Complete substitution of Sr for Ca in Bi$_2$Sr$_{2+x}$Ca$_{1-x}$Cu$_2$O$_{8+\delta}$

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We have systematically substituted Sr for Ca as spacer of the CuO$_2$ planes in Bi$_2$Sr$_{2+x}$Ca$_{1-x}$Cu$_2$O$_{8+\delta}$ thin films deposited by molecular beam epitaxy, from $x=0$ (2212 phase) to $x=1$ (2302 phase). From dc transport measurements we have found a decrease of T_c-zero from 88 K for $x=0$ down to 55 K for $x=1$. The remarkable result reported here is the presence of superconductivity when Ca is completely replaced by Sr. Comparison of structural and transport data shows that the enlargement of the unit cell due to the substitution has no dramatic effect on the onset of superconductivity. This result is compared to previous studies and existing results on bilayer systems.

One of the enduring questions surrounding superconductivity in cuprates is that of the physical dimensionality of the coherent dynamical system and how this system undergoes a transition to the superconducting state. While there is a great deal of evidence that macroscopic quasiparticle transport in the c-axis direction is incoherent and of a hopping nature in the normal state, the role of c-axis coupling between planes in contributing to a pairing mechanism continues to be debated. Different approaches to the mechanisms of high-T_c superconductivity have been formulated, for example Anderson's interlayer tunnel theory[1] and Leggett's MIR scenario.[2] In both cases the parameters of the theory are sensitive to the spacing between the planes and this has motivated several groups to systematically vary this quantity and find out its role in determining the transition temperature.

The intramultilayer (IML) distance in cuprates, i.e., the distance between two CuO$_2$ planes in the same half unit cell, has been changed either by intercalation, pressure or by making artificial superlattices.[3,4] Besides YBCO-based compounds,[5,6] all other HTS multilayered materials undergo the superconducting transition only if the spacing ion is Ca. Partial substitution of Ca was performed, sometimes by rare earths,[7,8] inevitably inducing disorder and valence change. Following the general idea of changing as few experimental parameters as possible, substitution of Ca by alkali earths is particularly interesting. However, so far no samples are known to be superconducting with Ca *fully* substituted by other alkali earths. Previous work has investigated Sr substitution of the nominal Ca layer in two layer cuprates. Sleight *et al.* substituted Sr for Ca in Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+\delta}$ (Ref. 9) and Sr for Y in Bi$_2$Sr$_{3-x}$Y$_x$Cu$_2$O$_{8+\delta}$ (Refs. 10 and 11) single crystals. In the case of Bi$_2$Sr$_{3-x}$Ca$_x$Cu$_2$O$_{8+\delta}$ the onset of T_c remains almost the same (95 K) in the range $x=0.4$–0.9. A different behavior is found in Bi$_2$Sr$_{3-x}$Y$_x$Cu$_2$O$_{8+\delta}$ samples, where superconductivity is restricted to the interval $x=0.2$–0.4 with a variation of T_c of 7 K, presumably due to carrier doping. For $x=0.5$–1 a semiconducting temperature dependence of the resistance was observed. The c axis decreased by 0.6 Å from $x=0.3$ to 1, which as we show is large compared to what we observe in our Bi$_2$Sr$_{2+x}$Ca$_{1-x}$Cu$_2$O$_{8+\delta}$ films (Fig. 1). The substitution of Y^{3+} for Sr^{2+} or Ca^{2+} involves also a change in the valence

that would need to be balanced by the introduction of oxygen in the Bi-O sheets, if the average carrier doping is to remain unchanged.[9]

