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Pre-sintering densification phenomenon of $YBa_2Cu_3O_{7-y}$ in the presence of non-equilibrium Ba–Cu–O compounds

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The dynamic sintering behaviour of $YBa_2Cu_3O_{7-y}$ containing Ba–Cu–O and other non-equilibrium impurity phases was investigated through dilatometry. It revealed the occurrence of subsidiary shrinkage just prior to the solid-state sintering. Densification tests also showed a rapid increase in the apparent density in the temperature range between 920 and 940 °C. X-ray diffraction analysis and optical microscope observations verified the correlation with the Ba–Cu–O phases. The phenomenon was attributed to the effect of rearrangement densification exerted by the transient liquid from Ba–Cu–O and to the reaction sintering densification when Ba–Cu–O reacts with other phases during heating.

1. Introduction

The $YBa_2Cu_3O_{7-y}$ (denoted 1–2–3) superconducting ceramics are usually produced by the powder method. This process is characterized by a high temperature and long reaction time to homogenize the composition and to assist the densification. There are drawbacks to using the process since incomplete reaction, excessive heating or prolonged soaking may all result in the formation of unwanted phases and inadequate microstructures. Distortion or even cracking frequently occurs if the sintering parameters are not well programmed especially in the presence of liquid phases, which strongly influence the shrinkage behaviour and cause abnormal grain growth.

Ba–Cu–O compounds are commonly seen as retained impurity phases in solid-state reacted 1–2–3. They can also be found in chemical-solution prepared materials despite the elaboration on homogeneity. The retention of Ba–Cu–O can be traced back to the off-stoichiometry of Cu [1–5], incompleteness of reaction, and local fluctuation in composition as well as in the processing conditions. Since the compounds could form various liquid phases at high temperatures, detailed investigations were done for the better understanding of their effect on densification.

2. Experimental procedure

Powders with nominal 1–2–3 composition were prepared by solid-state reaction using 99% purity Y_2O_3 (Merck), $BaCO_3$, CuO (both from Riedel-de Haen) as starting materials. After mixing and grinding in a micronizer with ethanol as medium, the slurry was dried in air. Calcination was done at 900 °C for 16 h (powder A) and at 950 °C for 8 h (powder B). Both conditions were extensively used for the preparation of the 1–2–3 material. After calcination, the products were reground in a high-purity alumina mortar.

Specimens for the densification test were die-pressed into 8 mm diameter discs using 0.45 g powder charge and under a pressure of 98 MPa. The test bars for the dilatation test (powder A) were die-pressed and cold isostatically pressed under a pressure of 196 MPa. For the densification test, the discs were heated in a tube furnace at a heating rate of 5 °C min^{-1} to temperatures ranging from 880 to 970 °C. Upon reaching the specific temperature, the discs were taken out without soaking and quenched in air. The as-quenched apparent density of those discs free from distortion or cracking was measured to follow the progress of densification. For the dilation test, the specimens were heated at the same heating rate as in the densification tests to 910, 920 or 960 °C and held at the temperature for 4 h.

The dilation test was performed in a Netzsch 402E electronic dilatometer equipped with 414/1 data acquisition system. The results were analysed to give the relationship between shrinkage rate and heating time. The morphology of the starting 1–2–3 powders and the as-quenched microstructures after the densification test were examined under the scanning electronic microscope (SEM) and the optical microscope (OM). Phase identification by X-ray diffraction (XRD) was carried out on a Philips PW 1700 powder diffractometer using a Cu target.

3. Results and discussion

3.1. Powder characterization

Fig. 1 shows the morphology and relative size of mortar-ground powders after calcination under different conditions. It is apparent that the powder calcined at 900 °C was finer and less agglomerated, whereas the 950 °C calcination had resulted in coarse platelet particles with a lot of dense aggregates. Both powders A and B contained Ba–Cu–O which was the only impurity phase that could be differentiated in the XRD spectrum. Its composition was identified as $BaCuO_2$ by comparing with JCPDS Powder Diffraction File 38-1402, but the possibility of Ba–Cu–O as $Ba_2Cu_3O_5$ [6, 7] could not be excluded. Other impurity phases were also considered to exist since the starting composition was in stoichiometric ratio. OM observations further indicated that the particles were bonded together by the Ba–Cu–O to form clusters.

