

Applications of electron-doped cuprates: Preparation of $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$ thin films and their sensitivity of physical properties to oxygen content

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We discuss possible applications of electron-doped cuprate superconductors. Thin films of the T'-phase cuprate, $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$, were prepared by reactive molecular beam epitaxy on NdGaO_3 (110) substrates with various doping concentrations of Ce. In-situ annealing in vacuum was necessary in order to obtain superconducting films. We also describe the post-deposition annealing procedures used to achieve optimal T_c for each Ce concentration. The films were characterized by x-ray diffraction and temperature dependent resistance measurements for each Ce and O content. For a fixed Ce concentration, we varied the oxygen content from well below to well above the optimum. The behavior of the electronic transport as a function of oxygen content cannot be explained purely by carrier doping of the CuO_2 planes. Both for maximally reduced and maximally oxygenated samples non-metallic behavior was observed. We also noted a correlation between superconductivity and the c -axis lattice parameter. When T_c is maximum the c -axis value is minimum. The physical properties of the T'-phase are very sensitive to oxygen content. The oxygen content in these materials has an intrinsically different effect compared to the hole-doped cuprates.

§1. Electron-doped cuprates

Most of the high T_c thin films developed for superconducting electronic applications are $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO). The reasons why YBCO is popular is that films with high critical temperature and high critical currents can easily be produced. However, there are also disadvantages of this material. The quality of the films, for example, is very sensitive to subsequent processing. In order to make devices it is important to be able to combine superconducting films with normal conductors and insulators. The deposition and subsequent processing of the other materials must be compatible with the superconducting films. Complete compatibility and clean interfaces require that the conductors or insulators are grown epitaxially on the superconductor. This limits the number of materials that can be used in a superconducting circuit. For this reason it is useful to explore superconducting cuprate films other than YBCO to see if their compatibility with conductors and insulators and manufacturability is superior to YBCO.

An interesting class of cuprate materials to consider are the electron-doped superconductors, such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$. The electron carriers are presumed to be donated to the system both by Ce^{4+} substitution for Nd^{3+} and by the formation of oxygen vacancies.¹ In this article, we describe the growth of the T'-phase cuprate superconductor, $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$. These materials have lower critical temperatures than YBCO, but they are easily grown in thin film form with the c -axis perpendicular to the substrate. Unlike YBCO, the superconducting properties of $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$ can be tuned continuously by changing the Sm/Ce ratio. Non-superconducting films can be produced either by underdoping or overdoping the films. The characteristics of the underdoped materials approach those of the insulating parent compound, Ln_2CuO_4 . Unlike the hole-doped cuprates, the electron-doped materials are also more conventional metals.² Overdoping produces a better conductor which is not superconducting. Furthermore, the coherence length in these superconductors is also longer than in YBCO.³ Since this class of materials consists of insulators, 20 K superconductors, and normal metals, all with the same crystal structure, they may prove useful for some applications where a combination of materials with different electronic properties is essential.

Recent microwave measurements of these materials indicate conventional BCS behavior of the magnetic penetration depth as well as the microwave surface resistance.³ More conventional superconducting behavior could make these materials better suited for applications in Josephson junctions, as well as for microwave devices. Additionally, these cuprates have some material properties which make them more attractive compared to YBCO. They do not have the mobile oxygen atoms, such as the chain oxygen in YBCO. This could help to make the grain boundaries more homogeneous. Moreover, the structure of the T'-phase cuprates does not contain any alkali earth layers. The alkali earth oxides, such as BaO or CaO, are extremely reactive to water or carbon dioxide. This makes these materials also less reactive in air or water compared to YBCO.⁴ They possess a longer lifetime and greater reproducibility, which are important considerations in applications.

