

# Influence of cation $\text{Si}^{4+} \leftrightarrow \text{Ge}^{4+}$ and $\text{P}^{5+} \leftrightarrow \text{Ge}^{4+}$ substitution on the mechanical parameters of single crystals $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$ and $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$

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**Abstract.** Herein we present the results of microhardness investigations aimed at monocrystalline samples of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.2, 0.4, 0.6, 0.8, 1) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.25, 0.5, 0.75, 1) solid solutions. The dependence of microhardness  $H$  on the load  $P$  and composition were investigated. It has been observed that the microhardness dependence on the applied load is characterized by a tendency to decrease with increasing the load. It indicates a presence of “normal” size effect in both  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.25, 0.5, 0.75, 1) solid solutions. The revealed size effects of hardness in single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions have been analyzed within the framework of the gradient theory of plasticity. The corresponding parameters of the model of geometrically necessary dislocations have been determined.

**Keywords:** argyrodite, single crystal, microhardness.

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## 1. Introduction

Currently, there is an increasing interest in solid-state conductors, driven by the strong demand for portable electronic devices and electric vehicles [1–3]. This is due to a number of advantages associated with solid-state conductors: stability, non-flammability and current density. Solid-state conductors based on argyrodites are promising superionic materials, because they have high ionic conductivity values commensurate with those of liquid electrolytes [4, 5]. Argyrodites are a class of ternary and quaternary complex chalcogenides based on a multivalent element, most commonly  $\text{Si}^{\text{IV}}$ ,  $\text{Ge}^{\text{IV}}$ ,  $\text{P}^{\text{V}}$ , and single-charged cations, such as  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Li}^+$  [6–9]. Multivalent elements and anions form a rigid anionic framework, and the resulting voids are occupied by single-charged cations. Unlike multi-charged cations, the coordination of single-charged cations is changeable and varies from linear to tetrahedral (with different degrees of distortion). Monovalent elements have partial occupancy of positions, which, along with variable coordination, provides high mobility of these ions and efficient ionic transport necessary for superionic conductors. The conductivity of argyrodites lies within the range of  $10^{-2}$  to  $10^{-3}$  S/cm [8–12], exceeding the parameters of most solid-state conductors [4].

Quaternary Ag-containing argyrodites are characterized by high ionic conductivity and chemical resistance [10, 11]. The ionic conductivity (at 25 °C) of single crystals of phases based on  $\text{Si}^{4+}$  and  $\text{Ge}^{4+}$  ions is  $8.13 \cdot 10^{-3}$  S/cm ( $\text{Ag}_7\text{SiS}_5\text{I}$  [10, 13]),  $7.98 \cdot 10^{-3}$  S/cm ( $\text{Ag}_7\text{GeS}_5\text{I}$  [10, 14]), and  $1.79 \cdot 10^{-3}$  S/cm ( $\text{Ag}_6\text{PS}_5\text{I}$  [15]). All three phases of  $\text{Ag}_7\text{SiS}_5\text{I}$ ,  $\text{Ag}_7\text{GeS}_5\text{I}$ ,  $\text{Ag}_6\text{PS}_5\text{I}$  are isostructural and crystallize in cubic crystal system, space group (SG) F-43m with cell parameters of 10.6316(6) Å [10], 10.6832(4) Å [14] and 10.4745(1) Å [15], respectively. In the case of both isovalent ( $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$ ) and heterovalent ( $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$ ) substitution, the formation of solid solutions with the structure of argyrodite is observed [10, 12].

Microhardness is one of the important functional properties of materials and is related to the crystal structure of the material. This paper presents the results of studying the mechanical properties of single-crystal samples of solid solutions with isovalent  $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$  ( $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$ ) and heterovalent  $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$  ( $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$ ) substitution with an argyrodite structure. The microhardness of the monocrystalline samples was measured and the effect of cationic substitution on the mechanical properties of the studied samples was determined.