3.2. Densification phenomena

The as-pressed density of powder B (4.07 $g\,cm^{-3}$) showed a higher value than that of powder A (3.91 $g\,cm^{-3}$). The difference seemed to be related to the characteristic double size distribution and to the existence of large, dense agglomerates in powder B. For powder A, the finer particle size was thought to be responsible for the lower packing efficiency.

After the densification test, almost all the quenched discs preserved bulk integrity and showed no discernible distortion. A plot of the as-quenched apparent density against temperature clearly revealed a transition step as shown in Fig. 2. At temperatures below 900 °C, the as-quenched apparent density seemed to be constant as specimens were heated. Starting from 910 °C, the as-quenched apparent density of both materials A and B rose rapidly but with different speeds. After reaching 940 °C, the densification slowed down and the curves became flattened again around

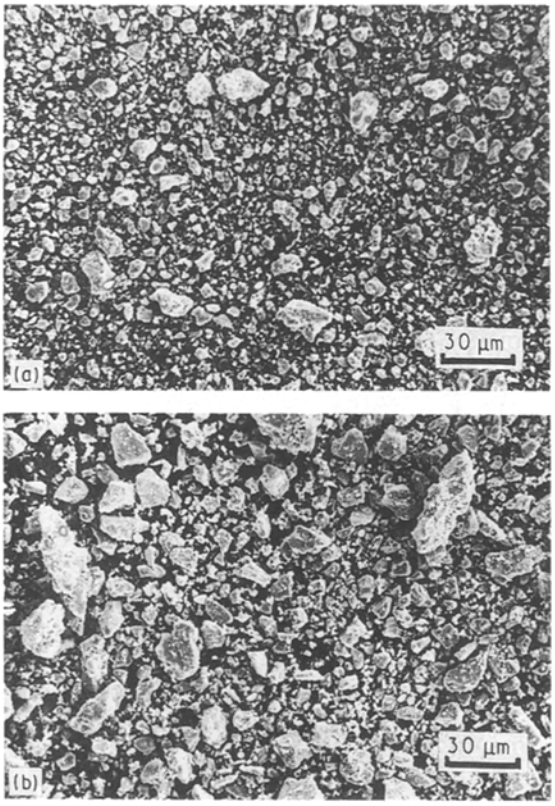

Figure 1 SEM pictures of 1–2–3 powders, (a) powder A and (b) powder B, after different calcination conditions showing that powder A is finer and less agglomerated than powder B. The faceted and plate-like morphology of powder B came from the effect of grinding on the high-temperature reacted material.

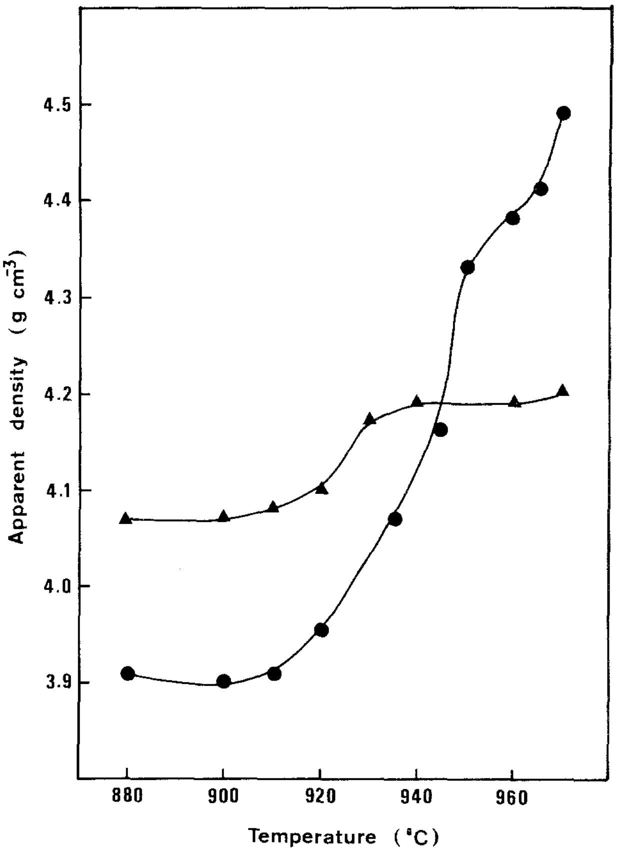

Figure 2 The as-quenched apparent density associated with the quenching temperature in densification tests, revealing a transition step in the temperature range between 920 and 940 °C. Calcination conditions (●) 900 °C, 16 h and (▲) 950 °C, 8 h.

