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INFLUENCE OF Ca DOPING ON THE SUPERCONDUCTIVITY OF $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$

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ABSTRACT

Here, we report the effect of Ca doping on the superconducting transition temperature (T_c), crystal structure and microstructural properties of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x \leq 0.05$). It was found that the variation of c-axis lattice parameter remains almost constant. However, a slight decrease in both a and b axes are noticeable leading to the reduction of orthorhombicity of Y-123 phase. The superconducting transition temperature decreases with Ca^{2+} substitution at the Y^{3+}. The T_c of $YBa_2Cu_3O_{7-\delta}$ (Y-123) was reduced from 91 K for x = 0.00 to 84 K for x = 0.05. The degradation of T_c is attributed to the decrease in oxygen content in the CuO chains. The superconducting transition breadth, ΔT, increases with Ca substitution indicating the degradation of crystallinity or the presence of inhomogeneity. Changes in grain size and grain boundary were also observed by SEM. As the concentration of Ca increases, the grain size becomes larger giving rise to the reduction of porosity in the system.

Keywords: Y-123; Ca substitution; Orthorhombicity; superconducting transition temperature;

INTRODUCTION

Up to date, various superconducting materials have been discovered that show high superconducting transition temperature, T_c. They are useful for the development of advanced technologies for a wide range of applications. In particular, the discovery of superconductivity in $YBa_2Cu_3O_{7-\delta}$ (Y-123) has revolutionized solid state physics research as this material shows T_c above the boiling point of nitrogen (77K). The significance of the discovery of YBCO is the much lower cost of refrigerant used to cool the material below T_c. According to previous studies, it has been recognized that in the fully-oxygenated $YBa_2Cu_3O_{7-\delta}$, Ca doping on Y decreases T_c.

The rationale is that Ca doping changes the relative charge within the CuO_2 planes by reduction of oxygen content [1, 2]. The level of this charge can be verified either by control of oxygen vacancies in the Cu–O chain through application of pressure or by atomic substitution [3, 4]. Because of smaller valence of Ca^{2+} compared to Y^{3+}, Ca doping is likely to introduce mobile holes into the CuO_2 planes and substitution of Ca^{2+}

for every Y^{3+} ion enhances carrier concentration with 1/2 hole per plane [5]. In addition, the transport properties of YBCO can be improved by Ca doping as more holes are created near the grain boundaries. The strong elastic strain field around the grain boundaries has an important role in the segregation of dopants [6]. Recently, Haibin *et al*. [6] reported that Y^{3+} ions are replaced by Ca^{2+} ions accompanied by creating holes in the CuO_2 planes. With the increasing of hole content, the screening effect by mobile holes increases. The strong screening effect (much shorter screening length) helps to reduce the area of influence of the grain boundaries.

So far, most of the reported work on Ca doping in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ has focused on larger x ($x > 0.2$). In this study, we attempt to dope smaller range of x ($0.00 \leq x \leq 0.05$) on Y site. It is expected that smaller amount of Ca doping at Y site may lead to a smaller reduction of T_c while improving the electronic properties of microstructure especially at grain boundaries. The results on crystal structure and phase formation analysis as well as on the superconducting transition temperature are reported.

EXPERIMENTAL DETAILS

Solid state reaction technique was employed to produce a series of polycrystalline samples of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x = 0.00 - 0.05). The starting powders were Y_2O_3 (99.9%), $BaCO_3$ (99.8%), CuO (99.7%) and CaO (99.95%). All starting materials were mixed thoroughly according to the nominal stoichiometric ratio. Afterwards, the mixed powders were ground by using a mortar and a pestle for one hour. The well mixed powders were calcined at 950 ^oC for 24 hours air and were slowly cooled down to room temperature. The black shining powders were then crushed and pelletized at a pressure of 5 tons by using a hydraulic press. Then, the pellets were sintered at 950 ^oC for 12 hours in air, slowly cooled down to 450 ^oC for 24 hours sintering and then furnace cooled. Those powders were heated at 2 ^oC/ min while cooled down at 1 ^oC/ min as most materials are sensitive to the heating rate used.

