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High T_C superconducting powders synthesis from aerosol

Lidija Mančić[a,*], Olivera Milošević[a], Nebojša Labus[a], Momčilo Ristić[b]

[a]*Institute of Technical Sciences of the Serbian Academy of Sciences of Arts, Knez Mihailova 35/IV Belgrade, Yugoslavia*
[b]*Center for Multidisciplinary Studies, University of Belgrade, Belgrade, Yugoslavia*

Abstract

Spray pyrolysis, as one of the novel powder processing methods, has been applied for the synthesis of 2223 phase of the Bi-based high T_c superconducting oxide ceramic materials. The process is performed through heterogeneous chemical reactions in dispersed system (aerosol) formed from common nitrates solution ultrasonically with the resonant frequency of 1.7 MHz. Synthesis through aerosol enables generation of ultrafine multicomponent particles with improved compositional homogeneity provided by higher surface reaction and the absence of compositional segregation. Consequently, spherical, solid, slightly agglomerated submicronic particles (below 400 nm) with the uniform particle size and the particle size distribution are produced. The obtained particle morphology is discussed in terms of precursor chemistry and processing parameters.

Keywords: Electron microscopy; Oxide superconductors; Spray pyrolysis

1. Introduction

Since the discovery of high T_c superconducting oxide, tremendous efforts have been made in the synthesis and characterization of these materials. Research today clearly indicates that their demanded properties are related to the ultrafine microstructure and extra purity. In the case of microwave applications the domain device characteristics that have to be obtain are low input impedance, a transresistent gain mechanisms and sufficient output impedance to allow a direct interface with semiconductor circuitry. The first step in providing of these properties is improvement of precursor characteristics determined by applied synthesis method. Under conventional preparation conditions in the Bi-based high temperature superconducting system, the 2212 phase ($Bi_2Sr_2CaCu_2O_x$) is the most stable, while either partial substitution of bismuth with lead[1] or reduction of oxygen partial pressure during sintering[2] enhances the 2223 phase ($Bi_2Sr_2Ca_2Cu_3O_x$) formation. Ultrasonic spray pyrolysis, as a dispersion phase powder processing method is capable to produce nanophased particles with improved structural homogeneity when Bi–Pb–Sr–Ca–Cu–O system is considered.[3] The process involves aerosol formation ultrasonically from the precursor salt solutions and control over aerosol decomposition in the high temperature flow reactor through different processes of evaporation, drying, precipitation and decomposition. High surface reaction generally enables complete conversion of the starting to the final material in a short reaction time and also retains precursor cations stoichiometry in the final particles[4], but some problems related to outstanding phase segregation in the droplet during multicomponent powders synthesis from aqueous (pure nitrates) precursors are still present.[5]

In this work the interests are focused on 2223 ($Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$) phase synthesis from a pure nitrates solution with the purpose to provide the control over chemical stoichiometry, purity, shape and size of synthesized particles and to define the influence that the precursor solution and processing parameters have on particle morphology and structure.

2. Experimental

Precursor solutions were prepared by dissolving the appropriate amounts of corresponding metal nitrates [$Bi(NO_3)_3\times5H_2O$, $Pb(NO_3)_2$, $Sr(NO_3)_2\times4H_2O$, $Ca(NO_3)_2\times H_2O$ and $Cu(NO_3)_3\times3H_2O$] in 5% nitric acid, in order to obtain a 1 mol/dm^3 solution. The starting cation ratio was Bi:Pb:Sr:Ca:Cu = 1.8:0.2:2:2:3. Characterization of the prepared solution included measuring the pH value (0.64), density (1.17 g/cm^3), viscosity (0.68×10^3 Pas) and surface tension (67 mN/m^2). Based on these results, the aerosol mean droplet size[6] (2.71 μm) and aerosol droplet density[5] (8.28×10^6 droplets/

* Corresponding author. Fax: +381-11-637239.
E-mail address: lydia@itn.sanu.ac.yu (L. Mančić).

