High-T_c superconductivity in the $RBa_{2-x}Sr_xCu_3O_7$ system for $R \equiv Y$, Gd, Sm and Nd

L. PARENT*, C. MOREAU
National Research Council Canada, Industrial Materials Institute, 75 blvd de Mortagne, Boucherville, Québec, Canada, J4B 6Y4

$RBa_{2-x}Sr_xCu_3O_7$ samples where $R \equiv Y$, Gd, Sm and Nd were synthesized in oxygen between 930 and 1070 °C. The effect of the Ba substitution by Sr on the sample optimum synthesis temperature, microstructure and electrical properties was investigated for $0 \leqslant x \leqslant 1.0$. The magnitude of the resistivity increase and of the T_c decrease due to the Ba substitution by Sr is found to depend on the R ionic radius. Moreover, the Sr addition has a decreasing effect on J_c for all R elements.

1. Introduction
In the search for superconductivity above 90 K many substitutions have been done in the Y–Ba–Cu–O system. The effect on T_c of the Y substitution by other rare earth elements is very weak [1]. On the other hand, T_c is decreased or the superconductivity disappears when copper is substituted by other transition elements [2, 3]. Moreover, the replacement of Ba by smaller alkaline ions also fails to increase T_c. The complete replacement of Ba by Sr results in samples exhibiting two superconducting transitions one at 40 and another at 80 K in the Y–Sr–Cu–O system [4]. However, only a small amount of information has been reported on the effect of the Ba substitution for systems other than $YBa_{2-x}Sr_xCu_3O_7$ [5–8] or $GdBa_{2-x}Sr_xCu_3O_7$ [9]. We reported here the effect of the Ba substitution by Sr on the electrical properties of R–Ba–Sr–Cu–O system for $R \equiv Y$, Gd, Sm and Nd.

2. Experimental procedure
R_2O_3 and CuO (each 99.999%), BaO_2 (99%) and SrO (99.5%) powders were sieved through a 32 μm screen, weighed and mixed under an inert atmosphere according to a method described elsewhere [10]. Green pellets were obtained by pressing the mixture at 200 MPa. The pellets were heated to the chosen temperature at a rate of 4 °C min^{-1}, kept at this temperature for 24 h and cooled to the room temperature at 2 °C min^{-1}. All the heat treatments were done under flowing oxygen.

The resistivity measurements were obtained using the four point probe method. The critical current values (J_c) were measured in boiling liquid nitrogen using $12 \times 2 \times 2$ mm^3 bars cut from the sintered pel-

lets. Four electrical contacts were made by sputter depositing a gold layer on the bar surface forming four conducting pads on which copper wires were attached using an indium solder [11]. J_c values were obtained when a difference of 1 μV appears between the two voltage contacts.

The CuK_α line was used for the X-ray diffraction analyses. Phases were analysed with an energy dispersive X-ray system (EDX) using a standardless software whose expected accuracy is of the order of a few per cent.

3. Results and discussion
The reactivity of Sr-substituted 123 compounds has been checked by X-ray analysis. The diffraction patterns of $RBa_{2-x}Sr_xCu_3O_7$ samples synthesized at 950 °C indicate that the reaction is nearly completed. An example is shown in Fig. 1 for $NdBaSrCu_3O_7$. The diffraction pattern is characteristic of the perovskite structure with small extra peaks attributable to secondary phases. The sintering behaviour of Sr-substituted compounds are different from the Sr-free ones. The $RBa_{2-x}Sr_xCu_3O_7$ compounds for $x = 0.5$ or 1.0 need a higher reaction temperature to produce pellets that can be manipulated easily. Fig. 2 shows the microstructure of $NdBa_{2-x}Sr_xCu_3O_7$ pellets for $x = 0$ and 1.0 after synthesis at 1030 °C. The porosity is higher in pellets containing Sr compared to those without Sr. A similar behaviour is observed for the other lanthanides. It is not surprising that the effect of the reaction temperature is different on Sr-substituted compounds since their melting points are increased. For example, the incongruent melting points of $YBa_{2-x}Sr_xCu_3O_7$ compounds are 1030, 1051 and 1061 °C in oxygen for
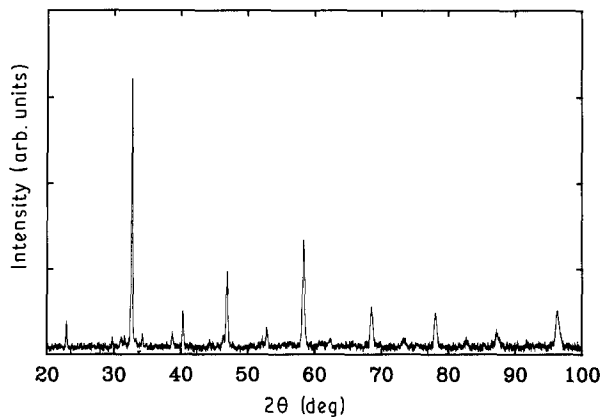
Figure 1 X-ray diffraction pattern of a $NdBaSrCu_3O_7$ sample synthesized at 950 °C for 1 h.

