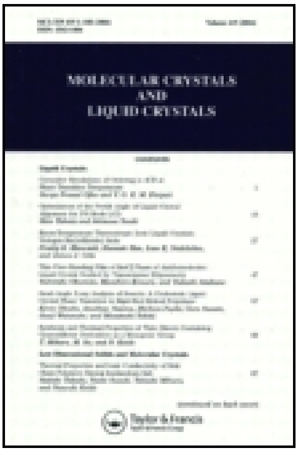

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Superconductivity Above 100 K in Tl-Pb-Ca-R-Sr-Cu-O System

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SUPERCONDUCTIVITY ABOVE 100 K IN Tl-Pb-Ca-R-Sr-Cu-O SYSTEM

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Abstract Bulk superconductivity with zero resistance temperature up to 108 K in $Tl_{0.5}Pb_{0.5}Ca_{0.8}A_{0.2}Sr_2Cu_2$ oxides (A = Y and lanthanides La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was achieved. For $Tl_{0.5}Pb_{0.5}Ca_{0.9}B_{0.1}Sr_2Cu_2O_y$ with B = Ce and mischmetal, superconducting transition temperatures were found to be 95 K and 101 K, respectively. Both powder x-ray diffraction profiles and electron diffraction results indicate that each monophasic sample crystallizes in the $YBa_2Cu_3O_{7-x}$-like tetragonal structure with space group P4/mmm. Magnetic property studies evidenced the coexistence of superconductivity and paramagnetism in magnetic rare-earth element containing compounds.

INTRODUCTION

For recent three years or so considerable theoretical and experimental interest has focused on the high-T_c superconductors both scientifically and practically. In the presently known high-T_c oxide superconductors, one possible new phenomenon is the interplay between the enhancement of superconductivity and the mixed-valence electronic states of Cu.[1-6] For example, the presence of the high-valent state Cu ions is one of the interesting characteristics of the high-T_c superconductor $YBa_2Cu_3O_{7-x}$. The introduction of Pr in its tetravalent state in the pseudoquinary $Y_{1-x}Pr_xBa_2Cu_3O_{7-x}$ compound will destroy the superconductivity, which can be accounted for the reduction of Cu valence.[7] Some similar results can also be found in the recent literature.[8-12]

Manako et al. discovered that the semiconductor $TlYBa_2Cu_2O_7$ resembled the $YBa_2Cu_3O_y$ structure with Tl occupying the corners of the modified Perovskite structure.[11] For the system $TlCa_{1-x}Y_xSr_2Cu_2O_y$, T_c was found to increase with Y substitution of Ca.[13] X-ray diffraction patterns indicate that these samples with x = 0.2, 0.5 and 0.7 are of $YBa_2Cu_3O_y$-like structure. However, the highest zero resistance temperature was found to be 80 K in this series, a result very much like the so-called 1122 TCBCO system.[14] Since by suitable elemental substitution we might get an optimal Cu valence state and we noted the previously reported $Tl_{0.5}Pb_{0.5}Ca_2Sr_2Cu_3O_y$ and $Tl_{1-x}Pb_xCaSr_2Cu_2O_7$ system in which Pb and Tl were found to share the corner positions of the unit cell,[15-16] a partial replacement of Tl with Pb in the $TlCa_{1-x}Y_xSr_2Cu_2$ oxide therefore was made. Fortunately, bulk superconductivity with zero resistance temperature above 100 K in the optimal stoichiometry $Tl_{0.5}Pb_{0.5}Ca_{0.8}A_{0.2}Sr_2Cu_2$ oxides (A = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was observed. For $Tl_{0.5}Pb_{0.5}Ca_{0.9}B_{0.1}Sr_2Cu_2O_y$ with B = Ce and mischmetal, superconducting transition temperatures were found to be 95 K and 101 K, respectively. In this paper, we discuss the crystal structure, lattice parameters and T_c values of polycrystalline Tl-Pb-Ca-R-Sr-Cu-O, R = rare-earth element. In addition, some interesting magnetic properties also have been investigated.

EXPERIMENTAL TECHNIQUES

Samples were prepared by first weighing approximate amounts of high purity $CaCO_3$, rare-earth oxide, $SrCO_3$ and CuO powders. After grinding in an agate motar, the well-mixed oxides were then calcined at 920 °C in air for 12 hours to obtain mixtures of Ca-R-Sr-Cu-O powders. The final specimens were prepared by mixing the approximate amounts of powders of PbO, Tl_2O_3 and Ca-R-Sr-Cu-O to yield products of nominal cation compositions of $Tl_{0.5}Pb_{0.5}Ca_{0.8}A_{0.2}Sr_2Cu_2$ or $Tl_{0.5}Pb_{0.5}Ca_{0.9}B_{0.1}Sr_2Cu_2$ oxides. The mixtures were ground and pressed into a cylindrical pellet under a pressure of about 2 tons/cm^2 with a dimension of 10 mm x 2 mm. To alleviate the possible decomposition of Tl_2O_3 to Tl_2O and O_2, the gold-foil-wrapped pellets were sintered in flowing O_2 at 950 °C for 3 hours and cooled to room temperature by controlled cooling (2 °C/min), furnace cooling or air quench. Electrical resistivity measurements were performed by a standard dc or ac four-probe technique. The magnetization measurements were carried out in a commercial SQUID magnetometer[17] in which the sample is moved slowly through the pick-up coil. X-ray diffraction analysis was performed by a Philip x-ray diffractometer. The lattice parameters of the unit cell were determined by the method of least squares[18] using the 14 most intense reflections for $2\theta < 50^\circ$ and including an internal silicon (a = 0.543083 nm). JEOL-2000EX and JEOL-2000FX transmission electron microscopes operating at 200 KV were used. The atomic concentrations of the samples were determined by an EDAX 9100/70 energy dispersive spectrometer (EDS). Quantitative analysis was performed using standardless techniques with composition-absorption-fluorescence correction factors from EDAX 9100 program developed by EDAX Laboratories.[19]

