

# Study of the Effect of the Sr/Ca Ratio on the Microstructure and Critical Current Density of BSCCO 2212 Ag-Sheathed Tapes

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**Abstract--** The effect of the Sr/Ca ratio and Bi content on the microstructure and  $J_c$  of Ag-sheathed 2212 tapes was studied. Changing the Sr/Ca ratio changed the melting temperature of 2212 phase, the phase assemblage in the melt, and the nonsuperconducting phases in the fully processed tape. In tapes with Sr/Ca=2.75, the 2201 phase crystallizes from the melt before 2212 during cooling, and this 2201 remains in the microstructure. In tapes with Sr/Ca=1.3, there is more liquid left after cooling, and it converts to 2201 as the tape cools to room temperature. Fully processed tape with overall composition 2.1:2:1:2 had the most homogeneous microstructure and highest  $J_c$ .

## I. INTRODUCTION

Improving HTSC coil performance depends mainly on improving the critical current density ( $J_c$ ) of the superconducting tape. This in turn requires improving the microstructure of the superconductor. Studies have been conducted to explore ways to affect the microstructure by controlling the melt processing atmosphere and by varying the composition (Bi and Cu) and (Sr, Ca) of the starting powder [1-4]. These methods have increased  $J_c$ .

Varying the Sr/Ca ratio in the 2212 phase has been done in phase diagram and crystal structure studies. Endo [2] varied the Sr/Ca ratio to process 2212 tapes in 1%  $O_2$ . They reported  $J_c$  of up to  $1.5 \times 10^5$  A/cm<sup>2</sup> at 4.2K, 0T in the Sr rich composition ( $Bi_2Sr_{2.3}Ca_{0.85}Cu_2O_x$ ). In the present study, we investigated the effect varying the Sr/Ca ratio has on the microstructure and  $J_c$  of 2212 in Ag-sheathed tapes melt processed in 100%  $O_2$ , which we found in a previous study [3] to be the best atmosphere to melt process 2212 tape.

## II. EXPERIMENTAL PROCEDURES

Nine powders with the compositions listed in Table 1 were prepared by aerosol spray pyrolysis (ASP) [5] from  $Bi_2O_3$ ,  $SrCO_3$ ,  $CaCO_3$  and  $CuO$  (> 99.9%). Details of powder preparation, and wire drawing and rolling were reported previously [4]. The final thickness of the tape is 150 $\mu$ m and the carbon content of the powder was about 200~250 ppmwt. TG-DTA (5°C/min heating) was used to investigate the melting point of each tape in 100%  $O_2$  (50 ml/min). The onset temperature was interpreted as the melting temperature of the 2212. Quenched tapes were prepared by dropping sections of tape into an oil bath at a desired point in the melt process schedule to freeze in the high-temperature micro-

TABLE 1  
THE NINE COMPOSITIONS USED IN THIS STUDY (Bi/Sr/Ca/Cu)

Sr/Ca	Bi=2.0	Bi=2.1	Bi=2.18
2.75	2/2.2/0.8/2	2.1/2.13/0.77/2	2.18/2.2/0.8/2
2	2/2/1/2	2.1/1.93/0.97/2	2.18/2/1/2
1.3	2/1.7/1.3/2	2.1/1.64/1.26/2	2.18/1.7/1.3/2

structure. Fig. 1 shows melt processing schedules used in this study. Fig. 1a (HT1) shows the typical heat treatment schedule, and Fig. 1b (HT2) shows an modified heating schedule. Phases present in the tape were identified by X-ray diffraction, SEM-EDS, and EPMA.  $I_c$  was measured by standard four probe method at 4.2K, 0T with 1 $\mu$ V/cm criteria, then converted to  $J_c$  using the cross sectional area of the oxide core.

## III. RESULTS

Fig. 2 shows the melting temperature of the 2212 in the tape as a function of Sr/Ca ratio and Bi content. The melting temperature was about 10°C higher for tapes with Sr/Ca=1.3 compared to Sr/Ca=2 and 2.75, which were about the same. The Bi content had only a small effect on the melting temperature.

