

## 1. Introduction

The synthesis of a high-temperature superconductor  $Y_3Ba_5Cu_8O_x$  (Y-358) with a superconducting transition temperature ( $T_c$ ) > 100 K [1] aroused great interest in further studies of the Y-Ba-Cu-O system. Many research groups have devoted their research to the study of induced fluctuation of conductivity [2], determination of stoichiometry [3], thermoelectric power and thermal conductivity [4], study of superconducting properties [5], structural and transport properties [6]. But, the determination of particle sizes by a complex of different methods has not been studied.

Despite the existence of other high-temperature superconductors (HTSC) with higher  $T_c$ , yttrium cuprates have a number of advantages. This is the ease of obtaining (less energy-intensive), the absence of toxic and volatile oxides Hg, Bi, Tl and Pb (environmentally friendly), the ability to easily grow single crystals with good magnetic and microstructural properties [7]. And the creation of materials with new qualitative properties and the improvement of the characteristics of existing compounds is the main goal of modern synthetic science. The basis for successful forecasting of new materials is the study of the dependence "Composition– Structure– Properties". Analysis of the dimensional, morphological, and structural characteristics of compounds shows that they largely depend on the synthesis method. Determining the size, structure, and morphology of superconducting phases provides even more opportunities for studying the mechanisms of superconductivity. This expands the knowledge in the field of studying superconducting compounds.

Determination of the size, structure and morphology of particles is usually carried out by methods such as scanning and transmission electron microscopy, high-resolution microscopy, tunneling and atomic force microscopy. However, methods based on integral characteristics of the powder can also be useful. These methods are based on the analysis of the expansion and shape of X-ray diffraction lines, methods of small-angle scattering of X-rays and neutrons, dynamic light scattering, the method for determining the specific surface of powders.

The methods based on the analysis of X-ray structural data have a fairly wide range of parameters determination: phase composition, structure, average size, and morphological characteristics of crystals [8].

## DETERMINATION OF THE SIZES OF PARTICLES OF SUPERCONDUCTING CUPRATE $Y_3Ba_5Cu_8O_x$ BY MEANS OF DIFFERENT METHODS

Anastasiia Bolotnikova

PhD

Department of Medical and General Chemistry  
Bogomolets National Medical University  
13 Tarasa Shevchenko Boulevard, Kyiv, Ukraine, 01601  
pylypenko.anastasiia@gmail.com

**Abstract:** The superconducting cuprate  $Y_3Ba_5Cu_8O_x$  was obtained with the help of sol-gel technology (sample C), co-precipitation of hydroxocarbonates (sample B) and solid-phase synthesis methods (A). Based on the results of scanning electron microscopy and methods based on the analysis of X-ray diffraction data: the Williamson-Hall construction and the Scherrer formula, features of the microstructure of the synthesized samples are established. The smallest particle size has a sample that has been synthesized by the sol-gel method. The tendency to aggregation and sedimentation for this sample is the smallest. The sample obtained by the co-precipitation method has larger grains and a higher tendency to aggregate. The size of the micro-particles and the tendency to aggregate for the sample synthesized by the solid-phase method are greatest. The morphology of particles was studied using three methods: SEM, Scherrer and Williamson-Hall formulas and the following results were found: particle size depends on the synthesis method, but a relatively narrow size distribution within one synthesis method remains, the value of crystal lattice microdeformation for samples increases in a line: C sample – A sample – B sample. Thus, the work was carried out for determining the size, structure and morphology of superconducting phases. It expands knowledge in the field of research of superconducting compounds.

**Keywords:** size of particles, Williamson-Hall method, Scherrer formula, sol-gel technology, solid-state method, co-precipitation of hydroxocarbonates, high-temperature superconductors, SEM, Y-358 phase, X-Ray analysis.

Each of these methods has both certain advantages and some limitations. Thus, it can be stated that for a reliable assessment of the size, morphology and structure of particles, it is necessary to use certain sets of methods. Therefore, the purpose of this work was to study the features of the morphology of superconducting cuprates by three methods: using scanning electron microscopy, the Williamson-Hall method, and using the Scherrer formula.

## 2. Methods

The reagents were qualified "chemically pure" for all methods of synthesis.

