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THE INFLUENCE OF Pr-Ca SUBSTITUTION ON PHASE FORMATION, MICROSTRUCTURE AND OXYGEN CONTENT IN *YBCO* BULK SAMPLES

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We have investigated Pr and Ca substitution for Y in $Y_{1-y}Pr_yBa_2Cu_3O_z$ and $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ bulk samples, where $x = 0.25$; 0.30 and $y = 0.04$; 0.05. The effects of this substitution on the phase formation, microstructure and oxygen content in these samples were studied. The observed dependences are discussed.

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Keywords: Pr, Ca substitution, Total oxygen content (z), Non-stoichiometric oxygen parameter (δ)

1. Introduction

Substitutions in the YBCO system are extensively interesting, because of the possibilities for improving the superconducting properties [1,2], structure and technical workability [3].

The substitution for Y by Ca decreases the *c*-parameter of the crystal lattice, while it increases the loss of oxygen and the distance between the Cu and O planes. As a result, the highest reported critical temperature for $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ is T_c = 80K [1]. This substitution generates additional carriers. It was observed that substituted YBCO is superconducting with T_c = 34K, while it is in a tetragonal phase with a total oxygen content $z = 6$ [4].

The investigation of the substitution of Pr on the Y-sites in the YBCO system addresses the question of the extent to which chemical elements with magnetic properties can exist in a particular superconducting sample, without damaging its superconductivity. Values of the critical current density, two orders of magnitude higher, have been obtained in $Y_{0.95}Pr_{0.05}Ba_2Cu_3O_z$ bulk samples [5]. This is due to the creation of magnetic pinning centers which have a stronger capability to pin Abrikosov vortices.

The current study estimates the optimal concentrations of substituted elements in $Y_{1-y}Pr_yBa_2Cu_3O_z$ and $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ bulk samples, having maximum values of the superconducting parameters. We treat this question from the maximum total oxygen content and the critical temperature, T_c.

2. Experimental details

2.1. Sample preparation

A series of $Y_{1-y}Pr_yBa_2Cu_3O_z$ and $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ samples ($x = 0.25$; 0.30, $y = 0.04$; 0.05) were prepared by a standard solid state reaction. The appropriate amounts of high purity (all 99.99% pure) powders of Y_2O_3, Pr_6O_{11}, $CaCO_3$, $BaCO_3$ and CuO were mixed, ground, pressed into

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pellets and calcinated in oxygen. The calcination was repeated three times. The first sintering was at 900 ºC, in flowing oxygen for 21h. After grinding, the powder was sintered at 930 ºC for the second time with the same atmosphere, followed by slow cooling and additional annealing at 450 ºC for 2h. The pellets were pressed at 5-6 MPa, sintered for a third time at 950 ºC for 23h, and subsequently annealed at 450 ºC for 23h.

2.2. Sample investigation

Standard X–ray power diffraction analysis with CoK_{α} radiation was used to investigate the material structure. The surface morphology of the samples was examined by scanning electron microscopy (SEM) and optical microscopy (OM), on a JEOL SSM-840A and a Nikon, Microphot-FX, respectively. The total oxygen content was obtained by the spectrophotometric method described previously [6]. It was determined as a sum of the oxygen stoichiometric and non-stoichiometric coefficients.

The critical temperature was obtained from resistivity measurements, by the four probe contact method.

3. Results

From the X-ray powder diffraction analysis, it is observed that we need a three stage sintering process and 90 h to obtain minimum secondary phases. The XRD spectra after the third sintering stage are shown in Fig. 1, for all samples.

