Processing of Bi-2223 Ceramics in the System BPSCCO

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Abstract

Systematic studies of the development of the superconducting properties for air or Ar/O_2(8%) preparation of 2223 ceramics via a sol/gel, solid state or melt process indicate that (i) 2223 has the tendency to grow beneath a superficial 2212 layer, (ii) the growth rate is drastically accelerated in a reduced oxygen atmosphere, (iii) the sol/gel technique is superior to the solid state route, (iv) for melt processing the 2223 content of product and precursor is directly correlated.

1. Introduction

The triple Cu-O layered Bi cuprate 2223 with the highest T_c (≈ 110 K) among the Bi series is the focus for the development of technical applicable materials in form of wires, tapes, thick films and ceramics for 77K applications. To date, a conclusive correlation between superconducting properties and the conditions of processing is missing due to the multitude of parameters. For this reason the present study examines systematically the development of the superconducting properties for air or Ar/O_2(8%) preparation of 2223 ceramics via a sol/gel, melt or solid state process. It is demonstrated that (i) 2223 has the tendency to grow beneath a superficial 2212 layer, (ii) the growth rate is drastically accelerated under a reduced oxygen partial pressure, (iii) the sol/gel technique is superior to the solid state methode, (iv) the employment of precursor powder with a high 2223 content improves the velocity of the 2223 formation via a melt process.

2. Experimental

Ceramic 2223 and 2212 materials of various cation ratios were prepared from $Bi(NO_3)_3 \cdot 5H_2O$, PbO, $Sr(NO_3)_2$, $CaCO_3$ and CuO via the sol/gel as well as the solid state route in air or Ar/O_2(8%) in corundum boats between 835 and 865°C for 15 to 400 h [1,2]. For the melt process, pellets were melted on Ag substrates or in Ag envelops at 920°C/20min and post-annealed. All samples were checked by XRD (Philips

powder diffractometer, CuKα radiation, Au standard). The oxygen content was calculated via the average oxidation state of the cations determined by a redox titration. The susceptibility measurements were performed with a SQUID magnetometer. For the transport measurements a $1\mu V/cm$ criterion was applied.

3. Results and discussion

3.1. Sol/gel and solid state route

Ceramics of identical cation ratio were processed in air via either the sol/gel or the solid state technique and submitted to identical post-treatments. From the data collection in Table 1 (No. 1 to 7) follows that the X-ray data as well as the overall oxygen content is not affected by either the preparation route or the post-treatment. Consequently, the hole concentration can be considered as constant and accordingly the transition to superconductivity is uniformely at about 108 K. From a comparison of the data for sample No. 1 to 4 follows the benefical role of post-treatment on the transport properties of the ceramic materials, likewise present for the sol/gel and the solid state route. However, significant differences between both methods get obvious from the χ(T) and M(H) traces. The χ''(T) data plotted in Fig. 1, which were obtained through derivation of the χ(T) curves, indicate a flux penetration of the intergrain material (T_m(j) according to [3]) at inferior temperatures for the solid state material. This effect is due to more copious 2212 seggregations at the grain boundaries; equally, observed for other Bi

Table 1. Lattice constants $(\text{Å})^a$ of the tetragonal 2223 subcell, oxygen content (O_2), transition temperature T_c (from $\chi(T)$) and critical current densities from $M(H)$ and transport measurements, $j_{cm}{}^b$ and j_{ct} $(H=0\,T)$ for 2223 ceramics

