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MECHANICAL PROPERTIES OF CERAMICS BASED ON $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$ SOLID SOLUTIONS

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$(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$-based ceramics were prepared by pressing and sintering from the micro- and nanopowders. The ceramic samples were investigated using microstructural analysis. The microhardness was measured using the method of pressing the Vickers pyramid. It has been shown that the microhardness of $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$-based ceramics essentially less ($\sim 50\%$) than that of the single crystals, but the tendency to the microhardness decrease with a decrease of the copper content at the $\mathrm{Cu}^+ \rightarrow \mathrm{Ag}^+$ cationic substitution is observed both for single crystals and ceramics. With the growth of microcrystallites' size in the range from 3 μm to 12 μm, the microhardness of ceramics increases. The compositional dependences and size effects of microhardness, electrical conductivity and density of $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$-based ceramics are analysed.

Key words: argyrodite; superionic conductor; ceramic; microhardness; ionic conductivity.

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I. INTRODUCTION

$\mathrm{Cu_7SiS_5I}$ and $\mathrm{Ag_7SiS_5I}$ superionic conductors belong to the wide family of compounds with the argyrodite-type structure [1, 2]. Electrical conductivity of $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$ solid solutions was investigated in Ref. [3]. It has been revealed that an increase in the silver atoms content in $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$ solid solutions leads to a nonlinear increase in electrical conductivity. Moreover, the ratio of ionic conductivity to the electronic one is nonlinearly increasing by almost five orders of magnitude at the transition from $\mathrm{Cu_7SiS_5I}$ to $\mathrm{Ag_7SiS_5I}$ [3]. Due to the high ionic conductivity, $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$ crystals are promising materials for different areas of solid state ionics (development of effective energy power sources, new electrode materials, supercapacitors etc) [3].

Recently, the ceramics based on superionic conductors with an argyrodite structure have benn investigated [4]. It should be noted that for a practical application the superionic materials in the ceramic form are more suitable. Therefore, the ceramics are more intensively applied in the production of functional components for different electronic devices.

Here we present the results of compositional studies of mechanical parameters and dimensional effects in superionic ceramics based on $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$ solid solutions.

II. EXPERIMENTAL

$\mathrm{Cu_7SiS_5I}$ and $\mathrm{Ag_7SiS_5I}$ compounds were synthesizad from simple substances: copper, silver, silicon, sulfur, and pre-synthesized binary copper (I) iodide and silver (I) iodide, further purified by vacuum distillation and directional crystallization, respectively, taken in stoichiometric ratios in evacuated to 0.13 Pa quartz ampoules. The synthesis regime of $\mathrm{Cu_7SiS_5I}$ and $\mathrm{Ag_7SiS_5I}$ included step heating up to 723 K at a rate of 100 K/h (ageing during 48 h), a further increase in temperature to 1470 K for $\mathrm{Cu_7SiS_5I}$ and 1230 K for $\mathrm{Ag_7SiS_5I}$ at a rate of 50 K/h and ageing at this temperature for 24 hours.

Alloys of $\mathrm{Cu_7SiS_5I}$–$\mathrm{Ag_7SiS_5I}$ system were synthesized using a direct one-temperature method from the pre-synthesized $\mathrm{Cu_7SiS_5I}$ and $\mathrm{Ag_7SiS_5I}$ compounds. The synthesis mode included step heating at a rate of 100 K/h to 1023 K and ageing at that temperature for 24 hours, a further increase in temperature to 1470 K at a rate of 50 K/h and ageing at that temperature for 72 hours. The annealing was performed at the temperature of 873 K during 120 hours. Cooling to room temperature was carried out in the mode of the switched off oven.

The ceramic samples were prepared from powders of different dispersion. The microcrystalline powders with an average particle size of $\sim$ 10–50 μm were obtained by grinding in an agate mortar. The nanocrystalline powders were ground in a planetary ball mill PQ-N04 for 30 min and 60 min with the speed of 200 rpm. The structural properties of $(\mathrm{Cu}_{1-x}\mathrm{Ag}_x)_7\mathrm{SiS}_5\mathrm{I}$ powders and ceramic samples were studied using XRD technique and microstructural analysis. The XRD measurements were performed using the diffractometer DRON 4-07 with CuK_α radiation, angle scanning speed 2θ was 0.02 degree, exposure was 1 s.