Synthesis of the polycrystalline sample A was carried out using a standard solid-phase method. As starting compounds, oxides of copper (II), yttrium and barium peroxide were used. The solid reagents were thoroughly homogenized in an agate mortar to a homogeneous mass (taken in a molar ratio of 3:5:8=Y:Ba:Cu). The resulting mixture was placed in porcelain crucibles and calcined at 950 °C for 24 hours in a muffle furnace. After that, the powder was re-triturated, compressed into tablets at a pressure of 100 MPa and subjected to a heat treatment for 24 hours at 950 °C. The final calcination was carried out at a temperature of 500 °C for 24 hours.

Sample B was prepared by the method of co-precipitation of hydroxocarbonates. The co-deposited mixture was obtained by precipitation of aqueous solutions of nitrates of the corresponding metals, mixed in stoichiometric proportions, 1M  $Na_2CO_3$  solution in the ratio 1:1.75. Precipitation was carried out with intensive mixing on a magnetic stirrer. After aging and analysis of the ion precipitate completeness, the precipitates were filtered off and washed with distilled water. The precipitate was dried in air, triturated in an agate mortar, and subjected to a heat treatment at 800 °C for 36 hours with intermediate rubbing after 12 and 24 hours of heat treatment. After that, the powdered samples were compressed into tablets, sintered at 800 °C in the open air, and conducted electrical measurements.

Sample C was synthesized by the sol-gel technique. Appropriate amounts of solutions of yttrium, barium, and copper nitrates were mixed in a glass-graphite cup. The citric acid monohydrate was used as a gelling agent. The solution of ammonia was added to maintain pH=6. The mixture was evaporated in a water bath to form a homogeneous gelatinous mass. The subsequent heating of the formed substance was accompanied by self-ignition. The resulting mixture was calcined with gradual heating from 400 to 800 °C at a rate of 100 °C/hour.

The powder was then grinded, pressed into tablets and investigated electrical properties.

The phase composition and the crystallographic characteristic of this compounds were determined by X-ray powder diffraction on a diffractometer Shimadzu XXRD-6000 (CuK $\alpha$  – radiation,  $\lambda=0.154056$  nm, range of angles  $5 \leq 2\theta \leq 90^\circ$ ). Diffraction patterns were analyzed using the database of the International Center for Diffraction Data (JCPDS PDF-2) [9]. The shooting was carried out at a speed of  $1^\circ/\text{min}$ . Indexing of the diffractograms, determining the spaces group and calculating the crystallographic parameters were established by using programs INDEX and X-Ray. The diffraction patterns were analyzed and corrected using Peak Fit selection program [10]. The morphology of the surface, the relief and the size of the grains were studied using a scanning electron microscope (SEM) of the JEOL JSM-35C brand and an open-source image processing software for scientific multidimensional ImageJ images [11].

In the calculations of the particle size were used the method of Williamson-Hall construction, based on the ratio:

$$\frac{\beta \cdot \cos \theta}{\lambda} = \frac{1}{D} + \epsilon d^*$$

where  $\beta$  – the physical expansion of the diffraction maximum;  $\theta$  – the Bragg reflection angle;  $\lambda$  – the wavelength of radiation (CuK $\alpha$ 1), which equal to 0.1541 nm;  $D$  – the average size of the coherent scattering region;  $\epsilon$  – the average length of microdeformation;  $d^* = \frac{(2 \sin \theta)}{\lambda}$  – the length of the vector of the return lattice [12].

Also, calculations of particle size were carried out using the Scherrer formula:

$$d = \frac{k \cdot \lambda}{\beta \cdot \cos \left( \frac{2\theta}{2} \right)},$$

where  $d$  – the participle diameter, nm;  $\beta$  – the width of X-ray maximum at half-height;  $\lambda$  – the wavelength of radiation, nm;  $k$  – some coefficient, which is considered to be  $\approx 1$  [13].

### 3. Results

#### 3. 1. Study of the morphology of Y<sub>3</sub>Ba<sub>5</sub>Cu<sub>8</sub>O<sub>18- $\delta$</sub> using SEM

Surface morphology and grain size in the samples were investigated using SEM and ImageJ. Grains in all samples, as shown in Fig. 1, are freely packaged and randomly oriented. The surface of the test compound is homogeneous and contains irregularly shaped particles, in some areas of microphotographs aggregation and agglomeration of particles is observed. Fig. 1, *a* shows an image typical of a sintered ceramic sample, with disordered grains having an average size of 2–3  $\mu\text{m}$ . The powder contains a significant amount of agglomerates. The size of the agglomerates reaches 5  $\mu\text{m}$ . Fig. 1, *b* shows that the sample contains a smaller number of agglomerates and the size of these formations does not exceed 3  $\mu\text{m}$ . The grain size of this compound has an average size of 1  $\mu\text{m}$ . The surface morphology of sample C (Fig. 1, *c*) is fine and even visually porous.