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cm^3) were calculated. The obtained values predict that particle formation could be considered as the case when one particle is obtained from one droplet.[7] The experimental set-up employed to study the $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ synthesis process consisted of an aerosol generator operated at 1.7 Mhz, a twin-zone tubular flow reactor (1.7 m long, 3.2 cm dia quartz tube) and a membrane filter where the produced particles were collected. The carrier gas (N_2) flow rate was 1 dm^3/min and the temperature profile in the reactor was increased-humped. The maximum temperature was 350 °C in the first zone and 840 °C in the second one. The filter temperature was maintained above 100 °C to avoid the condensation process. The droplet velocity was 0.02 m/s and the droplet/particle residence time in the heated zone was 63 s, while aerosol decomposition at maximum temperature proceeded in a few seconds.

Thermal analysis of the dehydrated precursor and as-prepared powder were performed in accordance to DTA analysis (Shimatsu DTA-50) using alumina crucible and nitrogen as a purging gas. During the analysis, the temperature was increased from room temperature to 900 °C at a constant heating rate of 10 °C/min.

The morphology and compositional homogeneity of obtained powder were determined in accordance to scanning electron microscope (SEM) analysis and qualitative and semi-quantitative energy dispersive X-ray spectroscopy (EDS). SEM analysis was applied on the two types of produced powder specimens: loose powder and polished section. The powder surfaces were coated by conducting films (carbon for magnifications 1:2000 and 1:3000 and gold for magnifications 1:20,000 and 1:30,000). For the preparation of polished specimens an epoxy resin was added to the powders and a conventional metalographic polishing process was applied. Polished specimens were coated with carbon and analyzed with a magnification of 1:30,000. Semi-quantitative EDS analysis was carried out through standard ZAF correction with cobalt specimen as the reference material. Oxygen content is determined as element by difference.

3. Results and discussion

In accordance to the differential thermal analysis of the dehydrated precursor mixture and obtained powder, (Fig.1), as well as, previously published data for the investigated system,[7] it was noticed that nitrates decomposition was finished in the temperature range up to 300 °C. Further changes in the phase composition of the samples take places at the temperatures 480 °C (CuO and Cu_2O crystallization) and 590 °C (Ca_2PbO_4 and $Bi_2Sr_2CuO_x$- 2210 phase formation).[8] According to literature,[9] the mechanisms of the 2223 phase formation is not well understood but generally this phase exists at all temperatures above 820 °C. Comparison of our

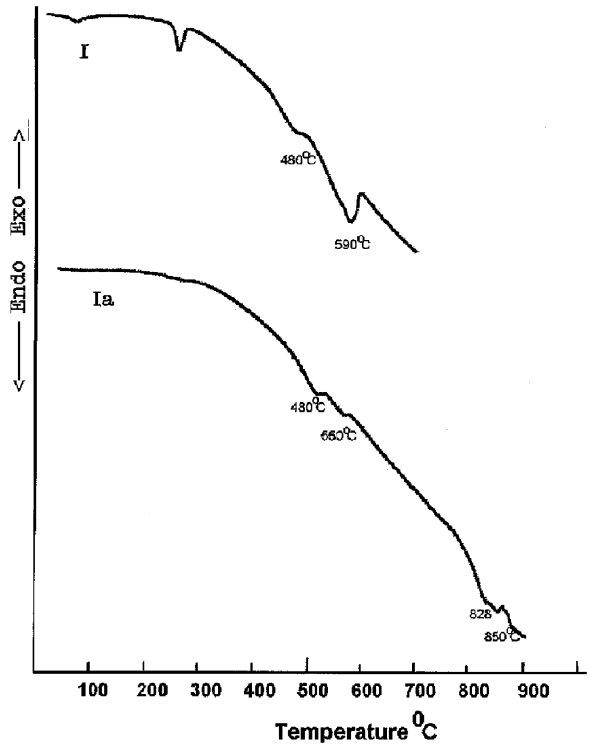

Fig. 1. DTA curves of the dehydrated precursor (I) and as-prepared powders (Ia).

experimental results with studies of others autors[8–10] implies 2223 high T_c phase formation in the temperature range up to 820 °C through disproportional and simultaneous precipitation of 2212 and 2223 phase in the presence of liquid (probably rich in Pb, $(Ca,Sr)_2PbO_4$ and 2201). DTA data of powders obtained through pyrolysis indicates uncompleted reactions in the temperature range around 550 °C pointing out insufficient particles residence time in the reaction zone and further 2223 phase formation up to 820 °C, (curve Ia on Fig. 1). Presence of several eutectics in this temperature area (peaks at 828 and 850 °C) suggests that 2223 phase formation takes place until this liquid exist in appropriate stoichiometry and quantity. Appearance of liquid phase during synthesis process increases the contact area among particles and accelerate 2223 phase formation.[10] As the phase development study was not performed results pointed above should take as tentative suggestions for the reaction mechanisms.

