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Preparation of polycrystalline samples of solid solutions Sm_{1+x}Ba_{2-x}Cu₃O_{6+v} (x = 0.0-0.7) and a study of their structural and superconducting properties

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Single-phase polycrystalline samples of $Sm_1Ba_2Cu_3O_{6+y}$ (123 SmSS) with x = 0.0-0.7 were prepared in air by solid state synthesis with precisely controlled technological parameters (the heating and cooling rates, temperature-time regime). Microstructural, structural, and superconducting properties were studied. It is shown that cation stoichiometric samples of Sm₁Ba₂Cu₃O_{6+v} with a high temperature superconducting transition (89-92 K) can be obtained in air. By increasing the Sm/Ba ratio in Sm_{1+x}Ba_{2-x}Cu₃O_{6+y} the orthorhombic-to-tetragonal phase transition is observed. The orthorhombic phase loses its stability at x > 0.125, and the solid solution decomposes by a spinodal mechanism to form layered microstructures with a variable Sm/ Ba ratio. The data obtained are useful for understanding the mechanisms of the formation of possible vortex pinning centers in Ln_{1+x}Ba_{2-x}Cu₃O_{6+v} phases.

Key words: A. inorganic compounds, B. chemical synthesis, C. electron microscopy, C. X-ray diffraction, D. superconductivity.

Introduction

A phenomenon of an unusual increase in the critical current density at moderate or high magnetic field (peak effect) for high temperature superconducting systems LnBa₂ Cu_3O_{6+v} (123Ln) containing light lanthanides (Ln = Nd, Sm and Eu) was discovered recently. Many investigations were carried out for the 123Nd system (see, for example, [1-6]). A close relationship between the anomalous parameters of these materials and their ability to form solid solutions of Nd_{1+x}Ba_{2-x}Cu₃O_{6+y} (123 Nd_{SS}) was established. However, the cation and anion disordering, which occurs in the lattice, has been shown to decrease T_{c} ; to prevent this, the synthesis should be carried out at a low partial pressure of oxygen [5, 6]. Nevertheless, attempts to prepare samples with the required properties in air are being continued.

To solve this problem, studies are being carried out on systems containing other lanthanides such as Sm and Eu, which have an ionic radius close to that of Nd [7, 8], as well as on complex systems with two or more rare-earth elements [9, 10].

The samarium system was studied in several investigations [7, 8, 11-14] but the results obtained by different authors do not agree with each other. A comparison of the data from Ref. [7] and Ref. [8] provides an example to illustrate the influence of synthesis conditions. In Ref. [7] the homogeneity area for solid solutions $Sm_{1+x}Ba_{2\text{-}x}Cu_3O_{6+y}$ (123 Sm_{ss}) was found to be 0 < x < 0.7 for samples obtained by heating at 850 °C for 72 h in air, while in Ref. [8] the degree of substitution x is no more than 0.4 under the same temperature and synthesis conditions but with $P_{O2} = 1$ atm.

A comparison of the published data points to the importance of the preparation procedure of the initial reaction mixtures. In Ref. [7] the sol-gel method for preparing the precursor, which guaranteed a high homogeneity of the mixture, allowed one to obtain a single phase 123 Sm specimen even at 800 °C, whereas the interaction of the initial components begins only at $T \ge 900$ °C in the standard solid state synthesis [15]. Conclusions on the "orthorhombic -tetragonal" phase transition also disagree: in Ref. [16] (no synthesis conditions are given) the phase transition was observed for $Sm_{1+x}Ba_{2-x}Cu_3O_{6+y}$ at x = 0.3-0.4; whereas in Ref. [7, 12] it was found at $x \ge 0.2$.

The interest in studying the structural transformations of the solid solutions is directly associated with the question of the nature of defects that can play a role of flux pinning centers. Detailed investigations of the evolution of stoichiometric samples and solid solutions in the neodymium system gave rise to several models of their defect structure based on an advanced stage of anti-structural disordering for Nd and Ba cations [17]. These models should also be acceptable for samarium system. However, it was shown in Ref. [13, 18] that the probability of the anti-structural defects appearing in the cation stoichiometric samples 123 Sm is small. The real structure of the $Sm_{1+x}Ba_{2-x}Cu_3O_{6+y}$ solid solutions may have specific features too. The present study is devoted to the preparation of Sm_{1+x}Ba_{2-x}Cu₃O_{6+y} solid

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solutions with x = 0.0-0.7 by sintering in air and to the study of the structure, microstructure and superconducting properties of the samples obtained.

Experimental

Sample preparation

High temperature solid state synthesis was used for the preparation of the samples in air. Original high purity (not less than 99.99%) compounds, Sm_2O_3 , CuO and BaCO₃, were preliminary heated at 800, 700, 400 °C, respectively. The same amount of the original reaction mixture (3 g) was used each time. Before annealing, the samples were ground thoroughly with acetone in an agate mortar. The high temperature solid state synthesis of the samples was carried out in an electrical furnace with a temperature control of ± 1 °C. The temperature was changed at a given rate.

