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Revival of superconductivity by Y^{3+}/Ca^{2+} substitution in $YBa_2Cu_{2.7}Co_{0.3}O_7$ without reported phase transformation

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Results of phase formation, resistivity (ρ), and thermoelectric power (S), are reported on $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ compounds with $x=0.1$ and 0.2 . Pristine compound, i.e., without Co or Ca substitution crystallizes in orthorhombic structure with space-group P/mmm . The Cu-site Co substituted compound, i.e., $YBa_2Cu_{2.7}Co_{0.3}O_7$ is tetragonal. With simultaneous doping of Ca at the Y site in Co substituted compound, i.e., $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ the tetragonal nature still remains. $\rho(T)$ measurements showed superconducting transition temperature (T_c) to decrease from 90 K ($YBa_2Cu_3O_7$) to 33 K for $YBa_2Cu_{2.7}Co_{0.3}O_7$, which with further Ca substitution increases from 33 to 53 K ($Y_{0.9}Ca_{0.1}Ba_2Cu_{2.7}Co_{0.3}O_7$) and 67 K for $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.7}Co_{0.3}O_7$. T_c decreases first with Cu-site Co substitution by hole filling and later recovers by simultaneous hole creation by Y site Ca substitution. Room temperature thermoelectric power S (300 K), which is an indirect measure of mobile carriers shows the decrease of carriers with Co doping and creation by Ca substitution. Our results demonstrate the hole filling by Co substitution is compensated by simultaneous Ca substitution. © 2005 American Institute of Physics. [DOI: 10.1063/1.1850383]

I. INTRODUCTION

Various on-site substitutional studies in high T_c superconducting (HTSc) compounds has attracted a lot of attention, for example, Ref. 1 and references there in. Basically all HTSc compounds in their ground state are antiferromagnetic insulators with Cu spins ordering above room temperature.¹ By doping of carriers through charge neutrality with various on-site aliovalent substitutions or oxygen content, one frustrates the Cu magnetic ordering and brings in the metallic behavior accompanied with superconductivity at low temperatures.¹ Phase diagrams are drawn in terms of doped carriers on the basis of mentioned substitutional studies for different HTSc families.^{1,2}

In a p -type (most HTSc compounds except a few) conductor higher valent on-site substitutions fill the mobile holes and decreases both conductivity and superconductivity of the parent system. The examples are Ba^{2+} site La^{3+} , Sm^{3+} , Pr^{3+} , and Cu^{2+} site Co^{3+} , Fe^{3+} , La^{3+} , Ru^{5+} substitutions in $YBa_2Cu_3O_7$ compound.¹⁻³ On the other hand, in a p -type conductor the lower valent on-site substitutions, viz. Y^{3+} site Ca^{2+} increases the carriers and improves the superconductivity of an under-doped system.^{4,5} This is however the most simplistic picture being given above. In reality with various aliovalent substitutions, the induction or reduction of carriers is accompanied with various structural changes and also

the charge neutrality is not as straight forward as the overall oxygen content of the system changes.^{6,7} For example, in the $Y_{1-x}Ca_xBa_2Cu_3O_7$ system, some of the carriers being introduced by Y^{3+}/Ca^{2+} substitution are compensated by a decrease in the overall oxygen content of the system,^{6,7} which is not the case when the parent system is under-doped viz. $Y_{1-x}Ca_xBa_2Cu_3O_{6.6}$.^{4,5} Hole filling by higher or hole creation by lower valent substitutions independently have been studied extensively over the years.⁴⁻⁷ At the same time, substitutional studies pertaining to simultaneous hole filling and hole creation in a composite HTSc system are still not fully explored.^{8,9} Moreover, in such a composite system viz. $Y_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_7$, the structural changes with both hole creating (Y^{3+}/Ca^{2+}) and hole filling (Cu^{2+}/Co^{3+}) taking place simultaneously might be complicated. In this short article we report the phenomenon of hole filling and hole creation in a composite system $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ compounds with $x=0.1$ and 0.2 . More interestingly we report the revival of superconductivity by Y^{3+}/Ca^{2+} substitution in $YBa_2Cu_{2.7}Co_{0.3}O_7$ without reported⁹ phase transformation. The results of phase formation [x-ray diffraction (XRD)], resistivity (ρ), and thermoelectric power (S), are reported on $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ compounds with $x=0.1$ and 0.2 .

