Structural Studies of the Superconducting
La$_{2.5}$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_7$O$_z$ (0 $\leq$ x $\leq$ 0.1)
Perovskite System by Neutron Diffraction

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We have investigated the effect of Fe substitution on the structural and superconducting properties of La$_{2.5}$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_7$O$_z$ system by Rietveld refinement of the neutron diffraction patterns of three samples with x = 0.02 (labelled B$_1$), x = 0.06 (B$_2$), and x = 0.10 (B$_3$) along with X-ray diffraction, resistivity, AC susceptibility, and oxygen-content measurements. Samples B$_1$, B$_2$, and B$_3$ are superconducting with $T_c$ values of 73, 62, and 41 K, respectively. Neutron diffraction studies confirm (i) the formation of a single phase tetragonal structure (space group P4/mmm) for all three samples, (ii) Ca and Y ions substitution at the La site concomitantly displaces La onto Ba sites, and (iii) increasing x from 0.02 to 0.10 increases oxygen content (the amount of oxygen per unit cell), as well as Cu(1)----O(4) and Cu(1)----O(1) bond lengths whereas Cu(2)----O(4) bond length decreases with corresponding decrease in $T_c$ to 41 K due to increasing occupancy of Fe ions at Cu(2) site. The change in bond lengths with oxygen content are essentially the same as those of Fe content (x). Present studies establish a correlation between the bond lengths (Cu(1)----O(1), Cu(1)----O(4), and Cu(2)----O(4)) and the measured $T_c$ values of three samples.

KEY WORDS: La$_{2.5}$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_7$O$_z$ system; Rietveld refinement; correlation between bond lengths and $T_c$ values.

1. INTRODUCTION

By simultaneously substituting both Ca and R (R = Nd, Gd, and Dy) for La and only Ca for Ba in the semiconductor La$_3$Ba$_3$Cu$_7$O$_{14}$, a series of superconductors with the nominal composition of La$_{3.5-\delta}$,R$_{\delta}$Ca$_{2}\delta$Ba$_{3.5-\delta}$Cu$_7$O$_{14}$ [LRCBCu] have been prepared by some of us [1] leading to the known superconducting system La$_3$CaBa$_3$Cu$_7$O$_{14}$ (La-3137) having a $T_c$ of 80 K [2–7] with a tetragonal triple-perovskite structure similar to that of the tetragonal YBa$_2$Cu$_3$O$_{7-\delta}$ [3]. The effect of substitution by foreign atoms on the chemical and physical properties of YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123) superconductor has been studied by many workers to investigate the origin of its superconductivity since the valency of the dopant plays an important role in determining the effective copper valence (the mobile carrier concentration) or the oxygen content of Y-123. As the results show, substitution at the Cu sites by Fe, Co, Ni, Zn, etc. reduces $T_c$ [8–13], while rare-earth substitution at the Y-site shows almost no effect on superconductivity [13]. Interestingly, partial rare-earth substitution at the La site in LRCBCu also exhibits almost no deleterious effect on superconductivity [1], similar to the situation for rare-earth substituted Y-123 [14].

To date no attempts have been made to substitute metal dopants like Fe, Co, Zn, etc. for Cu in the LRCBCu compounds in investigating the effect of substituents on superconductivity and structure except for a recent study of Fe substituted
La$_2$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_3$O$_y$ system (0.0 ≤ x = y ≤ 0.15) where some of us have shown [15] that increasing Fe concentration decreases $T_c$ and destroys superconductivity mainly due to magnetic pair breaking by local moments. Since one is not sure whether the Fe dopant occupies Cu(1) chain or Cu(2) plane sites, it is of interest to determine the same. Most of the studies mentioned above do not present detailed structural investigation, and so far, the exact atomic and some times lattice parameters are not known. Neutron diffraction provides an accurate determination of the oxygen atom positions, the bond lengths, and site occupancies. In this paper, we present the results based on the Rietveld refinements of neutron powder diffraction data on La$_2$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_3$O$_y$ for x = 0.02, 0.06, and 0.10 (three compositions here designated as B$_1$, B$_2$, and B$_3$, respectively) which

(i) confirm the existence of the correct tetragonal (P4/mmm) structure for the x = 0.02 (B$_1$), x = 0.06 (B$_2$), and x = 0.10 (B$_3$) superconducting samples,

(ii) determine accurately the oxygen atom positions, site occupancies, and bond lengths, and

(iii) show the exclusive presence of Fe ions on the Cu(2) plane site suppressing the superconductivity.

