

STRONG DEPENDENCE OF SUPERCONDUCTING TRANSITION TEMPERATURE (T_c) ON THE RARE EARTH IONIC SIZE IN REBaSrCu₃O₇ (RE = Y, Dy, Nd AND La) SERIES

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The REBaSrCu₃O₇ compounds with RE = Y, Dy, Nd and La have been synthesized by the standard solid-state reaction route. Superconducting transition temperatures (T_c), as measured by ac susceptibility technique, are 81 K, 79 K, 62 K and 45 K for samples with RE = Y, Dy, Nd and La, respectively. The rare earth dependence of T_c in the REBaSrCu₃O₇ series is quite different from that observed in the REBa₂Cu₃O₇ (RE:123) series where T_c is nearly independent of the choice of the RE (except when RE = Ce, Pr and Tb). Neutron diffraction studies have been carried out on the REBaSrCu₃O₇ compounds and structural details have been obtained from the Rietveld analysis of the room-temperature neutron diffraction data. The compounds with RE = Y, Dy are found to crystallize in the orthorhombic RE:123 structure (space group Pmmm) with orthorhombicity considerably smaller than that of the RE:123 compounds. In fact, the orthorhombicity reduces so much that the REBaSrCu₃O₇ compounds with light rare earths, RE = La and Nd, are tetragonal or almost tetragonal.

1. Introduction

There are several RE (rare earth)-based high temperature superconductor (HTSC) families of compounds. These include REBa₂Cu₃O₇ (RE:123), REBa₂Cu₄O₈ (RE:124) and RE₂Ba₄Cu₇O₁₄ (RE:247)^{1–3} compounds. The RE-based RE:123, RE:124 and RE:247 superconductors are known for all rare earths except Ce, Pr and Tb. While Ce and Tb do not form the required structure, the case of Pr is unique due to its magnetic interaction with neighboring Cu–O conduction band.^{4,5} The superconducting transition temperature (T_c) for all RE:123 compounds is almost similarly independent of the choice of the RE ion^{1,2} (with the exceptions noted

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above). In RE:124 and RE:247 compounds, the T_c is found to be somewhat dependent on the ionic radius of the host RE. For example, the T_c of Y:124 is typically about 80 K, but is only around 70 K for Nd:124 (Refs. 6 and 7). It is observed that the lower the ionic size of the host RE, the higher is the T_c . Similarly, this is the case in the RE:247 series.^{1-3,6,7} The ionic size of the host RE also plays a role in the T_c suppression due to Pr in RE_{1-x}Pr_x:123 compounds.^{8,9} Some recent reports also indicate that the T_c depression due to 3d metal substitutions at the Cu-site in RE:123 compounds is also host RE dependent.¹⁰ It is worth mentioning here that RE ions in RE:123, RE:124 and RE:247 systems remain in the trivalent state. This necessarily means that in stoichiometric, optimally oxygen-doped compounds of these families, charge neutrality would require that the level of p-type carriers in them remains the same for a particular family independent of the RE. A relatively less explored RE-based family of superconducting compounds is the REBaCaCu₃O₇ family called RE:1113. This family is unique in terms of phase formation and crystal structure. Unlike RE:123 and RE:124 compounds, the RE:1113 compounds form only with lighter rare earths such as La, Pr and Nd.¹¹ Moreover, the RE:1113 compounds crystallize in a tetragonal structure with an oxygen content close to 7.0 (Refs. 12-14). In this series of compounds, the T_c is also strongly dependent on the host RE. For example, the T_c of La:1113 is typically 70 K, but is only 40 K for Nd:1113 (Ref. 11).

In this paper, we discuss the structural details of another series of less explored RE:123-type compounds with the general formula REBaSrCu₃O₇. In this series, YBaSrCu₃O₇ has been reported to crystallize in the orthorhombic RE:123 structure with a T_c of around 82 K.¹⁵⁻¹⁷ We selected RE = Y, Dy, Nd and La in the REBaSrCu₃O₇ series as some representatives to cover nearly the entire lanthanide series, in order to look for T_c dependence on different REs in this series. Further, we have carried out detailed structural studies on all the samples through Rietveld analysis of the room-temperature powder neutron diffraction data. Results of superconductivity and structural details of REBaSrCu₃O₇ compounds are presented and discussed in this paper.