II. EXPERIMENT

Samples of a $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ system with $x=0.1$ and 0.2 synthesized by solid-state reaction route from ingredients of Y_2O_3 , $CaCO_3$, $BaCO_3$, CuO , and Co_3O_4 . Cal-

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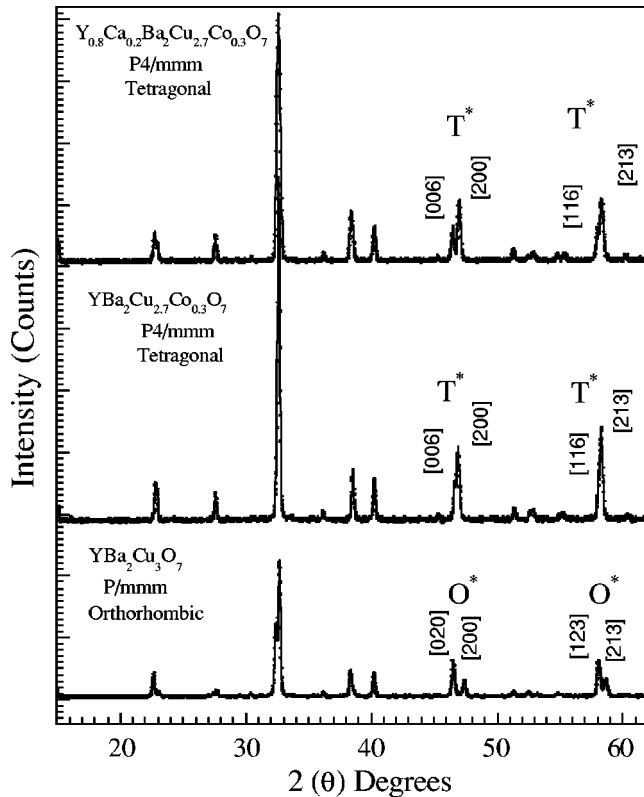


FIG. 1. XRD patterns for $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ system.

cinations were carried out on the mixed powder at 900, 910, 915, and 925 °C each for 24 h with intermediate grindings. The pressed circular pellets were annealed in a flow of oxygen at 920 °C for 40 h and subsequently cooled slowly to room temperature with an intervening annealing for 24 h at 600 °C. X-ray diffraction (XRD) patterns were obtained at room temperature (MAC Science: MXP18VAHF²²; $K\alpha$ radiation). Resistivity measurements were carried out by a conventional four-probe method. Thermoelectric power (TEP) measurements were carried out by a dc differential technique over a temperature range of 5–300 K, using a homemade setup. Temperature gradient of ~ 1 K is maintained throughout the measurement.

III. RESULTS AND DISCUSSION

Room temperature x-ray diffraction (XRD) patterns of $YBa_2Cu_3O_7$, $YBa_2Cu_{2.7}Co_{0.3}O_7$, and $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.7}Co_{0.3}O_7$ are shown in Fig. 1. A pristine $YBa_2Cu_3O_7$ (Y:123) system is orthorhombic with $a = 3.826(5)$ Å, $b = 3.892(4)$ Å, and $c = 11.6734(7)$ Å.

In Y: 123-type compounds, a sheet of Cu and O atoms with variable composition CuO_x interconnects the BaO/CuO₂/Y/CuO₂/BaO slabs. The oxygen sites in Cu–O₂ planes are identified as O (2) and O (3). The O (2) resides between two Cu atoms along the a axis, while the one toward the b axis is named the O (3) site. The copper atoms in Cu–O₂ planes are termed Cu (2), while in CuO_{*x*} chains are named Cu (1). 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 CuO_{*x*} strings, often called Cu–O chains, are named O (5) (along the a axis) and O (1)

