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GRAIN ORIENTATION IN HIGH T_c SUPERCONDUCTORS BY MOLTEN SALT POWDER SYNTHESIS

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ABSTRACT

The molten salt or the flux method is utilized in this study to fabricate a grain oriented $YBa_2Cu_3O_{7-x}$ (123) superconductor. Here we suggest a two stage approach in using the "green phase," Y_2BaCuO_5 (211), as seed crystals in the formation of $YBa_2Cu_3O_{7-x}$. The process uses Y_2BaCuO_5 formed by molten salt synthesis. The Y_2BaCuO_5 phase has been observed to be stable in water and in most of the salt systems. Salt processing can can form a small quantity of anisotropic particles of Y_2BaCuO_5. This material can form the 123 phase when tape cast and sintered in the presence of the required levels of Ba and Cu.

INTRODUCTION

The existing anisotropy in the critical current density of $YBa_2Cu_3O_{7-x}$ warrants a grain orientation processing which yields 'textured' microstructure with the aim to enhance the maximum current density of the ceramic[1,2]. Molten salt processing can yield single crystal particles with shape anisotropy which are subsequently aligned by techniques such as tape casting and hot forging. This technique has been applied successfully on a variety of ferroelectric systems[3-5].

Attempts at molten salt synthesis of $YBa_2Cu_3O_{7-x}$ in other ceramic systems has been largely unsuccessful. Studies by others[6,7] revealed the instability of the superconducting phase in NaCl-KCl, LiCl, $BaCl_2$-$CuCl_2$, $CuCl_2$, and Na_2SO_4-K_2SO_4 salts. Certain studies[7] show that the stability of the $YBa_2Cu_3O_{7-x}$ phase might be favored in salt systems with small anion and large cation sizes. $YBa_2Cu_3O_{7-x}$ in powdered form reacts vigorously at room temperature with water[9]. The green phase, Y_2BaCuO_5, is one of the decomposition products of the reaction of $YBa_2Cu_3O_{7-x}$ with water. The stability of the green phase and the anisotropic nature of its grains led us to proceed further with this phase. Moreover molten salt processing of $YBa_2Cu_3O_{7-x}$ requires a complex process for removal of the salts, while in case of the green phase the salts can be removed by washing with water.

The two stage approach to the formation of $YBa_2Cu_3O_{7-x}$ by utilizing the green phase, Y_2BaCuO_5, formed by molten salt synthesis as seed crystals is reported here. The results of our tape casting experiments are also reported here.

EXPERIMENTAL PROCEDURES

Y_2BaCuO_5-Salt Equilibrium

The first experiment tested the stability of preformed 211 in vaious salts to determine the best salts for forming the 211 powders. In the first method precursor materials $BaCO_3$, Y_2O_3 and CuO were taken in stoichiometric proportions of Y_2BaCuO_5 and ball milled in ethanol for 12 hours with YTZ ceramic balls. After drying, the batch was calcined at 960°C for 12 hours and annealed at 530°C for 6 hours in flowing oxygen atmosphere. X-ray diffraction studies confirmed the phase purity of the sample. The preformed 211 powders was then mixed with various salt systems and heat treated in closed magnesia crucibles at temperatures above the melting point of the salt systems[10] used. Table 1 gives all the details of all salt systems used and the resultant phases after heat treatment.

