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MORPHOLOGY OF $Y_1Ba_2Cu_3O_z$ AND $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ BULK SAMPLES DEPENDING ON Ca – SUBSTITUTION

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The effects of calcium substitution on the microstructure, composition and morphology of superconducting bulk samples were analyzed by means of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) techniques. We have shown evidence that a Ca concentration 0.3 is the critical substituted value for YBCO system, in respect of the optimium superconducting properties.

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1. Introduction

It is well known that the substitution of Ca for Y increases the overall carrier concentration in $YBa_2Cu_3O_z$. According to many authors, such substitution increases the quantity of the carriers in the superconducting system, and therefore enhances the critical current density but reduces the temperature of the superconducting transition, T_c, - 80K [1,2]. The critical current densities in bulk phase material depend strongly on the phase purity, porosity, and the alignment of the superconducting crystallites and the composition of the grain boundaries.

Scanning electron microscopy (SEM), in combination with energy dispersive X-ray (EDX) analysis and optical microscopy (OM), are mutually complementary methods for investigating the microstructure of a superconducting material.

The aim of the present paper is to show the microstructure of $YBa_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$, and to discuss the effects of Ca-substitution on the composition and morphology of YBCO superconducting bulk samples.

2. Experimental details

2.1. Sample preparation:

$YBa_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ samples were prepared by a standard solid state reaction. The technological process is described in [1].

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2.2. Sample investigations

The surface morphology of the samples was examined by scanning electron microscopy (SEM) on a Jeol JSM-840A. The chemical composition of the samples was studied by X-ray microanalysis, using the method of energy dispersive spectroscopy (EDX) on a Link analytical AN 10/95S spectrometer. The qualitative and quantitative analyses were carried out at an accelerating voltage of 20 kV, due to the sample thicknesses. Optical images were taken with polarized light, using a Nikon, Microphot-FX optical microscope (OM).

3. Results

Fig. 1 shows optical micrographs of $YBa_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ samples, taken in polarized light. The SEM images and distributions in terms of each compositional element are in Fig. 2. The black areas are pores; the gray color shows randomly-oriented superconducting crystals in all pictures. The white zones in Fig. 2 present the distribution of a chosen element. Grain boundaries and micro-cracks are visible in both figures. The $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ sample shows higher porosity and larger grains.

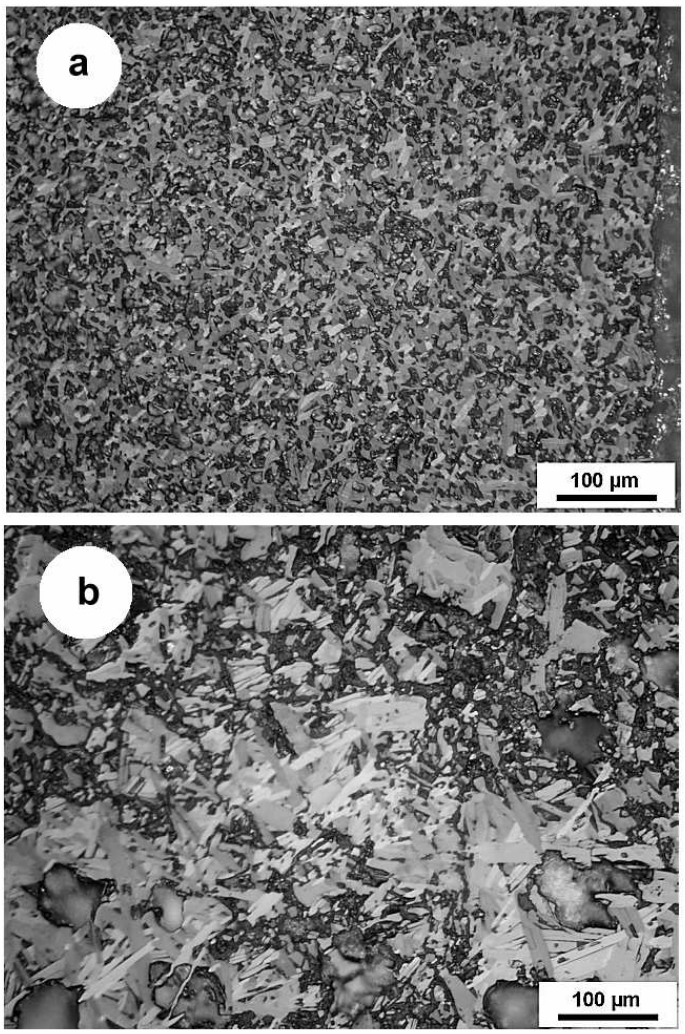
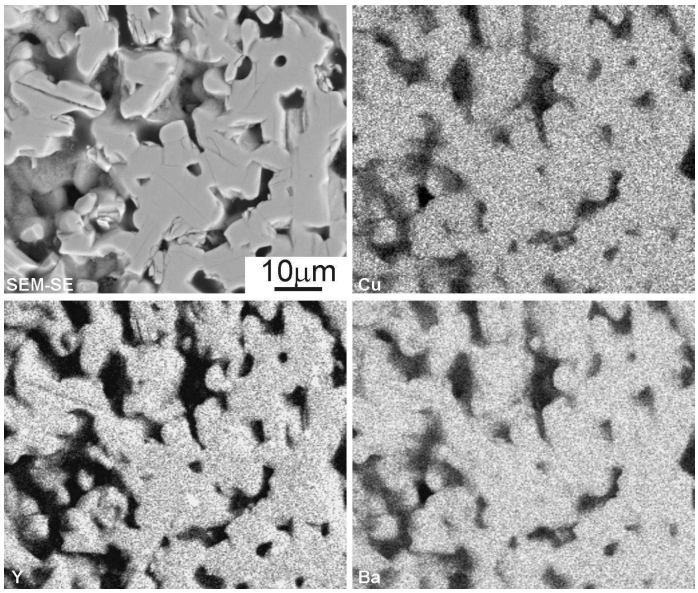
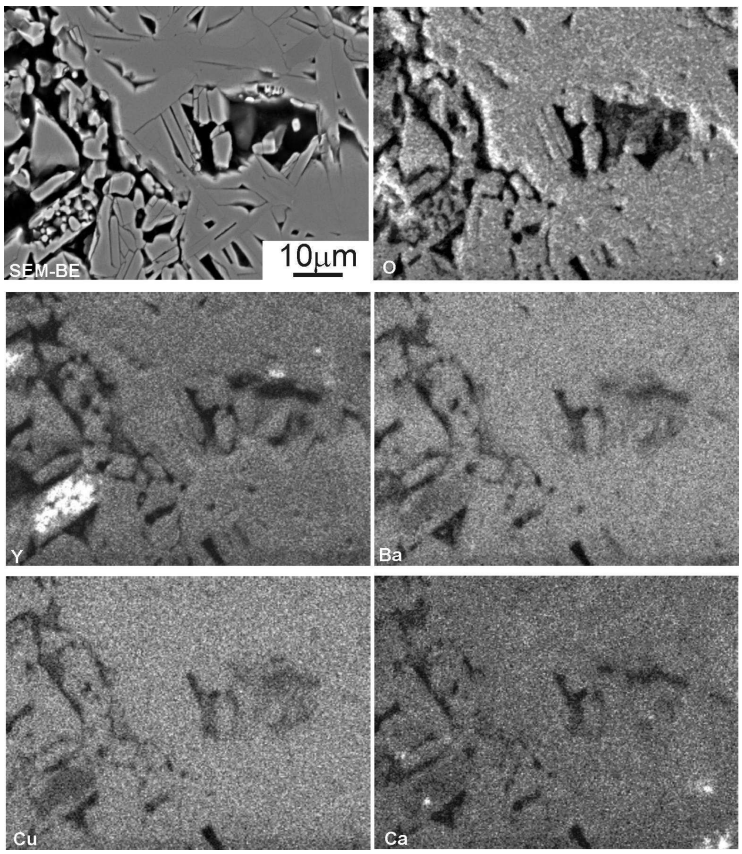


