Crystallographic analysis, transport features and magnetic properties of the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-\delta}$ superconducting material

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Results of structure, superconductivity and normal state magnetism of the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-\delta}$ superconductor are presented. A structural study was performed by powder X-ray diffraction and magnetic characterization by SQUID (Superconducting Quantum Interface Device) magnetometer. Electrical resistivity measurements were performed by using a low-frequency AC-technique. The transition temperature ($T_c$) of the pristine sample decreases with an increase in the doped Ga concentration. The main cause of the decrease in $T_c$ is the eating of holes due to the Cu$^{2+}$/Ga$^{3+}$ alli_barval substitution, along with the disorder created due to the ionic size mismatch between Ga and Cu ions. In the normal state, the molar susceptibility for several samples fit to the Curie-Weiss law, which permitted the obtainment of the corresponding magnetic parameters, e.g., the effective magnetic moment, the Curie temperature and the temperature independent term.

Keywords: Superconductivity; magnetic characterization; resistivity; substitution.

Se presentan los resultados de la estructura, superconductividad y magnetismo del estado normal presentes en el superconductor CaLaBaCu$_{3-x}$Ga$_x$O$_{7-\delta}$. El estudio estructural se realizó por difracción de Rayos X y la caracterización magnética con el magnetómetro SQUID (Superconducting Quantum Interface Device). Las medidas de resistividad eléctrica fueron realizadas usando una técnica-AC de baja frecuencia. La temperatura de transición ($T_c$) de las muestras disminuye prematuramente con el aumento en la concentración del dopado de Ga. La causa principal de la disminución en $T_c$ es la destrucción de agujeros debido a la sustitución Cu$^{2+}$/Ga$^{3+}$, junto con el desorden creado debido a la desigualdad en el tamaño iónico entre los iones de Ga y Cu. En el estado normal, la susceptibilidad molar para varias muestras se ajustó a la ley de Curie-Weiss, lo cual permitió la obtención de los correspondientes parámetros magnéticos p. e., el momento magnético efectivo, la temperatura de Curie y el término independiente de la temperatura.

Descriptores: Superconductividad; caracterización magnética; resistividad; sustitución.

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1. Introduction

Since the discovery of high temperature superconductors, the study of substitutions in several structural positions has been useful in order to understand the basic aspects of the superconductivity of these interesting materials [1]. Copper ions have great importance in the structure because the superconductivity is attributed to originate in the CuO$_2$ planes. Hence, all on-site substitutions in Cu-O stacks have a direct impact on the superconductivity. While in nearly all HTSC systems, there is only one type of Cu-site, called the planar Copper, in RE:123 (RE = Rare Earth) type of compounds there are two, one is the Cu-chain site called Cu(1) and the other is the planar site called Cu(2). Copper in chains has four fold nearest neighbor planar coordination, while the Cu planes have a five fold square pyramidal coordination. The coordination of the planar copper remains nearly invariant, except in unique cases [2], while that of Chain Cu changes with the substitutions or the oxygen content variations in the system. Cu-O planes run along the a-b direction, while the Cu-O chains run along the c-direction.

All the oxygen sites e.g., O(2) and O(3) are always fully occupied in Cu-O planes. In Cu-O chains for an ideal orthorhombic system, while the O(1) along the b-direction are fully occupied the, O(5) along a-direction are unoccupied, which gives rise to a situation where $b > a$, e.g., an orthorhombic distortion. For Cu-site substitutions in high $T_c$ cuprates, the 3d metals have their own importance due to their similar outer orbital structures and closer ionic sizes to that of Cu. A relatively new combination of the known RBa$_2$Cu$_3$O$_{7-\delta}$, which conforms a tetragonal structure, is the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-\delta}$ compound. In this system, 40% of the R=La site is occupied by the Ca ion; one Ba site is occupied by a distribution of Ca and La. As a consequence, the O(1) and O(5) oxygen sites at the chains are randomly occupied, forming a tetragonal structure, independently of the total oxygen contained in the sample.