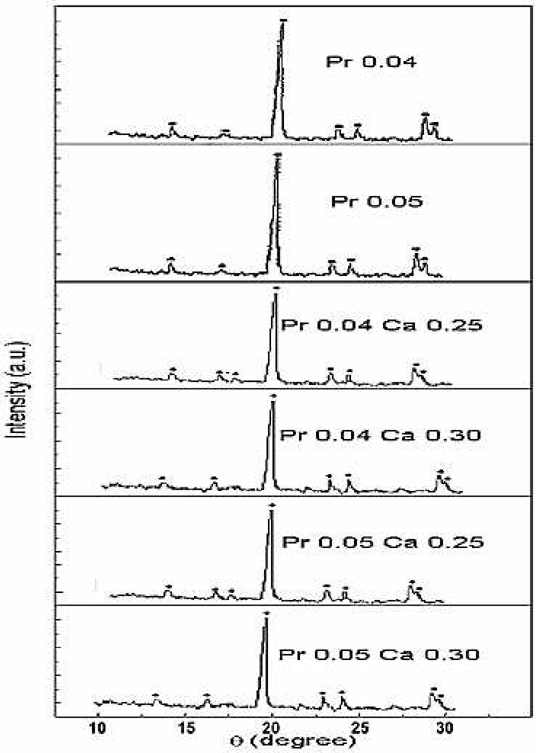

Fig. 1. XRD patterns using CoKα radiation for $Y_{1-y}Pr_yBa_2Cu_3O_z$ and $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ samples (x = 0.25; 0.30, y = 0.04; 0.05). The symbol (•) indicates main peaks of 1:2:3 $YBa_2Cu_3O_z$ phase.

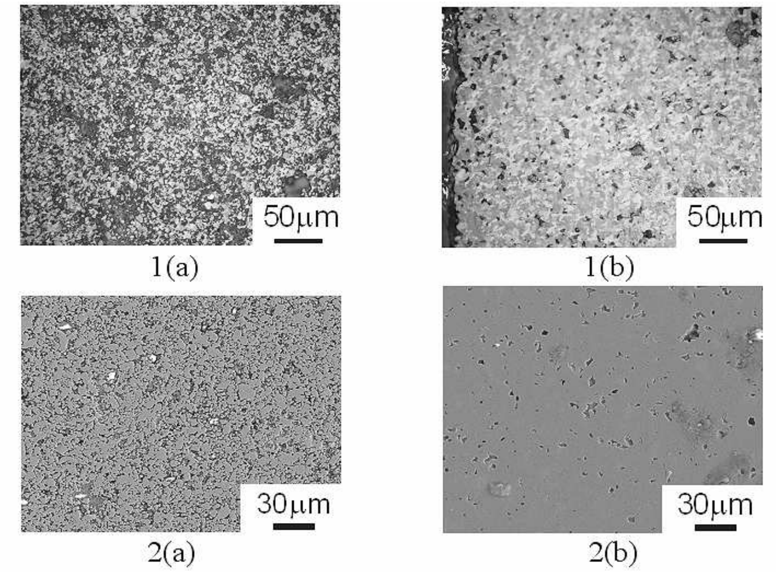

Fig. 2. OM and SEM data of $Y_{0.96}Pr_{0.04}Ba_2Cu_3O_z$ (1a, b) and $Y_{0.71}Ca_{0.25}Pr_{0.04}Ba_2Cu_3O_z$ (2a, b).

Typical optical microscopy and SEM photos of our samples are presented in Fig. 2. All results for experimental measurements of the oxygen content and critical temperature of our samples are presented in Table 1. The oxygen content dependence of the substituted concentration is shown in Fig. 3a. The curves are the best fits to our experimental data, plus data from [1]. The dependence of the substituted concentration for the $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ samples on the critical temperature is presented in Fig. 3b. This is a typical curve [2], from which we can estimate the value of $(x+y)$, for which the system has the optimal quantity of carriers and the highest critical temperature, T_c.

Table 1. Results for the oxygen coefficient in $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ samples.

x	y	Calculated value of the oxygen coefficient	Experimental value of δ	z	T_c [K]
0	0.04	6.500	0.42	6.920	91
0	0.05	6.500	0.46	6.960	90,8
0.25	0.05	6.375	0.43	6.805	78,5
0.30	0.05	6.365	0.47	6.835	77
0.25	0.04	6.375	0.43	6.805	77,6
0.30	0.04	6.350	0.48	6.830	77,2

