Influence of Cu-site substitution on La$_2$Ca$_1$Ba$_2$Cu$_5$O$_z$
superconducting system

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Abstract. We have prepared a series of La$_2$Ca$_1$Ba$_2$Cu$_{5-x}$Co$_x$O$_z$; x = 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 (La-2125) compounds by the standard solid state reaction method and characterized for their structural, superconducting, magnetic properties and oxygen content through X-ray diffraction, scanning electron microscopy, d. c. resistivity, magnetic susceptibility and iodometric titration respectively. All the compounds crystallize with the tetragonal LaBa$_2$Cu$_3$O$_z$ type structure, space group P4/mmm. Here the effect of higher Co substitution for Cu in the La$_2$Ca$_1$Ba$_2$Cu$_5$O$_z$ system has been studied. It is observed that only 2 at. % Co substitution for Cu destroys the superconductivity of the sample. For heavily doped samples (with x $\geq$ 0.1) are found non-superconducting presumably because of magnetic pair-breaking effect. These samples do not show superconductivity but are of interest for understanding the interplay between superconductivity and magnetism. Possible reasons for destruction of superconductivity are discussed in this communication.

1. Introduction
Since the discovery of high-$T_c$ cuprate superconductors [1], to understand the mechanism of superconductivity in high-$T_c$ oxides has been one of the most interesting research topics. Structurally there are many derivatives of R-123, made up by cation substitutions in the parent compound. Particular among them for the Ca-doped LaBa$_2$Cu$_3$O$_{7-\delta}$ compounds, where for a certain doping level of Ca, superconductivity appears along with the structural transition from orthorhombic to tetragonal [2]. The La$_2$Ca$_1$Ba$_2$Cu$_5$O$_z$ (La-2125) compound is obtained by the simultaneous addition of CaO and CuO to the non-superconducting LaBa$_2$Cu$_3$O$_z$, which has a tetragonal LaBa$_2$Cu$_3$O$_z$ (La-123) structure. The addition of CaO and CuO at the same time results in a superconducting compound with a $T_c$ of 79 K [3], which also has a structure similar to tetragonal La-123.

Substitutions at various crystallographic sites in the triple perovskite Y-123 structure has been a very popular approach of understanding the mechanism of superconductivity in these high temperature superconductors. The effect of substitution by various elements on the physical properties of RBa$_2$Cu$_3$O$_{7-\delta}$ (R=Y or rare-earth ion) superconductors have been studied to investigate the origin of superconductivity in such compounds. The $T_c$ of RBa$_2$Cu$_3$O$_{7-\delta}$ is not sensitive to rare-earth elements R [4]. Partial rare-earth substitution for La in La$_{2-x}$R$_x$Ca$_2$Ba$_2$Cu$_{4+2x}$O$_z$ also exhibits almost no effect on superconductivity [5], similar to the observations on rare-earth substituted R-123 systems [4], while the substitution of Fe$^{3+}$, Co$^{3+}$, Ni$^{2+}$, Zn$^{2+}$, Hf$^{4+}$, Mo$^{4+}$, etc. at the Cu site in R-123 suppresses the $T_c$ [6, 7, 8].
The valence state of the Cu ion is known to be higher than +2. Since a Co$^{3+}$ ion can be in either an S = 0 or 2 state, the substituted Co$^{3+}$ ion will work for removing spins from the two-dimensional CuO$_2$ planes and this may reduce the short-range correlations among Cu$^{2+}$ ions, having T$_c$ decrease as the Co content increases. Keeping mentioned facts in mind, we have initiated a systematic study of such kind of higher doping of Co at Cu site in La-2125 system for verifying the effect of magnetic Co using ρ-T, M(T) and grain growth measurements. Some systems like Y$_1$Ba$_2$(Cu$_{1-x}$Co$_x$)$_3$O$_{7-δ}$ and Bi$_2$(Sr$_{1-x}$Ca$_x$)$_2$(Cu$_{1-x}$Co$_x$)$_3$O$_{7-δ}$ are superconducting even when the Co content x is as high as 10 at. %. Therefore, the mechanism for annihilation of superconductivity in La$_2$Ca$_2$Cu$_{5-x}$Co$_x$O$_8$ with x = 0.1 - 5.0 samples should be different from these two systems [7, 9].