The powders were pressed at $\sim$400 MPa and annealed at 973 K during 36 hours. In such a way the polycrystalline ceramic samples were fabricated in the form of disks, 8 mm in diameter and 3–4 mm thick. The ceramic samples were investigated though microstructural analysis using metallographic microscope METAM-R1. It has been shown that the ceramic samples prepared by sintering a nanopowder obtained by grinding in a planetary ball mill are characterized by a more homogeneous microstructure, characterized by the distribution of particles in a narrower range, in contrast to the samples obtained by sintering a micropowder with a particle size of $\sim$ 10–50 μm. As a result of the recrystallization process, the average size of microcrystallites for the samples obtained from micropowder grinding in an agate mortar is ∼ 12 μm, while for the samples obtained from nanopowders grinding in a planetary ball mill for 30 min and 60 min is ∼ 5 μm and ∼ 3 μm, respectively.

We used the microindentation method using a Vickers indenter to study the mechanical properties of ceramics based on $(Cu_{1-x}Ag_x)_7SiS_5I$ solid solutions. This method is often used to investigate ceramic samples [5]. The measurements of microhardness using the method of pressing the Vickers pyramid were carried out in the load range of 0.1–2 N at room temperature. The microhardness PMT-3 meter with Vickers indenter (correct quadrangular pyramid with an angle of 136° at apex) was used to measure microhardness. The microhardness values were calculated by the equation [6]:

$$H = \frac{P}{S} = \frac{2P\sin\frac{\alpha}{2}}{d^2} = 1.854\frac{P}{d^2}, \qquad (1)$$

where α=136°, P is the load on the indentor, d is the diagonal of the imprint. The depth of indenter imprints was 1–10 μm (Fig. 1).

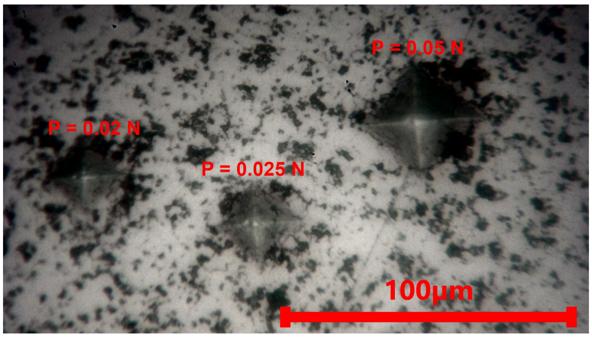

Fig. 1. Vickers indentor imprints and microstructure of ceramic sample based on $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ solid solution with an average crystallite size of ∼ 5 μm.

Electrical conductivity were measured though impedance spectroscopy [7] in the frequency range from 10 Hz to 2 × 10^6 Hz and temperature interval from 292 to 383 K using a combination of high-precision LCR meters: Keysight E4980A and AT-2818 [3]. The amplitude of the alternating current was 10 mV. Measurements were carried out using a two-electrode method, on blocking (electronic) gold contacts. Gold contacts for measurements were obtained by chemical precipitation from the solutions [3]. It has been revealed that with an increase in frequency the electrical conductivity grows, which is typical of materials with ionic conductivity in a solid state. For detailed studies of the frequency behavior of electrical conductivity as well as its separation into ionic and electronic components, a standard approach using electrode equivalent circuits (EEC) [7, 8] and their analysis on Nyquist plots was used. The parasitic inductance of the cell ($\sim 2 \times 10^{-8}$ H) has been taken into account during the analysis of all ceramic samples.

III. RESULTS AND DISCUSSIONS

Figure 2,a presents the compositional dependences of microhardness for the ceramic samples prepared on the basis of $(Cu_{1-x}Ag_x)_7SiS_5I$ solid solutions with $x=$ 0, 0.25, 0.5, 0.75, 1. Previously, mechanical properties of $(Cu_{1-x}Ag_x)_7SiS_5I$ single crystals were studied in Ref. [9].