The hypothesis of extra-oxygen inclusion in the structure when Ca is substituted by Sr has been also considered by Shaked *et al.*[12] in La$_{1.8}$Sr$_x$Ca$_{1.2-x}$Cu$_2$O$_{6-\delta}$ (LSCCO) samples. The unit cell of this compound contains two CuO$_2$ planes, nominally separated by Ca, representing in this sense an analog of Bi$_2$Sr$_{2+x}$Ca$_{1-x}$Cu$_2$O$_{8+\delta}$. Neutron diffraction experiments proved that in La$_{1.8}$Sr$_x$Ca$_{1.2-x}$Cu$_2$O$_{6-\delta}$ there is oxygen intercalation in the metal plane separating the CuO$_2$ sheets and a comparable occupation probability of the Ca^{2+} site by Sr^{2+} and La^{3+} ions. The overall effect of the substitution of Sr for Ca on the superconducting properties of these samples is that the T_c decreases from about 60K (no Sr in the structure) to zero (no Ca in the structure). When Sr is substituted for Ca, the structure of the unit cell is expected to change as a consequence of the larger ionic radius of Sr^{2+} as compared to Ca^{2+} (1.26 Å vs 1.12 Å in eightfold coordination[13]). A size effect was indeed observed in La$_{1.8}$Sr$_x$Ca$_{1.2-x}$Cu$_2$O$_{6-\delta}$ as a linear increase in the c axis of
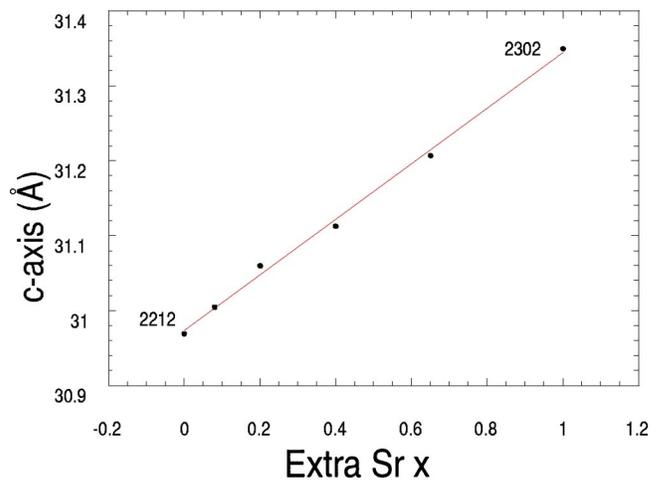
FIG. 1. c-axis dependence on the extra Sr x of Bi$_2$Sr$_{2+x}$Ca$_{1-x}$Cu$_2$O$_{8+\delta}$ thin films as measured by XRD. The unit cell expands linearly by $\Delta c = 0.19$ Å from 2212 to 2302 phases.

about 0.40 Å from the sample with $x=0$ to the sample with $x=0.8$. This c-axis variation is too big to be due only to different ionic radii of Sr and Ca. The inclusion of oxygen between the copper oxide planes could be related to increased available space after Sr substitution as well as to enhanced electrostatic attraction because of La^{3+} at the Ca^{2+} site.

In order to clarify the effect of substitution of the CuO_2 planes spacer in bilayer systems, we have replaced Sr for Ca inside the unit cell of thin films of double-layer BSCCO ($Bi_2Sr_2CaCu_2O_{8+\delta}$) with the intent to study the effect on the structural and electronic properties. It is our belief that by making substitution of Ca for Sr, the most obvious, and hopefully the most important difference between these two ions is that of their size, and that no important changes in details of band structure or dielectric constant are induced (as both Ca^{2+} and Sr^{2+} are closed shell ions with low polarizability). In this paper we report results of experiments in which thin films of $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_{8+\delta}$ are grown with x ranging from 0 to 1 using atomic layer-by-layer molecular beam epitaxy (ALL-MBE). When $x>0.8$ the compound is apparently thermodynamically unstable and can not be synthesized using equilibrium techniques.[11] By using atomic layering of each molecular layer, it is possible to grow samples of compositions that are otherwise impossible to obtain.[14] We find that a new superconducting phase 2302 (corresponding to x = 1) of BSCCO family can be artificially grown. The substitution of Sr on the Ca site in BSCCO-2212 slightly increases the spacing between the CuO_2 planes within each molecular layer.