## 2. Experimental

The synthesis of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  ( $x = 0.2, 0.4, 0.6, 0.8$ ) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  ( $x = 0.25, 0.5, 0.75$ ) solid solutions was carried out using the one-temperature synthesis in evacuated silica ampoules from the previously obtained quaternary  $\text{Ag}_7\text{SiS}_5\text{I}$  or  $\text{Ag}_6\text{PS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$  taken in the appropriate stoichiometric ratios [10, 12]. The latter were synthesized from high-purity elemental Ag (99.995%), Si (99.999%) or P (99.9999%) or Ge (99.9999%), S (99.999%) components and previously synthesized AgI. The detailed synthesis regimes to prepare  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions are described in Refs. [10, 12]. As a result of the synthesis, bulk polycrystalline samples weighing 20 g each were obtained, which were subsequently used to grow single crystals [10, 12] of the corresponding composition. Single crystals of solid solutions of the composition  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.2, 0.4, 0.6, 0.8, 1) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.25, 0.5, 0.75, 1) were grown using the method of directional crystallization (vertical zone technique) from the melt-solution according to the growth procedure described in Refs. [10, 12, 15].

Monocrystalline samples of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.2, 0.4, 0.6, 0.8, 1) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (0, 0.25, 0.5, 0.75, 1) solid solutions with the thickness close to 3-4 mm were polished to optical quality. Experimental data were obtained using a PMT-3 microhardness tester (Vickers diamond indenter – a regular quadrangular pyramid with an angle at the vertex  $136^\circ$ ) at room temperature within the load range from 0.05 to 2 N with an indentation time

of 10 s at each load (at least 5 indentations were made at each load). The indenter loading and unloading time was kept at 30 s. The maximum depth of indentation into the tested samples was  $\sim 9 \mu\text{m}$ .

The numerical values of microhardness were calculated using Eq. (1) [16]:

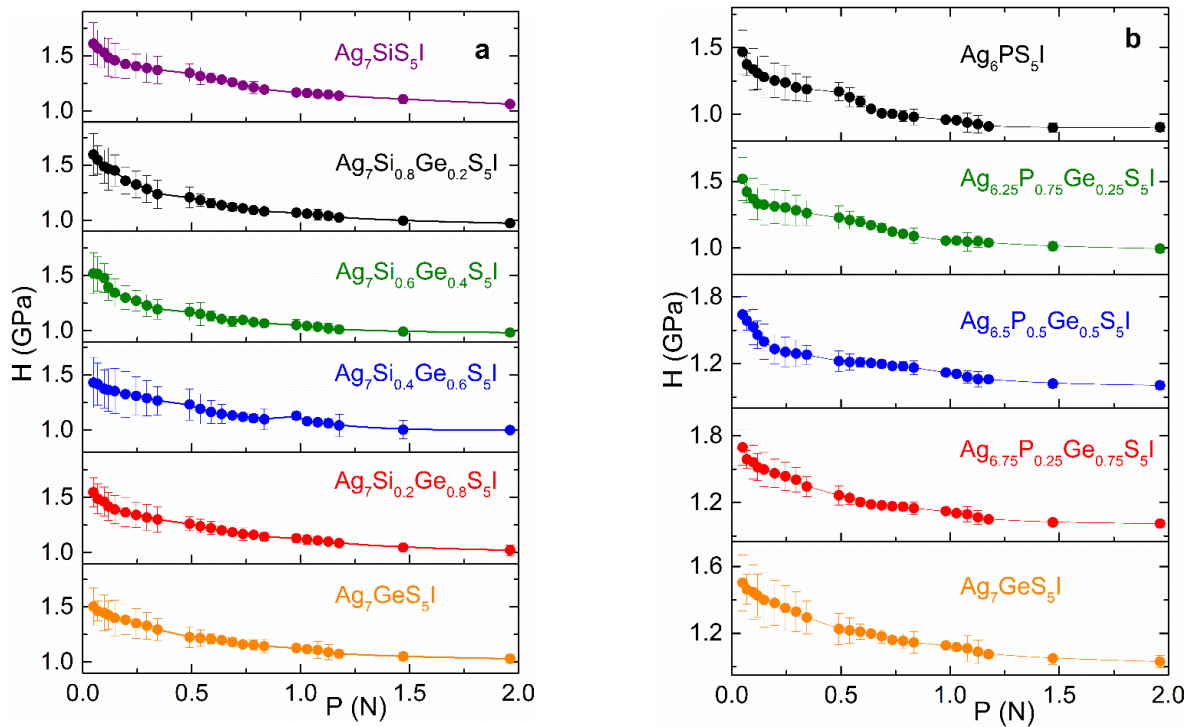
$$H = -\frac{2P \sin \alpha/2}{d^2} = 1.854 \frac{P}{d^2}, \quad (1)$$

where  $P$  is the load on the indenter, and  $d$  is the average of these two diagonals of the imprint.

