

# Notes

## Synthesis and Characterization of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Material by the Improved Gel Method

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Several methods of synthesis for high- $T_c$  superconducting materials have been employed to prepare monophasic cuprates with good superconducting properties. The most common method of preparation of cuprate superconductors is the traditional ceramic method which have been used for the preparation of a large variety of oxide materials.<sup>1-6</sup> The preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  material by the ceramic techniques typically involves mixing oxides with appropriate carbonates, oxalates or nitrates and firing the mixture. Because the reaction proceeds by diffusion in the solid state, temperatures as high as 950°C and reaction times of at least 48h are required for obtaining well crystallized  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . A major difficulty encountered in preparing the material by this method is in obtaining homogeneous and dense powders, even by repeated grinding and heating procedures. The heterogeneity of the ceramic may be responsible for poor superconducting properties of these compounds. Improved control of the chemistry and powder morphology will certainly enhance those properties, and the synthesis of these oxides *via* other techniques is therefore attractive. In order to solve those synthetic problems, other methods such as coprecipitation,<sup>7-11</sup> pyrolysis of nitrate salts,<sup>12-15</sup> hydroxides,<sup>16-18</sup> alkoxides,<sup>19-22</sup> acetates,<sup>23-27</sup> and freeze drying<sup>28-32</sup> have been studied.

This paper describes the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconducting oxides by the improved gel method and demonstrates in detail the process of decomposition of precursors as well as the crystallization of various phases. To obtain a smooth and controlled decomposition in this method acetates were used as starting materials instead of nitrates. Nitrates of yttrium, barium and copper are probably not the best choice, particularly in scaling-up, because nitrates in the presence of an organic substance can give rise to an abrupt and uncontrolled decomposition of the organic material, eventually leading to spontaneous combustion in the vessel in which the solution is being concentrated. This method offers an attractive route for several reasons; better homogeneity achieved through an intimate mixing at the molecular level in the solution, lowering the synthesis temperature because of the increased reactivity of the mixed precursors, and a high degree of control in the stoichiometry of the final product.

### Experimental

High purity metal acetates are obtained from commercial

sources and analysed to determine their levels of hydrated water before use. Metal acetates are converted to the corresponding oxides at sufficiently high temperatures (800-900 °C). The amount of water has been determined according to their stoichiometric reaction (Gravimetric analysis). The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  precursor solution has been prepared from the metal acetate salts dissolved in deionized water. 0.02 mol of  $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 3.75\text{H}_2\text{O}$ , 0.04 mol of  $\text{Ba}(\text{CH}_3\text{COO})_2$ , and 0.06 mol of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 1.08\text{H}_2\text{O}$  are dissolved in 500 mL of deionized water and the solution is stirred for several hours at room temperature. 0.03 mol of the tartaric acid dissolved in 40 mL of water is added to the aqueous solution and stirred another 3-4 hours. The molar ratio of the tartaric acid to copper is made to be 1/2. The aqueous solution has kept in a furnace at 80°C to evaporate water until it is gelled and dried. The dried gel is ground to a fine powder using a conventional mixer or a mortar and pestle. After the resulting precursor (dry gel powder) is heated at 500 °C for 6 h in air to remove volatile anions, the powder is calcined at 875 °C for 12 h to form the desired compound. Post oxygen annealing is done at 550 °C under a flowing oxygen for five hours, followed by slow cooling (1 °C/min) to room temperature.

The evolution of the gels as a function of temperature is followed by thermogravimetric analysis (TGA), and infrared spectra (IR) are used to study the decomposition mechanism as well as the phase transformation. The precursors, intermediates, and final products are characterized by powder X-ray diffraction (XRD). The dc electrical resistance of the pellet is measured by the standard four-probe method using silver paste as electrodes.

### Results and Discussion

Water has been evaporated from the aqueous solution of metal acetates and tartaric acid without using a vacuum dryer. Neither precipitation nor phase separation occur during the formation of the gel. Thermogravimetric analysis (TGA) in Figure 1 shows the gradual weight loss at first until 200 °C, then abrupt losses occur at around 200-400 °C. It means the major decomposition of organic compounds which corresponds to almost half of the total weight loss. The gradual weight loss above 400 °C must be the decomposition of residual organic compounds and carbonates formed during pyrolysis. This TGA diagram shows that most organics are removed by 500 °C.

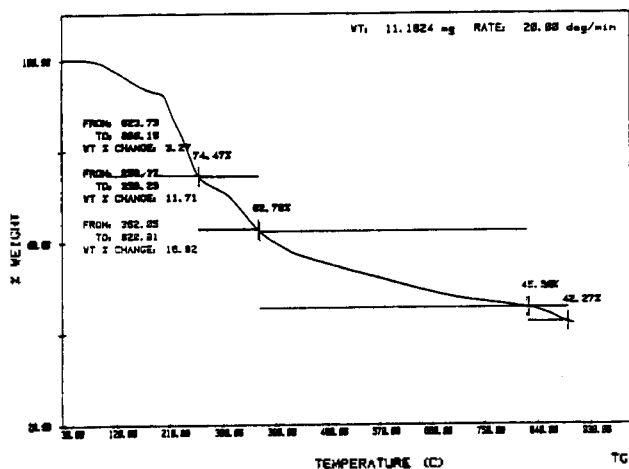


Figure 1. TGA thermodiagram for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  precursor.

