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Parallel, core and valence level photoemission studies of nominal (Bi0.9,Pb0.1)2Sr2Ca2Cu3010+x

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On the substitution of Y_2O_3 with ZrO_2 in the synthesis of $YBa_2Cu_3O_{7-\delta}$

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Abstract. It is shown that the substitution of Y_2O_3 with ZrO_2 in the synthesis of YBaCuO leads to a mixture of $BaZrO_3$, $BaCuO_2$, CuO and $YBa_2Cu_3O_{7-\delta}$. For zirconia percentages less than 50% the mixtures exhibit a conductor–superconductor transition at a temperature higher than 77 K, which is due to the presence of the orthorhombic phase, $YBa_2Cu_3O_{7-\delta}$ with δ less than 0.2. Between 50 and 70% zirconia, the materials are still superconductors at low temperature, but semiconductors above the transition, which then takes place over a broad range of temperatures lower than 77 K. Above 70% zirconia, the ceramics are semiconducting down to 4.2 K, and the YBaCuO present is tetragonal with an oxygen stoichiometry pretty close to 6.

It was found that zirconia improves the densification of the ceramic mixtures, presumably because it increases the wettability of the liquid phase present at the beginning of the sintering process.

1. Introduction

In a previous paper [1], we have shown that the partial replacement of Y_2O_3 with ZrO_2 in the basic ingredients required for the preparation of $YBa_2Cu_3O_{7-\delta}$, via the reactive sintering technique, leads to dense mixtures of ceramics, which are mechanically much stronger and chemically more resistant to atmospheric corrosion than $YBa_2Cu_3O_{7-\delta}$ itself, but are still superconducting at liquid nitrogen temperature for substitution percentages as high as 40%.

Similar resistivity–temperature curves were reported by others [2, 4] but in all cases, including ours, it was not established whether yttrium was really substituted with zirconium in the crystallographic cell of $YBa_2Cu_3O_{7-\delta}$ or merely used to synthesise secondary phases.

Because this question is of relevance for both understanding the mechanism of superconductivity in this class of materials and for deposition of $YBa_2Cu_3O_{7-\delta}$ thin films on zirconia substrates, we have extended the range of substitution percentages explored and carried out systematic micrographies, x-ray images, electron microprobe local analysis and x-ray powder diffraction on various ceramic mixtures over the complete range of substitution percentages of Y_2O_3 with ZrO_2.

2. Experimental procedure

All the specimens were prepared from appropriate mixtures of Y_2O_3, CuO and BaO_2 (not $BaCO_3$ as in our

previous paper) powders, which were first ground in an agate grinder for 16 h then compacted into pellets that were 3 mm thick and 25 mm in diameter by a force of 5×10^4 N applied through a hydraulic press. These pellets were sintered for 72 h at 980 °C under flowing oxygen and subsequently annealed for 48 h at 400 °C in the same run. The specimens so obtained were cut into rods of about 20 mm in length and cross section 1.5×1.5 mm^2. Their electrical resistance was measured in the temperature range 4–300 K by the four-probe technique, using high local pressure mechanical contacts. The tested rods were then diamond polished on a dry felt and examined by optical as well as scanning electron microscopy to observe their porosity and the size and shape of their grains.

To identify the phases present, the distributions of Y, Zr, Ba and Cu were systematically recorded through the x-ray intensities emitted from 100 μm $\times$ 100 μm spots scanned by the beam of an electron microprobe. This first check allows for repartition of the various zones of the observed spots into a few classes of relative abundance.

Chemical analysis of several representative zones of each class of abundance was then attempted by stopping the beam in the centre of them. Although electron microprobe analysis is a sensitive and reliable technique, the results were rather scattered, because most often secondary phases were finely dispersed into each major phase, so that it was only possible to get an indication of the composition of the major phases. Nevertheless, these indications, plus the knowledge of phase equilibrium diagrams and of the proportions of the starting ingredients, allowed us to formulate some

hypotheses on the composition of the present phases. To corroborate these hypotheses, each specimen was ground into a fine powder, of which an x-ray diagram was taken and compared with standards. In addition, some thin foils were prepared via dimpling plus ionic thinning for observations and analysis by transmission electron microscopy. Finally, it was checked that the composition of the various phases present, so deduced, was consistent with the observed volume fractions.

3. Results and discussion

As shown in figure 1, for replacement percentages of Y_2O_3 with ZrO_2 less than 5%, the curve of resistivity against temperature is little affected, with the same critical temperature and almost the same resistivity value at 100 K of $\sim 3 \times 10^{-4}$ Ω cm, a value which is one of the lowest ever published for sintered $YBa_2Cu_3O_7$.

