Magnetic properties of high-oxygen pressure prepared \( \text{PrBa}_2\text{Cu}_3\text{O}_{7-y} \) cuprates

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High oxygen pressure annealed \( \text{PrBa}_2\text{Cu}_3\text{O}_{7-y} \) \((y \sim 0)\) cuprates were prepared in order to study the effect of oxygen stoichiometric parameter \(y\) on the unusual \(\text{Pr}/\text{Cu}\) magnetic properties and/or recently reported superconductivity. The oxygen-rich orthorhombic 123-chain phase is highly unstable under high-oxygen pressure synthesis and decomposes completely in 10 bar pressure. For a smaller 2 bar prepared sample a relatively clean phase was preserved with an oxygen parameter \(y = 0.05\), as compared with \(y = 0.11\) from a conventional 1 bar flowing oxygen method. No superconductivity can be detected for all high-oxygen pressure prepared samples. Instead, Mott-insulator behavior with anomalous high \(\text{Pr}\) ordering \(T_N(\text{Pr}) = 19\) K was observed for \(\text{PrBa}_2\text{Cu}_3\text{O}_{6.95}\). Comparison with other \(\text{Pr}/\text{Ba}\) intersubstituted \(\text{Pr}_{1-y}\text{Ba}_y\text{Cu}_3\text{O}_7-y\) cuprates is discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1357859]

Superconductivity with \(T_c\) above 90 K were observed for most orthorhombic 123-chain \(\text{RBa}_2\text{Cu}_3\text{O}_7\) or 1212-chain (rewritten as \(\text{CuBa}_2\text{RCu}_2\text{O}_7\)) to emphasis the \(\text{CuO}_2\) bilayers and \(\text{CuO}\) chain rare earth cuprates \((R = \text{Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, or Lu})\), except for insulating \(\text{PrBa}_2\text{Cu}_3\text{O}_7\), where \(\text{Cu}^{2+}\) magnetic moments ordered antiferromagnetically with a Néel temperature \(T_N(\text{Cu})\) above room temperature and \(\text{Pr}^{4+}\) moments ordered with an anomalous high \(T_N(\text{Pr}) \sim 18\) K.\(^1\sim^5\) However, indications of inhomogeneous superconductivity with \(T_N(\text{Pr})\) around 90 K in \(\text{PrBa}_2\text{Cu}_3\text{O}_7\) were reported recently in some thin films, powders, or single crystals.\(^6\sim^7\) These results are in sharp contrast to earlier works and detailed study is thus necessary to clarify this puzzle.\(^8\sim^9\)

In this report, through high-oxygen pressure annealing, we have investigated the high-oxygen content \(\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}\) cuprates \((y \sim 0)\) in order to study the effect of oxygen stoichiometry on the complex interplay among crystal symmetry, unusual \(\text{Pr}\) magnetic property and possible unconventional superconductivity in the \(\text{Pr}-123\) system.

The \(\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}\) samples with nominal composition were synthesized by a standard solid-state reaction method using high-purity \(\text{Pr}_6\text{O}_{11}(99.99\%\)), \(\text{BaCO}_3(99.99\%\)), and \(\text{CuO}(99.99\%\)) powders. Powders were thoroughly mixed and carefully calcined at 870 °C in air for 2 days with several intermediate regrinding. The calcined powder was then pressed into pellets and sintered in flowing Ar at 890 °C for 1 day in order to suppress the formation of unwanted magnetic impurity \(\text{PrBaO}_3\). The as-sintered samples were annealed in flowing \(\text{O}_2\) at 400 °C for 1 day then slowly furnace cooled to room temperature.

To achieve higher oxygen content, samples were further annealed under high-oxygen pressure of 2–10 bar at 400 °C for 1–5 days in a Morris HPS-5015P high pressure furnace. The block diagram for the high-oxygen pressure furnace system is shown in Fig. 1. The oxygen content parameter \(y\) was determined from the standard iodometric titration method.

The powder x-ray diffraction data were obtained with a Rigaku RotaFlex 18 kW rotating anode diffractometer using graphite monochromatized \(\text{Cu} K\alpha\) radiation with a scanning step of 0.02° in 2θ. The electrical resistivity measurements were performed using the standard four-probe method with a Linear Research LR-700 ac (16 Hz) resistance bridge from 5 to 300 K. The low field (10 G) magnetic susceptibility data were obtained through a quantum design \(\mu\)-metal shielded magnetic property measurement system 2 (MPMS 2) superconducting quantum interference device magnetometer from 2 to 300 K.

![FIG. 1. Block diagram of high-oxygen pressure furnace system.](image)
valence for Pr ions. However, an intermediate valence of 3 + δ for Pr is more reasonable considering strong Pr–O wave function hybridization. The orthorhombic lattice parameters for relatively clean PrBa$_2$Cu$_3$O$_6.95$ cuprate are $a$ = 0.3870, $b$ = 0.3926, and $c$ = 1.1706 nm.

For conventional gas flowing (1 bar) prepared PrBa$_2$Cu$_3$O$_{7-\delta}$ samples, oxygen deficiency was generally observed with clean single phase samples. For example, oxygen-deficient orthorhombic 123-chain phase sample PrBa$_2$Cu$_3$O$_{6.89}$ ($\delta$ = 0.11, with lattice parameters $a$ = 0.3872, $b$ = 0.3926, and $c$ = 1.1710 nm) was obtained in 400°C flowing oxygen with furnace cool and severe oxygen-deficient tetragonal $T$ phase (space group $P4/mmm$) sample PrBa$_2$Cu$_3$O$_{6.22}$ ($\delta$ = 0.78) was obtained in 890°C flowing argon annealing with liquid nitrogen quench. The orthorhombic–tetragonal phase transition boundary was observed around $\gamma$ = 0.5.

