JOURNAL OF SOLID STATE CHEMISTRY **105**, 609–612 (1993)

$LaBaCuO_2BO_3$: A New Single Layer Cuprate Containing BO_3^{3-} Anion Groups as Connecting Elements

LI RUKANG,* R. K. KREMER, AND J. MAIER

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany

Received February 17, 1993; accepted March 11, 1993

A new cuprate compound with the composition of $LaBaCuO_2BO_3$ has been synthesized. The X-ray powder diffraction patterns of the compound suggest that it is a structure analogue of a recently reported single CuO layer compound $Sr_2CuO_2CO_3$. The lattice parameters of the compound have been determined as: $a = 3.943$ Å, $c = 7.508$ Å from the X-ray diffraction patterns. The structure can be viewed as an alternate stacking of the $[CuO_{4/2}]$ layers and the layers of distinct BO_3 groups. Although it contains complete CuO planes in the structure as in common high-T_c cuprates, bulk superconductivity has not been observed in the system yet.

All of the high-T_c cuprates can be thought of as composed of copper–oxygen layers and additional connecting and separating layers (*1, 2*). The cuprate superconductors can generally be derived from the parent antiferromagnetic and insulating compounds by tuning the carrier concentrations. Recently, several cuprate compounds containing the structural units, such as $TaO_{6/2}$ layers, $GaO_{4/2}$ chains, and CO_3 groups, have been found to be new superconductors (*3–5*). Especially, the superconducting $BaSrCuO_2CO_3$, which was derived from $Sr_2CuO_2CO_3$ reported first by von Schnering *et al.* (*6*), can be assigned to the simple 1201 family of the layered cuprates. Based on the X-ray diffraction data of a single crystal, the same group (*7*) obtained an oriented disordered structure as shown in Fig. 1a. Powder neutron diffraction results of the same compound have also been interpreted in terms of other different ordered (*8*) or disordered (*9*) structure models (Fig. 1b). All models agree in that the structure of $Sr_2CuO_2CO_3$ contains single $[CuO_{4/2}]$ layers and layers of distinct CO_3 groups (Figs. 1a, 1b).

Since many mineral carbonates and borates are isostructural (*10*) (e.g., dolomite $(MgCa(CO_3)_2)$–nordenskiolite$(CaSn(BO_3)_2)$, huntite $(CaMg_3(CO_3)_4)$–$YAl_3(BO_3)_4)$, it seemed worth investigating whether a compound containing BO_3^{3-} anions and being isostructural to $Sr_2CuO_2CO_3$ could be synthesized. In the following, the preparation and characterization of such a compound, namely $LaBaCuO_2BO_3$, is reported.

Samples of the nominal composition $La_{1-x}Ba_{1+x}CuO_2BO_3$ ($-0.2 \le x \le 0.2$) were prepared from two groups of starting materials: (1) La_2O_3, $BaCO_3$, CuO, H_3BO_3; (2) La_2O_3, BaO_2, CuO, H_3BO_3 (carbonate free). The well mixed starting compounds were first heated at 870°C for 48 hr in air. After cooling down to room temperature, the samples were reground, pressed into pellets, and then sintered at 950°C for 72 hr in an alumina crucible (interrupted by several intermediate grindings). The X-ray diffraction patterns of the samples were recorded with

* On leave from Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China.

0022-4596/93 $5.00

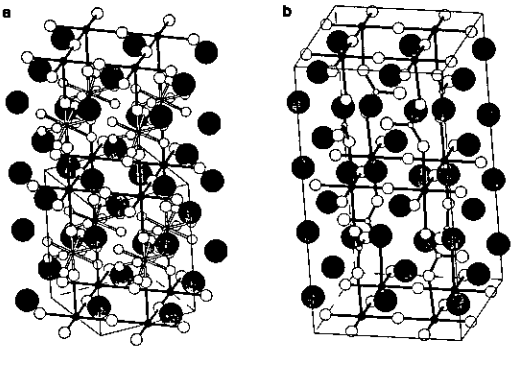

FIG. 1. Two structure models of $Sr_2CuO_2CO_3$ and $LaBaCuO_2BO_3$ (according to (a) Ref. (*7*), (b) Ref. (*8*)). The shaded large circles denote Sr ions or La/Ba ions and small shaded circles are C or B atoms. The larger open circles denote oxygen and filled circles are Cu respectively. Different selections of the unit cells are also shown in the figure.

a Philips PW1710 diffractometer, and the lattice constants were obtained from a Guinier film with silicon powder as an internal standard. The dc magnetic susceptibilities of the samples were measured by using a MPMS SQUID magnetometer (Quantum Design).