From the SEM photomicrograph of powder synthesized by the spray pyrolysis method, (Fig. 2a), two types of particles are visible. Large polyhedral-like particles with smooth surface and longer axes with a size around 15 μm are presented together with the slightly agglomerated particles with the mean particle size ranging below 400 nm. In accordance to the present results, Fig. 2b, spherical particles are characterized by relatively smooth surface and uniform size. Qualitative EDS analysis taken from the point marked 1 (at Fig. 2a), corresponding to

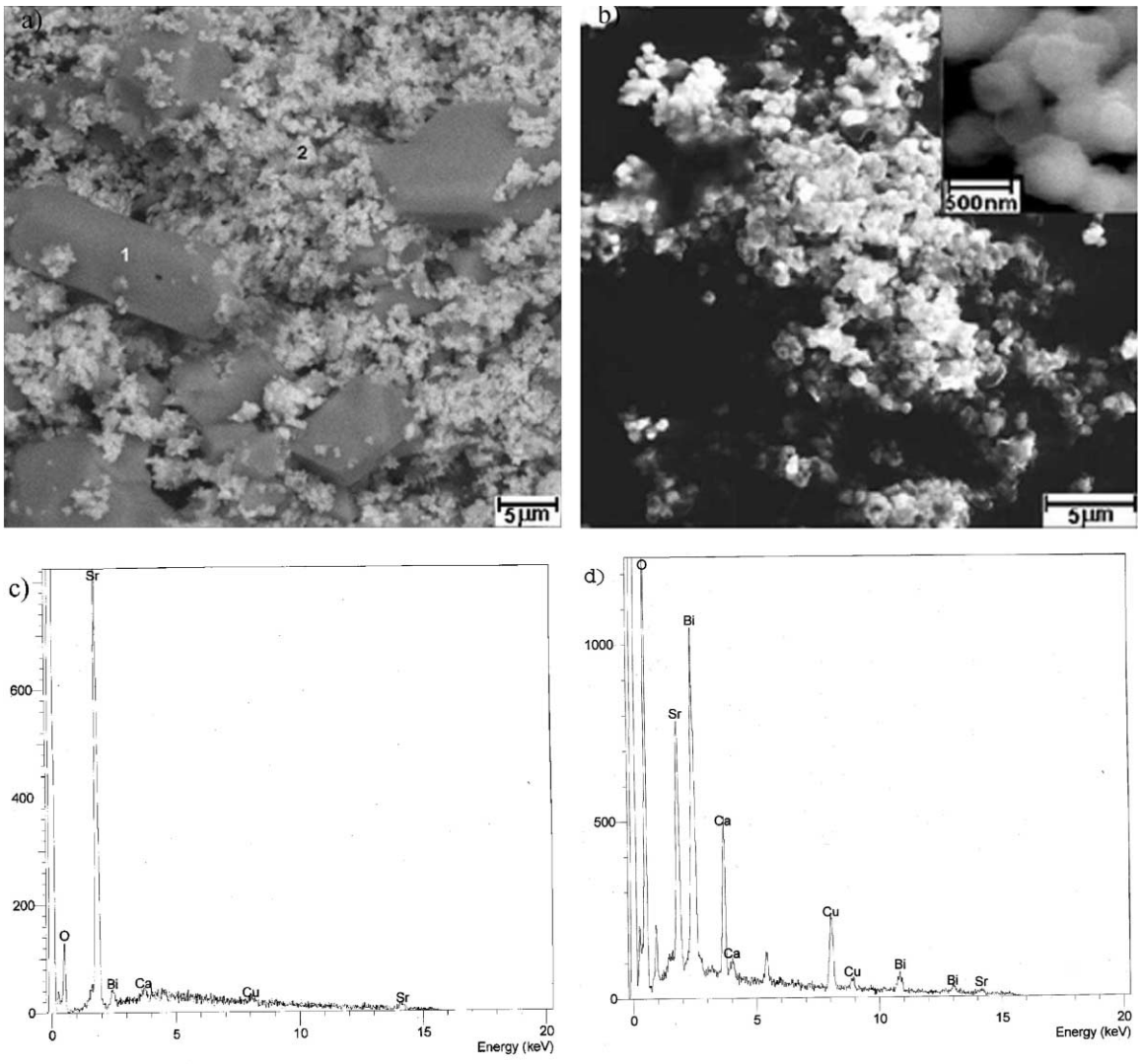

Fig. 2. SEM photomicrographs [magnifications 1:2000 (a), 1:3000 (b) and 1:20,000 (inset on b)] and EDS spectra taken at the point 1 (c) and at the point 2 (d).

the polyhedral-like particles, indicates a high strontium content, Fig. 2c. The evidence of other elements in traces probably relates to the surface contamination due to the presence of smaller particles in the investigated area. Against the fact that there are many physico-chemical processes which may affect the final particle morphology in the spray pyrolysis process, short droplet/particle residence time in reaction zone suggests that the only possible explanation for the presence of such large Sr-rich particles in produced powder could be the