Fig. 1. Optical micrographs of $YBa_2Cu_3O_z$ (a) and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ (b).

The integral EDX data for the distribution of elements are summarized in Table 1 for $YBa_2Cu_3O_z$, and in Table 2 for $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$



(a)



(b)

Fig. 2. SEM images of $YBa_2Cu_3O_z$ (a) and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ (b).

Table 1. Integral EDX data of $YBa_2Cu_3O_z$ for the elements, in atomic percents.

Analysis No	Y	Ba	Cu
1	7.25	12.24	21.08
2	7.12	12.46	21.13
3	7.25	12.52	20.71
4	7.22	12.32	21.02
Mean	7.21	12.39	20.99

Table 2. Integral EDX data of $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ for the elements, in atomic percents.

Analysis No	Y	Ca	Ba	Cu
1	5.42	2.12	12.85	20.95
2	5.61	1.93	12.80	21.21
3	5.47	2.25	12.40	20.25
4	6.30	1.85	12.90	20.95
Mean	5.70	2.04	12.74	20.84

4. Discussion

It is well known that a Ca concentration 0.3 is a critical from the point of view of the concentration of the secondary phases. For this value, the system has a minimum concentration of impurities [3]. When the fraction of Ca atoms is increased above 0.3, the impurity levels rapidly increase, and the superconducting properties deteriorate.

In Fig. 2b, one can see Y and Ca areas of non-reacted materials in a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ sample. This observation is in a good agreement with previous observations [3]. On the other hand, there is no evidence for non-reacted materials in the $YBa_2Cu_3O_z$ sample (Fig. 2a). The Y areas are bigger than the Ca zones, due to the differences in the initial concentrations of the compounds. The non-reacted Y is related to the appearance of a peak due to $BaCuO_2$ in the XRD pattern [1]. When we substitute Ca on the Y sites, we create a system which is a sum of $YBa_2Cu_3O_z$ and $CaBa_2Cu_3O_z$ unit cells. The fractional numbers of these cells are in the same ratio as the chosen concentration. The appearance of non-reacted Ca can again be explained by the formation of a $BaCuO_2$ phase, which has limited the synthesis of $CaBa_2Cu_3O_z$ in the unit cell scale.

From the data presented in Tables 1 and 2, one can see that our samples have the stoichiometric 1:2:3 phase.

5. Conclusions

We have prepared fully oxygenated $YBa_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ bulk samples, by astandard solid state reaction. They are superconducting with T_c values of 92K and 80K respectively. EDX analysis has shown that the samples are stoichiometric. We have observed more porosity and larger grains in a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ sample, by optical microscopy and SEM. Also, we have presented evidence for increasing levels of impurities as the Ca concentration increases.

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