Thin films of cuprates are important for their applications in electronics. Here we report on a part of a systematic study of the characteristics of $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$ films as a function of the Sm/Ce ratio and the oxygen content. Several research groups have already reported on the preparation of T' cuprate films by laser ablation and by activated reactive evaporation.⁵⁻⁷

§2. Sample synthesis and measurements

We have grown SmCeCuO thin films on $5 \times 5 \text{ mm}^2$ (110) NdGaO_3 substrates by reactive molecular beam epitaxy.^{8,9} Films were grown by coevaporation of elemental sources in an ozone beam at a substrate temperature of 750°C . By adjusting the relative evaporation rates for the different elements to a desired ratio, samples with different levels of doping were made. All our samples were made with the same thickness of 100 nm. We have systematically investigated our samples by x-ray diffraction θ - 2θ measurements. The oxygen content ($4\pm\delta$) was changed by a post-deposition anneal in vacuum or in a flow of oxygen. The absolute concentration of oxygen at each annealing stage, however, could not be determined. The in-plane resistance was measured in the temperature range 4.2 K– 300 K using a helium flow-cryostat. Four Au pads were evaporated onto corners of the sample at room temperature and wires were attached to the Au pads using silver paint.

§3. Annealing behavior

It is well known that the T'-phase cuprates are only superconducting after an oxygen reduction process. Therefore we have examined various anneals in order to optimize the superconducting properties of the samples. We utilized anneals in-situ directly after deposition, as well as ex-situ anneals in an oven. The annealing procedures used to obtain optimal samples of SmCeCuO at each Ce content are described in Table 1. We define the optimal properties as highest T_c and lowest resistance. All our films were deposited in the presence of ozone at 750°C . A typical result is shown in Fig. 1. This sample was annealed in situ at 700°C for 10 minutes. The as-made film had a T_c of ~ 10 K. After a further anneal in vacuum for 15 minutes at 390°C we were able to obtain a T_c onset of 23 K and $T_c(R=0) = 20.1$ K.

By doing a series of anneals in vacuum and in oxygen one can span the whole range of accessible oxygen contents. The longer anneals in oxygen are necessary to recover the starting properties of the fully oxygenated material. By doing further reducing anneals afterwards we were able to repeat the whole procedure. Optimal superconducting thin films of SmCeCuO were made after an in-situ anneal in vacuum for 20 mins at 700°C . These results are similar to the data of A. Gupta et al.,⁵ who reported for 250 nm NdCeCuO thin films that a reduction of 45 mins at 780°C was necessary in order to show optimal superconductivity.

Figure 2 shows a series of anneals done on sample B. In this case, the as-made sample had close to optimal transport properties, which corresponds to $T_c = 12$ K. From Fig. 2a it can be seen that the resistance of the sample increases as the sample's oxygen content is reduced, even though all the samples here show metallic behavior. Upon oxygenation of optimal samples, resistance will also increase. However, in this case the resistance has a different behavior as a

function of temperature. There is a resistance increase at low temperature, as can be seen in the top curve of Fig. 2b. Similar results have been reported previously by Jiang et al.¹⁰

These results indicate that there is an optimum oxygen content with respect to the transport properties. This optimum content has to be adjusted by doing anneals for very precise times, in our case of the order of a few minutes. Shorter or longer anneals produce oxygenated or reduced samples compared to the optimal one. In Fig. 3 we show the result of anneals starting with sample A in its fully oxygenated state. As the sample is reduced superconductivity appears and then disappears again. At either end, fully oxygenated and fully reduced, the samples are insulating.

The x-ray diffraction patterns of our samples can be indexed with the (0 0 2n) lines of the T' structure. This indicates that the *c*-axis lattice parameter is perpendicular to the substrate. The *c*-axis lattice constant is in the range 11.87 – 11.90 Å, which is comparable to the bulk values.¹¹ For two of the samples a second phase peak at a *d*-spacing of 2.338 Å was also observed. The various post deposition annealing treatments did not change the crystal structure of the films, but the change of the *c*-axis lattice constant is observed in all samples. Fig. 3 also shows the behavior of the *c*-axis lattice parameter for two of the reflections as a function of annealing. In all the measured samples, we have observed a correlation between the *c*-axis lattice constant and the transport properties. The optimal oxygen content corresponds to a minimum of the *c*-axis lattice constant. The absolute observed change of the *c*-axis in sample A is $\Delta c/c = 0.16\%$. This behavior contrasts with the hole-doped cuprates where oxygen annealing results in a monotonic dependence of the *c*-axis.