RESULTS AND DISCUSSION

(a) Crystal structure, lattice parameters and T_c[20-23]

Samples investigated for this work were found to be remarkably homogeneous both in composition and structure by EDS, XRD and TEM analyses. Powder x-ray diffraction patterns with CuK_α radiation indicate that each sample crystalizes in the $YBa_2Cu_3O_y$-like structure with space group P4/mmm. These results also have been revealed in the electron diffraction data and high resolution images of the Y-, La-, Pr- and Ce- containing compounds. A structure model of $Tl_{0.5}Pb_{0.5}Ca_{0.8}R_{0.2}Sr_2Cu_2O_y$ is shown in figure 1 and can be regarded as a derivative of $TlYBa_2Cu_2O_y$ structure. The lattice parameters a and c together with the zero resistance temperature T(R = 0) are listed in table 1. All the zero resistance temperature values obtained

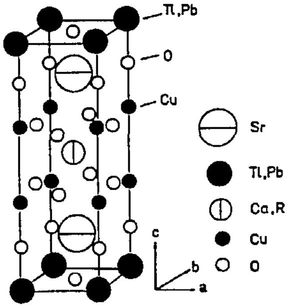

FIGURE 1 A structure model of $Tl_{0.5}Pb_{0.5}Ca_{0.8}R_{0.2}Sr_2Cu_2O_y$.

are consistent with the magnetic measurements. One point we must emphasize here is that the resistivity versus temperature curves for the samples investigated are not much dependent on the cooling conditions of the sample. This phenomenon is quite different from that of the well known $YBa_2Cu_3O_{7-x}$ compound. Though the T_c value of $Tl_{0.5}Pb_{0.5}Ca_{0.8}Ce_{0.2}Sr_2Cu_2O_y$ is only 49 K and much below than that of the rest samples, however, the T_c value can be increased to 95 K for $Tl_{0.5}Pb_{0.5}Ca_{0.9}Ce_{0.1}Sr_2Cu_2O_y$.[20] This result may suggest an optimal Cu valence state of +2.15 assuming full occupancy of oxygen sites.

Table 1. Lattice parameters, zero resistance temperature and μ_{eff} of $Tl_{0.5}Pb_{0.5}Ca_{0.8}R_{0.2}Sr_2Cu_2O_y$ compounds. The number given in the parentheses is the standard deviation in the least significant digit of the reported value.

R	a (nm)	c (nm)	T(R = 0) (K)	$\mu_{eff.th}$ (μ_B)	$\mu_{eff.exp}$ (μ_B)
Y	0.3806(2)	1.2078(6)	108	-	-
La	0.3813(1)	1.2133(3)	106	-	-
Ce	0.3814(1)	1.2056(3)	49	2.54	-
Pr	0.3817(3)	1.2127(11)	106	3.58	3.59
Nd	0.3812(2)	1.2104(6)	108	3.62	3.66
Sm	0.3810(1)	1.2109(3)	108	0.84	-
Eu	0.3809(2)	1.2098(7)	108	0	-
Gd	0.3808(1)	1.2093(5)	105	7.94	8.0
Tb	0.3807(3)	1.2069(11)	106	9.72	8.0
Dy	0.3810(3)	1.2103(10)	107	10.63	10.31
Ho	0.3807(2)	1.2098(6)	108	10.60	10.40
Er	0.3805(1)	1.2084(4)	104	9.59	9.50
Tm	0.3800(3)	1.2081(11)	107	7.57	7.32
Yb	0.3800(1)	1.2067(5)	106	4.54	4.43
Lu	0.3804(1)	1.2082(4)	105	0	-

(b) Magnetic property studies

Since the magnetic ion is believed to be very effective in breaking the superconducting pairs, this system provides an excellent opportunity to explore the intriguing question whether the magnetism and superconductivity are intimately connected. Very interestingly, we found that the magnetic susceptibility became positive below T_c when the applied magnetic field increased to 2 or 3 Tesla for the sample containing rare-earth element with larger effective moment ($> 7\ \mu_B$). Figure 2 and 3 present the temperature dependence of the static magnetic susceptibility for 7 samples measured in a field of 4 Tesla.

