

Synthesis and magnetism of $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y, Pr, and Tb}$) systems

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The problems of making phase-pure $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ systems, with $R = \text{Y, Pr, and Tb}$, are discussed in detail, particularly in the case of Pr and Tb. Complete substitution of these three rare earths at the Ca site is realized in this system. The c lattice parameter of the rare-earth-containing material decreases in comparison with that of the pure undoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. On-site ionic size differences and increased oxygen content due to aliovalent substitution are the possible causes of the decreased c lattice parameter. Magnetic-susceptibility (χ) measurements on these samples give an effective paramagnetic moment close to that of 3+ for Tb but intermediate between those of 3+ and 4+ for Pr. A change in slope in the χ^{-1} vs T curve for the Y compound at ~ 295 K and a dip in the same for the Pr compound at ~ 330 K may be indicative of the antiferromagnetic ordering of the Cu moments in these compounds.

I. INTRODUCTION

From the phase diagram of all the high- T_c cuprate superconductors, it is seen that they behave like Mott-Hubbard insulators in their ground state with antiferromagnetic ordering^{1,2} of the Cu moments. The insulating ground state of $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ ($R:123$) and of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($\text{La}:124$) systems is well established^{2,3} for decreased oxygen content ($y \approx 1$) and low Sr ($x = 0$) content, respectively, with antiferromagnetic ordering temperature in the range of 350–550 K. On the other hand, antiferromagnetic ground states of Bi- and Tl-based high- T_c cuprates are still to be fully explored. One of the ways to explore their ground states is by the substitution of rare earths for Ca in these compounds.^{4,5} In the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ($\text{Bi}:2212$) systems, many rare earths show complete substitution at the Ca site.^{6,7} Complete substitution of Ca by Y in $\text{Bi}:2212$ systems results in an insulating antiferromagnetic state having an ordering temperature in the range of 300–350 K.^{8,9} However, in this regard there are very few reports on the substitution of Ca by Ce (Ref. 10), Pr (Refs. 11–13) and Tb (Ref. 6).

The behavior of Ce, Pr, and Tb also seems to be unusual in $R:123$ superconducting oxide system. For instance, most of the $R:123$ compounds show high- T_c superconductivity in the 90 K range, but Ce, Pr, and Tb compounds of this series are still exceptions.^{14,15} The Pr:123 compound is not superconducting and shows an unusually large value of the electronic specific-heat coefficient and a high ordering temperature of Pr moments (for a review, see, for instance, Ref. 16). There is only one report which describes the synthesis of superconducting Pr:123 thin films with partial substitution of Pr by Ca.¹⁷ The mystery of the absence of superconductivity in pure Pr:123 is still a challenging problem with different experiments providing different and contradictory results about the nature of Pr ions in this system.^{18,19} In the case of Ce and Tb, the situation is even more interesting as they do not substitute isostructurally in $R:123$ systems.²⁰ Keeping in view the challenges of Pr and Tb in $R:123$ systems,

we have focused our attention on their substitution in $\text{Bi}:2212$ high- T_c systems. In this paper we present the results of synthesis, x-ray-diffraction data, and magnetic-susceptibility measurements on $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ systems, with $R = \text{Y, Pr, and Tb}$. Complete substitution of Y, Pr, and Tb for Ca is observed in this system. Magnetic-susceptibility measurements yield an effective moment close to that of 3+ ions for Tb, but intermediate between those of 3+ and 4+ for Pr. Moreover, there are high-temperature anomalies in the susceptibility which may be due to antiferromagnetic ordering of the Cu moments.

II. EXPERIMENTAL DETAILS

The samples of $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y, Pr, and Tb}$) were prepared by solid-state reaction of appropriate quantities of metal oxides and carbonates of purity better than 99.99%. For the calcination process all the samples were heated at least 10 times between a temperature of 820 and 930 °C, each time for 15 h and furnace cooled to room temperature over a span of 6 h, with intermediate grinding at every step. In the final sintering, Y, Pr, and Tb samples were heated at temperatures of 935, 950, and 945 °C, respectively, for 15 h and then quenched to room temperature. It is worth mentioning here that these temperatures are very crucial to avoid the formation of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ ($\text{Bi}:2201$) in the matrix which is superconducting at low temperatures.