The X-ray powder diffraction patterns (XRDP, Fig. 2) of $LaBaCuO_2BO_3$ turned out to be identical for the samples prepared from both groups of starting materials, and to be similar to the pattern of $Sr_2CuO_2CO_3$. The pattern can be successfully indexed with a tetragonal unit cell. The cell parameters, a = 3.9434(2) Å, c = 7.5077(6) Å, were obtained by a least squares fitting of the observed reflections in th 2θ range of 20–90° (Table I). The reduced cell parameters are related to those of $Sr_2CuO_2CO_3$ (a', c') by $a = a'/\sqrt{2}$, $c = c'$ (*7*) or $a = a'/2$, $c = c'/2$ (*8*). Such a reduced cell has also been adopted by Babu *et al.* (*9*) for $Sr_2CuO_2CO_3$ since apparent superstructure reflection peaks did not appear in their neutron diffraction patterns. Due to the lack of single crystals, we are not able to decide whether this simple model or the more complicated ones proposed in Refs. (*6, 7*) and (*8*) are applicable in the case of the boron analogue.

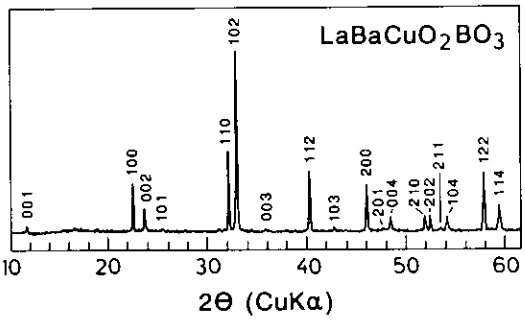

FIG. 2. The X-ray powder diffraction pattern of $LaBaCuO_2BO_3$.

Since both groups of starting materials led to the formation of the same compound and an attempt to prepare a hypothetical compound $LaBaCuO_2CO_3$ failed under analogous conditions, we are convinced that the BO_3 groups rather than CO_3 groups are indeed the relevant structure elements in the present compound. A chemical analysis of all the elements (La(28.78 wt%), Ba(34.51 wt%), Cu(15.67 wt%), B(2.76 wt%), O(18.14 wt%); totally 99.86 wt%) presented in the compound also ruled out the significant presence of CO_3 in the prepared samples. This is confirmed by the IR spectra showing expected BO_3 vibrations; the CO_3 signals could not be detected. In view of the above considerations, we may conclude that the structure of $LaBaCuO_2BO_3$ is similar if not identical to that of $Sr_2CuO_2CO_3$. Instead of CO_3^{2-}, the BO_3^{3-} anions now are acting as the connecting elements for the $[CuO_{4/2}]$ planes via sharing of the apical atoms.

Figure 3 shows the temperature dependence of the dc magnetic susceptibility(χ) of the as-prepared sample of $LaBaCuO_2BO_3$. The susceptibility decreases with decreasing temperature until a minimum at about 100 K, then it rises again at lower temperatures. The high temperature behavior of χ is very similar to that of other parent compounds of high-T_c superconductors (e.g., $Ca_{0.86}Sr_{0.14}CuO_2$, La_2CuO_4, and $YBa_2Cu_3O_{6.1}$) (*11*), which is a typical two dimensional(2d) antiferromagnetic (AFM)

TABLE I

CALCULATED AND OBSERVED X-RAY DIFFRACTION PATTERN OF $LaBaCuO_2BO_3$ (INDEXED WITH THE LATTICE PARAMETERS: a = 3.9434(2) Å, c = 7.5077(6) Å)

h k l	d_{calc}	d_{obs}	I_{obs}
0 0 1	7.5077	7.5165	4.3
1 0 0	3.9434	3.9414	32.5
0 0 2	3.7539	3.7520	13.7
1 1 0	2.7884	2.7875	47.5
1 0 2	2.7189	2.7181	100
1 1 2	2.2384	2.2378	35.2
1 0 3	2.1130	2.1127	3.0
2 0 0	1.9717	1.9714	25.1
0 0 4	1.8769	1.8764	8.2
2 1 0	1.7635	1.7631	9.2
2 0 2	1.7456	1.7453	8.6
1 0 4	1.6948	1.6943	9.2
1 2 2	1.5962	1.5961	34.4
1 1 4	1.5571	1.5569	15.8
2 2 0	1.3942	1.3944	7.3
2 0 4	1.3595	1.3595	6.9
2 2 2	1.3070	1.3066	2.7
2 1 4	1.2852	1.2854	6.7
1 3 0	1.2470	1.2470	15.5
3 0 2	1.2406	1.2405	6.1
1 0 6	1.1927	1.1927	3.9
1 3 2	1.1834	1.1836	5.2

behavior below $T_M(\chi^{max})$. Following Ref. (*11*), the change of slope of χ around 240 K may be assigned to a 3d AFM ordering induced by the interplanar interactions. The ordering temperature(T_N) also agrees with the larger interplane distance in $LaBaCuO_2BO_3$ (7.5 Å—T_N = 240 K, 3.2 Å($Ca_{0.86}Sr_{0.14}CuO_2$)—T_N = 540 K, 6.6 Å (La_2CuO_4)—T_N = 290 K). The increase of χ at lower temperature may be attributed to paramagnetic defects or traces of impurity phases. At present we do not have a clear explanation of the cusp observed in the temperature dependent susceptibilities at about 45 K. It may be due to some AFM impurities or a small fraction(5 ppm) of superconducting phase.

