

Preparation of superconducting-grade copper from commercial grade copper salt

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Abstract. Fine samples with nominal composition of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ have been produced by solid state method using various purity grades of starting copper oxide powder. Studies on T_c and high- T_c volume fraction measurements of these samples revealed that the samples produced using CuO powders obtained in laboratory after double purification of the commercially available copper salts have higher T_c (104.46 K) and increased percentage of high T_c volume fraction (58%) compared to even the samples prepared from Aldrich grade (99.99%) CuO. A simple and cost-effective chemical route for the purification of CuO from commercially available copper salts has been outlined.

Keywords. Superconductor; high purity copper; chemical purification.

1. Introduction

Ever since the discovery of superconductivity in perovskite ceramics (Bednorz and Muller 1986) and later extension of this discovery (Wu *et al* 1987), there have been large-scale research efforts in this direction the world over. The voluminous research publications in this field stand testimony to the global urge to understand and realize the potentials of these ceramic superconductors. Huge chunks of research funds worldwide are continuously being directed towards the large-scale production of ceramic superconductors having high critical current density (J_c) and transition temperature (T_c) into the superconducting phase.

Research into the basic chemistry of these materials are continuing as improvements on the superconducting properties are being sought for. However, some generalizations can now be made for these materials owing to the consistent replication of findings. One such generalized finding is that in all copper oxide based ceramics, the pairing of carriers in the Cu–O₂ planes are responsible for their high (T_c) superconductivity (Tarascon *et al* 1987). Thus any substitution on the copper site of these materials, which alters the electronic structures of the Cu–O₂ plane, would tend to strongly depress their (T_c) (the transition temperature into the superconducting phase or the zero resistance temperature) and the volume fraction of the high (T_c) superconducting phase (Jones *et al* 1989). Therefore, impurities, particularly the transition metals (3d), which have the requisite valencies and ionic radii would tend to replace copper in the Cu–O₂ planes and detriment the superconducting

properties (Ginsberg 1989; Maeda *et al* 1990). As a consequence, the purities of the starting materials, particularly the copper salts, used in the preparation of these ceramic superconductors, is expected to play a major role in obtaining a high T_c phase-pure product.

In this paper, we deal with the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ceramic superconductor system which is constituted of (2223) phase with T_c at 110 K, the (2212) phase with T_c at 80 K, and the (2201) phase with T_c at 20 K. To increase the critical current density (J_c) above liquid nitrogen temperature, it is important to increase the volume fraction of the high T_c phase (i.e. the (2223) phase with T_c at 110 K) and decrease that of the other phases. Here, we report results of the investigations on the effects of purity of the starting copper oxide on T_c and the volume fraction of the high T_c superconducting phase. We also report a cost-effective chemical route for the preparation of high purity grade ($\geq 99.99\%$) copper oxide from commercially available copper salts.

2. Experimental

Five different grades of copper oxide powders were used for the preparation of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples. The copper oxide powders used were: (i) Copper oxide (98%) supplied by LOBA Chemie, India, (ii) Copper oxide (98%) supplied by S.D. Fine Chemicals, India, (iii) Laboratory (single) purified copper oxide from commercially available copper chlorides/sulphates, (iv) Laboratory (double) purified copper oxide from single purified copper and (v) Aldrich grade (99.99%) copper oxide.

The $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples prepared using each of the five mentioned grades of copper oxide powders

