Phase formation and microstructure in Re$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_7$ (Re=Y, Eu, Er; x=0, 0.2, 0.3) superconducting ceramics

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Abstract: We have investigated the influence of Ca-substitution and different rare earths on the microstructure of RE$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-δ}$ (RE=Y, Eu, Er; x=0, 0.2, 0.3) superconducting ceramics. Scanning electron microscopy, X-ray microanalysis and energy dispersive spectroscopy have been used to study the microstructure and the chemical composition of the samples. A correlation was established between the polycrystalline microstructure and phase formation depending on the additive content. We observed that calcium is distributed uniformly in the crystals. The formation of minor impurity phases improved the sintering conditions.

Keywords: REBCO superconducting ceramics, Ca-substitution, microstructure, morphology

1 Introduction

Recently one of the most extensively studied substitution in REBa$_2$Cu$_3$O$_{7-δ}$ systems is divalent Ca$^{2+}$ for trivalent RE$^{3+}$ (RE=Y, Eu, Er) [1–3]. According to Hatada, et al.[1],

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Buckly, et al. [4] and Cao, et al. [5] the substitution of calcium into yttrium sites increases the hole concentration in the CuO$_2$ plane directly without provision of holes from the CuO chain-site. It was proven for YBCO that the values of critical current densities $J_c$, critical temperature $T_c$ and oxygen content depend on calcium doping [6]. In our previous reports it was established that the superconducting properties in REBCO ceramics with Ca-substitution depend strongly on the phase purity, porosity, the alignment of the crystallites, the peculiarity of the grain-boundaries and oxygen content ($\delta$) [7–9]. For this reason additional investigations of the microstructure of such ceramics could be very useful to accumulate new knowledge about the processing conditions of superconducting ceramics.

The object of this study is RE$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ (RE= Y, Eu, Er; x=0, 0.2, 0.3) ceramics. The purposes is to determine the influence of calcium substitution, and the kind of different rare earths on the polycrystalline microstructure, to find the correlation between the distribution of additives in the volume of samples and the phase formation during the solid state reaction and final sintering.

2 Experimental

2.1 Sample preparation

All RE$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ (RE= Y, Eu, Er; x=0, 0.2, 0.3) samples were synthesized by the optimised ceramic method which included solid-state reactions and sintering [7, 10]. The triple heat treatment regime with intermediate grindings was used. The first step included mixing and milling of appropriate amounts of Y$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, CuO, BaCO$_3$, CaCO$_3$and calcinations in flowing oxygen at 900 °C for 21h. The second step of the heat treatment was conducted at 930 °C for 21h at the same atmosphere, followed by annealing at 450 °C for 2h. The last step started with grinding and pressing of the powder in the pallets followed by sintering at 950 °C for 23 h, slow cooling to 450 °C and holding at that temperature for 23 h.

2.2 Sample analysis

The phase formation was studied by X-ray powder diffraction analysis using Bruker D5005 diffractometer with Cu K$\alpha$ – radiation. The microstructure of the samples was studied by means of Jeol JSM-840A Scanning Electron Microscopy (SEM). To examine the structure and the composition, cross-section polishes from the samples were made. The chemical composition of the samples was determined by the X-ray microanalysis, using the Energy Dispersive Spectroscopy (EDS) method on a LINK Analytical AN10000 system. The qualitative and quantitative analyses were carried out at an accelerating voltage 20 kV which is a normal condition for these purposes. The distribution of the elements inside the samples was visualized by X-ray mapping technique. Optical images were taken with polarized light, using a Nikon, Micro hot-FX optical microscopy (OM).
Fig. 1 XRD patterns using Cu-Kα radiation for RE$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ (RE=Y, Eu, Er; x=0, 0.2, 0.3) samples; a - RE=Y, 1-x=0, 2-x=0.3; b - RE=Eu, 1-x=0, 2-x=0.2, 3-x=0.3; c - RE=Er, 1-x=0, 2-x=0.2, 3-x=0.3; The symbol (●) indicates main peaks of 123 phase; (□) – 211, (○) – BaCuO$_2$. 
3 Results and discussion

All prepared $\text{RE}_1-x\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{\delta}$ (RE=Y, Eu, Er; x= 0) samples were essentially single-phased with 123 orthorhombic structure (Fig. 1). Partial transformation of orthorhombic to tetragonal structure was detected in YBCO samples when the Ca content increases to $x=0.3$, which is evaluated by splitting of the peaks in the range $2\theta$ (32-33), $2\theta$ (46-48), $2\theta$ (58-59), using the method of Yoshimi Kubo, et al [11]. For the samples with calcium content $x=0.3$ and RE=Y we detected the appearance of additional reflections, which are connected with the formation of impurity phases BaCuO$_2$ - (file JCPDS-ICDD 70-0441) and Y$_2$BaCuO$_5$ (211) - (file JCPDS-ICDD 81-1199), whereas in the samples with RE=Eu, Er at $x=0.2$, 0.3 we detected peaks of REBCO (123) and BaCuO$_2$.