We have observed the highest optimal T_c for the film with a Ce content of $x = 0.15$. The critical temperature decreases continuously and superconductivity disappears at about $x = 0.18$, as is also the case for NdCeCuO.¹² The highest T_c for each Ce concentration is plotted in Fig. 4. If we make a comparison between our data and those reported for the LnCeCuO (Ln = Pr or Nd),¹² we conclude that the SmCeCuO diagram (T_c, x) is very similar.

Table 1. Preparation conditions and optimization of the samples for their highest T_c 's.

Sample	preparation conditions	optimization conditions	Ce content x	optimal T_c (K)	<i>c</i> -axis lattice parameter at optimal oxygen content (Å)
A	made at 750 °C in ozone; cooled to 400 °C in ozone and then annealed and cooled to RT in vacuum	first anneal in a flow of O ₂ for 2 hours at 390 °C; then in vacuum for 2 hours at 340 °C and 10 mins at 380 °C	0.165	10	11.90
B	made at 750 °C and cooled to 700 °C in ozone; then annealed in vacuum for 20 mins at 700 °C	as made was optimal	0.16	12	–
C	made at 750 °C and cooled to 700 °C in ozone; then annealed in vacuum for 10 mins at 700 °C	optimized after one anneal at 390 °C for 15 mins in vacuum	0.15	20.1	11.89
D	made at 750 °C and cooled to 700 °C in ozone; then annealed in vacuum for 10 mins at 700 °C	this film showed no superconductivity for different anneals in vacuum and in oxygen	0.18	not sc above 4.2 K	11.87

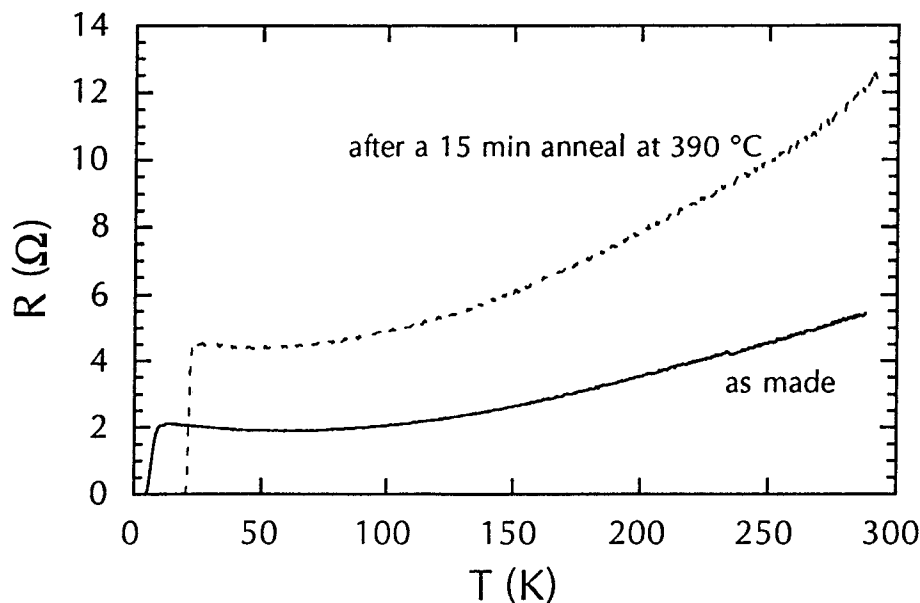


Figure 1: The temperature dependence of resistance of sample C, as-made and after a 15 minute anneal at 390 °C in vacuum.

