

High-temperature ceramic oxide superconductors⁺

C N R RAO

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

Abstract. High-temperature superconductivity in oxides of the type $\text{La}_{2-x}\text{Ba}_x(\text{Sr}_x)\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14}$ and Bi(Tl)-Ca-Sr(Ba)-Cu-O systems is discussed, with special emphasis on the experimental findings from the author's laboratory. The importance of holes on oxygen and of the Cu^{1+} (d^{10}) state is examined. A transition is shown to occur from chain- to sheet-superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ accompanying a change in oxygen stoichiometry. Some of the important material parameters and technological applications are briefly presented. There is every hope that materials with T_c close to room temperature will be discovered in the near future. All the high T_c oxides found hitherto have perovskite-related structures with two-dimensional Cu-O sheets.

Keywords. High-temperature superconductivity; ceramic oxide superconductors; bismuth cuprates; thallium cuprates; $\text{LnBa}_2\text{Cu}_3\text{O}_7$; rare earth cuprates.

1. Introduction

The phenomenon of superconductivity has been an area of vital interest for the past several decades, ever since Kammerlingh Onnes discovered in 1911 that mercury becomes superconducting at 4.2 K. Many materials, mostly metals and alloys, and more recently, molecular systems including organic charge-transfer compounds, have been investigated for superconductivity, but the superconducting transition temperature did not cross 23 K till 1986. The average rate of increase in T_c was about 3 degrees per decade and it appeared as though 23 K was the upper limit for the T_c . The highest T_c 's (in the 20 K region) were exhibited by the A15 compounds such as Nb_3Sn and Nb_3Ge . Some of the metal oxides also showed superconductivity, the highest T_c amongst them being exhibited by $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and LiTi_2O_4 , both around 13 K.

Bednorz & Mueller (1986) showed the possibility of high-temperature superconductivity in oxides of the La-Ba-Cu-O system. It was established in January 1987 that these oxides had the general formula $\text{La}_{2-x}\text{Sr}_x(\text{Ba}_x)\text{CuO}_4$ and possessed the K_2NiF_4 structure; T_c values in these oxides were in the 20–40 K region, the compositions corresponding to the maximum T_c in the Sr and Ba systems being $x=0.2$ and 0.15, respectively (Cava *et al* 1987; Chu *et al* 1987; Ganguly *et al* 1987a;

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Uchida *et al* 1987). Following on the heels of this discovery, superconductivity above liquid nitrogen temperature was reported in March 1987 in the Y-Ba-Cu-O system (Wu *et al* 1987). It was soon found that the oxide responsible for superconductivity in this system did not possess the K_2NiF_4 structure, but instead had the defect perovskite structure with the composition $YBa_2Cu_3O_{7-\delta}$ (Ganguly *et al* 1987b; Rao *et al* 1987b; Siegrist *et al* 1987). In the last few weeks, the big news has been the discovery of superconductivity in Bi and Tl cuprates containing alkaline earth metals; these oxides show T_c 's in the 100–120 K range (Chu *et al* 1988; Ganguli *et al* 1988; Rao *et al* 1988; Subramanian *et al* 1988; Sheng & Hermann 1988).

The discovery of superconductivity above the liquid nitrogen temperature in oxide materials has raised much hope because of its important technological implications. Equally importantly, this has given a big boost to research in ceramic oxides. In what follows, some of the highlights of research on high T_c oxide superconductors will be presented, with particular reference to the results obtained in the author's laboratory (Rao 1988). In addition, some of the special features of these ceramic oxides will be indicated along with their possible technological applications. It may be remarked here that research efforts in this laboratory related to the high-temperature superconducting oxides were initiated in the early part of January 1987, soon after information about the $La_{2-x}Ba_x(Sr_x)CuO_4$ system became available through the American participants in the International Conference on Valence Fluctuation held in Bangalore.

2. $La_{2-x}Ba_x(Sr_x)CuO_4$

Oxides of the general formula A_2BO_4 possess the quasi two-dimensional K_2NiF_4 structure (figure 1) wherein the B ions interact only in the ab plane. The structure and properties of the oxides of the K_2NiF_4 system have been examined in some detail recently by Ganguly & Rao (1984). It has been known for sometime that orthorhombic La_2CuO_4 is a relatively low-resistivity material (~ 1 ohm cm at 300 K, see figure 2) and becomes antiferromagnetic at low temperatures. Substitution of La by Ba or Sr in $La_{2-x}Ba_x(Sr_x)CuO_4$ ($x > 0.05$) makes the structure tetragonal (at room temperature) and superconductivity manifests itself at low temperatures (Rao & Ganguly 1987a). Superconductivity is also found in the 15–40 K region in oxides of the type $(La_{1-y}Ln_y)_{2-x}Ba_x(Sr_x)CuO_4$ where $Ln = Pr, Nd, Gd$ etc. (Ganguly *et al* 1987a; Mohan Ram *et al* 1987a). These oxides, containing planar CuO_2 units, show maximum T_c around a specific value of x (Sreedhar *et al* 1987). Electrical resistivity values of these oxides in the normal state above T_c are in the $10^{-2} - 10^{-3}$ ohm.cm range (figure 2) which correspond closely to Mott's minimum metallic conductivity (Rao & Ganguly 1985).

There have been several investigations of La_2CuO_4 and $La_{2-x}Ba_x(Sr_x)CuO_4$ in the last few months. Antiferromagnetism in La_2CuO_4 has been established by neutron scattering and diffraction studies, the T_N being close to 290 K with a low-temperature Cu-moment of $0.43 \mu_B$ (Mitsuda *et al* 1987). Besides establishing the magnetic structure, these studies have shown the occurrence of the orthorhombic-tetragonal distortion at 505 K. Muon spin rotation has also been employed to examine antiferromagnetism in La_2CuO_4 (Uemura *et al* 1987). The work of Shirane *et al* (1987) has shown that La_2CuO_4 is in a 2-dimensional *afm* quantum fluid state wherein spins are ordered instantaneously over long distances, but there is no

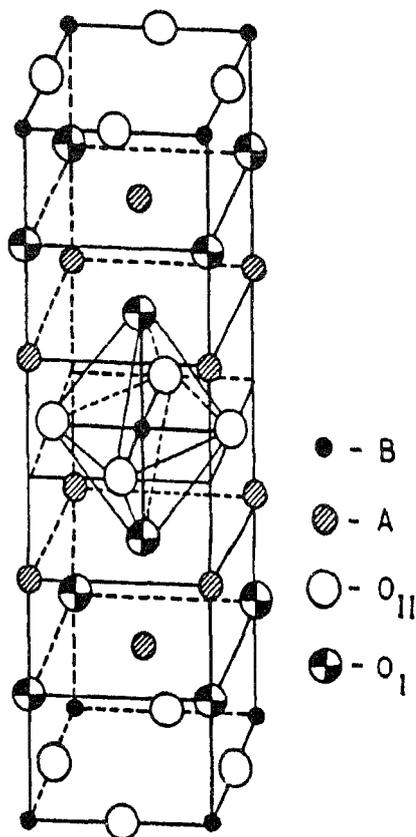


Figure 1. The K_2NiF_4 structure of oxides of the formula A_2BO_4 .

measurable time-averaged moment. More interestingly, studies of oxygen-excess La_2CuO_4 has shown it to be superconducting with a T_c of 40 K (Beille *et al* 1987); La-deficient samples also exhibit superconductivity in this temperature region.