It was found earlier that in the $Ln_{1+x}Ba_{2-x}Cu_3O_{6+y}$ systems the active phase formation takes place at 900-980 °C. However, account must be taken of the fact that at these temperatures the change-over may occur from a simple solid state synthesis to the interaction with the participation of a liquid phase. This, in turn, may cause local heterogeneities that will degrade the functional properties of materials. Consequently, we carried out the syntheses beginning at a relatively low temperature about 770 °C and gradually increasing temperature up to the 950 °C which was determined as a result of optimization. The second controlled parameter is the rate of cooling of the samples synthesized. It was within the limits of 50 Kh⁻¹ (in most cases, it was 10-15 Kh⁻¹), since, as was shown in Ref. [19] for the Nd system, quenching gives rise to many anti-structural defects. The third important parameter is the isothermal annealing time especially during the final stage of synthesis at 950 °C. Preliminary XRD data showed that after annealing for 40 (and more) hours the 123 Sm phase begins to decompose with the formation of BaCuO₂ and Sm₂BaCuO₅.

In order to maximize the oxygen content, all the samples obtained were annealed at 550 $^{\circ}$ C in an oxygen atmosphere (8.5 atm) for 45 h [20].

Experimental methods

The phase composition of the synthesis products was verified using the X-ray powder diffraction method (XRD) (a Philips PW-1700 diffractometer, Cu K α -radiation, step scanning $\Delta 2\Theta^{\circ} = 0.01$, storage time of impulses 10 s). The microstructure and chemical composition were studied using optical and scanning electron microscopy (SEM) (a LEO-420 scanning electron microscope) with an energy dispersive X-ray (EDX) microprobe (a Rontec). In measu-rements of the magnetic susceptibility in the temperature interval from 4.2 to 120 K the mutual inductance bridge method was used. The superconducting transition temperature T_c was determined by the onset of a diamagnetic signal.



Fig. 1. The unit cell parameters of solid solutions $123 \text{ Sm}_{\text{SS}}$ versus *x*. The data of [7, 12] are included for comparison.



Fig. 2. SEM micrographs of $Sm_{1+x}Ba_{2-x}Cu_3O_{6+y}$ samples with x = 0 (a) and x = 0.6 (b).

Results and Discussion

X-ray diffraction characterization

According to the XRD data the samples $Sm_{1+x}Ba_{2\cdot x}$ Cu_3O_{6+y} with $0 \le x \le 0.7$ are single-phase, and at x = 0.8certain impurity phases are observed. The stoichiometric compound $Sm_1Ba_2Cu_3O_{6+y}(x = 0)$ has an orthorhombic structure with the unit cell parameters a = 3.914 Å, b = 3.853 Å, c = 11.730 Å(b < a). Fig. 1 shows how the change in the unit cell parameters depends on the degree of substitution x. As the degree of substitution increases the unit cell parameters a and c decrease while b increases; near the excess samarium content of $x \approx 0.2$, the structure transforms from orthorhombic to tetragonal. Our findings are in a good agreement with the results of Refs. [7] and [12].

Microstructure and cation composition

SEM gives evidence that the samples with a stoichiometric composition and with low degrees of substitutions (x < 0.3) consist of crystallites of an elongated form with sizes about 30-50 micrometres (Fig. 2(a)). As the degree of substitution increases the microstructure of the samples changes: the form of crystallites becomes practically isometric, and the sizes decrease by almost an order of magnitude (Fig. 2(b)).

EDX microprobe data indicate that the cation composition of crystallites for the samples with x = 0 (Sm/Ba ratio in the



Fig. 3. EDX microprobe data for $Sm_{1+x}Ba_{2-x}Cu_3O_{6+y}$ samples (symbols) prepared from original mixtures with different Sm/Ba ratios (solid lines).



Fig. 4. Temperature dependence of magnetic susceptibility of samples 123 Sm_{SS} with different degree of substitution *x*.

starting material is equal 0.5) and x = 0.3 (Sm/Ba = 0.765) is rather homogeneous (Fig. 3). At x = 0.2 (Sm/Ba = 0.666), considerable variations in the elemental composition of separate grains are observed.

The superconducting properties

The temperature of the superconducting transition, T_{c} , of the stoichiometric samples is equal to 89-92 K (Fig. 4). The samples of practically all compositions are characterized by a wide transition to the super-conducting state. T_c decreases with an increase in the degree of Ba with Sm substitution for a series of solid solutions with 0 < x < 0.15, and remains practically constant (40-45 K) for the samples with 0.2 < x < 0.3, but the amount of superconducting phase seems to decrease in the last case. This may be caused by the variation in the oxygen content and distribution, or by the cation nonstoichiometry on a microscopic level. A repeated oxidizing annealing had no impact on the properties of the samples and thus the assumption of the nonuniform oxygen distribution was not justified. To clarify the presence of the cation nonstoichiometry, an additional analysis of experimental diffraction profile lines and microprobe data was carried out.

