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LETTER TO THE EDITOR

Depression of T_c with Rare Earth Substitution for La in $La_{2-x}Sr_xCuO_4$ Superconductors

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Phases of the type $La_{2-x-y}R_xSr_yCuO_{4-z}$, where R is Pr, Nd, Sm, Eu, or Gd, have been prepared for various values of x and y. All phases prepared had the La_2CuO_4 structure. The general trend for fixed y is that T_c decreases as the four coplanar Cu–O distances decrease. This unexpected correlation between T_c and Cu–O distance is explained by our finding that the Cu^{III} concentration also decreases as these R cations are substituted for La. The amount of R that can be substituted for La increases as R becomes larger. For R = Pr, the x value reaches about 0.8. Such phases, for example, $La_{1.05}Pr_{0.80}Sr_{0.15}CuO_4$, do not show a depressed T_c, indicating that Pr does not always adversely affect superconductivity in copper oxide based phases as it does in the $YBa_2Cu_3O_7$ type structure.

Introduction

For copper oxide based superconductors, good correlations have been established between T_c and both the carrier concentration (i.e., Cu^{III} or Cu^{I}) and the Cu–O distance for the four highly covalent coplanar bonds (*1*, *2*). In $La_{2-x}A_xCuO_4$ phases, where A is Ca, Sr, Ba, or Na, increasing x leads to an increase in T_c as the Cu–O distance decreases (*3*, *4*). However, the carrier concentration is also increasing with increasing x. Thus, it is not clear whether we should regard this as a T_c correlation with carrier concentration or as a T_c correlation with Cu–O distance. The fact that T_c also increases with pressure suggests that there is a correlation of T_c with Cu–O distance which is independent of carrier concentration (*5*). A way to confirm this correlation might be partially to substitute some of the smaller rare earth cations for La in a $La_{2-x}A_xCuO_4$ superconductor. Such substitutions would be expected to give shorter Cu–O distances without changing the carrier concentration.

Compositions of the type $La_{2-x-y}R_xSr_yCuO_{4-z}$ are also of interest because, at complete substitution of rare earths R for La, a new structure is produced which is our only example of n-type copper oxides which superconduct. Thus, a better under-

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standing of p-type $La_{2-x-y}R_xSr_yCuO_{4-z}$ phases might help us to better understand the n-type $R_{2-x}A_xCuO_4$ superconductors because we might better understand the influence of the R cations.

Experimental

Members of the $La_{2-x-y}R_xSr_yCuO_4$ series for various values of x and y were prepared by heating appropriate mixtures of La_2O_3, CuO, R_2O_3, and SrO_2 in air at 1100–1150°C for 24–36 hr in flowing oxygen atmosphere. Pr_2O_3 was prepared by hydrogen reduction of Pr_6O_{11} at 750°C. Formation of single phase products was checked by X-ray diffraction with Cu$K\alpha$ radiation. Unit cell dimensions were refined by least squares. The test for superconductivity was made by the ac mutual inductance technique. The Cu^{III} content was analyzed by titrimetry (*1*).

Results

Broad ranges of single phase compositions of the type $La_{2-x-y}R_xSr_yCuO_{4-z}$ were successfully prepared, where R is Pr, Nd, Sm, Eu, and Gd. Figure 1 shows the solid solution limits for various rare earths (R) and the shaded portion of the chart shows the superconducting range when y is 0.15. Attempts to prepare analogous phases with significant quantities of even smaller rare earth cations led to products which were not single phase. The room temperature symmetry of the $La_{2-x-y}R_xSr_yCuO_{4-z}$ phases prepared was usually tetragonal but was orthorhombic when y was 0.15 and $x > 0.4$ in the case of Nd, $x > 0.3$ in the case of Sm. None of the phases with room temperature orthorhombic symmetry became superconducting at low temperatures.

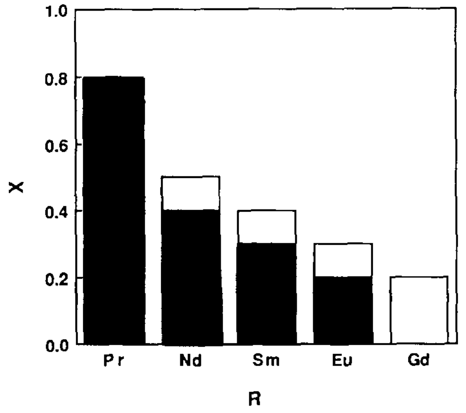

FIG. 1. Range of existence of single phase materials in the system $La_{2-x-y}R_xSr_yCu_2O_4$ when $y = 0.15$. The superconducting range is shaded.

