

# Effect of partial lanthanide substitutions of Gd123 submicronic powder

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**Abstract**—GdLn<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> (Ln = La, 0 ≤ x ≤ 0.6; Ln = Nd, Sm, Eu, 0 ≤ x ≤ 0.5) (Gd123:Ln) samples were synthesized using the sol-gel method. The homogeneity region, variation of the crystal lattice and oxygen stoichiometry of the Gd123:Ln solid solutions were studied as a function of the substitution degree x. It was shown that the homogeneity region becomes wider when going from Eu<sup>3+</sup> (x ≤ 0.35) to La<sup>3+</sup> (x ≤ 0.5), but for all lanthanides the symmetry changes from orthorhombic to tetragonal for x ~ 0.05. Measurements of the electrical resistance of Gd123:Ln samples in the temperature range 77–300 K revealed superconducting transition temperatures over 77 K only for x = 0 and x = 0.05.

**Keywords**—High-T<sub>c</sub> superconductors; Sol-gel synthesis; Crystal structure; X-ray diffraction; Lanthanide

## I. INTRODUCTION

Electronic systems are widespread in all aspects of modern life. Medicine, telecommunications, transport, computing and energy are just some of the key areas that contribute to the intensive growth of micro and nanotechnology. Improved functionality, performance and reliability at reduction costs are the driving forces in the research of electronic systems, regardless of their application.

Interest in investigation of high temperature superconducting (HTSC) compounds is growing due to the fact that many of them have found applications in microelectronics, medicine and development of efficient systems used for energy production, accumulation and transmission. For example, thin films of such HTSC compounds as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (Y123) (whose critical temperature T<sub>c</sub> is about 92 K) are used in making superconducting quantum interference devices (SQUIDS) and various microwave receiving facilities. Y123 was also used to produce superconducting foam that may serve as a basis for practically ideal dangerous current limiter in electric power industry, tapes that are more than 100 m long, carrying over 200 A/cm width at 77 K and others [1].

For some solid solutions of Ln<sub>1+x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> (whose structure is similar to that of Y123) the critical temperature is the higher. That can allow higher electric currents to transmit than YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>. Thus, it was found that partial substitution of Ln for Ba is possible for La, Nd, Sm, Eu, Pr and Gd. The GdLa<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub>, GdPr<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub>, Sm<sub>1+x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> and

Nd<sub>1+x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> systems have been comprehensively studied [2-7]. In [8] substitution of Gd<sup>3+</sup> for Ba<sup>2+</sup> was studied; it was shown that the homogeneity region is 0 ≤ x ≤ 0.25. In [8-9] a structural transition from orthorhombic to tetragonal was observed in the GdPr<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> and GdLa<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> systems at x = 0.2 and 0.25, respectively.

It is known that the critical temperature of GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (Gd123) is about 2-4 K higher. Thus, it can take good positions along with Y123 [10-12].

The objective of our work was the synthesis of GdLn<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub> (Ln = La, 0 ≤ x ≤ 0.6; Ln = Nd, Sm, Eu, 0 ≤ x ≤ 0.5) (Gd123:Ln) systems and the investigation of the structural and electrophysical properties and the oxygen stoichiometry.

## II. MATERIALS AND METHODS

Sets of samples were synthesized using the sol-gel technique [4, 13]. The main preferences of this method consist of simple preparation process, relatively inexpensive initial reagents and a resulting submicron or nano-sized powder with high homogeneity.

The starting substances for synthesis of superconducting ceramic were Gd<sub>2</sub>O<sub>3</sub> (99.0%, High Purity Chemicals), La<sub>2</sub>O<sub>3</sub> (99.0%, High Purity Chemicals), Eu<sub>2</sub>O<sub>3</sub> (99.0%, High Purity Chemicals), Nd<sub>2</sub>O<sub>3</sub> (99.0%, High Purity Chemicals), Sm<sub>2</sub>O<sub>3</sub> (99.0%, High Purity Chemicals), BaCO<sub>3</sub> (99.0%, High Purity Chemicals) and CuO (99.0%, High Purity Chemicals).

