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The Role of Heterovalent P^{+5}/Si^{+4} Substitution on the Microhardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ Single Crystals

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The dependence of the microhardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ (x = 0.25; 0.5; 0.75) single crystals on load and composition was investigated using the Vickers method. The investigation was performed in wide range of the applied loads 0.05…2 N at room temperature. It has been established that an increase in the load on the indenter leads to a nonlinear decrease in the microhardness values for all studied crystals. Observed dependences indicates a normal indentation size effect. The behavior of microhardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals were described using the geometrically necessary dislocations model. The corresponding parameters of the used model were determined. The influence of ionic radii and electronegativity on microhardness change were discussed. Using Meyer's law, the occurrence of a normal indentation size effect has been confirmed.

Keywords: argyrodite, single crystal, microhardness, heterovalent substitution.

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Introduction

Superionic conductors are characterized by exceptional ion-conducting properties in solid state, making them indispensable for a wide range of scientific and technological applications. Thanks to their high ionic conductivity, these materials open up new possibilities for the creation of advanced energy systems, including solid-state batteries, fuel cells, and other devices where the speed and reliability of ion transport play a key role. The use of superionic conductors contributes to the improvement of the efficiency and safety of energy technologies, reducing the risks associated with electrolyte leakage and degradation of electrode materials. [1-5]

In addition to the energy sector, superionic conductors are being actively researched in the fields of electrosynthesis and catalysis, providing new approaches to optimizing chemical processes. Their ability to efficiently transport ions improves the selectivity and speed of reactions, opening up prospects for the creation of new technologies in the chemical industry and materials science. Due to their high ion mobility, these materials can also be used in sensor systems, functional electronics, and other innovative areas [6].

However, for the widespread introduction of superionic conductors into technological processes, it is necessary to ensure their adequate mechanical stability. The ability of such materials to withstand mechanical loads determines their operational reliability, durability, and stability in real-world conditions. Optimizing the composition and structure of superionic conductors is critical for increasing their mechanical strength, which is especially important for applications in high-tech industries, including solid-state batteries and microelectronics components.

One of the key methods for determining the mechanical properties of superionic conductors is microhardness measurement, which allows assessing their resistance to local deformations and surface damage at the microscopic level. Microhardness analysis provides information about the behavior of the material under load, which contributes to its improvement and adaptation to various operating conditions. Since the interphase contact between the solid-state conductor and the electrode is critical in solid-state battery technology, it is difficult to achieve the required degree of contact for materials with high hardness [7].

Promising superionic materials include quaternary chalcogenides with an argyrodite structure [8-11], which have high ionic conductivity values. According to [10,11], the ionic conductivity of individual quaternary compounds Ag_7SiS_5I, Ag_7GeS_5I and Ag_6PS_5I is at the level of 10^{-3} S/cm, and when solid solutions are formed, an increase in ionic conductivity to 5.00×10^{-2} S/cm ($Ag_7(Si_{1-x}Ge_x)S_5I$ [10]) and 2.9×10^{-2} S/cm ($Ag_{6+x}(P_{1-x}Ge_x)S_5I$ [11]) is observed. The common motif of the crystal structure determines the close values of the cell parameters of compounds with an argyrodite structure. Thus, the compounds Ag_6PS_5I, Ag_7SiS_5I, and Ag_7GeS_5I are characterized by the same space group - F-43m, Z=4) with similar cell parameters: a = 10.4745 Å [11], 10.6543 Å [10], and 10.7116 Å [10], respectively. The close values of the cell parameters indicate the possibility of forming solid solutions. The mechanical parameters of these and similar compounds in the form of single crystals are poorly studied and are limited to several series of solid solutions based on halogen-containing $Ag_7(Si_{1-x}Ge_x)S_5I$, $Ag_{6+x}(P_{1-x}Ge_x)S_5I$, and halogen-free compounds $Ag_{7+x}(P_{1-x}Ge_x)S_6$ and $Ag_{7+x}(P_{1-x}Si_x)S_6$. The microhardness of these phases is in the range of 0.90–1.15 GPa [12] and 0.64–0.88 [13,14], respectively.