Superconducting $La_{2-x}Ba_x(Sr_x)CuO_4$ undergoes a tetragonal-orthorhombic distortion around 180 K (Day *et al* 1987; Paul *et al* 1987). ESR studies have thrown light on microscopic magnetic interactions in these oxides (Thomann *et al* 1987). Static and dynamic aspects of the tetragonal-orthorhombic distortion in $La_{2-x}Sr_xCuO_4$ have been studied by neutron scattering and related studies and a classical soft phonon behaviour involving CuO_6 octahedra has been observed (Birgeneau *et al* 1987).

3. $YBa_2Cu_3O_{7-\delta}$ and related oxides

Wu *et al* (1987) reported superconductivity above liquid N_2 temperature in $Y_{1.2}Ba_{0.8}CuO_4$. This composition was actually biphasic, consisting of green Y_2BaCuO_5 and a black oxide. We had initiated studies (Ganguly *et al* 1987b) on the Y-Ba-Cu-O system with compositions of the type $Y_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ by analogy with $La_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ (Er-Rakho *et al* 1981). This was because Y_2CuO_4 (unlike La_2CuO_4) does not crystallize in the K_2NiF_4 structure. By comparing the X-ray diffraction patterns of $Y_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ and Y_2BaCuO_5 , it was possible to identify the phase responsible for the high T_c (90–95 K) superconductivity as

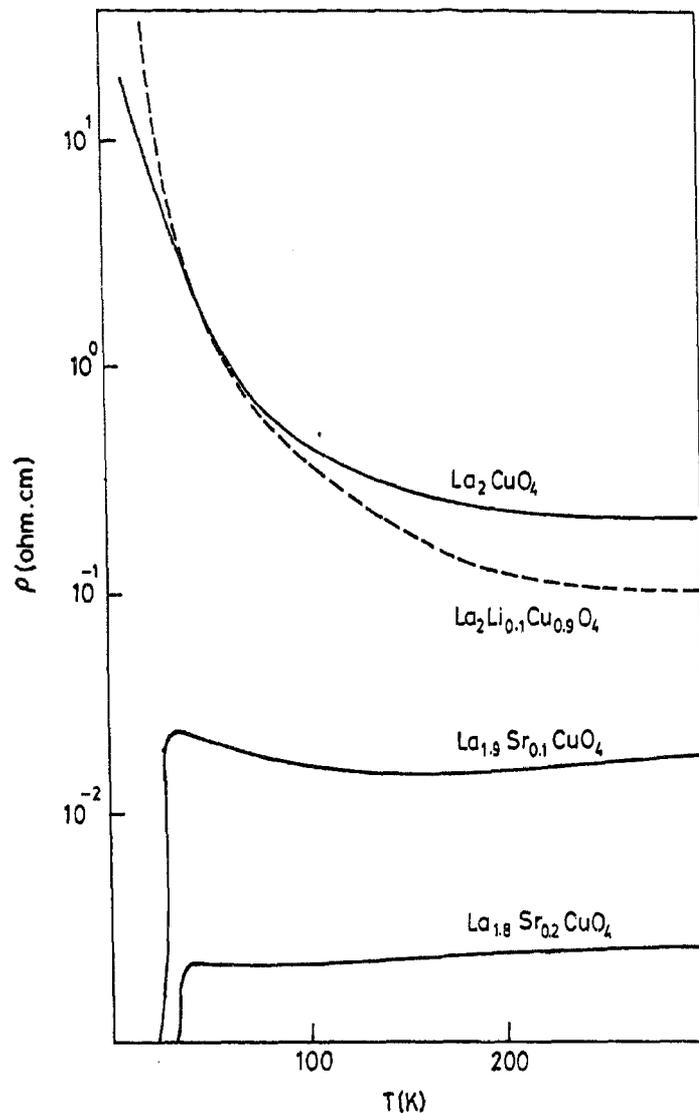


Figure 2. Electrical resistivity behaviour of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and La_2CuO_4 (from Ganguly *et al* 1987a).

orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Rao *et al* 1987b). AC susceptibility (Meissner effect) measurements showed the superconductivity to be a bulk property. Soon, many other related oxides such as $\text{Y}_{1-x}\text{Ln}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\text{Ln}=\text{La}, \text{Lu}$ etc) as well as $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\text{Ln}=\text{Er}, \text{Dy}, \text{Gd}$ etc.) were found to be high T_c superconductors, all with $T_c \approx 90$ K (Mohan Ram *et al* 1987b; Raychaudhuri *et al* 1987; Tarascon *et al* 1987; Xiao *et al* 1987). Obviously Y and Ln ions play no role in the superconductivity; they only help to keep the structure together.

Superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is extremely sensitive to oxygen stoichiometry (Rao *et al* 1987a, 1988a; Rao & Ganguly 1987b). Thus, the $\delta \geq 0.6$ sample is non-superconducting and tetragonal. Oxygen is readily intercalated into the $\delta \geq 0.5$

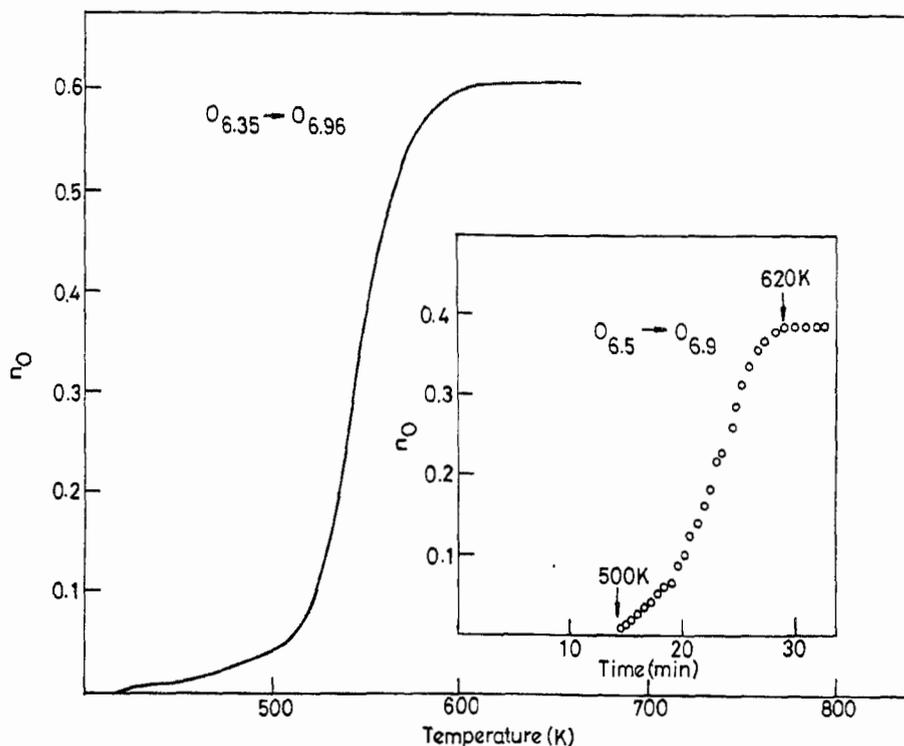


Figure 3. TGA curves showing the oxidation of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ to $\text{YBa}_2\text{Cu}_3\text{O}_7$. Inset shows the rate of oxygen intercalation in a $\text{O}_{6.5}$ sample (from Rao *et al* 1988a).