2. Experimental

All the samples of La$_2$Ca$_2$Ba$_2$Cu$_{5-x}$Co$_x$O$_8$ series (x = 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0) were prepared by standard solid state reaction method. The high purity (>99.9%) starting compounds of La$_2$O$_3$, CaCO$_3$, BaCO$_3$, CuO, CoC$_2$O$_4$•2H$_2$O were taken in the stoichiometric quantities and thoroughly ground under acetone using agate and mortar. The mixture was calcined at 940°C for 24h. The resultant black powder was then palletized and sintered at 950°C for 24h in muffle furnace and slowly cooled to room temperature. The sintered samples were then annealed at 500°C in flowing oxygen gas for 24h and then slowly cooled (1°C/min) to room temperature.

The structure and phase purity of synthesized samples were checked by powder X-ray diffraction (XRD). A JEOL JSM 5600 scanning electron microscope (SEM) was used to study the microstructure of the ceramic samples. The chemical composition was confirmed by energy dispersive analysis of X-ray (EDAX) for all the samples. Electrical resistivity was measured as a function of temperature (5-300 K) with the standard four-probe technique. Electrical contacts were made with silver paste. Magnetic susceptibility was measured as a function of temperature between 5 to 100 K. The oxygen content was determined by iodometric double titration method.

3. Results and Discussion

Figure 1 shows the Rietveld refined and indexed XRD patterns for the La$_2$Ca$_2$Ba$_2$Cu$_{5-x}$Co$_x$O$_8$ (x = 0.0, 0.1) system. The phase purity and structural characteristics of samples were confirmed by Rietveld analysis using the FULLPROF program on XRD data (λ = 1.5412 Å), based on the refined Wyckoff positions at room temperature. The pseudo-voight function was used to analyze the peak profiles. The analysis of XRD pattern shows that x = 0.0 sample exhibit tetragonal structure with the space group P4/mmm. All the samples retain tetragonal structure without transforming to the orthorhombic structure, whereas structural transition from orthorhombic to tetragonal have been observed for the Co-doped Y-123 at a Co concentration of x ~ 0.025 [10]. For x = 0.1 and above samples, small amount of secondary phase is detected and may be identified as La-Cu-Co compound phase. The amount of the secondary phases increased with increasing Co-doping. Tellez et al. found that the Co, Ga, Ni substitution takes place isostructurally at Cu-site in CaLaBaCu$_7$O$_{17}$ compound at least up to 8 at. % of the substituent concentration in the material, where as in La-2125 limit is below 2 at.% [11].

Figure 1. Rietveld refined XRD Plots for La$_2$Ca$_2$Ba$_2$Cu$_{5-x}$Co$_x$O$_8$ (x = 0.0, 0.1)
Table 1 shows values for the lattice constants – $a$, $c$ and the unit cell volume $V$, with respect to the Co content $x$. For the lower substitution ($x = 0.1 - 2.0$), the value of $a$, $c$, and $V$ are remains almost level off to constant but increases for the higher substitution ($x = 5.0$). The increment in $a$ and $V$ for the higher substitution suggests Co$^{3+}$ ion is in its high-spin configuration state. This is due to the ionic radius of Co$^{3+}$ ion for high-spin state ($r = 0.061\text{nm}$) is larger than that of Cu$^{2+}$ ion ($r = 0.057\text{nm}$) \[12\].

Table 1. Values of $a = b$, $c$, $V$, X-ray density and oxygen content $z$ for La$_2$Ca$_1$Ba$_2$Cu$_{5-x}$Co$_x$O$_z$ ($x = 0.0 - 5.0$).

| Concentration ($x$) | Unit cell parameters | X-Ray Density (g/cm$^3$) | Oxygen Content ($z$) |
|---------------------|----------------------|--------------------------|---------------------|
|                     | $a = b$ (Å$^3$) | $c$ (Å$^3$) | $V$ (Å$^3$) |                     |
| 0.0                 | 3.869               | 11.641          | 174.21        | 10.46               | 11.75               |
| 0.1                 | 3.931               | 11.635          | 179.79        | 10.09               | 11.45               |
| 0.2                 | 3.923               | 11.614          | 178.73        | 10.12               | 11.29               |
| 0.5                 | 3.899               | 11.392          | 173.18        | 10.48               | 11.54               |
| 1.0                 | 3.882               | 11.359          | 171.17        | 10.54               | 11.32               |
| 2.0                 | 3.909               | 11.381          | 173.90        | 10.35               | 11.42               |
| 5.0                 | 5.450               | 13.680          | 406.33        | 4.38                | 11.54               |

Figure 2 shows the SEM micrographs for $x = 0.1$, 1.0, 5.0. The microstructure of the heat-treated pellets shows a uniform grain growth but does not show dense packing of individual particles during heat treatments. The homogeneous packing of tiny crystallites aggregates favours a high sintering activity in the samples. It is also observed that the major phase in the samples is La-2125 with well shaped grains. Microstructure of $x = 5.0$ shows comparatively smaller grain size than the $x = 0.1$ sample and segregation is observed. The staff gauge is 1µm.