2. Experimental Details

Samples of the series REBaSrCu₃O₇ (RE = Y, Dy, Nd and La) were synthesized through a solid-state reaction route. The ingredients Y₂O₃, Dy₂O₃, Nd₂O₃, La₂O₃, BaCO₃, SrCO₃, and CuO of 99.99% purity were thoroughly mixed in the required proportions for each sample and calcined between 900° and 970°C in air for a period of 24 hours each, in steps of 10°C with intermediate grindings at each stage. The resulting powders were ground, mixed, pelletized and annealed in flowing oxygen at 950°C for a period of 24 hours, and then furnace cooled to room temperature with an intervening annealing for 16 hours at 600°C. AC susceptibility measurements were carried out in the temperature range of 4.2-300 K using a Quantum Design SQUID magnetometer in an applied rms field of 0.01 mT at a frequency of 117 Hz. Neutron

diffraction patterns at room temperature were obtained at the research reactor facility of the University of Missouri using neutrons of wavelength 1.4875 Å. The experimental details are reported elsewhere.¹⁸ The diffraction data were collected from 5° to 105° (rebinned at 0.05° intervals), using a 5-element position-sensitive array covering an angle of 20° at a time.

3. Results and Discussion

3.1. AC susceptibility

Figure 1 depicts the ac susceptibility (χ_{ac}) versus temperature plots for REBaSrCu₃O₇ samples with RE = Y, Dy, Nd and La. The superconducting transition temperatures (T_c), defined as the onset of diamagnetic transition, are nearly 81 K, 79 K, 62 K and 45 K for Y, Dy, Nd and La samples, respectively. The T_c for all the samples is also seen clearly from the distinct single peak in the imaginary part of the ac susceptibility measurements (upper part of Fig. 1). A T_c of about 82 K has been widely reported for a YBaSrCu₃O₇ compound.^{15–17} Our present T_c of around 81 K for the same compound is in good agreement with this result. Among the four samples investigated in this study, T_c is lowest for the La sample (45 K) and goes up to 81 K in a systematic way as one moves from La (larger ionic size) to Y (lowest ionic size). For the NdBaSrCu₃O₇ sample, we found a T_c of around 62 K. For this compound, the T_c values of 74 K and 58 K are reported respectively in Refs. 19 and 20. In both cases, the samples were annealed in flowing oxygen at 450°C for 48 hours.^{19,20} Later, it was observed that a T_c of up to 75 K can be achieved in this compound by heating the sample in argon prior to oxygen annealing.²¹ All the samples of composition NdBaSrCu₃O₇ discussed above, with their T_c values ranging from 58 to 75 K do have interestingly same oxygen contents close to 7.0 and similar lattice parameters.^{19–21} The wide range of T_c variation of about 20 K, without any change in oxygen content (no change in p-type carriers) for NdBaSrCu₃O₇ compound, goes against the so-called universal relation between T_c and the number of p-type carriers,²² about which the pitfalls are already pointed out earlier.^{23,24} As discussed briefly in Ref. 21, the reordering of oxygen sites in Cu–O chains might be the cause for such a change in T_c without changing the p-type carriers. In the present study, we have followed a similar annealing procedure for all the samples to guarantee their comparison with each other. In fact, even in the case of the widely understood RE:123 compounds, conflicting results are reported, where T_c is either enhanced^{25–27} or lowered^{28–31} between 92 and 99 K with an increase in rare earth ionic radius (moving from Er:123 to La:123). Interestingly, in the case of RE:124, there is an agreement, at least for the time being, among different research groups, that T_c goes down from rare earths with smaller ionic radius to their bigger ionic size counterparts,^{6,7,32} the same is true about RE:247.^{7,33}

In Fig. 2, we plot the T_c values obtained from χ_{ac} data shown in Fig. 1 against the ionic radius of the corresponding RE³⁺ in their existing coordination number of eight in the RE:123 structure (ionic radius are taken from Ref. 34). For

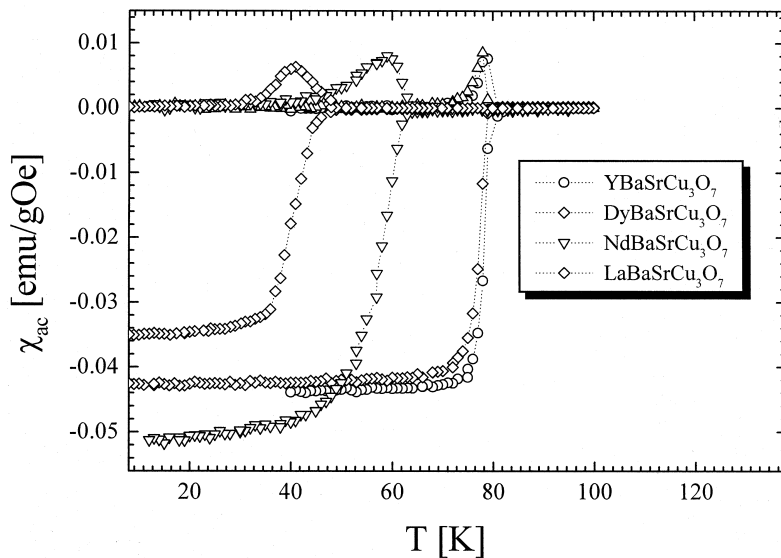


Fig. 1. AC susceptibility versus temperature plots for REBaSrCu₃O₇ (RE = Y, Dy, Nd and La) compounds.