Single crystal $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_{8+\delta}$ thin films with x = 0, 0.08, 0.2, 0.4, 0.65, and 1 were grown by ALL-MBE, all using the same optimized growth conditions. The details of the system deposition are described elsewhere.[14] We deposited 40 monolayers of $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_{8+\delta}$ on top of two monolayers of 2201 phase which serve as a buffer layer on top of the $SrTiO_3$ substrate, for a total thickness of about 600 Å for all the samples. The oxidation was obtained using a beam of pure ozone and the growth pressure was kept at a value of 8×10^{-6} Torr, while the substrate was heated to a temperature of 720–730 °C, as measured by an optical pyrometer. A quartz crystal monitor and atomic absorption spectroscopy were used to monitor the atomic fluxes. In particular, the atomic absorption spectroscopy is fast enough to be used for feedback control of the shuttering times during the growth and the reproducibility is well within 1%.[15] In addition, information about the crystalline structure, coherence and flatness, given in real time by reflection high-energy electron diffraction (RHEED), allows the modification of the deposition parameters. The RHEED analysis has shown a layer-by-layer growth mode under optimal conditions and atomically smooth surfaces for x in the range 0–0.4. A typical large area root mean square value of the surface roughness of about 8 Å, caused by terrace steps, as measured by atomic force microscopy (AFM) performed after the growth, characterizes the degree of atomic flatness of the surfaces. The structural properties of the films were studied by x-ray diffraction (XRD) performed by a Philips
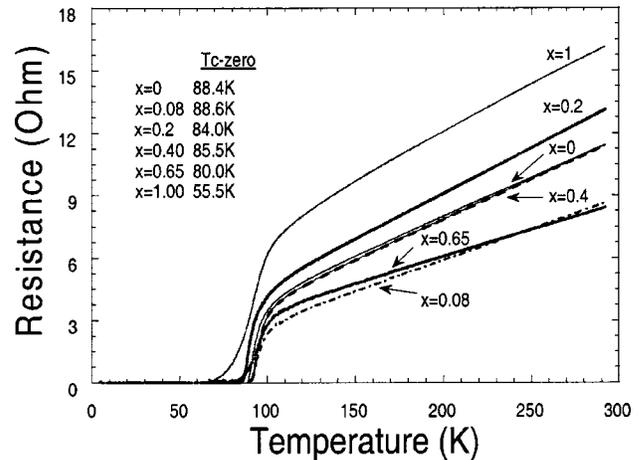
FIG. 2. Resistance vs temperature curves of $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_{8+\delta}$ with $x=0-1$. A complete superconducting transition (zero resistance) is observed in all the films, included the 2302 sample.

X'Pert diffractometer in high-resolution optic configuration. The superconducting properties were measured by dc transport.

The dependence of the formula unit c-axis lattice constant on Sr substitution is shown in Fig. 1. We find a linear increase of the c-axis lattice constant as the Sr content in our films increases, as measured from the (0010) diffraction peak in $2\theta-\omega$ scans. The c axis varies by 1.2% between full Ca (2212) and full Sr (2302). The observed linear dependence of c on the Sr content is similar to the observations in $La_{1.8}Sr_xCa_{1.2-x}Cu_2O_{6-\delta}$,[12] and in $Bi_2Sr_{3-x}Y_xCu_2O_{8+\delta}$,[11] but in those cases a larger variation of the c axis (2.3%, and 2%, respectively) was found in the range of substitution investigated. The ω scan rocking curve of the (0010) reflection of the 2212 phase measures 0.02°. The presence of Kiessig fringes around the (0010) in the $2\theta-\omega$ scan confirms the high degree of structural order throughout the thickness of the samples, and specifically the high quality of the unit cell interfaces. The same features are observed in the $2\theta-\omega$ and ω scans at least until the $x=0.4$ sample.

Figure 2 shows the resistance vs temperature curves $R(T)$ of the samples. The first important observation is that the $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_{8+\delta}$ films are all superconducting. In contrast to Ref. 12 we find superconductivity even when Ca is completely replaced by Sr as the spacer between the CuO_2 planes obtaining a new superconducting phase in BSCCO family compounds, the 2302 phase, in correspondence with $x=1$. The difficulty in obtaining 2302 by just thermodynamic processes[11] has been overcome by using nonthermodynamic, kinetically controlled growth typical of molecular beam epitaxy. The T_c zero of the new superconducting phase is about 55 K. This value is lower than in 2212, but still higher than in the single layer compound [38 K (Ref. 16)].