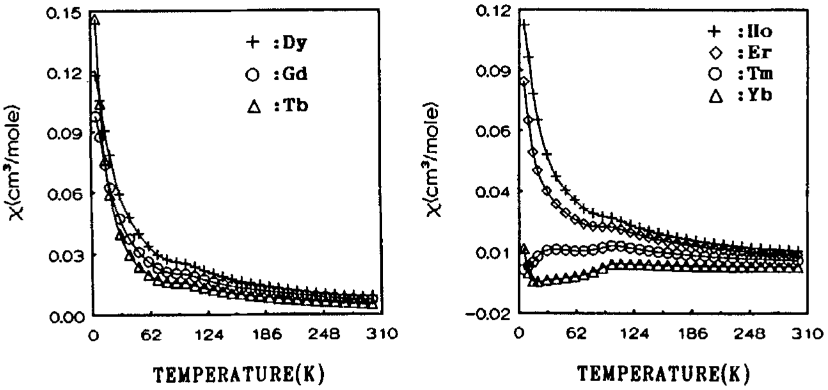

FIGURE 2 and 3 DC magnetic susceptibility measured in a field of 4 Tesla between 5.0 and 300 K for 7 samples in the $Tl_{0.5}Pb_{0.5}Ca_{0.8}R_{0.2}Sr_2Cu_2O_y$ system, R = Dy, Gd, Tb, Ho, Er, Tm and Yb.

Since a kink is seen in each curve around $T = T_c$, the diamagnetic signal of the superconducting state is assumed to be burried incompletely by the magnetic field induced paramagnetism in the magnetic rare-earth system. This assumption can be confirmed by the electrical resistivity measurements under magnetic field.[24] In other words, the superconductivity in the presence of strong paramagnetism can be observed in the $Tl_{0.5}Pb_{0.5}Ca_{0.8}R_{0.2}Sr_2Cu_2O_y$ (R = magnetic rare-earth element) compounds. The effective moment of the rare-earth ion obtained from the Curie-Weiss law are reported in table 1. It is found that the experimental $\mu_{eff.exp}$ is very close to that calculated from the theoretical formula $\mu_{eff.th} = g_J[J(J + 1)]^{1/2}$.

(c) The effects of substituting Ca by mischmetal[25]

As mentioned above, the $Tl_{0.5}Pb_{0.5}Ca_{0.8}R_{0.2}Sr_2Cu_2O_y$ compounds are highly reproducible and stable. Therefore, a suggested economical way to prepare the high-T_c superconductors is to use the mischmetal oxide as the starting material instead of the rare-earth oxide. Experimental results show that the superconducting transition temperature of $Tl_{0.5}Pb_{0.5}Ca_{0.9}M_{0.1}Sr_2Cu_2O_y$ can reach to 101 K irrespective of the considerable high concentration of Ce^{+4} and Pr^{+4} in the mischmetal oxide. Figure 4 shows the zero field cooling (ZFC) and field cooling (FC) magnetization data for the sample $Tl_{0.5}Pb_{0.5}Ca_{0.9}M_{0.1}Sr_2Cu_2O_y$ measured in a field of 10 Oe between 5 and 130 K. A surprising result is the observation of the induced paramagnetism by low-field-cooled measurements, which may be due to the increased trapped flux by some unknown effects.

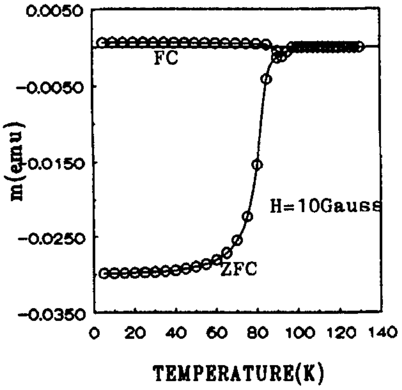

FIGURE 4 Zero-field-cooled (ZFC) and field-cooled (FC) magnetization data of $Tl_{0.5}Pb_{0.5}Ca_{0.9}M_{0.1}Sr_2Cu_2O_y$ sample measured in a field of 10 Oe between 5 and 300 K.

CONCLUSIONS

In summary, the effect of partial substituting Cu by Tl and Pb, Y by R and Ca, Ba by Sr in the $YBa_2Cu_3O_{7-x}$ is quite intriguing. A suitable elemental substitution can result in the increase of T_c up to 108 K in the system investigated because of the optimal control of Cu valence. If the oxygen sites in $Tl_{0.5}Pb_{0.5}Ca_{1-x}R_xSr_2Cu_2O_7$ are supposed to be fully occupied, experimental results suggest an optimal valence of Cu to be +2.15. However, further analyses of the exact valence state of Cu as well as the oxygen concentration and distribution in the compound are required.

In the present contribution we wish to draw attention to the fact that the synthesis conditions for the system investigated are found to be much less rigid than those of other high T_c oxide superconductors. This system also provides an excellent opportunity to study the coexistence problem of superconductivity and paramagnetism.

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