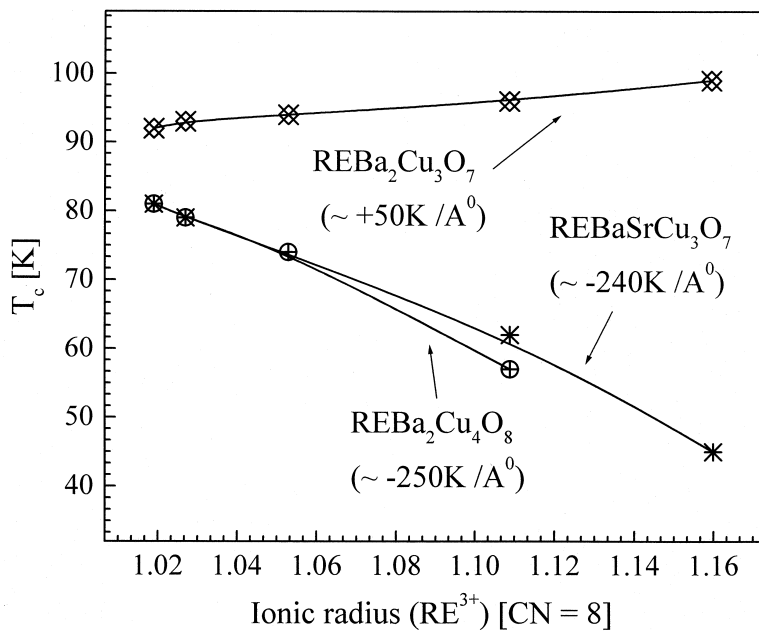


Fig. 2. Rare earth (RE) ionic size versus T_c plots for the RE:123, RE:124 and REBaSrCu₃O₇ systems.

comparison, we also include the reported T_c data on RE:123 (as mentioned in earlier paragraph, conflicting reports do exist, so we pick up comparatively recent data from Ref. 27) and RE:124 (Ref. 32) compounds. Data for RE:247 is similar to that as of RE:124, and data for RE:1113 (REBaCaCu₃O₇) is not included because in this series, the RE substitutes at both the Ba and the nominal RE sites with the two different coordination numbers. In the case of RE:123, RE:124 and REBaSrCu₃O₇ compounds, the RE stays with full occupancy between two Cu–O planes with the same coordination number of eight. Hence, for these three systems, the ionic radius of RE remains the same due to the same chemical environment of RE in these structures which facilitates comparison of their T_c values as a function of RE ionic radius from one series to another. It is clear from Fig. 2, that among the systems discussed, the change in T_c with rare earth ionic radius (dT_c/dr_{RE}) is ~ 50 K/Å for RE:123, ~ -250 K/Å for RE:124 and ~ -240 K/Å for the REBaSrCu₃O₇ system. In fact, for RE:123 compounds, the RE ionic size dependence of T_c is least, but positive. For other RE-based HTSC compounds, viz. RE:124, 247 and the presently studied REBaSrCu₃O₇, the dT_c/dr_{RE} values are negative. Also, for RE:123 compounds, the ionic size dependence of T_c is opposite to that as observed for other families, viz. RE:124, 247 and the presently studied REBaSrCu₃O₇ compounds.

3.2. Neutron diffraction

The REBaSrCu₃O₇ compounds with RE = Y, Dy, La and Nd crystallize in the orthorhombic structure (space group Pmmm). In the orthorhombic RE:123 structure, the RE cation resides between the copper–oxygen sheets of the double layer in an eightfold coordination with oxygen. Barium ions are located above and below these Cu–O₂ sheets. The BaO/CuO₂/RE/CuO₂/BaO slabs are interconnected by a sheet of Cu and O atoms with variable composition CuO_{*x*}. The oxygen sites in the Cu–O₂ planes are identified as O(2) and O(3). The O(2) resides between two Cu atoms along *a*-axis while the one towards the *b*-axis is named O(3) site. The copper atoms in the Cu–O₂ planes are denoted as Cu(2) while those in the CuO_{*x*} chains are named as Cu(1). In an orthorhombic RE:123-type compound, the *b*-axis is larger than *a*, resulting in Cu(2)–O(3) > Cu(2)–O(2). In the tetragonal RE:123 structure, both O(2) and O(3) become identical, resulting in *a* = *b* or Cu(2)–O(2) = Cu(2)–O(3). The oxygen site in the Ba–O plane is named as O(4), while the RE-plane is found to be devoid of any oxygen. The oxygen sites in the CuO_{*x*} strings, often called as Cu–O chains, are named as O(5) (along *a*-axis) and O(1) (along *b*-axis) sites. In orthorhombic RE:123, O(1) sites are nearly fully occupied, while O(5) sites are nearly unoccupied, giving rise to *b* > *a*. The RE:123 system can become tetragonal either by removing oxygen from the O(1) site (RE:123 oxygen deficient, oxygen < 7.0) or by filling the O(5) site (which can be achieved by Fe, Co, Ga, Nb, V, etc. substitutions at the Cu(1) site), often resulting in oxygen > 7.0 (Ref. 35). Besides this, an interesting situation can occur through redistribution of oxygen at the O(1) and O(5) sites with oxygen content close to 7.0, which is