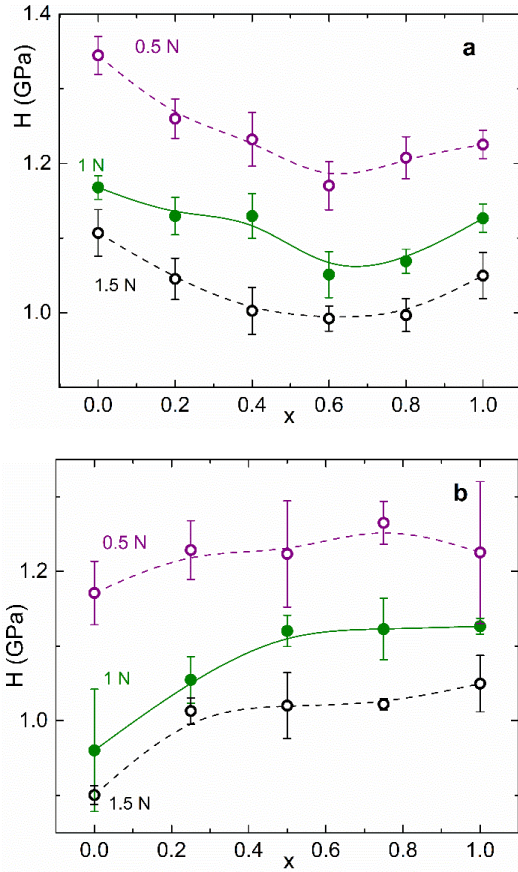
## 3. Results and discussion

The variation of microhardness  $H$  from the applied load  $P$  on the indenter for single crystals of the initial quaternary chalcogenides  $\text{Ag}_7\text{SiS}_5\text{I}$ ,  $\text{Ag}_6\text{PS}_5\text{I}$ , and  $\text{Ag}_7\text{GeS}_5\text{I}$ , as well as solid solutions of the composition  $\text{Ag}_7\text{Si}_{0.8}\text{Ge}_{0.2}\text{S}_5\text{I}$ ,  $\text{Ag}_7\text{Si}_{0.6}\text{Ge}_{0.4}\text{S}_5\text{I}$ ,  $\text{Ag}_7\text{Si}_{0.4}\text{Ge}_{0.6}\text{S}_5\text{I}$ ,  $\text{Ag}_7\text{Si}_{0.2}\text{Ge}_{0.8}\text{S}_5\text{I}$ ,  $\text{Ag}_{6.25}\text{P}_{0.75}\text{Ge}_{0.25}\text{S}_5\text{I}$ ,  $\text{Ag}_{6.5}\text{P}_{0.5}\text{Ge}_{0.5}\text{S}_5\text{I}$ , and  $\text{Ag}_{6.75}\text{P}_{0.25}\text{Ge}_{0.75}\text{S}_5\text{I}$  are characterized by a tendency to decrease with increasing the load (Fig. 1). At high values of indenter loads, the decrease in microhardness occurs to a lesser extent (Fig. 1). Such a dependence of the microhardness  $H$  on the load  $P$  indicates that for single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions, a “normal” size effect is observed [17].

According to the results of experimental studies (Fig. 2a), it was found that cationic  $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$  substitution for single crystals of  $\text{Ag}_7\text{Si}_{1-x}\text{Ge}_x\text{S}_5\text{I}$  ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1$ ) solid solutions leads to a monotonic



**Fig. 1.** Dependence of microhardness  $H$  on the applied load force  $P$  for single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (a) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (b) solid solutions.