Fig. 3 summarizes the phase assemblages in the tapes in 100%  $O_2$  as a function of temperature. These data show that the tapes contain different phase assemblages before and after the melt process. The initially essentially phase pure 2212 phase contained different nonsuperconducting phases after melt processing. The phase assemblage is different in

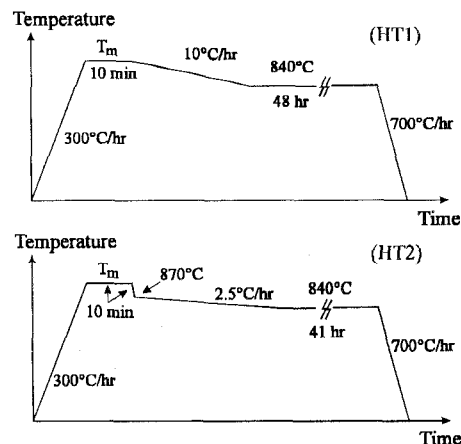


Fig. 1 Heat treatment schedules used in this experiment

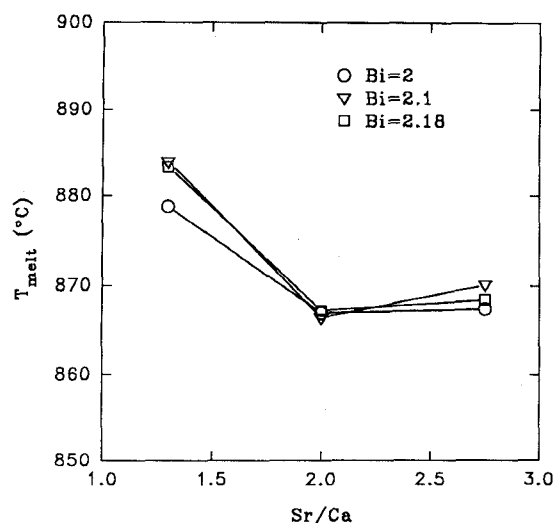


Fig. 2 Melting temperature of 2212 tapes as a function of Sr/Ca ratio and Bi content.

samples with different Sr/Ca ratio, but is the same for samples with different Bi content.

The following sections discuss tapes with different Sr/Ca ratios. Fig. 4 shows typical microstructure of tape with Sr/Ca=2.75 processed using HT1. Above the melting temperature ( $\sim 870^\circ\text{C}$ ) for these tapes, the melt contains liquid,  $(\text{SrCa})_{14}\text{Cu}_{24}\text{O}_x$  (14:24 AEC) and  $\text{Bi}_2(\text{SrCa})_4\text{O}_x$  (2:4 CF). The 2:4 CF grains were small immediately after melting, but grew to large size during the subsequent slow cooling. In these tapes,  $\text{Bi}_2\text{Sr}_2\text{CuO}_x$  (2201) is the first crystalline phase that comes out of the melt on cooling. After cooling to  $870^\circ\text{C}$ , Fig. 4(a) shows that a lot of 2201 had formed, whereas only a small amount of 2212 had formed. The 2201 crystals that formed grew to large size and were present in fully processed tape along with 14:24 AEC and 2:4 CF. Even after holding for 2 days at  $840^\circ\text{C}$ , 2201 was still present in the microstructure (Fig. 4b). Prelimi-