samples and the stoichiometry reaches close to $\text{YBa}_2\text{Cu}_3\text{O}_7$ on intercalation (figure 3). Structures of the orthorhombic ($\delta=0.0$) and the tetragonal ($\delta=1.0$) phases differ in an interesting manner. Besides the CuO_2 sheets, the stoichiometric ($\delta=0.0$) phase contains Cu-O-Cu chains (or corner-linked CuO_4) units which are absent in the non-superconducting ($\delta=1.0$) sample (David *et al* 1987; Bordet *et al* 1987). In figure 4 we compare the orthorhombic and tetragonal structures of the $\delta=0.0$ and the $\delta=1.0$ samples. In the $\delta=0.6-1.0$ range, it seems that the tetragonal phase has disordered oxygens giving rise to distorted CuO_6 octahedra as indicated in figure 4c (Jorgensen *et al* 1987). In general, oxygen non-stoichiometry in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system has to be understood in terms of both disorder and structural distortion.

The variation of the superconducting transition temperature of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with δ (in the δ -range 0.0–0.5) is most interesting. In figure 5, the resistivity data of a few members with different δ values is shown while in figure 6, the T_c values from the resistivity data are plotted against δ (Rao *et al* 1988a). In figure 6, we also show results from the magnetic measurements of Johnston *et al* (1987). Although the actual T_c values vary in the different sets of data (figure 6), we see that the T_c is nearly constant around 90 K at low δ (0.0–0.2) and drops to a lower value (~ 60 K) above $\delta=0.2$ showing a plateau-like behaviour. The T_c in the plateau region is similar to that of $\text{La}_{2-x}\text{Ba}_x(\text{Sr}_x)\text{CuO}_4$ (of the K_2NiF_4 structure). Since in this composition range, the Cu-O-Cu chains of $\text{YBa}_2\text{Cu}_3\text{O}_7$ will be depleted, we believe that the ~ 60 K plateau is characteristic of superconductivity due to CuO_2

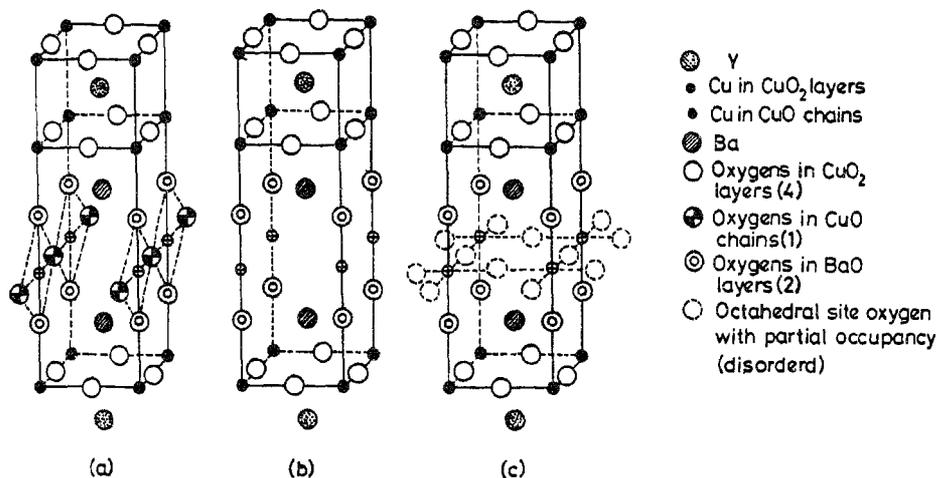


Figure 4. Structures of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: (a) Orthorhombic structure of the superconducting phase with $\delta=0.0$; (b) tetragonal structure of the non-superconducting phase with $\delta=1.0$; (c) disordered structure of the tetragonal phase with CuO_6 octahedra (where the site occupancy is small).

sheets while the 90 K T_c is characteristic of the sheets in the presence of Cu-O-Cu chains. Figure 6 may therefore be taken to represent a transition from chain-type to sheet-type superconductivity brought about by the change in oxygen stoichiometry.

Several workers have in recent months synthesised derivatives of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where Cu is substituted by Zn, Ni, Co, Fe and such ions or Ba is substituted by La and other ions. Such substitution in general lowers T_c or destroys the superconductivity, the oxide generally being tetragonal and oxygen-deficient. It should be noted that non-superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compositions also possess the tetragonal structure. Weakly orthorhombic or nearly tetragonal samples prepared by low-temperature methods are non-superconducting as well. Bulk superconductivity has, however, been recently reported in tetragonal $\text{YBa}_2(\text{Cu}_{0.96}\text{Co}_{0.4})_3\text{O}_{7-\delta}$ (Langen *et al* 1988).

4. Other La-Ba-Cu-O and related systems

The $\text{La}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14+\delta}$ family of oxides were considered to be high T_c superconductors (Mitzi *et al* 1988) even though they did not possess Cu-O chains (Er-Rakho *et al* 1981). It is now known that these oxides are related to the 123 oxides (Segre *et al* 1987), the relative occupation of the O1/O5 sites determining the orthorhombicity. Truly high T_c is found in this system only in the orthorhombic structure when $x=1$, $\delta \approx 0.0$ (Ganapathi *et al* 1988). All other compositions ($x \neq 1$, $\delta \neq 0.0$) are generally tetragonal. In figure 7, the various rare-earth-containing families of oxides investigated by us for superconductivity are shown.

