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T_c enhancement versus rare-earth size in $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ (R = Sm, Eu, Gd, Dy, Ho, and Er)

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Six compounds of general formula $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ (R = Sm, Eu, Gd, Dy, Ho, and Er) have been synthesized. They crystallize in a structure isomorphous with $YBa_2Cu_4O_8$. All these Ca-substituted 1:2:4 compounds are superconducting. The highest $T_c = 88$ K was found for Er, the smallest ion. T_c decreases systematically with larger rare earths to 72 K for the Sm compound. In all cases, the T_c is increased by Ca substitution. The enhancement in T_c (ΔT_c) is the highest (10 K) for the Er compound and decreases as the rare-earth size increases; for Sm the enhancement in T_c is only 3 K. The lattice constants a, b, and c and the unit-cell volume V increase with rare-earth size, whereas b/a decreases until the structure is nearly tetragonal for R = Sm. The systematic change in T_c and in the T_c enhancement by Ca substitution seemed to be a consequence of the increase in lattice constants with larger R ion. Larger Cu-O distances in the CuO_2 sheets will reduce the charge transfer into the sheets. Thus when the rare-earth ion is large, and the Cu-O bonds are larger, the charge transfer is reduced. This explains why addition of holes by Ca doping at the 0.1 level will be less effective in raising T_c for large rare earths.

INTRODUCTION

The discovery of a significant T_c enhancement in $YBa_2Cu_4O_8$ by a partial substitution of Ca for Y (Refs. 1 and 2) has generated a lot of interest in this $Y_{1-x}Ca_xBa_2Cu_4O_8$ series of compounds. A number of papers about this $Y_{1-x}Ca_xBa_2Cu_4O_8$ series, describing the superconducting properties, structure, phase diagram and J_c have been published during the last two years.[1-7] It is generally conjectured that this increase in T_c is due to an increase in number of holes on the CuO_2 sheets arising from Ca doping. It was thought that the origin of this enhancement can be clarified if we had a number of similarly substituted compounds with different structural features, which can be correlated to variation in T_c. With this end in view, six calcium substituted $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ (R = rare-earth ion) 1:2:4 compounds were synthesized. In all cases the T_c is enhanced by calcium substitution, with respect to the T_c of the parent compound.[8] Furthermore, the T_c value as well as the enhancement by calcium substitution (ΔT_c) decrease with increasing size of the rare-earth ion. A similar decrease in T_c with increasing ionic radius of the rare earth has been seen earlier in $R_1Ba_2Cu_4O_8$ (1:2:4) (Ref. 8), $R_2Ba_4Cu_7O_{15}$ (2:4:7) (Ref. 8), and in (Pb,Cu)Sr_2(Ca,R)Cu_2O_7 (Ref. 9), but not for $R_1Ba_2Cu_3O_7$ where T_c remains unaffected on replacing Y by any of the rare earths which form the 1:2:3 structure.[8,10] For $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ we also observe a decrease in orthorhombicity b/a of the compounds with increasing rare-earth radius and this result was also observed earlier for 1:2:3 and 1:2:4 compounds.[8,10]

SAMPLE PREPARATION

We attempted to prepare compounds of the general formula $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ with fourteen rare-earth elements (R). However, we were successful in getting compounds with the 1:2:4 structure in only six cases, namely Sm, Eu, Gd, Dy, Ho, and Er. Further studies were therefore restricted to these six rare earths. The concentration of calcium was fixed at 0.1 atom per formula unit in view of the known results from Ca substitution in yttrium 1:2:4, where the maximum enhancement of T_c is found at 0.1 Ca. The 1:2:4 compounds were formed by solid-state reaction. Appropriate amounts of the rare-earth oxide, calcium oxide, barium peroxide, and copper oxide (CuO) were weighed on an accurate single-pan balance and mixed in an agate mortar and pestle under acetone. The mixed powder was dried and pressed into tablets of 6 mm diam × 2 mm thickness and fired in a commercial high-oxygen-pressure furnace[11] at 930°C for 30 h under an oxygen pressure of 200 bars. The firing was repeated several times to ensure as complete a reaction as possible. Between each run the pellet was ground to a fine powder and repressed.

