Local cation non-stoichiometry in $Y_1Ba_2Cu_3O_{7-z}$ from citrate combustion and conventional routes

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Abstract. Local deviations of Y:Ba:Cu ratio from the stoichiometric value 16.7:33.3:50.0 in single-phase superconducting samples of $Y_1Ba_2Cu_3O_{7-z}$ have been studied by EDXS in grains and grain boundaries. Two types of single-phase pellets, sintered from solution derived citrate complex and mechanically ground powders, are studied here.

Keywords. High temperature superconductors; local cation composition; EDAXS.

1. Introduction

Atomic per cents for $Y_1Ba_2Cu_3O_7$ can be calculated to be Y:Ba:Cu:O = 07.7:15.4:23.1:53.8. It is well known that the superconducting transition temperature, T_c , is about 90 K for O-content approaching 53.8 at%, and reduces with loss of oxygen. A small decrease of only 2.2 at% in O-content (implying reduction of oxygen mole-fraction to 6.4) makes the compound non-superconducting (Rao 1990). Therefore any variation in the at% of any of the components (cation or anion) even on a microscopic scale may affect the superconducting and other properties. A local non-stoichiometry of cations may affect the physical properties either indirectly (by adjustment of O-content to attain charge balance) or directly. Once detected (De *et al* 1988), this should be studied in a systematic manner. This has been done in the present work.

Our preliminary experiment (De *et al* 1988) of EDXS with an electron beam (diameter $\leq 0.2 \mu$) showed different grains (few microns in size) of the same sintered pellet to have significantly different cation compositions: the best (sample 1) of the 4 ground and fired pellets studied, showed a variation of about 3.5 at% around the stoichiometric value of 7.7 at% for Y, of about 2.3 at% around 15.4 at% for Ba, and of about 2.6 at% around 23.1 at% for Cu. Babcock *et al* (1988) showed that in 123 or $Y_1Ba_2Cu_3O_{(7-z)}$ grains the local at% can deviate from the average by as much as 1.9 for Y, 4.6 for Ba, 8.1 for Cu and 10.2 for O. The rest of the work is, however, devoted to grain boundary regions, where composition variations are less unexpected. Therefore, even in the 123-phase, the local composition variations seem to be large. Hence these have been investigated in this work. Here we check (i) whether cation inhomogeneity exists for samples made from solution-derived powders, specifically the citrate combustion samples obtained by Pankajavalli *et al* (1988), (ii) whether the cation inhomogeneity is different for (a) inter- and intra-grain points, and (b) freshly broken and original surfaces, and (iii) that the earlier observed (De *et al* 1988) inhomogeneity is not an artifact of the EDXS experiment, specifically of the unevenness of the sample surface. Our work concentrates on $Y_1Ba_2Cu_3O_{7-z}$ grains of essentially single-phase pellets, with a few readings on grain boundaries.

2. Experimental outline

Both sample preparations, starting from Y_2O_3 , $BaCO_3$ and CuO in 1:4:6 molar ratio, involved repeated grinding (G), pelletizing (P), prolonged firing or heating, and a slow-cooling (S-CL). Flow-chart for the ground-and-fired samples is as follows (Subba Rao *et al* 1987): G, 24 h at $950^\circ C$ in air, G, P, 24 h at $900^\circ C$ in air, G, P, 24 h at $900^\circ C$ in air, 24 h at $900^\circ C$ in O_2 flow, 24 h at $600^\circ C$ in O_2 flow, and S-CL in 15 to 18 h to room temperature. No attempt was made to improve on the preparation conditions of Pankajavalli *et al* (1988).

EDXS was done in a Philips scanning electron microscope with EDXS 711 B analyser, and X-ray intensities for Y, Ba and Cu lines were converted to at% (De *et al* 1988). The readings and scanning electron micrographs, showing the grains subjected to EDXS, were taken for 2 ground-and-fired samples and 3 citrate-route-samples. Sample I was broken into 2 parts, and EDXS done on freshly broken surfaces. One part was mounted on an araldite mould. Polishing was done with diamond paste and kerosene in steps, starting with diamond particle size of 5μ and ending with 0.5μ particles. Methanol was used for washing at each stage. The other part of sample I was powdered and its a.c. susceptibility measured down to 4 K, confirming superconductivity. EDXS was done on polished form (called sample PI) of sample I and another polished citrate-route-sample, sample IV.

