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SYNTHESIS AND PROPERTIES OF NEW FAMILY OF SUPERCONDUCTING COPPER OXIDES BASED ON GaO LAYERS*

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ABSTRACT

We have discovered the first layered superconducting copper oxide with small, fixed oxidation state cations separating the conducting CuO_2 planes. This material, $GaSr_2Y_{1-x}Ca_xCu_2O_7$, is similar to $YBa_2Cu_3O_7$ with the square planar copper chains replaced by chains of edge-shared GaO_4 tetrahedra. Thus, oxidation can occur only for the copper ion located in square pyramidal coordination in the CuO_2 plane. The undoped parent compound, x = 0, does not show magnetic order above 4K, probably due to the presence of the thick, ionic region separating the CuO_2 planes. However, this ionic region does not suppresses high T_c superconductivity (~70K) for the doped compositions.

INTRODUCTION

All known copper oxide superconductors have an anisotropic structure containing two-dimensional CuO_2 planes with the copper ion in square planar, square pyramidal or octahedral coordination by oxygen. The CuO_2 planes are bounded in the third dimension by metal-oxygen layers, AO, containing large and strongly electropositive (A = Ba, Sr and La-Ga) metal ions, thus forming AO-CuO_2-AO structural blocks. For many superconducting compounds there are frequently multiple CuO_2 planes, separated by metal layers, A′ (A′ = Ca, lanthanides and Y), within the block. All superconducting compounds can be divided into two general structural classes depending on the block stacking sequence. For the first class, blocks are stacked directly together (e.g. La_2CuO_4, Nd_2CuO_4 and $La_2CaCu_2O_6$)[1]. The second class, contains an additional intermediate region, separating the blocks, consisting of mixed oxidation state cations covalently bonded to oxygen (e.g. structures based on Cu, Tl, Pb and Bi)[1].

The best known superconducting copper oxide $LnBa_2Cu_3O_7$ (Ln = lanthanides and Y) contains square planar coordinated copper ions in the intermediate region (frequently referred to as the chain region) between the AO-CuO_2-A'-CuO_2-AO blocks[2]. It was shown for Ln = La that it is possible to substitute this square planar copper site with tantalum and niobium resulting in the distinct, but very similar $LaBa_2TaCu_2O_8$ structure, with octahedraly coordinated Nb and Ta[3]. This latter structure shows the importance of the coordination preference of small ions leading either to the formation of ordered CuO_2 planar compounds or mixing with copper on both sites. Recent discussion of the ionic size and coordination factors that led to the formation of CuO_2 planes in $AA'BCuO_6$ (B = transition or post transition metal) compounds is given by Anderson et al.[4]. Several new layered copper oxides with ionic, fixed oxidation state, cations in the intermediate region between AO-CuO_2-AO structural blocks were found (e.g. single CuO_2 layer $AlSrLaCuO_5$, $GaSrLaCuO_5$ and $SnLa_2CuO_6$, and double CuO_2 layer $AlSr_2LnCu_2O_7$ and $GaSr_2LnCu_2O_7$). However, none of these compounds was superconducting when prepared in air.

The structural similarity of these compounds to the known hole-doped copper oxide superconductors and the possibility of controlling the carrier concentration by varying the oxygen content led us to synthesize the Ca-substituted compositions under high oxygen pressure. The combined calcium and oxygen doping could introduce the necessary charge to the CuO_2 layers. Recently, we have prepared the $GaSr_2Y_{1-x}Ca_xCu_2O_7$ compound that become superconducting after high pressure oxygen annealing[5]. While the undoped parent compound, x = 0, did not show three-dimensional magnetic order above 4K, probably due to the presence of the thick ionic region separating the CuO_2 layers, superconductivity with a high T_c (~70K) was observed for the doped compositions.

EXPERIMENTAL

Polycrystalline samples of $GaSr_2Y_{1-x}Ca_xCu_2O_7$ ($0 \leq x \leq 0.4$) were synthesized from stoichiometric mixture of oxides and carbonates in air at 980°C followed by fast cooling to room temperature. Samples were fired for 3 weeks with frequent intermediate grindings. High pressure annealing was done for 24 hours in pure oxygen using 200 atm. at 910°C for powdered samples and 300 atm. at 925°C for pressed dense pellets. Lattice parameters were determined using Rietveld refinement of powder x-ray diffraction data. Susceptibility measurements were performed using a Squid (Quantum Design Corp. MPMS) and an a.c. (Lake Shore Cryotronics) susceptometer. Resistivity was measured using a standard four-lead d.c. technique. Oxygen content was determined using thermogravimetric analysis measurements (Cahn TG 171).