Ratio	Salt	Temp	Time	Resulting Phases	
Salt:211	Systems	°C	Hrs.	Oxides	Other Phases
1:1	NaCl	825	3	211	NaCl
1:1	KCl	825	3	211	KCl
1:1	LiCl	825	3	$Cu_2Y_2O_5$, Y_2O_3	LiCl
1:1	NaCl-KCl-LiCl	825	3	$Cu_2Y_2O_5$, Y_2O_3	NaCl, KCl
1:1	Li_2SO_4	975	3	$Cu_2Y_2O_5$,	$BaSO_4$
1:1	Na_2SO_4	975	3	211	Na_2SO_4
1:1	Li_2SO_4-Na_2SO_4-K_2SO_4	975	3	211, $Cu_2Y_2O_5$,	$BaSO_4$
1:1	Na_2SO_4	1050	4	211	Na_2SO_4
1:1	K_2SO_4	1050	4	211	K_2SO_4
1:1	Li_2SO_4-Na_2SO_4-K_2SO_4	1050	4	Y_2O_3	K_2SO_4
1:1	Na_2SO_4	1100	4	211, Y_2O_3	Na_2SO_4
1:1	K_2SO_4	1100	4	211, Y_2O_3	K_2SO_4
1:1	NaCl-KCl	900	2	211	NaCl-KCl
2:1	NaCl-KCl	900	2	211	NaCl-KCl
3:1	NaCl-KCl	900	2	211	NaCl-KCl

Table 1: Stability of Preformed 211 Phase in Molten Salt systems

The salts promising the best stability of 211 phase were then studied as fluxes in producing 211 powders from raw materials. In this method precursor materials $BaCO_3$, Y_2O_3 and CuO in the stoichiometric proportions of Y_2BaCuO_5 were mixed with various salt systems and ball milled in ethanol for 12 hours. The dried batch was then heat treated in closed magnesia crucibles. Table 2 gives details of the salt systems used, the temperature and time of the heat treatment and the resultant phases.

Ratio Salt:211	Salt Systems	Temp °C	Time Hrs.	Resulting Phases	
				Oxides	Other Phases
1:1	NaCl-KCl	850	4	$Cu_2Y_2O_5$, Y_2O_3	$BaCO_3$, NaCl, KCl
1:1	NaCl	850	3	211	NaCl
1:1	NaF	1000	4	Y_2O_3, $Cu_2Y_2O_5$	NaF, $BaCO_3$
1:1	KI	825	4	211	KI
3:1	K_2SO_4	1050	4	211, Y_2O_3	K_2SO_4, $BaCO_3$
3:1	Na_2SO_4	1050	4	211, Y_2O_3	Na_2SO_4, $BaCO_3$
3:1	NaCl-KCl	1000	4	211, Y_2O_3	$BaCO_3$, NaCl, KCl

Table 2: Stability of 211 Phase in Precursor-Salt Systems

The high stability of Y_2BaCuO_5 in water enabled easy removal of the salts by repeatedly washing with water. X-ray diffraction studies were used to confirm the removal of the salts. The washed samples were then observed under the scanning electron microscope.

To test the proof of concept that the green phase, Y_2BaCuO_5 can be used as seed crystals in the formation of the superconductor, the resultant pure Y_2BaCuO_5 was mixed with reagent grade $BaCO_3$ and CuO in the required molar proportions as given by the following reaction:

$$Y_2BaCuO_5 + 3BaCO_3 + 5CuO \longrightarrow 2YBa_2Cu_3O_{7-x} + 3CO_2 \quad (1)$$

The batch was calcined at 960°C for 12 hours and annealed at 530°C for 6 hours in oxygen atmosphere. The results was positive and the 123 material was then formed by tape casting proceedure.

Tape Casting

To test the total concept, 123 ceramic was formed using tape casting technique. The batch containing the required amounts of Y_2BaCuO_5, $BaCO_3$ and CuO, was ball milled in ethanol for 12 hours to ensure homogeneity, dried and sized to 325 mesh to ensure uniform small particle size.

Commercially available binder (Metoramic Sciences, Inc., Clandan Product No. B73210) was used in order to supply the necessary rheological properties required in tape casting. Binder additions to the above batch were made in the amount of 40-45% by weight and Toluene in the amount of 5-7% by weight was also added to adjust the viscosity. This batch was then ball milled for 12 hours with zirconia balls and tape cast on glass using a hand held doctor blade. The blade height was consistently set at 0.25 mm. A solution of pure lecithin dissolved at a 1.5 weight percent ratio with 1,1,1 trichloroethane was used as a releasing agent.

