JOURNAL OF MATERIALS SCIENCE 31 (1996) 2987–2996

The effects of Cs addition and different sintering conditions on YBCO–123 superconductors made from precursor or commercial 123 powder

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Bulk $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors were prepared from initial mixtures of a precursor and CsI or commercial 123 Hoechst powder and CsI with the nominal composition $Y_1Ba_2Cu_3Cs_xO_y$ ($x = 0, 0.05, 0.1, 0.2$ and 0.3). Different synthesis regimes were applied in order to determine the influence of normal or reduced oxygen pressure as well as vacuum when isothermal heating at 800 °C is performed during sintering. It was found that heating at 800 °C with reduced oxygen pressure favourably affects the J_c and density of the samples in the case where 123 powder is used as the starting material. When the precursor is used the intensive dissociation of $BaCO_3$ at low pressure leads to higher porosity and deterioration of the superconducting properties. Adding Cs in small concentrations promotes higher J_c and density of specimens made from the precursor, but when commercial 123 powder is used, a negative effect is observed due to the chemical instability of the superconducting phase. Atomic absorption spectrometry reveals that the Cs disappears during sintering and, therefore, could be used in small concentrations as a fluxing additive without any risk of creating Cs-containing impurity phases.

1. Introduction

Since the discovery of the $Y_1Ba_2Cu_3O_{7-\delta}$ (123) superconducting phase many studies have been devoted to the influence of different doping elements on the microstructural characteristics and superconducting properties of the bulk materials. Among the different elements used as dopants the alkali metals (M^+) have been investigated [1–5]. In most of the studies the effect of the dopant on T_c was mainly studied and only in [5] more detailed data concerning the dependence of the type of alkali metal on the powder characteristics and morphology are given. No clear conclusions about the effect of M^+ on J_c have been published.

Recently, it was found that the different M^+ elements affect specifically the superconducting properties and phase composition in Bi-containing oxides [6, 7]. It was established that some of these elements and especially the heaviest ones, Rb and Cs, promote higher T_c as well as being completely evaporated during heating. On the other hand some authors [2, 3] suppose the presence of Cs dopant in the final Y–Ba–Cu–O (YBCO) superconductor after sintering even at higher temperatures. The effect of Cs in materials made only from precursor has also been studied [2, 3, 5]. From a practical point of view, however, it is interesting to investigate the interaction between Cs and commercial 123 Hoechst powder. Such powder is currently used for the production of 123 wires by suspension spinning method [8, 9].

In order to establish which facts and conclusions are valid for the Cs–YBCO system and to satisfy the need for a more complete investigation of this material a detailed study of YBCO superconductors with Cs addition, using different starting materials and applying various sintering conditions, was performed. The results obtained are described and discussed in the present article.

2. Experimental procedure

The bulk superconducting pellets were prepared from the precursor (mixed Y_2O_3, $BaCO_3$ and CuO with purity > 99%) and CsI or commercial superconducting 123-Hoechst powder and CsI with a nominal composition of $Y_1Ba_2Cu_3Cs_xO_y$ ($x = 0, 0.05, 0.1, 0.2$ and 0.3). Preliminary experiments using Cs_2CO_3 were also performed. It was established that the CO_2 produced by the decomposition of Cs_2CO_3 during the heat treatment, drastically destroys the 123 Hoechst phase, thus imposing the choice of CsI. To understand

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better the effect of the Cs additive on the formation and properties of the 123 phase, the materials were synthesized using three or four different synthesis regimes. The regimes, for the case of the precursor, are graphically presented in Fig. 1. For the materials made from 123 powder only regimes I, II and III were applied. They were slightly modified because the superconducting phase existed in the raw material: the temperature of the final isothermal heating was a bit lower, i.e. 950 °C (instead 955 °C), and the time to rise from 900 °C to the maximum temperature was 10 h (instead 18 h, as in the case of the precursor). The choice of sintering regime was made on the basis of the following arguments:

1. The first regime is performed under normal oxygen pressure ($P_{O_2} = 0.1$ MPa), and includes a 6 h isothermal heating at 800 °C to facilitate the full evaporation of Cs from the material. This could be important to avoid the destructive influence on the commercial 123 phase.
2. The second regime is like the first, but without isothermal heating at 800 °C.
3. The third regime is an application of the "improved" synthesis method described in [9] giving the possibility of increasing J_c of the product. This regime includes heating stages in vacuum ($P < 10$ Pa), and with reduced oxygen pressure ($P_{O_2} = 100$ Pa). The isothermal heating at 800 °C for 30 min is also performed with $P_{O_2} = 100$ Pa. A further thermal treatment is performed under normal oxygen pressure.
4. The fourth regime applied to precursor materials is similar to the third, but vacuum was used instead of reduced P_{O_2} in order to facilitate additionally the decomposition of $BaCO_3$.

To check the reproducibility of the results and dependencies obtained, as well as to determine the error bars for the measured J_c values, all syntheses were repeated keeping the technological conditions constant, and every time, three different pieces of each sample were measured independently. The error found was less than 2%.

The synthesized materials were analysed by X-ray diffraction (XRD) analysis, using CuK_α radiation, atomic absorption spectrometry (AAS), scanning electron microscopy (SEM) and wavelength dispersive X-ray (WDX) analysis as well as optical microscopy in polarized light. The electrical resistance R and critical current density J_c were measured by a standard four-probe technique in the range 77–300 K.

3. Results

Fig. 2 presents some typical $R(T)$ dependencies of materials synthesized by different regimes and using either precursor or 123 powder. Generally the $T_{c\,\mathrm{zero}}$ values are in the range 86–90 K. For some samples a broadening of the transition is observed. Similar to the results reported in [5], some samples with Cs addition show slightly higher T_c (1–2 K more) than the "pure" samples synthesized under the same conditions. The T_c values for the samples without Cs addition in the starting materials are shown in Fig. 3. Obviously, the effect of the different synthesis regimes is different for materials made from either precursor or 123 powder. The analysis of all the results will be

