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Relation between high T_c superconductivity and structure: A study of $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ and $YBa_2Cu_3O_{7-\delta}$ systems†

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Abstract. Superconductivity is found in tetragonal $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ and (La, Ba)$_{6-x}$Sr$_x$Cu$_6$O$_{14+\delta}$ even though they do not possess Cu–O chains or the K_2NiF_4 structure. Resistivity measurements confirm the occurrence of a transformation from chain-superconductivity to sheet-superconductivity in $YBa_2Cu_3O_{7-\delta}$ as δ is varied in the range 0·0–0·5.

Keywords. High-temperature superconductivity; $La_3Ba_3Cu_6O_{14}$; $YBa_2Cu_3O_7$.

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Ever since the discovery of high-temperature superconductivity in the La–Ba–Cu–O system by Bednorz and Müller (1986), there has been unprecedented interest in investigating superconductivity in various oxide materials. The first group of high-T_c oxide superconductors belonging to the La–Ba(Sr)–Cu–O family, possess the K_2NiF_4 structure (Chu *et al* 1987; Uchida *et al* 1987; Rao and Ganguly 1987; Ganguly *et al* 1987a). These oxides with T_c in the 20–40 K range contain planar CuO_2 units. The second group of oxides have the general composition $YBa_2Cu_3O_7$ or $LnBa_2Cu_3O_7$ (Ln = Dy, Gd, Ho, Er, etc). $YBa_2Cu_3O_7$ and related oxides contain Cu–O–Cu chains or corner-linked CuO_4 units (David *et al* 1987); these superconducting oxides have the orthorhombic structure. Removal of oxygen in the Cu–O–Cu chains destroys high T_c ($T_c \sim 90$ K) superconductivity in these oxides (Bordet *et al* 1987; Rao *et al* 1987b).

We initiated investigations of the Y–Ba–Cu–O system (Ganguly *et al* 1987b; Rao *et al* 1987a) by analogy with $La_3Ba_3Cu_6O_{14}$ (Er-Rakho *et al* 1981). $La_3Ba_3Cu_6O_{14}$ itself is an oxygen-deficient perovskite with a tetragonal structure. While in $YBa_2Cu_3O_7$, oxygen vacancies are in the Cu–O planes located between fully oxidised Ba–O layers, $La_3Ba_3Cu_6O_{14}$ has additional oxygen vacancies on the (La, Ba)–O planes between oxidised Cu–O planes. Along the *c*-axis of $La_3Ba_3Cu_6O_{14}$, the sequence is $|Cu_2O_4–A_2O\square–Cu_2O_4–A_2\square_2–Cu_2O_4–A_2O\square|_\infty$. We examined superconductivity in the $La_{3-x}Ba_{3+x}Cu_6O_{14}$ in the very early stages of our studies (Ganguly *et al* 1987a, b), but did not report these results because of our preoccupation with the Y–Ba–Cu–O system. We however reported the first perovskite oxide showing superconductivity (Ganguly *et al* 1987a). We have since

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learnt of the fine study of the $La_{3-x}Ba_{3+x}Cu_6O_{14}$ system by Mitzi *et al* (1987). In this communication we report results of our studies to show that members of (La, Ba)$_{6-x}$Sr$_x$Cu$_6$O$_{14}$ system possessing the $La_3Ba_3Cu_6O_{14}$ structure also exhibit superconductivity although their structure is different from either that of $La_{2-x}Ba_xCuO_4$ or $YBa_2Cu_3O_7$.

We prepared samples of the $La_{3-x}Ba_{3+x}Cu_6O_{14}$ and (La, Ba)$_{6-x}$Sr$_x$Cu$_6$O$_{14}$ systems starting with a mixture of stoichiometric amounts of La_2O_3, $BaCO_3$, $SrCO_3$ and CuO. The thoroughly ground mixture was first heated in air around 1200 K for 20 h. These were pelletized and again heated in air at the same temperature. Samples were finally annealed in oxygen around 700 K.