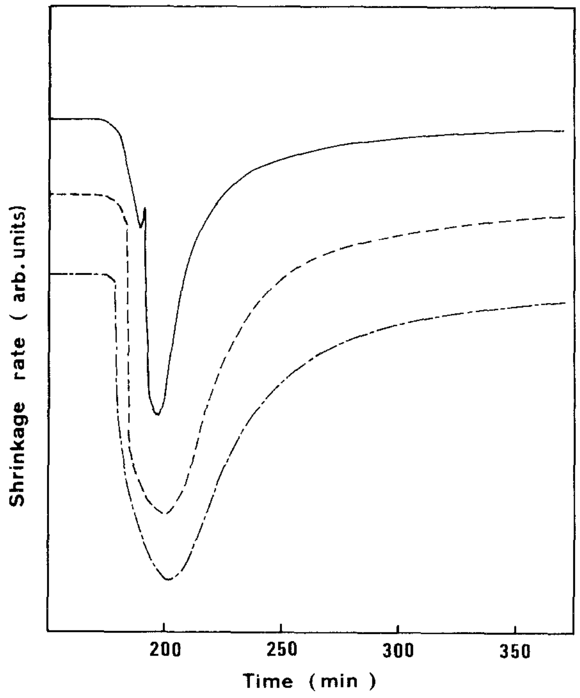

Figure 3 Dilatometric recordings for $YBa_2Cu_3O_{7-y}$ sintered under different conditions, displaying the subsidiary densification around 920 °C: (—·—) 910 °C, (– – –) 920 °C, (——) 960 °C. The time given corresponds directly to the temperature before soaking, since the heating rate was constant.