RESULTS

The orthorhombic structure of $GaSr_2LnCu_2O_7$ (noncentrosymmetric space group Ima2, No.46) is similar to $LnBa_2Cu_3O_7$ (see Fig.1)[5,6]. The square planar copper chains in $LnBa_2Cu_3O_7$ are replaced by chains of edge-shared GaO_4 tetrahedra. The large lanthanides and Sr are distributed over the A and A'-cation sites and the small lanthanides occupy only the A' site between the copper planes within the double CuO_2 layer.

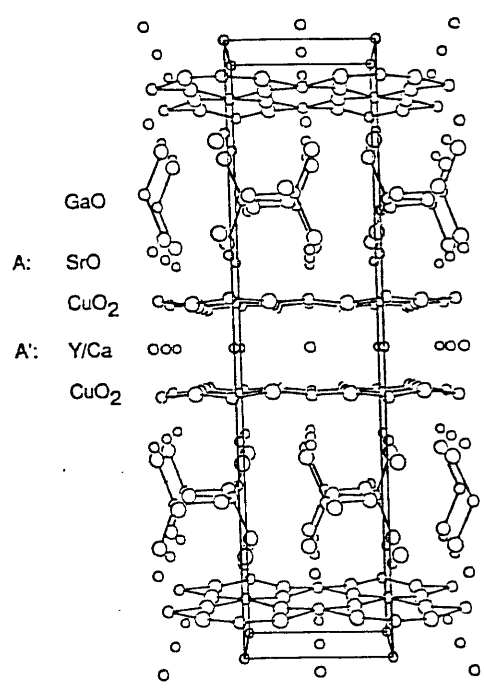

Fig.1 Layered structure of $GaSr_2LnCu_2O_7$ viewed along the b axis.

Air cooled samples with compositions $0 \le x \le 0.25$ were single phase. Larger doping levels led to the presence of small amounts of unidentified impurity phases. In general, a very small contraction of the in-plane and an expansion of the out-of-plane lattice parameters were observed with increasing doping. However, these lattice parameters changes were not continuous which indicates that the oxygen content and the cation distribution of the fast cooled samples may vary. The high pressure annealed samples showed a decreased amount of impurity phase for $x \ge 0.25$ and noticeable contraction of the in-plane lattice parameters, indicating an increased hole-doping of the CuO_2 planes.

High sensitivity, zero field cooled Squid susceptibility measurements using 100 Gauss were done for both powder and pellet high pressure annealed samples. For the dense pellets, a gradual development of a superconducting phase with an almost fixed transition temperature, T_c~20-25K, was observed with increased doping as shown on Fig. 2. For powder annealed samples different T_c's were observed with the highest T_c = 73K for x = 0.3 (see insert to Fig.2). The superconducting phase fractions, as determined from these measurements, were only a few percent. The Squid measurements performed for the fast cooled undoped material over an extended temperature range, 4-300K, showed that the parent compound, $GaSr_2YCu_2O_7$, is weakly paramagnetic with no magnetic order above 4K.

