═══ *Semiconductor physics* ═══

Microhardness of single-crystal samples of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions

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Abstract. This work presents the results of microhardness investigations of single-crystal samples of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ ($x = 0$, 0.1, 0.25, 0.33, 0.5, 0.75, 1) solid solutions. The dependences of microhardness H on load P and sample composition were investigated. The microhardness was found to decrease with applied load, which indicates presence of "normal" indentation size effect in $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions. The obtained results were approximated in the framework of the geometrically necessary dislocations (Nix–Gao) model, and the model parameters were found. The effect of heterovalent $P^{5+} \rightarrow Ge^{4+}$ substitution on the mechanical properties of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ crystals was determined.

1. Introduction

Superionic conductors exhibit a number of advantageous characteristics that make them important in the field of materials science, technology, and industry [1–4]. Superionic conductors have a wide range of applications covering areas from energy to electronics. They continue to attract attention of scientists and engineers due to their potential for innovation and technology improvement. In the energy sector, their high ionic conductivity makes them promising for use in solid-state batteries and fuel cells, where the efficiency of ion transport is important [3–5]. In the field of electronics, superionic materials can be used in the development of new ionic conductive electronic devices and sensors, expanding the capabilities of modern technology [6–9]. In the field of chemical research, superionic conductors are a key element for modern methods of photoelectrolysis and catalysis, which opens up new perspectives in chemical processes. Their unique properties and high ionic conductivity allow them to influence electrochemical reactions and contribute to the creation of more efficient and stable catalysts [6, 10, 11].

In developing and analyzing the properties of new materials researchers use microhardness data to optimize material compositions and processing routes to achieve the desired mechanical characteristics and analyze them to the highest possible extent. It is important to ensure stability and effectiveness of devices over a long period of time. Therefore, microhardness plays an important role in understanding and selecting materials for high-performance technologies, contributing to the optimal combination of strength, stability, and durability. In materials science, microhardness is a key indicator for determining the strength of materials at the microlevel. Measuring microhardness provides information about the material resistance to deformation and scratching. This is especially important when selecting materials for producing high-performance devices such as sensors, microelectronic devices, *etc.* [12, 13].

For high-performance device applications, where precision and stability are important, the materials must have high microhardness. This helps to avoid deformation and mechanical damage that may occur under external influences. Knowledge of microhardness is also important when developing new materials for high-performance devices, as it allows engineers to consider not only chemical properties but also mechanical aspects, thus contributing to improval of the device quality and durability [14].

This paper presents the results of the investigation of microhardness of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ ($x = 0$, 0.1, 0.25, 0.33, 0.5, 0.75, 1) single-crystal samples and the effect of heterovalent $P^{5+} \rightarrow Ge^{4+}$ substitution on their mechanical properties. The microhardness of the crystalline $Ag_{7+x}(P_{1-x}Ge_x)S_6$ samples was measured at different loads and described using the geometrically necessary dislocations (Nix–Gao) model.

2. Experimental

2.1. Materials and methods

$Ag_{7+x}(P_{1-x}Ge_x)S_6$ (x = 0.1, 0.25, 0.33, 0.5, 0.75) solid solutions were prepared from previously synthesized ternary Ag_7PS_6 and Ag_8GeS_6 compounds. The latter were synthesized from high-purity elemental Ag (99.995%), P (99.9999%), Ge (99.999%), and S (99.999%). Both initial compounds Ag_7PS_6 and Ag_8GeS_6 as well as the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions were synthesized by the one-temperature synthesis method in quartz ampoules evacuated to 0.13 Pa. The maximum synthesis temperature was 1000 °C, the heating rate to this temperature and the cooling rate to the room temperature were 50 °C/h. The synthesis regimes of the Ag_7PS_6, Ag_8GeS_6, and $Ag_{7+x}(P_{1-x}Ge_x)S_6$ (x = 0.1, 0.25, 0.33, 0.5, 0.75) solid solutions are described in detail in Refs [15, 16]. As a result of the synthesis, polycrystalline bulk alloys of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions were obtained. They were transferred to quartz growth containers with a conical bottom for growing single crystals with targeted compositions.