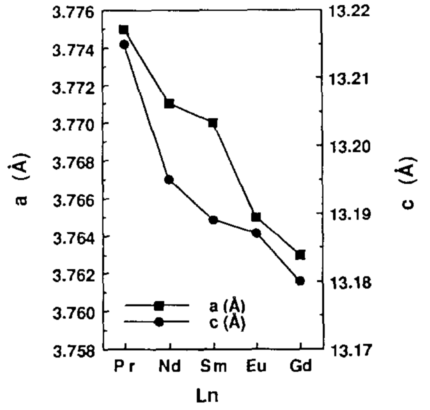

FIG. 2. Variation of a [or $(a + b)/2$] and c cell dimensions for $La_{1.85-x}R_xSr_{0.15}CuO_4$ as a function of R.

To study the trends of substituting R for La, y was fixed at either 0.15 or 0.20. For fixed x and y, the unit cell dimensions decreased as the size of the rare earth (R) decreased (Fig. 2). The Cu–O distance of interest is one-half of the a or b cell edge. As shown in Figs. 3 and 4, T_c decreases as R becomes smaller. Since T_c also decreases with increasing x, T_c is in fact always decreasing with decreasing Cu–O distance for these phases. Several other laboratories have reported essentially the same trends for more limited ranges of compositions (*6–11*). However, none of these other laboratories reported measurements of carrier concentration or Cu^{III} concentration. Our titrations show that the Cu^{III} concentration

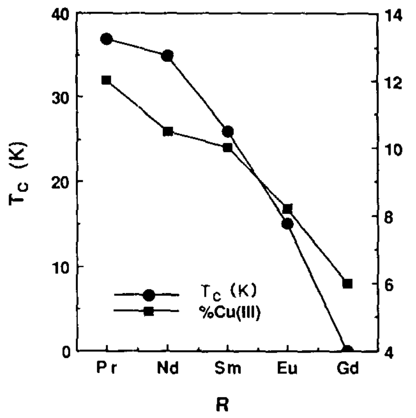

FIG. 3. Variation of T_c and carrier concentration (Cu^{III}) as a function of R for $La_{1.7}R_{0.15}Sr_{0.15}CuO_4$.

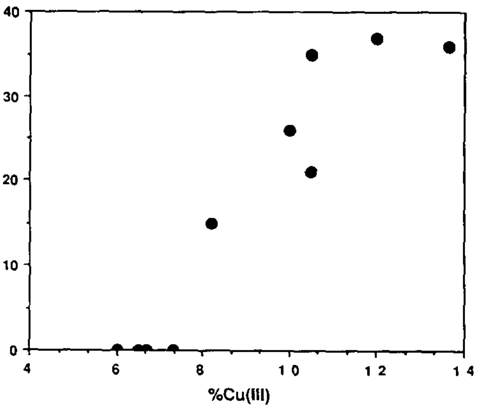

FIG. 5. Variation of T_c vs carrier concentration for $La_{1.85-x}R_xSr_{0.15}CuO_4$.

decreases as R becomes smaller and as x becomes greater (Figs. 3 and 4). There is a very good correlation between T_c and the Cu^{III} concentration (Figs. 5 and 6).

Our attempts to substitute Pr for La in $La_{1.85-x}Pr_xSr_{0.15}CuO_4$ showed that single phase samples with tetragonal La_2CuO_4-type structure exist for x values up to 0.8. Both a and c cell dimensions showed a slight decrease as x increases (Fig. 7). However, unlike other rare earth substitutions, T_c does not precipitously decline as x increases. Our titrations show that the Cu^{III} concentration is always high and nearly independent of x (Fig. 8). The behavior of $La_{1.85-x}Pr_xSr_{0.15}CuO_4$ phases is very much in contrast to $Y_{1-x}Pr_xBa_2Cu_3O_7$ phases where one observes a rapid disappearance of superconductivity as x increases from zero.

Discussion

One might have expected that $La_{2-x-y}R_xSr_yCuO_{4-z}$ phases would have yielded new information on the correlation between

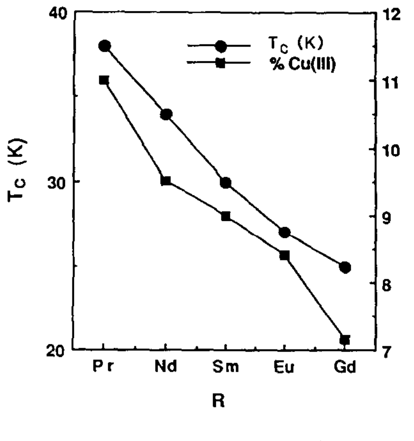

FIG. 4. Variation of T_c and carrier concentration (Cu^{III}) as a function of R for $La_{1.65}R_{0.2}Sr_{0.15}CuO_4$.