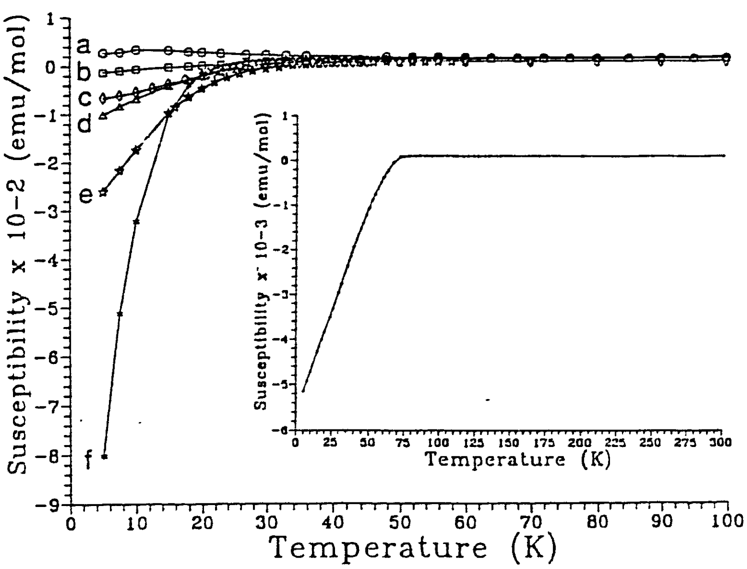

Fig.2 Squid susceptibility for dense x = 0 (a), 0.1 (b), 0.15 (c), 0.2 (d), 0.25 (e) and 0.35 (f) samples annealed under 300 atm. at 925^{o}C. Insert: susceptibility for x = 0.35 powder sample.

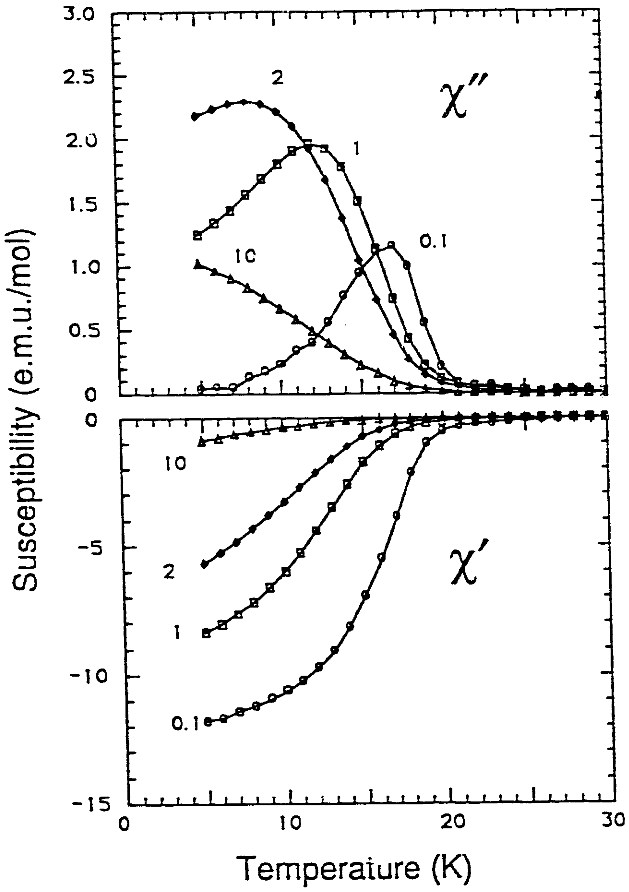

Fig.3 Real (χ') and imaginary (χ'') part of complex a.c. susceptibility for a x = 0.35 dense sample. The magnitude of an a.c. field is denoted on the graph in Gauss.

Additional low field measurements were performed using a.c. susceptibility. Figure 3 shows real and imaginary susceptibility for a x = 0.35 dense sample for various values of the a.c. field. Clearly, for low fields, ≤1 Gauss, the sample shows full diamagnetic behavior, proving that for this composition a large fraction of the sample becomes superconducting. Similar a.c. field dependence of the measured superconducting phase fraction was observed for the other compositions for either dense pellets or loose powders. The a.c. data also showed very good agreement for the onset T_c measured with the Squid.