For medium replacement percentages of 10–50% (see figure 2) the ceramics are still superconductors with an onset temperature close to 90 K, but the higher the
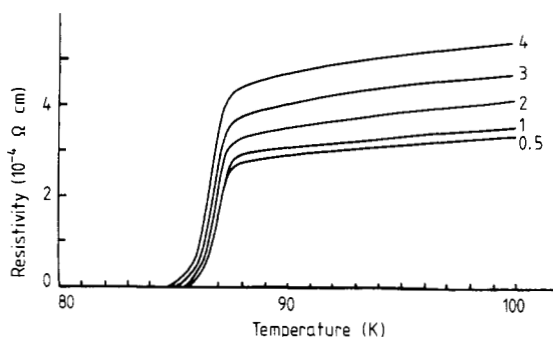

Figure 1. Plots of resistivity against temperature for ceramics synthesised with the replacement of less than 5% of Y_2O_3 with ZrO_2, $J = 1$ A cm^{-2}. The amount of ZrO_2 (%) is given for each curve.
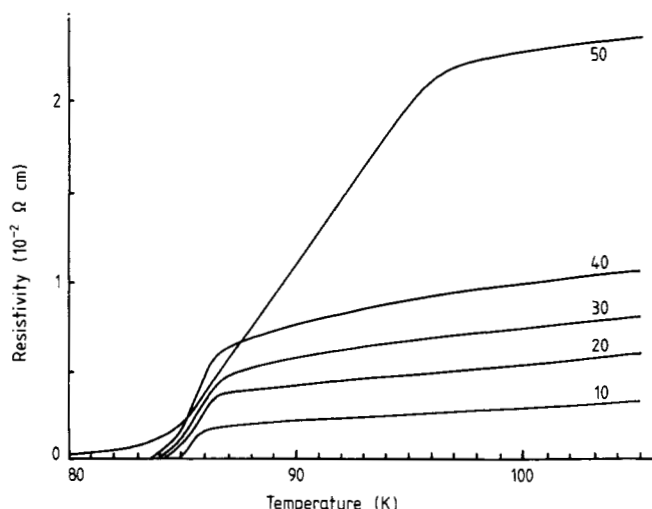

Figure 2. Plots of resistivity against temperature for ceramics synthesised with replacement percentages of Y_2O_3 with ZrO_2 between 10 and 50%. The amount of ZrO_2 (%) is given for each curve. $J = 1$ A cm^{-2}.
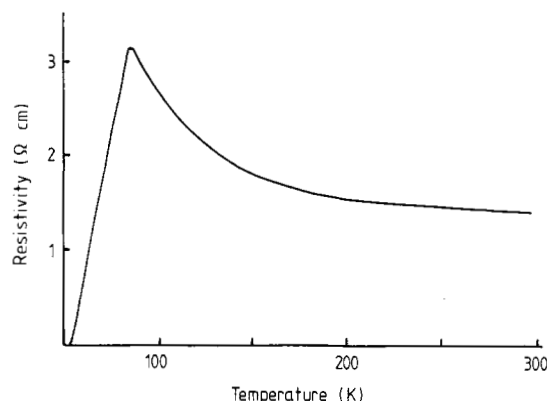

Figure 3. Plot of resistivity against temperature for a ceramic synthesised with the replacement of 70% of Y_2O_3 with ZrO_2. $J = 1$ A cm^{-2}.

replacement percentage the lower the offset temperature and the higher the resistivity above 90 K. This last set of results is in fair agreement with that of our first paper [1] obtained with $BaCO_3$ in place of BaO_2 as a starting ingredient. The only major difference is that superconductivity above 77 K was observed here up to replacements of 50%, whereas previously it was restricted to 40%. It should also be noted that the onset temperature of the 50% ZrO_2 specimen was surprisingly high (nearly 100 K). For 60% ZrO_2 (figure 3) the specimens were no longer conducting but semiconducting at high temperature, nevertheless their resistivity was still observed to drop from about 3 Ω cm at 80 K to zero at 50 K.

With 70% ZrO_2 and also with higher replacement percentages, the samples were observed to be more and more resistive and semiconducting down to 4 K. For example, the resistivity of the specimens substituted at 70 and 90% were, respectively, 30 and 95 Ω cm at 300 K and 190 and 6×10^5 Ω cm at 50 K.