In figure 1 we show part of the powder X-ray diffraction patterns of three compounds to illustrate how they all possess the same $La_3Ba_3Cu_6O_{14}$ (tetragonal) structure. We have found oxides of compositions $La_{3.3}Ba_{2.7}Cu_6O_{14}$, $La_3Ba_2SrCu_6O_{14}$, $La_{2.5}Ba_{2.5}SrCu_6O_{14}$ and $La_{2.25}Ba_{3.25}Sr_{0.5}Cu_6O_{14}$ also crystallize in the tetragonal structure of $La_3Ba_3Cu_6O_{14}$. Oxides of the type (La, Ba)$_{6-x}$Sr$_x$Cu$_6$O$_{14}$ have been reported here for the first time.

Resistivity measurements show superconductivity only in $La_{2.5}Ba_{3.5}Cu_6O_{14}$ and $La_2SrBa_3Cu_6O_{14}$. Superconductivity was not observed in $La_{3.3}Ba_{2.7}Cu_6O_{14}$, $La_3Ba_2SrCu_6O_{14}$, $La_{2.5}Ba_{2.5}SrCu_6O_{14}$ and $La_{2.25}Ba_{3.25}Sr_{0.5}Cu_6O_{14}$ (see figures 2 and 3). Although the T_c found by us is in the 40 K region, it is realized that it can be increased by heating the samples under high oxygen pressure (Mitzi *et al* 1987). What is important, however, is that superconductivity manifests itself in these oxides in the absence of one-dimensional Cu–O chains or of the K_2NiF_4 structure.

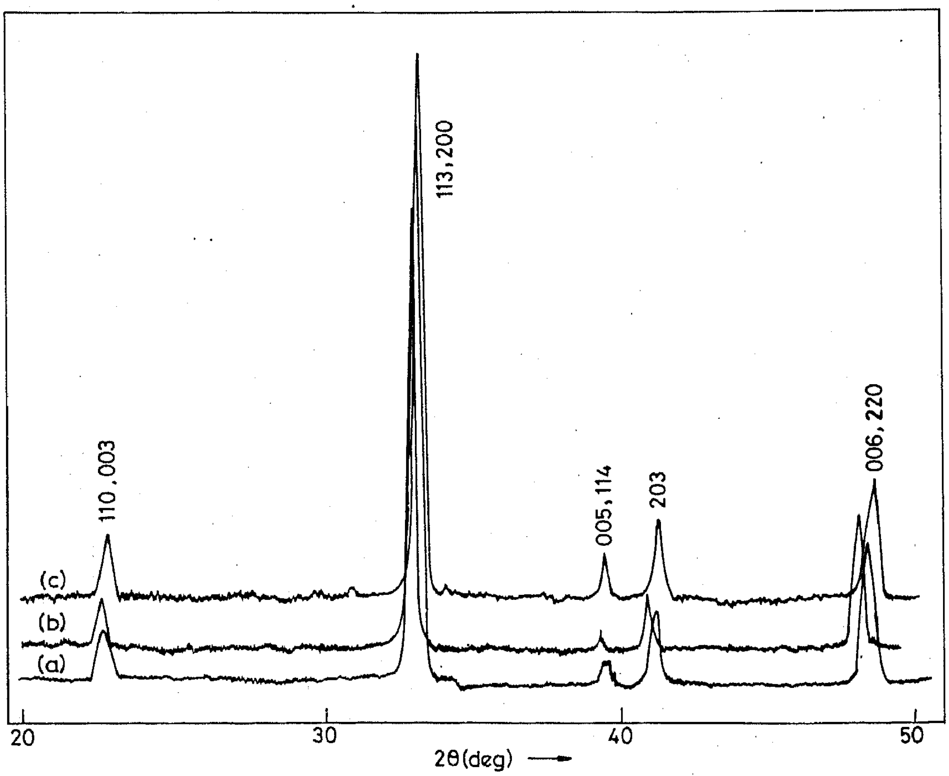

Figure 1. X-ray diffraction patterns of (a) $La_3Ba_3Cu_6O_{14}$ (b) $La_{2.5}Ba_{3.5}Cu_6O_{14}$ (c) $La_2SrBa_3Cu_6O_{14}$.

