

Kinetics of the sintering of superconducting ceramics $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}$

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Abstract

The densification kinetics of ceramics $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}$ (YBC, YBSC: doped with strontium) was studied at constant heating rate with a dilatometer. The different sintering regimes were clearly detected and analysed tentatively according to the available densification models. The data for the initial and intermediate stages fitted reasonably well with the Johnson and Coble models, and the average activation energies for grain boundary and volume diffusion, were roughly estimated. For YBC compositions, a satisfactory fit with a liquid-phase sintering model was obtained at temperatures higher than about 960°C.

INTRODUCTION

The present paper is part of a broader research program on the kinetics of sintering and grain growth in the superconducting ceramics $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ (LSC) and $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}$ (YBC, YBSC). Some of these results were presented at the Argentinian Physical Society Meeting in Tucumán, October 1991, and in ref. 1.

Here we consider the linear contraction and densification rate data obtained for ceramics YBC and YBSC at constant heating rate. The various densification equations employed for the interpretation of the results are listed in the Appendix and correspond to well-known models [2–8] for solid state (SS) and liquid phase (LP) sinterings.

EXPERIMENTAL

The nominal compositions were, in wt. %: YBC: 17.15 Y_2O_3 , 46.59BaO, 36.26CuO (1 : 2 : 3); and YBSC: 17.42 Y_2O_3 , 42.57BaO, 3.20SrO, 36.81CuO;

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Dedicated to Professor Joseph H. Flynn honour of his 70th birthday.

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and corresponded to $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}$ with $x = 0.0$ for YBC and $x = 0.2$ for YBSC. The powders were made through the solid-state reaction at 800°C of mixtures of Y_2O_3 (Sigma), BaO_2 (Mallinckrodt), CuO (Merck) and strontium hydroxide made in the laboratory. After repeated calcinations and grindings in an agate mortar, the powders (+4% PEG, MW 1000) were pressed at 90 MPa for 30 s and subjected to heating in air up to 850°C for 2 h; this yielded porous materials with negligible densification (less than about 2%), but strong enough for cutting pieces approximately $2 \times 4 \times 6 \text{ mm}^3$ in size, which were measured in the dilatometer (Netzsch 402) in the thickness (l) direction. The dilatometer head was made of alumina and no correction, due to the expansion of Al_2O_3 , was made to the $\Delta l (l_0 - l(T))$ data. The selected heating rate was $10^\circ\text{C min}^{-1}$ and the surrounding atmosphere was static air.

The $\Delta l/l_0$ versus T values were digitized and differentiated numerically to produce the corresponding $d(\Delta l/l_0)/dT$ versus T ($^\circ\text{C}$) data.

RESULTS, DENSIFICATION MECHANISMS AND DISCUSSION

Figure 1 shows the $\Delta l/l_0$ and $d(\Delta l/l_0)/dT$ versus T curves for the YBC and YBSC compositions.

For YBC, the linear contraction starts at about 925°C , and at 940°C there is an apparent change in mechanism, probably indicating the intermediate stage of sintering with a maximum densification rate in the range $950\text{--}960^\circ\text{C}$. The rate decreases slightly up to 970°C , at which point it increases and approximately levels off, probably indicating another change in densification mechanism.

According to the data in ref. 9 for the pseudo-binary-cut $\text{YCuO}_{2.5}\text{--BaCuO}_2$, for compositions to the right of 1:2:3 (i.e. richer in Ba and Cu

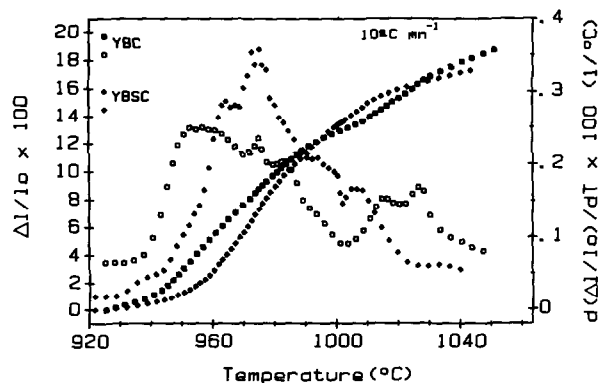


Fig. 1. $\Delta l/l_0$ and $d(\Delta l/l_0)/dT$ vs. T ($^\circ\text{C}$) curves for YBC and YBSC, presintered at 850°C for 2 h; heating rate, $10^\circ\text{C min}^{-1}$; surrounding atmosphere, static air.

