

# NOVEL PRECURSORS IN PREPARATION AND CHARACTERIZATION OF NANOSUPERCONDUCTOR $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$

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## ABSTRACT

In order to prevent agglomeration of high temperature  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) superconducting materials, the solid state processing method based on new and appropriate yttrium complex precursors that have high stability in air and compatibility in solution, was used without applying any surfactant. A new method of preparing yttrium precursors on the basis of coordination hydroxynaphthaldehyde, salicylaldehyde and acetylacetonate compounds has been suggested. These have been prepared by a reaction of yttrium acetate with three various coordination compounds for forming yttrium complex types. These techniques provide proper control on nanoparticles size distribution. The generated steric hindrance due to the structure of the novel precursors, acts like a protecting agent and prevents from agglomeration. We synthesized nanoparticles of a size about 30–50 nm with homogeneous grains distribution at high calcination temperature 920 °C. The maximum values of transition temperature into the superconducting state have been found to be  $T_c(0) = 84$  K with a temperature interval of  $\Delta T = 3$  K for YBCO nanosuperconductor. The synthesized products were characterized by powder X-ray diffraction, fourier transform infrared spectroscopy (FT-IR), transmission electron micrograph and scanning electronic microscopy.

**Key words:** superconductor, coordination compositions; solid state process; nanostructures;  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

## INTRODUCTION

Currently,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Y-123) is still the best suited high- $T_c$  superconductor for most applications [1]. A great effort has been made by scientists in both academia and industry to study this material. One of the most important and conventional synthesis techniques of YBCO is solid state reaction which despite some limitations and problems [2] in this method, due to its relative ease, is widely used for the synthesis of ceramics superconductors.

It has been found that several factors, such as the selection of the starting reactants, techniques employed and the calcination procedures play important

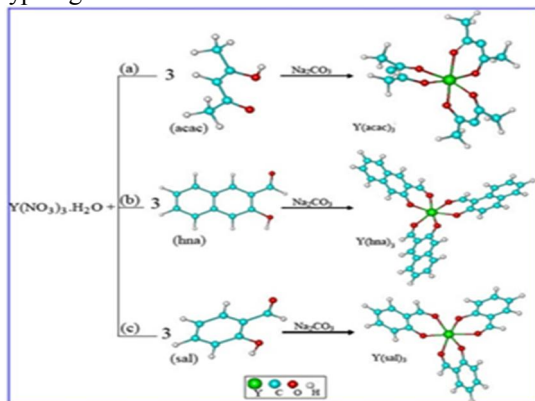
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roles in the phase formation and the characteristics of fabricated samples [3]. Most of the early fabricated compounds were synthesized by reacting  $Y_2O_3$  and  $CuO$  with  $BaCO_3$  [4–8] or  $BaO_2$  [3, 9, 10] and a long time calcination was required because the carbonates decompose with a slow rate. So, the particles were agglomerated with no a high quality structure. Another problem is carbon retention in sintered compacts that affected the critical current densities. In this work, for the first time we synthesized samples with various and new precursors of yttrium via solid state reaction method. By comparing XRD patterns of products, it was found that in samples synthesized with coordination composition of yttrium as the precursor instead of yttrium oxide,  $BaCO_3$  phase disappears at  $900\text{ }^\circ\text{C}$  and a rather pure Y-123 phase was obtained that consists of tiny particles with spherical shape and a homogeneous grains distribution.

### METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

At the first step, we synthesized three precursors of yttrium. These were prepared by the reaction of high-purity nitrate salt of Y with acetylaceton ( $C_5H_8O_2$ ), 2-hydroxo-1-naphthaldehyde ( $C_{11}H_8O_2$ ) or salicylaldehyde ( $C_7H_6O_2$ ) type ligand.



**Fig. 1** – Schematic diagram illustrating the formation of precursors: (a)  $Y(acac)_3$ , (b)  $Y(hna)_3$  and (c)  $Y(sal)_3$

**Table 1** – Chemical precursors used to obtain YBCO superconductor

| Samples no. | Initial materials     |
|-------------|-----------------------|
| 1           | BaO, CuO, $Y(acac)_3$ |
| 2           | BaO, CuO, $Y(hna)_3$  |
| 3           | BaO, CuO, $Y(sal)_3$  |

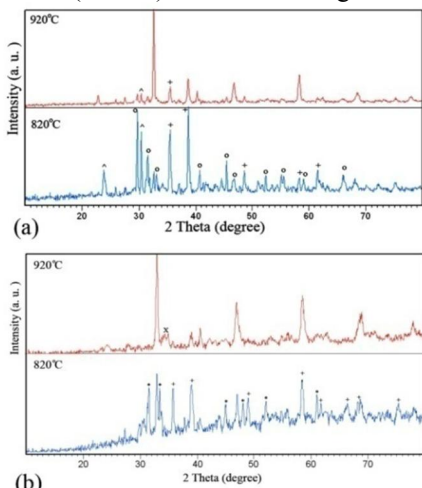
at temperatures  $820$ ,  $900$  and  $920\text{ }^\circ\text{C}$  for 10 h with intermediate grindings. Finally, the powder annealed to  $500\text{ }^\circ\text{C}$  in oxygen flow, then cooled down to room temperature.

After dropwise adding of sodium carbonate into the mixed solution and refluxing for about 2 h, the obtained precipitates were centrifuged and washed with ethanol for several times. *Fig. 1* shows a schematic molecular structure of the prepared complex precursors.