There are a few reports on substitutions of 3d metals in this material [3]. The effect of substitutions of Zn, Fe and Co at the Cu site on the superconducting properties was recently reported [4-6]. In this work we present the Ga substitution results at the Cu-site in the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-\delta}$ compound. We observe that this substitution decreases the $T_c$ of the pristine system nearly in a similar way as in orthorhombic RE:123 [1,7]. The c and a parameters increase with increases of Ga, and the system remains tetragonal even for the maximum doping level. The normal state magnetism of the Ga doped CaLaBaCu$_{3-x}$Ga$_x$O$_{7-\delta}$ compounds follows a Curie-Weiss trend in terms of an induced moment in the Cu ion present in the material.
2. Experimental

Samples with composition \( \text{CaLaBaCu}_{3-x} \text{Ga}_x \text{O}_{7-\delta} \) (where \( x = 0.0 \) to 0.18) were prepared by thoroughly mixing and grinding of \( \text{La}_2\text{O}_3, \text{BaCO}_3, \text{CaCO}_3, \text{CuO} \) and \( \text{Ga}_2\text{O}_3 \) in stoichiometric ratio and firing at 975°C for 12 hours. The samples were cooled to room temperature by air quenching. This exercise was repeated at least three times. Then, the powders were reground and heated at 975°C in air for 12 hours before furnace cooling to room temperature. After grinding again, this time the powders were pressed into pellets. These pellets were annealed at 575°C in flowing \( \text{O}_2 \) for 24 hours and were furnace cooled to room temperature. The X-ray diffraction (XRD) was used to determine the phase purity and lattice parameters of all the samples using a Siemens D-500 diffractometer with \( \text{CuK} \alpha_1 \text{ radiation. The XRD of all the samples was characteristic of a single phase tetragonal RE:123 structure. AC susceptibility measurements were performed by using a low-frequency AC-technique.}

\[ \lambda = 1.5406 \text{ Å} \]

In order to determine the nominal content of oxygen in the \( \text{CaLaBaCu}_{3-x} \text{Ga}_x \text{O}_{7-\delta} \) compound, we utilized the iodimetry technique. Results reveal a value around \( 7 - \delta = 0.95 \) for all analyzed samples (for several Ga concentrations). This value indicates that samples have the ideal oxygen content to obtain good superconducting properties.

3. Analysis and Results

In Fig. 1a the XRD patterns of the \( \text{CaLaBaCu}_{3-x} \text{Ga}_x \text{O}_{7-\delta} \) system with \( x = 0.0, 0.03, 0.06, 0.09, 0.12 \) and 0.18 are represented, being taken at room temperature. It is clear from Fig. 1a that all samples are the single phase with tetragonal RE:123 unit cell, and other crystallographic phases due to impurities in the samples do not exist. The structural parameters with \( T_c \) and \( \Delta T_c \) for all the samples used in the present study are shown in Table 1.

The AC susceptibility results for all samples of the \( \text{CaLaBaCu}_{3-x} \text{Ga}_x \text{O}_{7-\delta} \) compound, with \( x = 0.0, 0.03, 0.06, 0.09, 0.12 \) and 0.18 are shown in Fig. 1b. The transition temperature \( T_c \) for these systems has been defined as the onset of the diamagnetic transition. For pristine, e.g., the \( x = 0.0 \) sample also is 77.3 K, which agrees with the earlier reports [3-6]. Every curve exhibits a diamagnetic transition with characteristic behaviors corresponding to compositional single phases and homogeneity of the superconducting state, which is deduced by the volumetric superconductivity and saturation of the AC-susceptibility at low temperature values. Moreover, it is observed that the Meissner fraction decreases as \( x \) increases. With progressive substitution of Ga at the Cu-site, the \( T_c \) decreases monotonically in this system. This indicates that Ga solubility in the present system could be even larger than 6%.

In the normal state, the electrical resistivity of most of the samples is metallic, see Fig. 2a. At the normal region, for \( x < 0.12 \), the temperature dependent resistivity fits with the equation, which can be due to weakly localized regime for a two-dimensional system in a random potential [8]. Magnetic AC-susceptibility measurements corroborate the resistivity results for the critical temperatures \( T_c \). The magnetic properties in the normal state of \( \text{CaLaBaCu}_{3-x} \text{Ga}_x \text{O}_{7-\delta} \) have been investigated by measuring the DC magnetic susceptibility in the temperature range 5 to 300 K and at an applied magnetic field of 5 kOe. The magnetic susceptibility data

\[
\begin{array}{cccccc}
 x & a(\text{Å}) & c(\text{Å}) & \text{Volume}(\text{Å}^3) & T_c(\text{K}) & \Delta T_c(\text{K}) \\
 0.00 & 3.86(94) & 11.61(58) & 173.917 & 77.42 & 4.7 \\
 0.03 & 3.87(66) & 11.62(89) & 174.756 & 70.29 & 7.8 \\
 0.06 & 3.87(91) & 11.63(31) & 175.047 & 62.74 & 10.5 \\
 0.09 & 3.88(11) & 11.64(35) & 175.383 & 52.93 & 11.6 \\
 0.12 & 3.88(54) & 11.65(59) & 175.964 & 36.71 & 22.3 \\
 0.18 & 3.88(57) & 11.66(08) & 176.061 & 26.69 & 23.4 \\
\end{array}
\]

\[ T_c(\text{K}) \]

\[ \Delta T_c(\text{K}) \]
Figure 2. (a) Electrical resistivity for CaLaBaCu$_{3-x}$Ga$_x$O$_{7-δ}$
(b) Behavior of $T_c$ as a function of doping concentration $x$ for the
CaLaBaCu$_{3-x}$Ga$_x$O$_{7-δ}$ system.