Figure 3 shows the temperature dependence of resistivity of the La$_2$Ca$_1$Ba$_2$Cu$_{5-x}$Co$_x$O$_z$ ($x = 0.0, 0.1, 0.5, 5.0$) samples from 5 K to 300 K in the warming process. Resistivity for $x = 0.0$ shows $T_c$ onset at about 79 K. For $x = 0.1 - 5.0$, resistivity of each of the Co-doped samples increases with decreasing temperature and shows no superconducting transition between 5 and 300 K, even when the Co content $x$ is as low as 0.1. Here, only 2 at. % Co substitution for Cu in La-2125 system destroys superconductivity.

The magnetic property is measured for magnetic moment as a function of temperature. As shown in figure 4(a), for $x = 0.0$, the magnetic susceptibility measured at field of 500 Oe in the zero field cooled (ZFC) and field cooled (FC) states. As superconducting nature is observed in resistivity measurement for this sample, it exhibits diamagnetic signals near to transition temperature. FC-ZFC fork is also observed near transition temperature. Figure 4(b) shows the substitution of 2 at. % Co at Cu site results in the onset of magnetism in this compound. The plot of $M$ vs $T$ exhibits a broad transition from paramagnetic to antiferromagnetic state around 20 K. This fact indicates that in La-2125 compound, the substitution of a magnetic ion (Co$^{3+}$) at Cu site results in annihilation of superconductivity and at the same time results in the onset of magnetism. Oxygen content was determined through iodometric double titration method and values are listed in table 1.
4. Conclusions
The effect of substitution of 3d metal Co for Cu in a high temperature superconductor La-2125 was investigated by measuring lattice constant, dc resistivity, magnetic susceptibility, iodometric titration in normal and superconducting states. Superconducting state was observed only in pure copper compound. Only 2 at. % Co substitution at Cu-site in La$_2$Ca$_1$Ba$_2$Cu$_{5-x}$Co$_x$O$_z$ samples destroys superconductivity. Such annihilation of superconductivity presumably because of large local paramagnetic moments in the Co element which results into pair braking and high spin state of the Co ions may cause such destruction. However, at the same time the 2 at. % Co at Cu site induces the magnetism in this compound.

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6. References
[1] Bednorz J and Muller K 1986 Z. Phys. B 64 189
[2] Gu H, Fung K, Wei C, Zhang J, and Yin D 1993 Physica C 208 391
[3] Mankadia S, Dalsantiya S, Okram G, Igalwar P, Gonal M and Bhalodia J 2011 Proc. Of 55th DAE SSPS 2010 (Manipal) 1349 (American Institute of Physics) p 893
[4] Hor P, Meng R, Wang Y, Gao L, Huang Z, Bechtold J, Forster K and Chu W 1987 Phys. Rev. Lett. 58 1891
[5] Rayaprol S, Mavami K, Rana D, Thakar C, Thampi R, Kuberkar D, Kulkarni R and Malik S 2002 J. Supercond. 15 211
[6] Kulkarni R, Kuberkar D, Baldha G, Bichile G 1993 Physica C 217 175
[7] Maeda A, Yabe T, Takebayashi S, Hase M and Uchinokura K 1990 Phys. Rev. B 41 4112
[8] Bhalodia J, Shaikh A, Kuberkar D, Baldha G and Kulkarni R 1994 Mater. Res. Bull. 29 89
[9] Sonntag R, Hohlwein D, Hoser A, Prandl W, Schifer W, Kiemel R, Kemmlersake S, Losch S, Schlichenmaier M and Hewat A 1989 Physica C 159 141
[10] Wu X, Pan F, Huang X, Ye C, Jin X and Jiang S 1996 J. Mater. Sci. 31 6113
[11] Tellez D and Aguilar J 2001 J. Magn. Magn. Mater. 226 318
[12] Shannon R 1976 Acta Crystallogr. Sect. A. 32 751

Figure 3. Resistivity Vs temperature curves for x = 0.0, 0.1, 0.5 and 5.0 samples.

Figure 4. Magnetic susceptibility Vs. temperature for the samples La$_2$Ca$_1$Ba$_2$Cu$_{5-x}$Co$_x$O$_z$ (x = 0.0, 0.1).