Then, an appropriate amounts of BaO, CuO,  $[Y(acac)_3]$ ,  $[Y(hna)_3]$  and  $[Y(sal)_3]$  were adjusted (Y:Ba:Cu = 1:2:3) and mixed to obtain sample no. 1, 2 or 3 (*Table 1*). The powders were grinded and heated

## RESULTS AND DISCUSSION

FT-IR spectra of precursors of yttrium, confirm the formation of Y complexes because the stretching C=O vibration of aldehyde is shifted to lower frequency (about  $1600\text{ cm}^{-1}$ ) indicating the coordination of carbonyl group to the metal. Results of powder X-ray diffraction of sample no. 1 at different temperatures (*figure 3a – c*) show that at  $920\text{ }^{\circ}\text{C}$  intensity of YBCO phase with an orthorhombic structure becomes strong. EDX quantitative microanalysis indicates an average composition of Y (19 %wt), Ba (45.6 %wt), Cu (26.3 %wt) and O (9 %wt) before annealing.



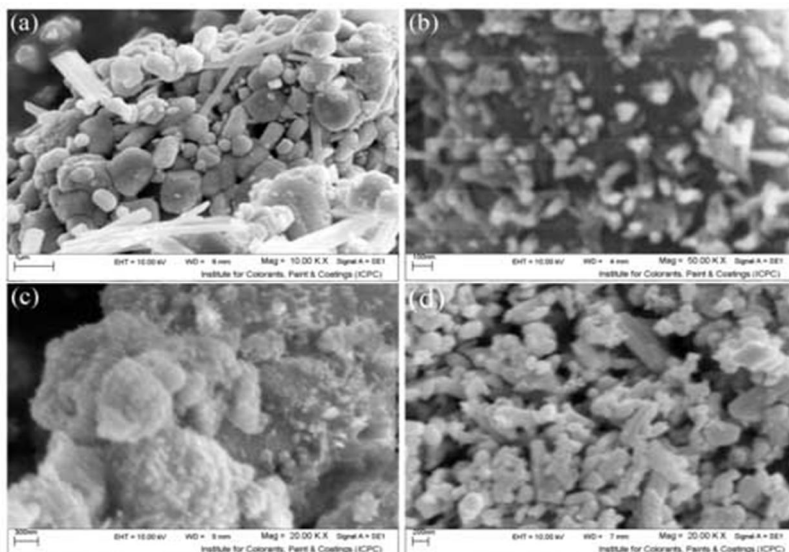
**Fig. 2** – XRD diffraction patterns for sample no. (a) 2 and (b) 3 at  $820\text{ }^{\circ}\text{C}$  and  $920\text{ }^{\circ}\text{C}$ . The peaks that do not correspond to YBCO phase are indexed by (+) CuO, (\*)  $\text{Y}_2\text{Cu}_2\text{O}_5$ , (^)  $\text{BaCuO}_2$ , (o) Y211 and (X) weak additional peaks.

of sample no. 3 was like to rods of a diameter about  $60\text{--}70\text{ nm}$ . Further observation at higher magnification in TEM image reveals that the size of nanoparticles obtained from the XRD diffraction patterns are in close agreement with the TEM studies which show average sizes of  $45\pm 5\text{ nm}$ .

The Resistance-Temperature (R-T) curve for as-prepared sample with 3 tons pressure showed that maximum values of transition temperature into the superconducting state have been found to be  $T_c(0) = 84\text{ K}$  with a temperature interval of  $\Delta T = 3\text{ K}$ .

*Figure 2* and *Figure 3* show XRD results of sample no. 2 and 3 that confirm at  $920\text{ }^{\circ}\text{C}$  nearly the single phases of YBCO were formed along with a little additional peak with low intensity. By the use of Debye-Scherrer equation ( $d = 0.9\lambda/\beta\cos\theta$ ), crystallite sizes were estimated and results were indicated:  $17.5\text{ nm}$  at  $900\text{ }^{\circ}\text{C}$ ,  $17.6\text{ nm}$  at  $920\text{ }^{\circ}\text{C}$  for sample no. 1,  $28.1\text{ nm}$  and  $17\text{ nm}$  at  $920\text{ }^{\circ}\text{C}$  for sample no. 2 and 3 respectively.

According to the SEM images (figures 3 a–d), at sample no. 1 nanoparticle of a size about  $30\text{--}50\text{ nm}$  with homogeneous grains distribution have been observed. Sample no. 2 consists of tiny, aggregated nanoparticles with spherical shapes and morphology



**Fig. 3** – Representative SEM images of: (a) and (b) sample no. 1 at 820 and 920 °C; (c) and (d) sample no. 2 and 3 at 920 °C respectively.

The obtained critical temperatures were slightly reduced compared with typically quoted values of bulk YBCO material (91 K) [4] but were enhanced compared with of nanosize YBCO reported elsewhere (80 K) [11].

### CONCLUSIONS

In summary, for the first time we have demonstrated the synthesis of YBCO nanoparticles on the basis of coordination hydroxynaphthaldehyde, salicylaldehyde and acetylacetonate compounds as new precursor via a thermal decomposition process. By using these novel precursors, it is possible to prepare nanoparticles of ceramic material at high calcination temperature. The presence of methyl groups and benzene rings around the metal centers (see *figure 1*), act like a protecting agent that cover the growing nanoparticles and prevents from agglomeration. After raising the temperature and decomposition of the complex, YBCO nuclei were formed and during the reaction, the growth of initial nuclei into nanoparticle occurred.

TEM images showed that the particle size of the as-synthesized powders was about 30–50 nm. The  $T_c$  of the obtained nanosuperconductor was determined about 84 K. The sintered material prepared with this powder showed clearly denser microstructure compared with that of other samples. As the magnetic field applied on the sample increased, due to the generated defects in

the superconductor structures, a visible decrease in  $T_c$  and  $T_c(0)$  temperature values were observed.

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