5. Bismuth and thallium cuprates

Two new families of superconducting cuprates with structures related to the

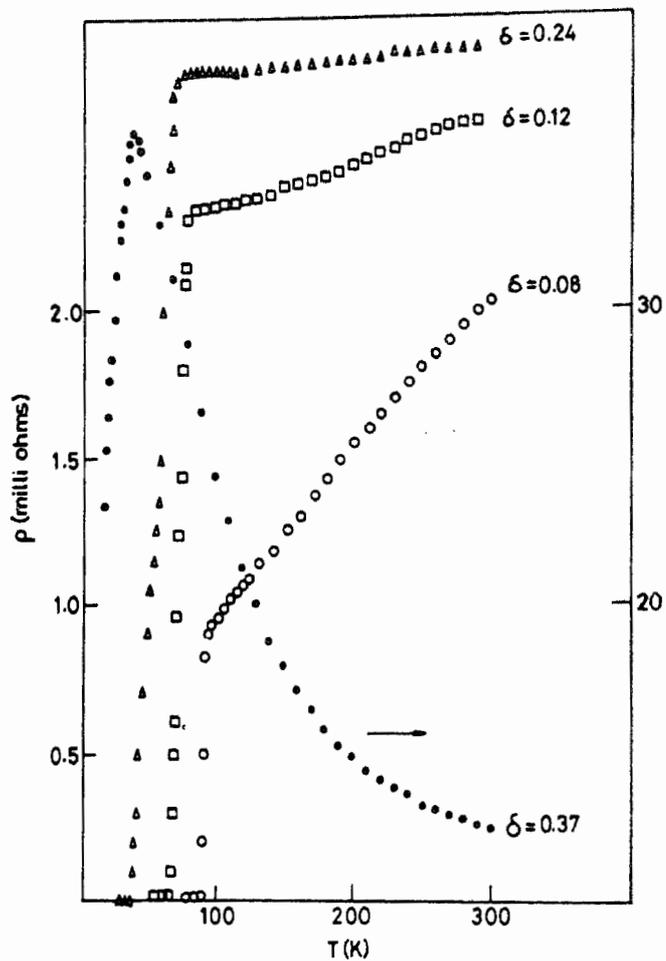


Figure 5. Electrical resistivity behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for different values of δ (unpublished results from this laboratory).

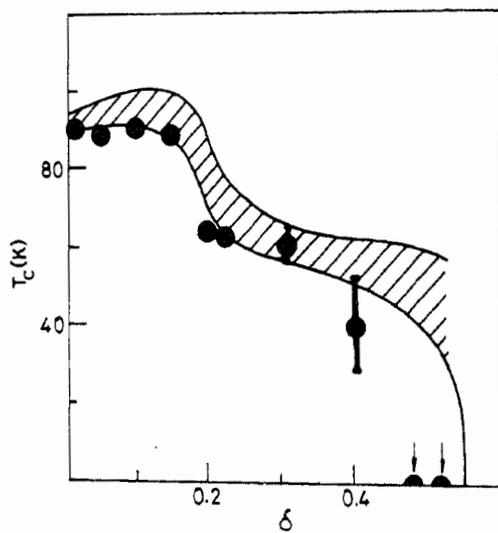
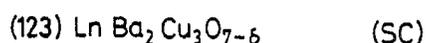
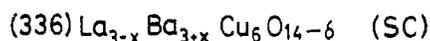
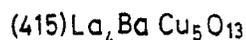
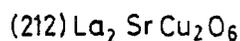
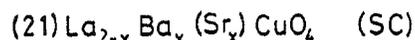


Figure 6. Variation of T_c of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with δ . Magnetic measurements of Johnston *et al* (1987) are indicated by the cross-hatched region. Our resistivity data are shown by full dark circles (from Rao *et al* 1988a).



(Ln = La, Y, Eu, Gd, Ho, Er etc)

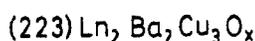
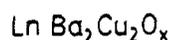
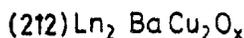
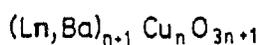


Figure 7. Various families of oxides investigated for superconductivity. SC stands for superconducting. Numbers in parenthesis on the left of each system are the popular designations.

Aurivillius family of oxides with T_c 's in the 100 K region have been discovered. The initial discovery of superconducting bismuth cuprates was by Michel *et al* (1987) who found T_c in the 7–22 K range in oxides of the type $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+\delta}$. Maeda *et al* (1988) then found high T_c (~ 100 K) in a Bi-Ca-Sr-Cu-O system. High T_c superconductivity (≈ 110 K) is exhibited by bismuth cuprates of the type $\text{Bi}_2(\text{Ca, Sr})_3\text{Cu}_2\text{O}_{8+\delta}$ (Chu *et al* 1988; Hazen *et al* 1988; Rao *et al* 1988; Subramanian *et al* 1988; Tarascon *et al* 1988). In figure 8, we compare the structures of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with that of $\text{Bi}_2\text{CaSr}_7\text{Cu}_2\text{O}_9$. In figure 9, we show the variation of resistivity and AC susceptibility of a sample to indicate the high T_c behaviour. The bismuth cuprates have less oxygen lability and seem to be more stable. The exact composition of the 110 K material is more complex than that indicated by the formula $\text{Bi}_2(\text{Ca, Sr})_3\text{Cu}_2\text{O}_{8+\delta}$.

Thallium cuprates of the Tl-Ba-Cu-O and Tl-Ca-Ba-Cu-O systems show high T_c superconductivity with onset in the 100–120 K range (Hazen *et al* 1988; Ganguli *et al* 1988; Sheng & Hermann 1988). In figures 10 and 11, we show the resistivity and susceptibility behaviour of typical members of the Tl-Ca-Ba-Cu-O system. The structure of the 2122 oxide is identical to that of the corresponding bismuth compound, $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$. All these oxides of Bi and Tl contain Cu-O sheets.

Electron microscopic studies of the Bi and Tl cuprates show the extensive presence of defects and dislocations just as in the Aurivillius family of oxides. Intergrowths are also present in these systems and they may be responsible for the high T_c 's (200–300 K) found in some of the samples in this laboratory.

6. Role of oxygen

Having established the crucial role of oxygen in the superconductivity of these ceramic oxides, we have further explored the mechanism of superconductivity by means of X-ray photoemission and related studies. Variable-temperature XPS studies

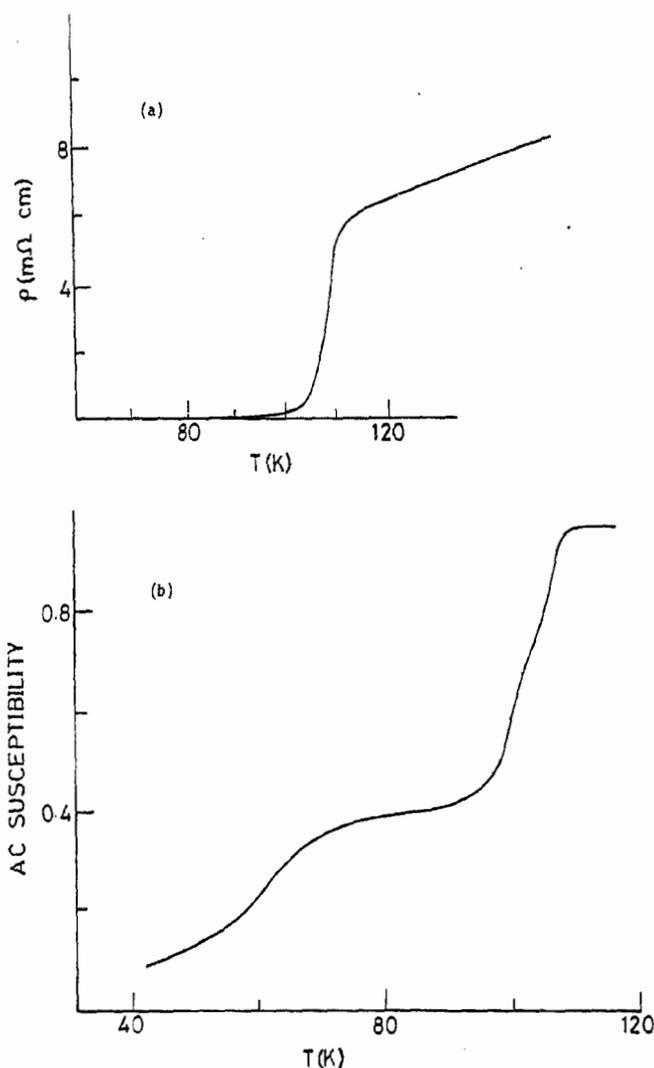


Figure 9. Resistivity and AC susceptibility data of a sample of $\text{Bi}_2(\text{Ca,Sr})_3\text{Cu}_2\text{O}_{8+\delta}$. (From Tarascon *et al* 1988.)

