

FORMATION OF LOW T_c SUPERCONDUCTING PHASE IN BSCCO SYSTEM

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The sol spray process (modified form of sol gel) has been used to prepare Bi-Sr-Ca-Cu-O (BSCCO) homogeneous powder. In sol spray process, the prepared sol solutions have been dehydrated directly into BSCCO ceramic powder by spraying into a preheated temperature controlled pyrex glass column by means of compressed air atomization without the addition of organic chelating agent or organic templates. The prepared BSCCO material was characterized by thermogravimetric (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) techniques. Elemental compositions of BSCCO oxide powder and calcined pellet were verified by inductively coupled plasma emission spectrometer (ICP-OES) and electron probe micro analyzer (EPMA) attached with SEM. The results of these techniques were compared and correlated statistically. Student t-test and variance ratio test (F-test) were performed for the significance of results by analysis of variance (ANOVA). The dependence of electrical resistance versus temperature was recorded by classical four probe technique. It has been observed that sol spray process did affect the physico-chemical properties of BSCCO superconductor oxide. The superconducting phase identified by above mentioned techniques mainly shows the higher %age of low T_c phase $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212) with transition temperature of 85 K.

Keywords: BSCCO, Sol spray process, Superconductors, 2212, ANOVA

1. Introduction

A number of investigations have been conducted on superconducting materials based on Bi-Sr-Cu-Ca-O (BSCCO) systems to improve their properties soon after its discovery by Maeda et al. [1]. This system has critical transition temperatures, T_c ranging from 22 to 125 K, according to the copper content [2]. In the BSCCO system three superconducting phases exist, with nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n=1-3$). These phases are 2201 phase ($n=1$, $c=24.6\text{ \AA}$, $T_c=10\text{K}$), 2212 phase ($n=2$, $c=30.94\text{ \AA}$, $T_c=85\text{K}$) and 2223 phase ($n=3$, $c=37\text{ \AA}$, $T_c=110\text{K}$). The current maximum T_c for this system is 110K for the 2223 phase [3]. These compounds are resistant to the environmental action and their properties are less dependent on the oxygen stoichiometry when compared with $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) superconducting materials. Several methods of synthesis have been employed for preparing the cuprate system, with the objective of obtaining pure monophasic products with good

superconducting characteristics. Such methods include conventional mixed oxide [4-5], combustion method or self-propagation high temperature synthesis [6], co-precipitation [7], use of organic precursors [8] and sol-gel method [9]. It has been stated in numerous investigations [8-19] that sol gel methods enable the preparation of superconducting materials Bi-Sr-Ca-Cu-O with better physico-chemical properties in comparison with conventional mixed oxide technique. The sol gel processing yields powder with smaller particle size, gives better homogeneity and stoichiometry control as well as permits lower sintering temperature and shorter heat-treatment. In the present study bismuth-cuprates superconductor oxide material was prepared by sol spray process (modified form of sol gel process) with an aim to determine the feasibility of the process for the production of phase-stabilized bismuth-cuprate superconducting oxide material to avoid the use of organic chelating agent or template and evaporation.

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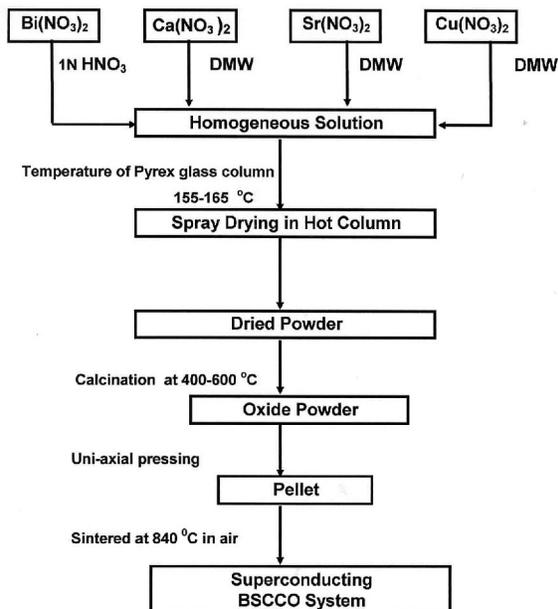


Figure 1. Flow sheet of sol spray process.