The green tapes were cut into one inch square pieces and laminated in a one inch square die with between 15-20 layers. The die was brought to a stable temperature near the glass transition of the binder through the use of heating plates on a hydraulic press. The lamination temperature used was between 60 and 65°C while the pressure was 5000 psi and the time

varied from 2 to 3 minutes. The resulting monolith showed no evidence of individual layers. The monoliths were then trimmed on all edges and diced into individual compacts. The rate of heating for the binder burnout, as determined from TGA analysis of the green tape, was regulated at 20°C per hour upto 500°C and held there for 1 hour. The compacts were then taken to the calcination temperature of 960°C at a rate of 100°C/hr and held there for 12 hours and then annealed at 530°C for 12 hours in flowing oxygen atmosphere. X-ray diffraction analysis revealed the presence of a nearly single phase $YBa_2Cu_3O_{7-x}$.

RESULTS AND DISCUSSION

Tables 1 and 2 show the stability of Y_2BaCuO_5 in most of the salt systems. This green phase was observed to degrade mostly in those salt systems that contained lithium salts. It was also observed that batches heat treated in uncovered crucibles showed appreciable weight loss, nearly an order of magnitude higher than those runs conducted with covered crucibles. The salts could be easily removed by repeated washing of the heat treated batch with water. The SEM micrographs shown in figures 1-3 are of the samples heat treated at 1000°C at times of 4, 12 and 32 hours respectively. From the micrographs it can be seen that there is a small presence of anisotropic particles at 4 hours which increases by a great amount at 12 hours while for still longer times they tend to be more rounded or equiaxed.

The process of combining the 211 powders from the salt synthesis with $BaCO_3$ and CuO and calcining revealed a phase pure $YBa_2Cu_3O_{7-x}$ with no or very little of Y_2BaCuO_5 phase.

Tape cast mixtures of 211 with $BaCO_3$ and CuO also revealed a nearly phase pure $YBa_2Cu_3O_{7-x}$. Figure 4 shows the XRD pattern of a calcined tape cast sample. From this X-ray diffraction plot it can be seen that peaks belonging to the 00l lines have increased intensity compared to a calculated pattern. This gives an idea of the degree of orientation and the Lotgering's factor[11] calculated for this pattern gives a factor of 0.27 which actually represents a moderate degree of orientation. The density of the calcined tapes was about 80-85% of the theoretical density. Resistivity measurements using a four point probe method performed on the tape cast samples show a T_c at 86 K for zero resistivity. The plot of resistivity against temperature is shown in figure 5. Figure 6 reveals the microstructure of a tape cast sample seen through a surface pore. The pore is surrounded by large grains with some platy morphology and appears consistent with a Lotgering orientation factor of 0.27.

CONCLUSIONS

The Y_2BaCuO_5 phase showed good stability in the salts and its stability in water facilitated in easy removal of the salts. Anisotropy depends on the growth kinetics as evident in times upto 12 hours. Longer soak times tended to produce more equiaxed particles. It was seen that the crucibles need to be covered during to minimize the weight loss of the batch on heat treatment. It has been shown here that Y_2BaCuO_5 can be used as seed crystals in the formation of $YBa_2Cu_3O_{7-x}$ superconductor. As further proof of concept we have shown

that tapes made of precursor materials can be easily converted to superconducting tapes. Moderate degree of orientation can be achieved in the tapes. Resistivity measurements show a T_c of 86 K for these tapes.