This work aims to investigate the behavior of microhardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ (x = 0.25; 0.5; 0.75) superionic crystals and describe it using the geometrically necessary dislocations model (Nix–Gao model) and Meyer power law.

I. Experimental

Solid solutions of $Ag_{6.25}P_{0.75}Si_{0.25}S_5I$, $Ag_{6.5}P_{0.5}Si_{0.5}S_5I$ and $Ag_{6.75}P_{0.25}Si_{0.75}S_5I$ composition, each weighing 20 g, were synthesized by a single-temperature method in quartz ampoules evacuated to 0.13 Pa from previously synthesized [15] Ag_6PS_5I and Ag_7SiS_5I, taken in the corresponding stoichiometric ratios according to the method described in Ref. [10,11]. The maximum synthesis temperature at which the solid solutions $Ag_{6+x}(P_{1-x}Si_x)S_5I$ were held for 72 hours was 950 ºC. The heating rate to the maximum temperature and cooling to room temperature was 50 ºC/hour. The corresponding single crystals were grown from the bulk polycrystalline alloys obtained as a result of synthesis by the method of directional crystallization from a melt. Crystals growth were carried out in evacuated conical quartz ampoules in a two-zone vertical resistance furnace with a crystallization front movement rate of 0.5 mm/hour. The detailed technological mode of single crystals $Ag_{6.25}P_{0.75}Si_{0.25}S_5I$, $Ag_{6.5}P_{0.5}Si_{0.5}S_5I$, $Ag_{6.75}P_{0.25}Si_{0.75}S_5I$ growth is described in Ref. [15]. The result was dark gray single crystals with a metallic luster, 1.2 cm in diameter and 3–4 cm in length.

The microhardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ (x = 0.25; 0.5; 0.75) single crystals was studied using a PMT-3 microhardness tester with a Vickers diamond indenter (a regular quadrangular pyramid with a vertex angle of 136°) at room temperature. The load on the indenter ranged from 0.05 to 2 N with an indentation time of 10 s for each load. For each load 5 measurements were made, the distance between which was at least three times greater than the length of the diagonal of the indentation. For experimental studies, flat parallel plates with a thickness of at least 2 mm were prepared, which were ground and polished to optical quality. The maximum depth of indentations of the studied samples ranged from 8.4 to 9 μm.

The load-dependent microhardness according to Vickers (H) was evaluated using the known ratio [16] (eq.1.):

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

where α is the angle of the apex of the Vickers pyramid, P is the load applied on the indenter, and d is the diagonal of the indentation.

II. Results and discussion

The results of the studies indicate the presence of an indentation size effect (ISE) in the studied single crystals of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ solid solutions. This is indicated by a non-monotonic decrease in microhardness (Fig. 1) during the increase in load on the indenter [17]. The occurrence of ISE is associated with the influence of plastic deformation at low loads (~0.05-0.5 N), which ultimately leads to the formation of dislocations in single crystals. In the graphical dependence of microhardness on the applied load on the indenter (Fig. 1), this is manifested in the form of a sharp decrease in microhardness. An increase in the load on the indenter gradually negates this effect, and the microhardness begins to approach its intrinsic value [18], which is reflected in the dependence (Fig. 1) by areas (above 0.5 N) where the microhardness begins to change within small limits.

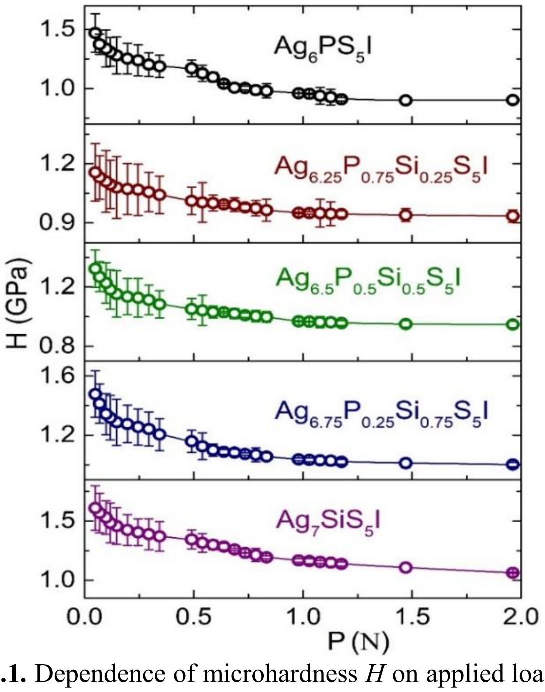

Fig.1. Dependence of microhardness *H* on applied load P for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals.