Ternary crystals Ag_7PS_6 and Ag_8GeS_6 were grown by the method of directional crystallization from melt, while the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ (x = 0.1, 0.25, 0.33, 0.5, 0.75) solid solutions were grown by directional crystallization using the melt-solution technique due to the nature of physico-chemical interactions in the Ag_7PS_6–Ag_8GeS_6 system [16]. Crystal seed was formed by collective recrystallization in the lower cone-shaped part of the ampoule for 48 hours. The temperature in the melt zone was 50 °C higher than the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ melting temperature. The temperature in the annealing zone was 2/3 of the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ crystallization temperature. The crystallization front movement rate was 0.5 mm/h. The cooling rate to the room temperature (from the annealing temperature) was 5 °C/h. As a result, $Ag_{7+x}(P_{1-x}Ge_x)S_6$ single crystals of dark gray color with a metallic luster, 25…30 mm long and 12 mm in diameter, were obtained [15, 16].

Using a PMT-3 microhardness tester with a Vickers diamond indenter (a regular quadrangular pyramid with an angle of 136° at the vertex), microhardness was measured at room temperature on the surface of plane-parallel and pre-polished single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ (x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1) solid solutions. The microhardness H was measured at the holding time of each indenter load of 10 s. At least 5 indentations were performed at each load. The microhardness was studied in the indenter load range of 0.05...2 N, which ensured the maximum depth of indenter impressions in the range of 0.8 to 0.85 µm. This range includes low and moderate load values, which allowed studying various effects on the mechanical properties of the single crystals. Thus, measurements at low indenter loads enable detecting sensitive changes in microhardness associated with the onset of plastic deformation of the material. Increasing the load opens up the possibility of determining the effect of strain on

changes in mechanical parameters. It should be noted that a wide range of loads provides a more complete and detailed analysis of the mechanical characteristics of the material under study. The load-dependent Vickers microhardness (H) was estimated by the following known relation [17]:

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

where P is the load on the indenter, d is the diagonal of the impression, and α is the angle of the Vickers vertex.

3. Results and discussion

The study revealed that microhardness of the Ag_7PS_6, $Ag_{7.1}P_{0.9}Ge_{0.1}S_6$, $Ag_{7.25}P_{0.75}Ge_{0.25}S_6$, $Ag_{7.33}P_{0.67}Ge_{0.33}S_6$, $Ag_{7.5}P_{0.5}Ge_{0.5}S_6$, $Ag_{7.75}P_{0.25}Ge_{0.75}S_6$ and Ag_8GeS_6 single crystals tends to decrease with increasing the indenter depth (h) (Fig. 1). The indenter depth is directly proportional to the increase in the force of the applied load on the indenter (P). It is noteworthy that at greater imprint depths (higher loads), the decrease in microhardness for the single crystals of all the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions has a lesser extent (Fig. 1). Such dependence indicates the presence of the "normal" indentation size effect for the single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions [18].

As a result, it was found that, regardless of the value of the indenter load, heterovalent $P^{5+} \leftrightarrow Ge^{4+}$ substitution in the single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions leads to a monotonic nonlinear increase in the microhardness values (Fig. 2). This indicates the increase in the stiffness of the crystal structure of these materials due to the increase in the ionic radii of the cations (R_I (P^{5+}) = 0.017 nm and R_I (Ge^{4+}) = 0.039 nm) [19] and the decrease in their electronegativities ($\chi(P) = 2.19$ and $\chi(Ge) = 2.01$) [20]. That is, the main influence on microhardness is caused by the characteristics of the elements (ionic radius and electronegativity), which form
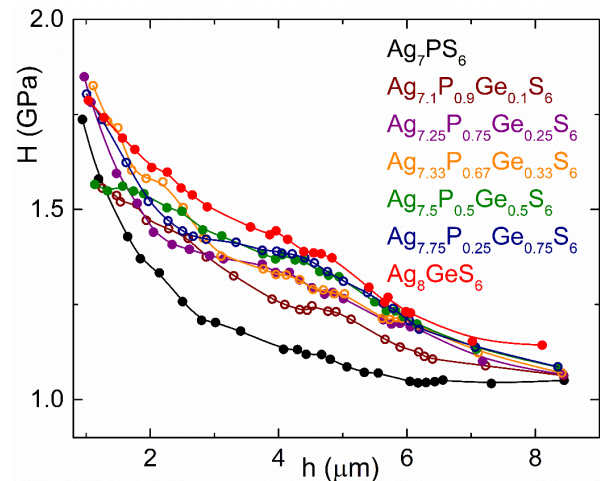

Fig. 1. Dependence of microhardness H on the imprint depth h for $Ag_{7+x}(P_{1-x}Ge_x)S_6$ single crystals.