the case for the presently studied (Nd or La)BaSrCu₃O₇ compounds. In the tetragonal RE:123 system with $a = b$, the O(1) and O(5) sites are indistinguishable and the same is true for O(2) and O(3) in the Cu–O₂ planes.

After giving details of the orthorhombic and tetragonal general structures of RE:123 compounds, we will now discuss the results of the presently studied REBaSrCu₃O₇ compounds. The neutron diffraction data were analyzed by the Rietveld refinement procedure using the generalized structural analysis system (GSAS) program and the pseudo-Voigt peak shape functions. Neutron scattering cross-sections used were (in units of fm) 7.75 for Y, 8.03 for Er, 7.69 for Nd, 8.27 for La, 5.25 for Ba, 7.202 for Sr, 7.72 for Cu and 5.81 for oxygen. The initial refinement of the neutron diffraction data for all the compounds was carried out in the orthorhombic structure (space group Pmmm). For the Y- and Dy-containing compounds, a good fit to the orthorhombic structure is obtained with considerably reduced orthorhombicity. Earlier, for a YBaSrCu₃O₇ compound, an orthorhombic symmetry is reported.^{15–17} The orthorhombicity reduces so much that the samples with RE = Nd and La may be considered tetragonal or pseudotetragonal.

In fact, due to the near tetragonal structure of La and Nd compounds, the refinement is unstable in the orthorhombic space group for these two compounds. For Nd compound, a tetragonal symmetry is reported earlier in the literature.^{19–21} In particular, the O(1) and O(5) occupancies, though close to each other, show large standard deviations in the Pmmm space group. Therefore, these were constrained to be equal (which is what it would be in the tetragonal structure), after which these were refined with much smaller standard deviation. For instance, in LaBaSrCu₃O₇, O(1) and O(5) occupancies in Pmmm space groups yield values of 0.52(18) and 0.48(18), respectively, but refined to 0.51(1) in P4/mmm space group. In the case of Nd compound, the refinement in Pmmm space group yields a and b lattice parameters equal to 3.8682(23) and 3.8693(24), respectively, after which the refinement becomes unstable and shows oscillations. Due to the closeness of a and b , the data on this compound were finally refined in the tetragonal space group P4/mmm in which the convergence was readily achieved. Some of the oxygen thermal parameters were ill behaved in some of the compounds and were constrained to the values obtained in other compounds of the same series. It is also worth mentioning here that unlike the REBa₂Cu₃O₇ system, the RESr₂Cu₃O₇-type compounds are formed only under high pressure and high temperature heat treatment.³⁵ The presently studied composition of REBaSrCu₃O₇ is intermediate to REBa₂Cu₃O₇ and RESr₂Cu₃O₇ and shows the presence of small amounts of secondary phase(s). High pressure oxygenation may be required to avoid formation of these secondary phases. In our analysis, we have included RE₂BaCuO₅ and RE₂O₃ phases as impurities in all the samples, and for Y, Nd and La counterparts, further inclusion of BaCuO₂ is invoked.

In Figs. 3 and 4, we show the observed and fitted neutron diffraction patterns of all the four presently studied REBaSrCu₃O₇ compounds (RE = Y, Dy, Nd and La).