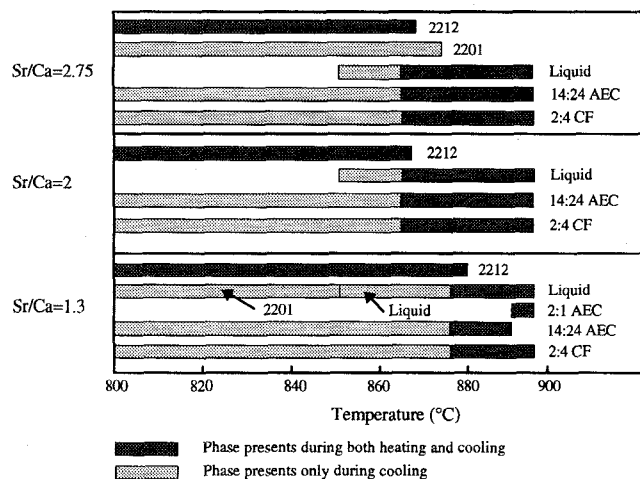


Fig. 3 Phase assemblages as a function of temperature and Sr/Ca ratio in  $\text{O}_2$ .

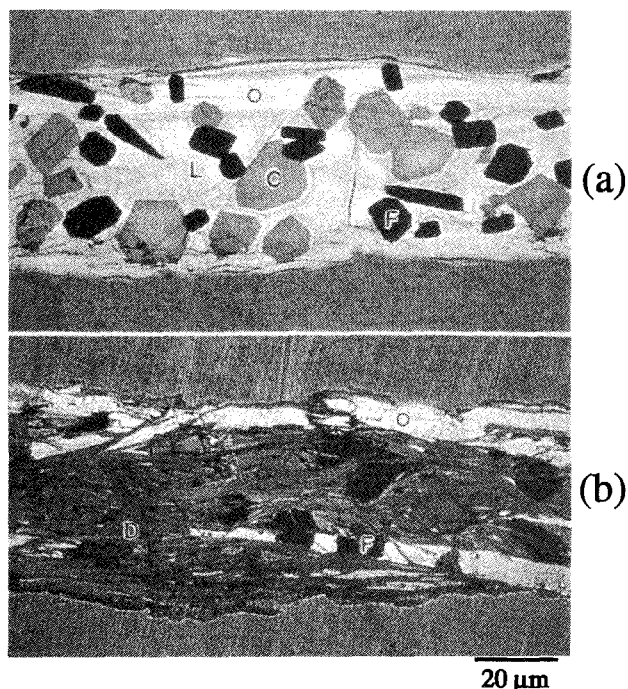


Fig. 4 Typical microstructures of tapes with Sr/Ca=2.75, Bi=2.1. Tapes were quenched during cooling at (a)  $870^\circ\text{C}$  and (b)  $840^\circ\text{C}$ . L=Liquid; F=14:24 AEC; C=2:4 CF; O=2201, D=2212

nary studies show that a 200hr anneal at  $\sim 860^\circ\text{C}$  is needed to fully convert 2201 to 2212 [6].

Fig. 5 shows typical microstructures of tape with Sr/Ca=2. The nonsuperconducting phases in the melt were the same as in tapes with Sr/Ca=2.75, that is 14:24 AEC and 2:4 CF.

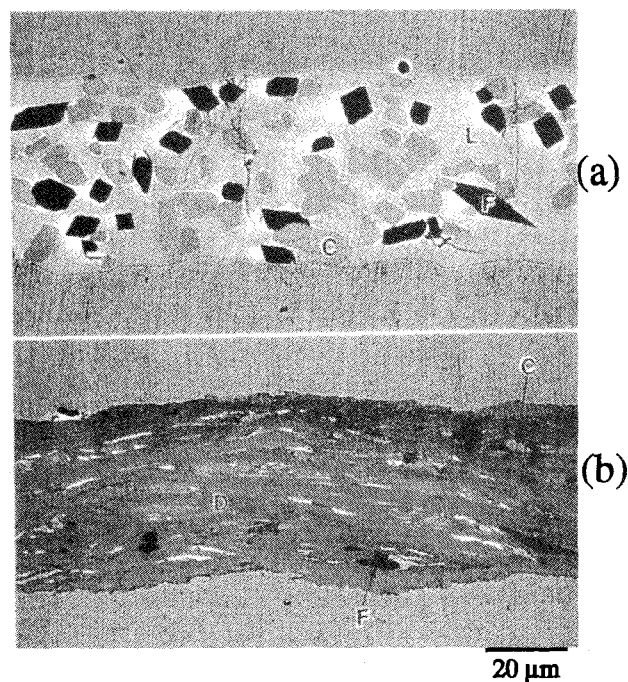


Fig. 5 Typical microstructures of tapes with Sr/Ca=2, Bi=2.1. Tapes were quenched during cooling at (a)  $870^\circ\text{C}$  and (b)  $840^\circ\text{C}$ . (see symbols in Fig. 4.)

