JOURNAL OF MATERIALS SCIENCE 37 (2002) 1557–1560

# Effect of Ar heat treatment on oxygenated $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (R = Y, Sm) superconductors

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The influence of heat treatment, at 450°C in Ar environment, on oxygenated ($6.72 < 7 - \delta < 6.93$) samples of $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (i.e. R(Ca)-123, with R = Y, Sm) with $0 < x < 0.3$ has been investigated. Measurements of oxygen loss, normal state resistivity behaviour $\rho(T)$, superconducting critical temperature $T_c$ and transition widths reveal that Ar treatment effects both the series differently. The Sm(Ca)-123 samples, for all values of $x$, show a considerable loss of oxygen ($\Delta\delta(x) = 0.4$ to 0.6) and decrease in $T_c$ ($\Delta T_c(x) = 35$ to 55 K). Whereas, surprisingly, the Y(Ca)-123 samples show a much smaller loss of oxygen ($\Delta\delta(x) = 0$ to 0.3), along with a decrease in $T_c$ for $x < 0.2$ and an increase in it for $x \geq 0.2$. In particular, the $x = 0.3$ sample shows a negligible change in oxygen content accompanied by an increase of 20 K in $T_c$. These and host of other observations suggest that the presence of Ca may influence the oxygen loss mechanism in these series.


## 1. Introduction

The peculiar dependence of structural, normal and superconducting state properties on oxygen content in $RBa_2Cu_3O_{7-\delta}$ (i.e., R-123, R = Y or rare earth) system [1, 2], and its qualitative insensitivity [3–5] to all R (except R = Ce, Pr and Tb) has been an interesting landmark in the field of high temperature superconductors (HTSC). It is well known that, with high temperature (~450°C) treatment in Argon environment, oxygenated R-123 system can lose oxygen from the chainer Cu—O plane, when the oxygen content $7 - \delta$ decreases from 7 towards 6. Typically the R-cation in R-123 structure has an 8-fold coordination and is sandwiched between two square-planar $CuO_2$ planes, which are supposed to stay unaffected by such heat treatments.

However, introduction of Ca at R-site may lead to oxygen loss from $CuO_2$ planes, due to its possible preference of different coordination number than that of R [6, 7]. The main idea has been that Ca in 8-fold coordination has an ionic radii of 1.12 Å and in 6-fold the same is 1.00 Å. Whereas, the ionic size of R-cation in 8-fold coordination can vary a lot depending on R. For instance, Y (Sm) has an ionic radii of 1.02 Å (1.09 Å), and Ca may prefer to substitute in 6-fold (8-fold) coordination at Y- (Sm-) site. To investigate such a possibility further, heat treatments similar to that known for R-123 system were given to oxygen treated series of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (i.e., Y(Ca)-123) and $Sm_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (i.e., Sm(Ca)-123). If the oxygen loss mechanism stays independent of R, then the changes in structure, total oxygen loss, normal and superconducting state properties should be at least qualitatively similar in both the series, as documented for pure (Ca-free) R-123 system. However, our results show that presence of Ca results in an entirely different set of properties for both the series, which is the highlight of present work.

## 2. Experimental details

Same oxygen treated polycrystalline samples of Y(Ca)-123 and Sm(Ca)-123 series as used in Ref. [6], with $x = 0.0$, 0.1, 0.2 and 0.3, were further heat treated in Ar environment at 450°C for 12 hours and furnace cooled to room temperature. X-ray diffraction (XRD), oxygen content (within ±0.02) determination by iodometric titration, resistivity $\rho(T)$ and $T_c(\rho = 0)$ (within ±1 K) measurements were carried out for all the samples. Typical current density for $\rho(T)$ measurements was kept less than 10 mA/cm$^2$.

## 3. Experimental results

After Ar heat treatment, all the samples of both Y(Ca)-123 and Sm(Ca)-123 series maintain a single phase XRD (see Ref. [6] for the XRD of the pristine samples before Ar treatment). In Figs 1a and 2a we show the orthorhombic distortion OD ($= (b - a)/b$), where $a$ and