**Fig. 2.** Compositional dependence of the microhardness  $H$  for single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (a) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (b) solid solutions at different loads.

decrease in microhardness values with a minimum value at  $x = 0.6$ . Whereas heterovalent  $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$  substitution, on the contrary, leads to a monotonic nonlinear increase in microhardness values (Fig. 2b). This may be due to different values of electronegativities  $\chi$  of the elements [18]:  $\chi(\text{Si}) = 1.90$ ,  $\chi(\text{P}) = 2.19$ ,  $\chi(\text{Ge}) = 2.01$ , which in the crystal structures of both, individual compounds  $\text{Ag}_7\text{SiS}_5\text{I}$ ,  $\text{Ag}_6\text{PS}_5\text{I}$ ,  $\text{Ag}_7\text{GeS}_5\text{I}$  and solid solutions based on them  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$ ,  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$ , form  $[\text{ES}_4]$  tetrahedra (E – Si, P, Ge). These  $[\text{ES}_4]$  tetrahedra are the basis of the rigid anionic sublattice of phases (compounds and solid solutions based on them) of the argyrodite structure [6]. Obviously, the higher the electronegativity of the element, on the basis of which the corresponding  $[\text{ES}_4]$  tetrahedra of the anionic framework are formed, the lower the microhardness values, which, for example, at the load 1.5 N are 1.11 GPa ( $\text{Ag}_7\text{SiS}_5\text{I}$ ), 0.90 GPa ( $\text{Ag}_6\text{PS}_5\text{I}$ ), and 1.05 GPa ( $\text{Ag}_7\text{GeS}_5\text{I}$ ) (Fig. 2). It should be noted that the cation isovalent  $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$  and heterovalent  $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$  substitution lead to an additional disorder [10, 12] of the anionic and cationic ( $\text{Ag}^+$ ) sublattices of the  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions, which most likely leads to a nonlinear change in the microhardness values (Fig. 2).

It is known that in the microcontact area between the indenter and the material under study, deformation zones are formed due to various mechanisms of crystal deformation during indentation. In particular, plastic deformation of the crystal is caused by the fact that the internal mechanical stress in the deformation zone exceeds the plasticity limit of the crystal.

The size effect is a consequence of the induced, *i.e.*, generated during indentation, plastic strain gradient in the microcontact zone [19]. This effect can be interpreted within the framework of the gradient theory of plasticity [20].

Plastic deformation in crystals is mainly caused by formation and movement of two types of dislocations. The first type is statistically distributed dislocations; the movement of these dislocations causes plastic deformation of crystals in the region of low internal stresses. The movement of these dislocations occurs when they are detached from their “anchor points” – point defects. The second type is geometrically necessary dislocations (GND), which are formed when statistically distributed dislocations are not sufficient for plastic deformation, and internal mechanical stresses exceed the plasticity limit and are used to adapt strain gradients. For geometrically necessary dislocations to be formed in the contact region, it is necessary that the internal mechanical stresses in the crystal exceed the plasticity limit. The change interval  $h$ , which separates the two regions of dimensional effects, is determined by the ratio between the densities of two types of dislocations in the microcontact region [17].

Nix and Gao explained the size effect by introducing the concept of geometrically necessary dislocations formed during the indentation process to distinguish them from internal dislocations existing in the material [20].

The revealed size effects of hardness in single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions were approximated within the framework of the gradient theory of plasticity based on the relationship between microhardness and imprint depth for single crystal materials in the model of geometrically necessary dislocations (Nix–Gao model). The dependence  $H(h)$  was approximated using Eq. (2) [20]:

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

where  $H$  is the experimentally determined hardness for a given indentation depth  $h$ ;  $H_0$  is the hardness at an infinite indentation depth (*i.e.*, at  $h \gg h^*$ , when the strain gradient under the indentation does not affect the hardness value),  $h^*$  is the characteristic indentation depth, which depends on the indenter shape, shear modulus, and hardness.  $H_0$  and  $h^*$  are the parameters of this model (Table).