Figure 3 Resistivity–temperature curves of $NdBa_{2-x}Sr_xCu_3O_7$ samples for $x = 0$, 0.5 and 1.0 synthesized at 1030 °C.

$x = 0$, 0.5 and 1.0, respectively [12]. In fact it is not only the compound sintering behaviour that is affected but the whole phase diagram equilibrium when Ba is substituted by Sr [13]. The solid solution limit in $YBa_{2-x}Sr_xCu_3O_7$ is reached for $x \approx 1.0$. Any attempts to substitute a larger proportion of Ba by Sr results in the formation of a four phase equilibrium [13]. The solid solution limit has not been established for other R elements. It is possibly different for each lanthanide. However, we have not been able to synthesize pure $RSr_2Cu_3O_7$ phase for any of the rare earth metals used in this work.

The pellet's normal state resistivity depends on the synthesis temperature. The synthesis temperature at which the resistivity is minimal is called optimum. The
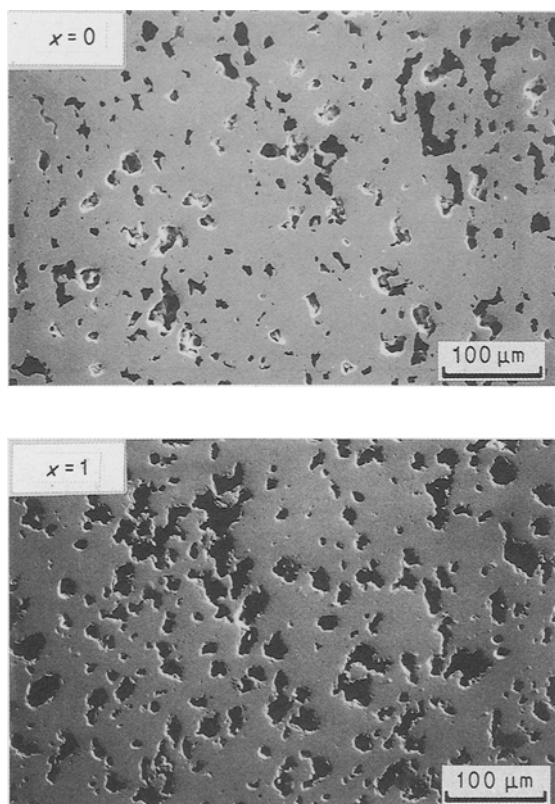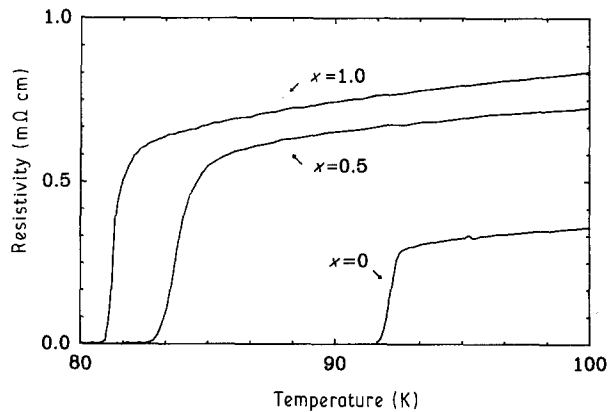
resistivity of pellets treated above the optimum temperature is higher due to the perovskite phase decomposition. For example, a CuO and an yttrium-rich phase have been found in $YBa_{1.5}Sr_{0.5}Cu_3O_7$ samples treated above the optimum temperature at 1030 °C. The optimum synthesis temperature is 990 °C for $YBa_{1.5}Sr_{0.5}Cu_3O_7$ and 1030 °C for all other Sr-substituted compounds. For comparison the optimum synthesis temperature for $RBa_2Cu_3O_7$ compounds has been determined to be 970 °C for $R \equiv$ Y, 970–990 °C for $R \equiv$ Gd, 1010–1030 °C for $R \equiv$ Sm and 1010–1050 °C for $R \equiv$ Nd [10, 14].