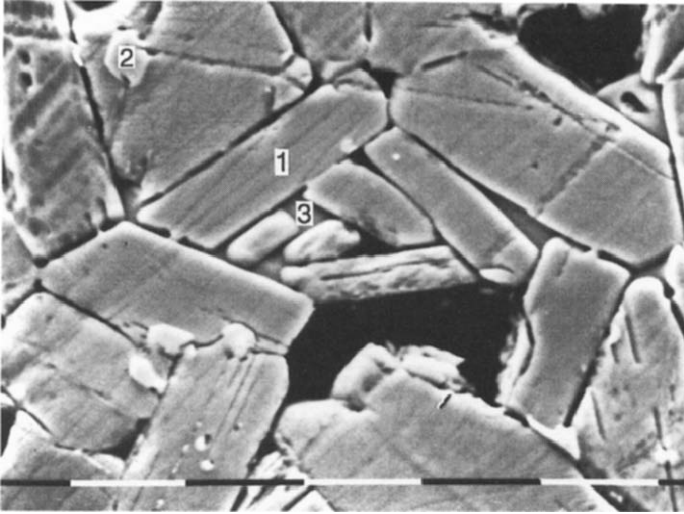


Fig. 2. Scanning electron micrograph for YBC sintered at 930°C for 21 h. (1) = 1:2:3 phase; (2) = 2:1:1 phase; and (3) = 0:1:1 phase. The white bar corresponds to 10 μm .

than 1:2:3), liquid phases should form at about 1000°C. For compositions to the left of phase 1:2:3, the formation of liquid phase should be detected at temperatures higher than about 950°C. The increase in densification rates detected at about 970 and 1005°C for YBC probably corresponds to the formation of liquid phases for the present compositions [9,13,16–18].

Summarizing, it may be suggested that from about 920 to 940°C the YBC system undergoes the first stage, e.g. the Johnson model in ref. 2, in the solid state sintering (SS); from 940 to approximately 970°C it may sinter following Coble's model [5], valid for densification concurrent with grain growth in SS; and for higher temperatures, the YBC may sinter through both SS and liquid phase sintering (LP) mechanisms.

Figure 2 shows a scanning electron micrograph of YBC sintered at 930°C for 21 h in O_2 ; and phases 1:2:3, 2:1:1 and 0:1:1 were detected. XRD analysis demonstrated that our YBC (850°C, 2 h) contained small but detectable amounts of 2:1:1, whereas the YBSC (similarly preheated) was made of "pure" 1:2:3 phase. Therefore, at this preliminary stage, it is difficult to ascertain whether the present $\Delta l/l_0$ data for YBC correspond to one or several compounds.

For the YBSC composition, there is a longer (920–955°C) initial stage, a higher rate second stage (from about 955 to 980°C) and a kind of single-mechanism third stage, roughly up to about 1015°C, at which point there is apparently another change in densification mechanism.

The various densification regimes were tentatively analysed according to the approximate models quoted in the Appendix, for the sintering of

TABLE 1

Approximate activation energies (kcal mol⁻¹) for YBC and YBSC, derived from fittings according to the models in the Appendix

YBC			YBSC		
Range (°C)	Model	Energy	Range (°C)	Model	Energy
924–952	Eqn. (A1)	900	920–936	Eqn. (A1)	1088
924–952	Eqn. (A2)	457	920–975	Eqn. (A2)	472
935–949	Eqn. (A3)	250	920–975	Eqn. (A3)	181
935–949	Eqn. (A4)	276	920–975	Eqn. (A4)	210
960–985	Eqn. (A5)	132	960–975	Eqn. (A5)	443

spherical grains under constant heating rate (CHR) conditions. This practice has been more or less successfully applied to other systems [2,3,8]. For instance in ref. 3 the sintering of silver grains was examined during the initial stage. Using eqns. (A1) and (A2), activation energies $Q_G = 28$ kcal mol⁻¹ and $Q_V = 25$ kcal mol⁻¹, were obtained for, respectively, grain boundary (GB) and volume (V) self-diffusion in silver. Because direct self-diffusion measurements [14] gave $Q_G = 20.2$ kcal mol⁻¹ and $Q_V = 49.5$ kcal mol⁻¹ for dense silver, the good agreement between the Q_G values for diffusion and from sintering suggests that the initial stage in the sintering of silver occurs via the grain boundary mechanism.