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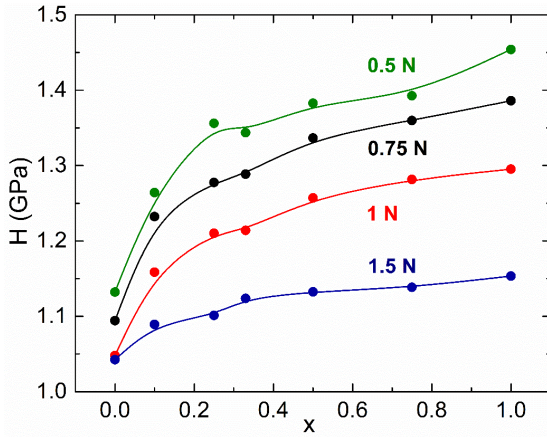**Fig. 2.** Compositional dependence of microhardness H for $Ag_{7+x}(P_{1-x}Ge_x)S_6$ single crystals at different indenter loads.

a rigid anionic framework of individual compounds and solid solutions of $Ag_{7+x}(P_{1-x}Ge_x)S_6$, forming corresponding $[ES_4]$ tetrahedra (E–P, Ge) [16]. A similar pattern of microhardness change was previously observed for single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions at $P^{5+} \rightarrow Ge^{4+}$ substitution [21].

Let us consider in more detail the effect of heterovalent cationic $P^{5+} \rightarrow Ge^{4+}$ substitution on the change in the mechanical parameters of the single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions in the framework of the gradient theory of plasticity. It should be noted that the size effect is the result of a plastic strain gradient in the microcontact region that occurs during indentation [22]. This effect may be interpreted using the geometrically necessary dislocations (Nix–Gao) model (GNDs) [23]. In the context of the GNDs model, the size effect arises due to the nature of the deformation, which depends on the size of the imprint or microcontact. The induced plastic strain gradient may be considered as a change in the mechanical properties of the material at the microscopic level due to the interaction of the indenter with the material. Thus, the GNDs model may be used to analyze movement of defects in the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions and to determine the effect of dislocations on the mechanical properties of single crystals.

Therefore, the detected size effects of microhardness in the single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions were approximated in the framework of the gradient theory of plasticity and analyzed in the framework of the GNDs model (Eq. (2)):

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

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

Here, H is the experimentally determined microhardness for a given indentation depth h, H_0 is the microhardness at an infinite indentation depth (the strain gradient under the indentation does not affect the microhardness value), h^* is the characteristic indentation depth (depends on the indenter shape, shear modulus, and microhardness), and H_0 and h^* are the parameters of the Nix–Gao model, respectively.

As can be seen from Eq. (3), H^2 should linearly depend on h^{-1}. Thus, by linearizing the linear section of the dependence $H^2 = f(h^{-1})$ (Fig. 3) using the Nix–Gao model, the intersection point of this section with the ordinate axis was found. This allowed us to determine the parameter H_0 [21]. Then the value of h^* was found from the slope of this line taking into account H_0 (Fig. 3).

As can be seen from Fig. 3, the experimentally determined microhardness (H^2) demonstrates a linear dependence on the imprint depth (h^{-1}) in a certain depth range. This indicates plastic deformation of the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ single crystals due to geometrically necessary dislocations. It should be noted that the values of H_{GND} and h_{GND} (Table), determined from the graphical dependences (Fig. 3) at the beginning of the deviation from the straight line, confirm the predominance of the plastic deformation mechanism due to the formation of geometrically necessary dislocations.

As a result of approximating the dependences of microhardness on imprint depth $H(h)$ in the framework of the model of geometrically necessary dislocations, the parameters of the studied samples shown in Table were determined. Here, H_0 is the limiting value of the crystal microhardness during its plastic deformation due to

Table. Parameters of the model of geometrically necessary dislocations for single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1$) composition.