Control of structural and composition homogeneity of the samples

Following Ref. [2], we have chosen some X-ray reflections



Fig. 5. Change of the profile forms of reflections 113 (a) and 007 (b) for samples 123Sm_{SS} depending on *x*.

as diagnostic diffraction peaks which can indicate the structural changes associated with the cation substitutions: the single peak 113 is selected to determine the particle distribution depending on the composition; the reflection 007 is taken to control the parameter c; the groups of reflections 006, 200, 020 are selected to identify the phases during the orthorhombic-to-tetragonal transition. Figs. 5 and 6 give the fragments of the diffraction patterns containing the selected reflections for the samples with x = 0.0-0.7. To compare the peak profiles easily, the intensities were normalized to the maximum at each angle interval and the peaks were shifted till the coincidence of their tops.

The single narrow peak 113 (Fig. 5(a)) found for the



Fig. 6. Changes of profile forms for diffraction reflections 006, 200, 020 for samples 123 Sm_{SS} depending on *x*.

whole series of solid solutions (a minor broadening for the samples with $x \ge 0.3$ is observed) denotes an absence of heterogeneity associated with a mechanical mixture of the particles of different compositions in the system.

The basal 007 reflection remains narrow up to x = 0.3 too, and becomes more broadened and weak with an increase in x. Most likely, this broadening is due to a decrease of the interferential coherence domain in the direction of the *c* axis; certain stacking faults are possible too [21]. With an increase in x the group of reflections 006, 200 and 020 (Fig. 6(a)) transforms from a triplet for x < 0.2, to a doublet for x = 0.2, and to a single peak for $x \ge 0.3$. This evolution of the profiles represents the transition process from the orthorhombic to the tetragonal and eventually to a pseudo-cubic ($a \approx b \approx c/3$) structure. The peak in samples with 0.4 < x < 0.5 has a slightly asymmetric form (a shoulder at the right hand side), because the c/3 value becomes unequal to a.

Fig. 6(b) presents the profiles of the 006, 200 and 020 reflections for a series of samples with 0 < x < 0.2, i.e. in the beginning of the structural transition. In the region of small substitutions (up to x = 0.1) the samples remain orthorhombic. The 020 peak position, which determines parameter b, remains almost unchanged. Beginning with x = 0.125, the 020 reflection moves into the field of the smaller angles, and at x = 0.15 only one asymmetric



Fig. 7. Microstructure (a) and elemental composition (b) on different parts of the particle (on the base surface, light and dark layers) of the sample with x = 0.2.

broadened peak remains in the XRD section considered. Qualitative modeling of the profiles of the diagnostic diffraction peaks using the PCW program shows that for sample with x = 0.15 one can create a model of the particle mixture of the orthorhombic phase with the unit cell parameters close to those of the sample with x = 0.125 (a = 3.8916 Å, b = 3.8760 Å, c = 11.7019 Å) and the tetragonal phase (a = 3.8947 Å, c = 11.6865 Å). The model of the latter (a = 3.8947 Å, c = 11.6865 Å) is suitable for a description of the diffraction profile of the sample with x = 0.3.

SEM observations revealed a different microstructure of the sample with x = 0.2. A considerable part of the crystallites look as a «sandwich pie» (Fig. 7(a)) in which the layers with a height of 0.5-0.8 micrometres differ in the Sm/Ba ratio (Fig. 7(b)).

Apparently, the changes of diffraction and microstructural characteristics observed can be interpreted in the framework of the mechanism of the decomposition of solid solutions [22].

In the samples with 0 < x < 0.125 the substitution of barium with samarium occurs in the entire volume of the orthorhombic phase. At $x \ge 0.125$, the orthorhombic phase becomes unstable, the solid solution decomposes according to a spinodal mechanism with the formation of layered microstructures with different Sm/Ba ratios

in the layers. The superconducting transition temperature decreases in comparison with the orthorhombic phase but remains practically unchanged for the samples with 0.2 < x < 0.3; the superconducting phase content in these samples decreases. At $x \ge 0.3$, the structure becomes tetragonal, the microcrystallites acquire an isometric form, and their sizes decrease by almost an order of magnitude in comparison with the samples containing a smaller amount of samarium; for these compositions the layered microstructure and superconductivity disappear.

To sum up, it is shown that $Sm_1Ba_2Cu_3O_{6+y}$ samples prepared in an air atmosphere can demonstrate a supercon -ductivity with $T_c \approx 92-89$ K. A qualitative analysis of the diffraction profiles together with the electron microscopy and EDX microprobe data allowed us to reveal some features of the structural changes of solid solutions. Data obtained here are useful for understanding the mechanisms of the formation of possible vortex pinning centers in $Ln_{1+x}Ba_{2-x}Cu_3O_{6+y}$ phases.

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