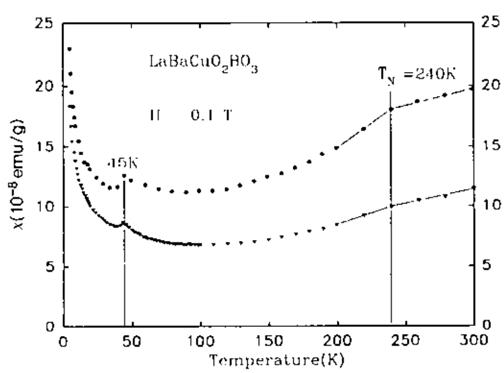

FIG. 3. The dc magnetic susceptibilities of the as-prepared (lower part) and high-O_2 pressure treated (upper part) $LaBaCuO_2BO_3$ samples.

In attempts to induce superconductivity in the $LaBaCuO_2BO_3$ system, the La/Ba ratios ($-0.2 \leq x \leq 0.2$) were varied and high oxygen pressure treatment (900°C, 500 bar, 60 hr) was applied. Unfortunately, the solid solution range of the $La_{1-x}Ba_{1+x}CuO_2BO_3$ was found quite limited ($-0.1 < x < 0.15$) under the present preparation conditions. For the Ba-rich samples, a 123-type compound $La_{1+x}Ba_{2-x}Cu_3O_y$ appears as a second phase, whereas $La_{2-x}Ba_xCuO_4$ forms for the samples with La excess. We have not found any significant superconducting transition in all the samples investigated. Our attempts to induce superconductivity by high O_2 pressure treatment of the stoichiometric and the single phase samples with small Ba excess were also not successful.

The fact that the bulk superconductivity has not been observed so far in the $La_{1-x}Ba_{1+x}CuO_2BO_3$ system may be due to the limitation of Ba vs La substitution. This may be overcome by the recent finding that it is possible to introduce holes by partial substitution of the CO_3 groups in $BaSrCu_{1+x}O_{2+y}(CO_3)_{1-x}$ by CuO_{2-x} groups. If, on the other hand, this BO_3 contained compound turned out to be nonsuperconducting at all whereas under comparable conditions the CO_3 contained compound is, this would provide further useful information with respect to possible mechanisms. In addition, it would also be of some importance to study the intraplane and interplane magnetic interactions of this single layered system and its relations to other parent compounds of cuprate superconductors.

Acknowledgments

The authors are indebted to U. Herterich, G. Dieckmann, and P. Senk for their kind help with high oxygen pressure treatments, to L. Viczian and F. Kögel for the recording of X-ray diffraction patterns, and to O. Buresch for the chemical analysis. The financial support from the Alexander von Humboldt foundation is gratefully acknowledged.

References

1. Y. Tokura and T. Arima, *Jpn. J. Appl. Phys.* **29,** 2388 (1990).
2. Li Rukang, *Appl. Phys. Commun.* **11,** 295 (1992).
3. R. J. Cava, J. J. Krajewski, H. Takagi, H. W. Zandbergen, R. B. van Dover, W. F. Peck, Jr., and B. Hessen, *Physica C* **191,** 237 (1992).
4. Li Rukang, R. K. Kremer, and J. Maier, *Physica C* **200,** 344 (1992).
5. K. Kinoshita and T. Yamada, *Nature* **357,** 313 (1992).
6. H. G. von Schnering, M. Hartweg, L. Walz, T. Popp, T. Becker, and M. Schwarz, "Annual Report of the Max-Planck-Institute für Festkörperforschung Stuttgart," p. 94 (1988).
7. T. Popp, Ph.D thesis, University of Stuttgart, Stuttgart (1990).
8. Y. Miyazaki, H. Yamane, T. Kajitani, T. Oku, K. Hiraga, Y. Morii, K. Fuchizaki, S. Funahashi, and T. Hirai, *Physica C* **191,** 434 (1992).
9. T. G. Narendra Babu, D. J. Fish, and C. Greaves, *J. Mater. Chem.* **1,** 677 (1991).
10. "Landoldt–Börnstein, New Series," Group 3, Vol. 7d2 (K.-H. Hellwege and A. M. Hellwege, Eds.) Springer-Verlag, Berlin (1980).
11. D. Vaknin, E. Caignol, P. K. Davies, J. E. Fisher, D. C. Johnston, and D. P. Goshorn, *Phys. Rev. B* **39,** 9122 (1989).