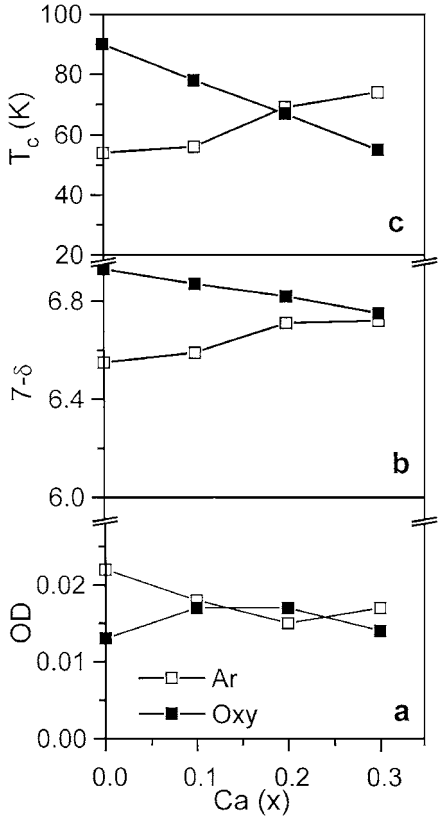


*Figure 1* (a) Orthorhombic distortion OD, (b) total oxygen content $7-\delta$, and (c) $T_c$ as a function of Ca content in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ samples. 'Oxy' and 'Ar' marked in the figure indicate the heat treatment of the samples in oxygen and subsequently in Ar atmosphere, respectively.

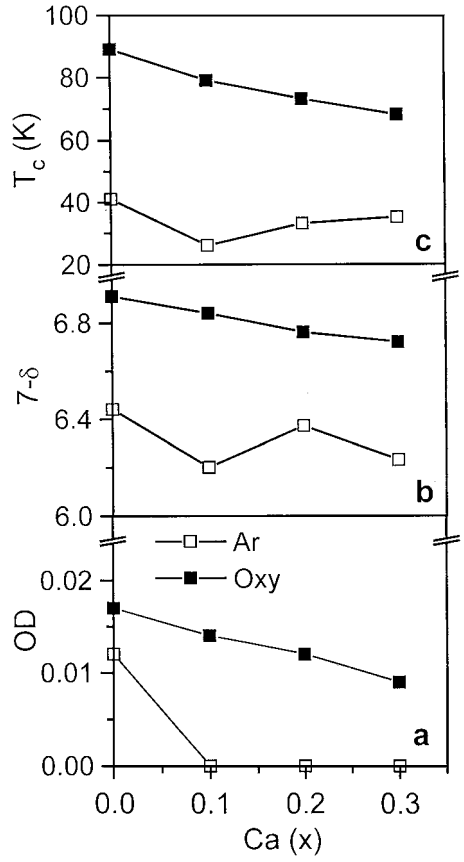


*Figure 2* (a) Orthorhombic distortion OD, (b) total oxygen content $7-\delta$, and (c) $T_c$ as a function of Ca content in $Sm_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ samples. 'Oxy' and 'Ar' marked in the figure indicate the heat treatment of the samples in oxygen and subsequently in Ar atmosphere, respectively.

$b$ are the lattice parameters) as a function of $x$ for both the series of samples before and after Ar treatment. The Y(Ca)-123, after Ar treatment, retains an orthorhombic structure with a finite OD for all the values of $x$ (see Fig. 1a). Whereas, the Sm(Ca)-123 becomes tetragonal with OD = 0 for all the values of $x \geq 0.1$ (see Fig. 2a).

In Figs 1b and 2b we plot the total oxygen content $(7-\delta)$ as a function of Ca concentration for both the series of samples before and after Ar treatment. For Y(Ca)-123 (see Fig. 1b), Ar treatment leads to a loss of oxygen $\Delta\delta = (7-\delta)|_{oxy} - (7-\delta)|_{Ar}$ (subscripts 'oxy' and 'Ar' denote the oxygen and subsequent Ar treatment), which decreases with increasing $x$. It is noteworthy that even after 12 hours of Ar treatment the $x = 0.3$ sample of Y(Ca)-123 shows only a negligible oxygen loss with $\Delta\delta = 0.03 \pm 0.02$. In contrast, the Sm(Ca)-123 samples for all values of $x$, after Ar treatment, show a relatively large loss of oxygen with $\Delta\delta(x) \approx 0.4$ to 0.6 (see Fig. 2b). Note that the total oxygen content $7-\delta > 6.5$ ($7-\delta < 6.4$) values for all the Ar treated Y(Ca)-123 (Sm(Ca)-123) samples gives credence to the their orthorhombic (tetragonal) structure as noted above.