sample number	composition Bi: Pb: Sr: Ca: Cu	method of processing and: post-treatment	a	c	O_z	T_c [K]	$j_{cm}(Acm^{-2})$ 5 K	77 K	$j_{ct}(Acm^{-2})$ 77 K
		sol/gel route							
1	1.8:0.2:2.0:2.0:3.0	air/ as prepared:	5.414	37.17	10.10	109	5.0×10^6	6.0×10^4	-
2	"	" / 24h/859°C	5.414	37.20	10.11	108	5.4×10^6	1.8×10^5	-
3	"	" / 72h/859°C	5.416	37.21	10.11	108	5.6×10^6	3.1×10^5	435
4	"	" /168h/859°C	5.410	37.19	10.13	108	5.8×10^6	2.7×10^5	600
		solid state route							
5	"	air/ as prepared:	5.414	37.18	10.08	109	-	-	-
6	"	" / 72h/859°C	-	-	-	-	5.2×10^6	2.1×10^5	-
7	"	" /168h/859°C	-	-	-	110	5.6×10^6	1.7×10^5	310
		solid state route							
8	1.8:0.2:1.9:2.1:3.0	air/ 48h/854°C	5.416	37.20	10.20	108	-	-	1850
9	1.8:0.4:1.9:1.9:3.0	air/115h/830°C	5.411	37.15	10.45	109	2.2×10^6	-	-
10	1.7:0.5:1.9:1.9:3.0	Ar/O$_2$(8%)/13h/830°C	5.405	37.13	-	108	-	-	-

^{a} ± 0.005 Å(a); ± 0.01 Å(c).

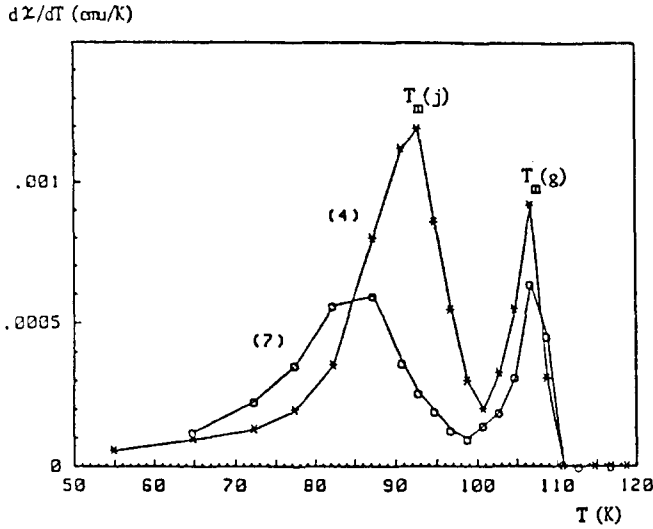^{b} calculated according the Bean model ($j_{cm} = 3M_r/2Vr$ with $r = 2 \times 10^{-4}$ cm).

Figure 1. χ'' vs. T for sample No.4 and No.7.

reduced oxygen content. As an example Table 1 gives the data for sample No. 9 and 10 with nearly identical cation ratio. The use of an $Ar/O_2(8\%)$ atmosphere reduces the firing time by about a factor of 10 to 13 h; likewise the Meissner fraction is drastically increased to 55% (No. 9: 30%; Fig. 2).

cuprates [4,5]. Consequently, the sol/gel route produces the better material with likewise improved critical current densities.

Furthermore, the transport properties are influenced by the Bi:Pb:Sr:Ca:Cu ratio. An exceptional high transport critical current density for a bulk material of $j_{ct} = 1.8 \times 10^3$ Acm^{-2} is obtained for a cation ratio of 1.8:0.2:1.9:2.1:3 (No. 8 in Table 1).