Fig. 3 depicts the effect of x on the resistivity–temperature curves for $NdBa_{2-x}Sr_xCu_3O_7$. The substitution of Ba by Sr increases the resistivity in the normal state and decreases T_c. The temperature at which the resistivity is zero $T_c(\rho = 0)$ is 91.5, 82.8 and 81.0 K while the 100 K resistivity increases from 360 to 725 and 830 $\mu\Omega$ cm^{-1} for $x = 0$, 0.5 and 1.0, respectively. Figs 4 and 5 present the resistivity–temperature curves of $RBa_{2-x}Sr_xCu_3O_7$ samples for $x = 0.5$ and 1.0, respectively. All samples were treated at 1030 °C except $YBa_{1.5}Sr_{0.5}Cu_3O_7$ which was treated at 990 °C. When $x = 0.5$ the zero resistivity temperature is 82.8, 85.5, 86.9 and 82.8 K while the 100 K resistivity is 270, 430, 595 and 725 $\mu\Omega$ cm^{-1} for $R \equiv$ Y, Gd, Sm and Nd, respectively.

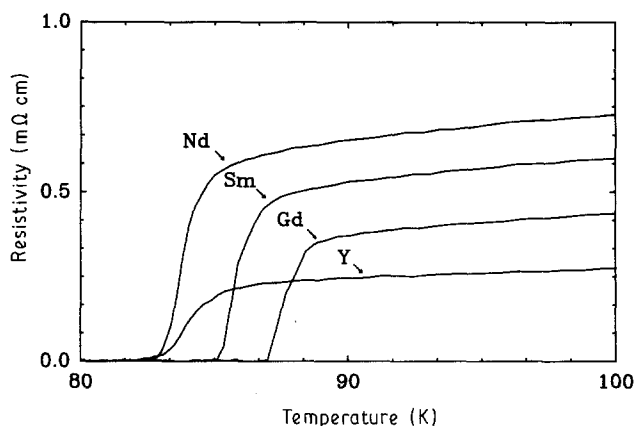*Figure 2* Micrographs of $NdBa_{2-x}Sr_xCu_3O_7$ samples for $x = 0$ and 1.0 synthesized at 1030 °C.

Figure 4 Resistivity–temperature curves of $RBa_{1.5}Sr_{0.5}Cu_3O_7$ samples for $R \equiv$ Y, Gd, Sm and Nd.
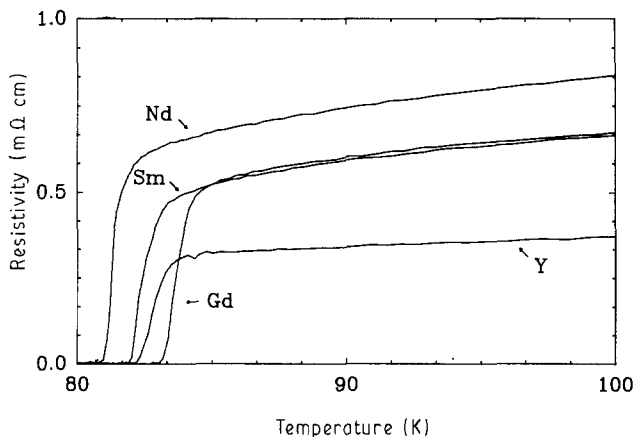
Figure 5 Resistivity–temperature curves of $RBaSrCu_3O_7$ samples for $R \equiv$ Y, Gd, Sm and Nd.