As can be seen from Eq. (2),  $H^2$  should depend linearly on  $h^{-1}$  (Fig. 3). Graphical dependence of  $H^2(h^{-1})$  (Fig. 3) shows the validity of the Nix–Gao model on a micrometer scale. From the linear approximation of the

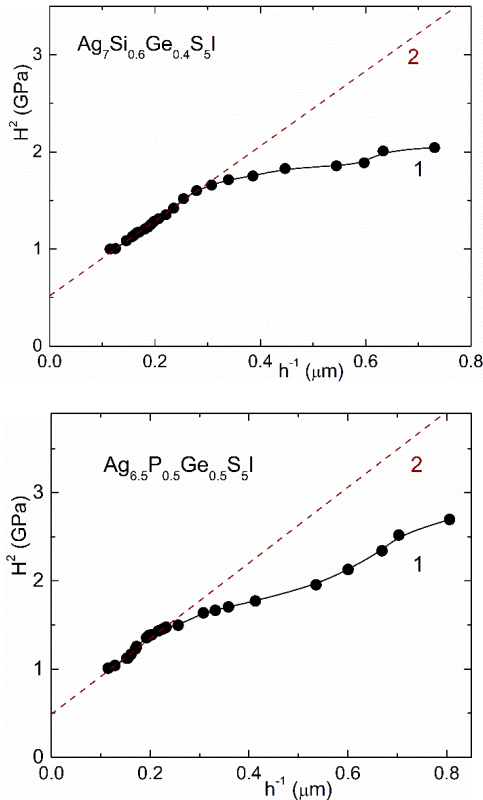
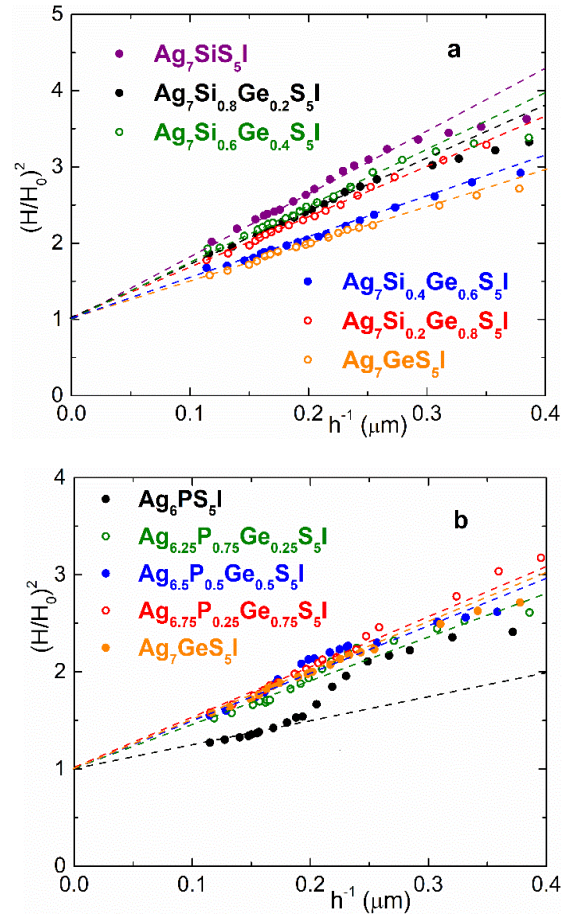


**Table.** Parameters of the GND model for single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions.

Composition	$h^*$ , $\mu\text{m}$	$H_0$ , GPa	$h_{\text{GND}}$ , $\mu\text{m}$	$H_{\text{GND}}$ , GPa
$\text{Ag}_6\text{PS}_5\text{I}$	0.14	0.81	4.87	1.04
$\text{Ag}_7\text{SiS}_5\text{I}$	0.12	0.75	3.76	1.34
$\text{Ag}_7\text{Si}_{0.8}\text{Ge}_{0.2}\text{S}_5\text{I}$	0.14	0.75	3.89	1.26
$\text{Ag}_7\text{Si}_{0.6}\text{Ge}_{0.4}\text{S}_5\text{I}$	0.17	0.76	3.58	1.27
$\text{Ag}_7\text{Si}_{0.4}\text{Ge}_{0.6}\text{S}_5\text{I}$	0.17	0.76	2.96	1.27
$\text{Ag}_7\text{Si}_{0.2}\text{Ge}_{0.8}\text{S}_5\text{I}$	0.18	0.77	2.86	1.32
$\text{Ag}_{6.25}\text{P}_{0.75}\text{Ge}_{0.25}\text{S}_5\text{I}$	0.099	0.81	4.18	1.21
$\text{Ag}_{6.5}\text{P}_{0.5}\text{Ge}_{0.5}\text{S}_5\text{I}$	0.086	0.80	4.31	1.21
$\text{Ag}_{6.75}\text{P}_{0.25}\text{Ge}_{0.75}\text{S}_5\text{I}$	0.082	0.80	5.09	1.16
$\text{Ag}_7\text{GeS}_5\text{I}$	0.21	0.82	3.23	1.30

dependence of  $H(h)$  (Fig. 1), the point of intersection of this line with the ordinate axis  $H_0$  was determined using this Eq. (2). According to the value of the tangent of the slope of this line to the abscissa axis and taking into account  $H_0$ , the value of  $h^*$  was found [20]:

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


**Fig. 3.** Approximation of normalized dependences of microhardness of single crystals on the example of  $\text{Ag}_7\text{Si}_{0.6}\text{Ge}_{0.4}\text{S}_5\text{I}$  and  $\text{Ag}_{6.5}\text{P}_{0.5}\text{Ge}_{0.5}\text{S}_5\text{I}$  solid solutions within the framework of the Nix–Gao model, where 1 – experimental curve, 2 – direct approximation (predicted hardness based on GND model).

**Fig. 4.** Normalized dependences of microhardness in the coordinates  $(H/H_0)^2-h^{-1}$  for single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (a) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (b) solid solutions.

It has been ascertained that for all the compositions of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions, the dependence of  $H^2$  on  $h^{-1}$  within a limited range is linear; therefore, Fig. 3 shows the dependence on the example of  $\text{Ag}_7\text{Si}_{0.6}\text{Ge}_{0.4}\text{S}_5\text{I}$  and  $\text{Ag}_{6.5}\text{P}_{0.5}\text{Ge}_{0.5}\text{S}_5\text{I}$  solid solutions. This behavior indicates the presence of plastic deformation that occurs due to geometrically necessary dislocations. The values of  $H_{\text{GND}}$  and  $h_{\text{GND}}$  at the beginning of the straight section indicate the beginning of the dominance of the plastic deformation mechanism due to formation of geometrically necessary dislocations.

As a result of approximating the dependences of the microhardness and the depth of the imprint  $H(h)$  for the single crystals of solid solutions of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$ , the parameters were determined, the values of which are given in Table:

(i)  $H_0$  is the limiting value of the crystal hardness during its plastic deformation due to formation of geometrically necessary dislocations (*i.e.*, at a large depth of indentation, where the dimensional effect does not prevent additional strengthening);

(ii)  $h^*$  is the correlation size in the ensemble of geometrically necessary dislocations, which depends on both material properties and indenter geometry, and

therefore depends on the density of statistically preserved dislocations (large values of  $h^*$  indicate that the size effect plays a role even for deep indentations);

(iii)  $H_{GND}$  is the microhardness of a crystal at which the contribution of geometrically necessary dislocations begins to appear in plastic deformation;

(iv)  $h_{GND}$  is the minimum depth of the indenter imprint, at which the value of internal mechanical stresses in the deformation zone is sufficient to form the geometrically necessary dislocations [20].

To verify the correctness of Eq. (2), the experimental dependences of  $H(h)$  for  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  crystals (Fig. 4a) were plotted in the coordinates ' $(H/H_0)^2$  versus  $h^{-1}$ '. A similar dependence was plotted for  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions (Fig. 4b). According to Eq. (3), the normalized dependences of  $(H/H_0)^2$  on  $h^{-1}$  at  $h \rightarrow \infty$  should be extrapolated to unity, i.e., if  $h \rightarrow \infty$ , then  $H \rightarrow H_0$  (Fig. 4).

It was found that the isovalent  $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$  cation substitution leads to a monotonic nonlinear increase in the parameters of the GND model –  $H_0$  and  $h^*$  (Table, Fig. 5a). On the contrary, heterovalent  $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$  cation substitution leads to a decrease in the values of the parameters  $H_0$  and  $h^*$ , which is manifested in the compositional dependence (Fig. 5b) in the presence of a minimum for  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions.

As a result, it can be concluded that  $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$  substitution in solid solutions of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  leads to a gradual decrease in the size effect and an increase in the dislocation density. The combination of these factors

causes an increase in elastic deformation. Instead, the minimum values of the parameters  $H_0$  and  $h^*$  observed for  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions (Fig. 5b) indicate an increase in the size effect and a decrease in the density of dislocations, which consequently reduces the elastic strain.

