Effect of the partial replacement of Ca by alkaline element Na on Tl-1223 superconductor

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Abstract We have investigated the effect of Na substitution at Ca sites on the lattice parameters, electrical resistivity, magnetic susceptibility and thermopower coefficient for TlBa₂Ca₂-xNaxCu₃O₉-δ; with 0 ≤ x ≤ 0.4. The lattice parameters elongate with increasing the Na-content. A little enhancement in the superconducting transition temperature Tc has been observed as x increases from 0 to 0.05 and then it depresses gradually for x > 0.05. This observation was attributed to the fact that Na has converted the Tl-1223 phase from over-doped regime to under-doped regime which is in conformity with the thermopower results, that found to change from negative (over-doped regime) to positive (under-doped regime). The inter-grain critical current density as function of Na has been also reported from ac magnetic susceptibility measurements.

Key words: Resistivity, magnetic susceptibility, thermopower, critical current density.

1- Introduction The effect of impurities, such as transition elements, rare earth elements and alkaline elements on high temperature superconductors gives important information about the origin of superconductivity phenomena and the structure of superconductors. Usually, transition metal elements and rare earth elements depress the transition temperature and critical current density [1] whereas alkaline elements are known in some cases to enhance: the transition temperature, the formation rate of the superconducting phase and critical current density [2]. Dong et al. [3] reported on the structure, transition temperature and superconductivity of Y₁₋ₓNaₓBa₂Cu₂₋ₓZnₓO₇₋δ, they found that the presence of Na in the samples had increased the transition temperature up to 60 K and decreased the oxygen content in the samples. The doping of MgB₂ bulk materials with sodium carbonate Mg₁₋ₓB₂(Na₂CO₃)ₓ, was studied by Ueda et al. [4]. A remarkable improvement in critical current density and irreversibility field at 20 K was observed up to x = 0.055 beyond which they decreased monotonically due to excess doping. Kayed [5] reported the stabilization of Tl-2223 phase by adding a small amount (0.3 mol.% of LiCO₃) to Tl₁₋ₓBa₃Ca₂₋ₓCuₓO₁₀₋δ and he succeeded to enhance the formation of Tl-2223 phase.

In this work polycrystalline samples of TlBa₂Ca₂₋ₓNaₓCu₃O₉₋δ; with 0 ≤ x ≤ 0.4 were prepared using a single step of solid state reaction and investigated using X-ray powder diffraction, electrical resistivity, thermopower and ac magnetic susceptibility.

2- Experimental technique Polycrystalline samples of TlBa₂Ca₂₋ₓNaₓCu₃O₉₋δ; with 0 ≤ x ≤ 0.4 were prepared using stoichiometric amounts of Tl₂O₃, BaO₂, CaO, Na₂O₂, and CuO by single step of solid state reaction technique [6]. The samples were characterized by X-ray using Philips PW-179 (CuKα-radiation) powder diffractometer. The electric resistivity and magnetic susceptibility were measured using a quantum design PPMS system equipped (physical property measurement system) with a 9-Tesla superconducting magnet. The electric resistivity of the samples was measured by the conventional four-probe technique in the temperature range from 300 down to
10 K. The samples were cut to have the shape of parallelepipeds with approximate dimensions $8 \times 2 \times 2 \text{ mm}^3$. A typical current of 1 mA was used to avoid heating effects on the samples. The ac-magnetic susceptibilities were measured on powder samples of typical masses 200 to 300 mg for five different values of the ac magnetic field between 0 and 15 Gauss.

The thermoelectric power (TEP) of the samples was measured using the standard differential technique. Sample of dimensions $1.5\times0.3\times0.2 \text{ cm}^3$ was clamped between two copper blocks serving as temperature reservoirs, one block is heated with a metal resistor and two T-type thermocouples were used to monitor the temperatures of both blocks. The thermoelectric motive force between the samples terminals obtained from the longitudinal temperature gradient was measured using a digital microvolt (Leybold–53213).

3- Results and discussions

Figure 1 shows the x-ray diffraction patterns for TlBa$_2$Ca$_{2-x}$Na$_x$Cu$_3$O$_{9-\delta}$ with $x = 0$, 0.05, 0.1 and 0.15. X-ray spectra indicate that the major phase present in the prepared samples is the Tl-1223 phase with very small amounts of impurities such as BaCuO$_2$ and Tl-1212 phases which are typical phases in samples primed by solid-state reaction [7]. The lattice constants “a” and “c” were found to slightly increase with increasing Na-content as shown in Table 1.

![Figure 1 X-ray diffraction patterns for TlBa$_2$Ca$_{2-x}$Na$_x$Cu$_3$O$_{9-\delta}$.](image)

![Figure 2 The variation of lattice parameters with Na content.](image)
Figure 3 displays the variation of electrical resistivity with the temperature for TlBa$_2$Ca$_{2-x}$Na$_x$Cu$_3$O$_{9-\delta}$ with $x = 0, 0.05, 0.1, 0.2$ and $0.4$. All the samples have a metallic behavior from room temperature down to 140 K, reflecting the conduction along the CuO$_2$ planes. The small curvature observed above $T_c$ in the resistivity plot is a characteristic of superconducting thermodynamic fluctuations [8]. For $x \geq 0.2$, the electrical resistivity behavior shows another superconducting phase at temperatures between 100 and 108 K indicating that at high Na-concentrations the formation of Tl-1223 was reduced while that of Tl-1212 was enhanced.