ceramic materials (and not metals). As mentioned earlier, in the normal state, they are poor conductors. While $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ seems to exhibit measurable ^{18}O isotope effect, there appears to be essentially no isotope effect in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system (Batlogg *et al* 1987). This means that the traditional BCS* theory is not valid in these oxide superconductors. While electron-phonon interaction could still play an indirect role, the actual nature of the role is not clear at present. The optical gap in $\text{YBa}_2\text{Cu}_3\text{O}_7$ seems to be $\sim 200 \text{ cm}^{-1}$ (Cardona *et al* 1987; Genzel *et al* 1987). A high-energy excitonic band (0.5 eV) whose intensity varies with T_c seems to be present in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and this may be of significance. Such bands need to be further explored. While a large number of papers on theoretical models have appeared in the

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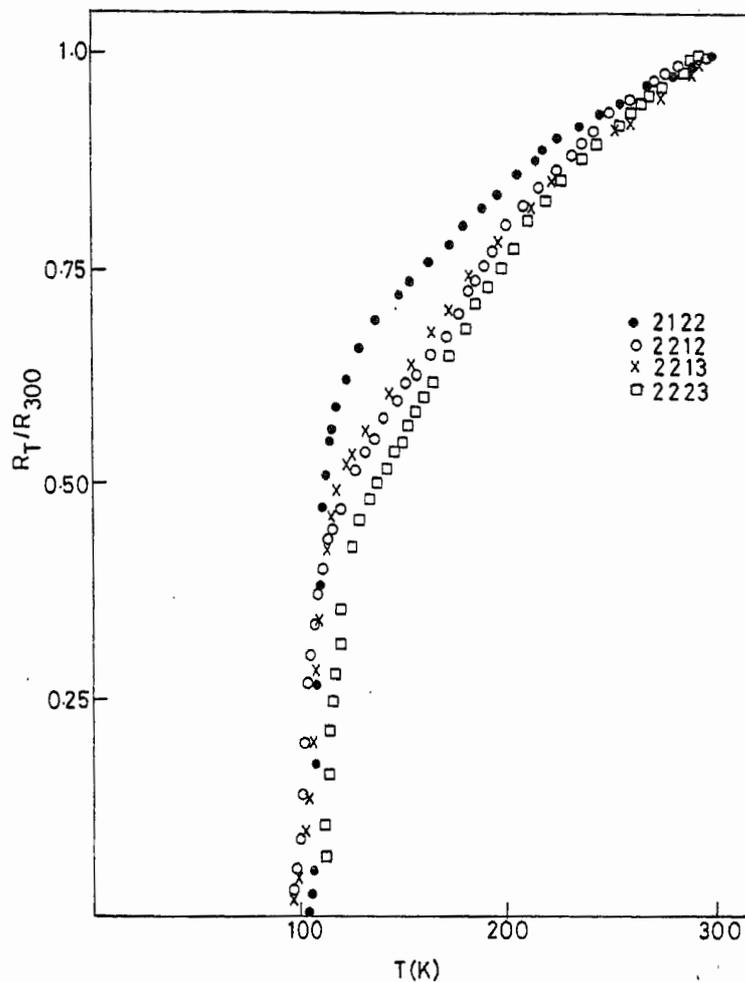


Figure 10. Resistivity behaviour of 2122, 2212, 2213 and 2223 members of the Tl-Ca-Ba-Cu-O system (from the author's laboratory). Better samples of 2223 show a T_c of 125 K.

literature in the last few months, there is yet no simple model or theory to explain high T_c in the oxide superconductors. It seems best to get good experimental data and look for models later. One of the noteworthy features is that T_c seems to increase with the number of Cu-O layers in the unit cell. The oxygen hole concentration also seems to increase in the same direction as T_c .

Electron microscopic studies of $\text{YBa}_2\text{Cu}_3\text{O}_7$ show the presence of certain domains (see figure 14) and twin boundaries in addition to other defects (see for example, Rao *et al* 1987c, 1988a; Subbanna *et al* 1987). The nature of the domains is causing curiosity. Noting that the coherence length is only a few angstroms, people are wondering about the origin and implications of such domains. Are they due to the co-occurrence of metallic and insulating phases (with different stoichiometry)? If so, what does the observed structure mean? The broad bands or domains (figure 14) found by us sometime ago (Rao *et al* 1987c), seem to be due to different orientations

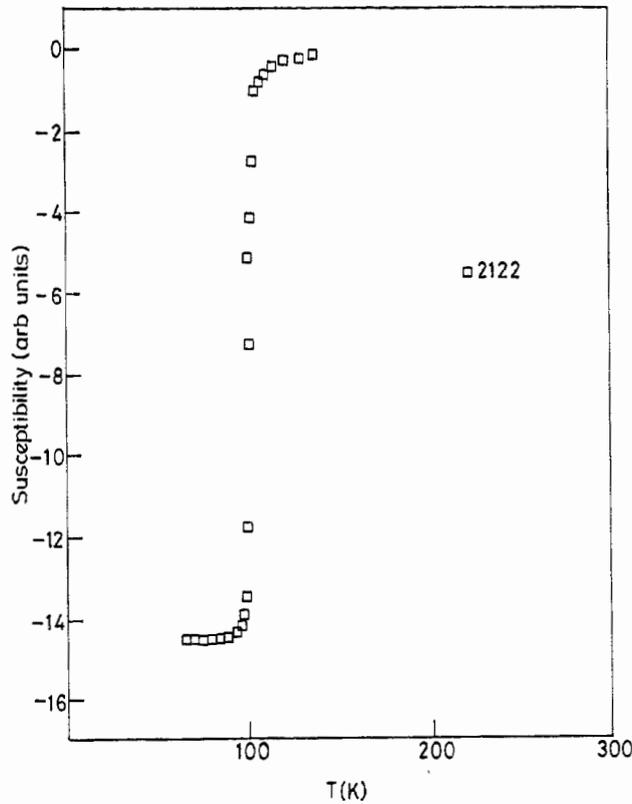


Figure 11. AC susceptibility data of the 2122 member of the Tl-Ca-Ba-Cu-O system (from the author's laboratory).

of the $(\text{CuO}_2)_\infty$ units (Rao *et al* 1988a). Such macroscopic features may be responsible for the unstable very high T_c (~ 300 K) behaviour of some oxides.