Furthermore, it was found that formation of RE-211 particles plays a significant role in the improvement of mechanical properties of these ceramics [12].

Fig. 2 Backscattering electron image of $\text{RE}_1-x\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE=Y, Eu, Er; x=0) samples, showing the composition map of different elements.

Backscattering electron image of $\text{RE}_1-x\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE=Y, Eu, Er; x=0; x=0.3) samples is shown in Fig. 2 and Fig. 3. Our result shows that the ceramic with RE=Er ($x=0-0.3$) has a high degree of porosity. The substitution of Ca in the Y site decreases
the porosity and keeps the grain size from 10 to 30 μm (Fig. 4).

We show that through microstructure analysis of each stage of synthesis it is possible to evaluate the steps of the synthesis and the technological characteristics of the superconducting ceramics mentioned above.

Fig. 3 Backscattering electron image of RE$_{1-x}$Ca$_2$Ba$_2$Cu$_3$O$_{7-δ}$ (RE=Y, Eu, Er; x=0.2; 0.3) samples, showing the composition map of different elements.
The calcium is distributed homogeneously in the samples, which proves its presence inside the grains. This result is an indirect confirmation of the diffraction data of other authors [1, 2, 4] for the incorporation of the Ca into the crystal structure. From the results presented in Table 1, one can see that all samples with Ca substitution correspond to the stoichiometric 1:2:3 phase. The barium is irregularly distributed in the samples in which RE= Eu, Er (Fig. 3). In the separate zones the ratio of Ba:Cu is nearly 1:1 which confirmed the appearance of the BaCuO$_2$ phase, established by X-ray phase analysis (Fig. 1). It is well known that the presence of BaCuO$_2$ (Cu$_2$O) phases simultaneously with main phase 123 causes a low-melting eutectic [13, 14]. In our case similar processes takes place. The liquid phase appears between the grains of REBCO which is visualized as small zones with irregular forms of the grain-boundaries.

That is why during the sintering at 900 - 950 °C the connectivity between the grains was improved, and better sintering is achieved. As a result, the porosity of the samples decreases, too.
Table 1 EDX data of $\text{RE}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_z$ (RE=Y, Eu, Er; x=0; 0.2; 0.3) for the elements.

| Samples            | $\text{RE}=$Y, Er, Eu, at. % | Ca at. % | Ba at. % | Cu at. % |
|-------------------|-------------------------------|----------|----------|----------|
| $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_5$       | 7.21                          | 0        | 12.39    | 20.99    |
| $\text{Eu}_1\text{Ba}_2\text{Cu}_3\text{O}_5$      | 9.15                          | 0        | 15.88    | 22.68    |
| $\text{Er}_1\text{Ba}_2\text{Cu}_3\text{O}_5$      | 6.86                          | 0        | 17.01    | 24.65    |
| $\text{Eu}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_5$ | 7.64                          | 1.71     | 15.81    | 22.94    |
| $\text{Er}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_5$ | 5.69                          | 1.69     | 16.81    | 24.39    |
| $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_5$ | 5.70                          | 2.04     | 12.74    | 20.84    |
| $\text{Eu}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_5$ | 7.29                          | 2.32     | 15.97    | 22.60    |
| $\text{Er}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_5$ | 5.29                          | 2.38     | 15.07    | 25.94    |

* The value of the data is average from five point analyses in different crystals.

4 Conclusions

- It is established that the microscopy analysis is appropriate to control the regime of the synthesis of dense $\text{RE}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_z$ (RE=Y, Eu, Er; x=0, 0.2, 0.3) superconducting ceramics as this method allows the detection of inhomogeneities in the microstructure due to the incomplete synthesis and sintering.
- It was found that the kind of the rare earth used influences the porosity in the ceramics subjected to a triple heat treatment regime. The samples with RE=Er have high porosity.
- It is observed that calcium is uniformly distributed in the grains. This study confirmed the X-ray diffraction data on Ca incorporation in the crystal lattice of REBCO (RE=Y, Eu, Er) [1, 2, 4].
- Ca substitution in the Y site initiated the partial separation of Ba in the BaCuO$_2$ phase, which improved sintering of the ceramics due to the appearance of the liquid phase.