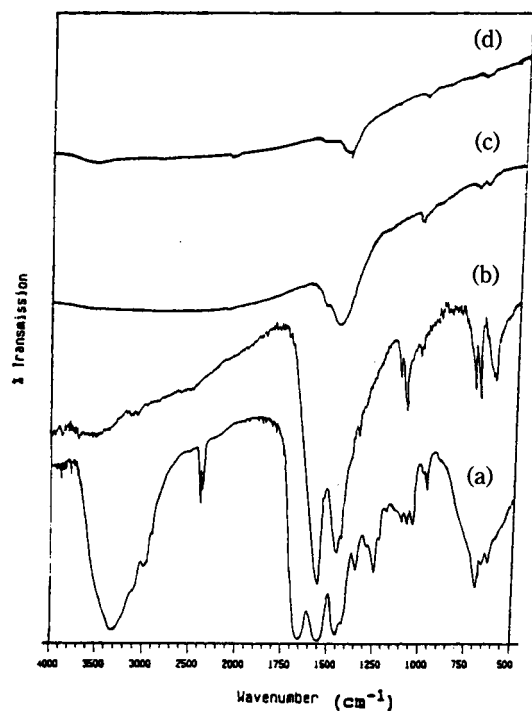


Figure 2. Infrared spectra of the precursor and its calcination products after heating at various temperatures. (a) precursor (b) 350 °C for 6h (c) 550 °C for 6h (d) 800 °C for 6h.

The IR spectra of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  precursor and its calcination products at various temperatures show their decomposition behavior, as shown in Figure 2. In the spectra of the precursor, there are several absorption peaks, given in  $\text{cm}^{-1}$ : 3400-3100 (O-H), 2900-3000 (C-H vibration), 1400-1600 (C=O and C-O asymmetric stretching), 1000-1280 (C-C), and 680 (C-O-M; M denotes metal). Figure 2 (b) shows the peaks from tartaric acid and water disappear; tartaric acid was decomposed and water evaporated. In the Figure 2 (c) of 350 °C, the bands attributed to C=O group of metal acetates are lost, and the peaks at  $1500\text{ cm}^{-1}$  and  $930\text{ cm}^{-1}$  attributed to carbonates (C-O for  $\text{CO}_3^{2-}$ ) appear. When the samples are heated to 750 °C, the absorption peaks of the carbonates become smaller, indicating the loss of carbonate

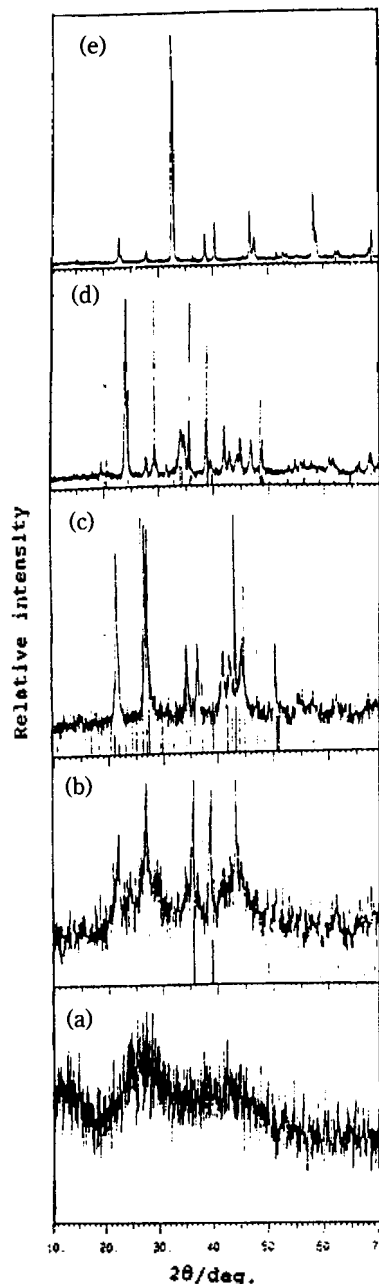


Figure 3. X-ray diffraction patterns of the powders heated at (a) room temperature. (b) 250 °C for 4h. (c) 350 °C for 4h. (d) 750 °C for 4h. (e) 875 °C for 4h.

in the heating process (Figure 2 (d)), finally leading to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  material.

The thermal treatment has been also investigated by X-ray diffraction analysis at different temperatures. A typical X-ray diffraction pattern of the precursor in Figure 3 (a) shows the broad peaks with low intensities, which suggests an amorphous state of the precursor and this material does not have long range order. The peaks corresponding to  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{BaCO}_3$  are identified at 250 °C and 350 °C (Figure 3 (b)-(c)). Superconducting phase was found to be present together with other second phases such as  $\text{BaCO}_3$ ,  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Y}_2\text{BaCuO}_5$ , and  $\text{BaCuO}_2$  at 750 °C, as shown in Figure 3 (d). There exists only tetragonal 123 phase in

the powder X-ray patterns heated at 875 °C for 12 hours as shown in Figure 3 (e). The formation of phase-pure 123 phase can be achieved at lower sintering temperature comparing to other methods. The precursor prepared using this gel method forms the 123 phase at least 50 °C lower temperature than that of other method due to the fine grain and intimately mixed microstructure of the material. The temperature dependence of the resistance was measured by the standard four probe method. A superconducting transition (on set) occurred from 92 to 84 K.