The average grain size is 0.5  $\mu\text{m}$ . The sample is slightly aggregated, but the size of the units does not exceed 2  $\mu\text{m}$ . In

addition, the grain boundaries in all samples are clear and have clean surfaces.

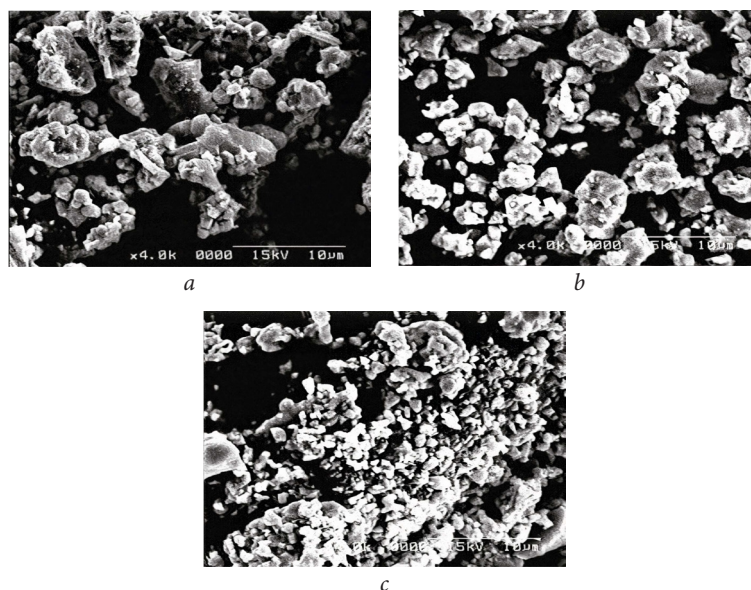


Fig. 1. Microphotographs of the compound Y<sub>3</sub>Ba<sub>5</sub>Cu<sub>8</sub>O<sub>18- $\delta$</sub>  (scale 10  $\mu\text{m}$ ) obtained by: *a* – the solid state reaction; *b* – the method of co-precipitated hydroxycarbonate; *c* – the sol-gel technology

The relationship between the susceptibility of the samples to agglomeration and the degree of their sintering can be traced. It turned out that as the degree of sintering of the samples decreases in the range from A to C, the number of agglomerates and their sizes decrease.

#### 3. 2. Clarification of cuprate grain sizes Y<sub>3</sub>Ba<sub>5</sub>Cu<sub>8</sub>O<sub>18- $\delta$</sub> by methods: Scherrer and Williamson-Hall

Diffractograms and their main characteristics were used to specify grain sizes. Table 1 presents the main reflexes of the synthesized phase.

Using PeakFit, the data obtained by X-ray phase analysis were prepared, systematized and refined. The standard deviation for the functions describing the diffractometric data was not less than  $r^2=0.98$ .

Table 1

The value of the width of the X-ray maximum at half height ( $\beta$ ) at the corresponding values of  $2\theta$  on the diffraction patterns of the samples

Sample C		Sample B		Sample A	
$\beta$ , nm	$2\theta$ , °	$\beta$ , nm	$2\theta$ , °	$\beta$ , nm	$2\theta$ , °
0.000247	15.17	0.000095	15.21	0.0000568	15.17
0.000251	22.88	0.000107813	22.87	0.0000572	22.90
0.000256	29.86	0.000122286	29.88	0.0000669	27.65
0.000259	32.85	0.000120191	32.88	0.0000682	32.67
0.000264	38.59	0.000125296	38.56	0.0000696	38.68
0.000266	40.41	0.000112463	40.43	0.0000698	40.30
0.000272	46.72	0.00012712	46.77	0.0000832	46.80
0.000286	58.27	0.000174569	58.24	0.0000781	58.30

#### 3. 3. Scherrer method

Scherrer formula is used only for compounds with grain sizes larger than 100–200 nm, so the objects of our study are suitable for the use of this method.