An interesting property of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the superconducting state is that it absorbs electromagnetic radiation over a wide range of frequencies from a few MHz to a few GHz (Bhat *et al* 1987). The absorption is extremely sensitive to temperature, particle size and the magnetic field and crucially depends on the presence of ambient oxygen. It is suggested that Josephson junctions formed by oxygen and the superconducting grains may be responsible for this effect.

8. Material parameters and applications

Since these new oxide superconductors are ceramic materials, there are inherent problems in obtaining them in the desired shape and form. However, there has already been considerable success in making wires, tapes and films. During the processing of these materials, there is a tendency to lose the labile oxygen which renders them non-superconducting; this can be solved by reheating the processed material in oxygen or by proper insulation in the initial stage itself. Another difficulty with these oxide ceramics is their chemical instability. Success in technological

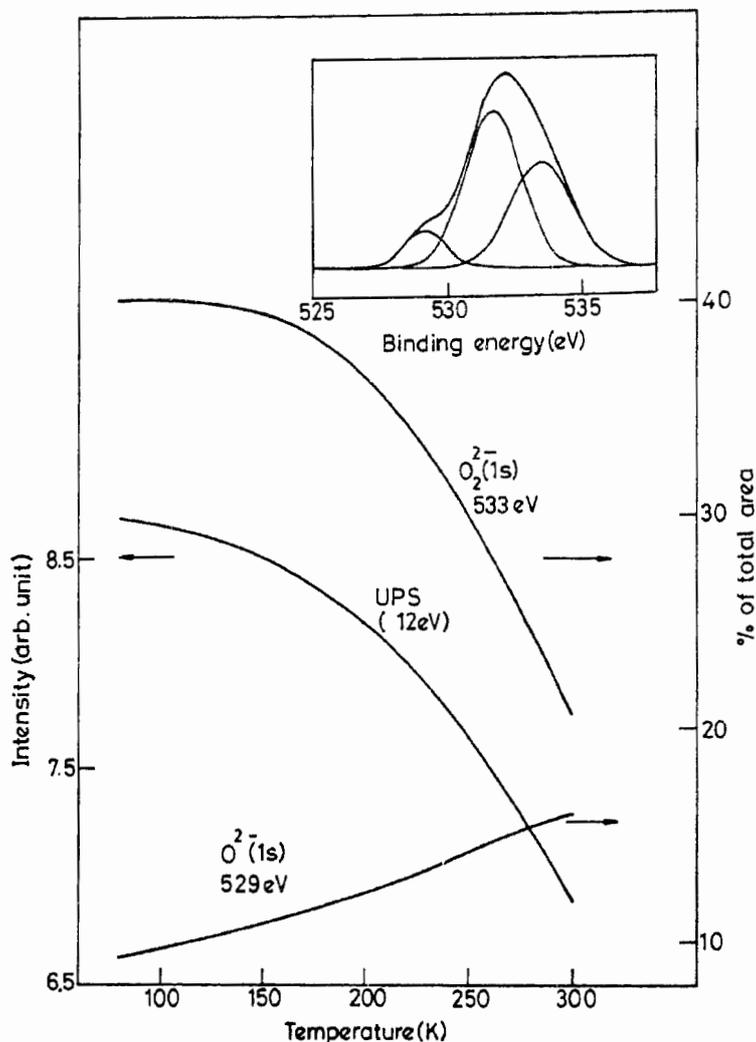


Figure 12. Temperature-variation of O(1s) peak intensity due to O^{2-} and O_2^{2-} species (at 529 and 533 eV respectively) in $YBa_2Cu_3O_7$. Temperature-variation of the intensity of He II spectrum at 12 eV is also shown. Inset shows the O(1s) signal at 80 K as consisting of three Gaussians peaking at 529, 531 and 533 eV, the one at 531 eV being due to O^- or impurity species (from Rao *et al* 1987a).

applications will depend on several factors (material parameters, cost etc.) as shown below.

Since $YBa_2Cu_3O_7$ is superconducting well above the liquid nitrogen temperature, it holds much promise. We shall briefly examine the material parameters of this ceramic oxide. Electronic properties of this oxide are anisotropic (just as the structure). Some of its important properties are as follows (Malozemoff *et al* 1987):

1. It is a Type II superconductor.
2. Hall carrier density: $4 \times 10^{21} \text{ cm}^{-3}$ (for a material of resistivity $\sim 400 \mu\Omega \text{ cm}$ just above the T_c).

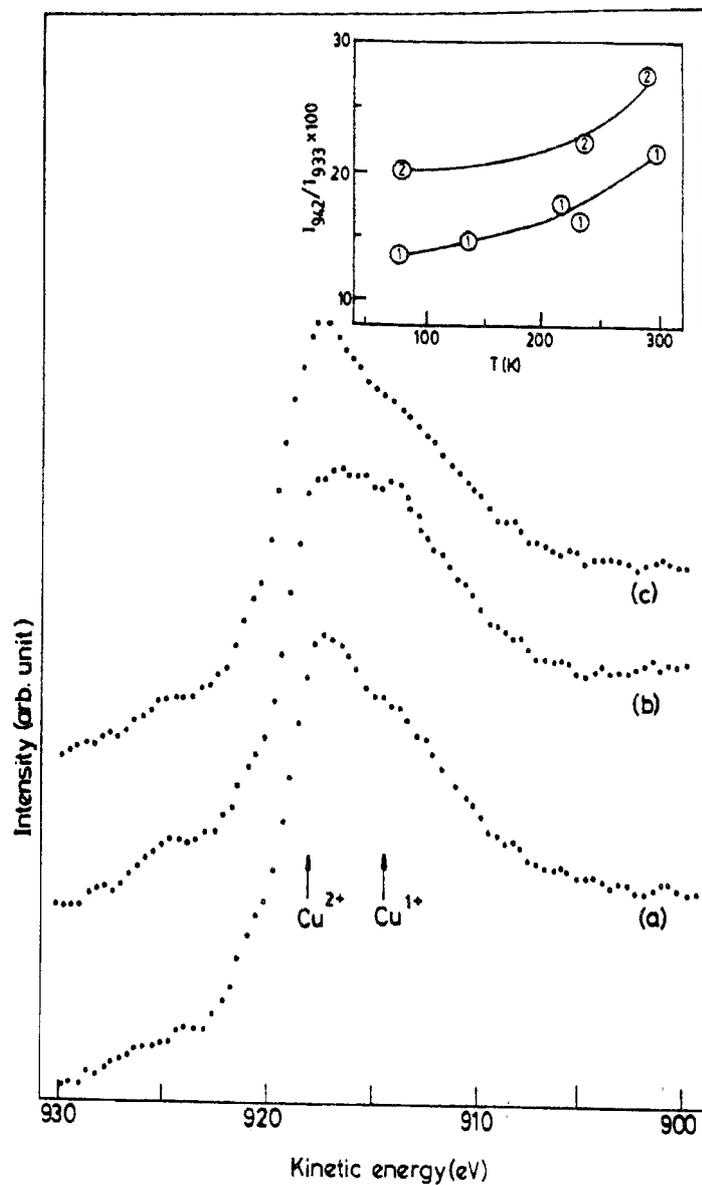


Figure 13. Cu(L₃ VV) Auger spectrum of YBa₂Cu₃O₇ at different temperatures. In the inset, the temperature variation of the intensity of the 942 eV feature relative to that of the 933 eV feature in the Cu(2p_{3/2}) spectrum is shown. 1 and 2 refer to independent sets of measurements (from Sarma & Rao 1987).