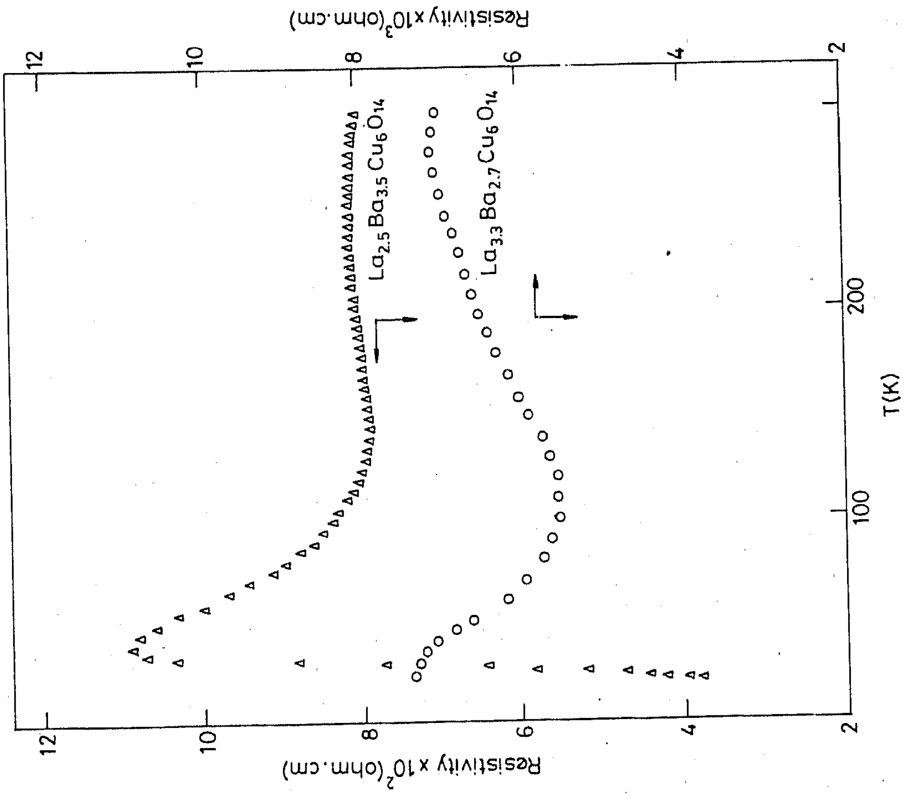

Figure 2. Resistivity data of $La_{2.5}Ba_{3.5}Cu_6O_{14}$ and $La_{3.3}Ba_{2.7}Cu_6O_{14}$.