It has been established that heterovalent $P^{+5}\rightarrow Si^{+4}$ substitution in the studied single crystals leads to a monotonic nonlinear increase in microhardness values at the high loads (Fig. 2). For example, at a load of 1.5 N on the indenter, microhardness values increase from 0.90 GPa (x = 0) to 1.06 GPa (x = 1). This trend is associated with different values of electronegativity of the elements (($\chi(P) = 2.19$; $\chi(Si) = 1.90$ and $\chi(S) = 2.58$ [19]), which form the basic structural polyhedral [PS_4] (Ag_6PS_5I), [SiS_4] (Ag_7SiS_5I) and [$P(Si)S_4$] ($Ag_{6+x}(P_{1-x}Si_x)S_5I$), or more precisely, with their difference ($|\Delta\chi|$ (P-S) = 0.39, $|\Delta\chi|$ (Si-S) = 0.68) and different ionic radii (R_I (P^{+5}) = 0.038 nm; R_I (Si^{+4}) = 0.040 nm [20]). Thus, the increase in the difference in electronegativity and the difference in ionic radii in $Ag_{6+x}(P_{1-x}Si_x)S_5I$ solid solutions leads to a gradual increase in the strength of chemical bonds, which leads to greater rigidity of the corresponding structural polyhedral, and ultimately leads to the trend observed in Fig. 2. It should be noted that a similar relationship between changes in the microhardness values of single crystals and the parameters of atoms/ions (ionic radius and electronegativity) is observed in the case of the cationic $P^{+5}\rightarrow Ge^{+4}$ ($Ag_{6+x}(P_{1-x}Ge_x)S_5I$ [12], $Ag_{7+x}(P_{1-x}Ge_x)S_6$ [13]), $Si^{+4}\rightarrow Ge^{+4}$ ($Ag_7(Si_{1-x}Ge_x)S_5I$ [12]) and $P^{+5}\rightarrow Si^{+4}$ ($Ag_{7+x}(P_{1-x}Si_x)S_6$ [14])) substitutions.

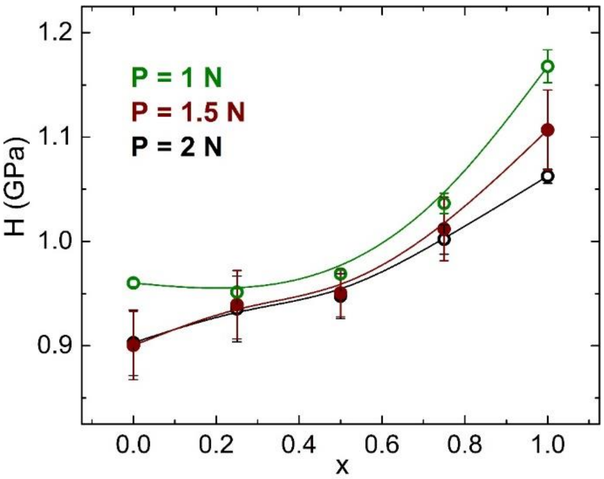

Fig. 2. Compositional dependence of microhardness *H* for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals under different loads.

Let us consider in more detail the microhardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals in the region of low indenter loads, i.e., in the region where plastic deformation occurs. The indentation size effect may indicate an increased number and activity of dislocations in the material, which affects its mechanical properties. Thus, higher microhardness values at low loads (Fig. 1) are explained by the increased density of dislocations in the plastic deformation zone. This phenomenon was explained in detail by Nix and Gao, who proposed the model of geometrically necessary dislocations (GND), which explains the size effect through the distribution of dislocations in the material during indentation [21,22] (eq.2., 3).

