

SYNTHESIS OF HIGH- T_c SUPERCONDUCTING CUPRATE MATERIALS THROUGH SOLID STATE REACTION ROUTE

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Abstract

Since the discovery of high- T_c superconductors in cuprate family considerable efforts have been inverted towards improving the synthesis process through solid state reaction technique. The preparation typically involves heating process of ceramic powders which must undergo special handling in order to control purity, particle size distribution and heterogeneity. In this paper, attempt has been made to describe the synthetic methods used to prepare the Y-, Bi-, Tl-, and Hg- based high- T_c cuprate superconductors through solid state reaction route.

Keywords: High- T_c Superconductors, YBaCuO, BiSrCaCuO, TlBaCaCuO, HgBaCaCuO, Sintering

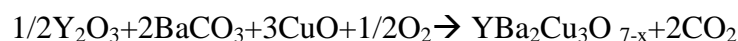
1. Introduction

The solid state reaction route involving mixing, calcinations and sintering is the most widely used method for the synthesis of polycrystalline bulk superconducting materials from a mixture of solid starting materials like oxides, carbonate etc. The starting high purity solid reactants powders in appropriate stoichiometric ratio have been weighed out to prepare superconducting materials. An agate mortar and pestle or ball mill (for large quantity sample) is usually employed for grinding process. The solid powders are calcined in good muffle furnace in the temperature range from 800°C to 950°C for several hours. A suitable container material

(crucible or boat, noble metals, platinum and gold) are usually used. The powder are cooled, reground and calcined again. This process is repeated several times to get homogeneous materials. The black powders are subsequently compacted to pellets and sintered at more elevated temperature for prolonged duration. The final temperature and duration of sintering may vary depending on the nature and properties of the sample under preparation. The sintering environment such as temperature, annealing time and cooling rate play a very important role in getting good high- T_c superconducting materials. The most commonly examined high- T_c superconducting materials with superconducting transition temperatures T_c above the temperature of liquid nitrogen are $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 90\text{-}95\text{K}$), $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ($T_c = 85\text{K}$), $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c = 110\text{K}$), $\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ($T_c = 110\text{K}$), $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, ($T_c = 127\text{K}$) and $\text{HgBa}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ($T_c = 134\text{K}$). In this paper the methods used to prepare the Y-, Bi-, Tl-, and Hg-based high- T_c cuprate superconductors through solid state reaction route has been presented.

2. Preparation of YBaCuO

For the preparation of YBCO high purity (99.99%) powders of Y_2O_3 , BaCO_3 and CuO were used as starting materials. Suitable amounts of these powders in the cation ratio Y: Ba: Cu = 1:2:3 were weighed and thoroughly mixed and grounded in a pestle mortar to form a homogeneous mixture. The powder was then cold pressed (3500 Kg/cm^2) into 2.5cm diameter pellets. These pellets were calcined in a programmable box furnace at 820°C for six hours. If there are any green colored particles, the compound must be reground and calcined again because the green color indicates non superconducting material typically copper oxide. These pellets were then grounded repressed into pellets, and calcined at 930°C (heating rate $10^\circ\text{C}/\text{min}$) for 30 hours in flowing O_2 . The step was repeated twice. Repeating the calcinations process assured complete removal of CO_2 by the reaction.



The pellets were calcined at a relatively high temperature in order to facilitate the decomposition of the precursors to oxides and to allow diffusional mixing for the formation of the stoichiometric superconducting phase. The calcined pellets were grounded and pressed again into

pellets. The compressed pellets were then sintered in electrical muffle furnace at 940°C for 24 hours in flowing O_2 . The orthorhombic superconducting phase of YBCO is unstable at temperature higher than 650°C . At $900\text{-}950^{\circ}\text{C}$, the oxygen content per formula unit is less than 6.5 and the structure is tetragonal. If quenched in this form the material is non-superconducting. To regain the oxygen to the desired value close to seven, the material should be given a long anneal in O_2 or air in the temperature range of $400^{\circ}\text{C}\text{-}500^{\circ}\text{C}$ to enable the oxygen pickup. Therefore, after sintering, the furnace was cooled slowly at the rate of $1^{\circ}\text{C}/\text{min}$ to 500°C . Slow cooling allows oxygen to be taken up by the sample and provides oxygen stoichiometry close to seven. At this temperature, the pellets were kept for 72 hours, and then cooled slowly to room temperature. The resultant YBCO pellets were black in color. The density of the pellets was $\sim 5.6 \text{ gm}/\text{cm}^2$. The T_c ($R=0$) of small pieces of pellets were 89K to 92K. The pellets have single (123) phase. The pellets were preserved in a desiccators to avoid atmospheric moisture and CO_2 degrading the samples [1].