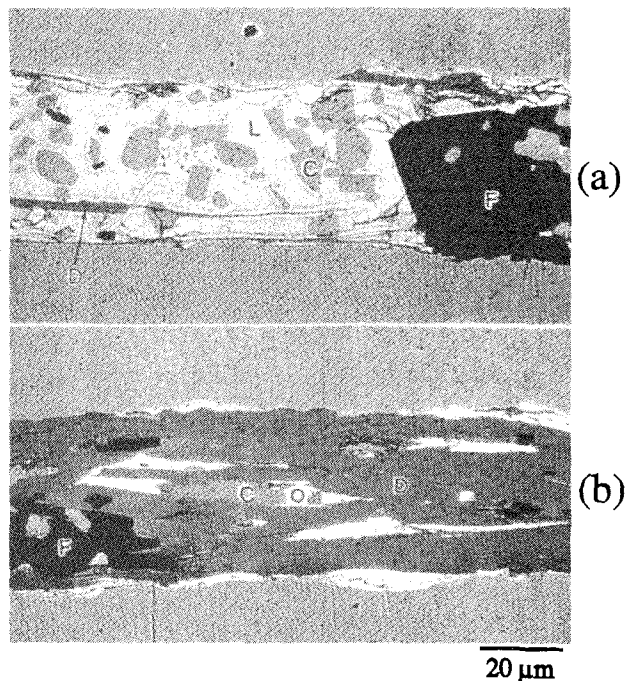


Fig. 6 Typical microstructures of tapes with Sr/Ca=1.3, Bi=2.1. Tapes were quenched during cooling at (a) 870°C and (b) 840°C. (See symbols in Fig. 4)

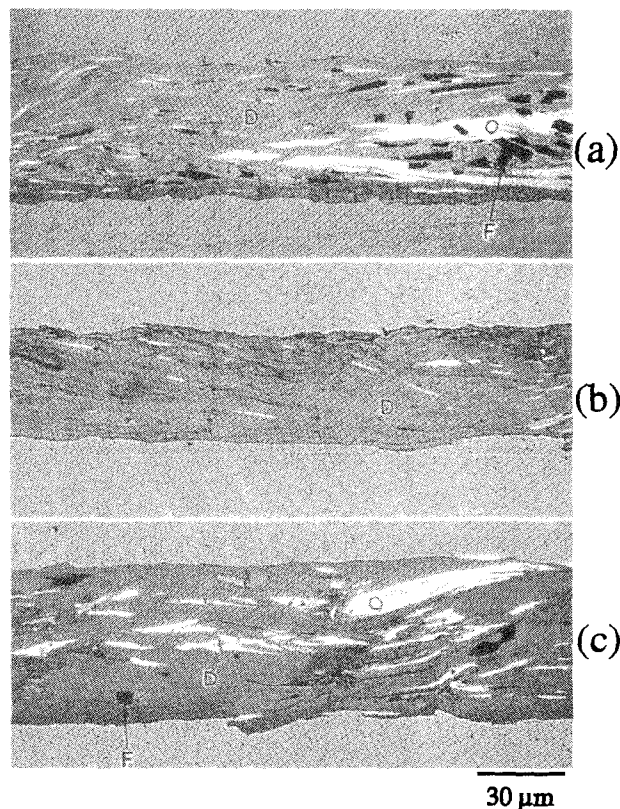


Fig. 7 Typical microstructure of tapes fully processed using HT2. The Sr/Ca ratios are (a) 2.75, (b) 2.0, and (c) 1.3, Bi=2.1. (see symbols in Fig. 4)

2201 does not form during cooling in these tapes. During cooling, the nonsuperconducting phases were consumed rapidly as 2212 crystallized out of the melt. There was only a small volume fraction of nonsuperconducting phases present in the fully processed tapes.