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} \qquad \text{(eq.2)}$$

$$H^2 = H_0^2 + \frac{H_0^2 \cdot h^*}{h} \qquad \text{(eq.3)}$$

where *H* and *h* are the measured microhardness and indenter penetration depth, H_0 is the intrinsic microhardness (related to the material properties and only to the presence of statistically distributed dislocations and the absence of geometrically necessary dislocations), and h^* is the correlation size related to the indenter geometry, the elastic shear modulus, and the mechanical hardening property of the material under study [22].

It has been established that on the dependencies (Fig. 3.a-c) in the coordinates H^2 vs (h^{-1}) for all studied crystals, a linear section is observed, which indicates the presence of plastic deformation. Thus, the analysis of the dependencies (Fig. 3.a-c) in the coordinates H^2 vs (h^{-1}) for all solid solutions allowed us to establish the parameters of the Nix and Gao model (Table 1). The intrinsic microhardness H_0 is established as a result of the intersection of the linear section with the ordinate axis; the value of the correlation dimension h^* is the tangent of the angle of the linear section relative to the abscissa axis, taking into account the value of the intrinsic microhardness; the values of the parameters H_{GND} and h_{GND} correspond to the areas on the dependencies (Fig.3.a-c) where a deviation from their linearity begins to be observed. It should be noted that the value of H_{GND} corresponds to the microhardness of the material, upon reaching which a significant contribution of geometrically necessary dislocations to plastic deformation begins to manifest itself in the process of indenting the material, and h_{GND} is the minimum indenter indentation depth required to initiate the active formation of geometrically necessary dislocations [21].

Table 1.

Parameters of the geometrically necessary dislocations model for $Ag_{6+x}(P_{1-x}Si_x)S_5I$

x	h^* (μm)	H_0 (GPa)	H_{GND} (μm)	H_{GND} (GPa)
Ag_6PS_5I	0.14	0.81	4.87	1.04
$Ag_{6.25}P_{0.75}Si_{0.25}S_5I$	0.42	0.82	4.55	1.01
$Ag_{6.5}P_{0.5}Si_{0.5}S_5I$	0.27	0.78	4.59	1.05
$Ag_{6.75}P_{0.25}Si_{0.75}S_5I$	0.18	0.76	4.32	1.14
Ag_7SiS_5I	0.12	0.75	3.76	1.34

The correctness of applying the Nix–Gao model for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals is indicated by the intersection of linearized sections (in coordinates $(H/H_0)^2$ vs h^{-1}) with the ordinate axis at a single point with a value of 1 (Fig. 3.d). This condition must be met because an increase in the indentation depth *h* leads to the measured microhardness *H* approaching the intrinsic microhardness H_0, i.e., if $h \rightarrow \infty$, then $H \rightarrow H_0$.

Let us consider the influence of cationic $P^{+5}\rightarrow Si^{+4}$ substitution on the change in the parameters of the GND model (Table 1, Fig. 4) for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals. It has been established that the value of the parameter h^* in the process of cationic $P^{+5}\rightarrow Si^{+4}$ substitution changes nonlinearly and nonmonotonically, which is associated with the presence of a maximum at *x* = 0.25 (Table 1). It should be noted that the value of the correlation parameter h^* for all solid solution compositions is higher than that of the initial compounds Ag_6PS_5I and Ag_7SiS_5I (Table 1). This indicates that solid solutions with x = 0.25, 0.5 and 0.75 contain a greater number of statistically distributed dislocations, which indicates their higher defectiveness compared to the initial quaternary phases. It is noteworthy that the heterovalent $P^{+5}\rightarrow Si^{+4}$ substitution leads to a nonlinear decrease in h_{GND} values and, accordingly, an increase in H_{GND} (with a slight minimum for the solid solution with x = 0.25) (Table 1), which indicates the increasing influence of geometrically necessary dislocations in the indentation process on the change in microhardness values.

For further analysis of microhardness and size effect of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ crystals, Meyer's power law $P = A\times d^n$ [23] was used. To determine the values of n, the linear form of Meyer's law was used, in which the values of $_n$ are determined from the slope of the obtained curve (Fig. 4) [23]:

$$\log P = \log A + n\times\log d \qquad \text{(eq.4)}$$

where P is the applied load on the indenter, d is the diagonal of the indentation, A is a constant characterizing the resistance of the material to the initial impact of the indenter, and n is the Meyer index, a measure of the effect of deformation on the hardness of the material [23].