incomplete dissolution of the strontium source in the precursor nitrates mixture and, consequently, nucleation and growth of strontium oxide. EDS spectra obtained for smaller, slightly agglomerated particles (point marked 2 at Fig. 2a) indicates an area of Bi–Sr–Ca–Cu–O rich particles, Fig. 2d.

The uniformity of particle size distribution in powder obtained by spray pyrolysis is easier to reveal from SEM photomicrographs taken from the polished samples, presented at Fig. 3a. The EDS spectrum of the whole-presented sections, Fig. 3b, indicates the existence of Bi–Sr–Ca–Cu–O rich particles, but the determined atomic ratio corresponds neither to pure 2223 phase nor 2221 phases. On the other hand, uniformity of compositional content over the samples is confirmed by the results of the quantitative EDS analysis taken from five random chosen points, Table 1. Obtained chemical content could be explained by 2212 and 2223 phase coexistence in particles (also confirmed by XRPD analysis[11]) and through variation of their amount along the specimen. The observed changes in the metal ionic ratio from point to point are presumed to be also the consequences

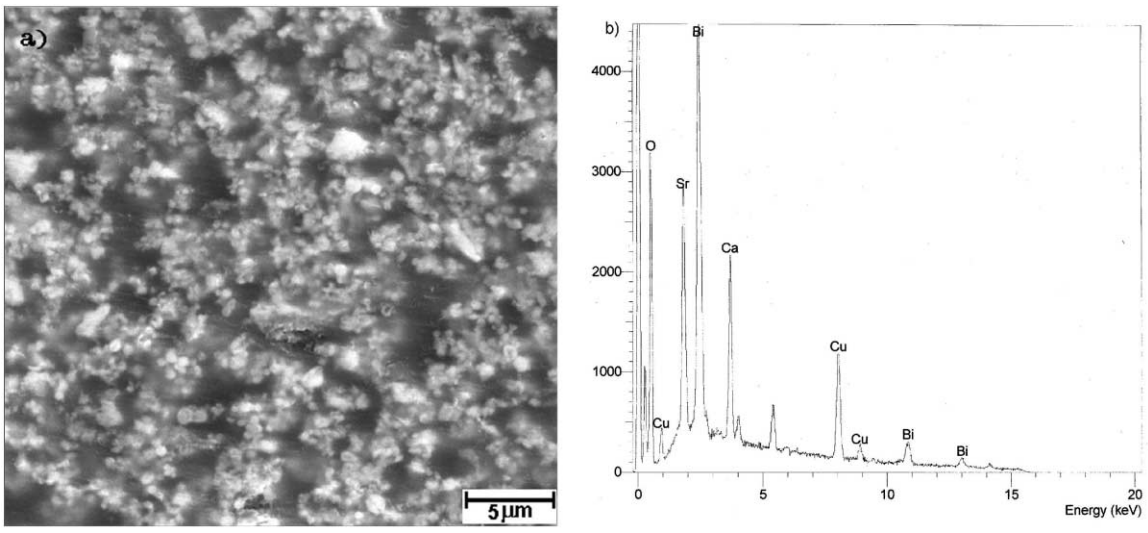

Fig. 3. SEM photomicrograph of polished samples (magnification 1:3000) and EDS spectra of presented section.