The $\rho(T)$ behaviour for the Ar treated samples of both Y(Ca)-123 and Sm(Ca)-123 series are depicted in Figs. 3a and 3b, respectively. For Y(Ca)-123 samples, as reflected by the change in curvature in Fig. 3a, the $\rho(T)$ behaviour continuously evolves from semiconducting- to metal-like with increasing $x$. The superconducting transitions continuously shift to higher temperatures with increasing $x$. In contrast, the Sm(Ca)-123 samples show an enhancement in the semiconducting- like $\rho(T)$ behaviour for all the values of $x$. The superconducting transition first shifts to a lower temperature with Ca substitution (compare the transitions for $x = 0$ and 0.1 samples in Fig. 3b). Subsequently, with increasing Ca ($x \geq 0.1$), the transition shifts to higher temperatures. Note that the latter result along with the fact that all the Ar treated Sm(Ca)-123 (for $x \geq 0.1$) samples are tetragonal ($7-\delta < 6.4$) agree with the earlier report of superconductivity in tetragonal R(Ca)-123 system [8].

Finally, in Figs 1c and 2c, we depict the results of $T_c(\rho = 0)$ as a function of $x$ for both the series of samples before and after Ar treatment. In the case of Y(Ca)-123, Ar treatment leads to a change in $T_c$ (see Fig. 1c), where $\Delta T_c = T_{c,oxy} - T_{c,Ar}$ decreases continuously with increasing $x$ and becomes negative (i.e., $T_{c,oxy} < T_{c,Ar}$) for $x \geq 0.2$. This result is especially significant for the $x = 0.3$ sample, where the Ar treatment results in an enormous increase in $T_c$ by 20 K along with only a negligible change in total oxygen content (see above). On the other hand, the Ar treated Sm(Ca)-123, for all the values of $x$, show a large decrease in $T_c$ with $\Delta T_c(x) \approx 35$ to 55 K (see Fig. 2c).

## 4. Discussion

For discussion, we note that the structure, $\delta(x)$ and $\rho(T)|_x$ in Sm(Ca)-123 samples after Ar heat treatment resemble the well established behaviour of pure (Ca-free) R-123 system. Whereas the behaviour of Ar

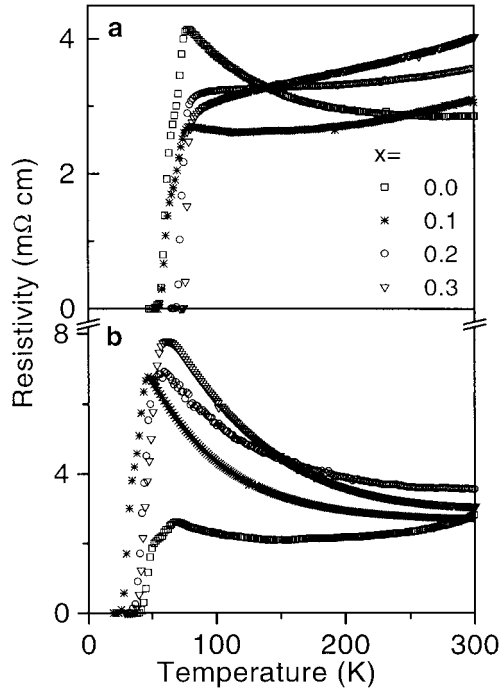


*Figure 3* Resistivity as a function of temperature for different values of Ca content in: (a) $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$; (b) $Sm_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$.

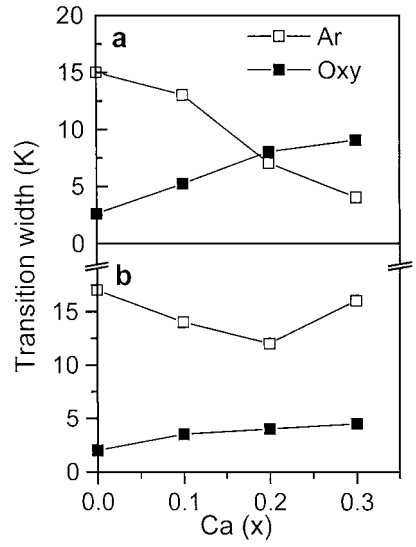


*Figure 4* Transition widths (defined as 10%–90% of the superconducting transition in $\rho(T)$) as a function of Ca content in: (a) $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$; (b) $Sm_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. 'Oxy' and 'Ar' marked in the figure indicate the heat treatment of the samples in oxygen and subsequently in Ar atmosphere, respectively.

