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DEVELOPMENT OF SUPERCONDUCTING PHASES IN BSCCO AND Ba–BSCCO BY SOL SPRAY PROCESS

S. K. Durrani[1], *A. H. Qureshi*[1*], *S. Qayyum*[2] *and M. Arif*[1]

[1]Materials Division, PINSTECH, P. O. Nilore, Islamabad, Pakistan
[2]Chemistry Department, University of Peshawar, NWFP, Pakistan

The effects of barium substitution for Bi or Sr sites on the growth of superconducting phases have been studied. The sol spray process has been used to synthesis the Bi–Sr–Ca–Cu–O (BSCCO) and Ba–BSCCO homogeneous ceramic powders. Thermogravimetric (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) techniques were employed to characterize the synthesized materials. The electrical resistance was measured by classical d.c. four-probe technique. It has been observed that sol spray process has affected the physico-chemical properties of the materials and also avoid the use of chelating agent as in the case of sol gel process. In addition to the $Bi_2Sr_2CaCu_2O_8$ (2212) phase Ba doped specimens also contained $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2223), $BaBiO_3$, $BaCuO_2$ and CuO phases.

The results revealed that the specific effect of barium-doping on either sites (Bi or Sr) seems to avoid the formation of higher volume fraction of the low T_c phase and promoting the formation of $BiBaO_3$, $BaCuO_2$ and CuO along with formation of a high T_c 2223 phase. The substitution of Ba on either sites (Bi or Sr) lower the sintering temperature for the formation of high T_c (small volume fraction) however, the Ba doped specimens also contained non-superconducting phases.

Keywords: *BSCCO system, d.c. four-probe, DTA, high T_c phase, SEM, sol–spray process, superconducting phases, TG, XRD study*

Introduction

A number of investigations have been conducted on bismuth-based superconductors to improve the properties of the system soon after its discovery by Maeda *et al.* [1]. It is evident that partial replacement of bismuth by lead (Pb) enhances superconducting properties such as J_c and T_c [2–7]. The substitution of different elements in the system and study of various related parameters are the subject of several communications [8–16], thus arousing much interest in this field. In the Bi–Sr–Ca–Cu–O (BSCCO) system three superconducting phases exist, $Bi_2Sr_2Cu_2O_7$ (2201) phase (T_c, 20 K), 2212 phase (T_c, 80 K) and 2223 phase (T_c, 110 K). These phases possess resistance to the environmental action and their properties are less dependent on the oxygen stiochiometry when compared with $YBa_2Cu_3O_x$ (YBCO) superconductor materials. For the preparation of BSCCO superconducting materials many methods have been introduced, such as conventional solid state reaction [17], combustion method or self-propagation high temperature synthesis, co-precipitation, use of organic precursors [18] and sol-gel technique [19]. From the processing point of view, sol-gel technique enable the preparation of superconducting BSCCO material with better physico-chemical properties in comparison with conventional solid state reaction as reported by many researchers [20–28]. The sol-gel processing yields powder with smaller particle size improving better homogeneity and stiochiometry control besides, permitting lower sintering temperature and shorter heat-treatment. Apart from usual Pb substitution on the Bi sites, only a few substitutions, such as Ba on Bi or Sr sites or Ni on Cu sites, have been realized in BSCCO. The appropriate amount of added Ba in BSCCO had the affect of raising T_c to a higher temperature region and a single transition phase [29].

The aim of present work is to investigate the effect of barium substitution on physico-chemical properties of bismuth-cuprates superconducting oxide materials using sol spray process. The sol-spray process (modified form of sol gel process) was developed to avoid the use of complexing agent such as citric acid and ethylenediaminetetraacetic (EDTA) acid. It is appealing to study the effect of barium addition on (BSCCO) system, because these belong to the same alkaline earth metal group as strontium and calcium, having different ionic radii. In addition, barium is known to be incorporated as $(Bi_2O_3)^{2+}$ M_{n-1} R_{3n-1}, where M represent Ba^{2+} and R represent Tl^{4+} [30]. It is also intended to observe the effectiveness of sol spray process for achieving highly reactive

* Author for correspondence: ammadqureshi@yahoo.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

and homogeneously mixed precursors which may lead to improvement on the formation kinetics superconducting phases in short span of time and at the lowest possible temperatures.