X-RAY DIFFRACTION

X-ray-diffraction analysis was carried out on a Scintag PAD-V diffractometer using Cu $K\alpha$ radiation and an intrinsic Ge solid-state detector with 200-eV energy resolution. Three typical patterns are shown in Figs. 1 and 2. The powder-diffraction patterns in case of all the six rare earths mentioned above could be indexed on the basis of the known 1:2:4 structure, except for some low-intensity

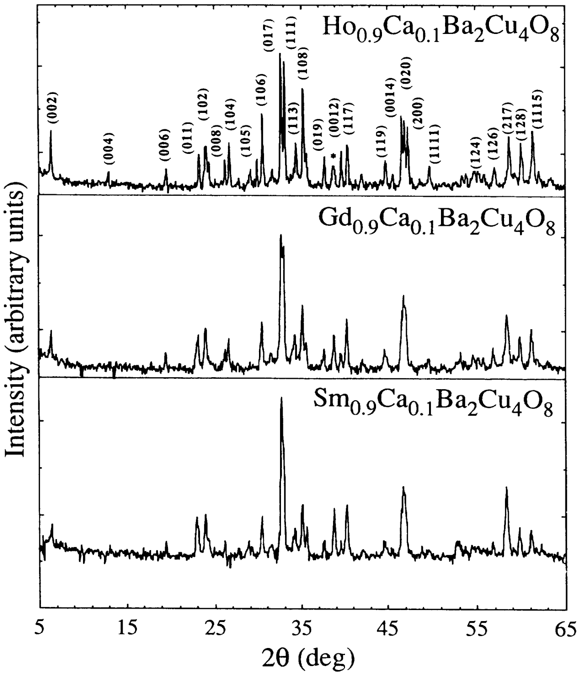

FIG. 1. X-ray-diffraction pattern of $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ with R = Sm, Gd, and Ho synthesized at 930°C under 200-bar oxygen pressure. The CuO peak is marked *.

peaks due to CuO and some other unidentified phase, both in case of the parent R 1:2:4 as well as the Ca-substituted R 1:2:4.

The lattice parameters were calculated by fitting the x-ray-diffraction peak positions of at lease 15 diffraction peaks using a standard least-squares reduction method. The lattice parameters of these calcium substituted R 1:2:4 compounds are similar to those of pure R 1:2:4 reported by Morris *et al.*[8] Several systematic trends can be seen in these results. The a, b, c, and the volume of the unit cell V rise with the increasing ionic radius of the rare earth as one goes from Er to Sm (see Fig. 3). This is indeed to be expected. On the other hand, the b/a ratio, a measure of the orthorhombicity, decreases from Er to Sm. This is interesting particularly in light of the fact that the superconducting transition temperature T_c also shows a similar trend.

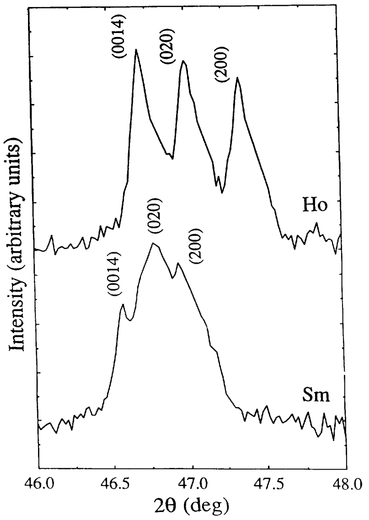

FIG. 2. Part of the x-ray-diffraction patterns ($46 \leq 2\theta \leq 48$) of $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ with R = Sm and Ho. Note the decrease of orthorhombicity b/a with increasing ionic radius.