Table 1
Quantitative EDS analysis taken from five random chosen points of the samples

at.%	1	2	3	4	5
Bi	7.29	7.97	9.56	6.91	3.90
Sr	1.04	3.04	0.51	4.37	8.73
Ca	3.48	5.67	3.40	4.76	5.67
Cu	12.69	11.98	3.85	7.72	4.60
O	75.71	71.35	82.69	76.23	77.09

of incomplete 2223 phase formation process (confirmed by DTA analysis) due to very short particle residence time in reaction zone.

4. Conclusion

This paper demonstrates the ability of aerosol synthesis of multicomponent Bi-based high T_c superconducting particles from pure nitrate solutions with improved compositional homogeneity all over the powder. Spherical, solid, Bi–Sr–Ca–Cu–O rich particles, with the mean particle size around 400 nm are obtained from common nitrates solution. Determined stoichiometry implies good homogeneity and co-existence of the 2212 and 2223 phases due to the insufficient particle residence time at the reaction temperature and uncompleted 2223 phase formation process. The uniformity of particles size and shape, and the absence of hard agglomeration formation were provided by maintaining of aerosol droplet density value below 10^8 droplets/cm.^{3} The existence of SrO rich large polyhedral like particles (15 μm) in the powder is a consequence of the incomplete dissolution of strontium source in the precursor solution (confirmed also by determined Sr-deficit composition in Bi–Sr–Ca–Cu–O particle). The results imply the possibility of powders morphology and size control by optimizing the processing conditions.

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References

1. Takano, M., Takaeda, J., Oda, K., Kotaguchi, H., Miura, Y., Ikaeda, Y., Tomii, Y. and Mazaki, H., Sperconductor with T_c equals to 117 K in the BiPbSrCaCuO system. *Jpn. J. Appl. Phys,* 1988, **27**, 1041–1044.
2. Endo, U., Koyama, S. and Kawai, T., Preparation of the high T_c phase of BiPbSrCaCu superconductors. *Jpn. J. Appl. Phys.,* 1988, **27**(8), L1476–L1479.
3. Tohge, N., Tatsumisago, M. and Minami, T., Preparation conditions and morphology of superconducting fine particles in the Bi–Sr–Ca–Cu–O system prepared by sprat pyrolysis. *J. Am. Ceram.Soc.,* 1991, **74**, 2117–2122.
4. Kodas, T. T., Generation of complex metal oxides by aerosol process: superconducting ceramic particles and films. *Chem. Advanced Mater.,* 1989, **101**(6), 814–826.
5. Messing, G. L., Zhang, S. C. and Jayanthi, G. V., Ceramic powder synthesis by spray pyrolysis. *J. Am. Ceram. Soc.,* 1993, **76**, 2707–2726.
6. Lang, R. J. and Ultrasonic atomization of liquids, J., Acoust. *Soc. Am,* 1962, **35**, 7–10.
7. Mančić, L. and Milošević, O., Morphology of the multicomponent particles in the Bi–Pb–Sr–Ca–Cu–O system system

prepared by the spray pyrolysis method as a functional of aerosol characteristics. *J. Sci. Sint,* 1988, **30**, 1 73-83.
8. Grivel, J. C., Kubel, F. and Flukiger, I., DTA/TG study of the formation of the $(BiPb)_2Sr_2Ca_2Cu_3O_{10+x}$ superconductor. *J. Therm. Anal,* 1997, **48**, 665–674.
9. Zhu, W., Kuo, C. K. and Nicholson, P. S., Kinetic and formation of the 110K phase in the Bi–Pb–Sr–Ca–Cu–O system. *J. Am. Cer. Soc.,* 1997, **80**, 1975–1980.
10. Lehndorff, B., Hardenbicker, P., Hortig, M. and Helmut, P., Evidence for enhanced grain connectivity due to second phase reduction of Bi-2223/Ag tapes. *Physica C,* 2223, **1999**, 312 105-111.
11. Mančić, L., Žakula, Z. and Milošević, O., Structural properties of ultradispersed Bi–Pb–Sr–Ca–Cu–O particles synthesized from aerosol. In *Advanced Science and Technology of Sintering*, ed. V. Skorokhod et al. Plenum, New York, 1999, pp. 153–158.