

## Synthesis and characterization of high-temperature ceramic YBCO nanostructures prepared from a novel precursor

S. Alikhanzadeh-Arani<sup>a</sup>, M. Salavati-Niasari<sup>\*, b</sup>

<sup>a</sup>Plasma physics Research Center, Science and Research, Islamic Azad University, Tehran, Iran

<sup>b</sup>Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317-51167, Iran

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### \*Corresponding author:

E-mail address:

Salavati@kashanu.ac.ir

Phone: +98 361 591 2383

Fax: +98 361 5552935

### Abstract

As a new precursor, [tris(2-hydroxyacetophenato)triaqua(III)], [Y(HAP)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]; complex was used in thermal decomposition process for the synthesis of rod-like high-temperature ceramic YBCO with length of about 320-350 nm and diameters 60–90 nm. The as-synthesized products were characterized by XRD, FT-IR, TEM, SEM and EDX analyses. The results showed that by using fine raw materials, the calcination temperature can be reduced to 870 °C. It was found that this type of precursor have clearly effects on the size and morphology of product because the organic ligands around yttrium center act like a protecting agent to prevent agglomeration.

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## 1. Introduction

The discovery of high-temperature superconductors with transition temperature ( $T_c$ ) above 77 K has opened up new vistas of potential applications. Since superconductors can function as strong quasi-permanent magnets, single-domain bulk superconductors are highly attractive for

industrial applications. The most efforts have been carried out by several methods on the fabrication of copper oxide systems such as Y–Ba–Cu–O (YBCO) [1], Er–Ba–Cu–O [2], Eu–Ba–Cu–O [3], Nd–Ba–Cu–O [4], Gd–Ba–Cu–O [5], Y–Sr–Cu–O [6], Sm–Ba–Cu–O [7], Bi–Pb–Sr–Ca–Cu–O [8] and others. Also, influence of various factors has been studied on the properties of superconductors

particularly on the famous YBCO superconductor [9–13].

In recent years, considerable endeavours have been done for the development of nanometer-sized superconductors [14, 15]. In order to study the physical effects at a dimension level of nanometer, superconductors should be made as small as possible. So, control over crystal morphology is of the uttermost importance in superconductor fabrication. The ideal morphology for superconducting nanodevices and for applications in computer circuitry is the nanowires and nanorods. The wet chemical techniques have been used in order to obtain a better morphology structure. Recently, nanowires of YBCO have been synthesized by sol-gel method and by using a biopolymer [16, 17] in order to control the nucleation of precursor nanoparticles of barium carbonate during the sol-gel processing. Also, YBCO nanofibers were synthesized by electrospinning a solution of metal nitrate and poly acrylic acid [18]. Although these techniques have usually higher cost and more complexity than the easy and conventional solid state thermal decomposition method but in the solid state decomposition of metals oxide, there are some fundamental problems. The most important of them are poor homogeneity, porosity and large particle size. By controlling the growth of the particles, surfactants play an important role in synthetic procedure leading to a homogenous atomic distribution of nanoparticles with controlled size. In addition to the important role of surfactants in size control of nanoparticles, precursors with special structures and shapes can prevent from agglomeration as well. Herein, we report a facile and low-cost process for synthesis of YBCO nanostructures via thermolysis of [tris(2-hydroxyacetophenato) triaqua(III)];

[Y(HAP)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]; complex as a new yttrium source by conventional solid state method. To the best of our knowledge, this is the first report on the synthesis of YBCO nanostructures via thermal decomposition of this new precursor.

In this work, nanorods of YBCO were synthesized by using of copper oxide, barium carbonate and [Y(HAP)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] complex. It was demonstrated that by using of the [Y(HAP)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] complex as a new raw material, it is possible to achieve the superconducting phase at lower calcination temperature because of compatibility of coordination compositions in solution. Also, there was no need to use any surfactant for size control and results suggest that sintering and agglomeration of the nucleated nanoparticles is prevented by the extended presence of the ligands (the so-called steric hindrance) to produce small, nanoparticulate centers for subsequent YBCO outgrowth.