2. Experimental

2.1. Materials

All the chemicals used i.e., bismuth, strontium, calcium and copper nitrate salts were reagent grade (99.9%) and used without further purification. Double distilled and demineralized water (DMW) was used as a solvent.

2.2. Production of specimens

During synthesis of BSCCO superconducting specimens the required amounts of each nitrate was dissolved in demineralized water (DMW) separately and were mixed together mildly to get desired sols. The prepared sol solutions were dehydrated directly into powder by spraying into a preheated temperature controlled pyrex glass column using compressed air atomization as shown systematically in Figure 1. The aqueous feed sol of sample was sprayed into upper end of vertical pyrex glass column at a rate of 40ml/ hour. The operating temperature of column was maintained at 155-165°C. The powder was deposited on the inner walls of pyrex glass column and finally the dried powder was collected in a glass collector placed at the lower open end of column using abrasive glass stick. Before grinding some of the powder specimens of bismuth-cuprate were first heated at 200°C in static air oven and

then calcined at 600 - 840°C for 3-4 hours using box furnace. The calcined specimens were furnace cooled and ground to fine powder. The oxide powder of bismuth-cuprate was used for pellet fabrication. The pellets were prepared using uniaxial hydraulic press of load capacity 10 ton/in² (1ton/in² = 15.444 Mpa). The green pellets designated as SD1, SD2, SD3, SD4 &SD5 were sintered in static air tube furnace at 800, 810, 830, 840 & 850°C respectively for different durations. The heating rate for the furnace during sintering of pellet was 10 °C/min. and for cooling was 50 °C/min.

2.3. Characterization of specimens

The elemental composition of sintered compacts was measured by wet chemical method and inductively coupled plasma emission technique by using ICP-OES spectrometer. Simultaneous thermal analyzer (STA NETZSCH STA-409) was used to study the thermal decomposition. A known amount of homogeneous specimen of BSCCO was placed into a special alumina crucible and weighed on balance pan, which was then transferred into the balance arm inside the furnace. The furnace was then switched on under the temperature programme via the TG processor. Specimens were scanned from 30 to 1000 °C in air at heating rate 10 °C/min. A horizontal high temperature differential dilatometer with an Al₂O₃ reference was used for dimensional change studies. Heating and cooling rates of dilatometer were 10°C/min and 50°C/min. respectively. Crystallinity and phase structure of all sintered and calcined specimens were determined by X-ray diffraction (XRD). Morphology of BSCCO phases was observed with SEM and phases were analyzed with electron probe micro analyzer (EPMA) attached with SEM. The d.c. electrical resistance was measured by employing standard four-probe technique. The electrical contacts were fixed and air conducting silver-paste was used as electrodes. The temperature was monitored by calibrated k-type thermocouple in the range of 77-300 K. The accuracy was 0.5K and measuring current was 5mA. The visual demonstration of the Meissner effect was checked before the d.c. electrical resistivity measurement by four probe technique.

Table 1: Percent elemental composition measured by ICP-OEC and SEM.

Sr.No.	Specimen BSCCO	Sintering Temperature °C	Sintering duration Hrs	% Elemental Composition			
				Bi	Sr	Ca	Cu
1.	SD1	800	24	13.16 ± 0.25	11.23± 0.18	5.36± 0.15	12.38± 0.12
2.	SD2	810	48	13.85± 0.22	12.47± 0.14	6.25± 0.11	12.86± 0.10
3.	SD3	830	72	14.11± 0.19	13.62± 0.13	6.91± 0.17	13.25± 0.16
4.	SD4	840	48	14.58± 0.44	13.92± 0.71	7.36± 0.26	13.92± 0.53
5.	SD5	850	72	16.25± 0.15	13.86± 0.09	7.45± 0.20	14.05± 0.21

Coeff. of variation = 2.82 for Bi Standard Error= 0.18 , Skewness = 0.35, P-values < .005, degree of freedom =4

3. Results and Discussion

The colour of prepared BSCCO superconducting specimens (SD1-SD5) was found pure greenish-brown. The pellets of powder specimens were sintered at temperature range 800-840°C. The sintered specimens SD1-SD5 were analyzed by ICP-OES & EPMA for chemical compositions and results are presented in Table 1. On the basis of these results it was found that specimen SD4 contain significant value fraction of low T_c phase. The latter results and discussion have been based on this specimen.