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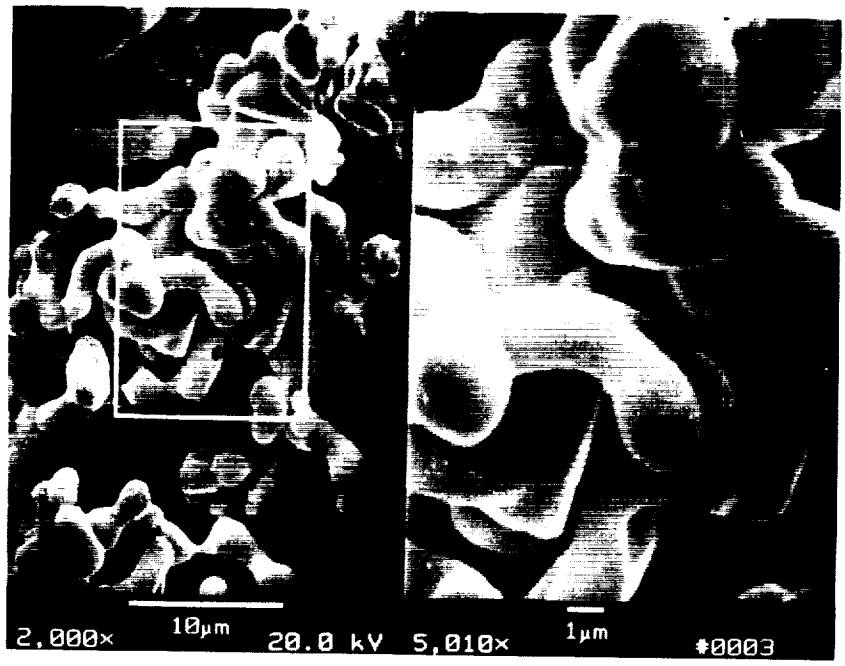

Figure 1: **SEM micrograph of sample containing precursor (211) materials and NaCl-KCl salt system heat treated at 1000°C for 4 hours**

Figure 2: **SEM micrograph of sample containing precursor (211) materials and NaCl-KCl salt system heat treated at 1000°C for 12 hours**

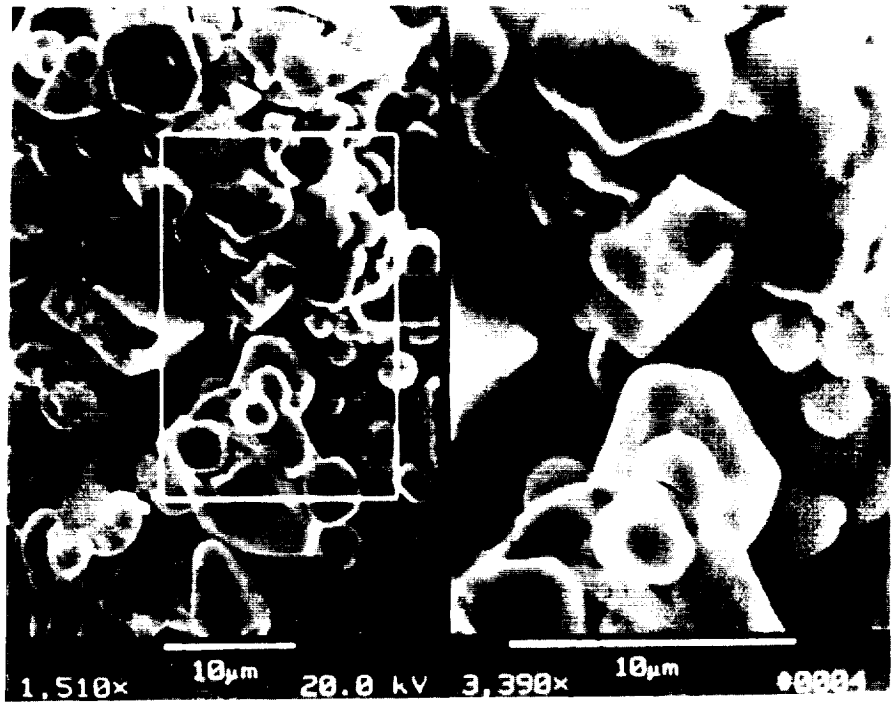

Figure 3: **SEM micrograph of sample containing precursor (211) materials and NaCl-KCl salt system heat treated at 1000°C for 32 hours**