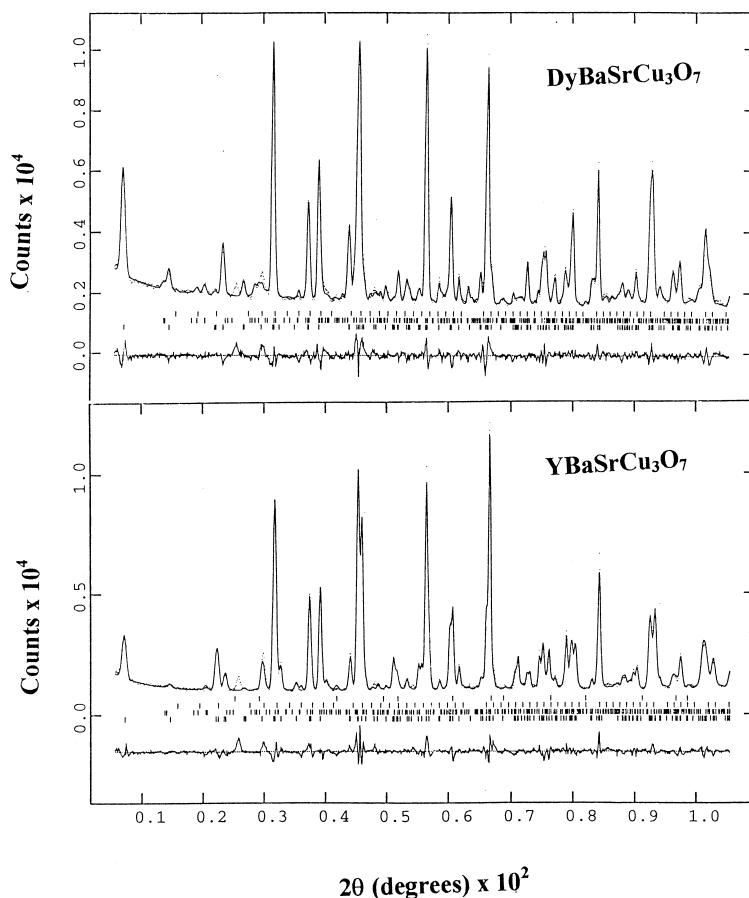


Fig. 3. Observed and fitted neutron diffractions for $REBaSrCu_3O_7$ ($RE = Y, Dy$) compounds. The line positions marked (starting from the bottom) are for RE_2BaCuO_5 , $REBaSrCu_3O_7$, RE_2O_3 and $BaCuO_2$ compounds, respectively.

The structural parameters obtained from the fits are listed in Tables 1–4 for various samples. For La and Nd compounds, we present the results in the $Pmmm$ space group with $a \cong b$ and $O(1)$ occupancy equal to $O(5)$ occupancy. The oxygen content obtained from the refinement of the data is close to 7.0 for all the compounds, being 7.07 for Y, 7.03 for Dy, 7.02 for La and 7.04 for Nd. Oxygen content of close to 7.0 has earlier been reported for Y and Nd counterparts.^{15–17,19–21} It is interesting that while the oxygen content is nearly the same in all the four $REBaSrCu_3O_7$ compounds, the two with $RE = La$ and Nd are nearly tetragonal while those with $RE = Y$ and Dy are orthorhombic, albeit with reduced orthorhombicity. As we discussed earlier, the orthorhombic to tetragonal phase transition takes place in the RE:123 structure either with substantial decrease/increase in oxygen content from 7.0, or with rearrangement of the $O(1)$ and $O(5)$ site occupancies in the Cu–O

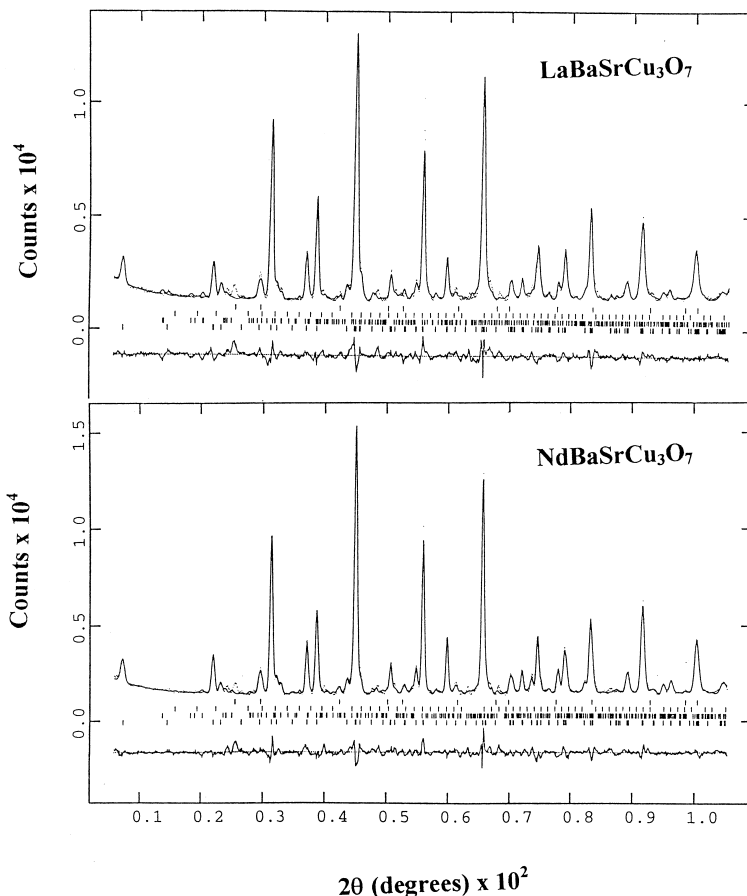


Fig. 4. Observed and fitted neutron diffractions for REBaSrCu₃O₇ (RE = Nd, La) compounds. The line positions marked (starting from the bottom) are for RE₂BaCuO₅, REBaSrCu₃O₇, RE₂O₃ and BaCuO₂ compounds, respectively.