treated Y(Ca)-123 for $x \geq 0.1$ deviates considerably from that of the latter. We believe that these results support our earlier work [6, 7], where we suggested the formation of oxygen vacancies in $CuO_2$ planes [9] and Cu—O chains in oxygen treated Y(Ca)-123 and Sm(Ca)-123, respectively. The different behaviour of Y(Ca)-123 and Sm(Ca)-123 samples, resulting from Ar heat treatment, may well be indicative of an oxygen loss mechanism operating differently in both the series. It is known that heat treatment of pure (Ca-free) oxygenated R-123 system, in Ar atmosphere, leads to removal of $O_2$ from the Cu—O chains [1, 2] to the environment. In case of Ar heat-treated Y(Ca)-123 system, it may be possible that the oxygen removed from Cu—O chains partially fills some of the existing oxygen vacancies in $CuO_2$ planes and partially lost to the environment. With increasing Ca, since the number of such vacancies increase in the pristine oxygen treated samples [6, 7], the amount of oxygen lost to the environment during Ar treatment may go down. The filling of oxygen vacancies in $CuO_2$ planes by Ar treatment can explain, with increasing $x$, the observed behaviour of a decrease in $(7-\delta)|_{oxy} - (7-\delta)|_{Ar}$ (see Fig. 1b), an improvement towards a metal-like $\rho(T)$ behaviour (see Fig. 3a), and a decrease in $T_c(x)|_{oxy} - T_c(x)|_{Ar}$ (see Fig. 1c) in Y(Ca)-123 system. For Ar treated Y(Ca)-123 ($x = 0.3$) sample, the rise in $T_c$ by 20 K accompanied by nearly no change in oxygen content can be understood as annealing out of the oxygen vacancies in $CuO_2$ planes. In contrast, in case of Sm(Ca)-123 for all values of $x$, as observed in the Ca-free pure R-123 system, the heat treatment in Ar plausibly leads to further removal of oxygen from Cu—O chains to the environment. This can explain the observed large decrease in oxygen content (see Fig. 2b), semiconducting-like $\rho(T)$ behaviour (see Fig. 3b), and a large decrease in $T_c$ (see Fig. 2c) in Ar heat treated Sm(Ca)-123 system for all values of $x$.

One aspect, which was not discussed, is the observed (see Fig. 3) significant change in the superconducting transition widths for both the Y(Ca)-123 and Sm(Ca)-123 samples after Ar treatment. Since the samples are polycrystalline, it is imperative to think whether it is not due to certain extrinsic factors related to grain boundaries. Bearing in mind that Ar treatment was carried at relatively low temperature of 450°C for 12 hours, no grain growth and texturing can be expected. The only extrinsic factor that may influence the transition width is a loss of oxygen from grain boundaries. However, a closer look at our results does not support this. Shown in Fig. 4 are the transition widths as a function of $x$ for both the series of samples before and after Ar treatment. For Y(Ca)-123 samples, interestingly, the transition widths decrease monotonically with increase in $x$ after Ar treatment (see Fig. 4a). Note that the $x = 0.3$ Y-based sample, which shows an enhancement in $T_c$ by 20 K along with nearly no change in oxygen content after Ar treatment, also shows a sharper transition. The transition width decreases from 7 K to 4 K after Ar treatment. These results, in fact, further support our suggestion that oxygen is lost from Cu—O chains to $CuO_2$ planes in case of Y(Ca)-123 samples. In contrast, for all values of $x$, the Sm(Ca)-123 samples after Ar treatment show considerable increase in the transition widths to values ≈15 K. As compared to the values before Ar treatment (see Fig. 4b), the increase in transition widths by around 10 K matches well with the values known [10] for pure (Ca-free) oxygen deficient R-123 system, and attributed to the loss of oxygen from Cu—O chains. Moreover, the observed changes in the structure and total oxygen content in both the series after Ar treatment cannot be accounted by a loss of oxygen only from the surface of the grains, i.e., grain boundaries. Considering these observations and the fact that both Y- and Sm-based series are prepared under identical synthesis conditions, we feel, the present analysis is justified.

## 5. Conclusions

In conclusion, the heat treatment of oxygenated Y(Ca)-123 and Sm(Ca)-123 in Argon environment at 450°C leads to a different evolution of the orthorhombic distortion, $\delta(x)$, $\rho(T)|_x$, $T_c(x)$ and transition widths in both the series. These results are at variance with a universal, independent of R-cation, change in these properties usually observed for pure (Ca-free) R-123 system. The applied heat treatment was expected to result in a loss of oxygen from chainer Cu–O planes to the environment. However, it seems, in the presence of Ca the actual oxygen loss mechanism depends on R-cation in R(Ca)-123 system.


## Acknowledgments

One of us (AVN) thanks CSIR for the Emeritus Scheme and is grateful to Professor Fernando for his hospitality and providing facilities and maintenance support during the visit.


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*Received 17 April*
*and accepted 11 December 2001*