3. $dH_{c2}/dT = 2T/K$,
BCS coherence length ≈ 1.4 nm,
London penetration depth ≈ 200 nm,
Mean free path ≈ 1.2 nm.
4. $H_c(O) \approx 1 T$.
5. $H_{c2}(O) \approx 120 T$.

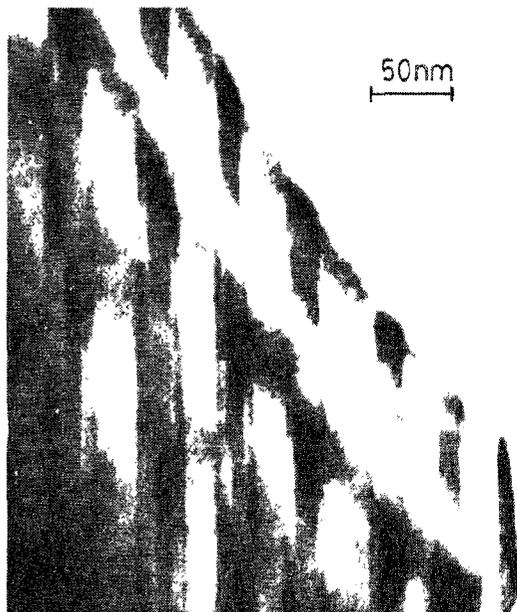


Figure 14. Bands (domains) in electron micrographs of YBa₂Cu₃O₇ (From Rao *et al* 1987c).

6. Critical current density: in ceramic samples $\sim 10^3$ A/cm² at 77 K,
 in films (on SrTiO₃) $\sim 10^5$ A/cm² at 77 K,
 in crystals and films $\sim 10^6$ A/cm² at 4.2 K.
 Depairing current density: $10^7 - 10^8$ A/cm² (estimated).

The big market for superconducting materials is in magnetic resonance imaging for medical applications. The other magnetic applications with commercial implications are in high energy physics, high field magnets for scientific investigations and magnetic separation. Magnetic confinement of plasma (fusion), levitating transportation vehicles and magnetohydrodynamics are some of the applications where commercialization will not be in the near future. In all these applications the factors that will determine the use of the new ceramics are cost advantages and material performance characteristics. The most crucial material parameter is the critical current density; it is necessary to obtain high values in large scale production of the ceramic material. Even if this becomes possible, the material cost per ampere metre will be crucial. The biggest factor is the refrigeration cost. At present, the cost of YBa₂Cu₃O₇ (for use at 77 K) seems to be much higher than traditional superconductors. It is however hopeful that the usable current density of YBa₂Cu₃O₇ will soon be higher than Nb₃Sn for high-field applications. In the mean time, problems of fabrication and chemical stability have to be sorted out.

Use of these superconducting oxides for power transmission lines is a possibility. While the cost factor (of the material and for refrigeration) has to be carefully examined, there is every hope that YBa₂Cu₃O₇ at 77 K can be used profitably in the long run at least for underground lines.

The most immediate application that seems realistic is the use of YBa₂Cu₃O₇ as interconnects in computers. Other electronic applications are in mm-wave detection, high-speed digital and analog signal processing and digital Josephson technology. Electronic instruments utilizing superconductivity such as sensitive SQUID magneto-

meters, high speed samplers and voltage standards based on Josephson effects as well as non-Josephson devices such as superconducting bolometers and SIS mixers are areas where success is likely. Transistor-like devices compatible with oxide superconductors need to be explored vigorously.

The new bismuth cuprates are promising since they are more stable chemically and with respect to oxygen stoichiometry; good films have already been made. Thallium cuprates may not be used as they are poisonous.

9. Concluding remarks

The tremendous possibilities for wide application of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other high T_c ceramic oxides make this area of research most exciting. Clearly, the high-temperature ceramic oxide superconductors constitute the most sensational discovery since the transistor; it has given a great boost to research in solid state science and engineering. There is no doubt that within a short time frame, some commercial applications will become a reality even with existing materials. The future offers unlimited vistas and opportunities in electromagnetic technology as well as in oxide ceramics research. Synthesis of materials with T_c 's close to room temperature or higher is no longer a remote possibility.

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References

- Batlogg B, Cava R J, Jayaraman A, van Dover R B, Kouroukis G A, Sunshine S, Murphy D W, Rupp L W, Chen H S, White A, Short K T, Muzsca A M, Rietman E A 1987 *Phys. Rev. Lett.* 58: 2333-2336
- Bednorz J G, Mueller K A 1986 *Z. Phys.* B64: 189-193
- Beille J, Cabanel R, Chaillout C, Chevalier B, Demazeau G, Deslandes F, Etourneau J, Le Jay P, Michel C, Provost J, Raveau B, Sulpice A, Tholence J, Tournier R 1987 *C.R. Acad. Sci. Paris* 18: 304-308
- Bhat S V, Ganguly P, Ramakrishnan T V, Rao C N R 1987 *J. Phys. C, Solid State* 20: L559-563
- Birgeneau R J, Chen C Y, Gabbe D R, Janssen H P, Kastner M A, Peters C J, Picone P J, Thio T, Thurston T R, Tuller H L 1987 (to be published)
- Bordet P, Chaillot C, Capponi J J, Chenavas J, Marezio M 1987 *Nature (London)* 327: 687-689
- Cardona M, Genzel L, Liu R, Wittlin A, Mattausch H, Garcia-Alvarado F, Garcia-Gonzalez E 1987 *Solid State Commun.* 64: 727-732
- Cava R S, van Dover R B, Batlogg B, Reitman E A 1987 *Phys. Rev. Lett.* 58: 408-410
- Chu C W, Bechtold J, Gao L, Hor P H, Huang Z J, Meng R L, Sun Y Y, Wang Y Q, Xue Y Y 1988 *Phys. Rev. Lett.* 60: 941-943
- Chu C W, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q 1987 *Phys. Rev. Lett.* 58: 405-407
- David W I F, Harrison W T A, Gunn J M F, Moze O, Soper A K, Day P, Jorgensen J D, Beno M A, Capone D W, Hinks D G, Schuller I K, Soderholm L, Segre C U, Zhang K, Grace J D 1987 *Nature (London)* 327: 310-312
- Day P, Resseinsky M, Prassides K, David W I F, Moze O, Siper A 1987 *J. Phys. C, Solid State*. 20: L429-434
- Er-Rakho L, Michel C, Provost J, Raveau B 1981 *J. Solid State Chem.* 37: 151-156
- Ganapathi L, Ganguli A K, Mohan Ram R A, Rao C N R 1988 *J. Solid State Chem.* 73: (in print)
- Ganguli A K, Subbanna G N, Umarji A M, Bhat S V, Rao C N R 1988 *Pramana-J. Phys.* 30: L483-L490
- Ganguly P, Rao C N R 1984 *J. Solid State Chem.* 53: 193-216
- Ganguly P, Mohan Ram R A, Sreedhar K, Rao C N R 1987a *Solid State Commun.* 62: 807-809