(along the b axis) sites. In orthorhombic Y:123, O(1) are fully occupied, while O(5) are unoccupied, giving rise to $b > a$. With 10% Co doping at Cu-site, i.e., $YBa_2Cu_{2.7}Co_{0.3}O_7$ both a and b lattice parameters become equal and the system turns to be tetragonal with $a=b=3.856(4)$ Å and $c = 11.6637(8)$ Å. With Co substitution at the Cu site in Y:123 the c -lattice parameter is decreased, due to lower ion $Co^{2+/3+}$ ion substitution at the Cu^{2+} site. This result is in agreement with previous reports on Cu/Co substitution.^{1–3,9} The explanation for tetragonal structure is the occupation of otherwise unfilled O(5) sites in CuO_{*x*} chains. The orthorhombic or the tetragonal structure of the Y:123 system can be identified by looking at some characteristic peaks intensity and nature of splitting. For an orthorhombic system, at $2(\theta)$ around 47.6° and 58.3° the split peaks appear with high-intensity, low-angle and low-intensity, high-angle sequence having indices [020], [200] and [123], [213], respectively. This is the case for the $YBa_2Cu_3O_7$ sample, see, bottom XRD in Fig. 1. As the orthorhombic distortion of the system decreases the split peaks start merging with each other. Interestingly when system becomes tetragonal the split peaks sequence of angle and intensity reverses. For tetragonal Y:123, though the sequence at $2(\theta)$ around 47.6° and 58.3° becomes low-intensity, low-angle and high intensity, high angle with indexing of [006], [200] and [116], [213], respectively. Please see middle XRD in Fig. 1 for $YBa_2Cu_{2.7}Co_{0.3}O_7$. When the splitting of these peaks is not clear, one has to deconvolute them and carry out the Reitveld analysis to confirm the structure. In the present case, as the splitting of these characteristic peaks is clear, the need for deconvolution or the Reitveld analysis is not necessary. The XRD of the $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.7}Co_{0.3}O_7$ compound is shown in the top part of Fig. 1. As seen from the splitting nature characteristic peaks in the XRD pattern the compound is tetragonal. According to some previous reports,⁹ Y^{3+}/Ca^{2+} substitution in the tetragonal $YBa_2Cu_{3-y}Co_yO_7$ system had brought about the tetragonal to orthorhombic phase transformation. On the contrary our XRD results clearly show that the $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.7}Co_{0.3}O_7$ compound is tetragonal.

With Co substitution at the Cu site in Y:123, the c -lattice parameter is decreased, due to lower ion $Co^{2+/3+}$ ion substitution at the Cu^{2+} site.¹ The lattice parameters for $x=0.10$ and 0.20 samples of series $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ are, respectively, $a=b=3.843(5)$ Å, $c=11.6691(9)$ Å, and $a=b=3.838(4)$ Å, $c=11.6703(8)$ Å, respectively. With Ca substitution in $YBa_2Cu_{2.7}Co_{0.3}O_7$, the a -lattice parameter has a slight decreasing trend. This is due to the fact that though the a -lattice parameter is supposed to increase slightly due to relatively bigger ion Ca substitution, the increasing number of carriers due to Y^{3+}/Ca^{2+} substitution decrease the in-plane Cu(2)–O(2) distance and hence the former effect is nullified. It is known that increasing p -type carriers in HTSC compounds increase the hybridization of the in-plane Cu($3d$) and O($2p$) orbitals resulting in a decrease both in Cu(2)–O(2) distance and the a -lattice parameter.¹⁰ The c -lattice parameter of Co doped samples increase monotonically with increasing x , indicating successful substitution of Y^{3+} by bigger ion Ca^{2+} . The ionic size of Ca^{2+} in the eightfold coordination number is 1.12 Å, while that of Y^{3+} in the same coordination is 1.02 Å. The system remains tetragonal over

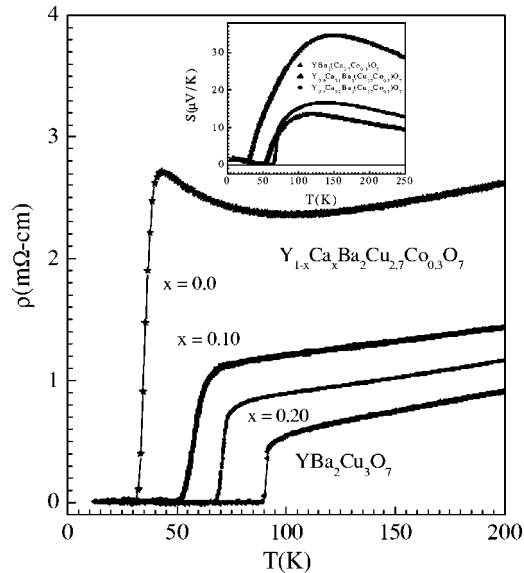


FIG. 2. $\rho(T)$ for $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ system, inset shows $S(T)$ for the same.

the whole range of doping (20% of Ca^{2+} at Y^{3+}). Monotonic increase of the c -lattice parameter with x in $Y_{1-x}Ca_xBa_2Cu_3O_7$ system guarantees the substitution of Ca^{2+} at Y^{3+} site in the same coordination number of eight.^{6,7}