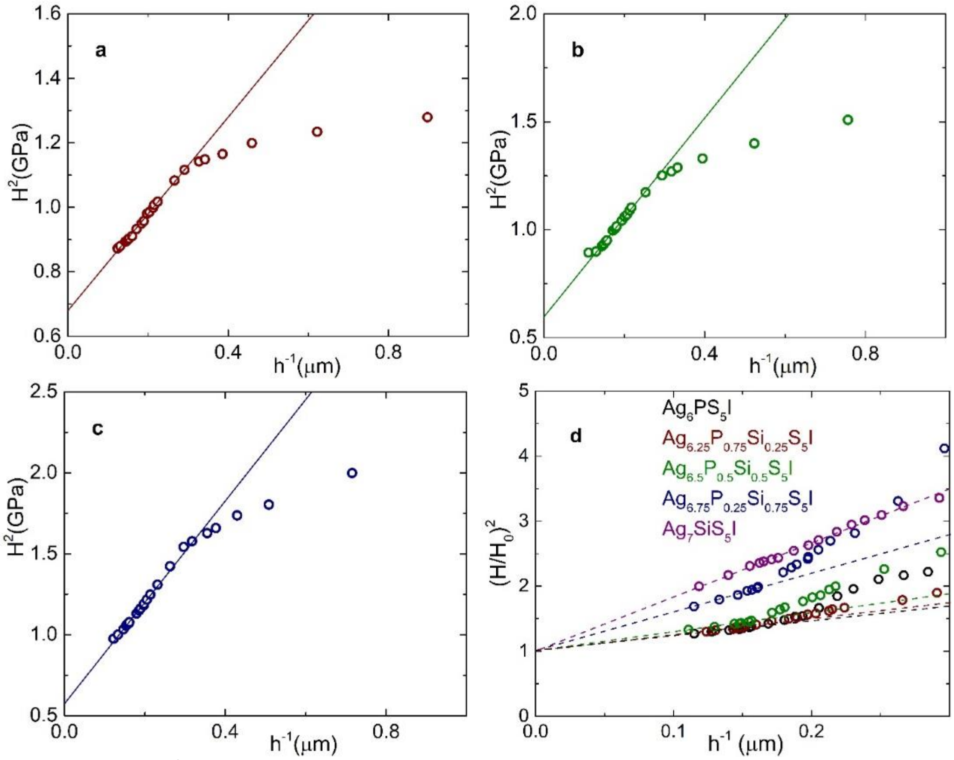

Fig.3. The Nix-Gao plots H^2 vs 1/h of $Ag_{6.25}P_{0.75}Si_{0.25}S_5I$ (a), $Ag_{6.5}P_{0.5}Si_{0.5}S_5I$ (b) та $Ag_{6.75}P_{0.25}Si_{0.75}S_5I$ (c) single crystals; dependences of the $(H/H_0)^2$ on the h^{-1} for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals (d).

