RBa$_2$Cu$_3$O$_Y$ crystal structure and properties

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Abstract. In this study, the effect of $R$ (R= Y, Pr, Nd, Sm, Eu, Lu) substitution on crystal structure and properties HTS compositions $R_{1-x}Ca_xBa_2Cu_3O_y$. The XRD results showed that the substitution of Y / R in Y-123 leads to the disappearance of spikes in the linear and volumetric coefficients of thermal expansion. Mechanical activation showed that the composition of Nd-123 demonstrates enhanced chemical stability with respect to water vapor and CO$_2$ when exposed to air.

1. Introduction

High-temperature superconducting materials (HTS) are interesting from the fundamental physical effects variety point of view, and from their applications in superconducting electronics. Currently, there is an active introduction of electrical equipment, superconducting power cables, current limiters, transformers and other unique technical devices based on HTS in various fields of electrical engineering. With the improvement of technologies, properties of current-carrying elements are improved. For HTS by X-ray and neutron diffraction observed structural anomalies, which appear as spikes in thermal expansion coefficients and in primitive cell parameters, as well as decrease of the Cu – O apical bond length which is non-monotonic by temperature. Such changes during thermal cycling can lead to deformations and destruction of superconducting products. When selecting a superconducting composition for a particular product and typical operating conditions, it is necessary to take into account the chemical stability of HTS materials with respect to the components of air and water.

2. Experimental Procedure

The objects of our study are $R_{1-x}Ca_xBa_2Cu_3O_y$, where R = Y, Pr, Nd, Sm, Eu, Lu. The following materials were used as starting materials: $R_2O_3$, $BaCO_3$, CuO, CaO in quantities corresponding to the desired composition. To remove the adsorbed water, the starting components were calcined at 600 ° C for 2 hours. The powders were thoroughly mixed in planetary monomill the Fritsch Pulverisette using agate balls $d = 15$mm. Afterwards, sample formulation into tablets on hydraulic press at a pressure of 15 MPa. Thereafter, annealed in a Nabertherm N11 furnace at temperatures of 860°C, 900°C, 920°C, 930°C, 950°C in during the 24 hours with intermediate grinding in a planetary mill with the addition of ethyl alcohol with agate balls $d = 35$ mm and pressing. After the final annealing, the samples were quenched on a copper plate. The phase composition was controlled using x-ray phase analysis. To obtain samples...
with various oxygen treatment, the phases were treated in a quartz boat placed in a quartz tube, to which an external gas flow (oxygen) was connected under the following conditions:

- 24 hours at 550 °C in an atmosphere of oxygen, quenched in a quartz tube under a stream of cold water;
- 24 hours at 500 °C in the atmosphere of air, quenched in a quartz tube under a stream of cold water;
- 24 hours at 700 °C in an air atmosphere with quenching on a copper plate in air.

Certification of chemical compounds was carried out on a XRD 7000 Maxima diffractometer by Shimadzu with CuKa radiation (wavelength = 1.5406 Å), graphite monochromator, scattering angle interval 2Θ = 15-80 degrees. According to X-ray phase analysis, samples of Y, Lu, Ca-123, Y, Eu-123, Nd, Eu-123 contained impurities of complex barium cuprates YBa3Cu4Ox (00-041-0454), Ba2Cu3Ox (00-047-0117), and also BaO (00-026-0178) in quantities not exceeding 3-5%. Sample Eu, Pr-123 had the same impurities, but in a larger amount ~ 10-12%. The list of investigated samples and their characteristics are given in table 1.

Using the powder X-ray diffraction method, we studied the effect of oxygen content and the degree of substitution on the crystal structure of HTS materials in the temperature range of 80–300 K. The temperature dependences of the primitive cell parameters, determined by the least squares method by 18–20 lines, are shown in Figure 1.