The samples were characterized for their phase composition by powder x-ray diffraction (XRD) technique performed by using a Phillips x-ray diffractometer with Cu-K_α radiation source. The data was collected over the diffraction angle of $2\theta = 20^o - 80^o$ with a scanning step size of 0.033^o. X'Pert Highscore Plus software was used to analyze the lattice parameter variation. The change of resistance versus temperature was measured by using four point probe technique in order to determine the superconducting transition temperature T_c. In order to record the change in voltage as the temperature went down, a small current of 0.03 A was applied to the sample. $T_{c(R=0)}$ was defined as the superconducting transition temperature for the resistance to drop to zero. The microstructure and elemental composition of those samples were investigated by Scanning Electron Microscope (SEM-LEO 1455 VPSEM).

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RESULTS AND DISCUSSION

X-ray powder diffraction patterns for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ where $0.00 \leq x \leq 0.05$ is shown in Figure 1. The XRD patterns reveal that all the samples are single phase in nature and correspond to orthorhombic structure of Y(Ca):123 phase [5]. Peaks which can be related to the dominant phase of $YBa_2Cu_3O_{7-\delta}$ (Y-123) have been labeled as shown in Figure 1. However, there are a few peaks which do not fit the standard index indicating the existence of impurities in the YBCO samples. One of the common impurities is Y_2BaCuO_5 as has been reported earlier by various research groups. Figure 2 shows the dependence of a, b, and c lattice parameters on various Ca concentrations in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. The lattice parameter is directly related to the unit cell volume of the crystal structure. It is obvious that the variation of the structure of YBCO unit cell is very small with Ca substitution on Y.

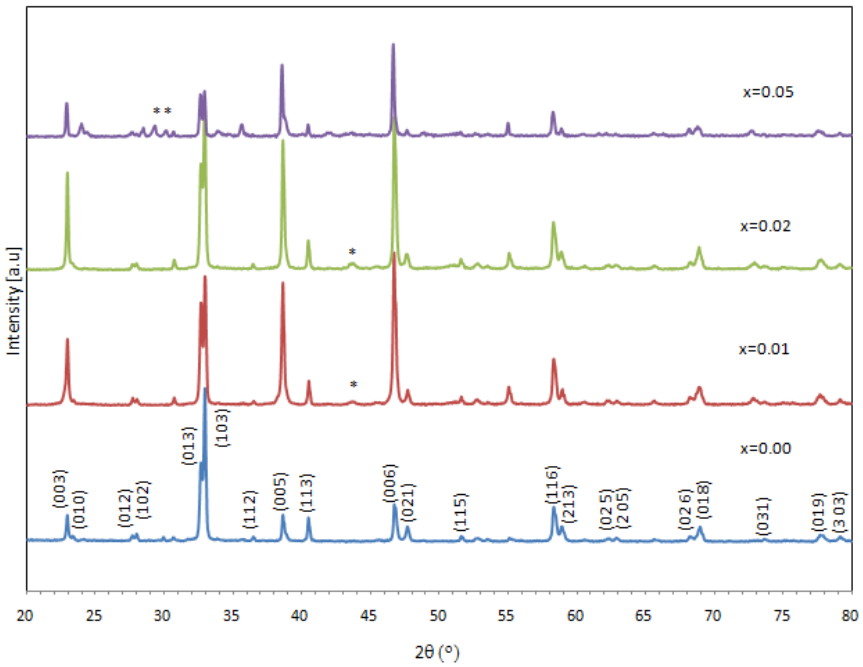

Figure 1: X-ray diffraction patterns for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ ($0.00 \leq x \leq 0.05$) samples

The change of lattice parameters of a, b, and c are insignificant in the whole doping range. It can be seen from Figure 2 that the lattice constants a and b decrease slightly with increasing Ca content while the lattice constant c remains nearly constant. Figure 3 shows that the decrease of a and b lattice constants by substitution of Ca in Y-sites reduces the orthorhombicity of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ system. The orthorhombicity of the structure as measured by (a-b)/(a+b), is calculated according to reference [5].

