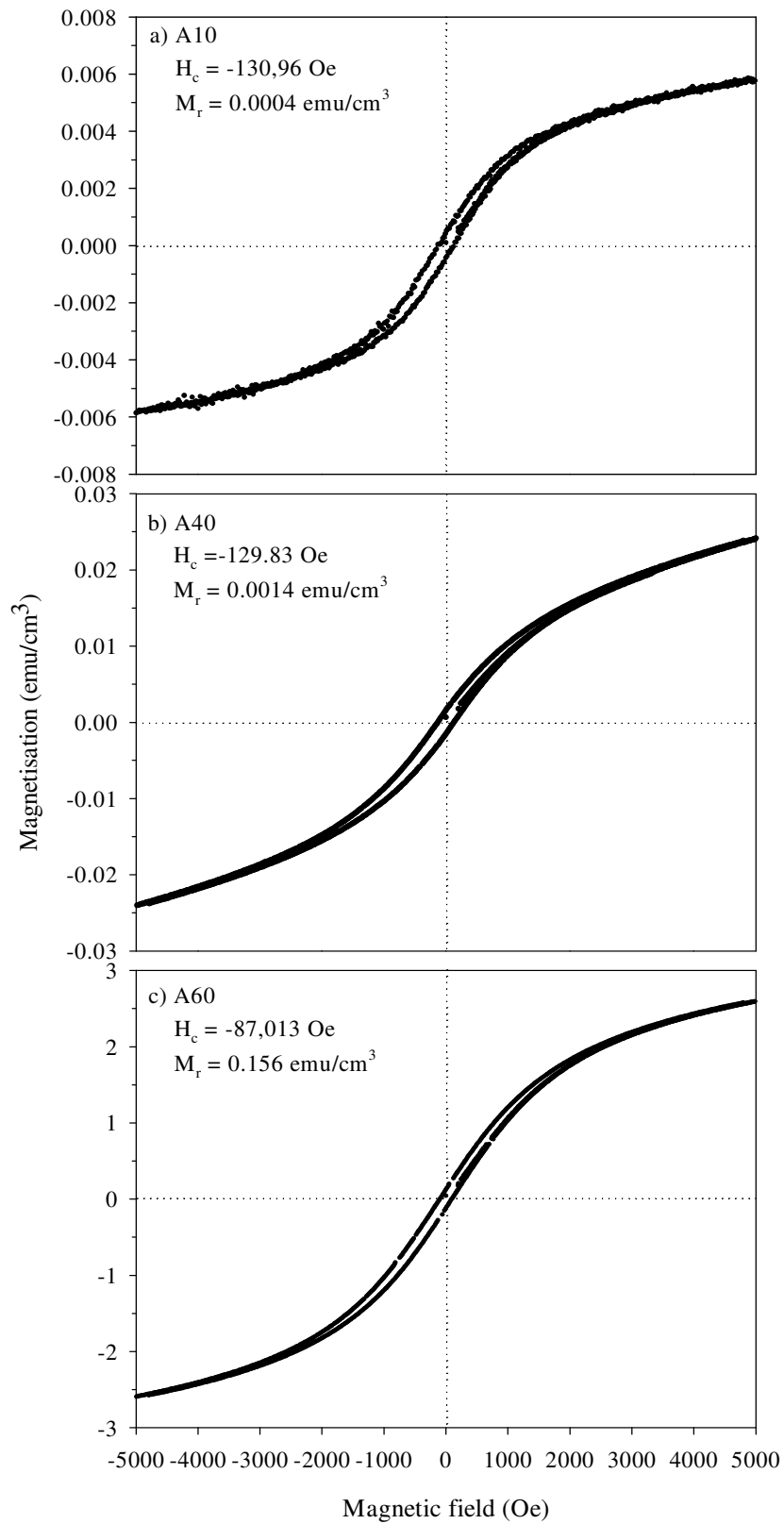
In order to determine the magnetic behaviour of our samples in more detail, the M-H loops of sample A10, A40 and A60 at 77K were taken, and are shown in Fig. 5. It can be clearly seen that the M-H loops indicate the hysteresis typical of ferromagnetic behaviour. The remanence magnetisation values of hysteretic loop increased when the milling time increased. The coercive force ( $H_c$ ) and

remanent magnetization ( $M_r$ ) values were determined at 77K for A60 sample to be respectively - 87.013 Oe and  $0.156 \text{ emu/cm}^3$  and values of other samples are as indicated in Fig. 5.