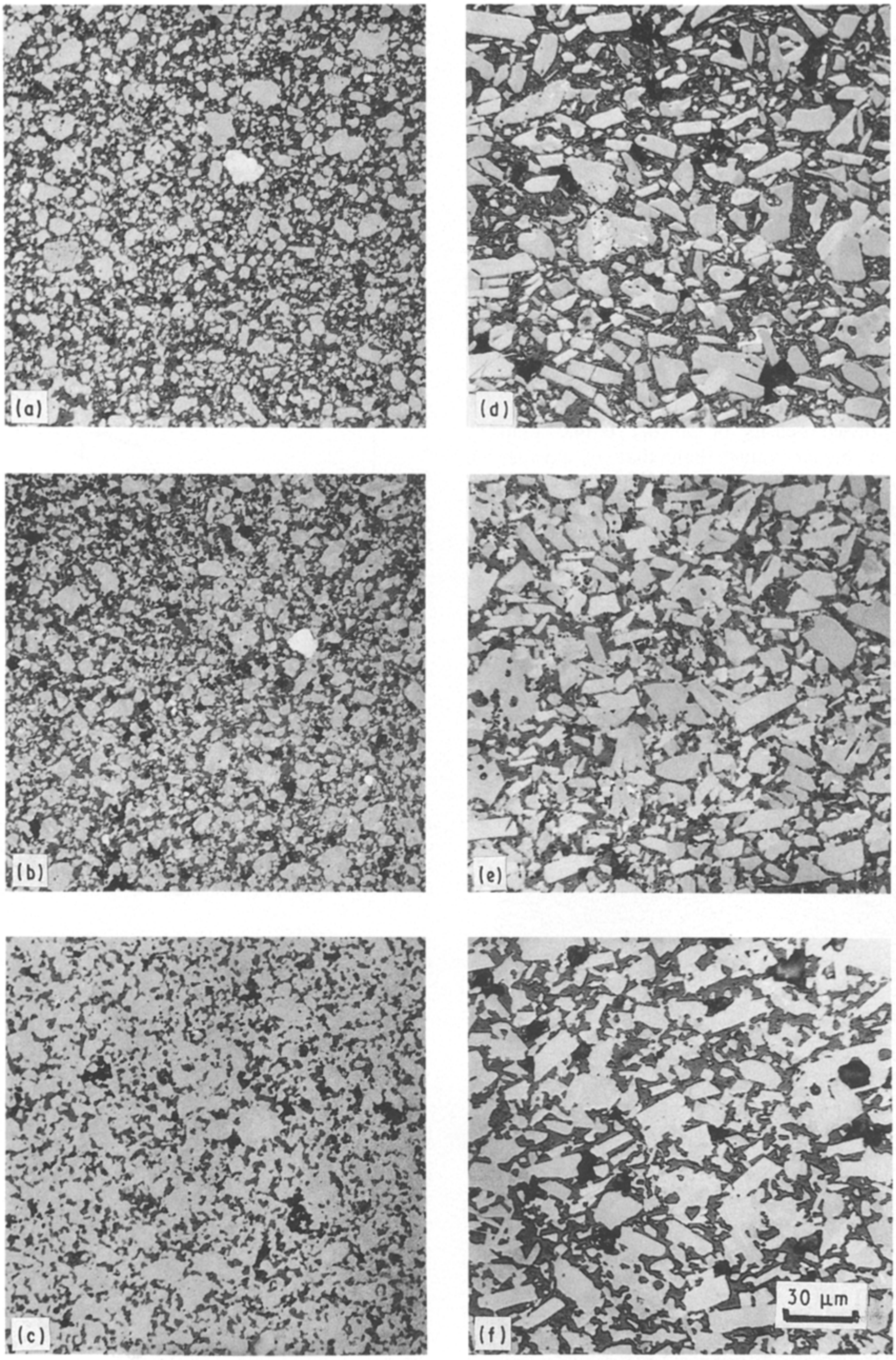

Figure 4 OM photographs of microstructure for discs quenched from different temperatures in the densification test. (a–c) Material A quenched at (a) 900, (b) 930 and (c) 960 °C; (d–f) Material B quenched at (d) 900, (e) 930 and (f) 960 °C.

950 °C before approaching another climb. The timespan associated with the transition step extended only for a few minutes. It was found that the temperature range for the transition overlapped with the reported melting range of Ba–Cu–O compounds [8]. It is also to be noted that the transition step was wider and the resulted densification was higher for material A. The climb at 970 °C might be associated with the incipient melting of the bulk material.

3.3. Dilatometric studies

The sintering behaviour as disclosed by the dilation test in Fig. 3 clearly indicated the appearance of