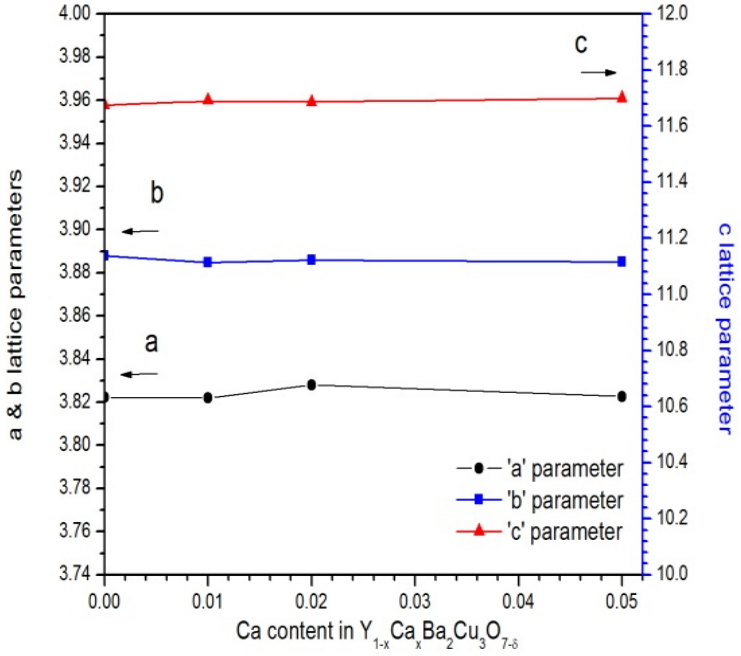

Figure 2: Evolution of lattice parameters versus Ca content for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, determine by Rietveld refinement of the x-ray powder diffraction data

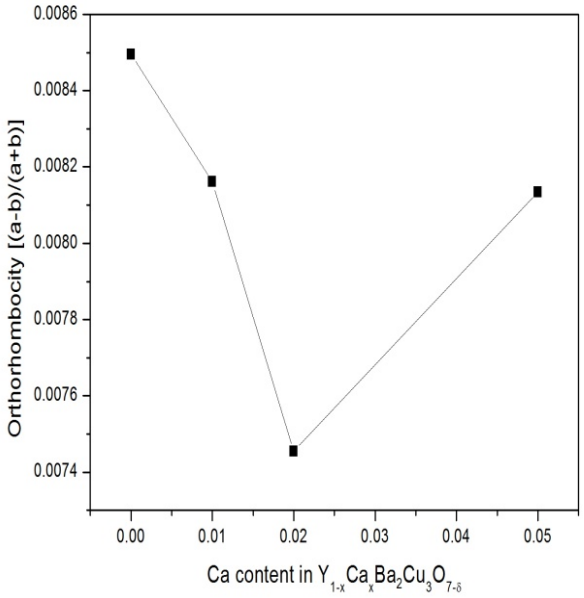

Figure 3: Dependence of orthorhombicity on Ca content for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ system