Composition	h^*, μm	H_0, GPa	h_{GND}, μm	H_{GND}, GPa
Ag_7PS_6	0.37	0.88	2.51	1.26
$Ag_{7.1}P_{0.9}Ge_{0.1}S_6$	0.19	0.83	3.89	1.28
$Ag_{7.25}P_{0.75}Ge_{0.25}S_6$	0.12	0.78	4.33	1.31
$Ag_{7.33}P_{0.67}Ge_{0.33}S_6$	0.10	0.75	4.55	1.30
$Ag_{7.5}P_{0.5}Ge_{0.5}S_6$	0.07	0.68	4.27	1.38
$Ag_{7.75}P_{0.25}Ge_{0.75}S_6$	0.06	0.65	4.22	1.38
Ag_8GeS_6	0.06	0.64	3.86	1.45

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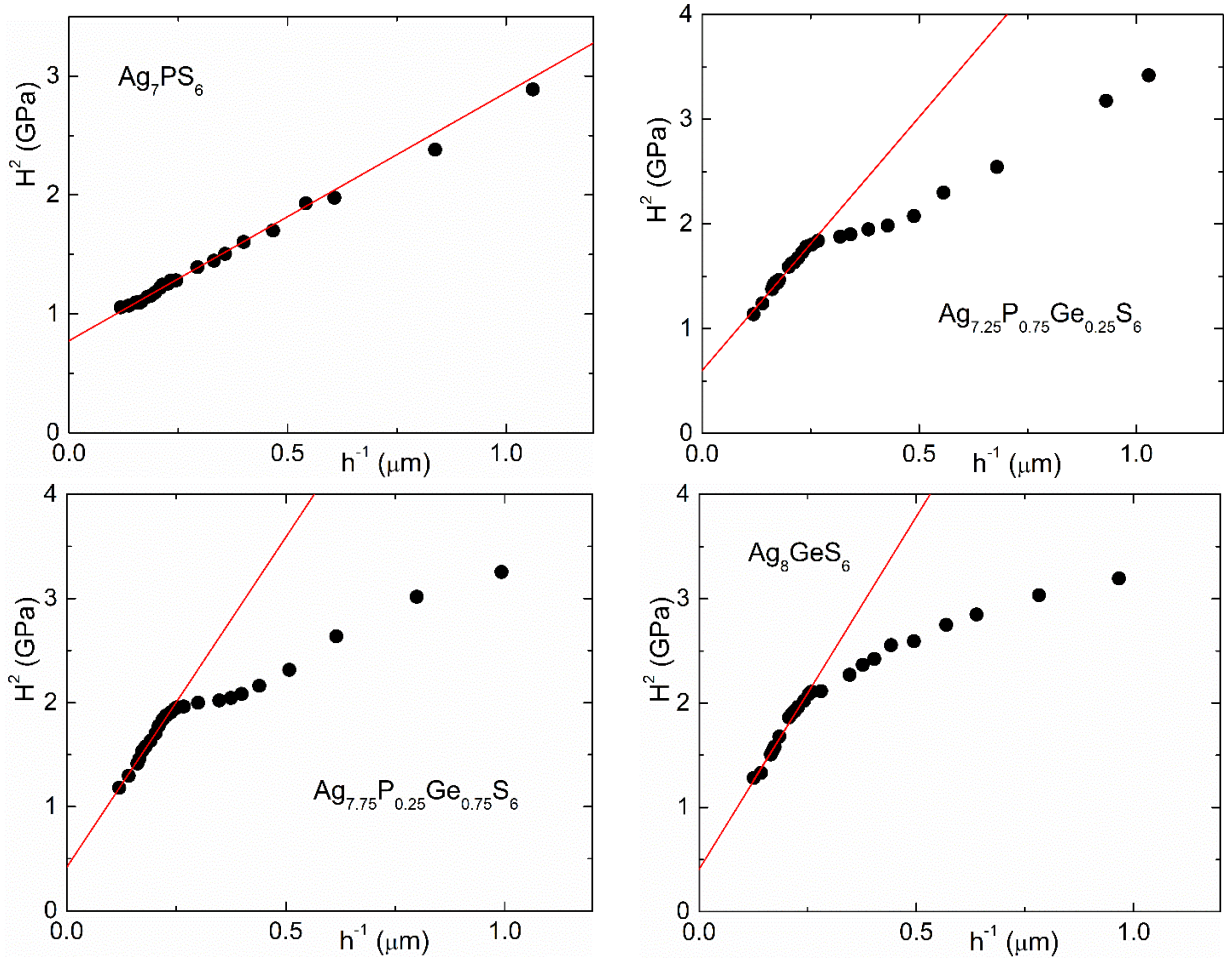**Fig. 3.** Linear approximations of the normalized microhardness dependences for $Ag_{7+x}(P_{1-x}Ge_x)S_6$ crystals (straight red lines) using the Nix–Gao model.
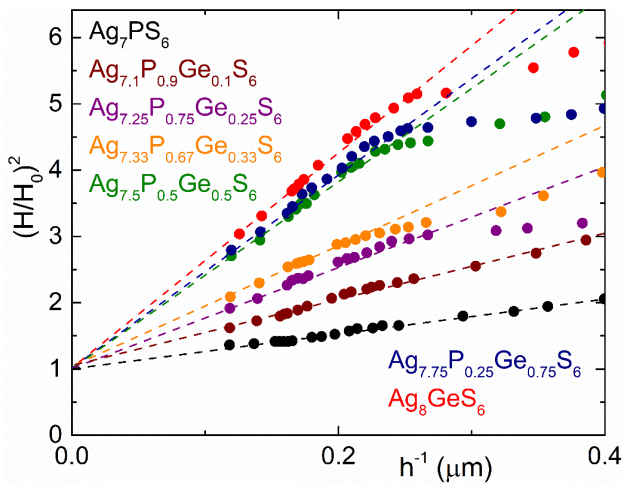