Table II. Magnetic parameters for the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-δ}$ system.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\chi_0 (10^{-4})$</th>
<th>$\theta_p$ (K)</th>
<th>$C$</th>
<th>$\mu_{\text{ion, cu}} (\mu_B)$</th>
<th>fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>3.9(94)</td>
<td>-4.570(58)</td>
<td>0.09434</td>
<td>0.504</td>
<td>85-300</td>
</tr>
<tr>
<td>0.06</td>
<td>1.1(66)</td>
<td>-4.573(89)</td>
<td>0.09335</td>
<td>0.503</td>
<td>85-300</td>
</tr>
<tr>
<td>0.09</td>
<td>5.7(91)</td>
<td>3.900(31)</td>
<td>0.07452</td>
<td>0.453</td>
<td>85-300</td>
</tr>
<tr>
<td>0.12</td>
<td>0.4(11)</td>
<td>2.080(35)</td>
<td>0.09440</td>
<td>0.511</td>
<td>85-300</td>
</tr>
<tr>
<td>0.18</td>
<td>4.9(54)</td>
<td>1.560(59)</td>
<td>0.08633</td>
<td>0.496</td>
<td>85-300</td>
</tr>
</tbody>
</table>

for all samples can be fitted well with the Curie-Weiss law
$\chi = \chi_0 + C/(T - \theta_p)$, where $C = N\mu_{\text{eff}}^2/3k_B$ is the Curie
constant, N is Avogadro’s number, $\mu_{\text{eff}}$ is the effective magnetic moment ($\mu_{\text{eff}} = P_{\text{eff}}/\mu_B$), $P_{\text{eff}}$ represents the effective Bohr magneton number, $\mu_B$ is the Bohr magneton, $K_B$
is the Boltzmann constant, $\theta_p$ is the paramagnetic Curie tem-
perature and $\chi_0$ is the temperature independent susceptibility term. The parameters obtained from the fitting are shown in
Table II. It is interesting to notice the negative characteris-
tic of the transition temperature $\theta_p$ obtained from the Curie-
Weiss fitting, for $x = 0.03$ and 0.06. These results permit us to
infer the occurrence of a paramagnetic-antiferromagnetic transition for these Ga-concentrations. On the other hand, for
other values of $x$, $\theta_p$ is positive, which is characteristic of a
paramagnetic-ferromagnetic transition. The $T_c$ versus dopant
concentration $x$ behavior for all samples is depicted in Fig.
2b. With progressive substitution of Ga at the Cu-site, the $T_c$
decreases monotonically in this compound.

The decrease in $T_c$ of a doped system can be explained
on the basis of the Ga$^{3+}$ substitution at the Cu$^{2+}$ site, which
is supposed to decrease the number of carriers in the system,
and then pushes back to the under-doped region with lower
$T_c$. Alloivalent substitutions in high $T_c$ systems give rise to
the charge imbalance, and hence, alter the effective copper
valence of the parent system, resulting in an alteration of the
number of carriers in them.

4. Conclusions
We have shown that the Ga substitution takes place isostruc-
turally at the Cu-site in the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-δ}$ com-
-pound, at least up to 6 % of the substituent concentration in
the material. The superconducting transition temperature, $T_c$
decreases with an increase in the concentration of doped Ga
in the CaLaBaCu$_{3-x}$Ga$_x$O$_{7-δ}$ compound, in a similar way
as in other RE:123 compounds. Our results suggest that the
pair breaking does not necessarily occur by the magnetic mo-
ment, but it may be due to other mechanism, as structural
disorder and hole-fulfilling. The main cause of the decrease
in $T_c$ is the eating of holes due to the Cu$^{2+}$/Ga$^{3+}$ aliova-
lent substitution, along with the disorder created due to the
ionic size mismatch between Fe and Cu-ions. The normal
state magnetism of the substituted samples shows a Curie-
Weiss temperature dependence to the magnetic susceptibility
in terms of an induced moment in the Cu ion present in the
material.

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