chains, making Cu(1)–O(1) = Cu(1)–O(5), resulting in $a = b$, with indistinguishable O(1) and O(5) occupancies. Because the oxygen content is nearly the same in all the samples, it is obvious to think that in the case of Nd and La samples, a rearrangement of O(1) and O(5) takes place in such a way that these site occupancies are nearly equal, resulting in a tetragonal structure for NdBaSrCu₃O₇ and LaBaSrCu₃O₇ compounds. A similar situation has been recently observed by some of us for LaBaCaCu₃O₇ (Ref. 14). However, in this compound, it is the mixing of Ca, Ba and La which brings the occupancies of O(1) and O(5) closer to each other, resulting in a tetragonal system despite an oxygen content close to 7.0. In the present case of Nd- and La-based RSBCO compounds, this possibility is ruled out. Though Nd and La can partially occupy the Ba site in the RE:123 structure, the possibility of Ba or Sr finding a place between the two Cu–O₂ planes is rather

Table 1. Structural parameters for YBaSrCu₃O₇, Wyckoff positions in the space group Pmmm, atomic coordinates, x , y , z , fractional site occupancies and the isotropic thermal parameters (U_{iso}). The numbers in parenthesis are the estimated standard deviations in the last digit(s). The lattice parameters are $a = 3.8040(2)$ Å, $b = 3.8502(3)$ Å and $c = 11.5829(9)$ Å. Those parameters, for which no standard deviation is given, were held fixed during the analysis.

Atom	Wyckoff position	x	y	z	Fractional site occupancy	$100 \times U_{\text{iso}}$ (Å) ²
Y	1h	0.5	0.5	0.5	1.0	0.7(1)
Sr	2t	0.5	0.5	0.18473(31)	0.5	1.7(1)
Ba	2t	0.5	0.5	0.18473(31)	0.5	1.7(1)
Cu(1)	1a	0.0	0.0	0.0	1.0	1.2(1)
Cu(2)	2q	0.0	0.0	0.35321(23)	1.0	0.4(1)
O(1)	1e	0.0	0.5	0.0	0.83(2)	5.4(4)
O(5)	1b	0.5	0.0	0.0	0.24(2)	5.4(4)
O(2)	2s	0.5	0.0	0.37655(18)	1.0	0.7(1)
O(3)	2r	0.0	0.5	0.37655(18)	1.0	0.7(1)
O(4)	2q	0.0	0.0	0.16064(37)	1.0	2.1(1)

$$wR_p = 0.0601, R_p = 0.0446 \text{ and total oxygen content} = 7.07(4).$$

Table 2. Structural parameters for DyBaSrCu₃O₇, Wyckoff positions in the space group Pmmm, atomic coordinates, x , y , z , fractional site occupancies and the isotropic thermal parameters (U_{iso}). The numbers in parenthesis are the estimated standard deviations in the last digit(s). The lattice parameters are $a = 3.8175(2)$ Å, $b = 3.8390(3)$ Å, $c = 11.5713(7)$ Å. Those parameters, for which no standard deviation is given, were held fixed during the analysis.

Atom	Wyckoff position	x	y	z	Fractional site occupancy	$100 \times U_{\text{iso}}$ (Å) ²
Dy	1h	0.5	0.5	0.5	1.0	1.0(1)
Sr	2t	0.5	0.5	0.18615(40)	0.5	1.3(2)
Ba	2t	0.5	0.5	0.18615(38)	0.5	1.3(2)
Cu(1)	1a	0.0	0.0	0.0	1.0	0.2(1)
Cu(2)	2q	0.0	0.0	0.35313(35)	1.0	0.2(1)
O(1)	1e	0.0	0.5	0.0	0.61(4)	5.0
O(5)	1b	0.5	0.0	0.0	0.42(4)	5.0
O(2)	2s	0.5	0.0	0.37615(26)	1.0	0.4(1)
O(3)	2r	0.0	0.5	0.37615(26)	1.0	0.4(1)
O(4)	2q	0.0	0.0	0.15993(54)	1.0	1.8(2)

$$wR_p = 0.0455, R_p = 0.0338 \text{ and total oxygen content} = 7.03(8).$$

remote. Also, the Rietveld analysis of neutron diffraction data shows full occupancy of the normal RE site by Nd and La in the RE:123 structure. It is worth mentioning that Sr at the Ba site in the RE:123 structure is next to the Cu–O chains where

Table 3. Structural parameters for NdBaSrCu₃O₇, Wyckoff positions in the space group Pmmm, atomic coordinates, x , y , z , fractional site occupancies and the isotropic thermal parameters (U_{iso}). The numbers in parenthesis are the estimated standard deviations in the last digit(s). The lattice parameters are $a = 3.8682(23)$ Å, $b = 3.8686(24)$ Å and $c = 11.6352(11)$ Å. Those parameters, for which no standard deviation is given, were held fixed during the analysis.