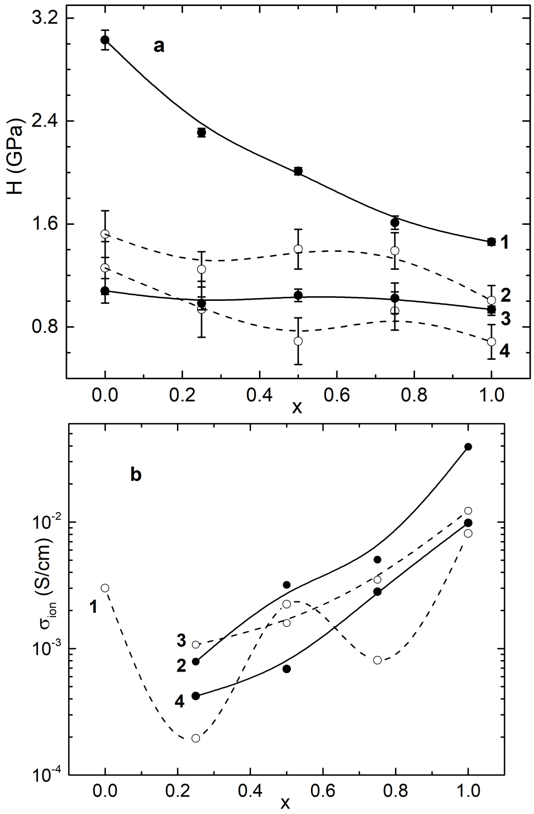

Fig. 2. The compositional dependences of microhardness at P = 0.5 N (a) and ionic component of electrical conductivity (b) for $(Cu_{1-x}Ag_x)_7SiS_5I$ crystals (1) and ceramics with different grain size: 12 μm (2), 5 μm (3), 3 μm (4).

It has been shown that the microhardness of the ceramic samples prepared on the basis of $(Cu_{1-x}Ag_x)_7SiS_5I$ solid solutions is essentially less (∼ 50%) than the same parameter determined for single crystals of the corresponding chemical composition. However, the tendency to the microhardness decrease with a decrease of the copper content at the $Cu^+ \rightarrow Ag^+$ cationic substitution is observed both for single crystals and the ceramics under investigation. The revealed compositional dependences of microhardness for abovementioned ceramics (Fig. 2,a) can be associated with the same reason as in the case of the single crystals — an increase in the ionic radius of cations at the $Cu^+ \rightarrow Ag^+$ isomorphic substitution [10]. The decrease of the microhardness of the ceramic samples in comparison with the single crystals of the same chemical composition can be related to the presence of pores, intercrystallites areas (with a great amount of structural defects) and, as a consequence, free volume. To determine the porosity of ceramic materials using a hydrostatic weighing method, density measurements were carried out. As a result, it was measured that the density of the ceramic materials is $\sim 3 - 11\%$ lower than the density of single crystals of similar chemical compositions (Fig. 3).

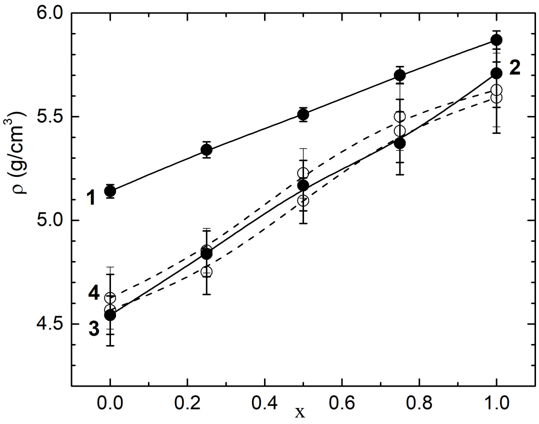

Fig. 3. The compositional dependences of density for $(Cu_{1-x}Ag_x)_7SiS_5I$ crystals (1) and ceramics with different grain size: 12 µm (2), 5 µm (3), 3 µm (4).