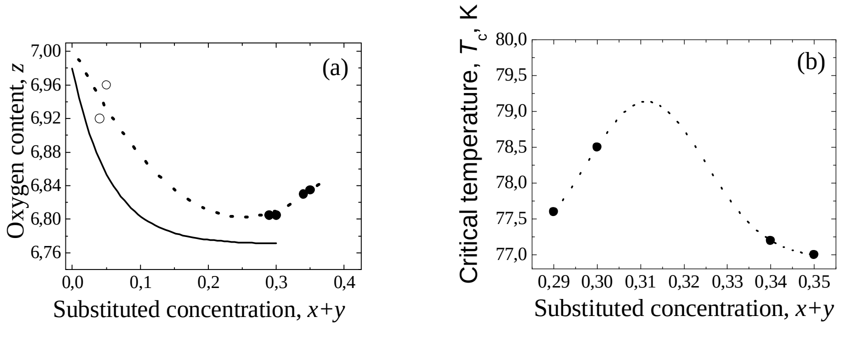

Fig. 3. Results for the oxygen content, z, (a) and critical temperature, T_c, (b) vs. doping concentration, $(x+y)$; $Y_{1-(x+y)}Ca_xPr_yBa_2Cu_3O_z$ (.), $Y_{1-y}Pr_yBa_2Cu_3O_z$ (o), the best fit to our data (...) and to the data from[1] (-).

4. Discussion

Upon introducing the Ca and Pr substitutions, we expect a different mechanism than that given in [1] for YCaBaCuO. In YCaBaCuO, there is an exponential decrease in the oxygen content with an increasing number of substituted ions (Fig. 3). This arises from the difference in the valence of Ca and Y atoms (Y- 3^+, Ca- 2^+). This is well explained by the bond valence sum rule [2]. In our case, we substitute Y by a Pr ion, which has the same 3^+ valence. Because of this, we do not expected any decrease in the oxygen content in YPrBCO samples, as is shown in (Table 1). Our $Y_{1-y}Pr_yBa_2Cu_3O_z$ samples have a T_c of around 91K (see Table 1).

The aim of Pr substitution is the creation of magnetic pinning centres for better pinning of Abrikosov vortices, because of its magnetic moment. This will increase the superconducting critical current density. The data for the critical current density of our samples $Y_{1-(x+y)}$ $Ca_xPr_yBa_2Cu_3O_z$ will be published elsewhere. The same effect is also expected from substitution by Ca atoms i.e. from doping with additional carriers. The great disadvantage of Pr substitution is the mechanism of localization of the carriers due to [1] the magnetic properties of the Pr atoms. This mechanism obviously limits the maximum substituted concentration in the studied material.

To solve this problem, we investigate $Y_{1-(x+y)}$ $Ca_xPr_yBa_2Cu_3O_z$, searching for optimal values of the substituted concentration which will give enhanced superconducting properties. In this case, we study the competition between these two mechanisms. From Fig. 3, one can see that different behaviours of the oxygen content fit functions of YCaBaCuO and YCaPrBaCuO actually occur, as we expected. The fit curve for YCaPrBaCuO does not decrease so dramatically as for YCaBaCuO. It is interesting to note that all samples with Pr substitution have higher total oxygen contents than samples with Ca substitution only.

As also shown in Table 1, we observed an unexpected fact that the non-stoichiometric coefficient, δ, is kept nearly constant for samples with Pr substitution only. The decrease in the total oxygen content comes only from the difference in the valence between Ca and Y, calculated by the bond valence sum. This might show that somehow the competition between additional and localized carriers leads to the over stoichiometric oxygen content.

From Fig. 3, we estimate the optimal substituted concentration ($x+y$) for our $Y_{1-(x+y)}$ $Ca_xPr_yBa_2Cu_3O_z$ samples as 0.31.

5. Conclusions

We have investigated fully oxidized $Y_{1-y}Pr_yBa_2Cu_3O_z$ and $Y_{1-(x+y)}$ $Ca_xPr_yBa_2Cu_3O_z$, (x = 0.25, 0.30; y = 0.04, 0.05) bulk samples. They were orthorhombic and superconducting, with T_c values in the range 91 to77K. For all of them, the total oxygen content determined by a spectrophotometric method was higher than for $Y_{1-x}Ca_xBa_2Cu_3O_z$ samples. From the critical temperature dependence of the doping, we obtained the optimal substituted concentration (x+y) for $Y_{1-(x+y)}$ $Ca_xPr_yBa_2Cu_3O_z$ samples.

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