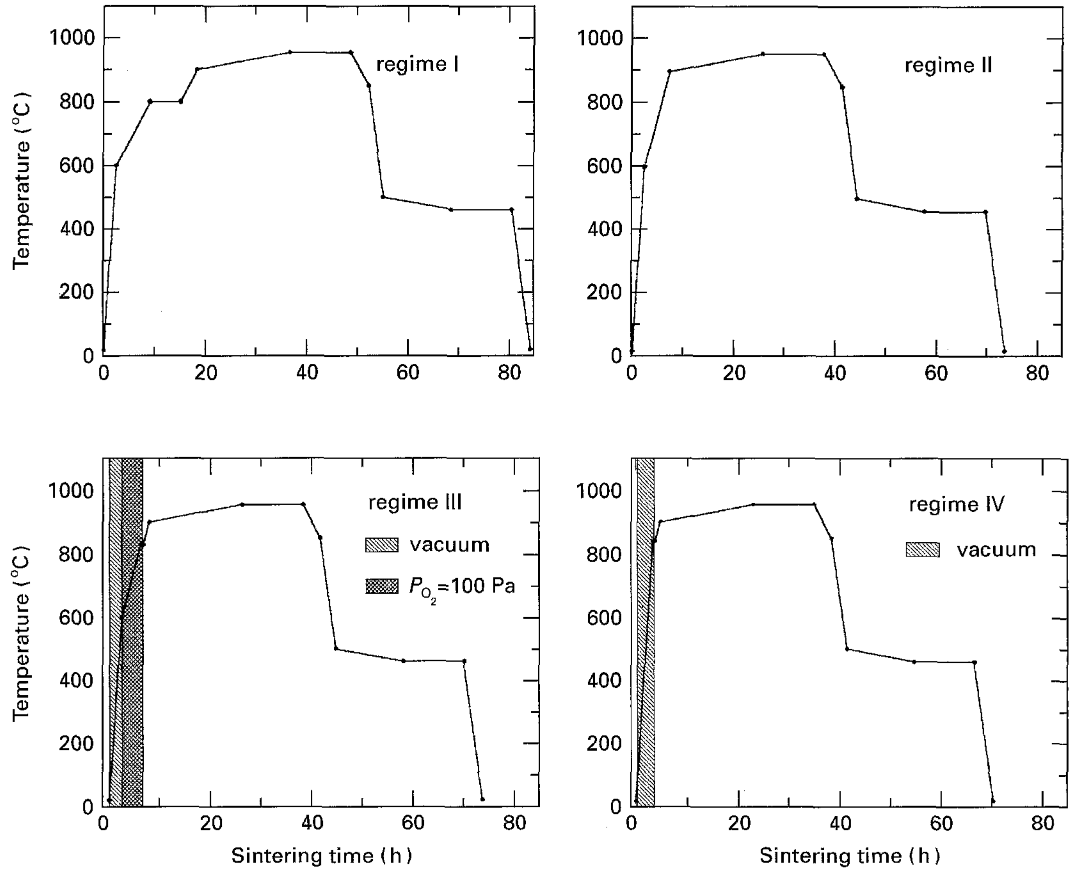

Figure 1 Sintering regimes applied to materials made from precursor.

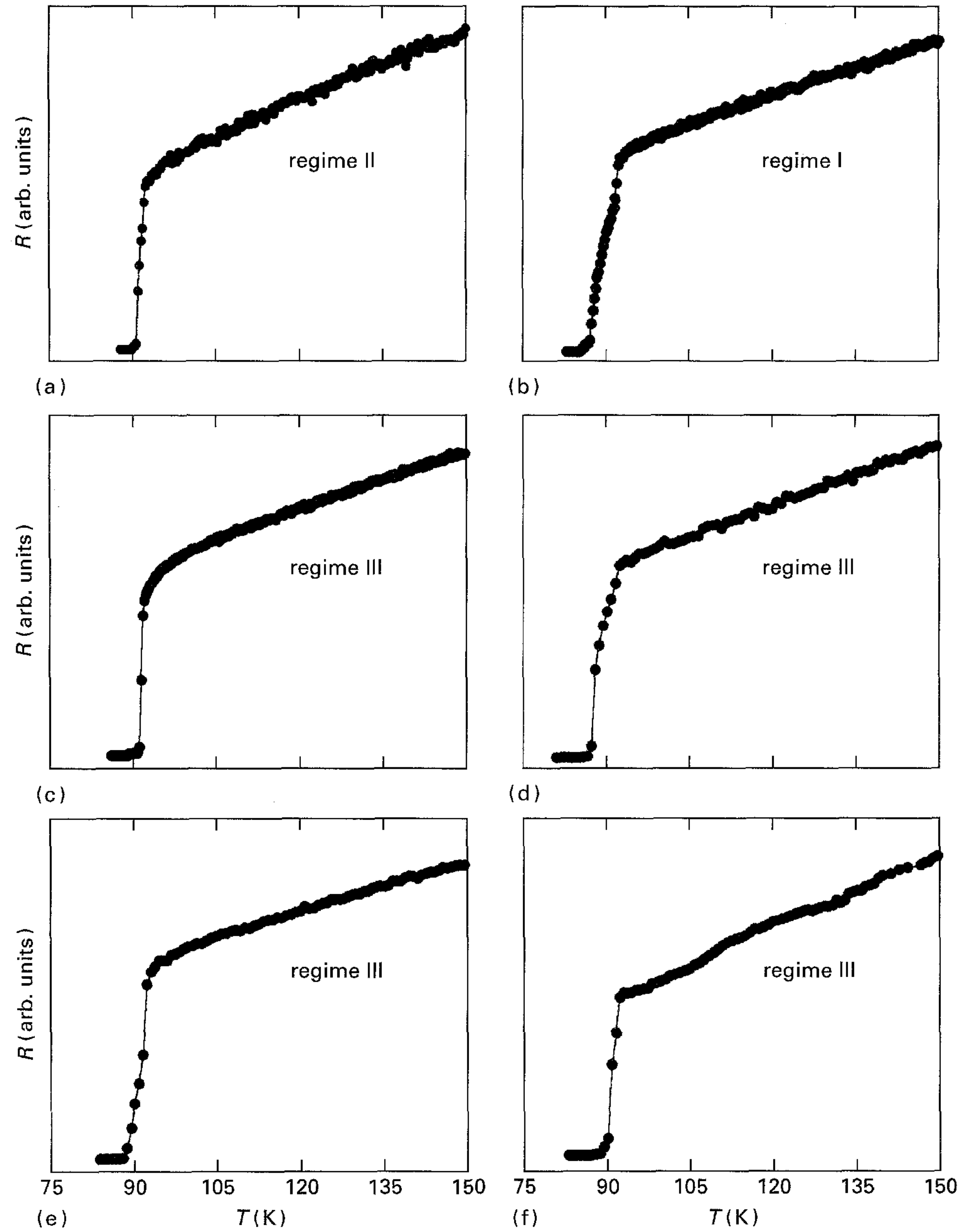

Figure 2 Typical $R(T)$ dependencies. The type of initial powder (precursor (P) or Hoechst (123)) and the content of Cs (X) are as follows: (a) P, 0.0; (b) P, 0.1; (c) 123, 0.0; (d) P, 0.0; (e) P, 0.1; (f) P, 0.3.

