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Changes in the Composition and Properties of High-T_c Superconducting Ceramics $YBa_2Cu_3O_{6.5+\delta}$ after Passage of a Direct Current

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DC treatment of '1:2:3' superconducting ceramics at low temperatures can cause the migration of light impurities and oxygen towards the appropriate electrode, accompanied by changes in their properties.

DC treatment of ceramics at temperatures over 200 °C has been found[1] to cause a loss of superconductivity in the part of the sample adjacent to the positive electrode, the phenomenon being ascribed to electromigration of oxygen towards the negative electrode. Other effects, such as migration of cations and impurities following DC treatment at low ($\leq$78 K) temperatures have been reported to occur.[2–4] Oxygen migration towards the positive electrode has been claimed[3,4] to take place under these conditions. All these unusual phenomena may be important in terms of the practical use of '1:2:3' superconductors.

In this communication the latest results of our investigations of the effect of DC on high temperature superconducting (HTSC) ceramics $YBa_2Cu_3O_{6.5+\delta}$ over a wide range of temperatures (77–295 K) are given. The changes in the oxygen indices δ, concentrations of impurities, HTSC phase relative volumes V_{HTSC} and intragranular critical current densities j_{cg} after DC treatment have been determined.

The experimental procedure has been described in detail elsewhere.[3,4] Briefly, the samples were superconductors with T_c = 92–94 K, critical current densities 60 A cm^{-2} and cationic compositions close to the '1:2:3' stoichiometry. DC treatments were carried out using current densities up to 30 A cm^{-2}. Before treatment, the samples were divided into 2 mm long sections, henceforth denoted according to their position ('+' and '−' for those near the electrodes and '0' for the middle section). For comparison, untreated reference samples cut from the same initial ceramic bar were also studied.

The δ values were determined by the iodometric titration method,[5] the concentrations of impurities were measured by laser-induced secondary ion mass-spectrometry and the V_{HTSC} and j_{cg} values were obtained from magnetization curves.[6]

The δ values were determined with $\pm$0.03 accuracy. In the reference samples the δ values were constant. After DC treatment variations in δ along the length of the samples were often observed. Since various types of δ distributions were registered, they were collected in three groups, consistent with the $\Delta\delta = \delta(+) - \delta(-)$ value: $\delta(+) > \delta(-)$ ($\Delta\delta > 0.07$), $\delta(+) = \delta(-)$ ($-0.07 \leq \Delta\delta \leq 0.07$) and $\delta(+) < \delta(-)$ ($\Delta\delta < -0.07$). The distributions registered at four different temperatures are given in Table 1. These statistics show that at low temperatures the δ values clearly tend to be higher at '+' than at '−'. It was observed that $\Delta\delta$ is enhanced when the duration of the treatment or the resistivities of the electrical contacts are increased. These facts indicate the operation of a diffusion process, initiated in the regions near the electrode, where heat and/or mass transfer may occur. Iodometric titration, however, is indirect and the changes in δ may be due to a redox process: $Cu^{3+} \rightarrow Cu^{1+}$. Nonetheless, it will be shown below that the phenomenon is likely to be associated with oxygen diffusion.

Table 1 Statistics for the δ distributions registered along the length of samples at various temperatures

T/K	$\delta(+) > \delta(-)$	$\delta(+) = \delta(-)$	$\delta(+) < \delta(-)$	Total
77	12	8	2	22
85–90	2	4	0	6
102	4	3	0	7
295	2	4	1	8
Total	20	19	4	43

In order to eliminate uncertainties associated with non-uniform distributions of impurities in the initial samples, they were each cut into two halves, one of which was then DC treated, while the other served as the reference sample. Both parts were cut into 5 sections, perpendicular to the current direction. The laser beam was scanned over the whole face of each section, providing values of the average concentration at particular positions along the length of the sample. The data

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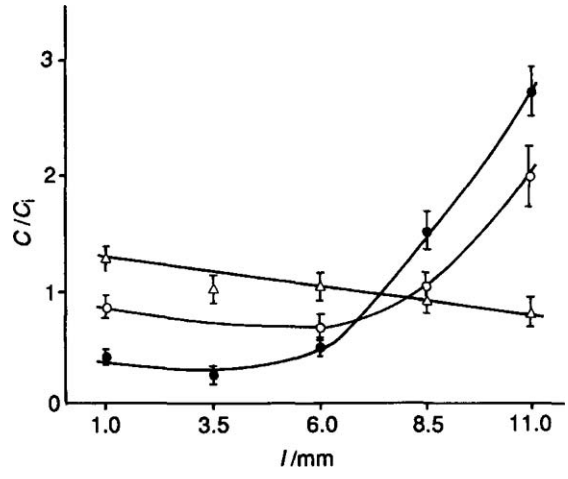

Fig. 1 Distributions of impurity concentrations along the length of the sample after DC treatment at 77 K, relative to those of the reference sample C_i. The distance k is measured from the '+' electrode. (●) Na; (○) K; (△) Cl.

could then be analysed relative to those obtained for the reference sample.