Experimental

The BSCCO and Ba substituted BSCCO materials were prepared from 'Analar grade' high purity (99.9%) barium, bismuth, strontium, calcium and copper nitrate salts. The required amount of each nitrate was dissolved in demineralized water separately and mixed together to get desired sols. The nominal compositions of the specimens were $Bi_2Sr_2CaCu_2O_{8\pm x}$, $Bi_{1.6}Ba_{0.4}Sr_2CaCu_2O_{8\pm x}$, and $Bi_2Ba_{0.4}Sr_{1.6}CaCu_2O_{8\pm x}$ designated as BSCCO-1, BSCCO-2 and BSCCO-3 respectively. In the present research work the 'sol-gel route' was modified into sol-spray process. Arrangement and characteristics of sol spray process are shown in Fig. 1. The aqueous feed sols of samples were sprayed into the upper end of the vertical Pyrex glass column at a rate of 40 mL/h with help of compressed air atomization. The operating temperature of the column was 155–165°C. The synthesized powder was deposited on the inner walls of Pyrex glass column and finally the dried powder was collected in a Pyrex glass collector placed at the lower open end of column using abrasive glass stick.

Thermal behaviour of the collected powder was studied by TG/DTA. The synthesized powders were first heated at 200°C in oven and then calcined at 600°C for 4 h using box furnace. The calcined powder was used for pellets fabrication using Uni-axil hydraulic press of load capacity 10 ton/in^2 (1 ton/in^2=15.444 MPa). The green pellets were sintered in tube furnace at 840°C in static air for 48 h.

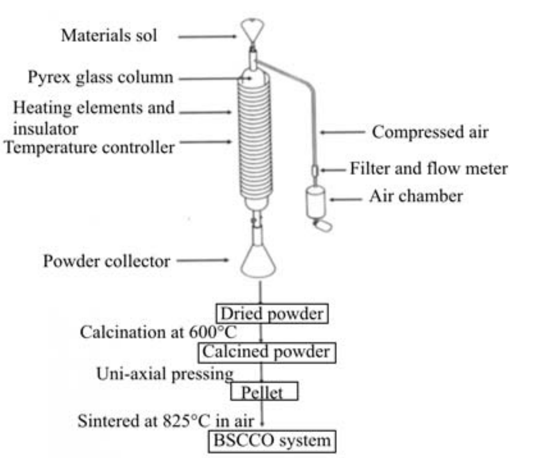

Fig. 1 Schematic diagram for sol spray process apparatus

Phase analyses of all sintered specimens were carried out by using X-ray diffraction (XRD). The morphology of sintered pellets was observed with scanning electron microscope (SEM) and phases analyzed by using electron probe micro-analyzer (EPMA) attached with SEM. The transition temperatures were determined by a conventional d.c. four-probe method using silver-paste to make electrical contact on the specimen. The visual demonstration of the Meisser effect was checked before the d.c. electrical resistivity measurements by four-probe technique.

Results and discussion

Thermal analyses (TG/DTA), Fig. 2a–c, were carried for the powders BSCCO-1, 2 and 3, which were collected at the bottom of the sol spray process. It can be inferred from figure that all the specimens decomposed completely in a series of steps. The curves revealed that after initial mass loss of water, large and small endothermic peaks in the DTA curves were occurred around 600 and 660°C, respectively, with major mass loss (TG curve) in all the

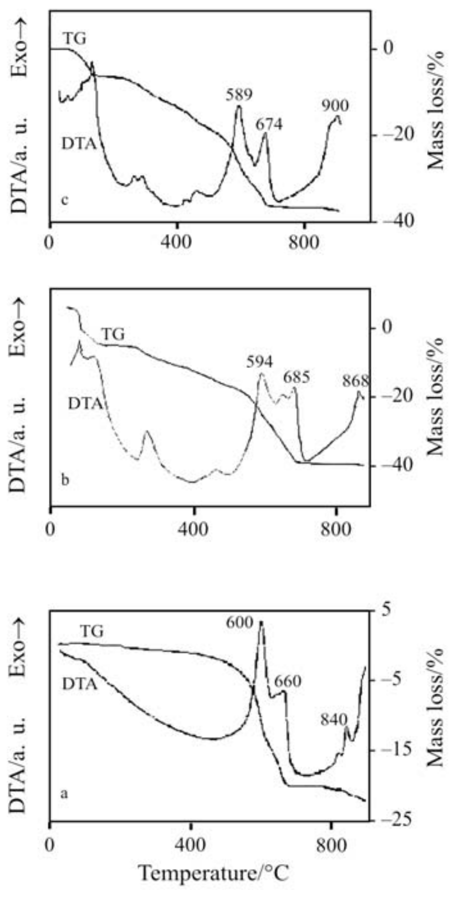

Fig. 2 TG/DTA curves of a – BSCCO-1, b – BSCCO-2 and c – BSCCO-3

specimens. Figures 2b and c show the identical behaviour with the substitutions of Ba either against Bi or Sr. However, the large endothermic peaks (Figs 2b and c) decreased down as compared to sample without the addition of Ba, Fig. 2a. It was also observed that the temperature of this peak reduced slightly with the addition of Ba against Sr relatively to Bi. The peaks around 600°C is corresponded to the formation of 2201 superconducting phase and impurities such as CaO and CuO [31]. The small endothermic peaks around 660°C might be attributed to the formation of $CaCuO_3$ phase. Another endothermic peak in DTA curve around 840, 870 and 890°C was also occurred in specimens BSCCO-1, 2 and 3 respectively. It has been observed [32] that at a temperature lower than 800°C the Ca_2CuO_3 is formed by the reaction between CuO and CaO and at a temperature above 800°C, the Ca_2CuO_3 reacts with 2201 in the presence of excess CuO to produce the 2212 phase. So, the endothermic peaks around 840, 870 and 890°C correspond to the formation of 2212 phase. The above results may be explained by the sequence of reactions as follows:

$$2CaO + CuO \rightarrow Ca_2CuO_3 \text{ followed by}$$

$$2(2201) + CuO + Ca_2CuO_3 \rightarrow 2(2212)$$

It has been noticed [18, 33, 34] that the optimum sintering temperature for the formation of superconducting phases in the BSCCO system occurred over the range from 840–870°C. DTA curve, Fig. 2a, revealed that 840°C is the effective temperature for the development of superconducting phases. For comparison, the pellets of the specimens BSCCO-1, 2 and 3 were sintered at 840°C to observe the formation of superconducting phases.

X-ray diffraction (XRD) patterns of specimens BSCCO-1, 2 and 3 sintered at 840°C for 48 h are shown in Fig. 3a–c. The characteristic peak d-spacing 15.3 Å indicates that major phase in the BSCCO-1, Fig. 3a, was 2212. However, high T_c 2223 phase was not found in this specimen but CuO and $CaCuO_3$ phases were observed. According to the XRD data the crystal structure obtained was orthorhombic with lattice parameters a=5.41, b=5.42 and c=30.9 Å. The lattice parameters values obtained for the 2212 phase are in good agreement to those reported [35, 36].

Figure 3b and c show the XRD patterns of specimens BSCCO-2 and 3. These specimens contained low T_c phase (2212) however, in a lesser amount relative to BSCCO-1. In addition to the 2212 phase these specimens also contained 2223, $BaBiO_3$, $BaCuO_2$ and CuO phases. These results revealed that the specific effect of barium-doping on either sites (Bi or Sr) seems to avoid the formation of higher volume fraction of the low T_c phase and promoting the formation of $BiBaO_3$, $BaCuO_2$

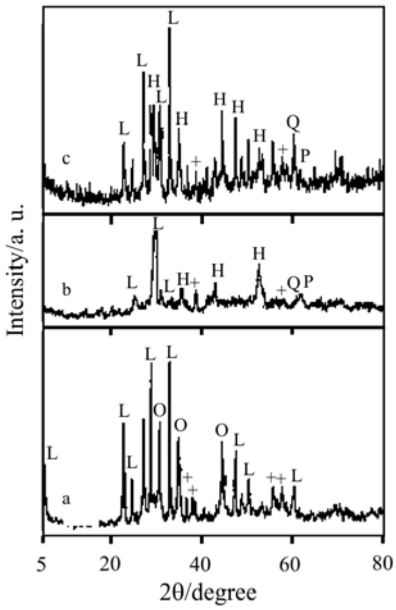

Fig. 3 XRD patterns of specimens a – BSCCO-1, b – BSCCO-2 and c – BSCCO-3 (H=2223, L=2212, O=Ca_2CuO_3, +=CuO, Q=$BaBiO_3$, P=$BaCuO_2$)

and CuO along with formation of a high T_c 2223 phase. The XRD results of specimens (BSCCO-2 and 3) were found to be close similar with earlier findings [37]. These results revealed that with the substitution of Ba on either sites (Bi or Sr) lower the sintering temperature for the formation of high T_c (small volume fraction) however, the Ba doped specimens also contained non-superconducting phases.

SEM micrographs for sintered pellets of BSCCO-1, 2 and 3 are shown in Fig. 4a–c. Plate like morphology was observed in BSCCO-1 specimen, Fig. 4a. The crystalline phases were observed in the sintered specimen BSCCO-2, Fig. 4b, which is consisted of randomly oriented plate-like morphology with 8–12 and 15–25 μm in size. Crystals with a needle shape were also observed which showed the presence of 2223 phase. The lamellar morphology was also observed in BSCCO-2 specimen. In Ba-doped (at Sr-site) specimen BSCCO-3, a Cu-rich 2223 phase was found along with plate like and quite different well-connected chain-like crystals, Fig. 4c. The black hole in the micrograph was indicated the presence of porosity. BSCCO-3 had a non-uniform crystal size in the range of 12–15 and 20–25 μm.