Further, results of X-ray diffraction (XRD), resistivity, and AC-susceptibility measurements on the same samples with x = 0.02 (B$_1$), x = 0.06 (B$_2$), and x = 0.10 (B$_3$) are presented, which complement the neutron diffraction data.

2. EXPERIMENTAL

A series of compounds having the composition La$_2$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_3$O$_y$ (x = 0.0, 0.02, 0.06, and 0.10) was prepared by the solid-state reaction route, under identical conditions. Stoichiometric quantities of fine powders of La$_2$O$_3$, Y$_2$O$_3$, BaCO$_3$, CuO, CaCO$_3$, and Fe$_2$O$_3$ (all at least 99.98% pure) were thoroughly mixed and heated twice in air at 950 °C for 24 h in a platinum crucible with an intermediate grinding. The resultant black product was pulverized and cold-pressed into pellets that were sintered under oxygen flow at 500 °C for 12 h followed by slow cooling at the rate of 1 °C min$^{-1}$ until room temperature was reached.

XRD patterns of all samples were taken at room temperature, using CuK$_\alpha$ radiation. The X-ray analysis revealed that all the samples were single phase, with an impurity level less than 1%. The stoichiometric composition of the constituents in the samples was confirmed by EDAX analysis, using a JEOL scanning microscope. The oxygen stoichiometry of the samples was determined by iodometric titration. Resistivity was measured as a function of temperature on rectangular bar shaped sample, using the standard four probe method. The AC-susceptibility measurements were accomplished in a system with a lock-in-amplifier and an APD cryocooler.

Neutron powder diffraction patterns were recorded at room temperature at the University of Missouri Research Reactor (MURR), Columbia, MO, using neutrons of wave length 1.4875 Å. The powdered samples were contained in a cylindrical vanadium can (∼2 g, 3 mm diameter, and ∼3 cm height). The patterns were analysed using Rietveld profile refinement program, GSAS [16].

3. RESULTS AND DISCUSSION

The observed XRD peaks were modeled by modified Gaussian functions and refined unit cell parameters, calculated using the standard least squares program based on the space group P4/mmm maintain a tetragonal-triple perovskite structure without a transition to the orthorhombic structure as is observed for Fe doped YBa$_2$Cu$_3$O$_{7-y}$ [Y-123] [8–10,17] and the Y-123 superconductor [18] during the cooling process. Therefore, the oxygen stability of these compounds is much higher than that of Y-123 when the samples are subjected to heat.

The oxygen stoichiometries, $z$ and $z'$, and the corresponding hole concentrations, $p$, are listed in Table I for the LYCBCuFe series. $z$ denotes the amount of oxygen per chemical formula of La$_2$Y$_{0.5}$CaBa$_3$(Cu$_{1-x}$Fe$_x$)$_3$O$_y$ and $z'$ is the amount of oxygen per unit cell. The formula could be written as (La$_{2y/3}$Y$_{2/3}$)(Ba$_{1.25}$La$_{0.25}$Ca$_{0.5}$)(Cu$_{1-x}$Fe$_x$)$_3$O$_y$, with $z' = (3/7)z$, similar to that of YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_y$.

The data in Table I make an assumption about the Fe oxidation state. The oxygen content of the phase can be determined from such data only if we assume that Fe is present as Fe$^{2+}$, for example. The hole concentration, $p$, of the LYCBCuFe series decreases with increasing Fe content from $x = 0.0$–0.10, which indicate

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