Figure 2 depicts the resistivity versus temperature (ρ versus T) behavior of the $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ compounds with $x=0.1$ and 0.2 . $\rho(T)$ measurements showed superconducting transition temperature (T_c) to decrease from 90 K ($YBa_2Cu_3O_7$) to 33 K for $YBa_2Cu_{2.7}Co_{0.3}O_7$, which with further Ca substitution increases from 33 K to 53 K ($Y_{0.9}Ca_{0.1}Ba_2Cu_{2.7}Co_{0.3}O_7$) and 67 K for $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.7}Co_{0.3}O_7$. T_c decreases first with Cu-site Co substitution by hole filling and later recovers by simultaneous hole creation by Y^{3+} site Ca^{2+} substitution. $\rho_{300\text{ K}}$ is least for pristine the $YBa_2Cu_3O_7$ sample and highest for the $YBa_2Cu_{2.7}Co_{0.3}O_7$ sample. This shows that with $Co^{2+/3+}$ ion substitution at Cu^{2+} the hole filling had taken place and hence the normal state resistivity is increased. With Y^{3+} site Ca^{2+} substitution in $YBa_2Cu_{2.7}Co_{0.3}O_7$ the $\rho_{300\text{ K}}$ is decreased, suggesting the creation of mobile holes in the system. Besides the T_c and $\rho_{300\text{ K}}$ values, the normal state conduction is semiconductor-like for $YBa_2Cu_{2.7}Co_{0.3}O_7$ and it changes to metallic with further Y^{3+} site Ca^{2+} substitution. Interestingly though the Y^{3+} site Ca^{2+} substitution in underdoped (due to hole filling) $YBa_2Cu_{2.7}Co_{0.3}O_7$ compound revives superconductivity by increasing T_c , decreasing $\rho_{300\text{ K}}$ and improving normal state conduction, but the same is not reached to the level of $YBa_2Cu_3O_7$. This shows that the hole filling ($Co^{2+/3+}$ ion substitution at Cu^{2+}) and hole creation (Y^{3+} site Ca^{2+} substitution) either do not compensate completely with each other, or there are other negative effects taking place simultaneously.

The results of thermoelectric power (S) measurements on $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ with $x=0.0, 0.10$, and 0.20 are shown in inset of Fig. 2. The value of S at room temperature (290 K) is found to be positive for all the samples, indicating

them to be predominantly hole- (p) type conductors. $S_{290\text{ K}}$ is least for $YBa_2Cu_3O_7$ ($\sim 6\text{ }\mu\text{V/K}$, plot not shown) and maximum ($\sim 30\text{ }\mu\text{V/K}$) for $YBa_2Cu_{2.7}Co_{0.3}O_7$. Further, the value of $S_{290\text{ K}}$ decreases with x for $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$. Implying that the number of mobile p -type carriers increase with an increase in x for $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ system. For strongly correlated systems the absolute value of S is reported to be inversely proportional to the number of mobile carriers.¹¹ However this may not be the fact in all the situations, and should be considered with reservations.¹² For example though in the $x=0.20$ sample of presently studied $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ series, the overall number of carriers is more, but its $S_{290\text{ K}}$ value ($\sim 12\text{ }\mu\text{V/K}$) is also more than as for $x=0.10$ ($\sim 10\text{ }\mu\text{V/K}$). Yet the general convention holds that decreasing the value of S implicates for an increase in mobile carriers. Further with decreasing temperature S passes through a maximum (S_{max}) and later starts decreasing with a further decrease in temperature. The temperature corresponding to S_{max} , i.e., $T(S_{\text{max}})$ decreases monotonically with increasing x . Thermoelectric power measurements below $T(S_{\text{max}})$, exhibit transitions to $T_c^{S=0}$ at around 90, 29, 51, and 65 K, respectively, for $YBa_2Cu_3O_7$, $YBa_2Cu_{2.7}Co_{0.3}O_7$, $Y_{0.9}Ca_{0.1}Ba_2Cu_{2.7}Co_{0.3}O_7$, and $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.7}Co_{0.3}O_7$ samples. In brief, one can conclude that thermoelectric power measurements corroborate the resistance versus temperature results shown in Fig. 2.

IV. CONCLUSION

Results of phase formation, resistivity (ρ), and thermoelectric power (S), for $Y_{1-x}Ca_xBa_2Cu_{2.7}Co_{0.3}O_7$ compounds with $x=0.1$ and 0.2 , showed the revival of superconductivity by Y^{3+}/Ca^{2+} substitution in $YBa_2Cu_{2.7}Co_{0.3}O_7$ without previously reported phase transformation.

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