Metallographic examination of all the specimens tested has indicated that the samples were nearly as porous as $YBa_2Cu_3O_{7-\delta}$ itself for replacement percentages lower than 5%, but turned out to be quasi-compact for replacement percentages of 10 and higher (cf figure 4). In agreement with observations by light microscopy, the measured density of the substituted samples was found to be high: 6.32 ± 0.03 for the 30% ZrO_2 specimen, for example, but this figure is less significant than that obtained by the metallographic examination since the specimen is multiphased. The grain size was also much affected by the presence of zirconia. Starting from the elongated slabs of about 10×100 μm, usually observed in plane sections of $YBa_2Cu_3O_7$ sintered at temperatures higher than 950 °C, the grains become smaller and smaller with higher and higher zirconia content, with the exception of some large and very bright ones seen by optical microscopy, which were identified as CuO by electron microprobe analysis (EMA). Because most of the grains were smaller than the lateral resolution of our EMA (~ 1 μm) and of different composition, our local analyses were very scattered; nevertheless we
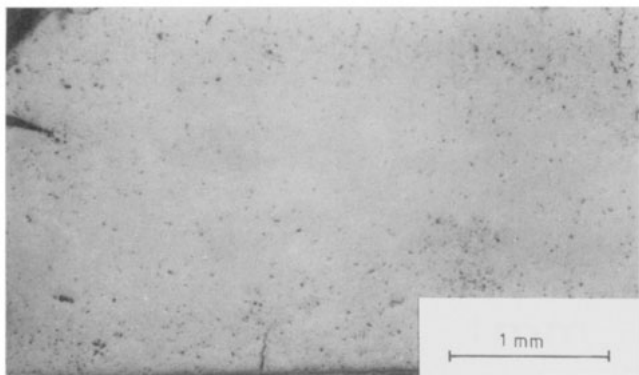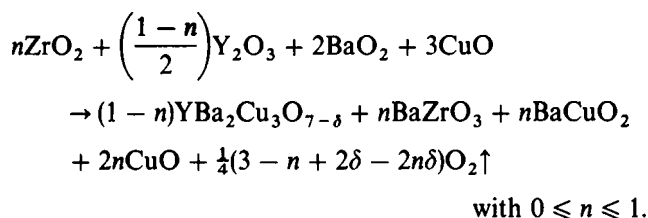
Figure 4. Metallographic examination of a ceramic synthesised with the replacement of 10% of Y$_2$O$_3$ with ZrO$_2$.

occasionally found some results close to those of BaZrO$_3$ or BaCuO$_2$. This allowed us to formulate the hypothesis that whatever the percentage of zirconia, the following chemical reaction held:

$$n\text{ZrO}_2 + \left(\frac{1-n}{2}\right)\text{Y}_2\text{O}_3 + 2\text{BaO}_2 + 3\text{CuO}$$

$$\rightarrow (1-n)\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + n\text{BaZrO}_3 + n\text{BaCuO}_2$$

$$+ 2n\text{CuO} + \tfrac{1}{4}(3 - n + 2\delta - 2n\delta)\text{O}_2\uparrow$$

$$\text{with } 0 \leqslant n \leqslant 1.$$

This hypothesis was fully confirmed by the comparison of x-ray powder diffraction diagrams recorded on each specimen with those of pure YBa$_2$Cu$_3$O$_7$, BaZrO$_3$, BaCuO$_2$ and CuO which were specially prepared for that purpose. The identification of BaZrO$_3$ and CuO was very accurate and, doubtless, that of BaCuO$_2$ a bit less, because of the very high natural background given by this compound. As for YBaCuO, for zirconia percentages $\leqslant 40\%$, the orthorhombic structure corresponding to $0 \leqslant \delta \leqslant 0.2$ [5] was observed. With higher zirconia content the structure became less and less orthorhombic with increasing δ values, and finally turned out to be tetragonal for zirconia percentages $\geqslant 70\%$, with $\delta \simeq 1$ according to [4].

Unfortunately, the variation of the crystallographic cell of YBaCuO with zirconia content could alternatively be attributed to the incorporation of zirconium atoms in the lattice of YBaCuO. Hence to test this challenging hypothesis some thin foils suitable for transmission electron microscopy were prepared, observed and analysed for both the 30 and the 80% zirconia samples. Heavily twinned and elongated grains, typical of the orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$, were easily recognised in the 30% specimen. Microdiffraction, lattice images and local analysis of these grains were also consistent with this assertion and no trace of zirconium was detected. Furthermore, it is worth noting that most of the YBaCuO grains observed were connected, so that percolation of superconducting paths was evident.

