

Studying the mechanical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals by using the micro-indentation method

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Abstract. $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals were grown using the Bridgman–Stockbarger method. The hardness dependences on the indentation depth profiles in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals were investigated. The measurements of mechanical parameters were performed at the room temperature by using the micro-indentation method. Variations of the hardness of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals were interpreted in the framework of the deformation gradient model. The influence of cation $\text{Cu} \rightarrow \text{Ag}$ substitution on mechanical parameters of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals was studied.

Keywords: superionic crystals, cation substitution, mechanical properties, micro-hardness, micro-indentation.

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1. Introduction

$\text{Cu}_7\text{GeS}_5\text{I}$ and $\text{Ag}_7\text{GeS}_5\text{I}$ crystals belong to the compounds with argyrodite structure [1-3]. Their high electrical conductivity is typical for the advanced superionic conductors. Due to the high electrical conductivity, pure $\text{Cu}_7\text{GeS}_5\text{I}$ and $\text{Ag}_7\text{GeS}_5\text{I}$ crystals as well as $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals on their base are of practical interest, in particular, for solid-state ionics [1-3].

In the course of preparing the mixed crystals, the presence of defects and homogeneity can be estimated by measuring the crystal hardness. Using the standard indenters and measuring the micro-hardness under various loads on the indenter provides the opportunity to analyze the process of forming the plastic deformation in these crystals.

The purpose of this work is to study the micro-hardness changes in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals as dependent on the imprint depth as well as changes in the hardness of these materials depending on their chemical composition.

2. Experimental

For micro-hardness measurements, $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals grown using the Bridgman–Stockbarger method were used. Samples for investigations were prepared in the form of parallelepipeds with a natural upper plane on which micro-indentation was performed.

Measurements of the micro-hardness were carried out by means of PMT-3 micro-hardness machine with the

Vickers indenter (a diamond regular quadri-angular pyramid with a 136° angle at the vertex). Numerical values of micro-hardness were determined with account of the equation [4]:

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

where $\alpha = 136^\circ$, P is the load force on the indenter, d – diagonal of the imprint. The load force on the Vickers indenter was applied along the (001) crystallographic direction. The relative error in the micro-hardness determination did not exceed 10%.

3. Results and discussion

To determine the micro-hardness, the load on the indenter is usually maintained for 5 s [4]. With increasing the load time, the micro-hardness decreases because the depth of the imprint (and its diagonal) increases. It happens due to the growth of individual components of sample deformation under the indenter. For the crystals, the main contribution to this phenomenon is made by the plastic component of deformation. In general, time variation of the indenter immersion depth under the constant load can be given by the equation:

$$h(t) = h_0 + h_1 \exp\left(-\frac{t}{\tau}\right) + \frac{\Delta h_p}{\Delta t} \cdot t, \quad (2)$$

where h_0 is the elastic component of the deformation, h_1 – weight contribution of the relaxation component, t – relaxation time, h_p – plastic component of deformation. At the constant load, the component h_0 does not change

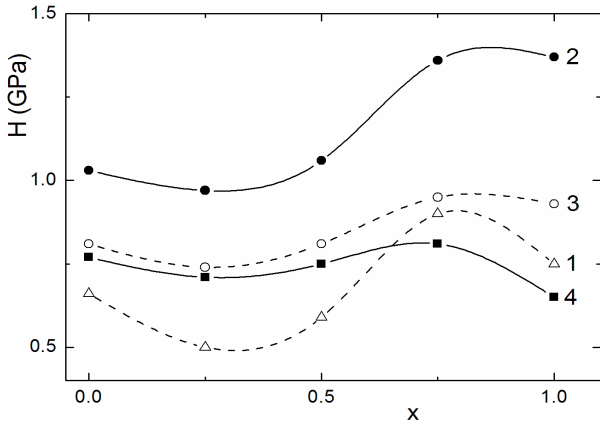


Fig. 1. Compositional dependences of mechanical parameters for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals: (1) micro-hardness H , (2) maximal value of micro-hardness H_{max} , (3) micro-hardness H_{200} at the load force $P = 2 \text{ N}$, (4) hardness H_0 at an infinite depth of the imprint (obtained when extrapolating $H(h)$ in the plastic deformation gradient model (MSG)).

[5]. The most significant component is h_p , since formation of the imprint under the load is largely related with plastic deformation of the material. It should be noted that the relaxation component $h_r(t) = h_1 \exp\left(-\frac{t}{\tau}\right)$ is essential for non-crystalline materials, glass and amorphous films. At crystals indentation, the relaxation component h_r is less significant.

Fig. 1 shows the dependence of micro-hardness on silver content for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals.