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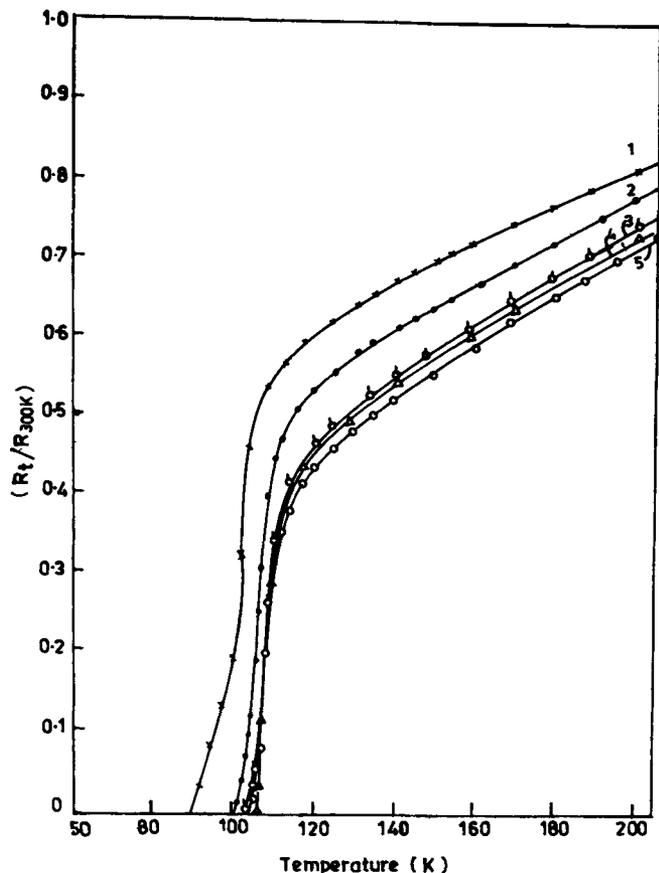


Figure 1. Resistance (R_t/R_{300K}) vs temperature (K) plots for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples prepared from CuO: (1) LOBA Chemie, (2) S.D. Fine Chemicals, (3) Laboratory single purification, (4) Laboratory double purification and (5) Aldrich.

are referred to in the text as samples 1, 2, 3, 4 and 5, respectively.

2.1 Sample preparation

Stoichiometric amounts of each of these copper oxides were separately taken and mixed with the required amounts of Bi_2O_3 , PbO , SrCO_3 and CaCO_3 . The mixed compositions were then calcined in air at 820°C for 24 h. On cooling, the powders were intimately mixed and again calcined in air at 820°C for 24 h. On cooling each of the powder compositions were pulverized and pressed into pellets. The pellets were finally sintered at 840°C for 100 h in an atmosphere of $\text{O}_2 : \text{N}_2 = 1 : 10$.

The resistance for each of the pellets were measured by a.c. method using a lock-in-amplifier by the standard four-probe contact method. The temperatures were recorded using a Cu-const thermocouple. The measurement of the (2223) phase volume fraction for each of the pellets were also carried out using a lock-in-amplifier.

2.2 Purification of copper oxide powders

To get single purified CuO, the commercially available copper sulphates (or, chlorides), with purity $< 98\%$, was dissolved in distilled water and complexed with sodium-potassium tartrate (Rochelle salt) in presence of optimum amounts of sodium hydroxide and sodium carbonate. The solution was filtered (to get rid of any turbidity or, suspended impurities) so as to get a clear blue coloured filtrate. The filtered solution then refluxed with 40%