In conclusion, ultrafine and homogeneous  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconducting material has been prepared successfully using an aqueous metal acetates and a tartaric acid. Water was removed from the aqueous solution of metal acetates without using a vacuum dryer. An amorphous state of the precursor was confirmed by X-ray diffraction analysis. Acetates were converted to carbonates when the precursor was heated to 350 °C. The carbonates disappeared slowly at higher temperatures. TGA diagram showed most organics were removed by 500 °C. The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  phase is already formed at 750 °C with other second phases. The formation of high purity 123 phase with a grain sizes about 1 to 3  $\mu\text{m}$  was achieved at relatively low sintering temperature of 875 °C due to the fine particles and the increased reactivity of the microscopically mixed precursor.

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### References

- Gallagher, P. K.; Sunshine, S. A.; Murphy, D. W. *Mat. Res. Bull.* **1987**, *22*, 995.
- Wu, J.; Bocarsly, A. *Inorg. Chem.* **1995**, *34*, 4262.
- Kini, A. M. *Inorg. Chem.* **1987**, *26*, 1836.
- Rao, C. N.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge Univ. Press: 1986; p 86.
- Jin, S.; Kammlot, G. W.; Tiefel, T. H. *Physica C.* **1993**, *181*, 57.
- Masuda, Y.; Ogawa, R.; Kawate, Y. *J. Mater. Res.* **1993**, *8*, 693.
- Wang, X. Z. *Solid State Commun.* **1987**, *64*, 881.
- Gotor, F. J.; Pellerin, N.; Odier, P.; Bonnet, J. P. *Physica C.* **1995**, *274*, 252.
- Dunn, B.; Chu, C. T.; Cooper, J. R. *Adv. Ceram. Mater.* **1987**, *2*, 343.
- Varanasi, C.; MaGinn, P. *Supercond. Sci. Technol.* **1994**, *7*, 10.
- Baiker, A.; Conder, K.; Kruger, C. *Physica C.* **1994**, *227*, 343.
- Stacy, A. M.; Badding, J. V.; Holland, G. F.; Keller, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 2528.
- Sargankova, I.; Diko, P.; Tweed, J. D. *Supercond. Sci. Technol.* **1996**, *9*, 688.
- Nagano, M.; Greenblatt, M. *Solid State Commun.* **1988**, *67*, 595.
- Goto, T.; Takahashi, K. *J. Mater. Res.* **1994**, *9*, 852.
- Barboux, P.; Greene, L. H.; Bagley, B. G. *J. Appl. Phys.* **1988**, *63*, 2725.
- Jacques, P.; Verbist, K.; Lapin, J. *Supercond. Sci. Technol.* **1996**, *9*, 176.
- Conder, K.; Kruger, C.; Kaldis, E. *Mater. Res. Bull.* **1995**, *30*, 491.
- Hayri, E. A.; Nagano, M.; Oliver, J.; Gerhart, R. J. *J. Mater. Res.* **1989**, *4*, 1099.
- Kumar, D.; Sharon, M.; Pinto, R. *J. Appl. Phys.* **1994**, *76*, 1349.
- Shibata, S. *Jpn. J. of Appl. Phys.* **1988**, *27*, L53.
- Zhang, P. X.; Zhou, L.; Wu, X. Z. *Supercond. Sci. Technol.* **1995**, *8*, 15.
- Kareiva, A.; Bryntse, I.; Karppinen, M. *J. Solid State Chem.* **1996**, *121*, 356.
- Wagner, A.; Gritzner, G. *Supercond. Sci. Technol.* **1994**, *7*, 89.
- Karppinen, M.; Linden, J.; Ninisto, L. *J. Alloys & Compounds* **1995**, *225*, 586.
- Kikkawa, S.; Kato, N.; Taya, N.; Tada, M. *J. Amer. Ceram. Soc.* **1995**, *78*, 1387.
- Heibel, M.; Kumar, G.; Wyse, C.; Bocarsly, A. *Chem. Mater.* **1996**, *8*, 1504.
- Horn, J.; Bernier, J. C. *Solid State Commun.* **1991**, *79*, 483.
- Johnson, S. M.; Gusmann, M. I.; Geballe, T. H.; Sun, J. Z. *Adv. Ceram. Mater.* **1987**, *2*, 337.
- Darracq, S.; Kang, S. G.; Demazeau, G. *J. Solid State Chem.* **1995**, *114*, 88.
- Wang, Z. L.; Goyal, A.; Kroeger, D. M. *Phys. Rev. B.* **1993**, *47*, 5373.
- Grasso, G.; Jeremie, A.; Flukiger, R. *Supercond. Sci. Technol.* **1995**, *8*, 827.