The samples were characterized for their phase purity by x-ray diffractometry (XRD) using a JEOL diffractometer equipped with $\text{CuK}\alpha$ radiation. Lattice parameters were obtained from a fit of the observed d values of the XRD patterns. Magnetic susceptibility of all the three samples was measured using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–400 K in an applied field of 5000 Oe. Susceptibility measurements were also made in a low field of 50 Oe to detect any superconducting $\text{Bi}:2201$ phase in the matrix.

III. RESULTS AND DISCUSSION

X-ray-diffraction patterns of the $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y, Pr, and Tb}$) samples are shown in Fig. 1. All the samples show single-phase Bi:2212 structure. While the complete solubility of Y at Ca sites in Bi:2212 had been established earlier,^{6,7} the situation regarding Pr and Tb was not clear prior to the present study. The c lattice parameter of each sample is given in the respective XRD patterns. The c lattice parameter of all the rare-earth-containing samples decreases in comparison to that of the superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ system ($c = 30.8 \text{ \AA}$).^{8,11} Earlier reports on the variation of c lattice parameters for the Pr sample have not been consistent. In Ref. 12, where the samples were prepared using a two-stage coprecipitation method with a final heat treatment at 850°C for several hours, it was reported that on complete substitution of Ca by Pr in Bi:2212, the c lattice parameter of the system remained nearly unchanged. However, another report,¹³ where the samples were prepared by solid-state reaction with a final heat treatment at 860°C for 24 h, indicated that the c lattice parameter of the system decreased with Pr substitution, as in our results (though the decrease observed in Ref. 13 was smaller than that observed in the present investigation). We find that the discrepancies observed in the variation of

the c parameter on substituting Pr for Ca in Bi:2212 are due to different heat-treatment schedules. We observed that when the samples are heat treated below 900°C , a small superconducting Bi:2201 phase appears with T_c below 10 K. The amount of the Bi:2201 phase is lower than the detection level of XRD, but this phase could be seen in 50 Oe magnetization measurements using a SQUID magnetometer. In fact, single-phase materials of these systems form only near their respective melting temperatures, i.e., near $930\text{--}950^\circ\text{C}$, which is also a function of the rare-earth concentration. The c lattice parameter of the Y-substituted sample, observed in the present investigation, is found to be consistent with that reported earlier.⁸ In the case of Tb, too, the c lattice parameter is found to decrease relative to that of pure Bi:2212. Substitution of divalent Ca by a rare earth in Bi:2212 gives rise to excess oxygen in the system, which may be partially responsible for a decreased lattice parameter c along with the on-site ionic size differences.²¹ It is thus interesting to note that though in $R:123$ the solubility of Tb is very limited, in Bi:2212 an isostructurally complete substitution is observed.

Figure 2 shows the temperature dependence of the susceptibility of $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y, Pr, and Tb}$) samples. These samples are not superconducting down to 2 K. It is seen that the susceptibility of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_{8+\delta}$ is fairly large in the temperature range investigated. In fact, this compound shows antiferromagnetic ordering of the Cu moments at a temperature of about 320 K,^{6,7} possibly due to the decreased holes on Cu in this case. In the case of fully substituted Pr or Tb compounds also, the holes on Cu are expected to decrease, due to on-site

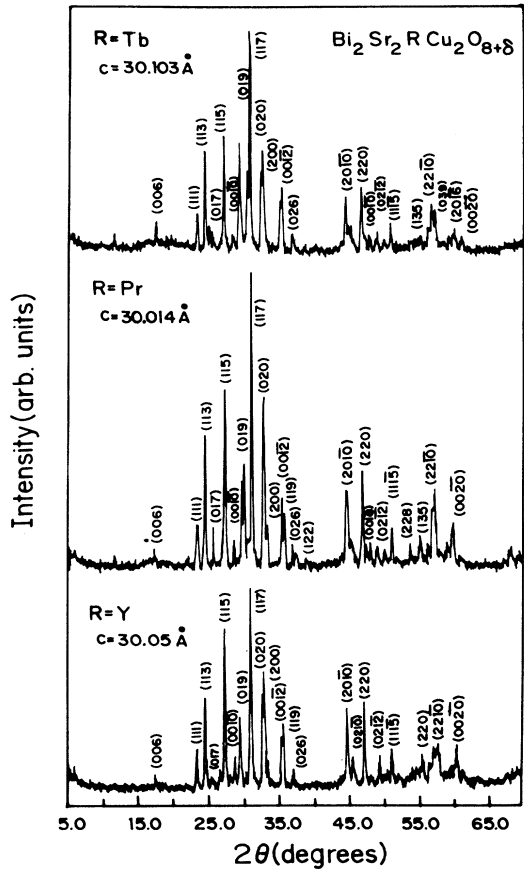


FIG. 1. X-ray-diffraction patterns of $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y, Pr, and Tb}$) compounds.