Table 1 lists the preliminary estimated results for activation energies derived from the equations in the Appendix and the data in Fig. 1. It should be noted that in several cases the ranges for the fittings were extended, covering slightly greater limits for the function-fittings than those corresponding to the visual breaks noted in Fig. 1. Nevertheless, the plots of ln(function) versus $1/T$ (K) were reasonably linear and the objective is to obtain an approximation of these possible activation energies.

For the YBC composition, it is noted in Table 1 that the Q_G value from eqn. (A1) of 900 kcal mol⁻¹ is much greater than the Q_V value (eqn. (A2)) of 457 kcal mol⁻¹. In view of the previous analysis for silver, and what appears to be an excessively high value for Q_G , it might be concluded that the initial stage in sintering is best described as a volume-diffusion mechanism.

The approximate fittings for the suggested (Fig. 1) second stage in densification, according to the probable Coble model, gave (Table 1) $Q_G = 250$ and $Q_V = 276$ kcal mol⁻¹, which seem to be more reasonable activation energies. In ref. 4 describing a similar analysis for barium titanate, a similar trend for $Q_G < Q_V$ was found, with the absolute values for these energies also being quite close in the range corresponding to the second stage of sintering. These fittings [4] were made after an initial densification that apparently obeyed Johnson's model (eqns. (A1) and

(A2)). Roughly, the overall behaviour and trends detected in this work for YBC and those described in ref. 4 for the ferroelectric, are about the same.

The following should be noted in relation to activation energies for YBC. The grain growth data in ref. 15 was analysed according to eqn. (A6) (Appendix), giving an activation energy of about 340 kcal mol⁻¹, valid for the range 925–950°C. The data in ref. 15 correspond to grain growth during sintering. In ref. 16, an activation energy of about 30 kcal mol⁻¹ is quoted for grain growth. In fact, in this study [16], the YBC ceramic was first sintered by slow heating between 920 and 990°C, giving grains of about 20–30 μm in size, and subsequently annealed at temperatures between 920 and 990°C for up to 72 h. Therefore, the results in ref. 16 correspond more to a recrystallization process related to grain boundary velocity controlled by curvature of the interface and the effective force on the interface, which may be related to impurity drag effects. In contrast, the data in ref. 15 relate more to a free growth of the crystals during the sintering of a much more porous body.

Other important data [11] relate to creep studies of YBC in the range 850–980°C. For this range, an activation energy of 232 kcal mol⁻¹ was obtained. A kinetic study [12] of the solid state reaction



gave an activation energy of 520 kcal mol⁻¹ in the 949–958°C range. Finally, in ref. 10 the diffusion of oxygen in YBC was analysed, giving an energy of 20.5 kcal mol⁻¹ between 300 and 600°C. At present, it is suggested that the densification and growth mechanisms may be related to the self diffusivities of cations, mainly Y and Ba ions; some degree of agreement between the sintering and growth activation energies and those corresponding to mechanisms involved in creep studies [11] and solid state reactions [12], is apparent.

Concerning liquid phase sintering, the data for YBC between 960 and 985°C were analysed according to eqn. (A5), and an activation energy of about 130 kcal mol⁻¹ was obtained. As discussed above [9,13,17,18], it is apparently possible at such temperatures for this system to develop phases other than the 1:2:3 phase, which could act as liquid phases. The energy calculated does not appear unreasonable. Thus, it is tentatively suggested that in this range, the YBC may sinter, at least partly, through LP mechanisms.

The situation for the YBSC composition is found (Table 1) to be much the same as for YBC. The main difference lies in the very high value obtained for the assumed activation energy for liquid-phase sintering in the 969–975°C range. This might be related to inhibition of liquid phase formation for temperatures lower than about 1000°C, due to the addition of strontium oxide.

It is clear that more work is needed to confirm these conclusions:

isothermal sintering studies are planned, in order to obtain cation diffusion data for the present preparations.

A further point of interest is related to sintering and grain growth under reduced partial pressure of oxygen.

CONCLUSIONS

Under controlled heating rate densification conditions of specially pre-heated YBC and YBSC compositions, it was possible to define clearly the various sintering regimes for these important high- T_c superconductors. For instance, replacement of some of the barium by strontium delays considerably the sintering with respect to YBC. From this approximate analysis of the sintering kinetics, it may be suggested that both the initial and intermediate stages involved in the solid state sintering can be reasonably described by the Johnson and Coble models.