In the 80% specimen, no twin was observed, but colonies of a few elongated grains nicely packed along their longest apparent dimension were present in mod-

erate abundance. Here again, microdiffraction, lattice images and local analysis were consistent with YBaCuO, but because of the absence of twins, it is clear that, in agreement with the x-ray diffraction powder diagrams, these grains are of the tetragonal YBaCuO phase and not of the orthorhombic YBaCuO phase. Most of the observed colonies in this foil were surrounded with BaZrO$_3$, BaCuO$_2$ or CuO grains, which led to the idea that the tetragonal phase does not percolate even in the bulk three-dimensional sample. The reason for the tetragonal phase formed during sintering being retained after annealing for 48 h at 400 °C under flowing oxygen is far from easy to understand. In fact, all the tetragonal-phase grains of the sintered pellets which contribute to the x-ray diffraction patterns have a free surface and consequently should be in equilibrium with oxygen despite the presence of neighbouring secondary phases. Nevertheless, these secondary phases, which are more abundant than the YBaCuO, constitute a rigid skeleton which probably prevents the YBaCuO grains embedded in them from shrinking due to extra absorption of oxygen.

It must be concluded that in our samples yttrium was not substituted with zirconium in the crystallographic cell of YBaCuO. More generally no atom was substituted with another in the various phases present; only pure YBaCuO, BaZrO$_3$, BaCuO$_2$ and CuO were observed. Consequently, there is no reason why partial replacement of some Y$_2$O$_3$ with ZrO$_2$ should increase the critical temperature for superconductivity, as claimed by [3]. Nevertheless this replacement is beneficial for the material since it considerably enhances its compactness and mechanical properties. The exact role of zirconia in the densification process is still under investigation in our laboratory. All we can say here is that, whatever the zirconia percentage, the densification occurs mainly between 880 °C and 930 °C during heating and so is practically terminated before the steady-state temperature (980 °C) is reached. This is because, whatever the zirconia percentage, the content of BaO$_2$ and CuO is constant. Hence there is always almost the same amount of liquid present to enhance the sintering process but the higher the zirconia the lower the amount of YBaCuO to be sintered, so the increased densification with increased ZrO$_2$ content may be simply due to the relative increase in the amount of liquid available for sintering. Unfortunately the composition of this liquid, the nature and the amount of secondary phases and the cold pressing are more or less dependent upon the exact zirconia content, which seriously complicates the situation. In particular, it is well known that zirconium, hafnium and titanium increase the wettability of the solders used for brazing oxide ceramics [6]. It is very likely that the addition of zirconia improves the sintering because it increases the wettability of the liquid phase present at the beginning of the process. Hence increased wettability could be responsible for sintering improvement, but this analogy of a metal melt with a solid oxide may not be applicable to an oxide melt.

It is worth mentioning that the fact that we observed the tetragonal phase for the highest zirconia percentages could explain why it is not so easy to get good superconducting thin films of $YBa_2Cu_3O_7$ deposited on zirconia. The interaction of ZrO_2 substrates with YBaCuO is an important topic from the standpoint of the deposition of thin films and there is a quite extensive literature on this point ([7–10] for example). In addition to the secondary phases reported here ($BaZrO_3$, $BaCuO_2$ and CuO), most of the relevant papers claim the presence of Y_2BaCuO_5, the well known green phase, which is easily recognised by optical microscopy and x-ray diffraction. This difference with our results is probably due to the large excess of ZrO_2 present during thin film deposition which increases the amount of $BaZrO_3$ synthesised, leaves less BaO_2 available for the formation of $YBa_2Cu_3O_{7-\delta}$ and consequently favours the formation of some Y_2BaCuO_5 (a barium poorer phase).

4. Conclusion

The partial substitution of Y_2O_3 with ZrO_2 in the synthesis of YBaCuO does not lead to the replacement of yttrium with zirconium in the crystallographic cell of YBaCuO.

The superconductor–conductor transition observed above liquid nitrogen temperature for substitution percentages lower than 50% is due to the usual $YBa_2Cu_3O_{7-\delta}$ orthorhombic phase with a δ value less than 0.2.

Nevertheless, for reasons which are not yet fully understood this replacement favours the densification of the ceramics and gives materials which are mechanically much more resistant than $YBa_2Cu_3O_7$ itself.

For zirconia percentages higher than 70% the YBaCuO present is no longer orthorhombic but tetragonal, which explains why the ceramics are no longer superconducting and sheds some light on the problems faced in the deposition of good superconducting YBaCuO thin films on zirconia.

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