- Ganguly P, Raychaudhuri A K, Sreedhar K, Rao C N R 1987b *Pramana-J. Phys.* 28: 1229-1231
- Genzel L, Wittlin A, Kuhl J, Mattausch H, Bauhofer W, Simon A 1987 *Solid State Commun.* 63: 843-846
- Hazen R M *et al* 1988 *Phys. Rev. Lett.* 60: 1657-1660
- Johnston D C, Jacobson A J, Newsam J M, Lewandowski J E, Goshorn D P, Xie D, Yelon W B 1987 *ACS Symposium Series* 351, chap. 14
- Jorgensen J D, Beno M A, Hinks D G, Soderholm L, Vohm K J, Hitterman R I, Grace J D, Schuller I K, Segre C U, Zhang K, Kleefisch M S 1987 *Phys. Rev.* (in print)
- Langen J, Veit M, Galfy M, Jostarndt H D, Erle A, Blumentoder S, Schmidt H, Zirngiebl I 1988 *Solid State Commun.* 65: 973-976
- Maeda H, Tanaka Y, Fukutomi M, Asano T 1988 *Jpn. J. Appl. Phys.* (to be published)
- Malozemoff A P, Gallagher W J, Schwall R F 1987 *ACS Symposium Series* 351, chap. 27
- Mohan Ram R A, Ganguly P, Rao C N R 1987a *Phase Transitions* 10: 107-121
- Mohan Ram R A, Vasantacharya N Y, Rao C N R 1987b *J. Solid State Chem.* 69: 186-188
- Michel C, Hervieu M, Borel M M, Grandin A, Deslandes F, Provost J, Raveau B 1987 *Z. Phys.* B68: 421
- Mitzi D B, Marshall A F, Sun J Z, Webb D J, Beasley M R, Geballe T H, Kapitulnik A 1988 *Phys. Rev.* (in print)
- Mitsuda S, Shirane G, Sinha S K, Johnston D C, Alvarez M S, Vaknin D, Moncton D L 1987 *Phys. Rev.* B36: 822-825
- Paul D M, Balakrishnan G, Bernhoeft N R, David W J F, Harrison W I A 1987 *Phys. Rev. Lett.* 58: 1976-1978
- Rao C N R 1987 *Progress in high-temperature superconductivity. Proc. Advantico Conference Trieste* (Singapore: World Scientific Co.)
- Rao C N R 1988a *J. Solid State Chem.* 73: (April issue)
- Rao C N R (ed.) 1988b *Chemistry of oxide superconductors* (Oxford: Blackwell Scientific Publishers)
- Rao C N R, Ganapathi L, Mohan Ram R A 1988a *Mater. Rev. Bull.* 23: 123-127
- Rao C N R, Ganguly P 1985 in *The metallic and non-metallic states of matter* (eds P P Edwards, C N R Rao) (London: Taylor and Francis)
- Rao C N R, Ganguly P 1987a *Curr. Sci.* 56: 47-49
- Rao C N R, Ganguly P 1987b *Jpn. J. Appl. Phys.* 26: 1882-1885
- Rao C N R, Ganguly P, Gopalakrishnan J, Sarma D D 1987a *Mater. Rev. Bull.* 22: 1159-1163
- Rao C N R, Ganguly P, Raychaudhuri A K, Mohan Ram R A, Sreedhar K 1987b *Nature (London)* 326: 856-857
- Rao C N R, Ganguly P, Sreedhar K, Mohan Ram R A, Sarode P R 1987c *Mater. Rev. Bull.* 22: 849-854
- Rao C N R, Umarji A M, Mohan Ram R A, Vijayaraghavan R, Nanjundaswamy K S, Somasundaram P, Ganapathi L 1988b *Pramana-J. Phys.* 30: 1359-1365
- Raychaudhuri A K, Sreedhar K, Rajeev K P, Mohan Ram R A, Ganguly P, Rao C N R 1987 *Philos. Mag. Lett.* 56: 29-34
- Sarma D D, Rao C N R 1987 *J. Phys. C, Solid State* 20: 1659-1661
- Sarma D D, Sreedhar K, Ganguly P, Rao C N R 1987 *Phys. Rev.* B36: 2371-2373
- Segre C U, Dabrowski B, Hinks D G, Jorgensen J D, Beno M A, Schuller I K 1987 *Nature (London)* 329: 227-229
- Sheng Z Z, Hermann A M 1988 *Nature (London)* 332: 55-58, 138-139
- Shirane G, Endoh Y, Birgeneau R J, Kastner M A, Hidaka Y, Oda M, Suzuki M, Murakami T 1987 *Phys. Rev. Lett.* 59: 1613-1616
- Siegrist T, Sunshine S, Murphy D W, Cava R J, Zahurak S M 1987 *Phys. Rev.* B35: 7137-7148
- Sreedhar K, Ramakrishnan T V, Rao C N R 1987 *Solid State Commun.* 63: 835-837
- Subbanna G N, Ganguly P, Rao C N R 1987 *Mod. Phys. Lett.* B1: 155-165
- Subramanian M A, Torardi C C, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew I R, Flippen R B, Chowdhry U, Sleight A W 1988 *Science* 239: 1015-1018
- Tarascon J M, McKinnon W R, Greene L H, Hull G W, Vogel E M 1987a *Phys. Rev.* B35: 3238-3242
- Tarascon J M *et al* 1987b *Proc. MRS Meeting, Anaheim*
- Tarascon J M *et al* 1988 (to be published)
- Thomann H, Johnston D C, Tindall P J, Goshorn D P, Klemm R A 1987 *Phys. Rev. Lett.* 59: 509-512
- Uchida S, Takagi H, Kitazawa K, Tanaka S 1987 *Jpn. J. App. Phys.* 26: 11-14
- Uemura Y J, Kossler W J, Yu X H, Kempton J R, Schone H F, Opie D, Stronach C F, Johnston D C, Alvarez M S, Goshorn D P 1987 (to be published)
- Wu M K, Ashburn J R, Toring C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q, Chu C W 1987 *Phys. Rev. Lett.* 58: 908-909
- Xiao G, Streitz F H, Gavrin A, Chien C L 1987 *Solid State Commun.* 63: 817-820