The starting materials dissolved in concentrated nitric acid. The content of lanthanides and copper cations were determined by complexometry with EDTA 0.05 M and xylenol orange as indicator, the Ba<sup>2+</sup> content by gravimetry. An ammonium citrate solution served as gel-forming substance (pH ~ 6-7). The resulting mixture was evaporated until the formation of a gel, which was then decomposed by gradually heating (100 °C/h) up to 800 °C. The ceramics obtained this way were ground and calcined in air at 830–850°C for 72 hours.

After this they were once again ground and pressed into pellets of 15 mm diameter and 1–2 mm thickness.

IR absorption spectra (in the 400-4000 cm<sup>-1</sup> range) of the products obtained after calcination were recorded with a

spectrophotometer Spectrum BX FT-IR (Perkin Elmer), using the pressing technique for tablets with KBr.

The pellets were sintered for 4 hours at 900 °C, then kept for 24 hours at 450 °C in oxygen atmosphere, and finally slowly cooled to room temperature in a flow of oxygen.

The oxygen content was determined by the iodometric titration technique [14]. The error in the determination of the oxygen content index  $y$  is believed to be 0.02 per formula unit Gd<sub>123</sub>:Ln.

The phase composition and crystal lattice parameters were determined using an X-ray diffractometer DRON-3 (CuK $\alpha$ -radiation, Ni filter). The diffraction patterns were recorded at a rate of 1 deg./min. For the refinement of the lattice parameters by the least-squares method, identical sets of reflections (7 for tetragonal and 11 for orthorhombic lattices) were used.

The microstructure of the compounds obtained was studied with a scanning electron microscope (SEM) Hitachi S – 2400.

The electrical resistance was measured in the temperature range 77–300 K, applying the standard four-probe technique method using indium-gallium eutectic.

### III. RESULTS AND DISCUSSION

The following homogeneity regions were found for the Gd<sub>123</sub>:Ln systems:  $0 \leq x \leq 0.5$  for Ln = La,  $0 \leq x \leq 0.45$  for Ln = Nd,  $0 \leq x \leq 0.4$  for Ln = Sm,  $0 \leq x \leq 0.35$  for Ln = Eu (Fig. 1). Thus, the homogeneity region becomes wider when going from Eu<sup>3+</sup> to La<sup>3+</sup>. This fact may be explained by the increase of the ionic radii of the lanthanides in the same sequence of Eu<sup>3+</sup> (1.066 Å), Sm<sup>3+</sup> (1.079 Å), Nd<sup>3+</sup> (1.109 Å), La<sup>3+</sup> (1.160 Å) [15].

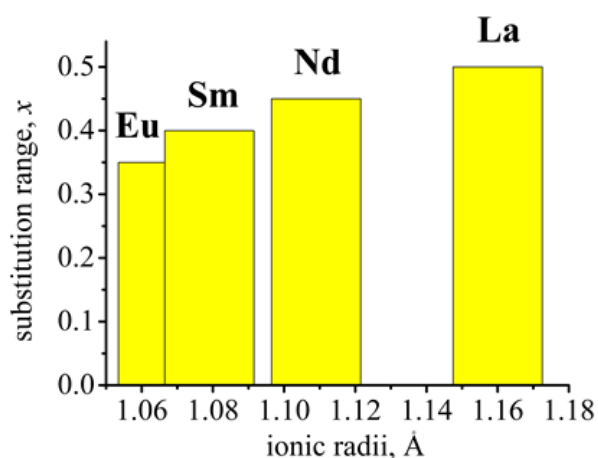


Fig. 1. Substitution ranges for Gd<sub>123</sub>:Ln solid solutions vs the ionic radius (in Å) of Ln<sup>3+</sup>.