The dependence of transport properties on x is more clearly evident from Fig. 3. In this figure three critical temperatures, chosen at different points of the $R(T)$ curves reported in Fig. 2, are plotted as a function of extra Sr. For each composition the top point is the onset temperature
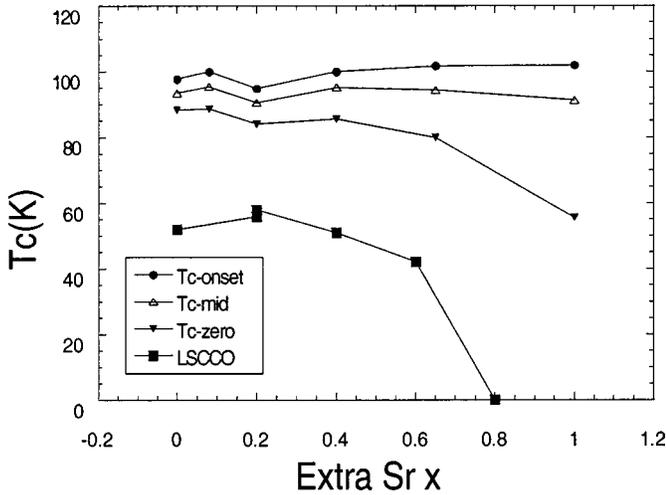
FIG. 3. Three temperatures corresponding to different points of the $R(T)$ curves reported in Fig. 2 are plotted vs extra Sr x: T_c onset, T_c mid (the midpoint of the transition), and T_c zero. Shaked *et al.*'s data are also reported as a comparison.

T_c-onset, defined as the intercept of the normal curve above the transition and the slope during the transition. The next temperature is T_c-mid, corresponding to the midpoint of the transition where the resistance value at the onset halves. The third line is T_c-zero, the temperature where the resistance is zero within the experimental detection limit. T_c-zero does not reduce very much from the 2212 sample (88.4 K at x =0) to 40% substitution (85.5 K at x=0.4). A decrease of T_c-zero of about 10% is reached at x=0.65, while a value of 55.5 K is found in the x=1 sample with 100% Sr substitution for Ca. The transition widens above x=0.60 and is much wider for the x=1 sample than for lower x samples. We attribute this to local lattice disorder which is related to growing a metastable phase. In the x=1 sample the onset is actually higher than in the other samples, but the transition extends to lower temperatures due to disorder. Since fluctuations can be enhanced by dimensional constraints, it is hard to uniquely attribute the higher onset temperature to an intrinsic response of the material to having a bigger spacer layer. In the same figure we also report Shaked *et al.*'s results.

The superconducting properties can be influenced by several factors. First of all, disorder. Some level of disorder is present also in our films for x=0.65 and 1, as is evident from the broadening of the $R(T)$ curves of Fig. 2. For the same samples, the RHEED patterns and the broadening of XRD rocking curves confirm an increase of disorder which reduces the flatness of the half unit cell interfaces. Nevertheless, this kind of disorder is not great enough to destroy superconductivity. It reduces T_c-zero, but the resistive onset is not influenced.

In the case of $La_{1.8}Sr_xCa_{1.2-x}Cu_2O_{6-\delta}$, the drastic decrease of T_c-onset down to zero has been attributed to the presence of oxygen in the Ca-substituted layer. This site is usually not occupied when Ca is the spacer, but a non-zero occupancy of 15% at x=0.8 was found by refinement on neutron scattering data in Ref. 12. Since our samples are thin

films, neutron scattering cannot be applied to detect possible intercalation of oxygen. Nevertheless, the XRD results about the expansion of the unit cell along the c direction by Δc =0.19 Å (comparable to the difference between the atomic diameters of Sr and Ca) is an indication that no extra oxygen is included in the Sr layer between the CuO_2 planes when the 2302 phase is stabilized. As discussed Ref. 12 the presence of extra oxygen is likely a consequence of electrostatic drive and large IML distance, but we believe that these conditions are absent in our sample and that the above estimate applies. In fact, the substitution of Bi for Sr is not very likely to happen in BSCCO,[19] especially since the atomic layering employed here provides the atoms sequentially to build up the molecular structure of each unit cell.