MEISSNER DIAMAGNETIC SUSCEPTIBILITY

Superconducting transitions were determined from measurement of Meissner diamagnetic susceptibility as a function of temperature using a Quantum Design superconducting quantum interference device magnetometer. The field was first set at 20 Oe (calibrated by a tin sphere) and was held constant throughout the measurement. The sample was then introduced into the magnetic field at 100

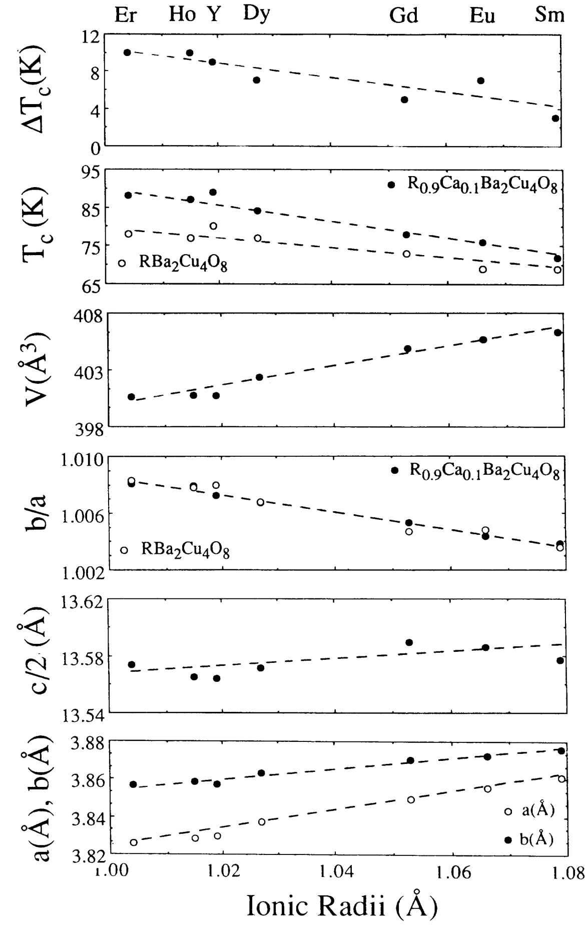

FIG. 3. Ionic radius dependence of lattice parameters a, b, c, b/a, V, T_c and ΔT_c. It can be clearly seen that: (i) the T_c in both the $RBa_2Cu_4O_8$ and $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ series decrease with increasing size of the rare-earth ion. (ii) The T_c of such calcium-substituted R 1:2:4 is higher than that of the corresponding calcium-free R 1:2:4. (iii) The difference between the T_c's (ΔT_c), i.e., the enhancement of T_c on calcium substitution, decreases with increasing size of the rare-earth ion just as the T_c does. (iv) The lattice parameters a, b, c, and V increase with increasing size of the rare-earth ion, but the orthorhombicity b/a decreases.

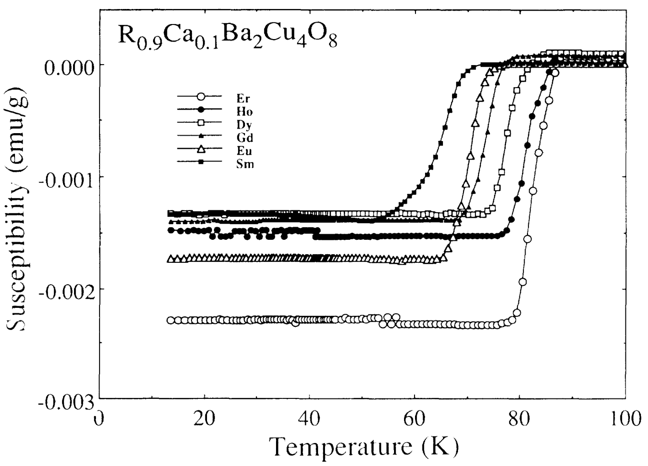

FIG. 4. Meissner (constant field cooled) diamagnetic susceptibility vs temperature for $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$, where R = Sm, Eu, Gd, Dy, Ho, and Er. The dependence of superconducting transition temperature on ionic radius of R can be seen.