The pure Gd<sub>123</sub> sample is crystallized in single phase with orthorhombic structure o-Gd<sub>123</sub>, belonging to the space group *Pmmm*. The calculated unit cell lattice parameters of pure Gd<sub>123</sub> are  $a = 3.895(1)$  Å,  $b = 3.871(2)$  Å,  $c = 11.697(2)$  Å. These crystallographic parameters are correspondent with the published previously [14].

In the Gd<sub>123</sub>:Ln solid solutions with increasing component concentration of lanthanide ions at substitution barium on lanthanide the changing from orthorhombic phase to tetragonal (space group *P4/mmm*) is observed. Consequently, for  $x = 0.05$ , we have an orthorhombic structure, and for  $x > 0.05$  - the tetragonal structure.

Surface morphology and microstructure characteristics of Gd<sub>123</sub>:Ln samples were investigated by SEM. Fig.2 shows SEM images of the samples with good granularity in its morphology and little grains of various sizes from 0.2 μm to 1.5 μm. Also, a small amount of agglomerated particles of different diameters are shown.

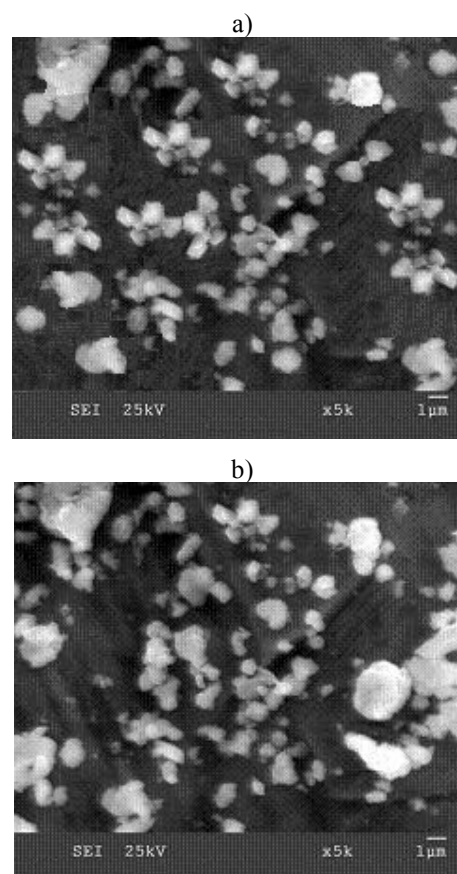


Fig. 2. The SEM photograph of Gd<sub>123</sub> (a) and GdEu<sub>0.05</sub>Ba<sub>1.95</sub>Cu<sub>3</sub>O<sub>y</sub> (b) samples.

Thus, the structure and superconducting properties of Gd<sub>123</sub> strongly depend on the stoichiometry of oxygen. The oxygen deficit causes a phase transition from the superconducting orthorhombic phase to the non-superconducting tetragonal phase.

For all the investigated Gd<sub>123</sub>:Ln it was found that an increase of the substitution degree  $x$  results in a reduction of the orthorhombic deformation of the crystal lattice and stabilization of the tetragonal phase. This is related to the increase of the electric charge in the Ba<sup>2+</sup> plane when part of the barium atoms are replaced by rare-earth atoms. The excess oxygen atoms occupy vacancies in the O(5) position on the axis  $a$  in the plane Cu(1). Thus, when the substitution degree  $x$

grows, the vacancies are redistributed between the O(1) and O(5) positions, the orthorhombic deformation of the lattice is removed, and stabilization of the tetragonal phase occurs at  $x \geq 0.05$  [4, 9]. Moreover, as the substitution degree  $x$  grows, the electric charge of the  $\text{Ba}^{2+}_{1-x/2}\text{Gd}^{3+}_{x/2}$  layer increases. The additional charge is compensated by the occurrence of additional oxygen atoms in positions O(5) on the  $a$  axis. The presence of these additional oxygen atoms increases the coordination number of the copper atoms Cu(1) from 4 to 5 (or even 6). The change from orthorhombic to tetragonal symmetry at a substitution degree  $x \geq 0.05$  can also result from the formation of stable  $\text{Cu}(1)\text{O}_5$  and  $\text{Cu}(1)\text{O}_6$  polyhedrons.

