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# INVESTIGATION OF THE DEPENDENCE OF ORTHOROMBIC FACTORS ON EFFECTIVE IONIC RADIUS IN THE $Ln_3Ba_5Cu_8O_x$ SYSTEM
## *(WHERE Ln– Y, Nd, Sm, Eu, Gd)*

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Four superconducting compounds are widely known in the Y-Ba-Cu-O system, namely: $YBa_2Cu_3O_{7-\delta}$ (Y-123), $YBa_2Cu_4O_{8-\delta}$ (Y-124), $Y_2Ba_4Cu_7O_{14+\delta}$ (Y-247) and $Y_3Ba_5Cu_8O_{18+\delta}$ (Y-358). They are characterized by a layered perovskite-like structure with different numbers of $CuO_2$ planes and CuO chains [1, 2]. It has been experimentally confirmed that as the number of $CuO_2$ planes for HTSCs – cuprate superconductors increases, the superconducting transition temperature increases [3, 4].

Thus, the various characteristics of superconducting materials, and especially the electrophysical and magnetic properties, are significantly influenced by their crystal structure, the parameters of the elementary lattice, the factor of orthorhombicity and the oxygen index. This work is devoted to the establishment of the parameters of elementary cells in the system: $Ln_3Ba_5Cu_8O_x$ (where Ln– Y, Nd, Sm, Eu, Gd), the calculation of the factor of orthorhombicity of the obtained phases and the establishment of dependences between these values.

The samples were synthesized by the classical solid-phase method. The oxides of the corresponding metals (Y, Nd, Sm, Eu, Gd, Cu) and barium carbonate in the appropriate molar ratios were ground in an agate mortar to form a homogeneous mass. The resulting mixture was calcined in the temperature range 600 - 950°C in increments of 50°C for 40 hours, with intermediate grinding. The polycrystalline powder was then compressed into tablets at a pressure of 100 MPa and kept for about 10 hours at 900°C in air.

The phase composition was investigated by X-ray powder diffraction on a Shimadzu LabX XRD-6000 diffractometer (CuKα - radiation, $\lambda$ = 1.54178 Ǻ, range of angles: $5 \le 2\theta \le 90°$), at room temperature. The International Powder Diffraction Standards Database (JCPDS PDF-2) was used to identify the phases. The index of X-ray diffraction pattern, determination of a wide group of crystallographic parameters was performed using an additional program INDEX and X-Ray.

The coefficient of orthorhombicity for the samples was performed according to the formula [5]:

$$\sigma = \frac{(b-a)}{(a+b)}$$

*where: a – is the numerical value of the unit cell parameter a;*
*b – is the numerical value of the unit cell parameter b;*
*σ – is the factor of orthorombicity.*

According to powder X-ray diffraction, it was found that in all samples the main phase $Ln_3Ba_5Cu_8O_x$ (Ln-358) crystallizes in orthorhombic syngony (sp. gr. Pmm2). Orthorhombic syngonia (sp. gr. Pmm2) was also determined for the yttrium phase (Y-

358), as well as oxygen parameters, average degree of copper oxidation and superconducting parameters [6].

The calculated data of elementary cells (Table 1) are close in values, but their difference correlates with the ionic radii of rare earth cations. The factor of orthorhombicity increase in a series: σ(Nd-358)< σ(Sm-358)< σ(Eu-358) < σ(Gd-358) < σ(Y-358) (Table 1).

*Table 1*

**Elemental cell parameters of superconducting phases Ln-358, values of effective ionic radius Ln and orthorhombic factors of systems**

| Sample | Elementary cell parameters | | | | Effective ionic radius, Å *(by Shannon and Pruitt)* | Orthorhombic factor |
|---|---|---|---|---|---|---|
| | *a*, Å | *b*, Å | *c*, Å | *V*, Å³ | | |
| Y-358 | 3,850(1) | 3,921(1) | 31,033(6) | 468,5(0) | 1,076 | 0,91(4) |
| Nd-358 | 3,881(1) | 3,941(1) | 32,011(5) | 468,5(8) | 1,163 | 0,74(2) |
| Sm-358 | 3,864(2) | 3,927(2) | 31,054(3) | 471,2(1) | 1,132 | 0,78(4) |
| Eu-358 | 3,861(3) | 3,924(3) | 31,064(2) | 470,6(4) | 1,12 | 0,80(9) |
| Gd-358 | 3,851(1) | 3,923(1) | 31,061(1) | 469,2(4) | 1,107 | 0,88(8) |

*[author's development]*

The dependences of the crystal lattice parameters of the obtained phases on the effective ionic radii of lanthanides show a linear directly proportional character. That is, with increasing metal radius there is an increase in the volume of the crystal cells (Fig. 1).