The decrease of $T_c(\rho = 0)$ for $RBa_{1.5}Sr_{0.5}Cu_3O_7$ compared to $RBa_2Cu_3O_7$ compounds reaches 8.7, 6.5, 3.4 and 2.9 K for $R \equiv$ Nd, Sm, Gd and Y, respectively. A similar behaviour with larger differences of $T_c(\rho = 0)$ is observed between $RBa_2Cu_3O_7$ and $RBaSrCu_3O_7$. These results, represented in Fig. 6, show that the T_c decrease observed in Sr-substituted compounds scales with the ionic radii of the R elements that are, respectively, 0.0995 nm, 0.0964 nm, 0.0938 nm and 0.0893 nm for $R \equiv$ Nd, Sm, Gd and Y [15]. For the $RBa_2Cu_3O_7$ structure, it has been established that the Cu(2)–Cu(2) distance across Ba decreases and the Cu(2)–Cu(2) distance across R increases with the R ionic radius [16]. This results in nearly constant cell dimensions independently of R. The Cu(2) plane responsible for the superconductivity is not affected by the R ionic radius. This is the reason why T_c is nearly constant in the $RBa_2Cu_3O_7$ system. On the other hand, the effect of the Ba substitution by Sr in $YBa_{2-x}Sr_xCu_3O_7$ compounds causes a distortion of the perovskite structure bringing about a shrinkage along the three axes [5, 8]. Moreover, the orthorhombic splitting of the lattice parameters is affected by the Sr content and is correlated to the T_c
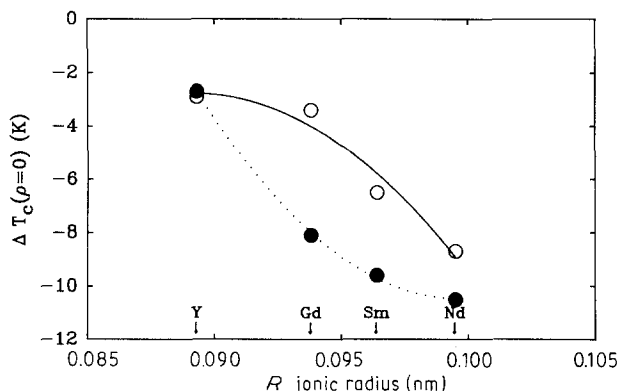

Figure 6 The $T_c(\rho = 0)$ decrease for $RBa_{2-x}Sr_xCu_3O_7$ compared to $RBa_2Cu_3O_7$ compounds as a function of the R^{3+} ionic radius for (○) $x = 0.5$ and (●) $x = 1$.

decrease observed in the Sr-substituted compounds [5, 7, 8]. According to Fig. 6, the T_c decline with x of the $RBa_{2-x}Sr_xCu_3O_7$ compounds increases with the R ionic radius. This is likely to be related to the more important effect on T_c of the perovskite structure distortion for larger R elements.

The normal state resistivity of $RBa_{2-x}Sr_xCu_3O_7$ compounds increases with the R radius for $x \neq 0$ but is nearly constant at $370 \pm 40 \, \mu\Omega \, cm^{-1}$ independently of R for $x = 0$ [10, 14]. To explain the dependence of the resistivity with R in Sr-substituted compounds it is necessary to consider many factors. One of these factors is the conduction path which is related to the sample density. Indeed, in more porous samples, the conduction path is decreased, giving higher values of resistivity. However, metallographic observations show that $RBa_{2-x}Sr_xCu_3O_7$ samples treated at the same temperature have a similar density independent of the R element. Therefore this effect cannot account for the resistivity increase. Another factor that influences the resistivity is the formation of secondary phases more resistive than the 123 phase. A secondary phase containing Sr and Cu has been found in all Sr-containing samples. We estimate that this phase represents only a few per cent of the sample composition. However, the relative proportion of the Sr–Cu phase in each $RBa_{2-x}Sr_xCu_3O_7$ sample may vary with R and be, in part, responsible for the resistivity increase. It does not exclude the fact that other phases like carbonate which have been found at grain boundaries of $YBa_2Cu_3O_7$ may also be formed in different amounts in $RBa_{2-x}Sr_xCu_3O_7$ samples increasing their resistivity. A third factor that can explain the R-dependent resistivity increase, is the structural modifications caused by Sr and R. The distortion of the structure produces a decrease in T_c which increases with the R ionic radius. The structure distortion can also have an effect on the resistivity. In fact the resistivity depends on the charge carrier density and their mobility. These two physical properties may be affected by the gradual structural distortion with R resulting in a significant resistivity increase.

The critical currents measured at the liquid nitrogen temperature in superconducting samples synthesized at different temperatures are given in Table I. For Sr-free samples, the critical currents do not strongly depend on the synthesis temperature in the following ranges: 950–1030 °C for $R \equiv$ Y, 930–970 °C for $R \equiv$ Gd, 930–1010 °C for $R \equiv$ Sm and 970–1050 °C for $R \equiv$ Nd. These temperature ranges overlap the temperatures at which the sample resistivities are minimal (the optimum temperatures). One notes also that the critical currents tend to decrease as the Sr content increases for all R elements. This J_c decrease is likely to be due to the formation of less dense samples when x increases as described above (Fig. 2) or to an increasing amount of secondary phases at the superconducting grain boundaries. The low critical current density values measured in our samples result certainly from the presence of weak links between superconducting grains (or twins) and do not permit us to conclude anything about maximum superconducting currents flowing in the grains themselves.