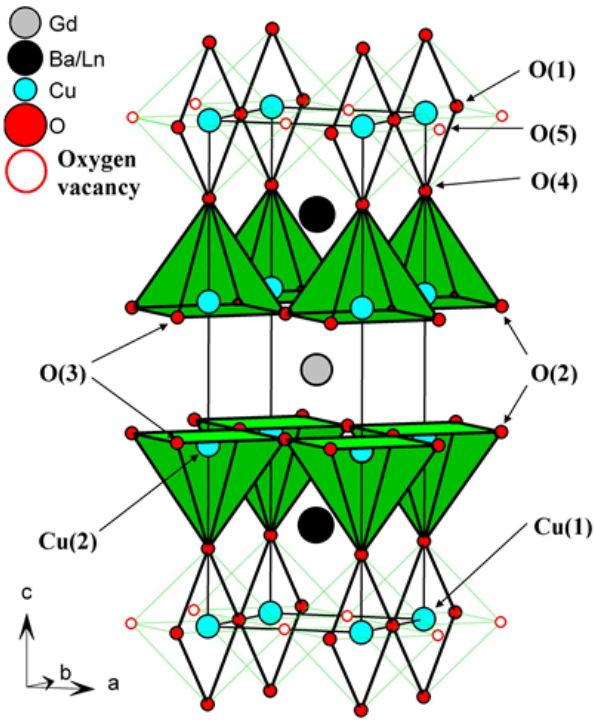


Fig. 3. Schematic crystal structure of Gd123:Ln.

To confirm the results of the X-ray studies, we determined the oxygen content in Gd123:Ln samples. The total oxygen content  $y$  involves oxygen atoms ( $6.5 + x/2$ ) that neutralize the charge of the cations assuming  $\text{Cu}^{2+} [(1+x)\text{Ln}^{3+} + (2-x)\text{Ba}^{2+} + 3\text{Cu}^{2+}]$  and mobile oxygen atoms ( $z$ ), connected with the presence of copper in oxidation state +3. Consequently

$$\psi = 6.5 + \xi/2 + \zeta.$$

Fig. 4a shows the dependence of the total oxygen content  $y$  on the substitution degree  $x$ . One can see that the oxygen content  $y$  increases with  $x$ , but the increase is not monotonic as it would be in agreement with the heterovalent character of  $\text{Ln}^{3+}$  replacing  $\text{Ba}^{2+}$ .

The dependence of the mobile oxygen content  $z$  on the substitution degree  $x$  is shown in Fig. 4b. The graphs indicate that for a substitution degree  $x$  in the range 0–0.05, additional oxygen (whose presence is due to lanthanide cation substitution for  $\text{Ba}^{2+}$ ) "replaces" mobile oxygen in the position O(1) in the

planes Cu(1). For values of  $x$  of about 0.3 ( $\text{Ln} = \text{La}, \text{Eu}$ ) or 0.2 ( $\text{Ln} = \text{Nd}, \text{Sm}$ ), a structural change of the crystal lattice occurs. This is the consequence of filling of vacancies in the positions O(5) on the axis  $a$  in the plane Cu(1) and a redistribution of oxygen vacancies between the positions O(1) and O(5). It is seen from Fig. 3 that a further increase of the substitution degree  $x$  produces a decrease of the mobile oxygen content. This is due to the replacement of mobile oxygen atoms (now from positions O(5)) by additional oxygen atoms that enter the lattice when barium is replaced by lanthanide.