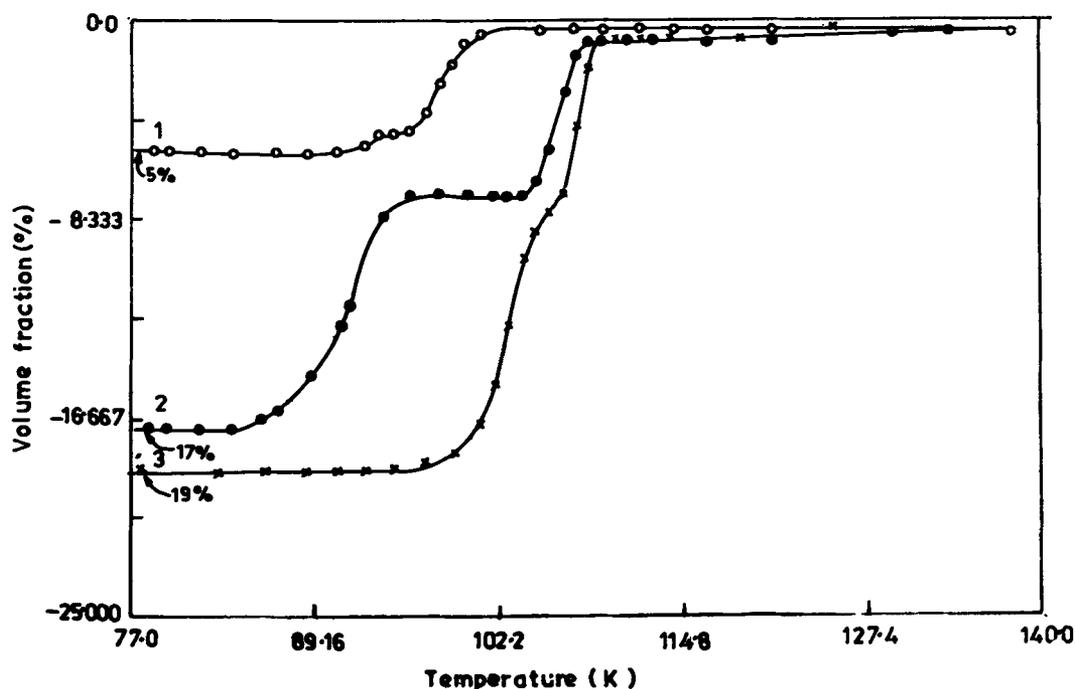


Figure 2. High T_c volume fraction (percentage) vs temperature (K) plots for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples prepared from CuO: (1) LOBA Chemie, (2) S.D. Fine Chemicals and (3) Laboratory single purification.

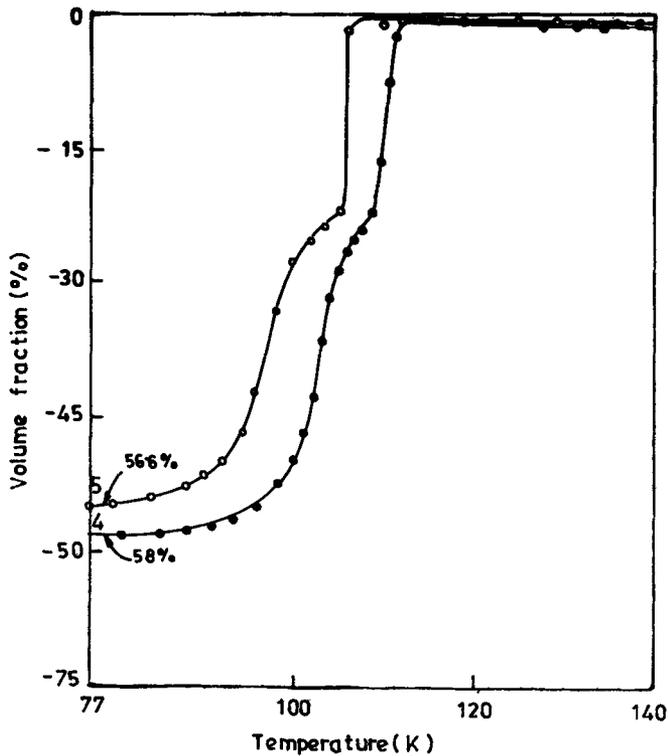


Figure 3. High T_c volume fraction (percentage) versus temperature (K) plots for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples prepared from CuO: (4) Laboratory double purification and (5) Aldrich.

formaldehyde (with ratio 5 : 1) over a water bath. Reddish metallic copper precipitated within 10–15 min of refluxing. The metallic copper was then separated and dried with acetone. Calcination (in air) at 400°C for 3 h, of the metallic copper gave the single purified CuO powder.

To obtain double purified CuO, the precipitated copper mentioned above was dissolved in chlorine water and the entire process from separation of copper from the solution to calcination in air was repeated.