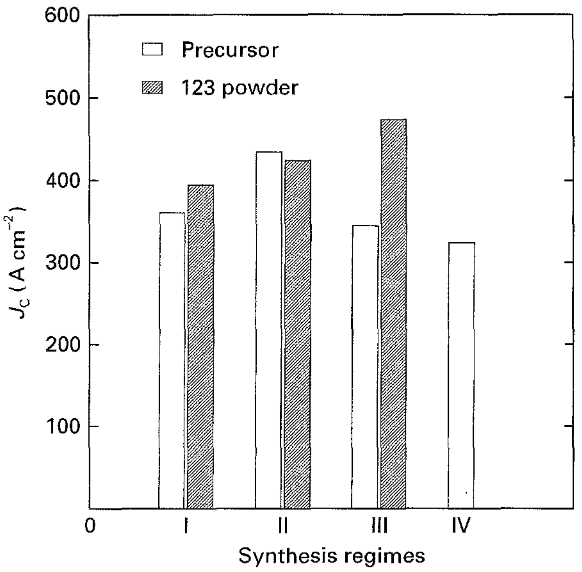

Figure 3 Dependence of J_c at 77 K as a function of the synthesis regimes for samples without Cs addition in the raw material.

presented later. The relationships between the J_c and Cs content in the raw material for different sintering regimes for 123 powder and precursor are shown on Figs 4 and 5, respectively. They generally show either a negative influence of Cs or a positive one for small concentrations of the additive. No positive effect is observed when 123 powder was used.

By AAS it was established that Cs is not present above the detection limit (2.5×10^{-3} wt %) in the samples after sintering, and obviously, there are no Cs containing impurity phases. These important results are similar to the results for Bi-superconductors [6, 7]. Previously, the Cs content had not been analysed and the results obtained had been explained as due to the presence of Cs somewhere in the 123 structure or in impurity phases [2, 3].

The XRD analysis reveals that in all cases the samples are pure 123 phase materials with only an indication of traces of CuO for some materials. Because normally the detection limit of XRD for impurities is estimated around 4–5% it is impossible to detect minor impurities (and to draw conclusions) as well as to explain the difference in the transport properties. For this purpose WDX analysis was applied. Detailed

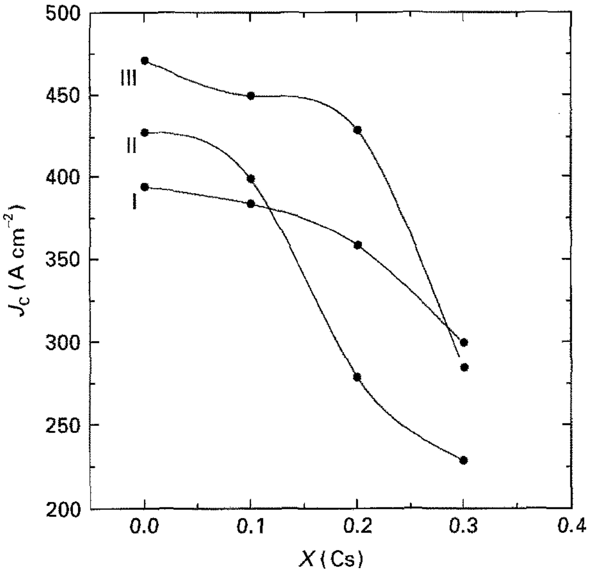

Figure 4 Dependence of J_c at 77 K as a function of the Cs content in the raw material and of the synthesis regimes for samples made from Hoechst 123 powder.

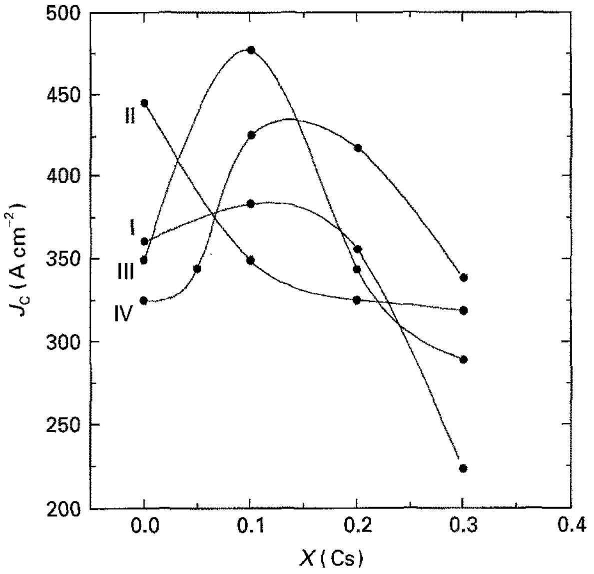

Figure 5 Dependence of J_c at 77 K as a function of the Cs content in the raw material and of the synthesis regimes for samples made from precursor.

TABLE I Impurities detected by WDX analysis in some bulk 123 superconductors prepared from starting materials with initial composition $Y_1Ba_2Cu_3Cs_xO_y$

X(Cs)	Initial powder: Hoechst (123); Precursor (P)	Regime of synthesis	Type and grain sizes of impurities
0.3	123	III	$BaCuO_2$ (2–5 μm); CuO (1–3 μm)
0.1	P	III	–
0.3	P	III	Y_2O_3 (5–10 μm); CuO (1–5 μm)
0	P	II	211 (< 1 μm)
0.1	P	II	CuO (1–30 μm)
0	P	I	–