3.2. Air and $Ar/O_2(8\%)$ preparation

Studies of the influence of the different gas atmospheres on the 2223 formation result for several processing routes uniformly in the superiority of a
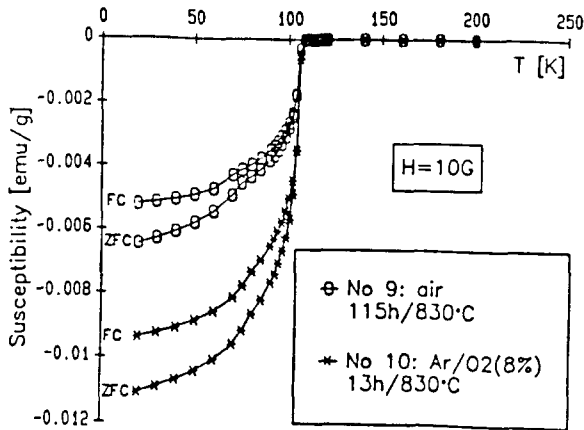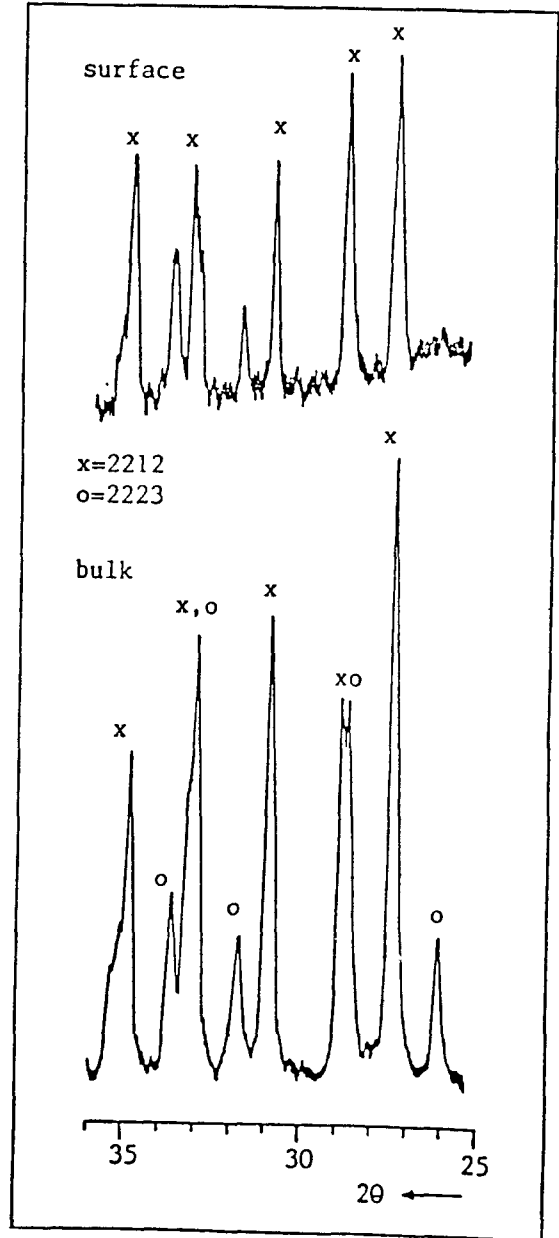

Figure 2. χ vs. T for sample No.9 and No.10.

Figure 3. XRD sections for sample B after post-annealing for 155h at 835°C.

3.3 Melt processing of ceramics

For a study of the 2223 formation via a melt process pellets with identical cation ratio 1.8:0.4:2:1.8:3 but prepared from precursor powders with different preannealing times were used (A: no preannealing, absence of 2212 or 2223; B: 60 h/835°C, 2212:2223 ≈ 9:1; C: 400 h/835°C; 2212:2223 ≈ 1:1). From X-ray investigations of the solidified melt follows the presence of small amounts of a 2201 crystalline phase in addition to a glassy majority phase. According to 3.2. the 2223 formation is significantly accelerated in an $Ar/O_2(8\%)$ atmosphere. Consequently, these data are only reported. XRD investigations of the composition of the surface and the interior of the recrystallized pellets indicate that on the surface nearly exclusively the 2212 (x) phase is produced, whereas 2223 (o) grows in the interior beneath this 2212 layer (cf. the corresponding XRD sections in Fig. 3). This observation demonstrates that the 2212 growth is not only favoured on a microscopic scale [4,5] at the grain boundaries but also in a macroscopic scale on the surface of a bulk material.

From a comparison of the 2223 quantity formed after a fixed time from the various precursor materials follows a clear correlation between the 2223 content of product and precursor. This effect is explainable by the high viscosity of the melt, which conserves the positional neighbourhood of the 2223 constituents despite the intermediate destruction of the 2223 crystal structure by melting. Accordingly, the largest 2223 proportion is obtained from a precursor with a 2223 content of about 90% (cation ratio 1.7:0.5:2.0:1.8:3). This ceramic is characterized by a very high critical current density j_{cm} of 1.4×10^7 Acm^{-2} at 5 K/0 T.

Acknowledgement

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