TABLE I Critical currents ($A\,cm^{-2}$) at 77 K in samples synthesized at various temperatures

Samples	Synthesis temperature (°C)							
	930	950	970	990	1010	1030	1050	1070
$NdBa_2$	58	83	122	127	167	137	146	42
$NdBa_{1.5}Sr_{0.5}$	–	14	–	11	–	42	–	–
NdBaSr	–	–	–	0	–	9	–	13
$SmBa_2$	140	146	120	158	103	86	117	–
$SmBa_{1.5}Sr_{0.5}$	–	–	–	53	–	38	–	–
SmBaSr	–	–	–	11	–	82	–	20
$GdBa_2$	127	133	172	101	88	88	–	–
$GdBa_{1.5}Sr_{0.5}$	–	61	–	164	–	114	–	–
GdBaSr	–	–	–	40	–	40	–	–
YBa_2	–	122	–	–	–	130	–	–
$YBa_{1.5}Sr_{0.5}$	–	74	–	119	–	1	–	–
YBaSr	–	6	–	9	–	–	–	–

Conclusion

Polycrystalline samples of $RBa_{2-x}Sr_xCu_3O_7$ were synthesized between 930 and 1070 °C for $R \equiv Y$, Gd, Sm and Nd and for x ranging from 0 to 1.0. The reaction of the starting powders was nearly complete after 1 h for a synthesis temperature above 950 °C. The Ba substitution by Sr is found to increase the sample resistivity and to decrease T_c and J_c values measured at the liquid nitrogen temperature.

References

1. J. M. TARASCON, W. R. McKINNON, L. H. GREENE, G. W. HULL and E. M. VOGEL, *Phys. Rev. B* **36** (1987) 226.
2. J. M. TARASCON, P. BARDOUX, P. MICELI, L. H. GREENE, G. W. HULL, M. EIBSCHUTZ and S. SUNSHINE, *Phys. Rev. B* **13** (1988) 7458.
3. G. XIAO, M. Z. CIEPLAK, D. MUSSER, A. GAVRIN, F. H. STREITZ, C. L. CHIEN, J. H. RHYNE and J. A. GOTAAS, *Nature* **332** (1988) 238.
4. M. K. WU, J. R. ASHBURN, C. A. HIGGINS, B. H. LOO, D. H. BURNS, A. IBRAHIM, T. D. ROLIN, F. Z. CHIEN and C. Y. HUANG, *Phys. Rev. B* **37** (1988) 9765.
5. B. W. VEAL, W. K. KWOK, A. UMEZAWA, G. W. CRABTREE, J. D. JORGENSEN, J. W. DOUINEY, L. J. NORWICKI, A. W. MITCHELL, A. P. PAULIKAS and C. H. SOWERS, *Appl. Phys. Lett.* **51** (1987) 279.
6. J. M. LIANG, L. CHANG, H. M. SUNG, P. T. WU and L. J. CHEN, *J. Appl. Phys.* **64** (1988) 3593.
7. Y. ZHAO, H. ZHANG, T. ZHANG, S. F. SUN, Z. Y. CHEN and Q. R. ZHANG, *Physica C* **152** (1988) 513.
8. M. F. TAI, S. W. HSU, J. R. HWANG, H. C. KU and K. H. LII, *Chi. J. Physics* **26** (1988) S146.
9. D. B. CURIE and A. M. FORREST, *Sol. State Comm.* **66** (1988) 715.
10. L. PARENT, B. CHAMPAGNE, K. COLE and C. MOREAU, *Supercond. Sci. Technol.* **2** (1989) 103.
11. J. W. EKIN, A. J. PANSON and B. A. LANKENSHIP, *Appl. Phys. Lett.* **52** (1988) 331.
12. D. NOËL, and L. PARENT, *Thermochim. Acta* **171** (1990) 57.
13. R. S. ROTH, C. J. RAWN, J. D. WHITLER, C. K. CHIANG and W. K. WONG-NG, *J. Amer. Ceram. Soc.* **72** (1989) 395.
14. L. PARENT, C. MOREAU and B. CHAMPAGNE, *J. Mater. Sci.* **26** (1991) 2359.
15. "Handbook of chemistry and physics" 65th Edn, edited by R. C. Weast (CRC Press, Florida, 1984) p. F-165.
16. Y. Le PAGE, T. SIEGRIST, S. A. SUNSHINE, L. F. SCHNEEMEYER, D. W. MURPHY, S. M. ZAHURAK, J. V. WASZCZAK, W. R. McKINNON, J. M. TARASCON, G. W. HULL and L. H. GREENE, *Phys. Rev. B* **36** (1987) 3617.