The calculated activation energies vary in a wide range but some acceptable agreement can be detected with the corresponding energies for other processes where similar diffusion mechanisms may operate. It appears possible that liquid phase sintering may operate for YBC at temperatures higher than about 960°C; in contrast, the high activation energy obtained for YBSC in a similar range may suggest that for YBSC, liquid phases may not form at temperatures lower than about 1000°C.

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APPENDIX

For the kinetics of sintering and grain growth, it is possible to derive the following equations [2,3–8]. Here we list the approximated expressions for the various stages in solid state sintering (SS) and liquid phase sintering (LP).

Initial stage in solid state sintering

This relates to the formation and growth of the neck without grain growth. The fractional contraction is $\Delta l/l_0 = (l_0 - l(T))/l_0$, with l_0 being the initial thickness, $l(T)$ the thickness at temperature T (K) and $d(\Delta l/l_0)/dT$ being the densification rate.

According to Young and Cutler [2] and González-Oliver [3], the following equation for initial densification owing to grain boundary diffusion (GB) can be derived

$$\ln X = \ln \left[T(\Delta l/l_0)^{2.06} d(\Delta l/l_0)/dT \right] = A_1 - Q_G/RT \quad (\text{A1})$$

with $A_1 = \ln[0.7\Omega\gamma D_0^G/ka^4c]$ and for volume diffusion (V)

$$\ln Y = \ln \left[T(\Delta l/l_0)^{1.03} d(\Delta l/l_0)/dT \right] = A_2 - Q_V/RT \quad (\text{A2})$$

with $A_2 = \ln(2.63\Omega\gamma D_0^V/ka^3c)$ where the diffusion coefficients for (GB) and (V) are given by $D_B = D_0^G \exp(-Q_G/RT)$ and $D_V = D_0^V \exp(-Q_V/RT)$, where b is the grain boundary width and Q_G and Q_V refer to the corresponding activation energies, Ω and γ are the atomic/molecular volume and solid–vapor interfacial energy, k is a geometric factor, a is the grain diameter, c is the heating rate and R is the gas constant.

Intermediate stage in solid state sintering

This applies to densification concurrent with grain growth. According to ref. 4, the following approximated equations can be derived following

Coble's model [5]

$$\begin{aligned} \ln W &= \ln \left[-T \left\{ 1 - 0.62 / (1 + y)^3 \right\}^{1/2} \left\{ 1 / (1 + y)^4 \right\} dy / dT \right] \\ &= -(Q_G / RT) + \left[\ln(860 \gamma \Omega D_0^G / k_0 S^4) - \ln(1.86 / c) \right] \end{aligned} \quad (\text{A3})$$

for (GB), and

$$\begin{aligned} \ln U &= \ln \left[-T \left(1 / (1 + y)^4 \right) dy / dT \right] \\ &= -(Q_V / RT) + \left[\ln(335 \gamma \Omega D_0^V / k_0 S^3) - \ln(1.86 / c) \right] \end{aligned} \quad (\text{A4})$$

for (V). In these expressions, $y = \Delta l / l_0$, S is the grain size and k_0 is a geometric constant.

Solution / precipitation in liquid phase sintering

This applies after the rearrangement stage, and relates to enhanced densification [6] owing to the accelerated solubility of the solid phase in the fully wetting liquid. The latter is accelerated by the extra interparticle compressive forces coming from the negative pressure at the pores, driving the densification of the compact.

For densification at constant heating rates, we obtain the approximated expression

$$\ln L = \ln(Ty^2 dy / dT) = -Q / RT + \ln(2(k_2 / k_1)c_0 D_0 \Omega \gamma_{LV} \delta / cRa^2) \quad (\text{A5})$$

where $D = D_0 \exp(-Q / RT)$ is the atomic diffusion coefficient of the solid in the liquid (of liquid/vapour surface tension γ_{LV}) and c_0 is the initial solid solubility in the liquid. It is assumed that the liquids completely wet the solid. The radius of the particles is r , k_1 and k_2 are geometric constants and δ is the boundary thickness.

Grain growth

The following kinetic equation applies to the majority of ceramic systems, with the exponent n ranging between 2 and 10. The nature of the value n is still controversial but several explanations can be noted in refs. 7 and 15:

$$S^n - S_0^n = a \exp(-Q_S / RT)t \quad (\text{A6})$$

where S_0 is the initial grain size ($t = 0$) and Q_S is the activation energy for the growth process.