#### 4. Conclusions

Single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions were used to prepare corresponding samples for microhardness measurements. The microhardness tests were performed at room temperature. It has been ascertained that with increasing of the applied load  $P$  on the indenter causes a decrease in the microhardness  $H$  values. This dependence of the microhardness  $H$  on the load  $P$  indicates that for the single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions, a “normal” size effect is observed. The compositional dependence of microhardness for isovalent  $\text{Si}^{4+} \rightarrow \text{Ge}^{4+}$  substitution is characterized by a monotonic decrease in microhardness values with a minimum value at  $x = 0.6$ . In the case of heterovalent  $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$  substitution, a monotonic nonlinear increase in microhardness values is observed. The revealed size effects of hardness in single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  solid solutions have been analyzed within the framework of the gradient theory of plasticity. The corresponding parameters of the model of geometrically necessary dislocations have been determined.

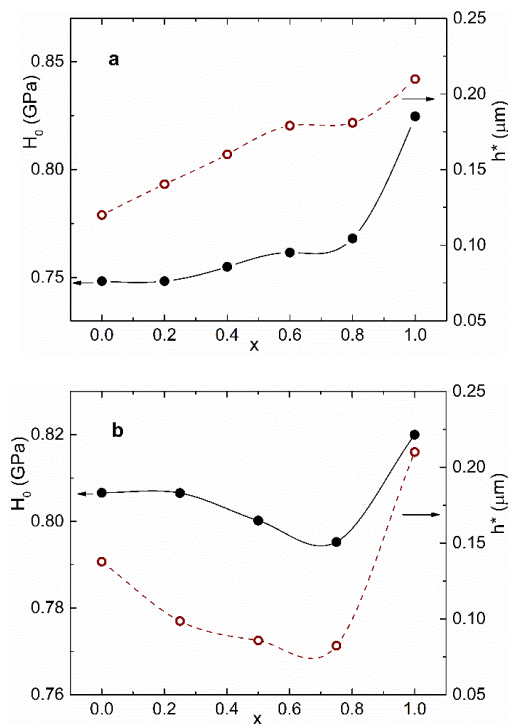
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**Fig. 5.** Compositional dependence of the parameters of the GND model  $H_0$  and  $h^*$  of single crystals of  $\text{Ag}_7(\text{Si}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (a) and  $\text{Ag}_{6+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_5\text{I}$  (b) solid solutions.



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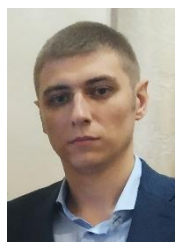
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**Вплив катіонного  $Si^{4+} \leftrightarrow Ge^{4+}$  та  $P^{5+} \leftrightarrow Ge^{4+}$  заміщення на механічні параметри монокристалів  $Ag_7(Si_{1-x}Ge_x)S_5I$  та  $Ag_{6+x}(P_{1-x}Ge_x)S_5I$**

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**Анотація.** У даній роботі наведено результати досліджень мікротвердості монокристалічних зразків твердих розчинів  $Ag_7(Si_{1-x}Ge_x)S_5I$  (0, 0.2, 0.4, 0.6, 0.8, 1) та  $Ag_{6+x}(P_{1-x}Ge_x)S_5I$  (0, 0.25, 0.5, 0.75, 1). З'ясовано залежність мікротвердості  $H$  від навантаження  $P$  та складу. Виявлено, що залежність мікротвердості від прикладеного навантаження характеризується тенденцією до зменшення зі збільшенням навантаження. Це свідчить про наявність прямого розмірного ефекту як у твердих розчинах  $Ag_7(Si_{1-x}Ge_x)S_5I$ , так і  $Ag_{6+x}(P_{1-x}Ge_x)S_5I$ . Виявлені розмірні ефекти зміни твердості у монокристалах твердих розчинів складу  $Ag_7(Si_{1-x}Ge_x)S_5I$  та  $Ag_{6+x}(P_{1-x}Ge_x)S_5I$  було проаналізовано в рамках градієнтної теорії пластичності. Визначено відповідні параметри моделі геометрично необхідних дислокацій.

**Ключові слова:** аргіродити, монокристали, мікротвердість.