The results showed that the obtained dimensions are slightly larger compared to other methods, because in addition to instrumental expansion and expansion due to the size of the crystallites, there are other factors that contribute to the width of the peaks on the diffractograms. For these samples, such factors may be distortion and defects of the crystal lattice, dislocations, packaging defects, twins, grain boundaries and chemical heterogeneity. Therefore, the particle sizes determined by the Scherrer formula are not accurate enough, because they take into account the expansion caused only by the particle size. Williamson-Hall method is used for more accurate determination. Calculations of the average particle sizes of the synthesized samples using the Scherrer formula are shown in Table 2.

Table 2

The results of calculations according to the Scherrer formula

Sample C	Sample B	Sample A
$\langle d, \text{nm} \rangle$	$\langle d, \text{nm} \rangle$	$\langle d, \text{nm} \rangle$
(average size)	(average size)	(average size)
553.25 (0.55 $\mu\text{m}$ )	1204.4 (1.20 $\mu\text{m}$ )	2134.8 (2.14 $\mu\text{m}$ )

### 3. 4. Williamson-Hall construction method

Graphically, the dependence  $s^* = \frac{\beta \cdot \cos \theta}{\lambda}$  on  $d^* = \frac{(2 \sin \theta)}{\lambda}$  a straight line (Fig. 2), on the segment cut off on the y-axis, determine  $1/D$ , and on the slope of the line  $-\epsilon$ , where  $D$  is the particle size, and  $\epsilon$  are microdeformations in the crystal lattice.

Numerical values for the obtained linear approximations are given in Table 3.

Table 3

The results of calculations of grain sizes and microdeformation values using the Williamson-Hall construction method

Sample C			Sample B			Sample A		
$\epsilon$	$1/D$	$D, \mu\text{m}$	$\epsilon$	$1/D$	$D, \mu\text{m}$	$\epsilon$	$1/D$	$D, \mu\text{m}$
$1 \cdot 10^{-5}$	0.0016	0.63	$6 \cdot 10^{-5}$	0.00053	1.89	$2 \cdot 10^{-5}$	0.00035	2.86

The values of microdeformation for the samples are presented in Table 4, the results are in the same order. However, the microdeformations of the crystal lattice for the samples increase in a number: C–A–B–samples. This fact correlates well with the results of X-ray phase analysis, because most of the impurities in the sample obtained by co-precipitation of hydroxocarbonates, slightly less in the solid-phase sample. Obviously, impurities cause more significant deformations and microdistortions.

The graphical dependence  $s^* = \frac{\beta \cdot \cos \theta}{\lambda}$  on  $d^* = \frac{(2 \sin \theta)}{\lambda}$ , the segment on the axis ( $1/D$ ) and the slope of the line  $-\epsilon$  for the three samples are presented in Fig. 2, a–c.

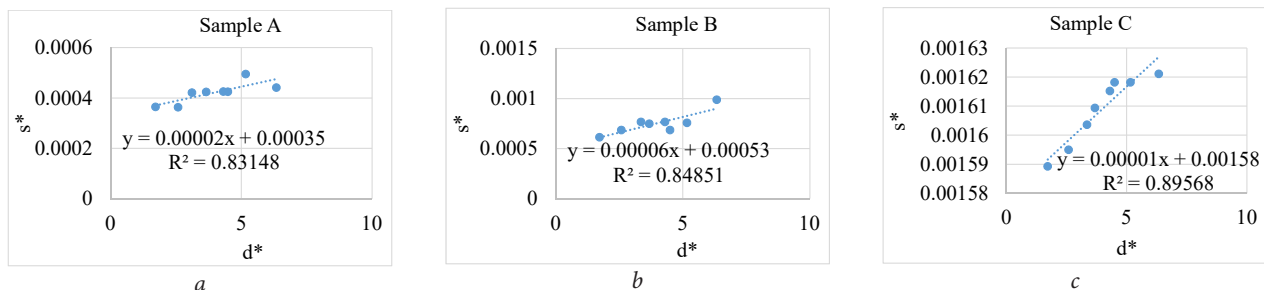


Fig. 2. Graphs of Williamson-Hall dependencies: a – sample A (solid-phase method); b – sample B (method of co-precipitation of hydroxocarbonates); c – sol-gel technique

## 4. Discussion

The results obtained by the scanning electron microscope have the same order of magnitude as in the other two methods, but are not identical. This difference can be explained by the ability of these samples to aggregate and agglomerate, so real microparticles can be smaller. The dispersion of microparticles of the obtained complex superconducting cuprates, thus, shows aggregative and sedimentation instability.