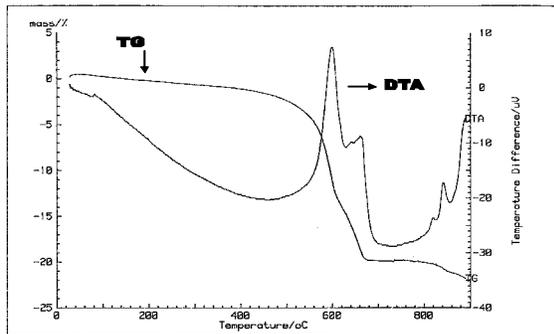


Figure 2. Thermal and differential analysis (TG/DTA) curve of powder specimen SD4 dried at 200 °C

TG-DTA thermograms of powder specimen SD4 dried at 200°C are presented in Fig. 2. It is revealed from TG-DTA thermograms that after initial weight loss of water, the first exothermic peak is believed to be due to the crystallization of CaO or CuO. The peak at around 599°C is due to crystallization of $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\xi}$ (2201) phase and phase such as Ca_2CuO_3 . The peak at around

620°C can be due to crystallization or phase transformation from 2201 to $\text{Bi}_2\text{Sr}_2\text{CaCu}_3\text{O}_{8+x}$ (2212). At higher temperatures the tendencies of crystallization of the 2201 phase decrease and at about 800°C disappear. There is one endothermic peak appearing at 790-830°C which corresponds to maximum weight loss i.e.~22.5% as shown in TG curve Fig. 2. The endothermic peak in DTA curve at temperature of 830 °C occurred due to the decomposition reaction of superconducting phase. It has been noticed [20-21] 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 revealed that 840°C is the effective temperature for superconducting phase.

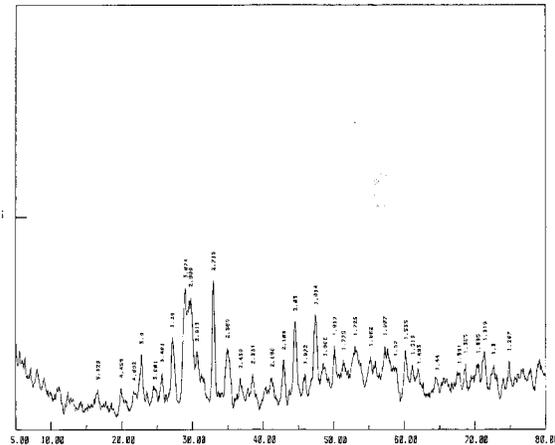


Figure 3. X-ray diffraction patterns of powder specimen SD4 dried at 200 °C.

Figures 3 & 4 represent X-ray diffraction patterns of powder specimen SD4 dried at 200°C

and sintered at 840°C for 48 hrs. The characteristic peak d-spacing 15.3 Å indicates that major phase in sintered specimen SD4 was 2212. However, high T_c 2223 phase was not found in this specimen. Some CuO and Ca_2CuO_3 phases were also present. There is no change in phase after sintering at higher temperature (840°C). This can be explained from DTA curve as shown in Figure 2, where it is evident that there was no change in the curve over temperature 840°C. This shows the stability of 2212 phase in the specimen SD4. XRD pattern values obtained for the 2212 phase are in good agreement to those reported [22-23]. SEM micrograph for sintered pellet of specimen SD4 is presented in Figure 5. The figure revealed that plate-like crystals have composition of 2212 phase with 8-12 µm in size.