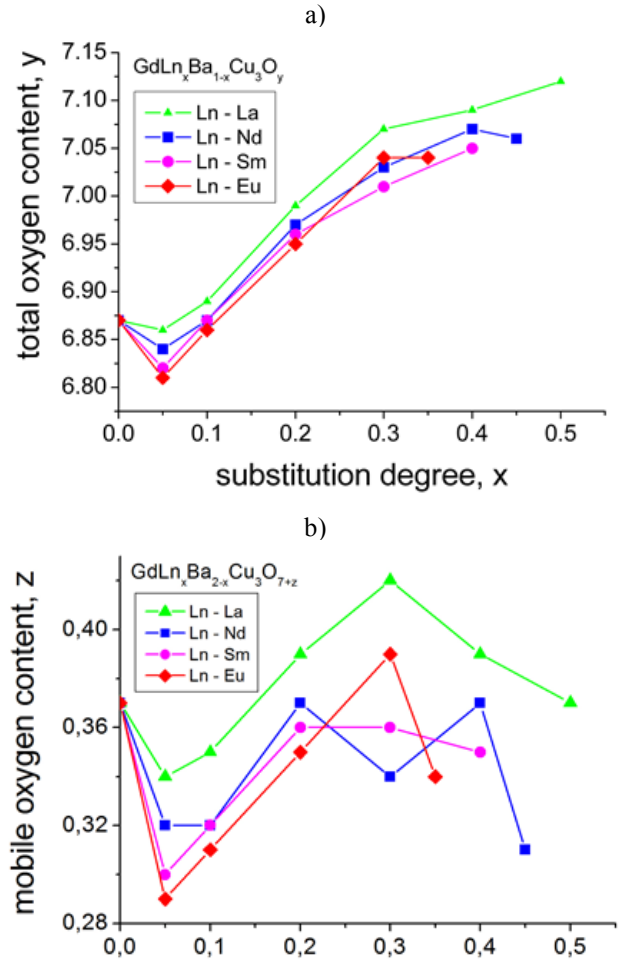


Fig. 4. Dependence of the total  $y$  (a) and mobile  $z$  (b) oxygen content on the substitution degree  $x$  for Gd123:Ln samples.

Measurements of the resistance of Gd123:Ln samples were performed in the temperature range 77–300 K. They showed that superconducting transitions at temperatures over 77 K are observed only for Gd123 ( $T_c = 94$  K) and for Gd123:Ln ( $x = 0.05$ ,  $T_c < 90$  K) (Fig.5a).

The samples with a substitution degree above 0.05 do not exhibit superconductivity at temperatures above 77 K. It is known from the literature that  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$  solid solutions can pass to the superconducting state for  $x$  values up to 0.5. This occurs, however, at temperatures considerably below the boiling point of liquid nitrogen [6].

For the samples with  $0 \leq x \leq 0.6$  ( $\text{Ln} = \text{La}$ ) and  $0 \leq x \leq 0.5$  ( $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$ ) the variation of the resistance in the temperature range 150–300 K is similar to that of a typical metal (Fig.5b). On further increasing the temperature, the resistance begins to increase, as in the case of semiconductors.