3. Results and Discussion

3.1. Crystal structure at 80-300 K

Substitution (Y3+/Ca2+) allows simplifying the technology for producing superconducting products, reduces the cost of electricity at the final stages of roasting, in some cases leads to an increase in the critical current [1-3]. The compositions of Nd, Eu-123; Sm, Ca-123; Eu-123; Y, Lu, Ca-123; Eu, Pr-123 with a high oxygen content (y > 6.8) demonstrate smooth monotonic dependences of lattice parameters on temperature, which are well described by quadratic dependences; that is, linear thermal expansion coefficients decrease with cooling. The Nd-123 and Y, Eu-123 compositions with low oxygen content (y <6.8) demonstrate a small maximum in the temperature dependence a(T) near 130 K, and the Sm-123 compositions with high oxygen content (y = 6.9) and Eu-123 with a low oxygen content (y = 6.64) demonstrate a maximum on the temperature dependences of the lattice parameters near ~ 250 K. Samples of the remaining compositions did not have pronounced features on the temperature dependence of the lattice parameters.

| Composition | Primitive cell parameters (T=293 K) | Obtaining conditions | Volumetric coefficient expansion, \( \times 10^5, K^{-1} \) |
|-------------|-----------------------------------|---------------------|-----------------------------------------------|
| NdBa2Cu3O6.75 | a = 3.8870, b = 3.8937, c = 11.6887 | 550 °C, O2 (93-173 K) | \( \alpha_1 = 1.9 \), \( \alpha_2 = 3.1 \) |
| Nd0.5Eu0.5Ba2Cu3O6.65 | a = 3.8693, b = 3.9123, c = 11.7636 | 700 °C, O2 (93-173 K) | \( \alpha_1 = 1.99 \), \( \alpha_2 = 3.43 \) |
| Nd0.5Eu0.5Ba2Cu3O6.76 | a = 3.8635, b = 3.9096, c = 11.7573 | 550 °C, O2 (93-173 K) | \( \alpha_1 = 2.48 \), \( \alpha_2 = 2.97 \) |
| Nd0.5Eu0.5Ba2Cu3O6.83 | a = 3.8607, b = 3.8607, c = 11.7495 | 550 °C, O2 (93-173 K) | \( \alpha_1 = 2.38 \), \( \alpha_2 = 3.44 \) |
| SmBa2Cu3O6.9 | a = 3.8615, b = 3.8936, c = 11.7160 | 550 °C, O2 (93-173 K) | \( \alpha_1 = 2.06 \), \( \alpha_2 = 3.02 \) |
| Sm0.9Ca0.1Ba2Cu3O6.8 | a = 3.8585, b = 3.9078, c = 11.7398 | 550 °C, O2 (93-173 K) | \( \alpha_1 = 2.3 \), \( \alpha_2 = 4.35 \) |
| EuBa2Cu3O6.64 | a = 3.8562, b = 3.9036, c = 11.7455 | 700 °C, O2 (93-173 K) | \( \alpha_1 = 1.87 \), \( \alpha_2 = 2.79 \) |
From the temperature dependences of the lattice parameters, the values of the thermal expansion coefficients are determined using the expression

\[
\alpha_X = \frac{1}{X} \frac{\Delta X}{\Delta T}
\]

where \(X\) is the volume or the primitive cell parameters. The obtained data are shown in Figure 1 for Eu-123 compounds with different oxygen content. For the remaining compositions, the results have a similar appearance.

| Sample                        | Lattice Parameters | Temperature | Oxygen Content | \(\alpha_a\) | \(\alpha_v\) |
|-------------------------------|--------------------|-------------|----------------|-------------|-------------|
| EuBa2Cu3O6.77                 | 3.8528             | 550         | -0.7 (air)     | 2.13        | 4.36        |
| EuBa2Cu3O6.85                 | 3.8523             | 550         | 0 (O2)         | 2.35        | 4.28        |
| Y0.5Eu0.5Ba2Cu3O6.6           | 3.8629             | 700         | -0.7 (air)     | 0.63        | 3.99        |
| Y0.45Lu0.45Ca0.1Ba2Cu3O6.8    | 3.8280             | 550         | -0.7 (air)     | 2.6         | 4.1         |
| Eu0.45Pr0.45Ca0.1Ba2Cu3O6.8   | 3.8580             | 550         | -0.7 (air)     | 1.31        | 3.44        |