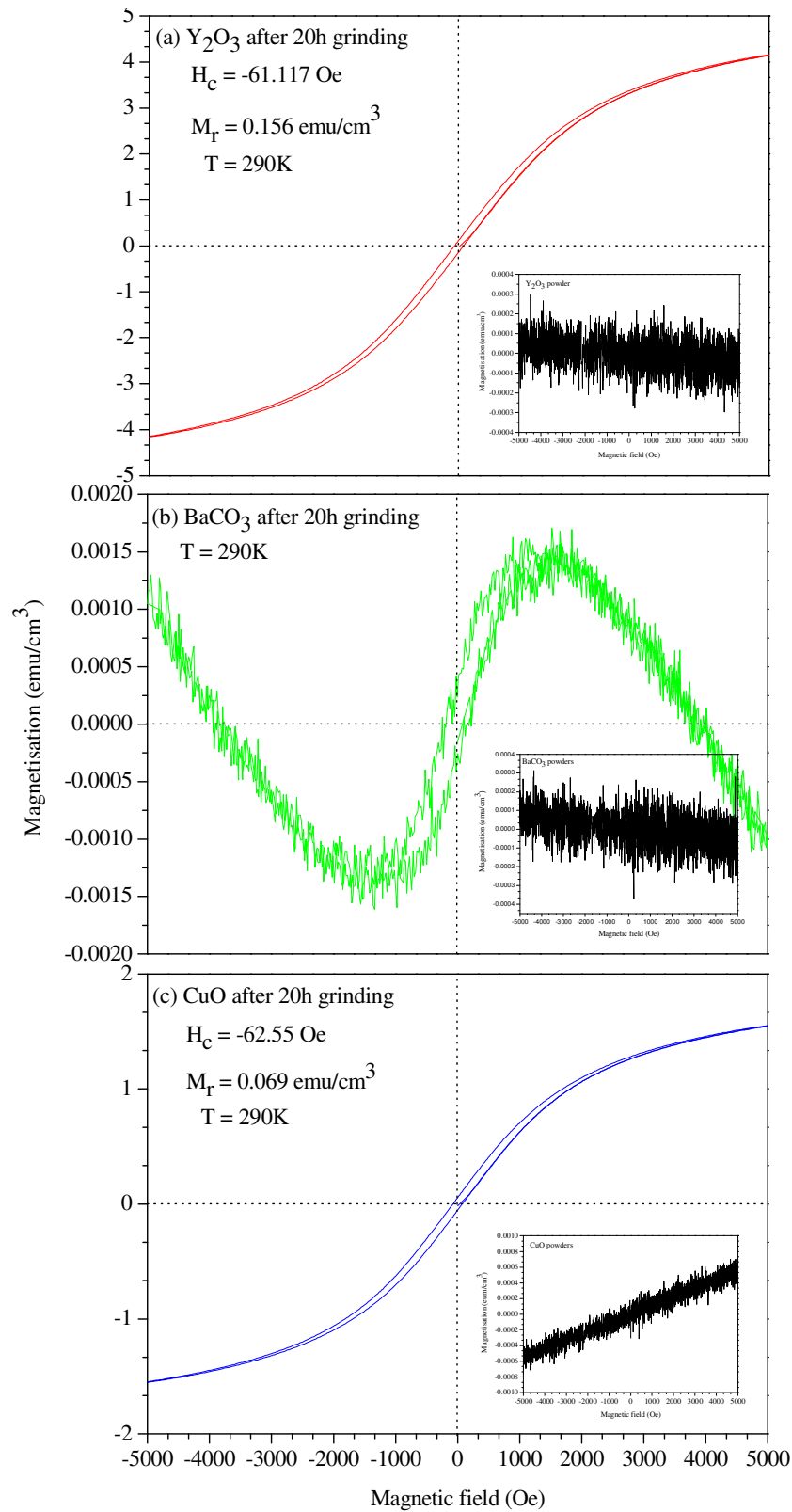
At this point, we decided to find out which compound is responsible for the ferromagnetic character after long grinding times. 10g of the starting  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  powders were separately subjected to grinding for 20 hours under same condition as all the samples described above. XRD and M-H measurements were then performed on each compound. Firstly, the peak intensities in the X-ray diffraction patterns decreased (not included here). Secondly,  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  powders after 20 h grinding were attracted to the magnet at 290 K as we seen before, but  $\text{BaCO}_3$  powders did not show any unusual behaviour. Then we measured the M-H loops of the three compounds before (insets of Fig. 6) and after 20h grinding, as shown in Fig. 6. As can be seen in the insets of Fig. 6, none of starting compounds show ferromagnetism. After 20h grinding, however, both the  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  powders showed weak ferromagnetic hysteresis at 290K but the  $\text{BaCO}_3$  powders showed a typical antiferromagnetic behaviour with the superimposed to a diamagnetic signal. The remanent magnetization ( $M_r$ ) and coercive force ( $H_c$ ) values for ground  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$  are indicated in Fig. 6.

In summary, samples prepared by grinding a mixture of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  (series A) showed no sign of the superconducting Y-123 phase in the XRD spectra and no sign of a typical Meissner effect when cooled by liquid nitrogen. From the DTA analysis, a strong peak at around  $330^\circ\text{C}$  corresponds to a possible strain release temperature since the peak intensity is increasing with the grinding time. This clearly indicates that strain in the particles is induced during grinding. We conclude that mechanical alloying of starting oxides is not an effective process to produce nanoscale Y123 powder, partly because of the excess strain introduced after long grinding times. In addition long grinding times also cause decomposition of prereacted Y123 powder, and restoring of the Y123 phase by re-sintering was not possible. After 20h grinding oxide mixtures, prereacted Y123 or  $\text{CuO}$  or  $\text{Y}_2\text{O}_3$  separately all showed weak ferromagnetic hysteresis at 290K.

We believe that the XRD, SEM and magnetic measurements all provide evidence that extensive grinding of all these samples results in the formation of nanoscale  $\text{CuO}$  and/or  $\text{Y}_2\text{O}_3$ . Previous work has shown that weak ferromagnetism has frequently been discussed in nano scale  $\text{CuO}$  [7-8], but not yet in  $\text{Y}_2\text{O}_3$ .



**Figure 5.** The M-H loops measured at 77 K for samples (a) A10 (b) A40 and (c) A60.



**Figure 6.** The M-H loops of individual Y<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub> and CuO after 20h grinding measured at temperature 290 K. The insets of each curve indicate the M-H loops of powders before grinding.



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