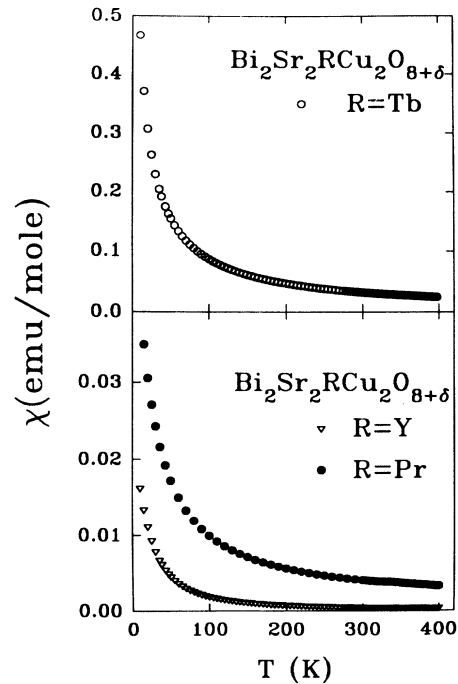


FIG. 2. Magnetic susceptibility vs temperature for $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y, Pr, and Tb}$) compounds.

aliovalent substitutions, and therefore Cu moments may also order magnetically in these compounds also. In the present susceptibility (χ) measurements on $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ we see a change in slope in the χ^{-1} versus temperature plot (Fig. 3) at about 295 K for $R = \text{Y}$ and a dip in χ^{-1} at about 330 K for $R = \text{Pr}$. In the case of $\text{Bi}_2\text{Sr}_2\text{TbCu}_2\text{O}_{8+\delta}$, a very feeble change of slope in susceptibility is discernible at about 380 K. All these features may be due to the antiferromagnetic ordering of the Cu moments.

In order to arrive at the correct susceptibility of the rare-earth ion in these compounds, it may be necessary to correct for the matrix susceptibility. As a first approximation, it is assumed that the matrix susceptibility in $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Pr}$ and Tb) compounds is essentially the same as that in their Y analog, Y being nonmagnetic. Therefore we have subtracted the susceptibility of $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_{8+\delta}$ from that of the corresponding Pr and Tb compounds. The measured and corrected susceptibilities are shown as a plot of χ^{-1} versus temperature in Fig. 3. The susceptibility can be well fitted to the Curie-Weiss behavior, given by

$$\chi = \chi_0 + C/(T - \theta_p), \quad (1)$$

where C is the Curie constant, θ_p is the paramagnetic Curie temperature, and χ_0 is the temperature-independent susceptibility. From the fit to the corrected susceptibility data, the parameters obtained for the Pr sample are: μ_{eff} , the effective paramagnetic moment, equal to $2.60\mu_B$, $\theta_p = -24.2$ K, and $\chi_0 = 1.1 \times 10^{-4}$ emu/mol; and those for the Tb sample are $\mu_{\text{eff}} = 8.44\mu_B$, $\theta_p = -9.91$ K, and $\chi_0 = 3.96 \times 10^{-4}$ emu/mol. It is worth mentioning here that in both the earlier reports^{12,13} on Pr systems, the above correction to the susceptibility has not been made and this may alter the final conclusion about the paramagnetic state of Pr ions in the system. For instance, the present uncorrected susceptibility data yield $\mu_{\text{eff}} = 3.20\mu_B$ and $\theta_p = -23$ K for the Pr compound in agreement with previous results^{12,13} and $\mu_{\text{eff}} = 8.47\mu_B$ and $\theta_p = -10$ K for the Tb compound. It is noted that the correction is not significant for the Tb compound, but is sizable for the Pr compound.