K. The amount of flux expulsion was recorded during the warm-up cycle. The susceptibility values (emu/g) were plotted as a function of temperature and T_c was read from the graph. The susceptibility-temperature plots are shown in Fig. 4. The values of diamagnetic onset temperature as read from this graph are presented in Fig. 3, plotted as a function of the ionic radii of the different rare-earth ions. A systematic decrease in T_c is seen with the size increase from Er to Sm. The corresponding values for the unsubstituted 1:2:4 compounds are also shown in this figure for comparison. Here too a similar trend of decreasing T_c is seen with increasing size of the rare earth. However, in each case the calcium-substituted compound has a higher T_c than the corresponding unsubstituted compound. Furthermore, the difference in the two T_c's (ΔT_c) increases with decreasing ionic radius of the R ion (see Fig. 3) from about 3 K for the Sm compound to about 10 K for the Er compounds.

The diamagnetic volume fraction ($4\pi\rho\chi$) was calculated from the value of the flux expulsion when the sample was cooled to 10 K in the constant field of 20 Oe. The density was calculated from the measured unit-cell volume. The diamagnetic volume fraction ranges between 11 and 19%; the largest value is for $Er_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ and the smallest for the Sm, Gd, and Dy compounds. A similar trend has been observed for the calcium-free R 1:2:4 series (Ref. 8). Generally, the volume fraction decreases as T_c decreases; the only noticeable exception seems to be the Eu compound.

DISCUSSION

The observations which seem to be of particular significance and interest are the following.

(i) The T_c in both the $RBa_2Cu_4O_8$ and $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ series decrease with increasing ionic radius of the rare-earth ion.

(ii) The T_c of the calcium-substituted R 1:2:4 is always higher than the T_c of the corresponding calcium-free R 1:2:4.

(iii) The difference between these two T_c's (ΔT_c), i.e., the elevation of T_c on calcium substitution, decreases with increasing ionic radius of the rare-earth ion just as the two T_c's do.

(iv) The lattice parameters a, b, c, and the volume of the unit cell V increase with increasing ionic radius of the rare-earth ion, but the orthorhombicity b/a decreases.

A. T_c dependence on the size of rare earth

For a proper insight into the reasons for these dependences, one would need to know the atomic positions (including those of oxygen) and thereby the interatomic distances in these compounds. The needed neutron-diffraction studies have not yet been completed. However, in spite of this serious handicap, one can still attempt to draw some tentative conclusions if one compares these results with those obtained from similar studies on R 1:2:3. For R 1:2:3, b/a decreases with increasing ionic radius of the rare earth just as in case of 1:2:4,[8,10] but unlike 1:2:4 the T_c remains nearly unchanged in case of 1:2:3. This would suggest that the change in T_c with R size in 1:2:4 and in Ca-substituted 1:2:4 is not a direct consequence of the decrease in b/a. A similar strong dependence of T_c on the ionic radius also appears in Pr-substituted 1:2:3 of the general formula $R_{0.8}Pr_{0.2}Ba_2Cu_3O_7$.[12] The effect of Pr substitution in 1:2:3 is to enhance[13] the pressure dependence dT_c/dp, which is small in pure 1:2:3, but becomes significantly higher in Pr-substituted Y 1:2:3. The Y 1:2:4 is also known to show a strong pressure dependence dT_c/dp, and it is reasonable to expect that the other rare-earth 1:2:4 compounds would also behave in a similar fashion. All these would suggest that the observed T_c dependence is a consequence of the "internal pressure," i.e., the change in interatomic bond length, caused by substitution of large or small R rare-earth ions. As seen experimentally, the placement of a larger rare-earth ion at the Y site increases the a and b parameters (in addition to the c axis). It is well known that the Cu-O bonds in the CuO_2 sheets in the high-T_c superconductors are compressed. This increase in a and b has the effect of decreasing the compression of the Cu-O bonds, i.e., the Cu-O bonds lengthen.