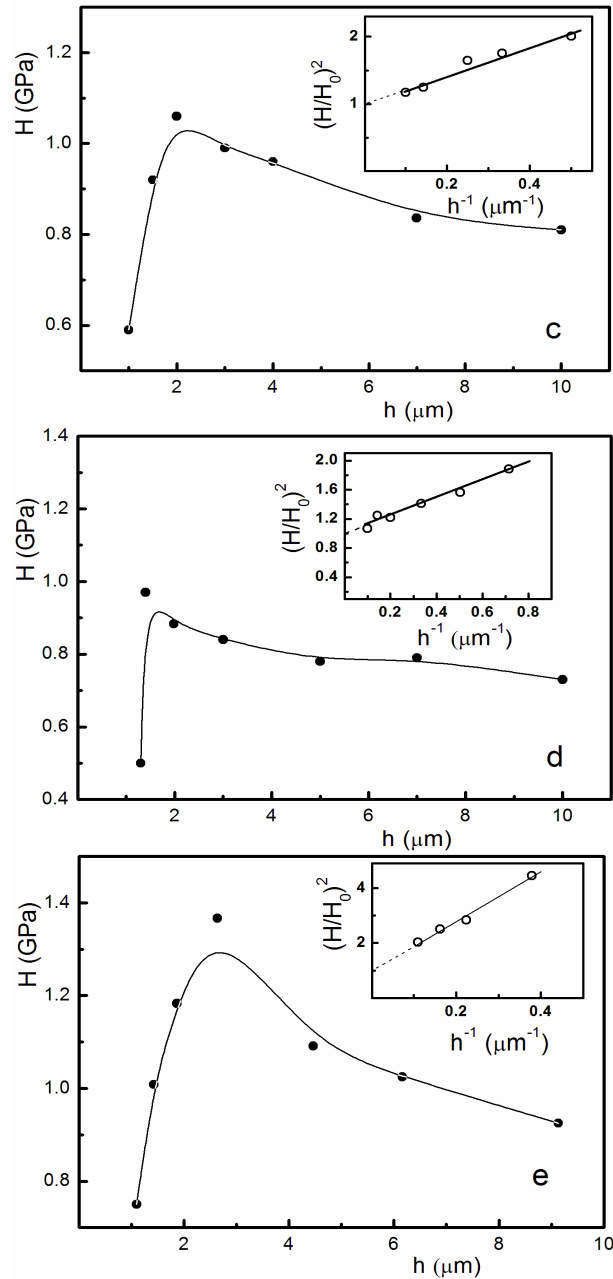
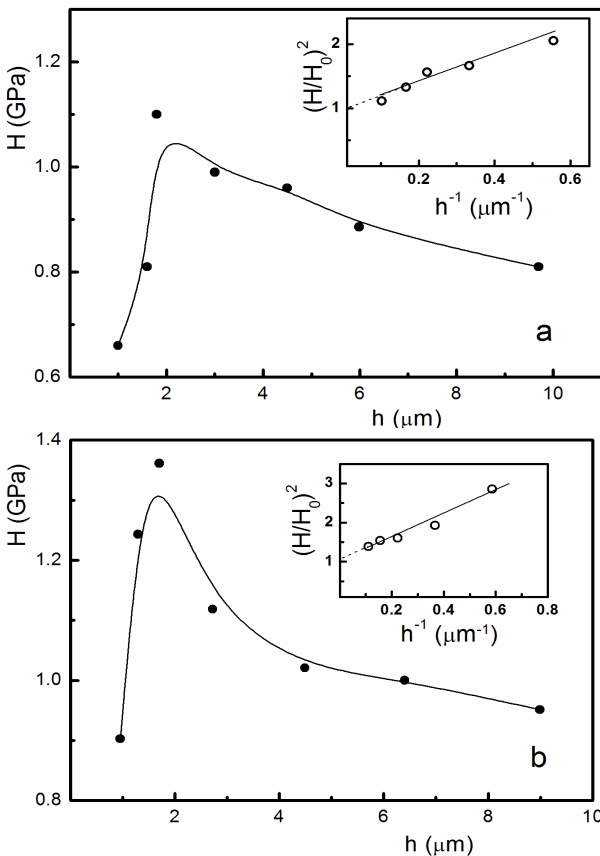


Fig. 2. Dependences of the hardness H on the penetration depth for indenter h in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals: (a) $\text{Cu}_7\text{GeS}_5\text{I}$, (b) $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeS}_5\text{I}$, (c) $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeS}_5\text{I}$, (d) $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeS}_5\text{I}$, and (e) $\text{Ag}_7\text{-GeS}_5\text{I}$. The curves present approximation of $H(h)$ dependences of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals in the deformation gradient model. The insets show the $H(h)$ dependence of the $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals, normalized to H_0 , in the “ $\left(\frac{H}{H_0}\right)^2 - h^{-1}$ ” coordinates (line is the result of linear approximation).