## 2 Experimental

### 2.1 Materials and characterization

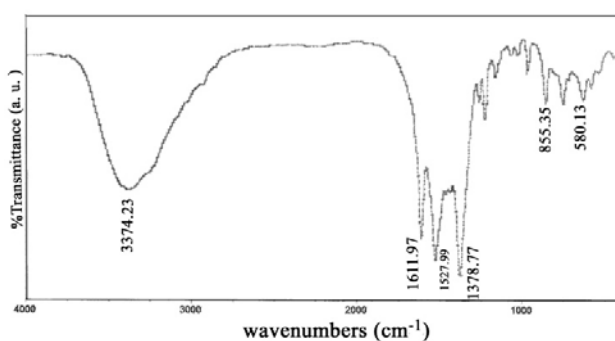
All the chemical reagents such as BaO, CuO, Y(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O, 2-hydroxyacetophenone and methanol used in our experiments were purchased from Aldrich and were used as received without further purification. Phase analysis of the samples was investigated using X-ray powder diffraction (Cu K $\alpha$  radiation). The compositional analysis was done by energy dispersive X-ray (EDX, KeveX, Delta Class I). Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The samples were ultrasonically vibrated to homogenize the mixing. Then, microstructural examination of the

samples was done using a scanning electron microscope (SEM). The morphology of the samples was observed with a transmission electron microscope (TEM). The C, H, N analysis results of the yttrium complex showed close similarity to the theoretical values. The molecular formulae of the complex have been assigned on the basis of the results of their elemental analyses.

## 2.2. Synthesis of yttrium complex precursor

We used the hydroxyacetophenone complex of yttrium as an active yttrium precursor. This was prepared by the reaction of high-purity nitrate salt of yttrium with 2-hydroxyacetophenone ( $C_8H_8O_2$ ). 6 g (8.22 mmol) of  $Y(NO_3)_3 \cdot 5H_2O$  and 6 ml of 2-hydroxyacetophenone were individually dissolved in methanol and thoroughly mixed. After drop-wise adding of sodium carbonate aqueous solution into the mixed solution, a precipitate was formed.

Anal. Calc. for  $C_{24}H_{27}O_9Y$ : C, 52.56; H, 4.96; Y, 16.21. Found: C, 52.43; H, 4.86; Y, 16.01%. The [tris(2-hydroxyacetophenato)triaqua(III)],  $[Y(HAP)_3(H_2O)_3]$ , complex was characterized by FT-IR (Fig. 1).



**Fig. 1.** FT-IR spectrum of as-synthesized  $Y(HAP)_3 \cdot 3H_2O$  complex precursor.

The absorption peaks at 3374.23 and 1611.97  $cm^{-1}$  is attributed to stretching vibration of O–H bond and the bending vibration of H–O–H

respectively, from water molecules on the external surface of the samples during handling to record the spectra. Also, the stretching C=O vibration at about 1527.99  $cm^{-1}$  and aromatic C=C stretching vibrations at 1378.77  $cm^{-1}$  confirm the formation of precursors indicating the coordination of carbonyl group to the metal [19]. The peak shown at about 580  $cm^{-1}$  in spectrum is attributed to the stretching vibration mode of metal-oxid [20].

## 2.3. Synthesis of nanostructured YBCO

Stoichiometric amounts of BaO, CuO and  $[Y(HAP)_3(H_2O)_3]$  complex were adjusted and mixed to obtain pure YBCO material. The powder was grinded and heated at temperatures 820 °C, 870 °C and 920 °C for 12 h, then slowly cooled down to room temperature in the furnace and crushed to a fine powder. Finally, the powder was annealed to 500 °C in oxygen flow and cooled down to room temperature.

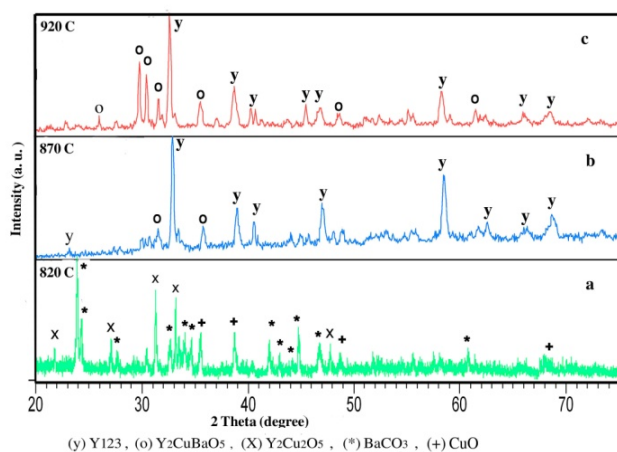
## 3. Results and discussion

According to the results of TG analysis, burning of 2-hydroxyacetophenato to acetone,  $CO_2$  and  $H_2O$  occurs from 250 to 460 °C [21]. Subsequently,  $Y_2Cu_2O_5$  was formed owing to the reaction between  $Y_2O_3$  and CuO. Also, BaO was consumed along with  $CO_2$  to produce  $BaCO_3$ .