As an example of how the IML distance d can affect the critical temperature, we have used Leggett's MIR scenario[2] to obtain a quantitative prediction of the expected decrease of the onset temperature T_c according with the expression

$$\Delta T_c^{(2)} = -\frac{\Delta d}{d}[T_c^{(2)}(d) - T_c^{(1)}(d)]. \tag{1}$$

Δd represents the change of the IML distance d, $T_c^{(2)}$ and $T_c^{(1)}$ are respectively the transition temperatures of the bilayer (2212) and single layer (2201) compounds in the same series. In our films taking $T_c^{(1)}$=38 K,[16] d=3.2 Å,[17] and other quantities from our experiments ($T_c^{(2)}=T_c$ onset=96 K for pure Ca-based compound, and Δd=0.19 Å for Sr-based one) we obtain $\Delta T_c^{(2)}$ of −3.4 K. This value is probably an upper limit on the T_c depression for two reasons. First of all, Bi-2201 is not a very good single layer HTS (as Tl- and Hg-ones), and therefore the difference ($T_c^{(2)} - T_c^{(1)}$) amplifies changes in the plane spacing. Second, any increase in polarizability of the spacer has been neglected, but in principle it would lead to small changes in the background screening properties.[2] The expansion of relevant quantities in d around Bi-2212 value inevitably leads to a small variation (decrease) of T_c with the values of Δd observed in our experiments.

It is interesting that MIR offers an explanation of suppression of T_c in the experiment of Shaked *et al.* According to (1), the variation of T_c in this case should be $\Delta T_c^{(2)}$ =−1 K. However, observed oxygen impurities were positioned between the Cu atoms in two adjacent planes, at a O-Cu distance not too different from the in-plane one. It has been conjectured that the nature of the O-Cu vertical bond is the same as the in-plane bond, and that the oxygen effectively acts as easy tunneling center between the planes, thus heavily suppressing T_c.[18]

An alternative explanation of the loss of superconductivity in $La_{1.8}Sr_xCa_{1.2-x}Cu_2O_{6-\delta}$ could be attributed to in-plane oxygen vacancies.[20] In fact, Shaked *et al.* revealed their presence up to 12% per unit formula (in the nonsuperconducting sample) by Rietveld analysis on neutron diffraction data. Nevertheless, although the amount of disorder induced by the above oxygen vacancy concentration can lower T_c it cannot drive it to zero. Finally, the extra oxygen could also contribute to pair-breaking mechanism, e.g., distorting the local structure of the planes, but no dramatic variation of T_c is expected in this case.[21]

In conclusion, the main result we have reported in this paper is the presence of superconductivity when the spacer of the CuO_2 planes is Sr and not Ca. We obtained this result in $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_{8+\delta}$ thin films grown by ALL-MBE. T_c zero is observed to decrease from 88 K in the sample with $x = 0$ (2212 phase) down to 55 K when $x = 1$, corresponding to an artificially synthesized superconducting phase. The Sr substitution apparently does not change the onset of the superconducting phase transition. We measured an increase of c-axis by 1.2% by high resolution XRD in 2302 compound respect to 2212. This increase, due to the larger ionic radius of Sr respect to Ca, is an indication that the CuO_2 planes are pushed apart from each other, but by a much smaller amount than that observed in other bilayer cuprates after the same substitution. When Sr is intercalated, the distance d_{Cu-Cu} is still too short to allow extra oxygen atoms to occupy the interplane space, unlike in LSCCO. This fact could be a possible explanation for the different electronic behavior of the two systems, with the loss of superconductivity in the case of LSCCO and its persistence in BSCCO. Calculations based on the MIR scenario predict a few degrees decrease for the onset of T_c, in both systems, if the only consequence of the Sr substitution is assumed to be an increased distance between the copper oxide planes. More quantitative predictions of the minimum value of d_{Cu-Cu} needed for the inclusion of oxygen would be interesting for understanding the role played by oxygen in the transport properties.

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