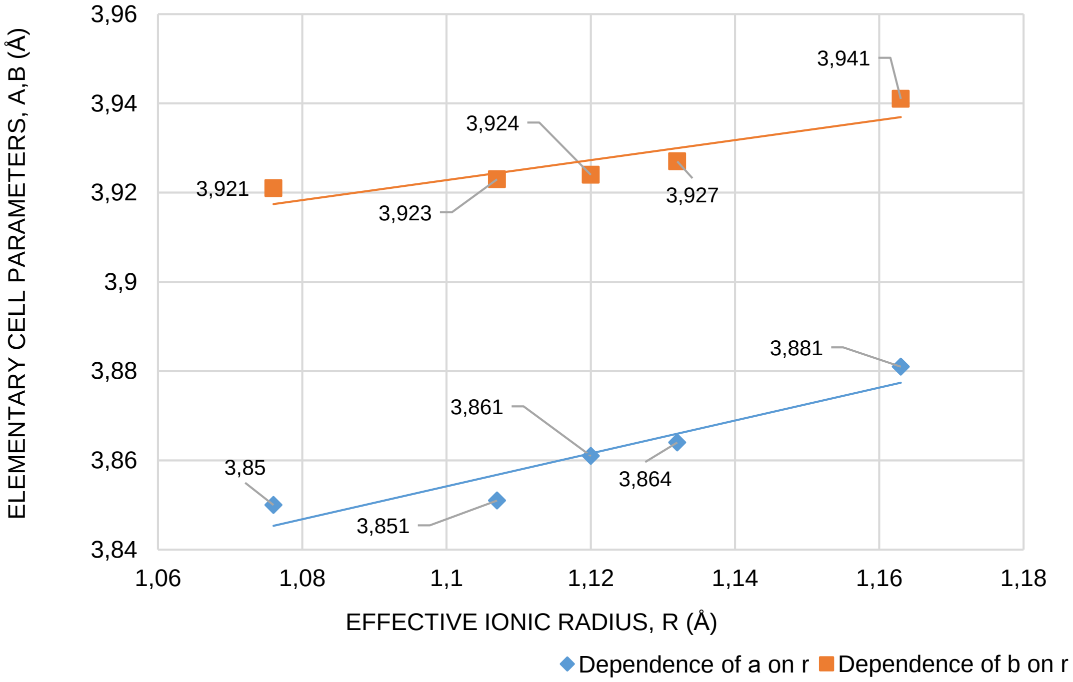


Fig. 1. **Dependences of crystal lattice parameters *a* and *b* on effective ionic radii Y, Nd, Sm, Eu, Gd**

The dependence of the orthorhombic factor on the ionic radius (Fig. 2) shows an inversely proportional character. That is, there is a decrease in the orthorhombicity of the system in the samples with an increase in their ionic radius.

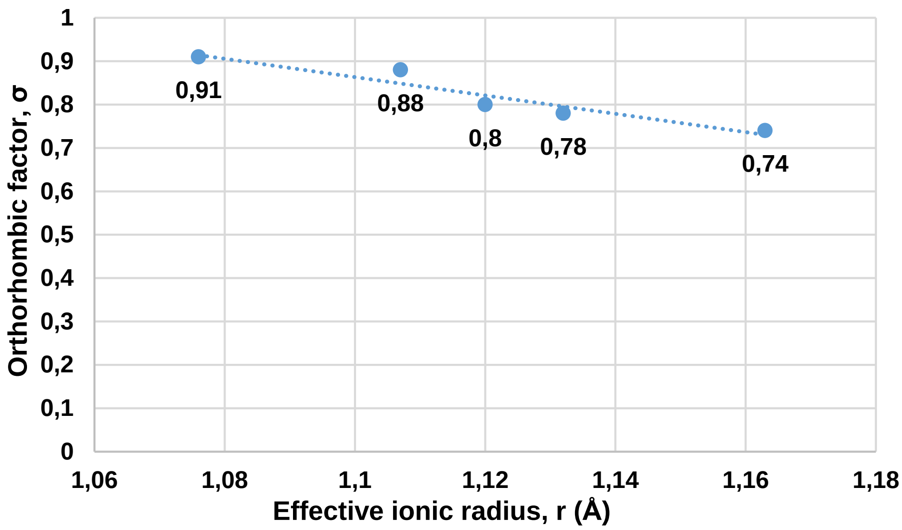


Fig. 2. **Dependence of the orthorhombic factor on the effective ionic radius Y, Nd, Sm, Eu, Gd**

**Conclusions.** Samples of Ln-358 (Ln: Nd, Sm, Eu, Gd and Y) were obtained using the solid phase synthesis method. It was found that in the samples: Nd-358, Sm-358, Eu-358, Gd-358, Y-358 – the main superconducting phase Ln-358 crystallizes in orthorhombic syngony (sp. gr. Pmm2).

The calculated unit cell data for the obtained samples are close in values and their difference correlates well with the ionic radii of rare earth cations. The dependences of the parameters of the unit cells of the obtained phases on the effective ionic radii of lanthanides show a linear direct proportional character (Fig. 1). However, the dependence of the orthorhombic parameters on the ionic radius shows an inversely proportional character (Fig. 2), ie there is a decrease in the orthorhombicity of the system in the samples with an increase in their ionic radius.

These results confirm that atoms close in radii (such as Y and Gd) replace each other in the cationic sublattice, forming phases with a high orthorhombic factor and sufficient oxygen content to obtain high-quality superconducting characteristics. Thus, compounds with a high orthorhombic factor (0.80-0.90) can have high values of the oxygen index and, accordingly, high values characterizing the superconductivity. However, phases with a deformated lattice ($\sigma$ <0.80) will have lower oxygen indices and lower values of Tc.

Therefore, atoms close in radii replace each other in the cationic lattice. It is obvious that the factor of obtaining the phase with orthorhombic structure is the size of the cation, which in turn affects the oxygen content of the compound and, subsequently, its superconducting properties.

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