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References

[1] K. Hatada and H. Shimizu: “Structural and superconducting properties of $\text{R}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{6+\delta}$ (R=Y, Er, Gd, Eu; 0< $\delta$ <1)”, *Physica C*, Vol. 304, (1998), pp. 89–95.
[2] P. Starowicz, J. Sokolowski, M. Balanda and A. Szytula: “The effect of calcium
substitution in deoxygenated $R_{1-x}Ca_xBa_2Cu_3O_{6,1}$ systems ($R=Y$, Eu): appearance of superconductivity, insulator to metal transition”, Physica C, Vol. 363, (2001), pp. 80–90.

[3] R.J. Cava, A.W. Hewat, E.A. Hewat, B. Batlogg, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck Jr and L.W. Rupp Jr: “Structural anomalies, oxygen ordering and superconductivity in oxygen deficient $Ba_2YCu_3O_x$”, Physica C, Vol. 165, (1990), pp. 419–433.

[4] R.G. Buckley, J.L. Tallon, D.M. Pooke and M.R. Presland: „Calcium- substituted superconducting $RBA_2Cu_4O_8$ with $T\sim90$ K prepared at one atmosphere”, Physica C, Vol. 165, (1990), pp. 391–396.

[5] Shixun Cao, Lingwei Li, Fen Liu, Wenfeng Li, Changyun Chi, Chao Jing and Jinchang Zhang: “Structure and charge transfer correlated with oxygen content for a $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_y$ (y=6.84-6.32) system: a positron study”, Supercond. Sci. Technol., Vol. 18, (2005), pp. 606–610.

[6] E.K. Nazarova, A.J. Zaleski, A.L. Zahariev, A.K. Stoyanova – Ivanova and K.N. Zalamova: “Effects of substituting calcium for yttrium on the superconducting properties of $YBa_2Cu_3O_y$ bulk samples”, Physica C, Vol. 403, (2004), pp. 283–289.

[7] S. Terzieva, A. Stoyanova-Ivanova, K. Zalamova, V. Mikli, Ch. Angelov and V. Kovachev: „Morphology of $Y_1Ba_2Cu_3O_7$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_7$ bulk samples depending on Ca – substitution”, J. Optoelectron. Adv. M., Vol. 7(1), (2005), pp. 477–480.

[8] L. Vladimirova, T. Nedeltcheva and A. Stoyanova-Ivanova: “Determination of oxygen stoichiometry in $Y_{1-x}Ca_xBa_2Cu_3O_y$ superconducting bulk samples”, J. Univ. Chem. Tech. Met., Vol. 38, (2003), pp. 955–956.

[9] A.K. Stoyanova-Ivanova, T.K. Nedeltcheva and L.K. Vladimirova: „Spectrophotometric determination of oxygen content in calcium substituted RBCO (R= Eu, Gd, Er) superconductors”, Eur. J. Chem., Vol. 3(3), (2005), pp. 432–440.

[10] C.N.R. Rao, R. Nagarajan and R. Vijayaraghavan: “Synthesis of cuprate superconductors”, Supercond. Sci. Tech., Vol. 6, (1993), pp. 1–20.

[11] Yoshimi Kubo, Tsutomu Yoshitake, Junji Tabuchi, Yukinobu Nakabayashi, Atsushi Ochi, Kazuaki Utsumi, Hitoshi Igarashi and Masatomo Yonezawa: „Effect of Oxygen Deficiency on the Crystal Structure and Superconducting Properties of the $Ba_2YCu_3O_y$”, Japan. J. Appl. Phys., Vol. 26(5), (1987), pp. 768–770.

[12] R. Cloots, T. Koutzarova, J-P. Mathieu and M. Ausloos: “From Re-211 to Re-123. How to control the final microstructure of superconducting single-domains”, Supercond. Sci. Technol., Vol. 18, (2005), pp. 9–23.

[13] Mehmet Sarikaya and B.L. Thiel: “Identification of Intergranular Cu$_2$O in polycrystalline YBa$_2$Cu$_3$O$_{7-x}$ superconductors”, J. Am. Ceram. Soc., Vol. 71, (1988), pp. 305–309.

[14] Judiyh L. McManus-Driscoll: “Materials Chemistry and Thermodynamics of ReBa$_2$Cu$_3$O$_{7-x}$”, Adv. Mater., Vol. 9, (1997), pp. 457–473.