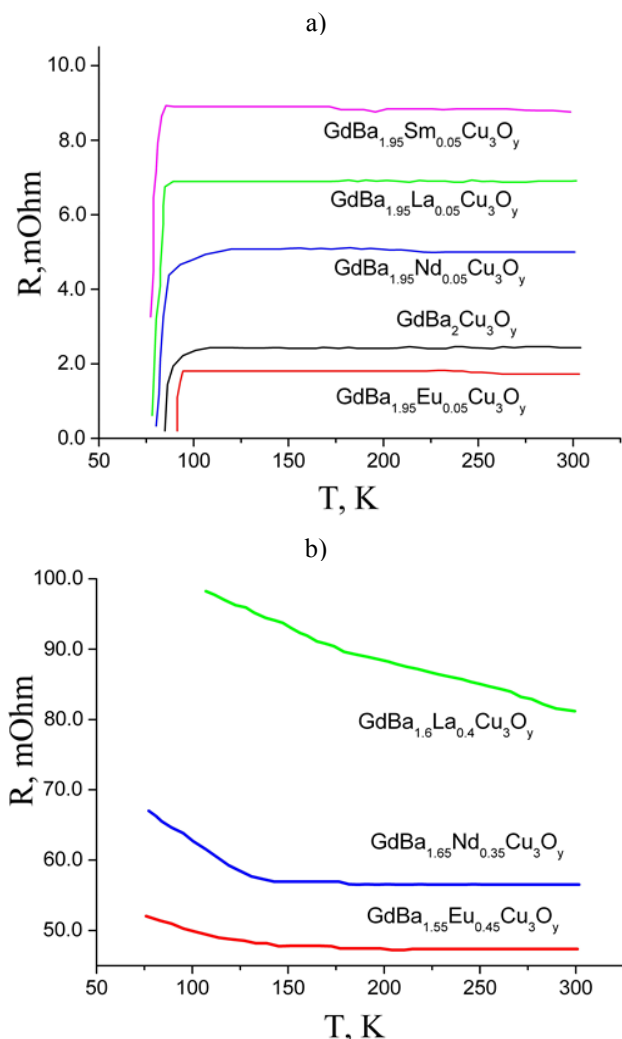


Fig. 5. Temperature dependence of electrical resistance for  $\text{GdBa}_2\text{Cu}_3\text{O}_y$ ,  $\text{GdLn}_{0.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_y$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$ ) (a) and  $\text{GdEu}_{0.45}\text{Ba}_{1.55}\text{Cu}_3\text{O}_y$ ,  $\text{GdNd}_{0.35}\text{Ba}_{1.65}\text{Cu}_3\text{O}_y$ ,  $\text{GdLa}_{0.4}\text{Ba}_{1.6}\text{Cu}_3\text{O}_y$  (b) solid solutions.

On the whole, the sample resistance increases with increasing substitution degree  $x$ . The increase of the resistance in the solid solutions may be explained by a decrease of the charge carrier concentration. In superconducting compounds of Y123 type, the electric current is realized by holes. During the heterovalent replacement of bivalent barium by trivalent cations of lanthanide, the latter supply additional electrons to the sample. As a result, the hole concentration decreases.

#### IV. CONCLUSIONS

We transitions at temperatures above 77 K have studied experimentally the variation of the oxygen content and lattice parameters of  $\text{Gd123}:\text{Ln}$  solid solutions with composition. The interrelation between the crystal structure and the oxygen

content was investigated. It was shown that the orthorhombic symmetry of  $\text{Gd123}$  is changed to tetragonal when barium is replaced by a lanthanide ( $x \geq 0.05$ ). The homogeneity region of the solid solution becomes wider when going from  $\text{Eu}^{3+}$  to  $\text{La}^{3+}$ . From resistivity measurements it was found that only  $\text{Gd123}$  and  $\text{GdLn}_{0.05}\text{Ba}_{1.95}\text{Cu}_3\text{O}_y$  exhibit superconducting properties.