Figure 3 The variation of electrical resistivity with the temperature for TlBa$_2$Ca$_{2-x}$Na$_x$Cu$_3$O$_{9-\delta}$ for $x = 0, 0.05, 0.1, 0.2$, and $0.4$.

Figure 4 Variation of transition temperature and thermopower coefficient as function of Na-content for TlBa$_2$Ca$_{2-x}$Na$_x$Cu$_3$O$_{9-\delta}$.

Figure 4 shows the variation of thermopower and transition temperature ($T_c$) as function of Na-content. A little increase in $T_c$ was observed as $x$ increases from 0 to 0.05 followed by a depression for $x > 0.05$. Since the preparation of our samples was carried out in closed tubes filled with air instead of vacuum tubes, then the un-doped sample, $x =0$, lies in the over-doped region. Na has a valence state of +1 and its substitution in Ca site would reduce the amount of
oxygen in the preparation tube implying that the substitution of Ca by Na may have changed the un-doped sample from over-doped regime to optimum-doped at x=0.05 and then to the under-doped regime for x > 0.05. These results are consistent with those obtained by thermopower measurements having negative values for the un-doped sample and positive values for the doped ones. This consistency is attributed to the fact that the superconducting domain of high-temperature superconducting cuprates is delineated by the minimum (p_{min}), under-doped regime, and maximum (p_{max}), over-doped regime hole concentration per planer Cu-atom. The over-doped samples have a low transition temperature and negative thermopower. As the hole density decreases, by the chemical substitutions or by lowering the oxygen, the optimum level of doping is reached which yields the highest transition temperature and the lowest positive thermopower value. With the further decrease in the hole concentration to under-doped regime the transition temperature has decreased and the thermopower attained larger positive value.

The complex ac magnetic susceptibility has been widely used in the investigations of high-temperature superconductors and was found to be strongly dependent on temperature and ac field amplitude especially for granular structure. Figure 5 shows the variation of the real \( \chi^\prime \) and imaginary \( \chi^\prime\prime \) parts of ac magnetic susceptibility as function of temperature for TlBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_9\)\(_\delta\). The curves of \( \chi^\prime \) data indicate that the transition temperature does not change with the increase of applied ac magnetic fields, however, a small broadening is observed as the ac magnetic fields was increased. Also, we notice that \( \chi^\prime\prime \) is small at high temperatures and exhibits a maximum that shifts to lower temperatures with increasing the external magnetic field.

![Figure 5](image)

Figure 5 The variation of real part \( \chi^\prime \) and imaginary part \( \chi^\prime\prime \) of an ac magnetic susceptibility for TlBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_9\)\(_\delta\) with the temperature.

The critical current density \( J_c \) at the temperature \( (T_p) \) corresponding to the maximum value of \( \chi^\prime\prime \) is related to the full penetration field \( B_p \) according to the equation [9]

\[
J_c = \frac{B_p}{\mu_0 R}
\]  

(1)

Where R is the average radius of grain estimated from Scanning Electron Microscope (SEM) measurements to be 10 \( \mu \)m, they were fitted according to the empirical scaling relation [10]:

\[
J_c(T) = J_c(0)(1 - \frac{T_p}{T_c})^\gamma
\]  

(2)

Where \( J_c(0) \) is the critical current density at 0 K and \( \gamma \) is the critical exponent. The values of \( J_c(0) \) and \( \gamma \) obtained from the best fitting to equation (2) are listed in Table 1.
Table 1: Variation of $J_c(0)$ and $\gamma$ with Na-content

| $X$  | $J_c(0) \times 10^9 A/m^2$ | $\gamma$ |
|------|---------------------------|----------|
| 0    | 1.5                       | 2.03     |
| 0.05 | 2.5                       | 2.08     |
| 0.1  | 2.1                       | 2.01     |
| 0.2  | 1.3                       | 2.00     |
| 0.3  | 0.85                      | 2.03     |
| 0.4  | 0.80                      | 1.93     |

The obtained values of $\gamma$ were found to be around 2, which are close to the values of other superconductors reported in the literature [11]. However, they are quiet different from what is expected ($\gamma=1.5$) from Ginzburg-landau theory for $J_c(T)$ of an infinite slab near $T_c$. The value of $\gamma=2$ indicates that the intergrain junctions are SNS type [12]. Moreover, the critical current density at 0 K increases as $X$ is increased from 0 to 0.05 and then it decreases in similar fashion to the transition temperature. The suppression in $J_c(0)$ at higher Na content is explained by the increase of the grain boundaries resistance and the reduction of the flux pinning inside the sample.

Conclusions

We have successfully studied the effect of partial replacement of Ca by Na in Ti-1223 phase. The x-ray, resistivity, and magnetization data showed that low Na-concentration enhances the formation of Ti-1223, and increases the critical current density whereas high Na-concentration enhances the formation of secondary phases and reduces the critical current density as well as the transition temperature. The resistivity and thermopower results indicated that the partial replacement of Ca by Na converted un-doped sample from over-doped regime to optimum-doped regime at about $x=0.05$ and to under-doped regime for $x > 0.05$.

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