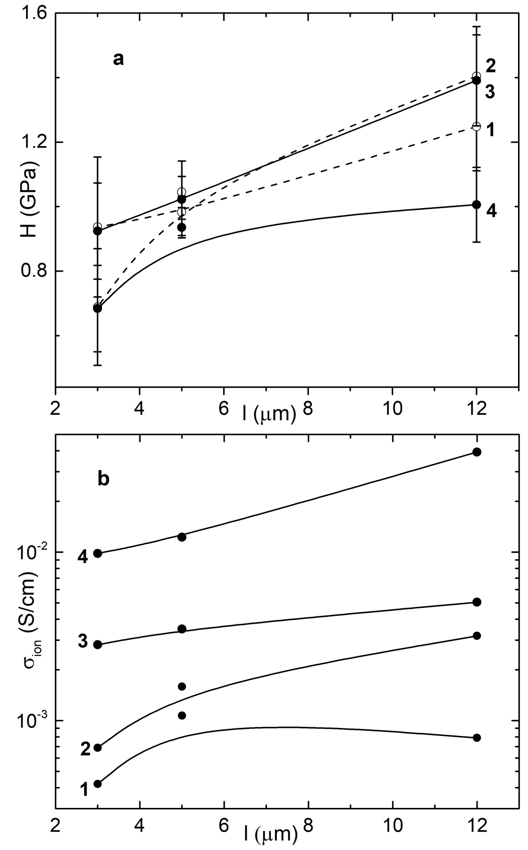

Fig. 4. Dependences of microhardness at $P = 0.5$ N (a) and ionic component of electrical conductivity (b) for ceramics on microcrystallites size: $(Cu_{0.75}Ag_{0.25})_7SiS_5I$ (1), $(Cu_{0.5}Ag_{0.5})_7SiS_5I$ (2), $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ (3), Ag_7SiS_5I (4).

Therefore, the microhardness of the ceramic samples is less than the microhardness of single crystals. It should be noted that the indentation the ceramic samples formed not only due to the plastic deformation of some areas in the microcrystal. The plastic deformation of ceramic samples under an indente can be caused by the contribution of intercrystallite areas with defects, as well as by the material densification into the area of pores and microvoids. It is well known that the following deformation regions are observed under an indenter in a near-contact zone: hydrostatic zone, plastic zone and elastic zone. The size of these zones depends on the mechanisms of the materials deformation as well as on the penetration depth of the indenter [11]. The parameters of the abovementioned zones formation and the microhardness are determined by the structural peculiarities of the samples. It should be noted that the microhardness of ceramics also depends on the average size of the microcrystallites which formed the ceramics after sintering nano- and micropowders.

The difference in the mechanical behavior of ceramics with different sizes of microcrystallites comparing to single crystals of the similar chemical composition is not only quantitative but also qualitative. As is known, during the formation of the imprint due to the plastic deformation of the material under the indenter, the dependence of the yield strength σ_T, as well as the microhardness H on the size of microcrystallites d for polycrystalline materials and ceramics is described by the Hall–Petch relation [12]:

$$\sigma_T = \sigma_0 + \frac{k}{\sqrt{d}}; \quad H = H_0 + \frac{k_h}{\sqrt{d}}, \qquad (2)$$

where σ_0 is the limit of (macro)elasticity, k characterizes the contribution of grain (microcrystallite) boundaries to the material seal under the indenter and depends on the resistance of the grain boundaries to the dislocations movement, k_h is some positive value. This relation holds in a wide range of grain sizes. It follows from this relation that when the grain size decreases, the hardness of the polycrystalline sample should increase. For the development of a plastic deformation in a single crystal, it is necessary to fulfil the force slip condition of the dislocation $\sigma > \sigma_0$, where σ is the external mechanical stress. In the case of polycrystals and ceramics, one more kind of barrier for the dislocation motion emerges in addition to the obstacles distributed inside the grains, namely, the grain boundaries. Therefore, in a polycrystalline material, the movement of dislocations is more complicated, which is explained by Eq. (2). However, in the formation of polycrystalline materials and, especially, ceramics, an important factor that influences the processes of deformation of the samples is the technological factor.