For tapes with Sr/Ca=1.3, the phase assemblage changed in the melt over a small temperature range. During heating, 14:24 AEC and 2:4 CF formed when 2212 melted at ~880°C. With continued increase in temperature, 14:24 AEC disappeared from the melt and  $(\text{SrCa})_2\text{CuO}_x$  (2:1 AEC) formed. During cooling, 2:1 AEC disappeared and grains of 14:24 AEC nucleated and grew. Fig. 6a shows that the 14:24 AEC grains that formed during cooling were much larger than the original 14:24 AEC grains and were not uniformly distributed in the melt. Because of the large size of the 14:24 AEC grains, the reaction to form 2212 did not go to completion, and there was a large volume fraction of nonsuperconducting phases in fully processed tape (Fig. 6b). 2201 present in the fully processed tape crystallized from the liquid as the tape was cooled to room temperature (< 840°C). The 2212 grains in these tapes were much larger and there was less 2201 intergrowth in the fully processed tape than in tapes with Sr/Ca = 2.75 or 2.0.

The reaction to form 2212 depends on the size of the nonsuperconducting grains in the melt; large grains impede the reaction. HT2 was developed to minimize the growth of the nonsuperconducting grains during melt processing. It does this by rapidly cooling the tape from  $T_{\text{max}}$  to 870°C, where 2212 begins to form from the melt. This minimizes the time during which the nonsuperconducting grains could grow. Fig. 7 shows the microstructure of tapes fully processed using HT2. The grains of 14:24 AEC and 2:4 CF were much smaller than in tapes made with HT1, but the 2201 in Sr/Ca=2.75 tapes and in Sr/Ca=1.3 did not change significantly between the two heat treatments.

Table 2 shows the measured cation composition of the 2212 phase in fully processed tape as a function of Sr/Ca ratio and Bi content. The Sr/Ca ratio varies from ~1.44 to ~2.77. The Bi content of 2212 increases with increasing

TABLE 2.  
CATION CONTENT OF THE 2212 PHASE IN SEVERAL TAPES  
MEASURED BY EPMA. (CATION MOLE %)

Sr/Ca	Bi=2 (initial)			Bi=2.1 (initial)		
2.75	32.1(5)	29.9(5)	10.8(5)	27.6(4)	32.3(4)	29.8(2)
2	30.6(4)	28.6(8)	13.9(3)	27.6(1)	30.9(5)	27.7(7)
1.3	29.9(3)	25.0(8)	17.1(4)	28.0(1)	30.3(3)	24.4(8)

Sr/Ca ratio, whereas the Cu content remains relatively constant. The measured Bi content in the 2212 phase is almost the same in tapes that have the same initial Sr/Ca ratio independent of the initial Bi content.

$J_c$  of fully processed tapes made using both heat treatments was measured and is shown in Fig. 8. Tapes with Sr/Ca=2,

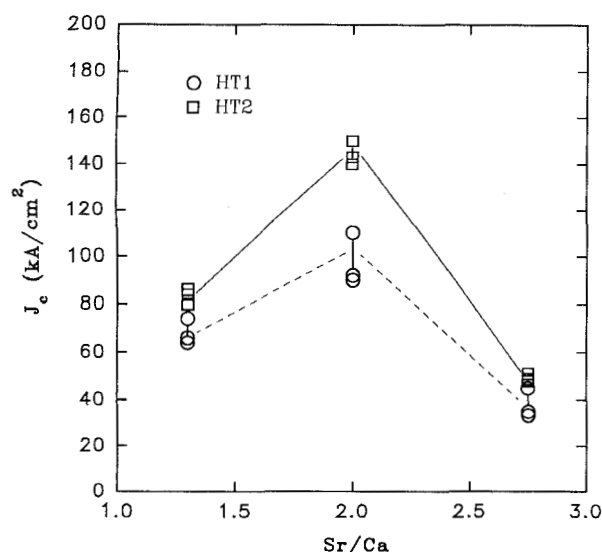


Fig. 8  $J_c$  as a function of Sr/Ca ratio for tapes with Bi=2.1 (4.2K, 0T).