The phases exist in the specimens BSCCO-1, 2 and 3 were analyzed by using electron probe micro-analyzer (EPMA) attached with SEM and these results (mass%) are tabulated in Table 1. The mass relationships among reacting chemical species i.e., empirical formulae (number of atoms per unit cell) of BSCCO-1, 2 and 3 were calculated using chemical stiochiometry method [38]. It was revealed from

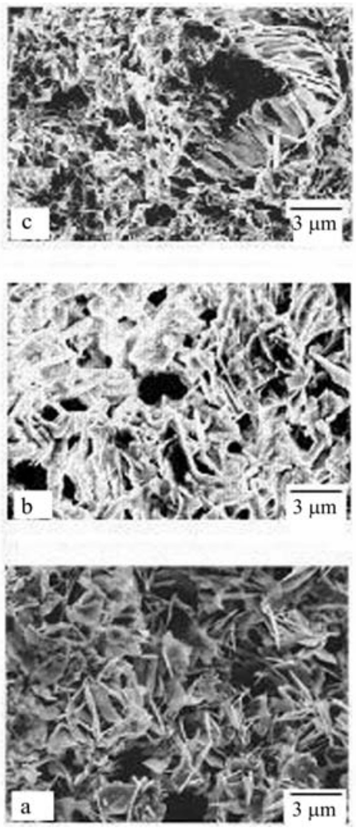

Fig. 4 SEM micrographs of sintered specimens a – BSCCO-1, b – BSCCO-2 and c – BSCCO-3

Table 1 that plate like crystals have composition of 2212 phase.

The temperature-resistance curves for sintered specimens of BSCCO-1 and barium-doped BSCCO-2 and 3 specimens are shown in Fig. 5. The two slope changes can be seen with T_c of 80 and 108 K for the specimens BSCCO-2 and 3, which indicated that these specimens contained both the low (2212) and high (2223) T_c phases. In contrast to these specimens BSCCO-1 sintered at same heating rate and duration showed T_c at about 74 K, which inferred that this specimen has only 2212 phase. These results

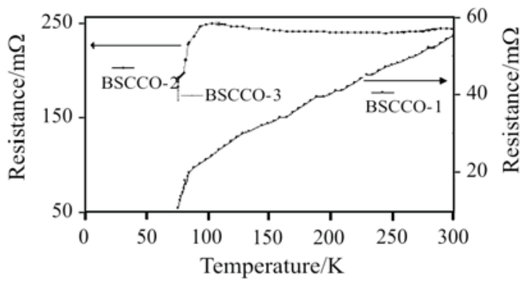

Fig. 5 Electrical resistance *vs.* temperature of BSCCO-1, BSCCO-2 and BSCCO-3

are in good agreement with the XRD data as discussed earlier.

Conclusions

- Superconducting material has been successfully prepared by sol spray process, which is to be more convenient route as compared to purely sol-gel process because in the present process mixed nitrate solution (without addition of complexing agent) are directly convert to powder rather than gel. This process has advantages of good homogeneity, ease of compositional control, low temperature processing and versatile shaping over other techniques.
- DTA results revealed that the peaks move toward lower temperature in the sample in which barium is substituted against the strontium site.
- XRD results showed that only 2212 phase is present in BSCCO-1 while both 2212 and 2223 phases are existed in Ba doped specimens (BSCCO-2 and 3).
- SEM micrographs and EPMA results showed the presence of plate-like crystals in all specimens which have the composition of 2212 phase. Crystals with a needle shape were also observed in

Table 1 EPMA analysis of specimens BSCCO-1, 2 and 3

Specimens	Mass%					
	Ba	Bi	Ca	Cu	Sr	Oxygen
BSCCO-1	–	14.69±0.34	7.36±0.26	13.57±0.51	13.92±0.7	50.46±1.5
BSCCO-2	2.65±0.5	10.43±0.03	7.82±0.02	13.65±0.55	13.44±0.24	55.01±1.7
BSCCO-3	3.09±0.08	14.43±0.09	7.91±0.13	13.86±0.11	12.43±0.20	56.11±1.8

	Number of atoms						Oxide formulae	Phases
	Ba	Bi	Ca	Cu	Sr	Oxygen		
BSCCO-1	0.00	1.99	1.0	1.84	1.86	6.86	$Bi_{1.99}Sr_{1.86}Ca_{1.0}Cu_{1.84}O_{6.86}$	2212
BSCCO-2	0.39	1.53	1.0	1.86	1.82	8.06	$Bi_{1.53}Ba_{0.39}Sr_{1.82}Ca_{1.0}Cu_{1.86}O_{8.06}$	2212
BSCCO-3	0.40	1.91	1.0	1.85	1.55	8.13	$Bi_{1.91}Ba_{0.4}Sr_{1.55}Ca_{1.0}Cu_{1.85}O_{8.13}$	2212

the specimens BSCCO-2 and 3, which showed the presence of 2223 phase.

- D.C four-probe method indicated that both the phases 2212 and 2223 are present in BSCCO-2 and 3, however only 2212 phase is present in BSCCO-1.

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