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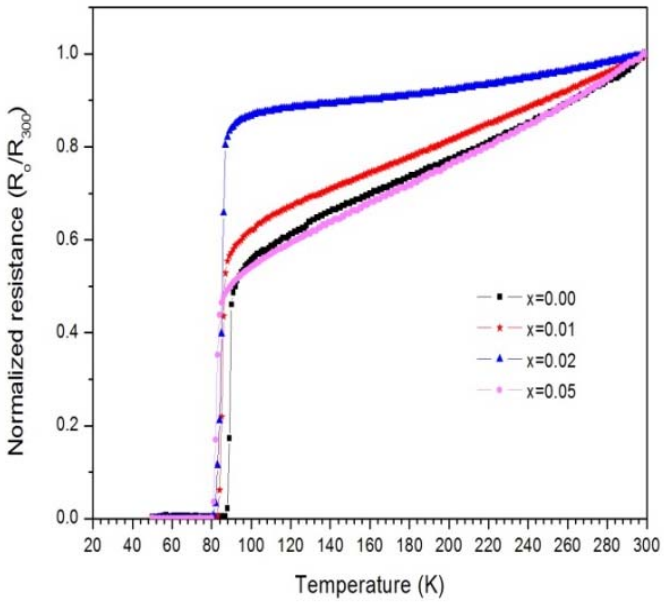

Figure 4: Normalized resistance versus temperature plots for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ system

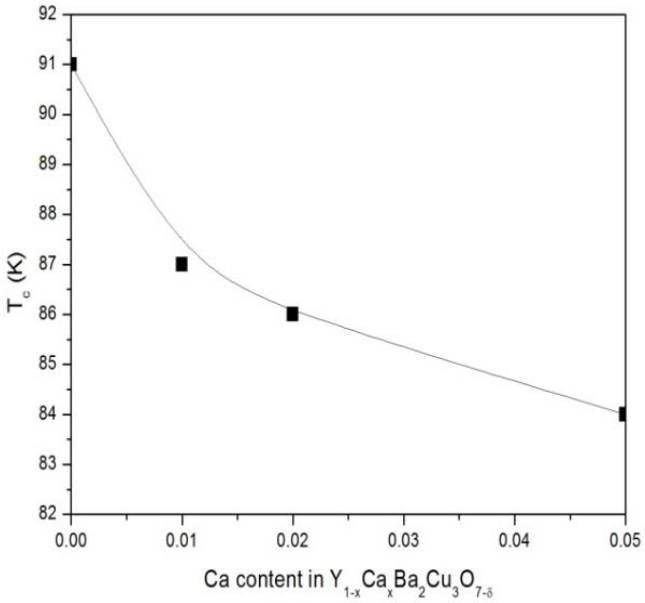

Figure 5: Variation in critical transition temperature (defined at zero resistance, $T_{c(R=0)}$) versus Ca content in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ system

