REACTIONS BETWEEN YBa$_2$Cu$_3$O$_{7-\delta}$ AND La$_2$O$_3$ AND SrCO$_3$

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Abstract

Solid state reactions at 925°C between the high-$T_c$ ceramic superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ and La$_2$O$_3$ and SrCO$_3$, respectively, mixed in various molar ratios $r = \text{MeO}/\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, were studied using X-ray powder diffraction and scanning electron microscopy. The reaction between YBa$_2$Cu$_3$O$_{7-\delta}$ and La$_2$O$_3$ yielded (La$_{1-x}$Ba$_x$)$_2$CuO$_{4-\delta}$, with $x \approx 0.075-0.10$, La$_{2-x}$Ba$_{1+x}$CuO$_{6-\delta}$, with $x \approx 0.2-0.25$ and La-doped (Y$_{1-x}$La$_x$)$_2$BaCuO$_5$, with $x \approx 0.10-0.15$. For $r = 3.0$, Y-doped La$_2$BaCuO$_5$ resulted also. The reaction between YBa$_2$Cu$_3$O$_{7-\delta}$ and SrCO$_3$ yielded (Sr$_{1-z}$Ba$_z$)$_2$CuO$_3$, with $z \approx 0.1$, Y$_2$(Ba$_{1-z}$Sr$_z$)CuO$_5$, with $z \approx 0.1-0.15$, and a nonsuperconducting compound with an approximate composition of Y(Ba$_{0.5}$Sr$_{0.5}$)$_3$Cu$_{3.5}$O$_{10.5}$. At values of $r \leq 2.0$, unsubstituted YBa$_2$Cu$_3$O$_{7-\delta}$ was found in the reaction products.

Keywords: La$_2$O$_3$, SrCO$_3$, YBa$_2$Cu$_3$O$_{7-\delta}$, superconductors

Introduction

Isomorphic substitutions for host ions in the ceramic superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ (labeled below as YBCO or Y$_{123}$) are possible for a great variety of ions which have ionic radii and oxidation states close to those of the host ions.

In a couple of previous papers solid state reactions between YBCO and oxides of potential substituents for yttrium, such as Eu, Ca, Th, Sc and Ce – [1] – and for copper, such as Fe, Co and Zn [2] were studied. It was concluded that the existence of substituted Y$_{123}$-phases seems to largely depend on chemical stability relations between the substituted YBCO and compounds of the oxide of the particular substituent ion with oxides of Ba, Y and Cu.

The purpose of this work is to study the solid state reactions between YBa$_2$Cu$_3$O$_{7-\delta}$ and compounds of elements which have been reported to substitute at the Ba-site, i.e. cations such as La$^{3+}$ (with ionic radius $R_X = 1.28\,\text{Å}$) and Sr$^{2+}$ ($R_X = 1.32\,\text{Å}$). Given the differences in ionic radii between La$^{3+}$, Sr$^{2+}$ and
$\text{Ba}^{2+} (R_x = 1.52 \text{Å})$ the main effect of the La and Sr-substitution for Ba is a shortening of the lattice parameters, especially the $c$-axis [3, 4].

La-substituted $\text{Y(Ba}_{1-x}\text{La}_x\text{)}_2\text{Cu}_3\text{O}_{7-\delta}$ was reported to have orthorhombic structure for values of $x < 0.15$ and tetragonal structure for values of $0.15 < x < 0.36$ [3, 5]. These solid solutions are superconducting, with reduced $T_c$ in the tetragonal state too.

Sr can replace Ba in $\text{Y(Ba}_{1-z}\text{Sr}_z\text{)}_2\text{Cu}_3\text{O}_{7-\delta}$ up to $z = 0.4$. A linear depression of the $T_c$ in combination with stabilization of the tetragonal crystalline phase with increasing Sr concentration has been reported. For $z > 0.4$ impurity phases, such as $\text{Y}_2\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Cu}_2\text{O}_5$ and $(\text{Sr}_{2/3}\text{Ba}_{1/3})_{14}\text{Cu}_{24}\text{O}_{41}$ emerge [6, 7].

The phase analysis of the reaction products requires a thorough knowledge about the compounds in the investigated systems. The Y–Ba–Cu–O system exhibits three quaternary phases at 925–950°C, in air or oxygen: the black, high-$T_c$ superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with orthorhombic structure (Y123) [8], the green $\text{Y}_2\text{BaCu}_2\text{O}_5$ with orthorhombic structure (Y211) [9] and one barium-rich compound with approximate composition $\text{YBa}_3\text{Cu}_2\text{O}_x$ (Y132), $\text{YBa}_4\text{Cu}_3\text{O}_{8.5-\delta}$ (Y143) or $\text{Y}_{1.0-1.33}\text{Ba}_3\text{Cu}_4\text{O}_{13.5-\delta}$ (Y184), having cubic or tetragonal structures [10–17].

In addition to the 30K-superconductor $(\text{La}_{1-x}\text{Ba}_x)\text{CuO}_{4-\delta}$, with $x \approx 0.075$ [18–20] and 90K-superconductor $\text{La}_{3-x}\text{Ba}_x\text{Cu}_6\text{O}_{14+\delta}$, with $0.0 \leq x \leq 0.8$ [20–22], there have been reported three other quaternary phases in the La–Ba–Cu–O system at 925–950°C, i.e. $\text{La}_4\text{BaCu}_5\text{O}_{13+\delta}$, labeled La415 [20, 23, 24], $\text{La}_{4-2x}\text{Ba}_{2-2x}\text{Cu}_2\text{O}_{10-2x}$, with $0.0 \leq x \leq 0.25$ (La211) [20, 25, 26] and $\text{La}_{2-2x}\text{Ba}_{1+x}\text{Cu}_2\text{O}_{6-x/2}$, (La212) with $0.2 \leq x \leq 0.8$ [7, 20, 26, 27].

Solid solutions of the type $(\text{Sr,Y,Ba})_{14}\text{Cu}_{24}\text{O}_{41}$ and $\text{Y}_2(\text{Ba,Sr})\text{Cu}_2\text{O}_5$ were reported to exist in the Y–Ba–Sr–Cu–O system [28]. However, no quaternary compounds were reported in the Y–Sr–Cu–O system [29].

**Experimental**

Solid state reactions between $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (the coefficient $\delta$ in this article is only a qualitative indication of the oxygen nonstoichiometry of the oxide compounds) prepared by standard ceramic method, and $\text{La}_2\text{O}_3$ and $\text{SrCO}_3$, respectively, both of p.a. quality (Merck), were performed by heat treatment of tablets of well homogenized powdered mixtures, for values of the molar ratio $r = \text{MeO}_x/\text{YBCO} = 0.1, 0.2, 0.4, 1.0, 2.0$ and $3.0$, respectively, at $925 \pm 10°\text{C}$, in air, for $18–24$ h in an electric furnace. The samples were allowed to cool slowly to room temperature, reground and subjected to a second heat treatment in flowing oxygen at the same temperature for 1 h, followed by heat treatment in oxygen at $450°\text{C}$ for 24 h.

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