Increasing the Cu-O distance in the CuO_2 planes decreases the Cu-O $d_{x^2-y^2}$-p_σ molecular orbital overlap. This may decrease the hole density in the CuO_2 planes. We also note in Fig. 3 the a parameter increases rapidly with R size, increasing the separation between the Cu-O chains and changing their energy levels, which may alter the degree of charge transfer into the CuO_2 sheets, so that the situation is quite complicated.

B. T_c enhancement on Ca doping and its dependence on the size of rare earths

The increase in T_c on calcium doping in R 1:2:4 compounds conforms to the earlier findings in $YBa_2Cu_4O_8$, which was explained by increased carrier (hole) density resulting from the substitution of a divalent Ca^{2+} ion in place of a trivalent Y^{3+} ion, while maintaining eight oxygens per formula unit. Recent collaborative neutron-diffraction studies on $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ (Ref. 14) do indeed confirm that: (i) Ca^{2+} substitutes at Y^{3+} sites and (ii) the oxygen content per formula units remains at eight. This indicates that the total hole concentration does increase from one per formula unit in $YB_2Cu_4O_8$ to 1.1 in $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. We can safely assume that at least a fraction of these additional holes distribute themselves over the CuO_2 planes and this is the cause of the observed increase in T_c. However, when the rare-earth ion is larger, the added holes from Ca doping are less effective in raising T_c in $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. It appears that in the large rare-earth compounds the additional holes are not effectively transferred into the CuO_2 sheets.

CONCLUSIONS

Calcium substitution increases T_c in six $R_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ that have been successfully synthesized with the well-known 1:2:4 structure. This increase is attributed to the increase in carrier (hole) density. T_c is found to decrease with increasing ionic radius of the rare-earth ion in the series just as in the case of parent compounds $RBa_2Cu_4O_8$. This is attributed to the increase in the lattice parameters and a resultant decrease in the charge transfer in CuO_2 sheets.

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[1] T Miyatake, S. Goto, N. Koshizuka, and S. Tanaka, Nature **341**, 41 (1989).

[2] D. E. Morris, P. Narwankar, A. P. B. Sinha, K. Takano, B. Fayn, and V. T. Shum, Phys. Rev. B **41**, 4118 (1990).

[3] D. E. Morris, P. Narwankar, A. P. B. Sinha, K. Takano, and V. T. Shum, Appl. Phys. Lett. **57**, 715 (1990).

[4] R. G. Buckley, D. M. Pooke, J. L. Tallon, M. R. Presland, N. E. Flower, M. P. Staines, H. L. Johnson, M. Meylan, G. V. M. Williams, and M. Bowden, Physica C **174**, 383 (1991).

[5] T. Waka, N. Suzuki, A. Ichinose, Y. Yaegashi, H. Yamauchi, and S. Tanaka, Jpn. J. Appl. Phys. **29**, L915 (1990).

[6] P. K. Narwankar, M. R. Chandrachood, D. E. Morris, and A. P. B. Sinha, Appl. Phys. Lett. **58**, 651 (1991).

[7] R. G. Buckley, J. L. Tallon, D. M. Pooke, and M. R. Presland, Physica C **156**, 391 (1990).

[8] D. E. Morris, J. H. Nicel, J. Y. T. Wei, Naggi. G. Asmar, J. S. Scott, U. M. Scheven, C. T. Hultgren, A. G. Markelz, J. E. Post, P. J. Heaney, D. R. Veblen, and R. M. Hazen, Phys. Rev. B **39**, 7347 (1989).

[9] H. B. Liu and D. E. Morris, Phys. Rev. B **44**, 5369 (1991).

[10] J. M. Tarascon, W. R. Mckinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, Phys. Rev. B **36**, 226 (1987).

[11] Morris Research, Inc., 1918 University Ave. Berkeley, CA 94704.

[12] H. D. Yang, P. F. Chen, C. R. Hsu, C. W. Lee, C. L. Li, and C. C. Peng, Phys. Rev. B **43**, 10568 (1991).

[13] *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989), p. 303.

[14] M. C. Chandrachood, P. K. Narwankar, D. E. Morris, and G. Kwei (unpublished).