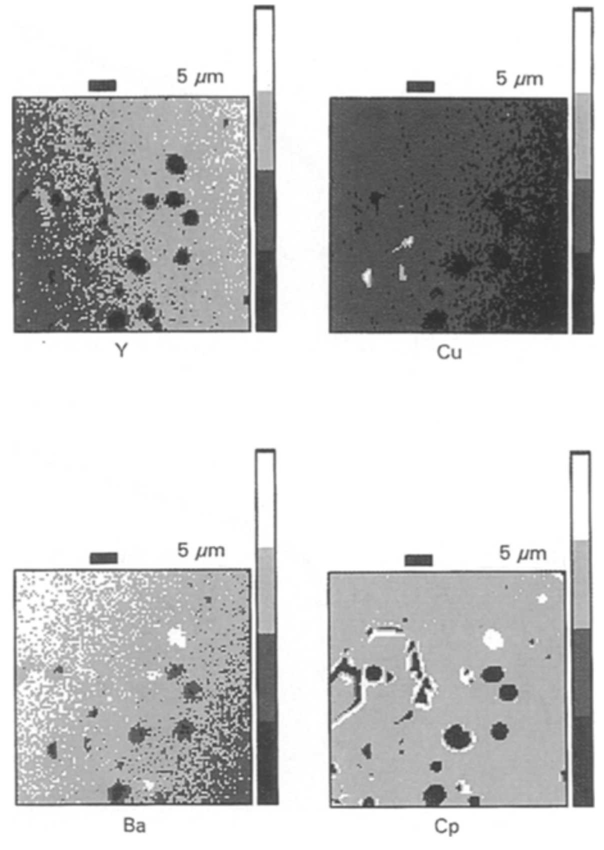

Figure 6 Characteristic X-ray maps for samples made from 123 powder with Cs content $X = 0.3$ under regime III. The concentrations increase from black to white. The compositional (Cp) images of Figs 6, 7 and 8 were obtained by back-scattered electrons.

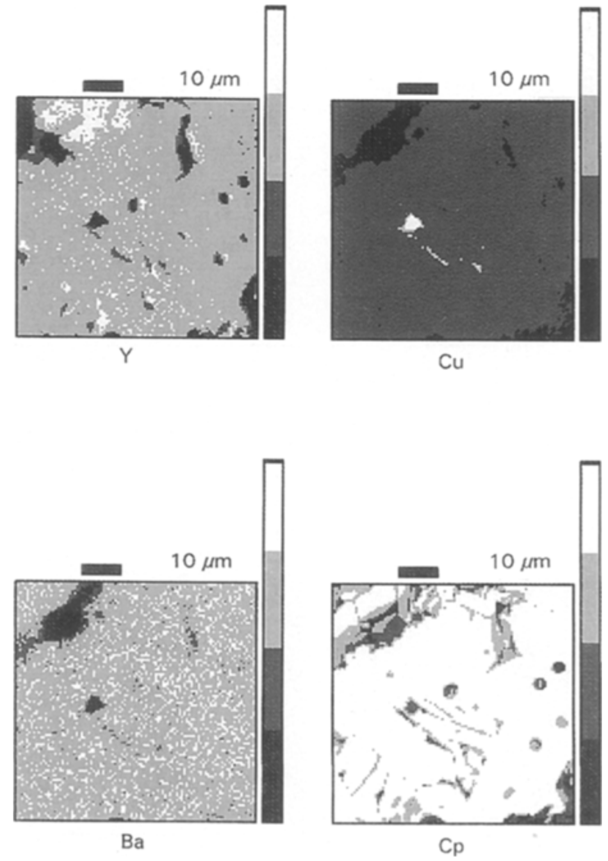

Figure 7 Characteristic X-ray maps for samples made from precursor with Cs content $X = 0.3$ under regime III. The concentrations increase from black to white.

searches were performed in line or in spot mode as well as by X-ray mapping. The kind of impurities detected and their range of grain sizes are presented in Table I. They vary for the different materials. Generally for samples prepared with maximum content of Cs in the initial powders the level of impurities is higher (Figs 6 and 7). For materials with low Cs concentration in the starting powder only CuO grains are observed, but the large ones are probably unreacted grains from the initial CuO powder (Fig. 8).

The morphology and grain sizes of the 123 phase were analysed by SEM and optical microscopy. Fig. 9 shows the typical microstructure of samples made from 123 powder. Characteristic features of the samples are in higher density and grain size in comparison with the superconductors made from precursor under similar conditions (Fig. 10). For these samples changes in the sintering conditions or Cs content in the starting materials lead to significant differences in morphology and grain size (Figs 10–12).

4. Discussion

4.1. Effect on J_c of sintering conditions and type of initial material without Cs addition

The correct selection of starting materials for synthesis of 123 superconductors is very important when samples with good transport properties and specific microstructural characteristics are required. Of