Atom	Wyckoff position	x	y	z	Fractional site occupancy	$100 \times U_{\text{iso}}$ (Å) ²
Nd	1h	0.5	0.5	0.5	1.0	0.3(1)
Sr	2t	0.5	0.5	0.18330(39)	0.5	0.9(1)
Ba	2t	0.5	0.5	0.18330(39)	0.5	0.9(1)
Cu(1)	1a	0.0	0.0	0.0	1.0	1.6(2)
Cu(2)	2q	0.0	0.0	0.34909(37)	1.0	0.6(1)
O(1)	1e	0.0	0.5	0.0	0.52(1)	5.1(5)
O(5)	1b	0.5	0.0	0.0	0.52(1)	5.1(5)
O(2)	2s	0.5	0.0	0.36602(30)	1.0	1.0(1)
O(3)	2r	0.0	0.5	0.36602(30)	1.0	1.0(1)
O(4)	2q	0.0	0.0	0.15919(62)	1.0	3.3(2)

$wR_p = 0.0581$, $R_p = 0.0454$ and total oxygen content = 7.04(2).

Table 4. Structural parameters for LaBaSrCu₃O₇, Wyckoff positions in the space group P4/mmm, atomic coordinates, x , y , z , fractional site occupancies and the isotropic thermal parameters (U_{iso}). The numbers in parenthesis are the estimated standard deviations in the last digit(s). The lattice parameters are $a = 3.8754(8)$ Å, $b = 3.8830(9)$ Å and $c = 11.6989(15)$ Å. Those parameters, for which no standard deviation is given, were held fixed during the analysis.

Atom	Wyckoff position	x	y	z	Fractional site occupancy	$100 \times U_{\text{iso}}$ (Å) ²
La	1h	0.5	0.5	0.5	0.89(1)	0.02
Sr	2t	0.5	0.5	0.18295(46)	0.5	0.8(2)
Ba	2t	0.5	0.5	0.18295(46)	0.5	0.8(2)
Cu(1)	1a	0.0	0.0	0.0	1.0	1.6(2)
Cu(2)	2q	0.0	0.0	0.34605(51)	1.0	0.7(1)
O(1)	1e	0.0	0.5	0.0	0.51(1)	5.0
O(5)	1b	0.5	0.0	0.0	0.51(1)	5.0
O(2)	2s	0.5	0.0	0.36064(45)	1.0	1.4(1)
O(3)	2r	0.0	0.5	0.36064(45)	1.0	1.4(1)
O(4)	2q	0.0	0.0	0.15710(81)	1.0	2.6(2)

$wR_p = 0.0676$, $R_p = 0.0509$ and total oxygen content = 7.02(2).

oxygen reordering takes place. This reordering seems to be influenced by the ionic size of the rare earth ion and is more for larger ionic size rare earths, La and Nd. As far as YBaSrCu₃O₇ is concerned, its orthorhombic distortion is less than that

observed in fully oxygenated Y:123 and this is in good agreement with other reports on this compound.¹⁵⁻¹⁷

4. Summary and Conclusions

Compounds in the series REBaSrCu₃O₇ (RE = Y, Dy, Nd, and La) have been synthesized. The superconducting transition temperature (T_c) of REBaSrCu₃O₇ series is substantially less for lighter (larger ion size) rare earths than that for heavier rare earths (Y, Dy). The strong ionic size dependence of T_c for REBaSrCu₃O₇ with various REs is a unique property of this system. The samples in the REBaSrCu₃O₇ series crystallize in the orthorhombic RE:123 structure for RE = Y and Dy, and tetragonal or near tetragonal RE:123 structure for RE = La and Nd, with oxygen content close to 7.0 for all of them.