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#### REFERENCES

- [1] N Martucciello, F Giubileo, G Grimaldi, and V Corato, "Introduction to the focus on superconductivity for energy," *Supercond. Sci. Technol.*, vol. 28, 2015, Art. no. 070201.
- [2] M. Sumadiyasa, I.G.A.P. Adnyana, N. Wendri, P. Suardana "Synthesis and Characterization of GLBCO-123 Phase:  $\text{Gd}_{1-x}\text{Ln}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $x = 0.0 - 0.5$ )", *MSCE*, vol. 5, 2017, pp. 49-57.
- [3] M. Rivera, A.M.G. Cuaspud, J.A.P. V'argas, C.A. Brijaldo, M.H. Ramirez, "Synthesis and characterization of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system, by combustion technique", *J. Supercond. Nov. Magn.*, vol. 29, 2016, pp. 1163-1171.
- [4] V.A. Drozd, I.L. Baginsky, S.A. Nediilko, V.S. Mel'nikov, "Oxygen stoichiometry and structural parameters of  $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$  solid solutions versus composition and temperature", *J. Alloys Compd.*, vol. 384, 2004, pp. 44-50.
- [5] J. Maňka, A. Cigán, J. Polovková, A. Koňakovský, "Effects of slight non-Stoichiometry in  $\text{Sm-Ba-Cu-O}$  systems on superconducting characteristics", *Measurement science review*, vol. 11, 2011, pp. 9-14.
- [6] J. Mozhaeva, A. Khoryushin, A. Puriy, J. Hansen, J. Bindlev, S. Claus, "Structure and electrical properties of  $\text{NdBa}_2\text{Cu}_3\text{O}_y$  thin films by laser ablation at low oxygen partial pressure", *J. Supercond. Nov. Magn.*, vol. 30, 2017, pp. 1781-1794.
- [7] A. Stoyanova-Ivanova, St. Georgieva, T. Nedeltcheva, L. Dimova, B. Shivachev, "Variation of the unit-cell parameters of the  $\text{REBa}_2\text{Cu}_3\text{O}_y$  ( $\text{RE} = \text{Gd}, \text{Er}$ ) ceramics in function of the oxygen content", *Bulg. Chem. Commun.*, vol. 43, 2011, pp. 320-324.
- [8] M. Mizadeh, M. Akhavan, "Pr at Gd or Ba site in  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ : Appearance of superconductivity", *Phys. Rev. B*, vol. 68, 2003, pp. 1045161-10451613.
- [9] M. Mirzadeh, M. Akhavan, "Electrical and magnetic properties of  $\text{Gd}(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{7+\delta}$ ", *Eur. Phys. J. B*, vol.43, 2005, pp. 305-318.
- [10] V.S. Vinila, R. Jacob, A. Mony, H.G. Nair, S. Issac, S. Rajan, A.S. Nair, D.J. Sathesh, J. Isac, "Ceramic nano-crystalline superconductor gadolinium barium copper oxide ( $\text{GdBaCuO}$ ) at different treating temperatures", *JCPT*, vol. 4, 2014, pp. 168-178.
- [11] B. Kang, D.H. Tran, W.N. Kang, "Scaling of pinning forces in  $\text{BaSnO}_3$ -added  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$  superconducting thin films", *Thin Solid Films*, vol. 624, 2017, pp. 16-20.
- [12] Y. Park, M. Lee, H. Ann, Y.H. Choi, H. Lee, "A superconducting joint for  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ -d-coated conductors", *NPG Asia Materials*, vol. 6, 2014 6, e98(1-5).
- [13] A.O. Pilipenko, S.A. Nediilko, O.G. Dziuzko, T.A. Voitenko, I.V. Fesich, M. Zelenko, N.Yu. Strutynska, Y. Galagan, O. Golovchenko, "High-temperature superconducting nanocomposites and their stability", *Proceedings of the 7th International Conference Nanomaterials: Applications and Properties*, 2017, pp. 03NNSA24-1 - 03NNSA24-4.
- [14] H. Asano, K. Takita, T. Ishigaki, H. Akinaga, H. Katoh, K. Masuda, M. Imai, M. Nishino, "Crystal structure of the high- $T_c$  superconductor  $\text{LnBa}_2\text{Cu}_3\text{O}_7$ -d ( $\text{Ln} = \text{Sm}, \text{Eu}$  and  $\text{Gd}$ )", *Jpn. J. Appl. Phys.*, vol. 26, Part 2, 1987, pp. 1410-1412.
- [15] P. Scherrer, "Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen", *Nachr. Ges. Wissen. Göttingen. Math.-Physik. Klasse*, 26, 1918, pp. 98-100.