The temperature dependence of electrical resistivity for $pO_2 = 2$ bar prepared PrBa$_2$Cu$_3$O$_{6.95}$ and 1 bar flowing oxygen prepared PrBa$_2$Cu$_3$O$_{6.89}$ were shown collectively in Fig. 3. These two samples show typical Mott-insulator behavior and no superconductivity can be detected down to 2 K. The logarithmic resistivity plotted against $T^{-1/4}$ in Fig. 3 indicates a variable-range hole hopping mechanism in the low temperature regime for these Mott insulators. The slightly higher resistivity for $\gamma$ = 0.05 with room temperature resistivity $p$(RT) = 290 m$\Omega$·cm as compared to $\gamma$ = 0.11 sample [$p$(RT) = 38 m$\Omega$·cm] may be due to the presence of minor insulating impurity phases of PrBaO$_3$ and CuO as indicated in the powder x-ray diffraction for PrBa$_2$Cu$_3$O$_{6.95}$ (Fig. 2).

The temperature dependence of molar magnetic susceptibility $\chi_m(T)$ and inverse susceptibility $\chi_m^{-1}(T)$ for the PrBa$_2$Cu$_3$O$_{6.95}$ sample was shown in Fig. 4. An unusually high antiferromagnetic Pr ordering temperature $T_N$(Pr) = 19 K was observed. Below 250 K, the data can be well fitted by a Curie–Weiss law $\chi_m(T) = \chi_0 + C/(T - \theta_p)$ (solid line) with a negative paramagnetic intercept $\theta_p$ of −7.98 K. An effective magnetic moment $\mu_{eff}$ of 2.65 $\mu_B$ per Pr ion can be deduced if the small saturation Cu moments of ~0.5 $\mu_B$ is neglected ($Cu^{2+}$ moments order antiferromagnetically above 300 K). The anomalous high Pr ordering with strong Pr–O–Pr superexchange interaction is due to large wave function overlap between extended light rare earth Pr-4f orbital and O-2$p_x$ orbital in the CuO$_2$ bilayers.

The low temperature magnetic susceptibility for PrBa$_2$Cu$_3$O$_{6.95}$ and PrBa$_2$Cu$_3$O$_{6.89}$ were shown collectively in Fig. 5. No superconducting diamagnetic signal can be detected down to 2 K for both high-oxygen content samples. The Curie–Weiss fitting as well as $d\chi_m(T)/dT$ derivative minimum gives a slightly lower $T_N$(Pr) of 18.5 K for lesser-oxygen content PrBa$_2$Cu$_3$O$_{6.89}$, indicates the sensitive effect of oxygen content on the subtle structural arrangement and the Pr-4f–O-2$p_x$ hybridization. Larger effective magnetic moment $\mu_{eff}$ of 2.89 $\mu_B$/Pr for single phase PrBa$_2$Cu$_3$O$_{6.89}$ is deduced as compared with 2.65 $\mu_B$/Pr for PrBa$_2$Cu$_3$O$_{6.95}$ sample with minor Pr$^{4+}$-impurity PrBaO$_2$. Again, an inter-

![FIG. 2. Powder x-ray diffraction pattern for four PrBa$_2$Cu$_3$O$_{7-\delta}$ samples annealed under different oxygen pressure. Impurity phases indicate that the orthorhombic 123 phase is highly unstable under oxygen pressure annealing.](Image)

![FIG. 3. Logarithmic electrical resistivity plotted against $T^{-1/4}$ for two high-oxygen content PrBa$_2$Cu$_3$O$_{6-\gamma}$ samples ($\gamma$ = 0.05 and 0.11).](Image)

![FIG. 4. Temperature dependence of molar magnetic susceptibility $\chi_m(T)$ and inverse susceptibility $\chi_m^{-1}(T)$ for PrBa$_2$Cu$_3$O$_{6.95}$ sample in a small applied magnetic field of 10 G.](Image)
mediate valence of $3 + \delta$ is more reasonable for 123-chain cuprates considering strong Pr–O wave function hybridization.

Mott-insulating behavior as observed not only on these high-oxygen pressure prepared PrBa$_2$Cu$_3$O$_{7-y}$ ($y \approx 0$) cuprates, but also on the whole PrBa$_2$Cu$_3$O$_{7-y}$ system ($-0.1 < y < 0.9$) as well as on the Pr/Ba intersubstituted Pr$^{3+}$Ba$_{2-x}$Cu$_3$O$_{7-y}$ system ($-0.2 < x < 1$; $-0.4 < y < 1$). These cuprates show that, regardless of the structural phase transitions, a systematic variation of anomalous Pr ordering $T_N(\text{Pr})$ from 19 K down to below 2 K with no superconductivity detected in the whole system.$^8$$^9$ The lack of metallic state for all samples studied indicates that the superconducting state, if it exists, may exist only in a very narrow annealed pressure/temperature/time range in order to ensure the specific optimum composition involving oxygen stoichiometry $y$, oxygen chain structure, Pr/Ba ratio and/or vacancy.

This work was supported by the National Science Council of R.O.C. under Contract Nos. NSC89-2112-M-007-088 and NSC89-2112-M-007-090.