3. Results and discussion

X-ray diffraction of both types of samples showed 123-pattern with clear orthorhombic splitting, and the impurity phase, if any, was $< 5\%$. The ground-and-fired samples showed zero resistance at 90.5 K (De *et al* 1988). Compared to these samples, the susceptibility measured for one of the citrate samples showed its T_c to be lower by about 4 K.

These citrate-combustion samples (figure 1) are seen to have longer grains, typically 100μ long and 10μ wide, compared to the samples studied by De *et al* (1988). Each might be a single crystal. In fact the freshly broken surface in the lower half of figure 2 shows sharp and clear crystalline edges.

As mentioned earlier, the diameter of the probing electron beam is much smaller than even the grain width. As shown in figure 1 for sample I, EDXS was done for several locations in each of the few grains studied. The resulting Y:Ba:Cu data points are plotted in figure 3 as a pseudo-ternary $YO_{1.5}$ -BaO-CuO diagrams for a freshly broken surface. The inset shows observations on an original surface of the pellet.

The three points taken on the grain boundary regions (figure 3) were the farthest from the 1:2:3 point. Such data from boundaries are excluded in the following discussion of at% $p(j)$, $j = Y, Ba$ and Cu and with $\Sigma p(j) = 100\text{ at}\%$. Let us define $s(j)$ as the difference of the maximum and minimum observed $p(j)$. Table 1 is compiled from our observations on 7 samples of 3 types. $p(Y):p(Ba):p(Cu)$ for the stoichiometric case is 16.7:33.3:50.0, as we exclude oxygen in the at% count from now on.

Comparing the cation spreads for UGF and UCR types of samples we see that these citrate-route-samples are more inhomogeneous than GF samples. It is possible that other citrate route samples are of better homogeneity. Still it is evident that the production of the precursor from a solution does not ensure molecular level

Figure 1. SEM of a part of the original surface. Numbers identifying four grains, correspond to the grain numbers in figure 3. ($\times 500$).

Figure 2. SEM showing the edge between an original surface (top portion) and a freshly broken surface ($\times 500$).

Figure 3. Pseudo-ternary plot of Y:Ba:Cu, as determined by EDXS for different locations on different grains seen on freshly broken surfaces of our $Y_1Ba_2Cu_3O_{7-z}$ pellet. Similar readings for the original surface of the pellet are given in the inset by re-drawing the part ABDC of the ternary diagram and using symbols explained within the inset. Most of the known binary and ternary phases are indicated as standard points (cross symbols) and new standard points (half-filled square symbols).

Table 1. Spread, $s(j)$, of local cation at% $p(j)$, where $p(Y) + p(Ba) + p(Cu) = 100$.

Sample Type	Sample no.	No. of EDXS pts.	$s(Y)$	$s(Ba)$	$s(Cu)$
UGF	1	30	6.8	5.2	10.3
	2	10	15.1	2.6	10.8
UCR	I	42	14.4	8.6	20.3
	II	30	18.6	2.3	13.6
	III	30	17.4	7.0	14.6
PCR	PI	96	8.7	6.3	10.4
	IV	20	12.5	3.6	9.2

UGF; unpolished grind-and-fire samples; UCR; unpolished citrate route samples; PCR, polished citrate route samples.

homogeneity. By comparing the heat treatments for the two types of samples, it appears that the higher number of intermediate grindings and the longer time of heat treatment at the optimum high temperature made the ground-and-fired samples somewhat more homogeneous.

On comparing the UCR and PCR samples in the table, we see that polishing removes only a minor part of the cation inhomogeneity. The spread remaining after polishing is significant. This confirms our earlier conclusion that the 123-phase is an area, and not a point on the $\text{YO}_{1.5}\text{--BaO--CuO}$ diagram.

4. Conclusion

Figure 3 shows that the cation composition varies at different points or locations of even the same $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{(7-z)}$ grain. Also, the intra-grain points and inter-grain points have variations of a similar degree. This figure also shows the spread in cation composition to be of similar degree for the freshly broken surface as the original pellet surface.

Since the cation inhomogeneities have been observed in differently proposed samples deep inside and even on polished surfaces, we conclude this type of cation inhomogeneity to be intrinsic to the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{(7-z)}$ compound. This can be explained by local but extensive lattice defects, like the extra Y-layers, being reported by various TEM studies (Ourmazd *et al* 1987).

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