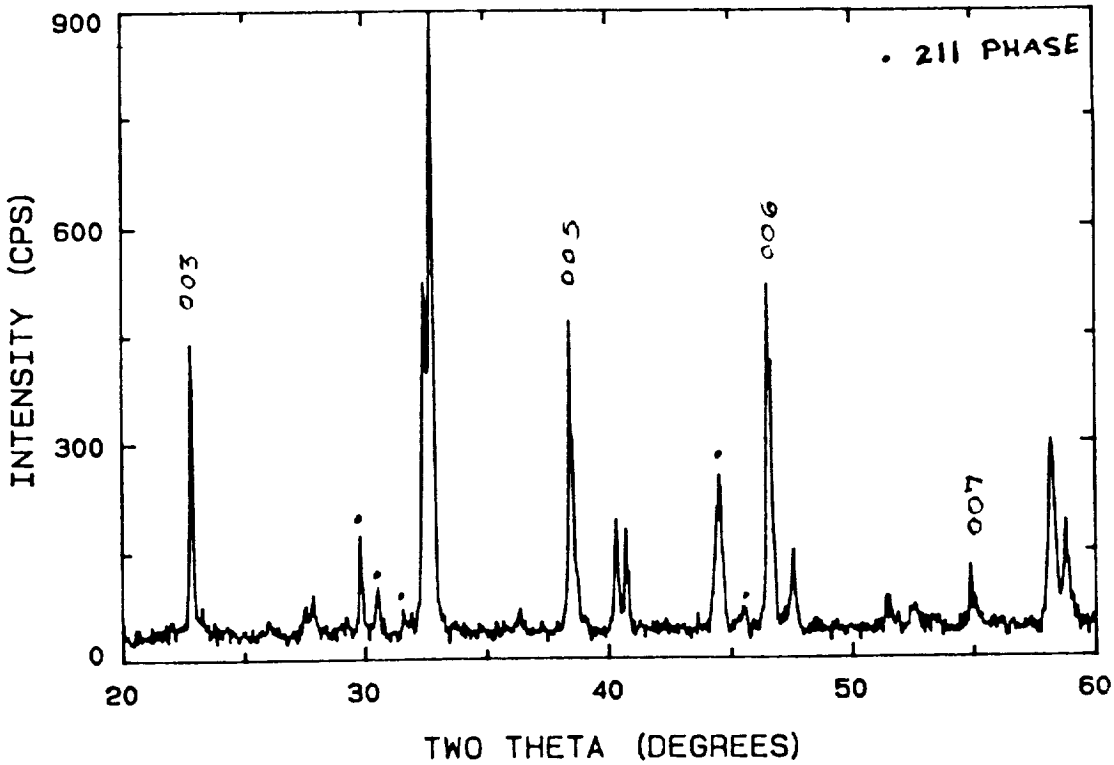

Figure 4: **XRD pattern for $YBa_2Cu_3O_{7-x}$ formed from calcination of tapes of Y_2BaCuO_5 with $BaCO_3$ and CuO**