The relative Na, K and Cl concentration distributions measured along the length of the sample at 77 K and room temperature are given in Figs. 1 and 2, respectively. The experiments were repeated twice and the curves were reproduced quite satisfactorily. The distributions unambiguously

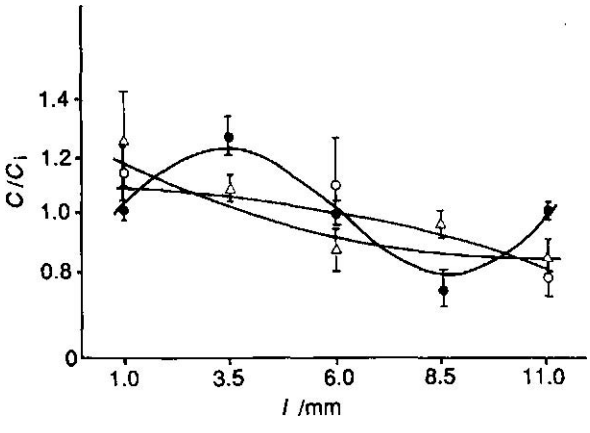

Fig. 2 Distributions of impurity concentrations along the length of the sample after DC treatment at room temperature, relative to those of the reference sample C_i. The distance k is measured from the '+' electrode. (●) Na; (○) K; (△) Cl.

show that DC treatment at 77 K causes impurities to migrate along the sample. The direction of ion migration is consistent with the electrode polarities, which allows one to conclude that the driving force is electrical in origin. It is surprising that this process takes place at low temperatures, when the sample is superconducting and no electric field is expected to exist inside the sample. On the contrary, at room temperature, when an electric field does exist within the sample, the effect is hardly discernible. This observation is qualitatively similar to that described above (Table 1), hence we conclude that the observed changes in δ are due to oxygen migration, driven by the same force as the migration of impurities. Given these assumptions, the exponential factor in the expression for the diffusion driving force must be small in comparison with that which is inversely proportional to temperature. This might be so if the activation energy was close to zero. Some theoretical predictions indicate that such diffusion paths may be present in $YBa_2Cu_3O_{6.5+\delta}$ samples,[7] but the nature and the mechanism of these processes are unclear at present.

Magnetization curves were measured and the magnitudes of j_{cg} and V_{HTSC} at 77 K were determined by this procedure.[6] It was found that after DC treatment at '0' the V_{HTSC} values are on average 8–12% higher, while the j_{cg} values are 10–30% lower than those observed near the electrodes. The differences between '+' and '−' are small. These phenomena may be accounted for by an enhanced occurrence of defects in the sample regions near the electrodes as compared to that in the middle of the sample, resulting from DC treatment. Once again, we conclude that electrical contacts play an important role in these processes.

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References

1 K. Govinda Rajan, P. Parameswaran, J. Janaki and T. S. Radhakrishnan, *J. Phys. D: Appl. Phys.*, 1990, **23**, 694.
2 A. M. Prokhorov, Yu. M. Gufan, A. E. Krapivka, E. N. Lubnin, G. N. Mikhailova, E. G. Rudashevskii, A. S. Seferov, V. N. Sumarokov, V. A. Tarasenkov and A. G. Chistov, *Pis'ma Zh. Eksp. Teor. Fiz.*, 1990, **51**, 132.
3 V. I. Nefedov, A. N. Sokolov, N. K. Belskii, L. I. Ochertyanova, A. T. Kozakov, A. V. Dem'yanchenko and G. I. Ramendik, *Sverkhprovodimost'. Phys., Khim., Tekhnol.*, 1991, **4**, 987.
4 V. I. Nefedov, A. N. Sokolov, N. K. Belskii, L. I. Ochertyanova, A. T. Kozakov, A. V. Dem'yanchenko, G. I. Ramendik, A. V. Filatov and E. A. Volkov, *Mod. Phys. Lett. B*, 1991, **5**, 1019.
5 K. Kishio, J. Shimoyama, T. Hasiegawa, K. Kitazawa and K. Fuelki, *Jpn. J. Appl. Phys.*, 1987, **26**, 1228.
6 E. A. Volkov, A. V. Filatov and V. M. Novotortsev, *Zh. Neorg. Khim.*, 1990, **35**, 2451 (English translation in *Russ. J. Inorg. Chem.*, 1990, **35**, 1393).
7 M. Ronay and P. Norlander, *Physica C*, 1988, **153–155**, 834.