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References

1. H. Oesterreicher and M. Smith, *Mater. Res. Bull.* **22**, 1709 (1987).
2. L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre and I. K. Schuller, *Nature* **328**, 604 (1987).
3. J. Herrmann, U.-C. Boehnke, M. Krotzsch and B. Lippold, *Physica* **C221**, 76 (1994).
4. A. Kebede, C.-S. Jee, J. Schwegler, J. E. Crow, T. Mihalisin, G. H. Myer, R. E. Salomon, P. Schlottmann, M. V. Kuric, S. H. Bloom and R. P. Guertin, *Phys. Rev.* **B40**, 4453 (1989).
5. See, for instance, S. K. Malik and C. V. Tomy, in *Physical and Material Properties of High Temperature Superconductors*, eds. S. K. Malik and S. S. Shah (Nova Science, New York, 1994), p. 283.
6. S. K. Agarwal, R. Lal, V. P. S. Awana, S. P. Pandey and A. V. Narlikar, *Phys. Rev.* **B50**, 10265 (1994).
7. R. G. Buckley, J. L. Tallon, D. M. Pooke and M. R. Presland, *Physica* **C165**, 391 (1990).
8. Y. H. Xu and W. Y. Guan, *Phys. Rev.* **B45**, 3176 (1992).
9. S. K. Malik, C. V. Tomy and P. Bhargava, *Phys. Rev.* **B44**, 7042 (1991).
10. S. S. Ata-Allah, Y. H. Xu and Ch. Heiden, *Physica* **C221**, 39 (1994).
11. R. Singh, A. V. Narlikar, V. P. S. Awana, J. Horvat and S. X. Dou, *Physica* **C301**, 48 (1998).
12. W. T. Fu, H. W. Zandbergen, C. J. Vander Beek and L. J. de Jongh, *Physica* **C156**, 133 (1988).
13. J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, P. A. Hahn, L. Bernardez and M. Costantino, *Phys. Rev.* **B39**, 9074 (1989).

14. V. P. S. Awana, O. F. de Lima, S. K. Malik, W. B. Yelon and A. V. Narlikar, *Physica* **C314**, 93 (1999).
15. C. Mitros, V. Psycharis, A. Koufoudalis, H. Gamri-seale and D. Niarchos, *J. Less-Common Mat.* **164&165**, 892 (1990).
16. A. Das and R. Suryanarayanan, *J. Physique* **15**, 623 (1995).
17. J. M. Liang, L. Chang, H. M. Sung, P. T. Wu and L. J. Chen, *J. Appl. Phys.* **64**, 3593 (1988).
18. V. P. S. Awana, S. K. Malik and W. B. Yelon, *Physica* **C262**, 272 (1996).
19. X. Z. Wang, B. Hellerbrand and D. Bauerele, *Physica* **C200**, 12 (1992).
20. V. Badri, U. Varadaraju and G. V. Subba Rao, in *Physical and Material Properties of High Temperature Superconductors*, eds. S. K. Malik and S. S. Shah (Nova Science, New York), to be published.
21. R. Suryanarayanan, A. Nafidi and A. Das, *J. Appl. Phys.* **76**, 598 (1994).
22. H. Zhang and H. Sato, *Phys. Rev. Lett.* **70**, 1693 (1993).
23. V. P. S. Awana and A. V. Narlikar, *Phys. Rev. Lett.* **71**, 303 (1993).
24. D. Goldshmidt, Y. Direkovitch, A. Knizhnik and Y. Eckestein, *Phys. Rev. Lett.* **71**, 3392 (1993).
25. H. Saked, B. W. Veal, J. Faber, R. L. Hitterman, U. Balachandran, G. Tomlins, H. Shi, L. Morss and A. P. Paulikas, *Phys. Rev.* **B41**, 4173 (1990).
26. T. B. Lindemer, B. C. Chakoumakos, E. D. Specht, R. K. Williams and Y.J. Chen, *Physica* **C231**, 80 (1994).
27. G. V. M. Williams and J. L. Tallon, *Physica* **C258**, 41 (1996).
28. Z. Henkie, T. Cichorek, H. Drulis and J. Klamut, *Physica* **C214**, 138 (1993).
29. P. H. Hor, R. L. Meng, Y. Q. Wang, La. Gao, Z. J. Huang, J. Bechtold, K. Foster and C. W. Chu, *Phys. Rev. Lett.* **58**, 1891 (1987).
30. M. J. Kramer, S. I. Yoo, R. W. Callum, W. B. Yelon, H. Xie and P. Allenspach, *Physica* **C219**, 145 (1994).
31. A. V. Narlikar, S. K. Agarwal and C. V. Narsimha Rao, in *Studies of High Temperature Superconductors*, ed. A. Narlikar (NOVA Science Pubs., New York, 1989), p. 343.
32. D. E. Morris, J. H. Nickel, J. Y. T. Wei, N. G. Asmar, J. S. Scott, U. M. Scheven, C. T. Hultgren, A. G. Markelz, J. E. Post, P. S. Heaney, D. R. Veblen and R. M. Hazen, *Phys. Rev.* **B39**, 7347 (1989).
33. T.-M. Chen, Y.-L. Lai and F. S. Kao, *Physica* **C282-287**, 789 (1997).
34. R. D. Shannon, *Acta Cryst.* **A32**, 751 (1976).
35. J. M. Tarascon and B. G. Bagley, in *Chemistry of High Temperature Superconductors*, ed. T. A. Vanderah (NOYES Publishers, New York, 1993), p. 310.
36. B. Okai, *Jpn. J. Appl. Phys.* **29**, L2180 (1990).