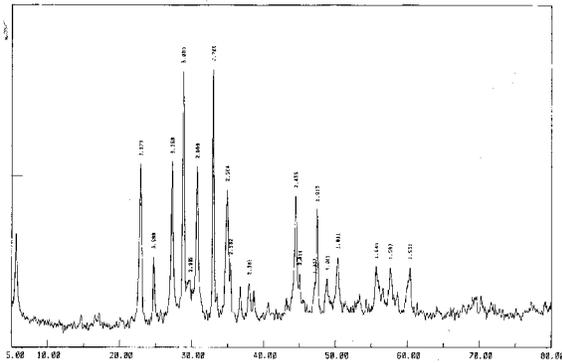


Figure 4. X-ray diffraction patterns of specimen SD4 sintered at 840 °C.

The temperature-resistance curve for sintered specimen SD4 is given in Figure 6. The ceramic pellet of specimen SD4 indicate only 2212 phase near T_c 75 K, which showed that T_c is dependent on sintering time and duration time. These results are in good agreement with the XRD data.

The statistical analysis was performed for the selected specimen SD4 and element bismuth only for verification of accuracy and reliability of the techniques. It was revealed from Table 1 that the chemical composition of specimen SD4 was found statistically significant and reliable at 5% level. Standard deviation (s), co-efficient of variation, skewness were calculated from one set of five determinations and from another six measurements. The difference between the means results of two techniques was correlated and ANOVA was applied to regression using F- and t-test with help of VisualStat and TC-plot software.

The precision was expressed as a 95% confidence limit. The results of statistical analysis and ANOVA for regression are presented in Table 2. Since the calculated F-values are greater than the tabulated values at 5% level of confidence, the results of means are significant. The normality, constant variance and power of performed tests are signifying positive values [24-25].

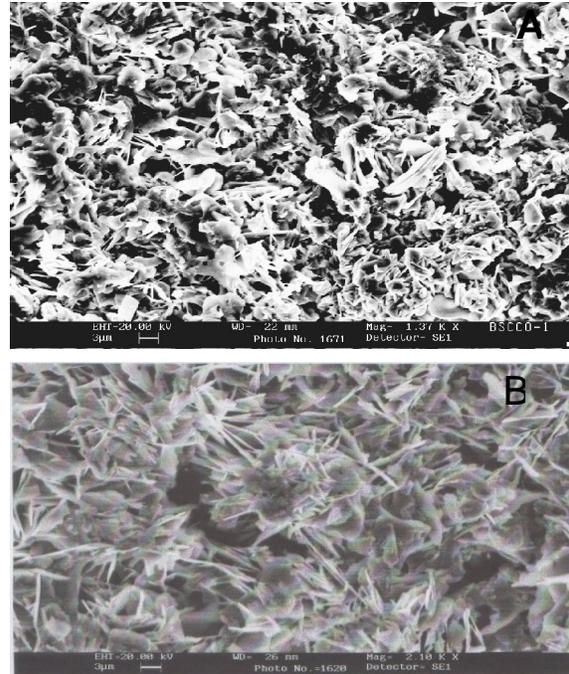


Figure 5. scanning electron micrographs of specimen SD4 (A) sintered at 820 °C, (B) sintered at 840 °C

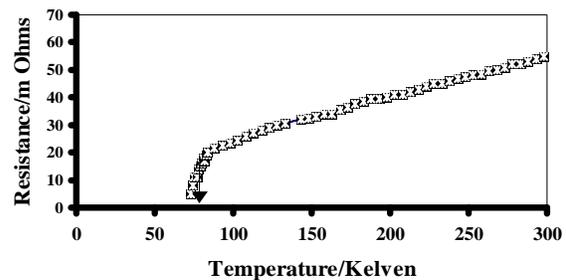


Figure 6. Electrical resistance vs. temperature of specimen SD4.

The characteristics of sintered ceramic specimen SD4 are given in Table 3. The weight relationships among reacting chemicals species i.e., empirical formulae (number of atoms per unit cell) of specimen SD4 was calculated using chemical stoichiometry method [26].