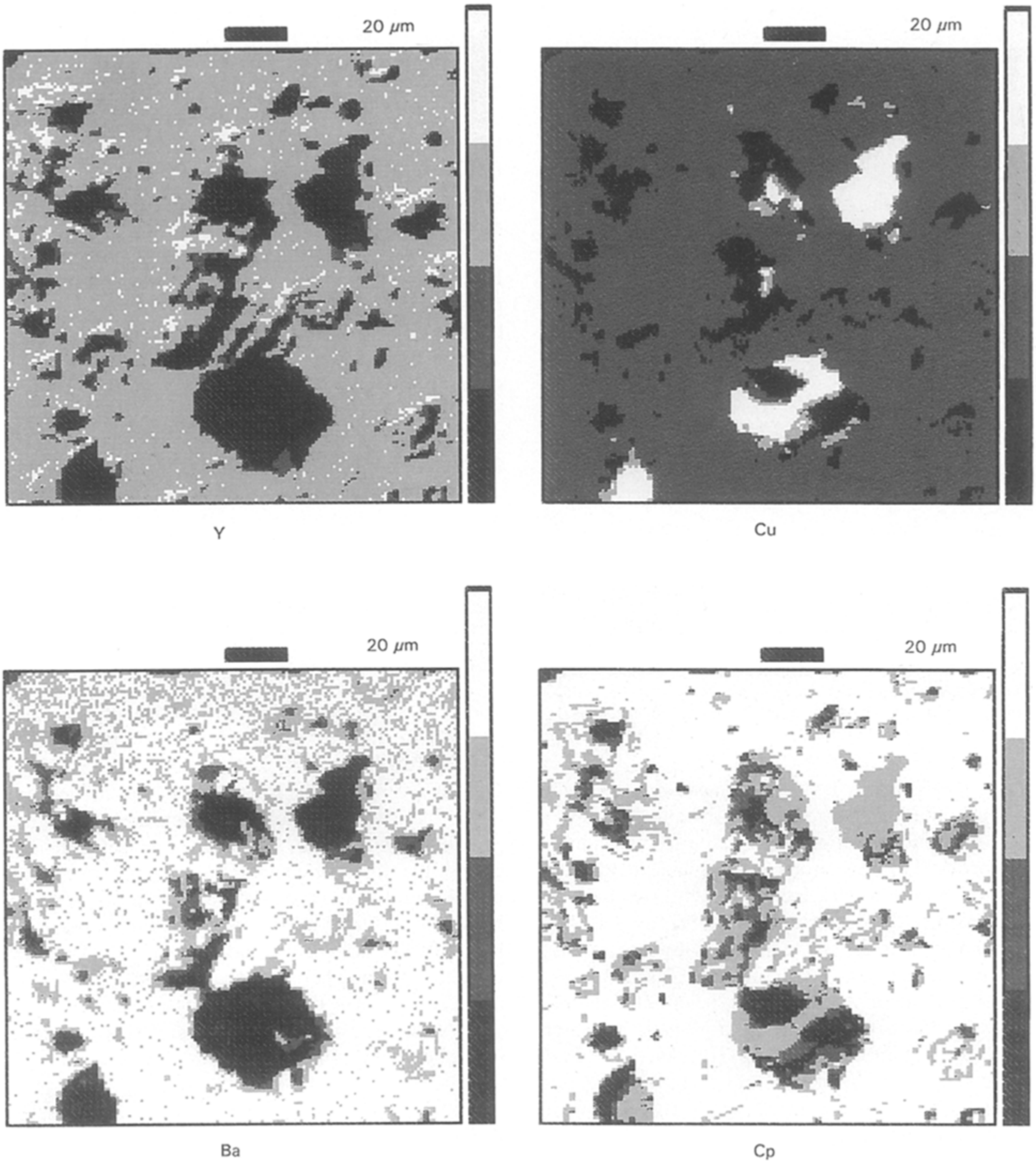

Figure 8 Characteristic X-ray maps for samples made from precursor with Cs content $X = 0.1$ under regime II. The concentrations increase from black to white.

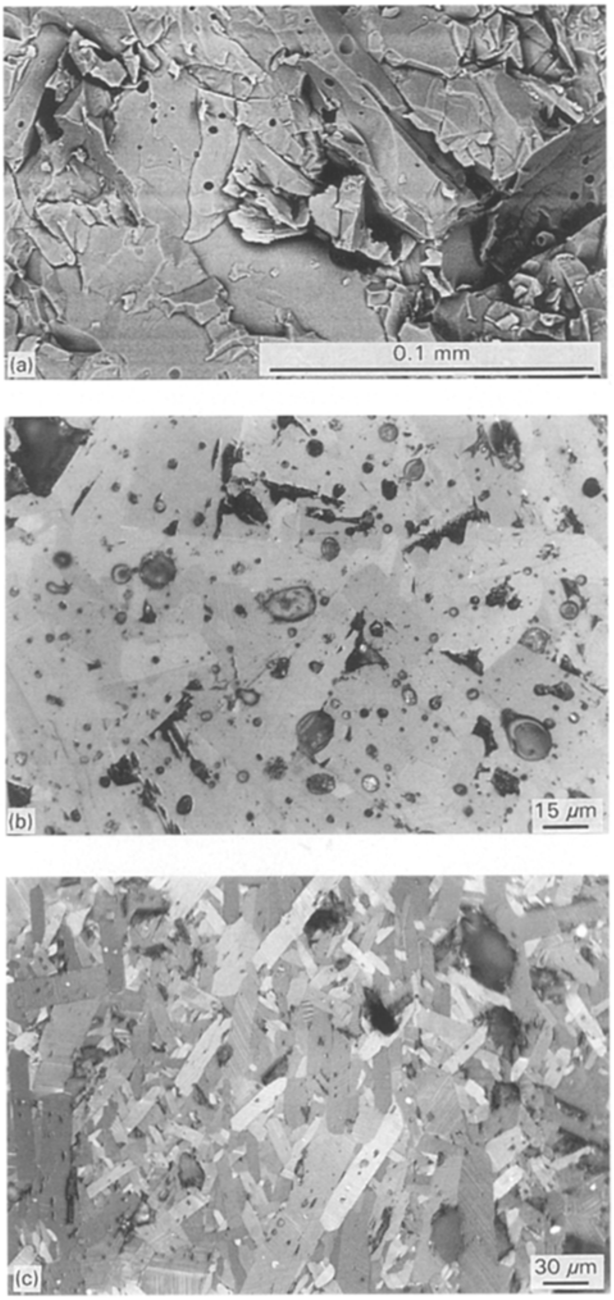

Figure 9 (a) SEM and (b) optical photographs of a sample without Cs addition, and (c) optical image of a sample with Cs content $X = 0.3$. The samples were made from 123 powder under regime III.

course, these properties also depend on the right choice of sintering conditions. For instance, the properties of superconducting wires made from commercial Hoechst 123 powder are strongly affected by the sintering conditions [9]. In the present investigation, a similar sintering regime (regime III) was applied, but additionally this sintering regime was investigated using precursor as the initial material. Fig. 3 clearly demonstrates the influence of the type of initial material on J_c. When Hoechst powder is used, the best results are obtained for regime III which includes heating stages under vacuum and under low oxygen pressure. This result is completely in agreement with the conclusions from [9].

The influence of the sintering regime on J_c for 123 samples made from precursor is quite different. The highest J_c is achieved by heating under normal oxygen pressure (regime II). When heating under reduced pressure or under vacuum (regimes III and IV) the J_c values obtained are the lowest (Fig. 3).

The negative effect of reduced oxygen pressure or vacuum on J_c, in the case for the precursor, can be explained by analysing the SEM photographs (Fig. 10a, Fig. 11a and Fig. 12a). When reduced pressure is applied (Fig. 10a) the intensive dissociation of $BaCO_3$ leads to much higher porosity in comparison with that for normal pressure (Fig. 11a and Fig. 12a) which will depress J_c. This negative effect is logically still more pronounced for the case of vacuum (regime IV). Another significant difference for the samples treated under regime III is evident from both SEM and optical micrographs of Fig. 10a and b. The grains with generally rectangular shape have sizes mainly in the range of 4 μm × 6 μm–7 μm × 24 μm. The size of the grains for samples heated under normal oxygen pressure is bigger (range from 11 μm × 13 μm to 13 μm × 30 μm in Fig. 11b or 5 μm × 7 μm to 11 μm × 27 μm in Fig. 12b). Such conclusions have also been made in [10]. This indicates a change in the kinetics when the pressure is changed and is in agreement with the conclusions obtained in [11] proving different reaction pathways when oxidizing or inert atmospheres are applied. It is also worth mentioning that heat treatment in oxygen flow may lead to $Ba_2Cu_3O_5$ instead of $BaCuO_2$ as an intermediate phase which affects favourably the further growth of the 123 phase according to [12].