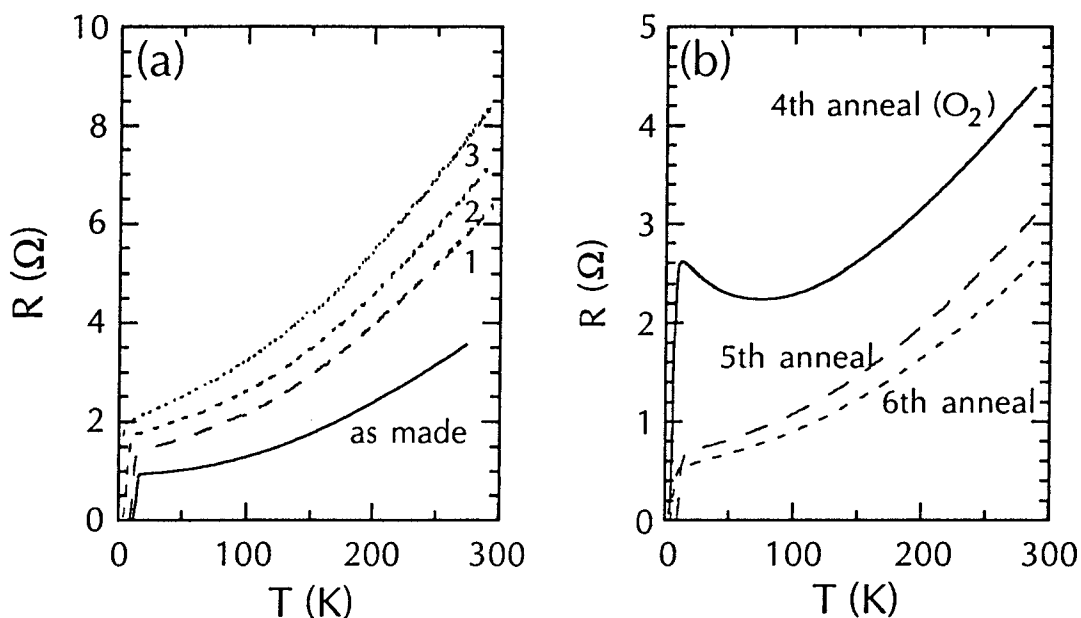


Figure 2. R vs T for sample B as a function of the order of the anneal, for reduced, (a), and oxygenated, (b), compared to optimal oxygen content. All the anneals except for number 4 were carried out in vacuum at 390 °C for 15 minutes. Anneal number 4 was done in a flow of oxygen at 390 °C for 2 hours.

§4. Discussion of oxygen dependency

It has been suggested that a small number of oxygen atoms removed by reduction come from key sites which when occupied strongly suppress superconductivity.¹⁰ It seems plausible that these are interstitial apical oxygen sites. When occupied they produce localized transport at low temperatures. This is likely the cause of the upturn in resistance observed in our oxygenated samples, Fig. 2b. Furthermore, as the samples are reduced beyond the optimal oxygen content superconductivity is again destroyed. This could be due to excessive hole doping. The small