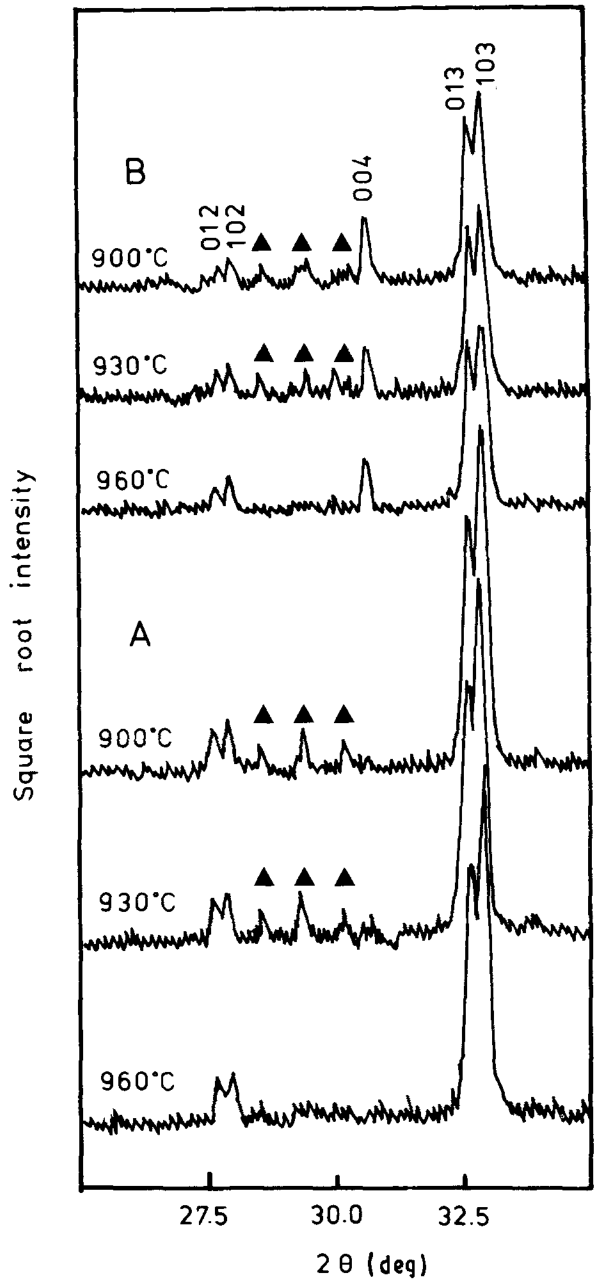

Figure 5 XRD patterns for material B (upper) and material A (lower) during densification tests. The peaks (▲) between (0 0 4) and (0 1 2, 1 0 2) are associated with the Ba–Cu–O compound. Other impurity phases may also be present in the same region but could not be identified due to the low peak intentisy.

subsidiary shrinkage just prior to the major densification maximum. The phenomenon implied the existence of an additional densification mechanism other than the solid-state one which was well recognized as the dominant mechanism for sinter densification in 1–2–3. For specimens sintered at 910 °C, this subsidiary densification was barely discernible. At 920 °C, it was visible but not very well developed. At 960 °C, it resulted in preliminary shrinkage and was partially mixed with the main one, indicating overlapping of different densification processes. During the isothermal sintering stage, it was noted that under 960 °C the densification rapidly saturated within a relatively short period of time. In the other two sintering conditions, the shrinkage rate decreased with soaking time but never went to zero.

The preliminary densification can be best explained by correlating it with the density transition step around 920 to 940 °C in Fig. 2. Since the temperature ranges for the transition both coincided with the reported melting range of Ba–Cu–O, it is understood that both the rearrangement of particles by the liquid phase and the dissolution of fine particles into it could have resulted in the behaviour. Moreover, since the subsidiary shrinkage lasted only for a few minutes indicating immediate disappearance of the liquid by reacting with other materials, reaction sintering was also thought to have partly contributed to this presintering densification.

3.4. Microstructures and phase identification

Figs 4 and 5 depict the microstructure and XRD spectra, respectively, associated with the densification test. The "unsintered" microstructure at 900 °C revealed the difference in morphology, size and distribution of the starting materials. For material B which was calcined at higher temperatures, the structure showed somewhat aligned packing of platelet-shape crystals. This preferred orientation of grains was also responsible for the enhanced intensity of (0 0 1) peaks in the XRD spectrum. At 930 °C, around which the rapid transition in density had occurred, there seemed indications of an increasing number of fine particles. Although it became more closely packed and the particles were lightly joined, the structure as a whole was still lacking in connectivity at this stage. At 950 °C, consolidation or sintering became evident for both materials A and B but the microstructures differed appreciably. For material A which was calcined at a lower temperature not only was the density higher but the microstructure was also more uniformly developed. For material B, small particles seemed to be disappearing with large open pores left. XRD analysis verified that most of the Ba–Cu–O was consumed by transforming to 1–2–3 during the rapid densification period, as can be seen from the disappearance of the three characteristic peaks in between the (0 0 4) and (0 1 2, 1 0 2) peaks of 1–2–3. Since the microstructure development (or densification) took only several minutes, chemical reactions between Ba–Cu–O and other constituents in the system were considered to have taken place, thus giving further evidence of the reaction sintering process.

The release of additional fine particles and the denser packing are indications of the liquid-phase-assisted rearrangement process. This can be visualized by considering the disintegration of aggregated particles by the liquid. Dissolution of fine particles may have taken place at the same time, which also contributed to the denser packing.

For the "sintered" structures no appreciable Ba–Cu–O could be detected, indicating the effectiveness of the transformation reaction. Abnormal grain growth was generally not observed during the preliminary densification as usually expected when sintering in the presence of a liquid phase.

4. Conclusions

1. Non-equlibrium phases were invariably found in 1–2–3 materials synthesized by the solid-state method under different heating conditions. These impurity phases (especially the Ba–Cu–O compounds), while in limited content, appreciably influenced the sintering behaviour of the high-T_c oxide material.

2. When powders containing non-equilibrium impurity phases were reground, press-formed and sintered, liquid phases originated from the remanent Ba–Cu–O at temperatures around 920 °C either by melting or by reacting with other phases. The presence of liquid caused rearrangement of particles and was partly responsible for the pre-sintering densification.

3. The highly reactive liquid quickly diminished through interaction with other constituents in the system and transformed to 1–2–3, thus further contributing to the pre-sintering densification by reaction sintering.

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