Finally, the presence of small Y_2BaCuO_5 (2 1 1) grains in the precursor samples without Cs addition heated under normal oxygen flow has to be emphasized (Table I). This indicates the possibility of the existence of much smaller grains which cannot be detected by WDX. They could act as pinning centres which would explain the high J_c value (near to 450 A cm^{-2}) in this case. It seems that the application of a one-step sintering process (without intermediate grinding) can also lead to good superconducting properties.

4.2. Effect of Cs addition in the raw materials in dependence on the sintering conditions

One of the frequent mistakes when the influence of a given additive or dopant in a system is studied is that general conclusions for the positive or negative influence of the doping element are drawn without taking into account that only one specific kind of synthesis has been performed. The results in this paper show how different this effect could be in combination with variable parameters of synthesis. Moreover, the relationships between Cs concentration and J_c also depend on the type of initial materials. This separates the further discussion in two sections.

4.2.1. 123 Hoechst powder used as initial material

The dependencies plotted in Fig. 4 clearly show that the introduction of Cs in commercial superconducting

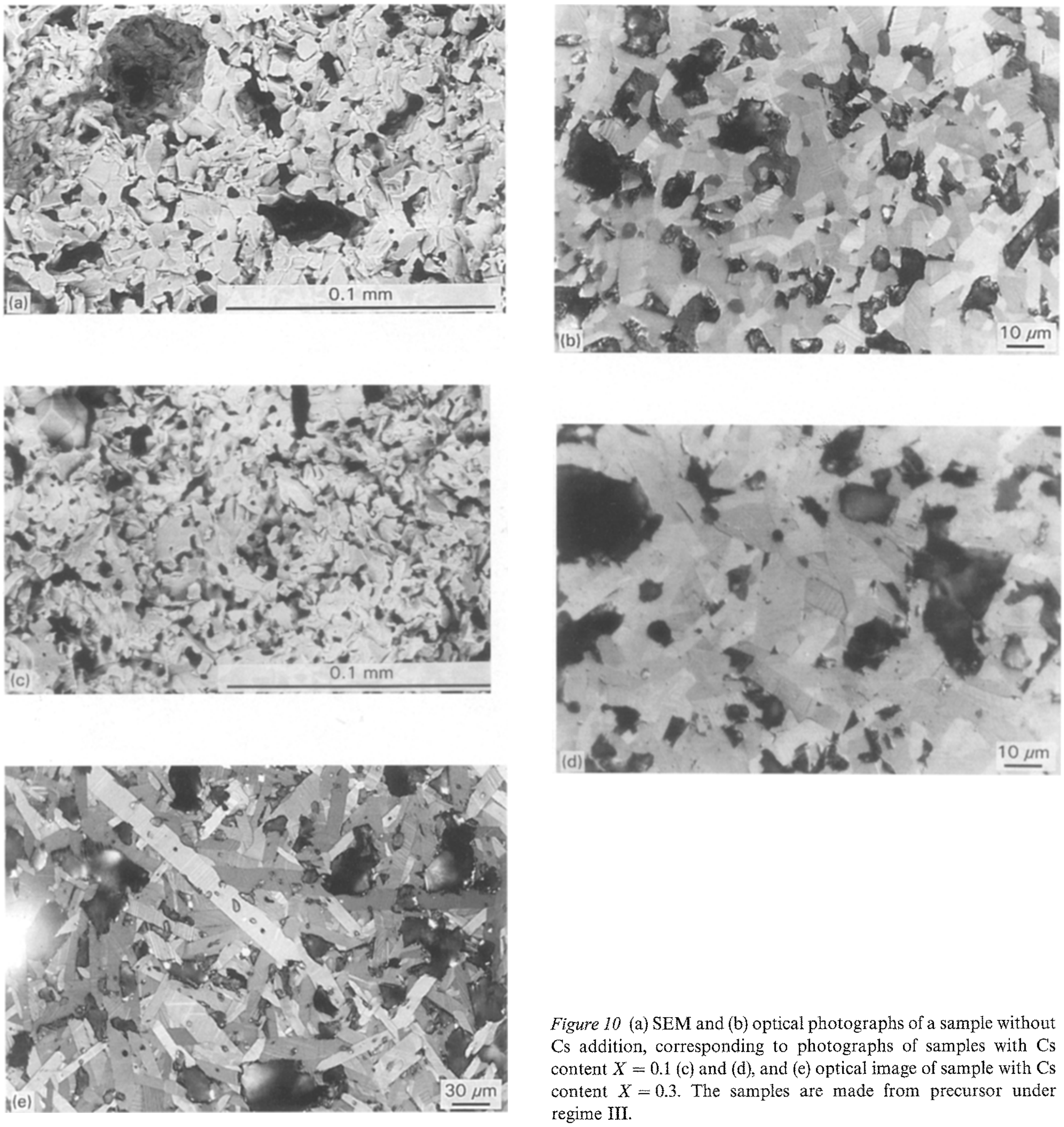

Figure 10 (a) SEM and (b) optical photographs of a sample without Cs addition, corresponding to photographs of samples with Cs content $X = 0.1$ (c) and (d), and (e) optical image of sample with Cs content $X = 0.3$. The samples are made from precursor under regime III.

123 leads to decreasing values of J_c at 77 K. Although the XRD results do not indicate decomposition of 123 and Cs becomes volatile at relatively low temperatures (below 900 °C), evidence for some decomposition of the 123 phase exists, and this reasonably explains the negative effect. The WDX maps on Fig. 6 reveal that both $BaCuO_2$ and CuO impurities are present in the case of high Cs content in the raw material. This proves that the decomposition of 123 is due to the fluxing action of the Cs additive. This conclusion is also supported from the analysis of Fig. 9b and c which show an increase in grain size from the range 5 μm × 8 μm to 14 μm × 50 μm for the sample without Cs addition (Fig. 9b) to 8 μm × 14 μm to 20 μm × 70 μm for the sample with Cs content, $X = 0.3$ (Fig. 9c). The large grain sizes for these samples are also a consequence of heating with reduced oxygen pressure [9].

When regime I is applied, the negative effect of Cs is less pronounced (Fig. 4) due to the additional isothermal heating at 800 °C for 6 h which promotes full Cs evaporation. When, however, direct heating to 950 °C is performed (regime II) a strong negative influence is observed. If heating under reduced pressure is applied (regime III), this dependence is not so pronounced, because low pressure also promotes fast Cs evaporation.