The ceramic samples obtained by recrystallization are characterized by the presence of a significant amount of pores. Therefore, in the process of microindentation, the deformation of ceramic samples under the indenter can largely occur by punching the material into the area of voids. As the sizes of the microimprints were much larger than the size of the ceramic grains d, the reduction of this parameter led to the formation of a more porous structure. As a result, its hardness slightly decreased. It is shown in Fig. 4,a that with the growth of the grain size from 3 µm to 12 µm, the microhardness of the ceramic samples increases. The reason may be that the dimension of the micro-indentations become equable with the dimension of the grains and in the micro-contact area the defect structure of the materials decreases. Therefore, the microhardness increases.

The microhardness value and the ionic component of electrical conductivity were compared with the help of the constructed compositional dependences (Fig. 2,b) and the dependences of the corresponding parameters on the size of microcrystallites (Fig. 4,b). As can be seen from Fig. 2,b, the value of ionic conductivity at the cationic $Cu^+ \rightarrow Ag^+$ substitution tends to increase, while the microhardness of ceramics decreases. When analyzing the values of the ionic conductivity and microhardness in the context of the microcrystallite size decrease 12 µm → 5 µm → 3 µm (Fig. 4), it is revealed that the tendency to decrease is preserved for both compared values, which is obviously related to the increase in the number of grain boundaries due to the decrease in the size of microcrystallites.

IV. CONCLUSIONS

The compositional dependences and size effects of the microhardness, electrical conductivity and density of $(Cu_{1-x}Ag_x)_7SiS_5I$ solid solutions are analyzed. It has been shown that at the isomorphic $Cu^+ \rightarrow Ag^+$ substitution, the microhardness of ceramics (as well as single crystals) decreases. With the growth of the microcrystallites size in the range from 3 µm to 12 µm, the microhardness of the ceramics increases.

The reduction in the microhardness value at the $Cu^+ \rightarrow Ag^+$ substitution correlates with a decrease in their melting temperature. These features can be caused by an increase in the ionic radius of the cation at the isomorphic substitution, which leads to an increase in the volume of the elementary cell and, as a consequence, to a decrease in the hardness of the crystal lattice.

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[1] W. F. Kuhs, R. Nitsche, K. Scheunemann, Mater. Res. Bull. **14**, 241 (1979); `https://doi.org/10.1016/0025-5408(79)90125-9`.

[2] T. Nilges, A. Pfitzner, Z. Kristallogr. **220**, 281 (2005); `https://doi.org/10.1524/zkri.220.2.281.59142`.

[3] I. P. Studenyak *et al.*, Solid State Ion. **345**, 115183 (2020);`https://doi.org/10.1016/j.ssi.2019.115183`.

[4] I. P. Studenyak *et al.*, Semicond. Phys. Quantum Electron. Optoelectron. **23(3)**, 260 (2020); `https://doi.org/10.15407/spqeo23.03.260`.

[5] J. B. Quinn, G. D. Quinn, J. Mater. Sci. **32**, 4331 (1997); `https://doi.org/10.1023/A:1018671823059`.

[6] P. Filho, T. Cavalcante, V. de Albuquerque, J. Tavares, J. Test. Eval. **38**, 88 (2010); `https://doi.org/10.1520/JTE102220`.

[7] M. E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy* (John Wiley & Sons, Inc., Hoboken, New Jersey, 2008); `https://doi.org/10.1002/9781119363682`.

[8] R. A. Huggins, Ionics **8**, 300 (2002); `https://doi.org/10.1007/BF02376083`.

[9] V. S. Bilanych, K. V. Skubenych, M. I. Babilya, A. I. Pogodin, I. P. Studenyak, Ukr. J. Phys. **65**, 453 (2020); `https://doi.org/10.15407/ujpe65.5.453`

[10] A. I. Pogodin *et al.*, Sci. Herald Uzhhorod Univ. Ser. Phys. **43**, 9 (2018); `https://doi.org/10.24144/2415-8038.2018.43.9-14`.

[11] Yu. I. Golovin, Phys. Solid State **50**, 2205 (2018); `https://doi.org/10.1134/S1063783408120019`.