Any method can be used to estimate the particle size of a substance, but a set of methods must be used to actually establish the morphology and grain size of the compounds. Comparative characteristics of the results of the three selected methods for calculating the size of microparticles are given in Table 4.

Table 4

 The results of determining the particle size of the superconducting cuprate  $\text{Y}_3\text{Ba}_5\text{Cu}_8\text{O}_x$  obtained by different methods ( $\langle d, \mu\text{m} \rangle$  – average size of microparticles)

Method of calculating the size of microparticles	Sample C, $\langle d, \mu\text{m} \rangle$	Sample B, $\langle d, \mu\text{m} \rangle$	Sample A, $\langle d, \mu\text{m} \rangle$
SEM	0.50	1.00	2.00
Williamson-Hall method	0.63	1.89	2.86
Scherrer method	0.55	1.20	2.14

Analysis of the data obtained by three methods of sizing showed that the particle size increases slightly under the influence of different methods of synthesis, but a relatively narrow size distribution within one method of synthesis is maintained. This difference can be explained by different temperature regimes during sintering of the samples.

The obtained results clearly correlate with the accuracy of determining the particle sizes of the selected methods. That is why a set of methods was used to reliably assess the size, morphology and structure of microparticles. This made it possible to estimate the size of the microparticles of this phase more broadly. In addition, a certain dependence of the particle sizes of powders on the method of their synthesis was observed. And in a number from A to C the sizes of microparticles decrease. The dependence of the number of microdeformations in the sample depending on the synthesis methods was established. The microdeformations of the crystal lattice for the samples increase in a number: C-sample – A-sample – B-sample. This fact correlates well with the results of X-ray phase analysis, because most impurities in the sample obtained by co-precipitation of hydroxocarbonates, slightly less in the solid-phase sample [14]. Obviously, impurities cause more significant deformations and microdeformations.



The determination of particle sizes for the superconducting phase Y-358 by the methods of Williamson Hall and Scherer was carried out for the first time. The obtained results allow to expand knowledge in the field of superconducting cuprates in the Y-Ba-Cu-O system.

After all, a special contribution to the study of the superconductivity mechanism is the determination of the number of micro-deformations in the synthesized samples. The number of micro-deformations can both increase the temperature of the transition to the superconducting state and reduce it. The further research will be devoted to the dependence of the electrical conductivity of samples on particle sizes. The correlation of such results can significantly affect the study of superconductivity mechanisms.

### 5. Conclusion

In this paper, the superconducting  $Y_3Ba_5Cu_8O_x$  cuprate was synthesized by sol-gel technology, co-precipitation hydroxocarbonates and the classical ceramic method. Using the scanning electron microscopy, the Williamson-Hall method and the Sherrer formula, the size of the microparticles of the superconducting powders obtained was established.

The features of morphology of superconducting cuprate according to the synthesis method are revealed. Thus, the smallest particle size has a sample C that was synthesized by the sol-gel method. The tendency to aggregation and sedimentation for this sample is the smallest, which can be explained by the conditions of synthesis. This sample had a relatively low baking temperature compared to the other two, and the homogenization of microparticles in this synthesis method was practically at the molecular level. The sample B because of a slightly higher treatment temperature, obtained by the method of co-precipitation, has larger grains and a high tendency to aggregate. In addition, this sample contains a small amount of impurity phases, which also affects the general morphology of the compound. Sample A was subjected to the highest temperatures of calcination and homogenization was carried out by mechanical grinding of the reaction mixture in the agate mortar. Therefore, the size of the microparticles for this powder is the largest, and this sample also has a significant propensity for aggregation. Consequently, the size of the grains varies depending on the methods of synthesis, but the relatively narrow size distribution within one synthesis method is preserved.