Fig. 2 shows the XRD patterns of the sample at different temperatures. As seen at 820 °C  $BaCO_3$ ,  $Y_2Cu_2O_5$  and CuO phases were observed. The XRD data clearly indicated that the barium carbonate phase remained stable in the heated reaction mixtures up to temperatures of approximately 820 °C. Increasing the temperature to 870 °C resulted in decomposition of  $BaCO_3$  and formation of YBCO phase (along with a weak

trace of  $Y_2CuBaO_5$  (Y-211) phase). After more heating the sample to 920 °C, nonsuperconductivity Y-211 phase became stronger indicating the optimum temperature for calcination was about 870 °C. So, it is found that the formation of YBCO happens at lower temperature by the new precursor due to compatibility of coordination compositions in solution by comparing with reported elsewhere [22, 11].

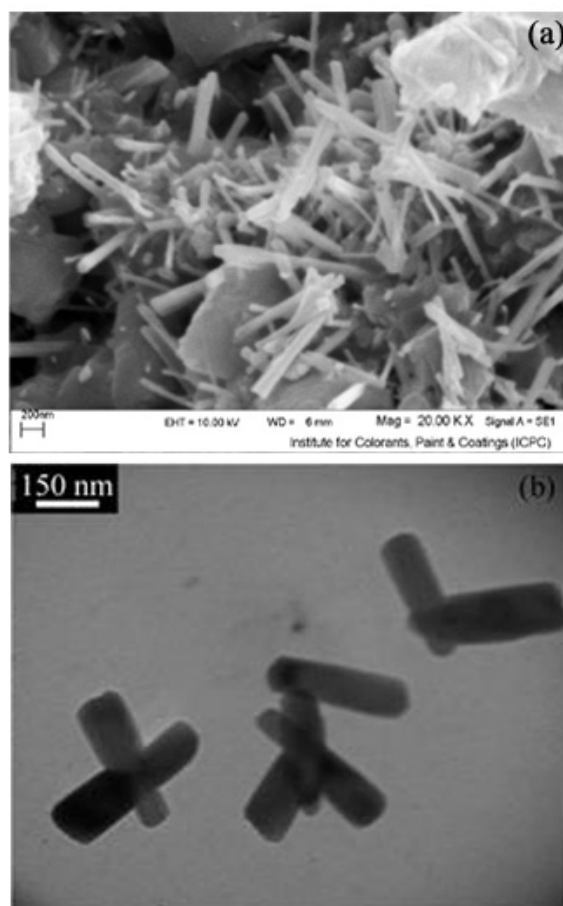
By the use of Debye-Scherrer equation, crystallite sizes of calcined samples were estimated and results indicated: 17.2 nm at 820 °C, 23.4 nm at 870 °C and 28.1 nm at 920 °C, so the extra heating makes the larger size of grains. The XRD investigation revealed that the prepared sample has an orthorhombic structure with lattice parameters  $a = 3.851 \text{ \AA}$ ,  $b = 3.879 \text{ \AA}$  and  $c = 11.644 \text{ \AA}$ . Nanostructural examination was done using a scanning electron microscope.



**Fig. 2.** XRD patterns of the calcined sample at 50 °C intervals from 820 °C to 920 °C.

Fig. 3(a) shows the SEM image of the prepared sample at 870 °C composing of nanorods that growth on the surface of sample. The TEM image of YBCO nanorods shows that the materials have rod-like shape (Fig. 3(b)) with a length of 320–