[12] A. S. Tana, F. H. Hammad, Phys. Status Solidi A **119**, 455 (1990); `https://doi.org/10.1002/pssa.2211190207`.

МЕХАНІЧНІ ВЛАСТИВОСТІ КЕРАМІК НА ОСНОВІ ТВЕРДИХ РОЗЧИНІВ $(Cu_{1-x}Ag_x)_7SiS_5I$

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Сплави системи $(Cu_{1-x}Ag_x)_7SiS_5I$ синтезували прямим однотемпературним методом із попередньо синтезованих тетрарних Cu_7SiS_5I та Ag_7SiS_5I. З одержаних унаслідок синтезу твердих розчинів складу $(Cu_{1-x}Ag_x)_7SiS_5I$ (x — 0.25, 0.5, 0.75, 1), методом твердофазного спікання пресованих зразків виготовлено керамічні матеріали відповідних складів. Нанокристалічні порошки отримано розмелюванням у планетарному кульовому млині PQ-N04 протягом 60 та 30 хвилин, тоді як мікрокристалічні зразки одержані механічним дисперґуванням в агатовій ступці. Отримані внаслідок помолів порошки $(Cu_{1-x}Ag_x)_7SiS_5I$ (x — 0.25, 0.5, 0.75, 1) досліджено з використанням методів XRD та SEM. Пресували зразки за тиску ∼ 400 МПа, відпал — за температури 973 K, протягом 36 год. Установлено, що внаслідок рекристалізації середній розмір кристалітів кераміки, одержаної з 10–50 µm порошку, становить ∼ 12 µm, із нанопорошків, одержаних розмелюванням протягом 30 min та 60 min, — ∼ 5 µm та ∼ 3 µm відповідно. Вимірювали мікротвердість методом удавлювання піраміди Віккерса в діапазоні навантажень 0.1–2 N. Досліджували електропровідність керамічних матеріалів твердих розчинів складу $(Cu_{1-x}Ag_x)_7SiS_5I$ (x — 0.25, 0.5, 0.75, 1) методом імпедансної спектроскопії в частотному $1 \times 10^1 - 2 \times 10^6$ Hz діапазоні. Результати досліджень показали, що мікротвердість керамік, виготовлених на основі твердих розчинів $(Cu_{1-x}Ag_x)_7SiS_5I$, суттєво менша ($\sim$ 50%) від аналогічного параметра, визначеного для монокристалів відповідних складів, однак тенденція зменшення мікротвердості за зменшення вмісту Cu в процесі катіонного $Cu^+ \rightarrow Ag^+$ заміщення в цих матеріалах зберігається як у монокристалах, так і в отриманих керамічних зразках. Зменшення мікротвердості досліджених керамічних зразків порівняно з монокристалами аналогічного хімічного складу може бути зумовлене наявністю в них пористості, міжкристалічних ділянок (із великою кількістю структурних дефектів) і, як наслідок, вільного об'єму. Як показали дослідження суперйонних керамік, їхня мікротвердість залежить також від середнього розміру мікрокристалів. Установлено, що зі збільшенням розміру мікрокристалів від 3 мкм до 12 мкм мікротвердість керамік зростає. Це може бути пов'язано з тим, що розмір мікровідбитків під час індентування стає співрозмірний із розміром кристалічних зерен, а в ділянці мікроконтакту дефектність матеріалу зменшується. Проведено порівняння значень мікротвердості та йонної компоненти електропровідності й побудовано концентраційну залежність та залежність відповідних параметрів від розмірів кристалітів. Установлено, що значення електропровідності в процесі катіонного $Cu^+ \rightarrow Ag^+$ заміщення, характеризується тенденцією до зростання, натомість мікротвердість керамік зменшується. Унаслідок аналізу значень йонної компоненти електропровідності та мікротвердості в контексті зменшення розмірів кристалітів 12 µm→5 µm→3 µm, встановлено, що тенденція до монотонного зменшення зберігається для обох порівнюваних величин, що очевидно пов'язано зі збільшенням кількості міжзеренних границь у зв'язку зі зменшенням розмірів кристалітів.

Ключові слова: аргіродит, суперйонний провідник, кераміка, мікротвердість, йонна провідність.