3. Results and discussion

The fall of resistance with temperature were recorded for each of the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ compositions prepared from varied purity of CuO and are depicted in figure 1. From the measurements, it was observed that the sample prepared from LOBA Chemie grade CuO (i.e. sample 1) had the lowest T_c ($R=0$) while the sample from double purified CuO (i.e. sample 4) and Aldrich CuO (i.e. sample 5) had higher and comparable T_c values. The fall in resistance with temperature (figure 1) in the case of samples 1 and 2 were not very sharp, reflecting the presence of phases other than the (2223) as the major phase. On the other hand, relatively sharper fall in resistance in samples 3, 4 and 5 were indicative of the realization of the (2223) as the major phase.

The details of the volume fraction of the (2223) phase for the various $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ samples are

Table 1. T_c ($R=0$) and percentage volume-fraction of the (2223) phase for various samples of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$.

Sample	Source of CuO	T_c	Percentage volume fraction
1	LOBA Chemie, India (98%)	89.30 K	5.0%
2	S.D. Fine Chemicals (98%)	99.20 K	17.0%
3	Single purified	102.98 K	19.0%
4	Double purified	104.46 K	58.0%
5	Aldrich Grade (99.99%)	104.44 K	56.6%

Table 2. Analysis of the impurities present in the various grades of CuO powder.

Impurity	Percentage present				
	LOBA Chemie	S.D. Fine Chemicals	Single purified	Double purified	Aldrich
Fe	0.1321	0.0580	0.0120	0.0020	0.0030
Zn	1.4250	0.0355	0.0246	0.0052	0.0040
Ni	0.0525	0.0135	0.0221	0.0060	0.0060
Co	0.0932	0.0162	0.0047	0.0032	0.0030
Mn	0.0324	0.0021	————	Not detectable	————
Cr	0.0201	0.0020	————	Not detectable	————
Se	0.0943	0.0240	————	< 0.001	————
Te	0.0762	————	————	< 0.001	————

represented in figures 2 and 3. The formation of steps in the volume fraction versus temperature curves are manifestations of the presence of (2212) phase along with (2223) phase. From figure 2, it is conclusive that in sample 1 very little of the (2223) phase exists in the sample. The striking feature of figure 3 reveals that the sample 4, prepared from double purified CuO, has a higher percentage volume-fraction of the (2223) phase compared to that of sample 5, which was prepared from Aldrich-grade (99.99%) CuO.

The T_c ($R=0$) values and their respective percentage volume-fraction of the (2223) phase for the various samples of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$, prepared from various grades of CuO are summarized in table 1.

The atomic absorption data for the various grades of CuO powders revealed the presence of Zn, Ni, Fe and trace amounts of Co, Se and Te as trace impurities. The impurities present were the maximum for the CuO powders supplied from the LOBA Chemie, India while it was the minimum for the double purified CuO. The analysis of impurities present in double purified CuO determined by atomic absorption spectroscopy (AAS) is given in table 2. The order of increase of purity in CuO powders were as follows:

LOBA Chemie < S.D. Fine Chemicals < Single purified
 << Aldrich-Grade \leq Double purified.

Presence of impurities, such as Zn, Ni and Fe, in the starting CuO powders provided scope for their substitution

for the Cu sites. With increased levels of impurities their chances of replacing Cu in the Cu sites were increased and the electronic structure of the Cu-O₂ plane was expected to get altered. Consequently, the T_c values and the percentage volume fraction of the (2223) phase got depressed.

Supplementing with the atomic absorption data, it can be concluded that higher purity of the starting CuO leads to higher values of T_c and increased volume fractions of high T_c phase. It can also be concluded that double purification of copper oxide by simple chemical route indeed leads to a better superconducting final material. The chemical route used for single and double purification requires commonly available and less costly chemical reagents such as formaldehyde, sodium-potassium tartrate, NaOH and Na₂CO₃ thus making the route cost-effective for large scale production of high-purity copper oxide.

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