which had the most homogeneous microstructure, had the highest  $J_c$ .  $J_c$  increased in tapes made using HT2, showing that fast cooling to 870°C followed by slow cooling, which improved the microstructure, also improved  $J_c$ .

#### IV. DISCUSSION

##### A. Thermodynamics and Kinetic Considerations

As mentioned above, different microstructures are present in tapes prepared by different heat treatments due to changes in the grain size of the nonsuperconducting phases and the cooling rate. This indicates that the "fully processed" tapes are not in thermodynamic equilibrium after melt processing. The approach to equilibrium is limited by the kinetics of the reaction to form 2212, which involves converting nonsuperconducting phases and liquid in the melt into the 2212 phase. Both the grain size of nonsuperconducting phases and the cooling rate through the temperature range in which the reaction occurs affect the kinetics of the reaction, resulting in different microstructures. The larger the grain size of the nonsuperconducting phases, the more difficult for it is for them to react completely, resulting in greater compositional inhomogeneity in the fully processed tape. Therefore, to optimize 2212 tapes, one must consider the thermodynamics (i.e., the phase diagram) and the kinetics of the reaction. Data are needed about the kinetics of the formation of 2212.

##### B. Composition of the 2212 phase that forms

Table 2 shows that the Sr/Ca ratio in the 2212 phase that forms during melt processing can vary from ~1.44 to ~2.77, which is in good agreement with previous work[7]. The Bi content in the 2212 that forms is the same in tapes with same Sr/Ca ratio regardless of their initial Bi content. The lowest Bi content measured in this experiment was about  $30 \pm 0.3$

mole% in tapes with Sr/Ca=1.3 and an initial Bi content of 28.57 mole% (Bi=2) and 30 mole% (Bi=2.1). This result indicates that the single phase region for 2212 is Bi rich, and the nominal composition  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.8}$  (Bi=28.57 mole%) appears to be outside the single phase region. On the other hand, the Bi content in the 2212 phase increases with increasing Sr/Ca ratio, as shown in Table 2. Holesinger et al. [7] reported that TEM studies showed 2201 intergrowths in the 2212 phase, resulting in a higher apparent Bi content in the grains of 2212. Comparing the microstructures of tapes with different Sr/Ca ratios in Figs. 6 and 7, shows that on the SEM scale the number of intergrowths of the 2201 phase between the 2212 grains decreases with decreasing Sr/Ca ratio, independent of the Bi content. In addition, the increase in the Bi content of the 2212 phase with increasing Sr/Ca ratio may be indirect evidence of 2201 intergrowths within the grains of 2212. TEM investigations are needed to study this hypothesis.

#### V. CONCLUSIONS

The effect of varying the Sr/Ca ratio and Bi content in 2212 tapes on the microstructure and  $J_c$  of fully processed tapes has been studied. The melting temperature of the 2212 phase changes with varying Sr/Ca ratio. The phase assemblages in the melt and in fully processed tape also change with variations in the Sr/Ca ratio. In tapes with Sr/Ca=2.75, during cooling, the 2201 phase forms from the melt before the 2212 phases. In tapes with Sr/Ca=1.3, there is more liquid phase left unreacted after cooling than for higher Sr/Ca ratios, and it converts to 2201 at lower temperature. The results suggest that the kinetics of the reaction to form the 2212 phase during melt processing play an important role in the formation of 2212 in fully processed tape. Thermodynamic (i.e., phase diagram) and kinetic information must be combined to fully understand and control the development of 2212 in Ag-sheathed tapes.

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