It has been shown that, with increasing the silver content, the micro-hardness of mixed crystals slightly increases. This may be caused by the fact that, with $\text{Cu} \rightarrow \text{Ag}$ isovalent substitution, the density and rigidity of the structure increases. Besides, the density of the crystal lattice arrangement grows.

Fig. 2 shows the dependences of micro-hardness on the depth of indenter immersion for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals. These dependences were obtained by changing the load on the indenter from 2 up to 200 g. The $H(h)$ dependences show that the micro-hardness of the investigated crystals non-monotonically depends on the depth of immersion. At the initial stage of indentation in the region of small h , the micro-hardness increases and reaches the maximum value H_{\max} at $h = h_{\max}$ (Fig. 2). The growth of H may be caused by the fact that the geometric factor plays a significant role at micro-indentation with the small depths of the indenter immersion [6]. In this area, the vertex of the indenter is a spherical surface with the radius R . Thus, it can be assumed that at $h < h_{\max}$ indentation is carried out by a spherical indenter, and the load P is localized in the wider area (as compared with the sharp peak of the Vickers pyramid). Therefore, deformation under the indenter at $h < h_{\max}$ will be predominantly elastic and, when the load P is removed, the imprint will be to much extent elastically restored. In addition, the strain hardening of the material under the imprint can take place as a result of movement and rectification of point defects [7].

Furthermore, with increasing $h > h_{\max}$, the hardness decreases. The indicated features of the $H(h)$ changes are associated with formation of various deformation zones in the contact area during indentation and with migration of structural defects [7]. As a result, as the indenter deepens into the crystal, mechanisms of its deformation change. In particular, in the investigated materials there appear the following areas of deformation under the sharp indenter, such as the hydrostatic zone, gradient zone, elastoplastic zone, elastic zone [7]. With the increase of the load force P on the indenter and its entrainment, these zones extend to the depth of the sample, and their volumes grow. Therefore, the contribution of different mechanisms to the overall process of forming the imprint changes, leading to changes in H .

The hardness decrease of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals with h increasing indicates that the main mechanism of crystals deformation at $h > h_{\max}$ is represented by plastic deformation [8], and the mechanical stress σ exceeds the materials strength limit. The mechanism of plastic deformation is represented by the movement of existing and formation of new extended defects, in particular dislocations in the area of micro-contact.

The change in the hardness of the investigated crystals at $h > h_{\max}$ can be interpreted within the framework of the plastic deformation gradient model (MSG) [9-11]. According to the MSG model, crystals indentation is accompanied by formation of circular loops of geometrically necessary dislocations (GND [8]) with Burgers' vectors perpendicular to the plane surface of the crystal [10].

According to this model, the dependence $H(h)$ can be described by the equation [12]:

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}}, \quad (3)$$

where H is the hardness for a given depth of imprint h ; H_0 – hardness at an infinite depth of the imprint, and h^* – characteristic depth of the imprint, which depends on the form of the indenter, shear modulus and hardness.

Thus, according to the MSG model H^2 should be linearly dependent on h^{-1} . To verify Eq. (3) for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals, the experimental dependences $H(h)$ were plotted in the coordinates “ $H^2 - h^{-1}$ ” (insets in Fig. 2). Fig. 2 shows that the dependence of $H(h)$ is well approximated by Eq. (3) in the area $h > h_{\max}$. It means that in this micro-area interval the dislocation mechanism of plastic deformation is implemented in accordance with the MSG model. From the linear approximation of the dependence $H(h)$ by the

equation $H^2 = H_0^2 + \frac{H_0^2 \cdot h^*}{h}$ in the $h > h_{\max}$ area, the point of intersection of the indicated line with the ordinate axis was found (insets in Fig. 2). From the value of the inclination angle of this straight line to the abscissa axis and with account of H_0 , the value h^* was obtained.

4. Conclusions

The micro-hardness of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals were determined by the method of micro-indentation. With the load on the Vickers indenter changing within the range from 2 up to 200 g, the dimensional effects are observed, which are manifested in a non-monotonic variation of the micro-hardness of crystals with increasing the depth of indenter immersion. Plastic deformation of crystals in the micro-area has a dislocation mechanism. The dimensional effects can be explained in the framework of the MSG model and are caused by formation of the circular loops of geometrically necessary dislocations with Burgers' vectors perpendicular to the plane surface of the crystal during indentation. Based on the approximation of the experimental data for $H(h)$, the H_0 and h^* parameters have been determined in the framework of MSG model.

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