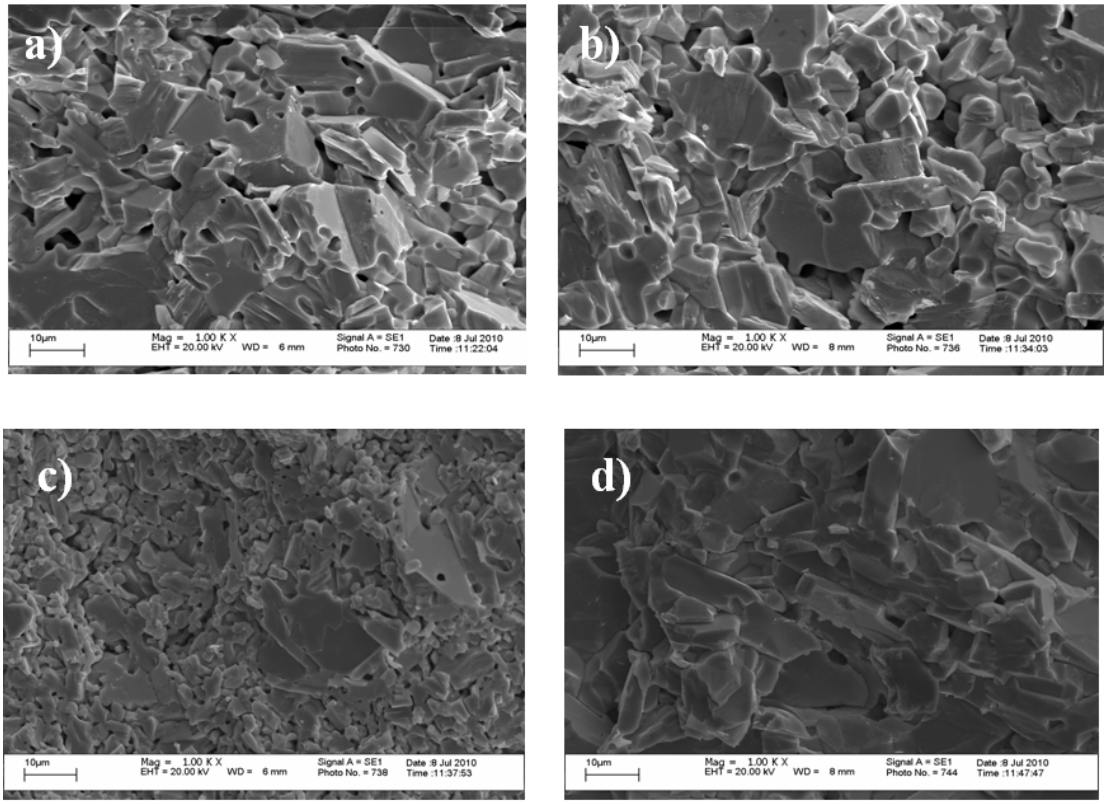

Figure 6: SEM micrographs of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ fracture surfaces with different Ca concentration (a) x=0.00, (b) x=0.01, (c) x=0.02, (d) x=0.05

Figure 4 shows the variation of normalized resistance versus temperature for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ samples (x = 0.00 - 0.05) in the temperature range of 50 K - 300 K. In normal state above the onset of T_c, all samples show metal-like behavior [5] with the resistance decreases as the temperature decreases. The pure sample of YBCO has the highest transition temperature $T_{c(R=0)}$ of 91 K. The decrease of transition temperature with the substitution of Ca^{2+} for Y^{3+} is shown in Figure 5. The degradation of T_c can be observed from samples $(Y_{0.99}Ca_{0.01})$:123, $(Y_{0.98}Ca_{0.02})$:123, and $(Y_{0.95}Ca_{0.05})$:123 which show $T_{c(R=0)}$ of 87 K, 86 K, and 84 K, respectively. Depression of T_c can be related to the decreasing of oxygen content in the CuO chain and also because of trapping of mobile holes due to oxygen vacancy disorder [6, 7]. In addition, the superconducting transition breadth, ΔT, increases with Ca substitution indicating inhomogeneity or degraded crystallinity of the samples.

The SEM micrographs for pure and substituted samples are shown in Figures 6 (a-d). As expected, for samples x=0.00 and x=0.01, the grains appear larger in size with noticeable porosity similar to x = 0.02. While for x = 0.05, the grain size became larger with less porosity indicating grain growth induced by Ca doping. Thus, bigger grain size would enhance continuity between grains by reducing the number of grain boundaries and thus diminish the porosity in the samples.

Solid State Science and Technology, Vol. 19, No2 (2011) 242-248
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CONCLUSION

Polycrystalline samples with nominal composition of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x = 0.00 – 0.05) were synthesized and their properties were evaluated in order to investigate the role of Ca doping on Y site in influencing the superconducting behavior. By increasing of Ca content, the reduction of orthorhombicity in YBCO is related to the slight decrease of 'a' and 'b' lattice parameters. A decrease of T_c with the increase in calcium content was observed. With the substitution of Ca^{2+} for Y^{3+}, the critical transition temperature decreases from 91 K for x= 0.00 to 84 K for x= 0.05. The superconducting transition breadth, ΔT, became wider with the increasing of Ca concentration. This can be related to the degradation of grain connectivity or sample inhomogeneity. Although Ca doping on Y sites introduces more holes as charge carrier, however this is suppressed by oxygen vacancy disorder. Finally, SEM micrographs revealed that Ca doping enhanced grain growth with improved link between grains.

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