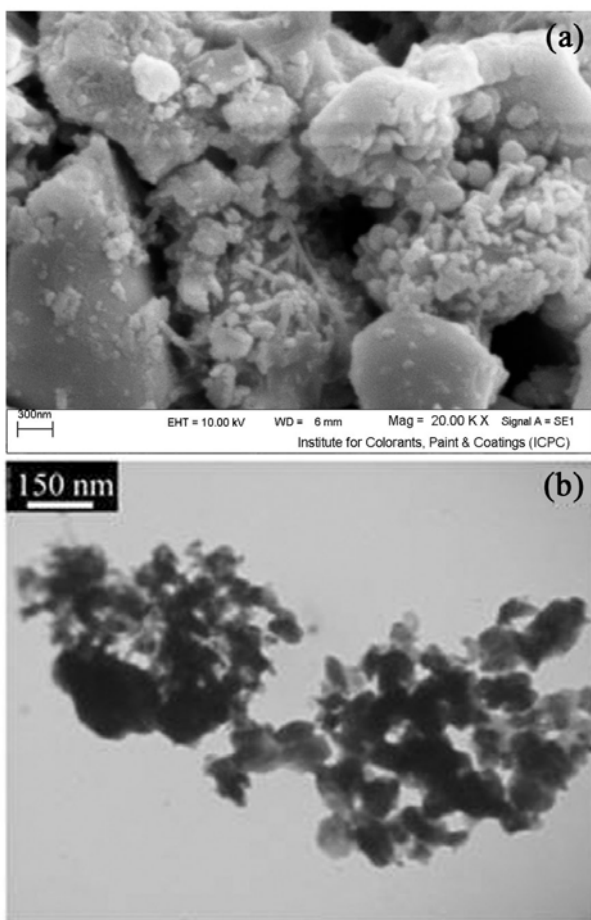
350 nm and a diameter of about 60-90 nm due to nucleation and growth of discrete nanoparticles. When we used  $[Y(HAP)_3(H_2O)_3]$  as yttrium source in the synthesis of YBCO via solid state method, fine structure of material is obtained. The effects of organic ligands around the central metal that remain up to 460 °C prevent from agglomeration in the initial stages of nucleation and growth of discrete nanoparticles.



**Fig. 3.** (a) SEM and (b) TEM micrographs of product calcined at 870 °C.

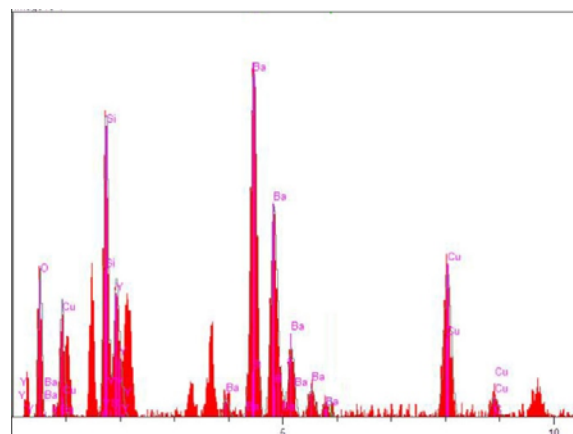
We propose that the generated steric hindrance around the Y atoms due to methyl groups and benzene rings in the structures of  $Y(HAP)_3$  plays role a surfactant. After the decomposition of

organic ligands, the concentrations of metal ions increase. Then, the YBCO nuclei start to form in a regular array of discrete sites. With the increasing number of the YBCO nuclei, nuclei begin to form small particles. Then, small particles aggregate to rod-like structures to eliminate the surface energy.



**Fig. 4.** (a) SEM and (b) TEM micrographs of product calcined at 920 °C.

So, we can limit the size of particles and restrict their spatial distribution using this precursor without using any protecting agent. By extra heating up to 920 °C, nanorods became aggregated resulting in large and irregular shaped grains (Fig. 4a). Also, TEM image of sample showed the sample consist of multi-micrometer-sized particles (Fig. 4b).



**Fig. 5.** EDX spectrum of the calcined sample at 870 °C. The Si line originates from the grid holding the sample.

Energy dispersive X-ray spectrum (EDX) analysis performed on the sample calcined at 870 °C confirmed the presence of Ba, Y, Cu and oxygen without any impurity as shown in Fig. 5. It is important to be able to prepare nanomaterials with a controlled size and size distribution. In addition of the important role of applied method in size control of nanoparticles, precursors with special structures can prevent of agglomeration as well. A major interest at the moment is the development of organometallic or inorganic compounds for preparation of nanoparticles [23, 24]. Using of the novel compounds can be useful and open a new way for preparing nanomaterials especially nano-sized superconductors .

#### 4. Conclusion

In conclusion, we have demonstrated the synthesis of YBCO nanostructures from the ([tris(2-hydroxyacetophenato)triaqua(III)], [Y(HAP)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]) as new precursor via a solid state process at different temperature for 12 h. It was found that by using the coordination compositions as new raw materials, it can be

possible to achieve the superconducting phase at lower calcination temperature (870 °C). Moreover, there was no need to use any surfactant or protective agent for controlling size of products due to steric hindrance of methyl groups around metal ion. From the results of XRD, FT-IR and TEM, the as-prepared sample shows good morphologies corresponding to rod-like nanostructures with length of about 320–350 nm and diameters about 60–90 nm.

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