3. Preparation of BiSrCaCuO

In the Bi-Sr-Ca-Cu-O system, the sample is prepared by solid state synthesis route. High purity Bi_2O_3 (99.9%), SrCO_3 (99.9%), CaCO_3 (99.9%) and CuO (99.9%) powder is taken in appropriate ratio Bi: Sr: Ca: Cu in 2:2:1:2 were first well mixed and grounded for 3 hours in an agate mortar. The powder is then put in the furnace at 700°C for 12 hour and allowed to cool naturally. It is then taken out and grinded for three hours and again put in the furnace at 770°C for 12 hr. After that the same grinding process is repeated and the sample is put in the furnace for calcinations at 820°C for 20 hours. Finally, the sample is pressed into pellet of 10 mm diameter and 5mm thickness by dry pressing method and sintered at 880°C for 12 hours. The temperature during calcinations was raised in steps to prevent the melting of oxides of low melting temperature. It is important that this initial heat treatment is carried out below the melting point of Bi_2O_3 ($\approx 825^{\circ}\text{C}$) to allow reaction of Bi_2O_3 before melting [2,3].

4. Preparation of TlBaCaCuO

The Tl based copper oxides are thermally unstable phases, and hence, are difficult to prepare pure phases. The primary difficulty in preparing the thallium based cuprate superconductor's lies in the toxicity and volatility of the reactant Tl_2O_3 and its decomposition products. Bulk samples of the 2201, 2212 and 2223 thallium based cuprate have been prepared by reacting Tl_2O_3 , $BaCuO_2$, dry CaO and CuO in stoichiometric amounts. The mixed reactants were pelletised, wrapped in gold foil and heated under flowing oxygen at $890^\circ C$ for 7 minutes for 2201, $905^\circ C$ for 7 minutes for 2212, and $910^\circ C$ for 7 minutes for 2223, followed by cooling at $10^\circ C/minute$. Essentially single phase $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2223) was obtained by heating stoichiometric quantities of the reactant at $890^\circ C$ for 1hr ; if this mixture was heated for more than two hour or at temperature above $900^\circ C$, a mixture resulted with 2212 as the major phase and 2223 as a minor phase confirm bulk superconductivity at 108 and 120K respectively[4,5,6].

5. Preparation of HgBaCaCuO

Single phase Hg-1223 ($HgBa_2Ca_2Cu_3O_{8-x}$) having $T_c \approx 133K$ (oxygen annealed) was successfully prepared by solid state reaction and short time annealing technique using mixtures of metal oxides HgO, BaO, CaO and CuO as starting reagents. The preparation has been done in sealed tubes because of highly volatile HgO compound. The powder mixture is homogenized in a dry container to prevent CO_2 and water absorption. A precursor material with the nominal composition $Ba_2CaCu_2O_5$ was obtained from a well ground mixture of respective metal nitrates, sintered at $900^\circ C$ in O_2 . After regrinding and mixing with powdered HgO, the pressed pellets were sealed in evacuated quartz tubes. These tubes were placed horizontally in tight steel containers and held at $800^\circ C$ for 5 hours. The obtained Hg-1201 and Hg-1223 samples were then heated and annealed in flowing O_2 at $300^\circ C$ for 24 h in order to increase their oxygen contents [7, 8, 9]

6. Conclusion

The preparation of Bi-, Tl-, and Hg- based high- T_c superconductors are difficult as compared to YBCO. Problems in these superconductors arise because of the existence of three or more phases having a similar layered structure. The syntactic intergrowth and defect such as stacking faults occurs during synthesis and it become difficult to isolate a single superconducting phase. Hg- and Tl- based systems involves toxic oxides and solid to vapor types of reaction. Therefore such materials are prepared in sealed a container, which makes the synthesis quite delicate. Poor compositional control, chemical inhomogeneity, time consuming process, coarse particle size, introduction of impurities during grinding and high temperature ($>1000^\circ\text{C}$) requirement are some inherent drawbacks of ceramic method.

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