The effective paramagnetic moment value of Tb in $\text{Bi}_2\text{Sr}_2\text{TbCu}_2\text{O}_{8+\delta}$ is very near to the value of free Tb^{3+} ions. However, the effective moment in $\text{Bi}_2\text{Sr}_2\text{PrCu}_2\text{O}_{8+\delta}$, without correction, is intermediate between the values of Pr^{3+} ($3.58\mu_B$) and Pr^{4+} ($2.54\mu_B$), but close to that of Pr^{4+} , with corrections, suggesting a possible mixed valent or near-tetravalent state for Pr in this compound. This appears to be consistent with the fast decrease in the c lattice parameter of the material with increasing Pr substitution.¹¹ In eightfold coordination, while the size of Pr^{3+} is comparable to that of Ca^{2+} , the size of Pr^{4+} in the same coordination number is smaller than that of Ca^{2+} , which is a possible reason for the faster decrease of the c lattice parameter of the system.¹¹ However, at the same time, the electronic

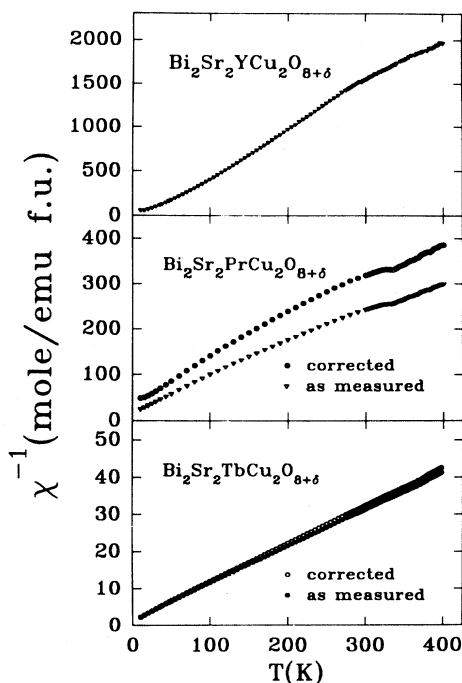


FIG. 3. Inverse susceptibility vs temperature for $\text{Bi}_2\text{Sr}_2\text{RCu}_2\text{O}_{8+\delta}$ ($R = \text{Y}$, Pr , and Tb) compounds. The corrected curves refer to those obtained after subtracting the susceptibility of the Y analog from the as-measured values.

specific-heat coefficient γ is not very high in $\text{Bi}_2\text{Sr}_2\text{PrCu}_2\text{O}_{8+\delta}$,¹² which would suggest a nearly stable Pr valence in this compound. It should be mentioned that an intermediate Pr moment is also seen in $\text{Pr}:123$ compounds and has been attributed to the effect of crystalline electric fields on Pr^{3+} ion.²² The electronic specific-heat coefficient, γ , is also large in $\text{Pr}:123$, yet spectroscopic measurements give no evidence of mixed valence Pr in this compound.²³ Clearly, therefore further work is necessary to ascertain the valence state of Pr in $\text{Bi}_2\text{Sr}_2\text{PrCu}_2\text{O}_{8+\delta}$ compounds also. In our measurements on $\text{Bi}_2\text{Sr}_2\text{PrCu}_2\text{O}_{8+\delta}$, we do not observe any antiferromagnetic ordering of the Pr moments down to 5 K. However, it is distinctly seen in $\text{Pr}:123$ systems near 17 K.¹⁶⁻¹⁸ As far as Tb in $\text{Bi}_2\text{Sr}_2\text{TbCu}_2\text{O}_{8+\delta}$ is concerned, its valence state is very near to $3+$; hence, it does not seem to be different from other magnetic rare earths.

In summary, the problems of synthesis of phase-pure Pr- and Tb-substituted Bi:2212 systems are discussed in detail. Complete substitution of Pr and Tb is observed by solid-state reaction in Bi:2212 systems. From high-field magnetic measurements, the magnetic state of Tb is confirmed to be $3+$, while Pr appears to be intermediate between $3+$ and $4+$ magnetic states. Furthermore, there are features in the susceptibilities of these compounds which may be due to magnetic ordering of the Cu moments.