Fig. 4. Normalized dependences of microhardness in the coordinates $(H/H_0)^2 - h^{-1}$ for $Ag_{7+x}(P_{1-x}Ge_x)S_6$ single crystals.

formation of geometrically necessary dislocations, h^* is the correlation size, which depends on both the material properties and the indenter geometry, H_{GND} is the

microhardness of the crystal at which the contribution of geometrically necessary dislocations begins to appear in the plastic deformation, and h_{GND} is the minimum indenter imprint depth sufficient for formation of geometrically necessary dislocations [23], respectively.

According to Eq. (2), the normalized dependences of $(H/H_0)^2$ on h^{-1} should be extrapolated to unity at $h \to \infty$, $i.e.$ $H \to H_0$ at $h \to \infty$, which is consistent with the experimental data (Fig. 4) and confirms the correctness of the Nix–Gao model.

Finally, let us consider compositional dependences of the parameters h^*, H_0, h_{GND} and H_{GND} of the geometrically necessary dislocations model (Fig. 5). It has been found that heterovalent cationic $P^{+5} \to Ge^{+4}$ substitution for the single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions leads to a monotonic nonlinear decrease in the parameters H_0 and h^* of the GND model (Fig. 5a). At this, the parameter H_{GND} (Fig. 5b) is characterized by a tendency to almost linear increase. It should be noted that the compositional behaviors of H_0, h^* and H_{GND} may indicate an increase in the size effect and a decrease in the dislocation density, which leads to a decrease in the elastic strain in the studied single crystals in the process
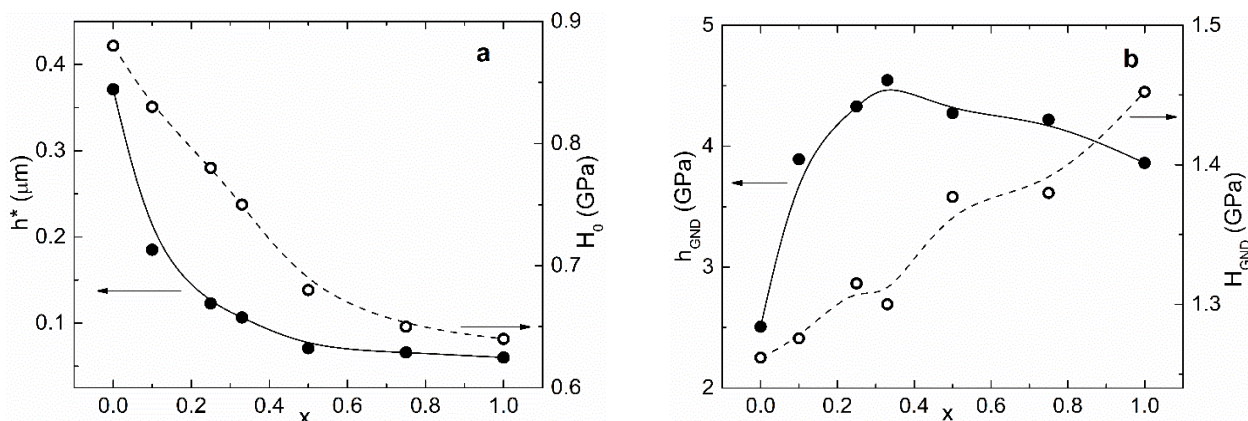
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Fig. 5. Compositional dependences of the geometrically necessary dislocations model parameters h^* and H_0 (a) as well as h_{GND} and H_{GND} (b) for $Ag_{7+x}(P_{1-x}Ge_x)S_6$ single crystals.