4.2.2. Precursor used as initial material

In this case the dependence of J_c on the Cs content in the raw materials for different sintering conditions varies greatly (Fig. 5) and differs from those for samples made from 123 powder. This is expected, as here the 123 phase is not present from the beginning and

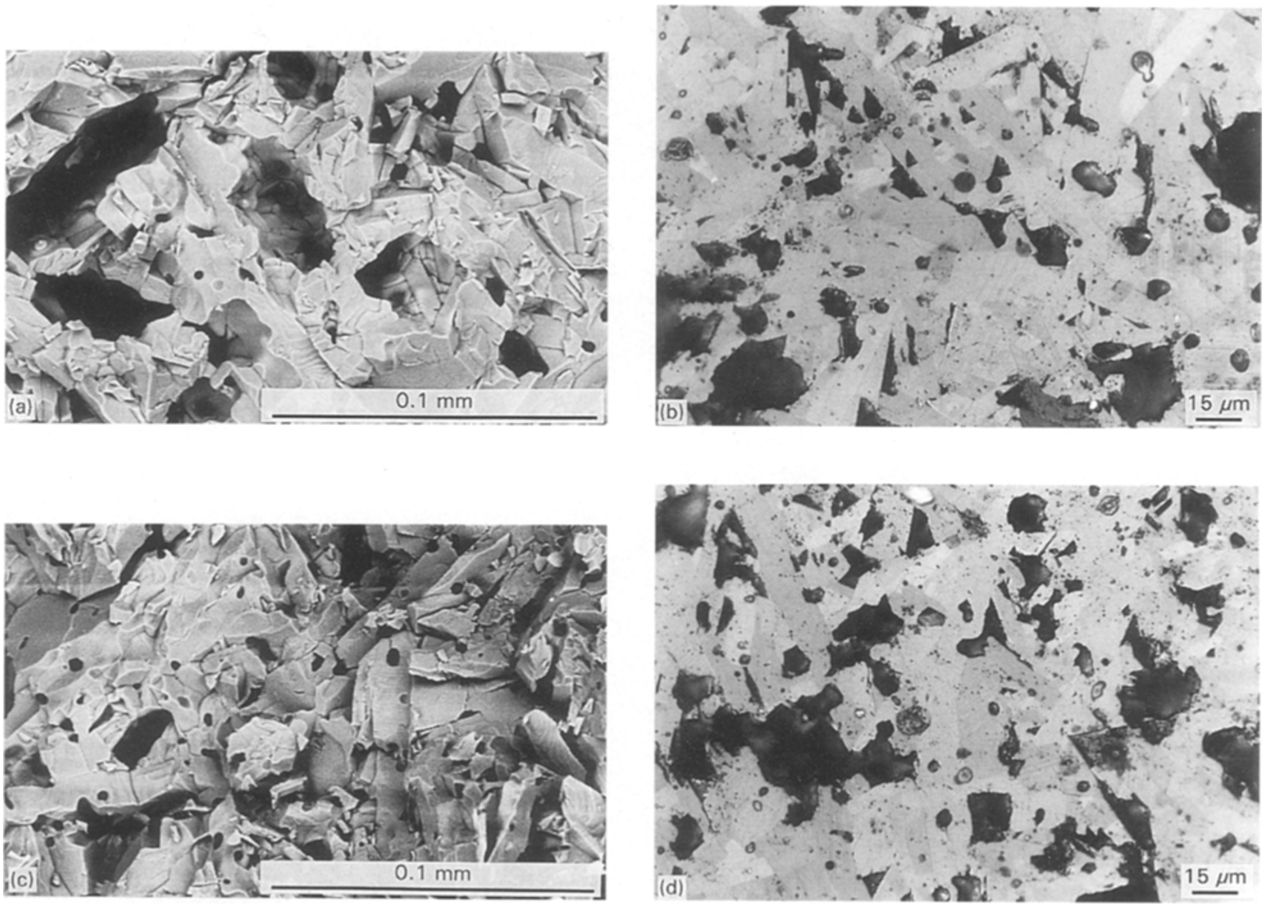

Figure 11 (a) SEM and (b) optical photographs of sample without Cs addition, and corresponding photos of sample with Cs content $X = 0.1$ (c) and (d). The samples are made from precursor under regime I.

there are many more possibilities of affecting the reaction processes and the kinetics of its formation. Comparing the $R(T)$ transitions (Fig. 2) we have to conclude that T_c is not very indicative of the J_c value. Samples with similar T_c and different J_c values are observed (for instance the samples prepared under regime II, Fig. 2a, and regime III, Fig. 2f).

For regimes I, III and IV a clear maximum for the J_c values is observed for $X = 0.1$. For regime II the effect is negative. To explain these facts it is worth remembering that J_c is influenced by a number of factors, e.g.:

- the density
- the presence of pinning centres
- the presence of impurities not acting as pinning centres
- the orientation relation between the grains (texturing)
- the presence of mechanical defects (for instance cracks introduced from temperature gradients etc.)

The positive effect of Cs addition with content $X = 0.1$ for regimes III and IV is well expressed (Fig. 5). In the case of regime III, the sample without Cs additive exhibits a porous microstructure and smaller grains (Fig. 10a and b), as discussed in Section 4.1. When Cs is added a more dense structure (Fig. 10c) and larger grains are observed (Fig. 10d). Increasing the Cs content from $X = 0.1$ to 0.3 leads to a strong increase in grain size from 4 μm × 8 μm–11 μm × 22 μm (Fig. 10d) to 6 μm × 17 μm–22 μm × 100 μm (Fig. 10e). This in combination with the absence of any impurities (Table I) for $X = 0.1$ can explain the high J_c (near to 500 A cm^{-2}). Increasing X further to 0.3, the grain sizes and density continue to increase, but now impurities consisting of unreacted Y_2O_3 and CuO are present (Table I, Fig. 7) and J_c has lower values (below 300 A cm^{-2}). The presence of unreacted initial oxides means that the reaction process is inhibited in the case of Cs content $X = 0.3$. Of course, as was mentioned in Section 4.1, an additional effect on the kinetics results from heating under reduced pressure, giving as a result samples with smaller grains, irrespective of whether Cs was added or not (Fig. 10c and d) in comparison with heating under normal pressure and analogous Cs content (Fig. 11c and d, Fig. 12c and d). Such facts and arguments are also valid for regime IV with the difference that the faster Cs evaporation due to the vacuum suppresses the Cs effect on J_c.