**Figure 1.** Temperature dependences of linear and volumetric coefficients of thermal expansion for samples EuBa2Cu3O\(_y\); \(y = 6.64\) (white characters), \(y = 6.67\) (gray characters) and \(y = 6.854\) (black characters).
3.2. Mechanical activation
The task of studying the stability of $\text{RBa}_2\text{Cu}_3\text{O}_y$ under the water vapor and carbon dioxide was solved using mechanical activation, since during mechanical activation there is a significant increase and activation of the free surface that is in contact with the atmosphere, $\text{RBa}_2\text{Cu}_3\text{O}_y$ particles also cleavage predominantly along the base plane of the crystallites, which brings chemically active structural layer of BaO to the open surface. The particle size of the resulting material, determined by analyzing images of a Carl Zeiss EVO 40 scanning electron microscope, was 3–5 μm. The particles were agglomerates consisting of coalescent crystallites ~ 0.3 microns in size. Mechanical activation during the first 1-2 minutes in the AGO-2 mill leads to a significant reduction in the size of coherent scattering regions, with an increase in the duration of grinding to 10 minutes, there is practically no further change. In the initial single-phase Y-123, with an increase in the grinding time, the amount of the impurity phase $\text{Y}_2\text{BaCuO}_5$ continuously increases, and in the Nd-123, on the contrary, a small amount of the impurity phase $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ present in the initial sample disappears in mechanically activated samples. This confirms the high chemical resistance of Nd-123 to the effects of atmospheric moisture and CO$_2$ compared to Y-123.

Thus, as a result of mechanical activation, the surface of Y-123 powders was covered with the products of hydrolysis and carbonization to a considerable depth. The process of chemical degradation occurs in the usual way — through the formation of the “green” phase of $\text{Y}_2\text{BaCuO}_5$. The study of chemical degradation for mechanically activated Nd-123 showed that the interaction of this oxide with CO$_2$ is not directly related to the hydrolysis process, as it happens in $\text{YBa}_2\text{Cu}_3\text{O}_y$. Carbonization of Nd-superconductor, in this case, is homogeneous, through the stage of carbon dioxide dissolution in the lattice. This mechanism now eliminates the usual hydrolysis reaction for $\text{RBa}_2\text{Cu}_3\text{O}_y$ with the formation of the characteristic “color” phase $\text{R}_2\text{BaCuO}_5$. As a result, the rate of chemical decomposition of mechanically activated Nd$\text{Ba}_2\text{Cu}_3\text{O}_y$ under the action of water is relatively low.

Thus, it was found that for Y-123 oxide, mechanical activation serves only as an accelerator of chemical degradation, while for Nd-123 it changes the mechanism of its interaction with moisture to less active, and superconducting characteristics close to the maximum.

3.3. Phase analysis
The stability of R-123 compounds in air at room temperature was investigated by comparing the initial X-ray diffraction data and after exposure on the air for several (3 to 7) years. The samples were kept in the form of powder or compressed tablets with a diameter of 1 cm and a thickness of 1-2 mm for Nd-123, as well as for all other R-123 studied, long exposure to air does not lead to the destruction of the superconducting phase, unlike the composition of Lu, Y, Ca-123, the tablet surface of which was found to be covered with heterogeneous formations. According to the XRF data, for the Lu, Y, Ca-123 superconducting phase completely disappeared, the decay products were determined using the PDF-2 database as $\text{Y}_1.4\text{BaCu}_{1.6}\text{O}_5$ (00–046–0895), $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ (00-040-0312) and CaCO$_3$ (00-001-0628), are shown in Figure 2.
Figure 2. XRD patterns of NdBa$_2$Cu$_3$O$_{6.83}$ samples (left) and Y$_{0.45}$Lu$_{0.45}$Ca$_{0.1}$Ba$_2$Cu$_3$O$_{6.8}$ (right) newly synthesized (grey line) and aged in air for 3 years (black lines).

4. Conclusion
The substitution of Y / R in Y-123 leads to the disappearance of spikes in the linear and volumetric coefficients of thermal expansion. The substitution (Y$^{3+}$/Ca$^{2+}$) is accompanied by an increase in the microhardness of the samples. The composition of Nd-123 demonstrates enhanced chemical stability with respect to water vapor and CO$_2$ when exposed to air.

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