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A universal trend in the structural correlation with oxygen content in $RBa_2Cu_3O_x$ systems

K MURALEEDHARAN

A.C.R.E., Indian Institute of Technology, Bombay 400076, India

Present address: Department of Physics, Indian Institute of Technology, Madras 600036, India

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Abstract. It is shown that the lattice parameters a, b and c in the superconducting perovskites $RBa_2Cu_3O_x$ are inter-related and well correlated to the total oxygen content. The correlation shows a universal trend.

Keywords. Ceramic superconductor; structural correlation; oxygen content.

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The superconducting cuprate perovskites are found to be structurally sensitive to the oxygen content (Jorgensen *et al* 1987; Cava *et al* 1987). In $RBa_2Cu_3O_x$ systems where R = Y or a rare earth atom, it is known that the superconducting orthorhombic phase is stabilized at room temperature for an oxygen content $6{\cdot}5 < x < 7$ (Jorgensen *et al* 1987). Below $x = 6{\cdot}5$, the high temperature tetragonal semiconducting phase is stabilized. The superconducting phase consists of 2-D Cu-O network in the a–b plane and linear chains resulting from ordered oxygen vacancies along the b direction of the unit cell. On oxygen depletion, either by quenching from high temperatures or by vacuum annealing, the linear chains are disrupted, and the oxygen atoms are rearranged in such a way that both (0, 1/2, 0) and (1/2, 0, 0) sites at the basal planes are equally occupied. This results in a tetragonal structure for $x < 6{\cdot}5$. Cava *et al* (1987) have reported a new orthorhombic phase with $T_c = 60$ K for $6{\cdot}2 < x < 6{\cdot}7$, as evident from a plateau region in the T_c vs x curve. The structural data reported, however, do not show any dramatic changes in the range of oxygen content $6{\cdot}2 < x < 6{\cdot}7$. In this letter, we report a universal trend observed in the correlation of the a, b and c parameters with oxygen content, in $RBa_2Cu_3O_x$ systems.

It is seen that in $RBa_2Cu_3O_x$ systems, the c parameter increases with decreasing oxygen content (Jorgensen *et al* 1987). The b parameter decreases and the a parameter increases till they become equal at the orthorhombic to tetragonal transition point. In figure 1 we show the variation of the quantity $q = (c/a) - (b/a)$, as a function of the oxygen content x, with the data taken from literature (Cava *et al* 1987; Tarascon *et al* 1987; Manthiram and Goodenough 1987; Segre *et al* 1987; Henry *et al* 1987; Yan *et al* 1987). The data for the $YBa_2Cu_3O_x$ systems are from Cava *et al* (1987) and for other rare earth-substituted systems $RBa_2Cu_3O_x$, where R = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb, the data are from Tarascon *et al* (1987). The two data points from the Y system at 77 K and 124 K are taken from Yan *et al* (1987).

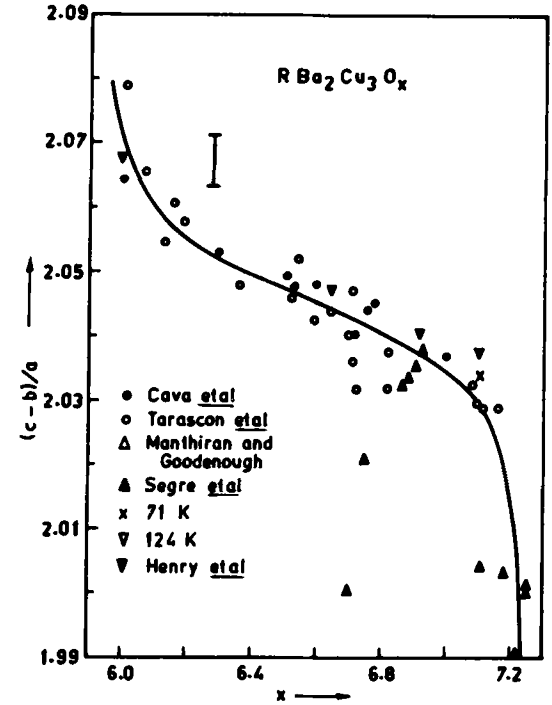

Figure 1. Variation of the quantity $q = (c/a) - (b/a)$, with oxygen content x in $RBa_2Cu_3O_x$ systems. The data points were collected from various references given. In the case of data from Segre *et al*, the system refers to $LaBa_{2-y}La_yCu_3O_x$.

The data for both the orthorhombic and tetragonal systems are plotted on the same figure. It can be easily seen that all the data points fall on a universal curve. (The solid line is only a guide to the eye). The q value initially decreases fast, up to $x = 6{\cdot}2$ and then decreases with a different slope till $x = 7{\cdot}0$, and, thereafter, rapidly falls for $x > 7{\cdot}0$. It is noted that the superconducting systems fall in the region $q < 2{\cdot}05$ and the 90 K region is limited to $q \sim 2{\cdot}03$–$2{\cdot}04$. There are some noticeable deviations also: the two points of the data taken from Manthiram and Goodenough (1987) are farther below the main curve. The lowest point near $q = 2{\cdot}0$ is a semiconductor, and that near 2·02 corresponds to $T_c = 60$ K. The particular sample with large deviation from the main curve had an oxygen content $x = 6{\cdot}7$, but was tetragonal in contrast to the usual observations. It was argued that the low temperature (< 780 C) synthesis technique they used could result in the presence of oxygen disorder and immobile peroxide units O_2^{2-}. One could thus conclude that the oxygen ordering is a crucial parameter determining T_c in addition to the total oxygen content. It is also to be noted that there is a large scatter in the data points around the main curve, which could result from the variation in the oxygen occupation ratio of (0, 1/2, 0) and (1/2, 0, 0) sites (Jorgensen *et al* 1987), which are unspecified in various samples having, nevertheless, almost the same total oxygen content.

We have plotted the data on $LaBa_{2-y}La_yCu_3O_x$ system (Segre *et al* 1987) also on the same figure. Even though these systems are expected to show a different behaviour regarding the $(c/a)-(b/a)$ ratio, the data points all fall about the same extrapolated smooth curve. The oxygen contents in these systems are greater than 7 but the T_c is lower than 90 K. The q values for these systems fall below 2·005. The T_c reported are all below 80 K and the transitions are very broad.

We do not attempt here any serious speculation on the significance of the q value, but only mention the following: the c/a ratio gives the deviation from the ideal perovskite structure in these systems. For an ideal tripled perovskite, $c/a=3$, and the b/a ratio gives an estimate of the deviation from the tetragonal structure. Thus, the quantity $(c/a)-(b/a)$ combines both these effects in real systems. From figure 1, we can conclude that there is a range of deviation from an ideal perovskite structure which is favourable for superconductivity, and this could be of some theoretical interest. The correlation observed above could also be of some use in estimating the approximate oxygen content from a, b and c values obtained from the powder X-ray diffraction measurements. It may also be stated that several new structural data which recently appeared in literature (see e.g. Cava *et al* 1988; Causa *et al* 1988) are also found to be consistent with the correlation discussed above.

In conclusion, we have demonstrated that in the high T_c ceramic perovskites of the type $RBa_2Cu_3O_x$, the structural parameters a, b and c are well correlated to the oxygen content, and the correlation shows a universal trend.

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