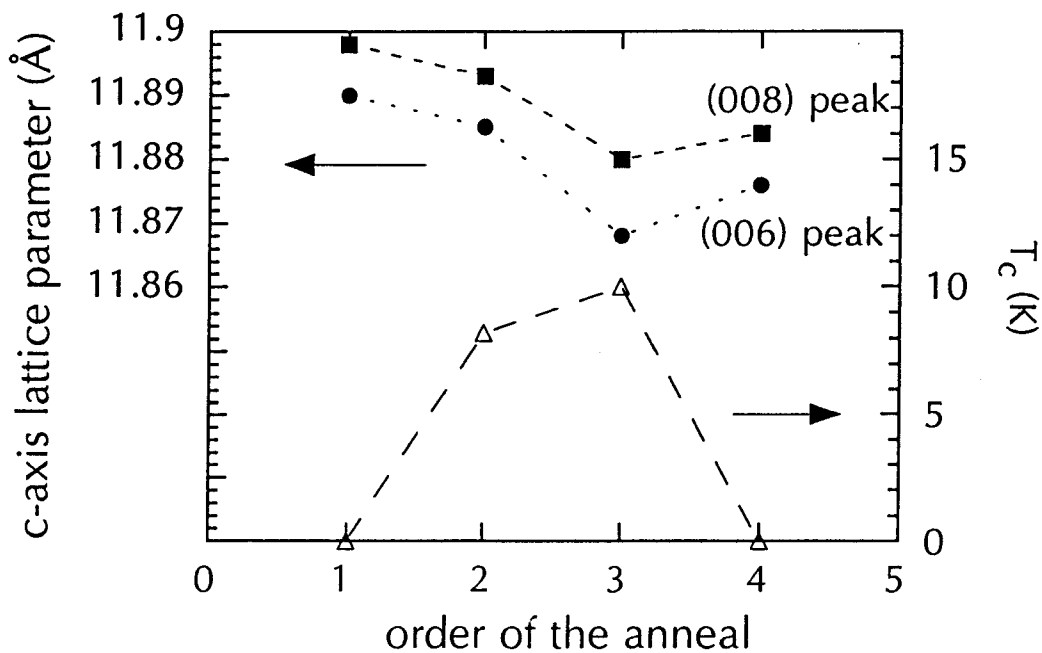


Figure 3: T_c and c -axis lattice parameter for sample A vs order of anneal in vacuum at 350 – 450 °C.

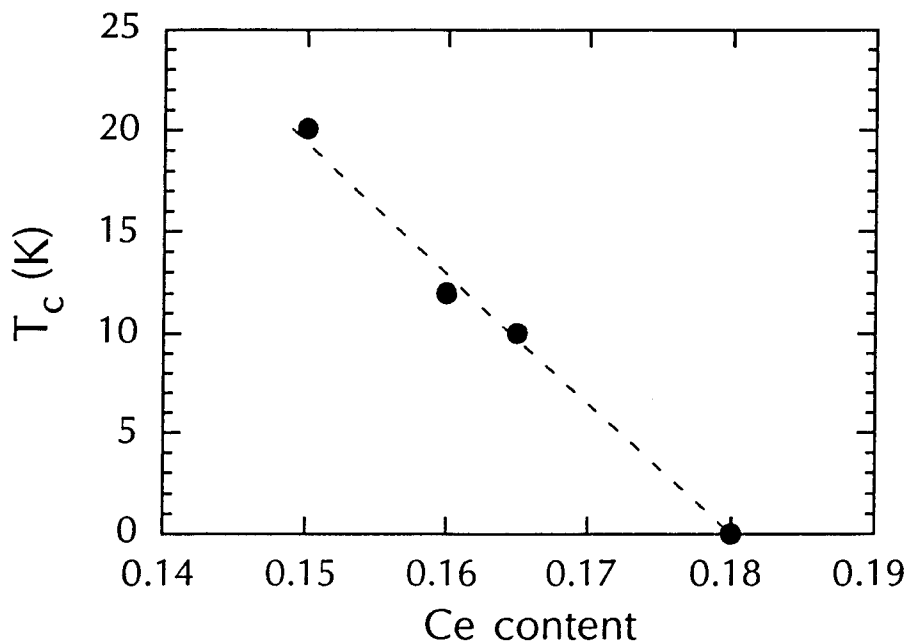


Figure 4. Optimum T_c vs Ce content for the $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$ samples studied here. The dashed line is a guide to the eye.

amount of oxygen content change, however, makes it unlikely that this is the only explanation. Furthermore, we observe an increase in resistance as the sample is reduced beyond optimal oxygen content. The increase is seen both in the residual resistivity as well as in the temperature dependent part. This indicates that in this regime the oxygen vacancies increase the scattering rate in the CuO_2 planes, in addition to any change in carrier doping that they may produce.