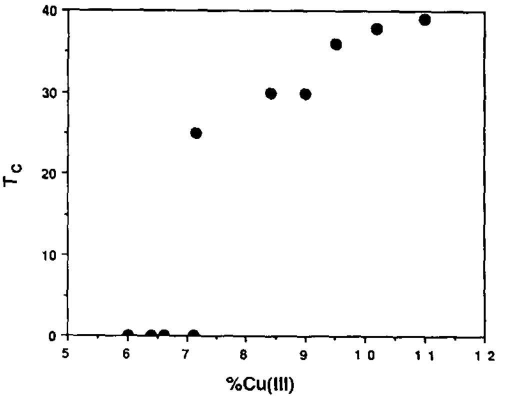

FIG. 6. Variation of T_c vs carrier concentration for $La_{1.85-x}R_xSr_{0.2}CuO_4$.

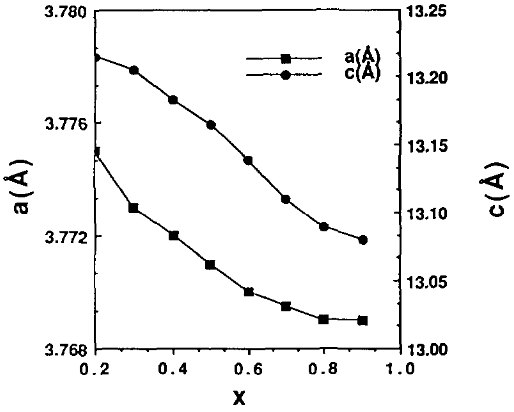

FIG. 7. Variation of a and c cell dimensions vs x for $La_{1.85-x}Pr_xSr_{0.15}CuO_4$.

T_c and the Cu–O distance. Instead, any such correlation is obscured by the obvious correlation between carrier concentration and T_c. The correlation between T_c and carrier concentration is, in fact, very good. Since oxidation of Cu^{II} to Cu^{III} represents removal of antibonding electrons from the Cu–O bonds, increasing the carrier concentration in p-type systems is expected to lead to shorter Cu–O distances. Thus, correlations of T_c with Cu–O distance may in general really be reflecting the correlation between T_c and carrier concentration which is frequently not well determined. Our results show that it is very easy for the correlation of carrier concentration with T_c to dominate the correlation of T_c with Cu–O distance. The observation that T_c decreases with increasing pressure for the n- type copper oxide superconductors (*12*) also indicates that there is no universal increase of T_c with decreasing Cu–O distance.

For the $La_{2-x-y}R_xSr_yCuO_{4-z}$ phases, the oxygen deficiency increases as R becomes smaller and more concentrated. In retrospect, this is not too surprising because we know that stabilization of Cu^{III} in oxides requires the presence of highly basic cations (*13*). The basicity of the rare earth cations decreases as their size decreases. Thus, the R cations become less effective in stabilizing Cu^{III} as their size decreases. This effect was previously apparent in attempts to dope the R_2CuO_4 phases p-type. Phases of the type $R_{2-x}A_xCuO_4$ in the T' structure, where R is Pr, Nd, Sm, Eu, or Gd and A is the divalent cation Sr or Ca, fail to produce superconducting or even metallic properties (*14*). This failure is presumably caused by the inability to stabilize sufficient quantities of Cu^{III} in such systems. The role of basic cations in stabilizing sufficient Cu^{III} for superconductivity was also noted for analogs of $Bi_2Sr_2CaCu_2O_8$ (*15*).

In the $YBa_2Cu_3O_7$ structure, substitution of Pr for Y causes a rapid disappearance of superconductivity (*16*, *17*). In fact, $PrBa_2Cu_3O_7$ is not even metallic. An obvious explanation would be that Pr is tetravalent instead of trivalent. However, the consensus is that Pr is essentially trivalent (*17*). In the $YBa_2Cu_3O_7$ structure, Pr on Y sites bonds only to oxygens that are strongly bound to copper in the CuO_2 sheets. However, in the La_2CuO_4 structure, Pr forms its strongest bonds to oxygen that is only weakly bound to copper. Thus, we may expect stronger Pr–Cu hybridization in the $YBa_2Cu_3O_7$

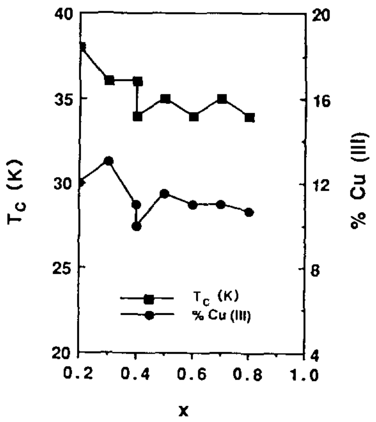

FIG. 8. Variation of T_c and carrier concentration (Cu^{III}) for $La_{1.85-x}Pr_xSr_{0.15}CuO_4$ as a function of x.

structure than in the La_2CuO_4 structure. The stronger hybridization would in turn adversely affect superconductivity.

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