- ¹J. B. Torrance, A. Bezing, A. I. Nazzari, and S. S. Parkin, *Physica C* **162-164**, 291 (1989).
- ²J. M. Taranquada, A. H. Moudou, A. I. Goldman, P. Zolliker, D. E. Cox, G. Shirane, S. K. Sinha, D. Vaknin, D. C. Johnston, M. S. Alvarez, and A. J. Jacobson, *Phys. Rev. B* **38**, 2477 (1988).
- ³J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. V. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **36**, 3608 (1987).
- ⁴T. Tamegai, K. Koga, K. Suzuki, M. Ichihara, F. Sakai, and Y. Iye, *Jpn. J. Appl. Phys.* **28**, L112 (1989).
- ⁵B. Jayaram, P. C. Lanchester, and M. T. Weller, *Phys. Rev. B* **43**, 5444 (1991).
- ⁶J. M. Tarascon, P. Barboux, G. W. Hull, R. Ramesh, L. H. Greene, M. Grioud, M. S. Hegde, and W. R. McKinnon, *Phys. Rev. B* **38**, 4316 (1989).
- ⁷J. M. Tarascon and B. G. Bagley, in *Chemistry of Superconductor Materials*, edited by Terrell A. Vanderah (Noyes, Park Ridge, NJ, 1993), p. 310.
- ⁸N. Nishida, S. Okuma, H. Miyatake, T. Tamegai, Y. Iye, R. Yoshizaki, K. Nishiyama, K. Nagamine, R. Kadono, and J. H. Brewer, *Physica C* **168**, 23 (1990).
- ⁹Y. Kimishima and H. Kittaka, *Physica C* **160**, 136 (1989).
- ¹⁰A. Sawa, T. S. Han, T. Iwamatsu, H. Uwe, and T. Sakudo, *Physica B* **165-166**, 1553 (1990).
- ¹¹V. P. S. Awana, S. K. Agarwal, A. V. Narlikar, and M. P. Das, *Phys. Rev. B* **48**, 1211 (1993).
- ¹²Y. Gao, P. Pernambuco-Wise, J. E. Crow, J. O. Reilly, N. Spencer, H. Chen, and R. E. Salomon, *Phys. Rev. B* **45**, 7436 (1992).
- ¹³Kuniyuki Koyama, Satoshi Kano, and Seiichiro Noguchi, *Jpn. J. Appl. Phys.* **28**, 1354 (1989).
- ¹⁴L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. V. Segre, and I. K. Schuller, *Nature (London)* **328**, 604 (1991).
- ¹⁵J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, *Phys. Rev. B* **36**, 226 (1987).
- ¹⁶S. K. Malik and C. V. Tomy, in *Physical and Material Properties of High Temperature Superconductors*, edited by S. K. Malik and S. S. Shah (Nova Science, New York, NY, 1994), p. 283.
- ¹⁷David P. Norton, D. H. Lowndes, B. C. Sales, J. D. Budai, B. C. Chakoumakos, and H. R. Kerchner, *Phys. Rev. Lett.* **66**, 1537 (1991).
- ¹⁸A. P. Reys, D. E. MacLaughlin, M. Takigawa, P. C. Hammel, R. H. Heffner, J. D. Thompson, J. E. Crow, A. Kebede, T. Mihalisin, and J. Schwegler, *Phys. Rev. B* **42**, 2688 (1990).
- ¹⁹J. Fink, N. Nücker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumier, and J. W. Allen, *Phys. Rev. B* **42**, 4823 (1990).
- ²⁰L. F. Schneemeyer, J. V. Waszczak, R. B. van Dover, and T. Siegrist, *Mater. Res. Bull.* **22**, 1467 (1987).
- ²¹S. B. Samanta, P. K. Dutta, V. P. S. Awana, E. Gmelin, and A. V. Narlikar, *Physica C* **178**, 171 (1991).
- ²²G. Hilscher, E. Holland-Moritz, T. Holubar, H.-D. Jostarndt, V. Nekvasil, G. Schaudy, U. Walter, and G. Fillion, *Phys. Rev. B* **49**, 535 (1994).
- ²³G. Wortmann, P. Sladeczek, G. Stadermann, I. Felner, and G. Kaindl, in *X-ray Absorption Fine Structure*, edited by S. S. Hasman (Ellis, Horwood, 1991), p. 386.