of heterovalent cationic $P^{+5} \rightarrow Ge^{+4}$ substitution. It is noteworthy that the compositional dependence of the parameter h_{GND} of the geometrically necessary dislocations model (Fig. 5b) is characterized by a nonlinear monotonic increase and presence of a maximum for the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ solid solutions with $x = 0.1, 0.25, 0.33, 0.5, 0.75$ as compared to the initial ternary Ag_7PS_6 and Ag_8GeS_6 compounds. The latter indicates that geometrically necessary dislocations for the $Ag_{7+x}(P_{1-x}Ge_x)S_6$ ($x = 0.1, 0.25, 0.33, 0.5, 0.75$) solid solutions appear in the region of higher indenter loads than for the initial Ag_7PS_6 and Ag_8GeS_6.

4. Conclusions

In this work, "normal" indentation size effects of microhardness in the single crystals of $Ag_{7+x}(P_{1-x}Ge_x)S_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1$) solid solutions are revealed. It is shown that the dependence of the microhardness of the crystals on the depth of imprints may be interpreted in the framework of the geometrically necessary dislocations model (according to the theory of Nix and Gao). The parameters of this model have been determined. It has been found that with a decrease in the ionic radius of cation at $P^{5+} \rightarrow Ge^{4+}$ substitution, the microhardness of the crystals increases due to the increase in the rigidity of the crystal structure of the materials under study. In the case of heterovalent substitution $P^{5+} \rightarrow Ge^{4+}$, a monotonic nonlinear decrease in the parameters of the GND model H_0 and h^* and a nonlinear nonmonotonic increase in the parameter H_{GND} are observed. Therefore, varying the load during microhardness measurements enables determining the plasticity limit of the material, at which transition from an elastic to a plastic state occurs (dominance of the plastic deformation mechanism due to the formation of geometrically necessary dislocations). Moreover, it makes possible to study both sensitive changes and effects at higher mechanical loads, which is important for understanding the mechanical properties of the material at the microscopic level.

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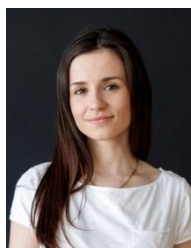
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Мікротвердість монокристалічних зразків твердих розчинів $Ag_{7+x}(P_{1-x}Ge_x)S_6$

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Анотація. У роботі наведено результати дослідження мікротвердості монокристалічних зразків твердих розчинів $Ag_{7+x}(P_{1-x}Ge_x)S_6$ (x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1). Досліджено залежність мікротвердості H від навантаження P та складу зразків. Виявлено зменшення мікротвердості зі збільшенням прикладеного навантаження, що свідчить про наявність "прямого" розмірного ефекту індентування в твердих розчинах $Ag_{7+x}(P_{1-x}Ge_x)S_6$. Отримані результати було апроксимовано в рамках моделі геометрично необхідних дислокацій (модель Нікса–Гао), та визначено параметри моделі. Встановлено вплив гетеровалентного заміщення $P^{5+} \rightarrow Ge^{4+}$ на механічні властивості кристалів $Ag_{7+x}(P_{1-x}Ge_x)S_6$.

Ключові слова: аргіродит, монокристал, мікротвердість.