The extreme sensitivity of the transport properties to the oxygen content and the particulars of the preparation anneals make the electron-doped cuprates difficult to work with. Unlike the hole-doped materials, the optimal superconducting properties of the T' cuprates are at an intermediate oxygen content, and not in an extremum. For YBCO, as well as other hole-doped materials, it is

usually sufficient to get the maximum oxygen content in order to get a superconducting phase. For the electron-doped cuprates maximum and minimum oxygen content correspond to insulating phases. One has to fine tune the oxygen content in order to get superconducting properties. The oxygen annealing clearly plays an important role beyond pure carrier doping, which is conventionally thought to be the case for the hole-doped materials. In the completely oxygenated material the oxygen atoms are likely interstitial and their disorder impedes extended electronic states. In the reduced regime they give rise to additional scattering.

The problem of oxygen content in the electron-doped cuprates will make any applications of these materials troublesome. Slight variations in the annealing processes will make reproducibility of transport properties difficult. We therefore see potential problems in applying these materials to any manufacturing process. Nevertheless, we believe that fundamental research into these materials will have to address issues such as their Josephson junction behavior and microwave losses.

§5. Conclusions

We have made films of the electron-doped cuprate superconductor $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4\pm\delta}$ by reactive molecular beam epitaxy in an ozone beam. A maximum T_c of 23 K was observed. In addition to the Ce content, another critical parameter which affects T_c in the T'-phase is the oxygen content. We have observed large, systematic changes in the transport properties with increasing degree of reduction at fixed cerium concentration of these thin films. The oxygen content was varied by successive anneals at different temperatures and for different times. An optimum oxygen content with respect to the transport properties was found for each Ce concentration. This also coincides with a minimum of the c -axis lattice parameter. These materials behave qualitatively differently as a function of oxygen annealing compared to the hole-doped cuprates. We attribute this to the different role that the oxygen plays. The necessity of tuning the oxygen content in order to obtain good superconducting properties makes these materials more difficult to work with.

References

1. Y. Tokura, H. Takagi, and S. Uchida, *Nature* **337**, 345 (1989).
2. C.C. Tsuei, A. Gupta, and G. Koren, *Physica C* **161**, 415 (1989).
3. D.H. Wu, J. Mao, S.N. Mao, J.L. Peng, X.X. Xi, T. Venkatesan, R.L. Greene, and S.M. Anlage, *Phys. Rev. Lett.* **70**, 85 (1993).
4. J.-P. Zhou, D.R. Riley, A. Manthiram, M. Arendt, M. Schmerling, and J.T. McDevitt, *Appl. Phys. Lett.* **63**, 548 (1993).
5. A. Gupta, G. Koren, C.C. Tsuei, A. Segmuller, and T.R. McGuire, *Appl. Phys. Lett.* **55**, 1795 (1991).
6. T. Terashima, Y. Bando, K. Lijima, K. Yamamoto, K. Hirata, K. Hayashi, Y. Matsuda, and S. Komiyama, *Appl. Phys. Lett.* **56**, 677 (1990).
7. S.N. Mao, *et al.*, *Appl. Phys. Lett.* **61**, 2356 (1992).
8. H.M. Appelboom, *et al.*, *Physica C* **214**, 323 (1993).
9. V.C. Matijasevic, H.M. Appelboom, F. Mathu, P. Hadley, D.v.d. Marel, and J.E. Mooij, *IEEE Trans. Appl. Supercond.* **3**, 1524 (1993).
10. W. Jiang, S.N. Mao, X.X. Xi, X. Jiang, J.L. Peng, T. Venkatesan, C.J. Lobb, and R.L. Greene, *Phys. Rev. Lett.* **73**, 1291 (1994).
11. E.A. Early, N.Y. Ayoub, J. Beille, J.T. Markert, and M.B. Maple, *Physica C* **160**, 320 (1989).
12. H. Takagi, S. Uchida, and Y. Tokura, *Phys. Rev. Lett.* **62**, 1197 (1989).