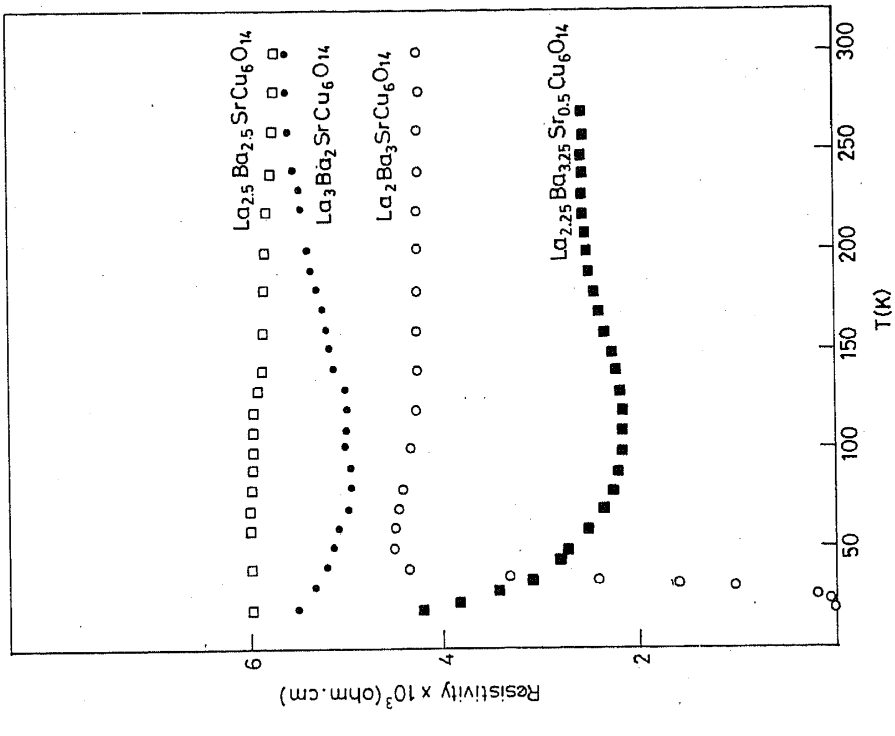

Figure 3. Resistivity data of $La_2Ba_3SrCu_6O_{14}$, $La_{2.5}Ba_{2.5}SrCu_6O_{14}$, $La_3Ba_2SrCu_6O_{14}$ and $La_{2.25}Ba_{3.25}Sr_{0.5}Cu_6O_{14}$.

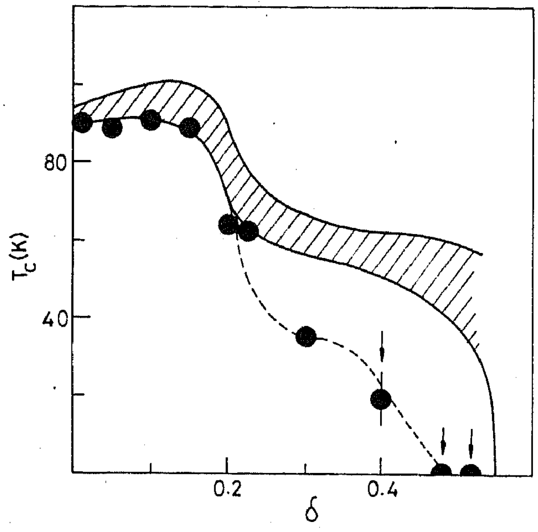

Figure 4. Variation of the superconducting transition temperature of $YBa_2Cu_3O_{7-\delta}$ with oxygen stoichiometry. The shaded region and full line are from magnetic measurements of Johnston *et al* (1987). Closed circles and dotted lines are based on resistivity data from this laboratory. Arrows indicate temperatures above which no superconductivity is observed.

Dependence of superconductivity on the structure of the oxide is of great relevance to the mechanism of superconductivity. We have mentioned above, three types of structures showing superconductivity. It is therefore interesting to see how the structural changes brought about by changes in oxygen stoichiometry in $YBa_2Cu_3O_{7-\delta}$ is reflected in the superconductivity of the system.

Superconducting $YBa_2Cu_3O_{7-\delta}$ is orthorhombic up to a δ value of 0·5. At $\delta \geqslant 0{\cdot}5$, the structure becomes tetragonal and the material is non-superconducting. The superconducting transition temperature of $YBa_2Cu_3O_{7-\delta}$ obtained by magnetic susceptibility measurements (Johnston *et al* 1987) shows an interesting variation with oxygen stoichiometry. The T_c is essentially constant at small values, but shows a change in behaviour above a $\delta \simeq 0{\cdot}3$, where we observe a plateau (figure 4). T_c values obtained by us from electrical resistivity measurements also show a somewhat similar behaviour although the transition temperatures found by us are lower than those from susceptibility measurements (for high δ oxides). The plateau in T_c above $\delta \simeq 0{\cdot}30$ is an important feature. In this composition range, $YBa_2Cu_3O_{7-\delta}$ would not have a sufficient number of oxygen atoms in the Cu–O chains. The superconductivity with T_c between 20 K and 40 K found in these compositions therefore probably arises from the CuO_2 planes as in $La_{2-x}Sr_x(Ba_x)CuO_4$. It appears that with the change in oxygen stoichiometry (or δ), we are actually observing the transformation of chain-superconductivity to sheet-superconductivity.

We are continuing our studies of $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ and other oxides prepared under high oxygen pressure.

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