### References

1. Aliabadi, A., Akhavan Farshchi, Y., Akhavan, M. (2009). A new Y-based HTSC with  $T_c$  above 100K. *Physica C: Superconductivity and Its Applications*, 469 (22), 2012–2014. doi: <https://doi.org/10.1016/j.physc.2009.09.003>
2. Esmaeili, A., Sedghi, H., Amniat-Talab, M., Talebian, M. (2011). Fluctuation-induced conductivity and dimensionality in the new Y-based  $Y_3Ba_5Cu_8O_{18-x}$  superconductor. *The European Physical Journal B*, 79 (4), 443–447. doi: <https://doi.org/10.1140/epjb/e2011-10814-x>
3. Topal, U., Akdogan, M. (2011). Further Increase of  $T_c$  in Y-Ba-Cu-O Superconductors. *Journal of Superconductivity and Novel Magnetism*, 24 (5), 1815–1820. doi: <https://doi.org/10.1007/s10948-011-1129-1>
4. Aksan, M. A., Kizilaslan, O., Aksan, E. N., Yakinci, M. E. (2012). Thermoelectric power and thermal conductivity study of the  $Y_3Ba_5Cu_8O_x$  system. *Physica B: Condensed Matter*, 407 (14), 2820–2824. doi: <https://doi.org/10.1016/j.physb.2012.04.035>
5. Topal, U., Akdogan, M., Ozkan, H. (2011). Electrical and Structural Properties of  $RE_3Ba_5Cu_8O_{18}$  ( $RE=Y, Sm$  and  $Nd$ ) Superconductors. *Journal of Superconductivity and Novel Magnetism*, 24 (7), 2099–2102. doi: <https://doi.org/10.1007/s10948-011-1176-7>
6. Ayaş, A. O., Ekicibil, A., Çetin, S. K., Coşkun, A., Er, A. O., Ufuktepe, Y. et. al. (2011). The Structural, Superconducting and Transport Properties of the Compounds  $Y_3Ba_5Cu_8O_{18}$  and  $Y_3Ba_5Ca_2Cu_8O_{18}$ . *Journal of Superconductivity and Novel Magnetism*, 24 (8), 2243–2252. doi: <https://doi.org/10.1007/s10948-011-1192-7>
7. Barakat, M. M. E., Awad, R., Abou-Aly, A. I., Roumié, M., Aly, N., Ibrahim, S. (2014). Determination of Stoichiometry and Superconducting Properties of  $Y_{3-x}Nd_xBa_{5-x}Ca_xCu_8O_{18-\delta}$  Samples. *Journal of Superconductivity and Novel Magnetism*, 28 (2), 453–458. doi: <https://doi.org/10.1007/s10948-014-2708-8>
8. Al'myasheva, O. V., Fedorov, B. A., Smirnov, A. V., Gusarov, V. V. (2010). Razmer, morfologiya i struktura chastits nanoporo-shka dioksida tsirkoniya, poluchennogo v gidrotermal'nyh usloviyah. *Nanosistemy: fizika, himiya, matematika*, 1 (1), 26–37.
9. The International Centre for Diffraction Data. Available at: <https://www.icdd.com/>
10. PeakFit - The Automatic Choice For Spectroscopy, Chromatography and Electrophoresis. Available at: <http://www.sigmaplot.co.uk/products/peakfit/peakfit.php>
11. ImageJ. An open platform for scientific image analysis. Available at: <https://imagej.net/Welcome>
12. Prabhu, Y. T., Venkateswara Methods Rao, K., Sesha Sai Kumar, V., Siva Kumari, B. (2013). X-ray Analysis of Fe doped ZnO Nanoparticles by Williamson-Hall and Size-Strain Plot. *International Journal of Engineering and Advanced Technology (IJEAT)*, 2 (4), 268–274.
13. Ginzburg, B. M., Tuichiev, S., Tabarov, S. K., Shepelevskii, A. A. (2007). Small-angle X-ray scattering study of the structure of powder fullerene C60 and fullerene soot. *Crystallography Reports*, 52 (2), 187–190. doi: <https://doi.org/10.1134/s1063774507020034>
14. Pilipenko, A. O., Nedilko, S. A., Dziačko, A. G., Fesich, I. V. (2017). Effect of Phase Composition of Superconductor  $Y_3Ba_5Cu_8O_{18+\delta}$  on Its Conducting Characteristics. *Theoretical and Experimental Chemistry*, 52 (6), 342–348. doi: <https://doi.org/10.1007/s11237-017-9488-8>

Received date 04.10.2020

Accepted date 06.11.2020

Published date 30.11.2020

© The Author(s) 2020

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0>).