Table 2 : Analysis of variance and regression coefficient for testing significance of means results of SEM and ICP techniques for the measurement of elemental composition of bismuth.

Regression Coefficients : ICP vs SEM							
	Coefficient	Standard error	Standard coefficient	t-values	Probability	Lower 95%	Upper 95%
Intercept	6.93	5.41		1.28	0.29	-10.28	24.14
SEM	0.50	0.35	0.63	1.42	0.25	-0.63	1.63
Analysis of Variance							
	Degree of freedom	Sum of square	Mean of square	F-distribution	Probability		
Regression	1	0.27	0.27	2.00	< 0.005		
Residual	3	0.40	0.13				
Total	4	0.67					

$$A = 6.93 + 0.50 * B$$

Densities of compact powders were estimated by using the equation given below.

$$\rho/\rho_{th} = \rho_o/\rho_{th} [1 - \Delta l/l_o]^{-3}$$

Where ρ_o/ρ_{th} was the initial density, $\Delta l/l_o$ was the total relatively thermal shrinkage measured from dilatometry and ρ/ρ_{th} was the relative density of the sintered compact [27]. It was observed that the value of sintered densities was greater than the green densities due to the shrinking and deterioration of the materials at the sintering temperature. The percent theoretical density ($86\% \pm 2.3$) was achieved at temperature 840°C . Above this temperature there was slight decrease in %theoretical density. Densification proceeds very quickly in these fine powders. No significant changes occurred in densities at higher firing temperature. Figure 7 illustrates the particle size distribution measured by laser particle size analyzer for specimens SD4. The particle size distribution curves indicate that median diameter of particles for powder specimen SD4 are in the range of $5.86 \pm 0.39 \mu\text{m}$.

Table 3. Physico-chemical characteristic of specimen SD4 superconducting material.

Physico-Chemical Properties	
Expected oxide formulae	$\text{Bi}_{1.99} \text{Sr}_{1.86} \text{Ca}_{1.0} \text{Cu}_{1.84} \text{O}_{6.86}$
Green density (gm. cm^{-3})	1.25 ± 0.05
Sintered density (gm. cm^{-3})	1.67 ± 0.14
Theoretical density (%)	86 ± 2.3
Expected phases	2212 (Cu-rich), 2223 (CuO , Ca_2CuO_3) phases
Phase morphology	Plate-like, needle-like and flake-like
Particle size (μm)	5-7.5
Sintered temperature $^\circ\text{C}$	840
Median diameter of particle (μm)	5.86 ± 0.39

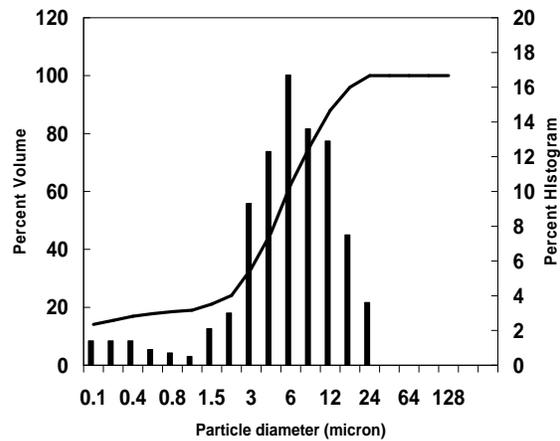


Figure 7. Particle size distribution of powder specimen SD4.

Conclusions

- Fine powder of Bi-Sr-Cu-Ca-O (BSCCO) superconducting oxide material has been obtained by sol spray process. Sol spray process is found to be more simple route as compared to sol-gel process because in this present process salt solutions are directly converted into oxide powder product rather than gel. The process can produce quite dense and significant control of the particle morphology. The prepared powder specimens can be sintered into uniform and fine grained ceramic at lowered temperature (840°C) compared to others methods.
- Sol spray process has advantages of good homogeneity, ease of compositional control and low temperature processing.
- SEM micrographs and EPMA results showed the presence of plate-like crystals in specimen SD4 which have composition of 2212 phase.

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