When regime I is applied, the J_c values and microstructures of samples with $X = 0$ and 0.1 are similar and no impurities were detected by WDX analysis. As was mentioned in Section 4.1, the isothermal heating at 800 °C will facilitate the evaporation of Cs and will diminish its influence. In the case of regime II the effect of Cs is negative, similar to the case for samples made

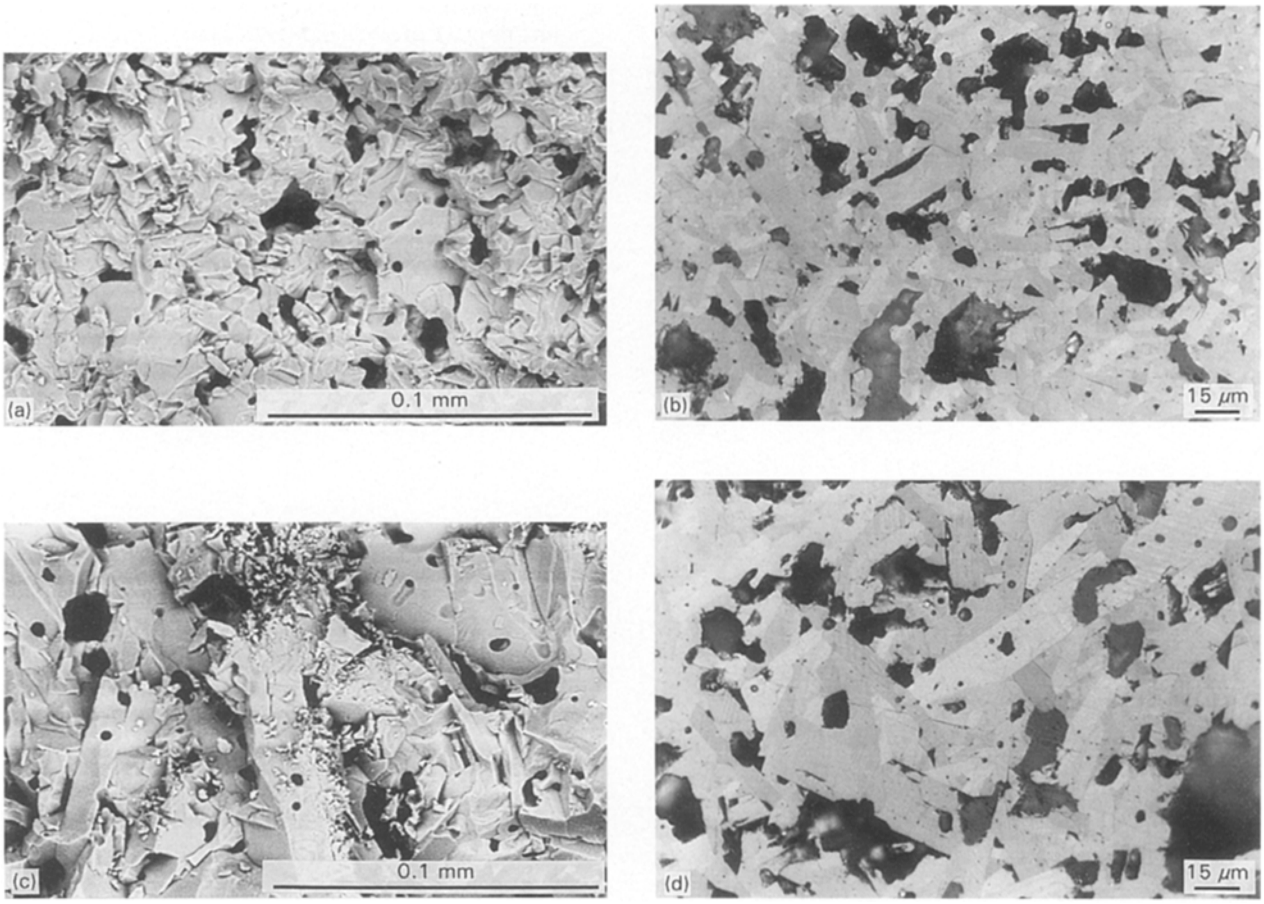

Figure 12 (a) SEM and (b) optical photographs of sample without Cs addition, and corresponding photos of sample with Cs content $X = 0.1$ (c) and (d). The samples are made from precursor under regime II.

from 123 powder. It is evident that direct heating to the sintering temperature is not an optimum condition if Cs is added. The impurities of CuO (Table I, Fig. 8), lead to an inhomogeneous microstructure (Fig. 12c), and negatively affects J_c (values about 350 A cm^{-2}). As for all other cases the Cs promotes the growth of 123 grains. The range of grain sizes shifts from 5 μm × 7 μm–11 μm × 27 μm (Fig. 12b) to 6 μm × 8 μm–15 μm × 60 μm.

5. Conclusions

Bulk $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors were successfully prepared from initial mixtures of precursor and CsI or commercial 123 Hoechst powder and CsI with nominal composition $Y_1Ba_2Cu_3Cs_xO_y$ ($x = 0$, $0.05, 0.1, 0.2$ and 0.3). Different synthesis regimes including heating under normal or reduced oxygen pressure as well as under vacuum were applied. It was found that the effect of Cs on J_c depends both on the type of starting material and on the sintering conditions. Where 123 powder is used Cs always affects J_c negatively. This is due to some decomposition of the 123 phase in the presence of Cs during heating. In the case of precursor, the Cs additive with content $X = 0.1$ in combination with heating under reduced pressure or vacuum improves J_c. The best J_c values for both superconductors made from 123 or precursor with Cs additive are near to 500 A cm^{-2}. In all cases the Cs act as a flux additive stimulating grain growth, and finally is completely evaporated after thermal treatment. It could be concluded that the combination of small additions of Cs to precursor material with heating under reduced pressure are possibly equivalent to the commerical 123 powder. Comparing the effect of different synthesis regimes on J_c for samples without Cs additive, it was found that heating under reduced oxygen pressure promotes higher J_c values if 123 powder is used. When precursor is used, heating under normal oxygen flux promotes higher density and J_c values.

Acknowledgements

This work has been carried out under the framework of the Incentive Programme High Temperature Superconductors, supported from the Belgian Government's "Federal Offices for Scientific, Technical and Cultural Affairs". The authors also thank Mrs M. Mertens for the XRD measurements and Mr R. Kemps for the SEM observations.

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Received 15 February
and accepted 8 September 1995