High temperature superconductivity in orthorhombic $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Abstract. High temperature superconducting $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been prepared by ceramic and nitrate methods to understand the influence of preparation conditions on superconductivity. The characterization was carried out by X-ray diffraction and magnetic susceptibility measurements. T_c onset was observed at 88 K. Meissner effect has been observed above the liquid nitrogen temperature.

Keywords. High temperature superconductivity; Meissner effect; ceramic method; nitrate method.

1. Introduction

Since the discovery of superconductivity around 90 K (Wu *et al* 1987) there has been tremendous interest for preparing materials belonging to Y–Ba–Cu–O system. The crystal structure of the superconducting phase has been shown to be oxygen-deficient distorted perovskite structure (Cava *et al* 1987; Rao *et al* 1987; Nagarajan *et al* 1987). These newly discovered high T_c superconductors have been classified into two groups based on their crystal structure. (i) $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) with tetragonal K_2NiF_4 structure with $0.1 \leq x \leq 0.3$ (Kishio *et al* 1987; Rao *et al* 1987; Cava *et al* 1987). Zero resistance T_c values in the range 20–48 K have been observed depending on the metal and its content. (ii) $\text{LaBa}_2\text{Cu}_3\text{O}_7$ with orthorhombic structure distorted, oxygen-deficient perovskite structure exhibiting a T_c of 95 K (Wu *et al* 1987; Ganguly *et al* 1987; Cava *et al* 1987; Sampathkumaran *et al* 1987; Kishio *et al* 1987; Murphy *et al* 1987; Engler *et al* 1987; Hor *et al* 1987). The superconducting properties of these two systems are sensitive to oxygen stoichiometry and in both systems, the mixed valence of copper ($-\text{CuO}_2$ -planes) is responsible for the metallic behaviour and high T_c superconductivity. Considerable work has been done by replacing yttrium by other rare earth materials like La, Gd, Dy, Eb etc in many laboratories. As the reported values of T_c are different, an attempt has been made in the present study to optimize the superconducting behaviour of $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$, by preparing this compound by ceramic and nitrate methods separately and characterizing them by X-ray and magnetic susceptibility measurements.

2. Experimental

In the ceramic method, the compound was prepared by solid-state reaction. Powders of La_2O_3 , BaCO_3 and CuO were mixed in molar ratio of 0.5:2:3 in agate mortar and pestle and were then calcined at 950°C for 10 h in air followed by grinding and reheating at 970°C in flowing oxygen for 10 h. The sample was cooled slowly in a

stream of oxygen to 400°C. At 400°C the sample was annealed in oxygen for 20 h and cooled down to room temperature.

In the nitrate method, La_2O_3 , BaCO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 0.5:2:3 mole ratio was dissolved in 6N HNO_3 . The resultant solution mixture was evaporated to dryness at 100°C. The nitrate precursor thus obtained was calcined at different temperatures. A minimum temperature of 850°C was sufficient for the formation of the 1–2–3 phase. The resultant oxide was again heat-treated at 970°C for about 4 h in O_2 to achieve good crystallinity. The nitrate-derived 1–2–3 material on oxygen annealing at 400°C for 20 h was employed to check its superconductivity. Oxygen content of the samples was estimated by reducing a known amount of the 1–2–3 material in flowing H_2 gas at 800°C to La_2O_3 , BaO and metallic copper. The samples were characterized by X-ray diffraction and magnetic susceptibility measurements.

3. Results and discussion

The ceramic method requires repeated heating and grinding schedules in general and also higher calcination temperature for longer durations to form the 1–2–3 phase. The resulting oxide, even after oxygen annealing, remained tetragonal. The peak at $2\theta = 32.3^\circ$ in XRD does not show any splitting as it is usually observed in orthorhombic YBC. From the oxygen estimation the composition of the sample was found to be $\text{LaBa}_2\text{Cu}_3\text{O}_{6.7}$. No Meissner effect was observed above 77 K for this sample. Several investigators, as in the present case, could not observe any superconductivity above 77 K for $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Subba Rao *et al* 1987).

Lanthanum-based 1–2–3 compound derived from nitrate method shows broad X-ray reflections. Though heat-treatment at 850°C is enough for the formation of 1–2–3 phase, a further increase in temperature is essential to achieve good crystallinity. The nitrate-derived materials show Meissner effect above liquid nitrogen temperature only after high temperature calcination and oxygen annealing. Thus, the nitrate-derived sample on calcination at 970°C for 4 h followed by oxygen annealing

Table 1. Method of preparation and characteristics of $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Sample	Method of preparation	Starting reagents	Ratio	Calcination in air temperature and time	Oxygen annealing	Cell dimension	T_c onset
$\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$	Nitrate	La_2O_3	0.5:2:3	850°C 10 h	400°C 20 h	$a = 3.90$	Not observed above 77 K
		BaCO_3				$b = 3.92$	
		$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 6N HNO_3				$c = 11.78$	
$\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$	Nitrate	La_2O_3	0.5:2:3	850°C 10 h	970°C 4 h and 400°C 20 h	$a = 3.90$	88 K
		BaCO_3				$b = 3.92$	
		$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 6N HNO_3				$c = 11.78$	
$\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$	Ceramic	La_2O_3 BaCO_3 CuO	0.5:2:3	950°C 10 h	970°C 10 h	—	Not observed above 77 K

Figures 1-3. X-ray (CuK_α) diffraction pattern of the LaBa₂Cu₃O_{7-δ} oxide superconductor annealing at 1. 800°C for 5 h. 2. 850°C for 10 h. 3. 970°C for 4 h.

Figure 4. Temperature dependence of the magnetic susceptibility of sample $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

at 400°C for 20 h showed diamagnetic behaviour with a T_c onset at 88 K (figure 4). The above observation is in agreement with Hor *et al* (1987). The XRD (figure 3) shows the presence of considerable impurity content in the sample along with the 1-2-3 phase. The (013) and (103) reflections are not distinctly separated. However the orthorhombicity was confirmed from the shouldered (200) reflection along with (020). The composition of the sample determined by oxygen estimation was found to be $\text{LaBa}_2\text{Cu}_3\text{O}_{6.8}$. The interesting feature is that only the nitrate-derived La 1-2-3 gives values above liquid nitrogen T_c values and observable orthorhombicity. It was found difficult to get rid off the impurities. Samples prepared at 850°C and 800°C show broad XRD reflections (figures 1 and 2). Though the (002) and (020) reflections are not separately seen in XRD, it is presumed to be orthorhombic from oxygen estimation and merger of broad X-ray reflections (020) and (200).

Table 1 summarizes the preparation conditions and characteristics of the samples prepared by ceramic and nitrate methods.

4. Conclusion

The method of preparation and calcination schedules seems to decide the site occupancy of Ba^{2+} and La^{3+} ions. In addition oxygen stoichiometry is also crucial for reproducible T_c values. Thus the optimum δ value to achieve near 90 K superconductivity in LBC is experimentally found to be 0.2.

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