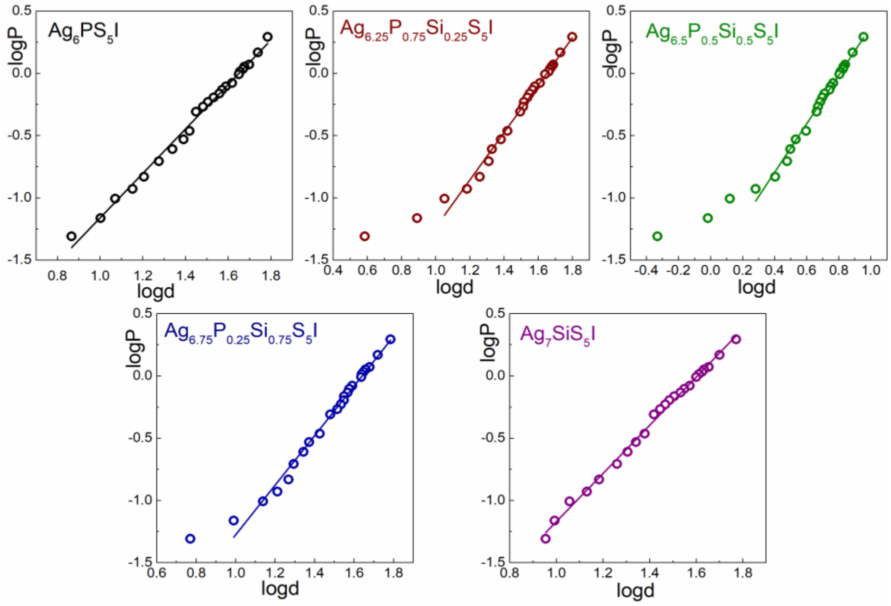

Fig.4. Plots of the dependence of log$P$ on log$d$ according to Meyer's law for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ crystals.

Meyer's index n is used to evaluate the normal size effect. The Meyer index n can take three values: when $n = 2$, microhardness does not depend on the load applied to the indenter, values of $n > 2$ indicate the existence of a tendency toward a reversible size effect (measured hardness increases with increasing indentation load), and when $n < 2$, the existence of a tendency toward a normal size effect (measured hardness increases as the indentation size decreases) [24,25].

The obtained values of the Meyer index for $Ag_{6+x}(P_{1-x}Si_x)S_5I$ crystals are within the range $n = 1.79$ ($x = 0$) ÷ 1.94 ($x = 1$), which indicates the realization of a normal size effect in these samples.

According to the classification presented in [24,25], materials with a value of $n = 1 \div 1.6$ are classified as hard materials, and $n > 1.6$ as soft materials. The results obtained indicate that the single crystals under study belong to soft materials.

Conclusions

The microhardness investigation by Vickers method was performed of the $Ag_{6+x}(P_{1-x}Si_x)S_5I$ ($x = 0.25$; 0.5; 0.75) single crystals. The indentation size effect was observed across the entire load range (0.05 to 2 N), manifested in a non-monotonic decrease in microhardness with increasing indenter load. The dependence of the micro-hardness of $Ag_{6+x}(P_{1-x}Si_x)S_5I$ single crystals on the imprint depth was interpreted within the framework of the geometrically necessary dislocations model (Nix and Gao theory). The parameters of this model were determined. Compositional dependence of the parameters of geometrically necessary dislocations model is nonlinear. The heterovalent $P^{+5} \rightarrow Si^{+4}$ substitution results in a nonlinear decrease in h_{GND} values and, accordingly, an increase in H_{GND}, which indicates the increasing influence of geometrically necessary dislocations in the indentation process on the change in microhardness values. The microhardness changes are associated with the difference in electronegativity and ionic radii of phosphorus and silicon, which leads to an increase in the strength of chemical bonds and the rigidity of structural polyhedra. Application of Meyer's law showed that the Meyer index (n) for the samples studied is in the range of 1.79 to 1.94, which confirms the presence of a normal ISE and classifies these materials as soft.

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Вплив гетеровалентного заміщення P^{+5}/Si^{+4} на мікротвердість монокристалів $Ag_{6+x}(P_{1-x}Si_x)S_5I$

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Залежність мікротвердості монокристалів $Ag_{6+x}(P_{1-x}Si_x)S_5I$ ($x = 0.25$; 0.5; 0.75) від навантаження та складу досліджено методом Віккерса. Дослідження здійснені у широкому діапазоні прикладених навантажень 0.05…2 Н при кімнатній температурі. Встановлено, що збільшення навантаження на індентор призводить до нелінійного зниження значень мікротвердості для всіх досліджуваних кристалів. Спостережувані залежності вказують на прямий розмірний ефект індентування. Поведінка мікротвердості монокристалів $Ag_{6+x}(P_{1-x}Si_x)S_5I$ була описана за допомогою моделі геометрично необхідних дислокацій. Визначено відповідні параметри використаної моделі. Також обговорено вплив іонних радіусів та електронегативності на зміну мікротвердості. За допомогою закону Мейєра було підтверджено наявність прямого розмірного ефекту.

Ключові слова: аргіродити, монокристали, мікротвердість, гетеровалентне заміщення.