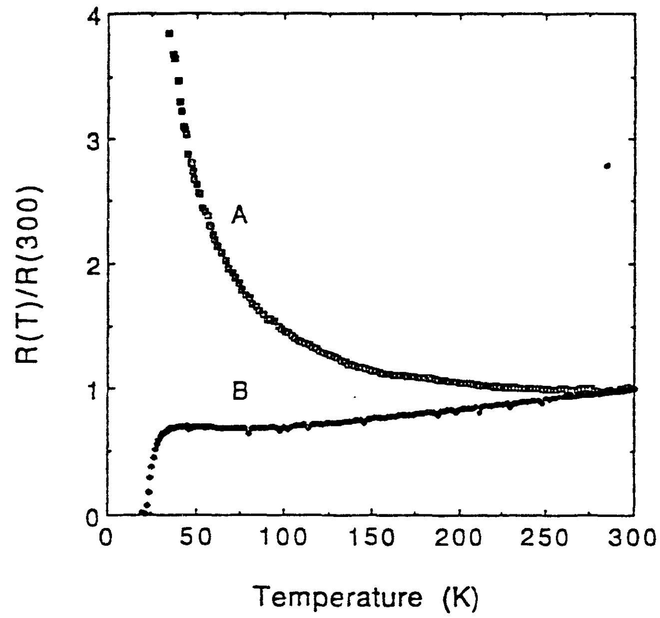

Fig.4 Normalized resistance for the fast cooled (A) and high pressure annealed (B) dense samples.

Resistivity measurements confirmed superconductivity for the high pressure annealed material. Typical R vs. T data for the fast cooled (A) and high pressure oxygen annealed (B) x = 0.35 dense samples is shown on Fig.4. The resistance changes from semiconductor-like to metallic when the sample is annealed under increasingly oxidizing conditions. The almost linear dependence of resistance on temperature for the superconducting sample is the same as observed for all other high temperature superconductors.

DISCUSSION

To verify that the presence of gallium is a necessary condition for superconductivity, we have prepared several samples without Ga and processed them under the same conditions as the Ga-containing material. None of these samples showed any traces of either superconductivity or metallic behavior. Also, in the x-ray diffraction patterns of $GaSr_2Y_{1-x}Ca_xCu_2O_7$ there was no indication for the formation of $YSr_2Cu_{3-x}Ga_xO_7$ impurity that could have superconducting properties. However, the reason the best superconducting properties are observed for $0.25 \leq x \leq 0.40$, i.e. beyond the apparent solubility limit at atmospheric pressure is still uncertain. It is possible, as frequently observed for oxide materials that the solubility limit depends on the synthesis conditions[7]. Therefore, the solubility limit could extend beyond x = 0.25 under high oxygen pressure annealing. The reduced impurity phase content after high pressure annealing indicates that some additional Ca might have been incorporated to the compound, however, the samples did not achieve full equilibrium during the 24 hour anneal. From thermogravimetric analysis there is a clear indication that the oxygen content increases slightly during cooling in oxygen over an extended temperature range for the doped compositions. Thus, the cooling rates are also very important and should be slow, <1°C/min., for maximum oxygen uptake or diffusion of cations, especially for dense samples.

The strong dependence of the superconducting phase fraction on the magnitude of the a.c. field may be related to the expected large anisotropy of the critical magnetic fields. At present, this behavior is not fully understood, but a similar field dependence has been observed for other highly anisotropic copper oxide superconductors (e.g. $Bi_2Sr_2CuO_6$)[8].

X-ray, neutron diffraction and thermogravimetric analysis, indicate that the undoped, x=0, material is stoichiometric in oxygen content and, thus, the copper ion should be in d^9 configuration. The absence of antiferromagnetic order above 4K in this material is significantly different from the parent compounds of other copper oxide superconductors in which the copper ion is unambiguously in a d^9 configuration, (e.g. La_2CuO_4 and Nd_2CuO_4). For these materials, the antiferromagnetic order develops at elevated temperatures (~300K). In fact, the presence of antiferromagnetism in the parent material and superconductivity for doped compositions has led to several theories of high temperature superconductivity based on magnetic coupling[9]. Two-dimensional antiferromagnetic fluctuations are possible in $GaSr_2YCu_2O_7$ but apparently the thick insulating, SrO-GaO-SrO, layer separating the double CuO_2 planes inhibits magnetic coupling between the planes suppressing the development of three-dimensional antiferromagnetic order.

CONCLUSION

We have synthesized the first layered superconducting copper oxide with small, fixed oxidation state cations separating the conducting $AO-CuO_2-A'-CuO_2-$

AO blocks, $GaSr_2Y_{1-x}Ca_xCu_2O_7$. This material may offer advantages for experimental and theoretical study because copper is the only mixed oxidation state ion and occurs only in one coordination. Several similar materials with ionic layers of AlO, NbO and TaO, may become superconducting once properly doped and annealed. These materials can provide important information concerning the nature of the superconducting state, in particular the relation between magnetic coupling and high temperature superconductivity.

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