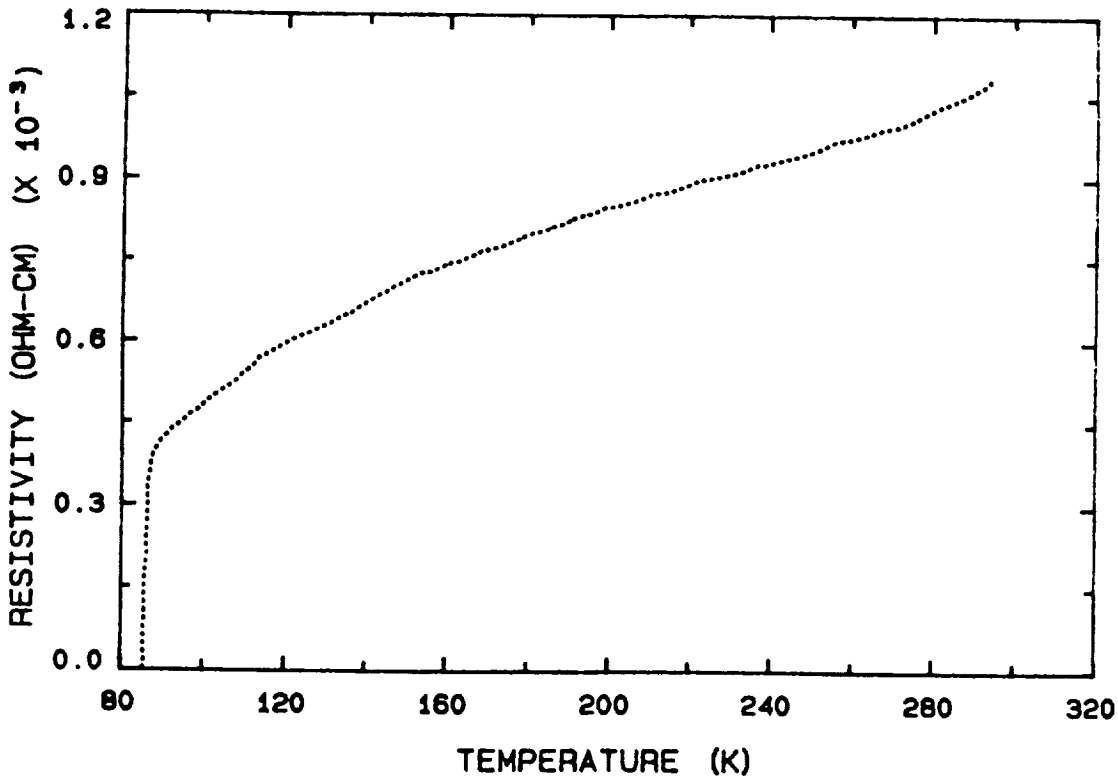

Figure 5: **Plot of resistivity versus temperature of a tape cast sample**

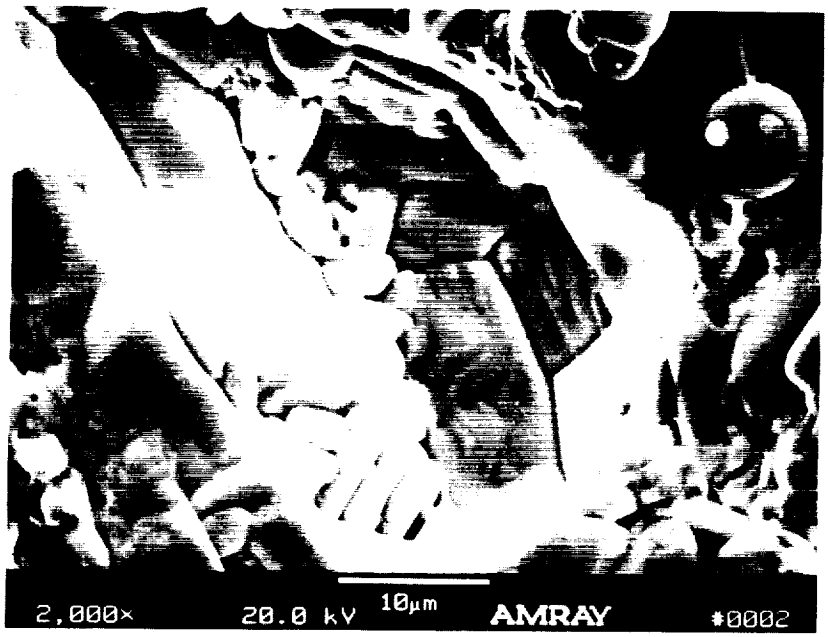

Figure 6: **SEM Micrographs of a tape cast sample as seen through a surface pore for ceramic sintered at 960°C for 12 hours**