Mechanical properties of superionic ceramics based on $(Cu_{1-x}Ag_x)_7GeSe_5I$ solid solutions

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Abstract. $(Cu_{1-x}Ag_x)_7GeSe_5I$-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 applying the indentation method with use of the Vickers pyramid. It has been shown that the microhardness of $(Cu_{1-x}Ag_x)_7GeSe_5I$-based ceramics decreases with copper content decrease at $Cu^+ \rightarrow Ag^+$ cationic substitution. The compositional dependences and size effects of microhardness inherent to $(Cu_{1-x}Ag_x)_7GeSe_5I$-based ceramics have been analyzed. The size effects of microindentation have been interpreted within the framework of the gradient theory of plasticity.

Keywords: solid solution, superionic conductor, cationic substitution, ceramic, microhardness.

1. Introduction

The development of non-traditional efficient energy sources stimulates the search and study of new materials with mixed ionic-electronic conductivity based on superionic conductors [1, 2]. For basic research and applied developments, superionic conductors with argyrodite structure are of interest, in particular, $(Cu_{1-x}Ag_x)_7GeSe_5I$ solid solutions and ceramics based on them, in which the high ionic conductivity is manifested against the background of predominant electronic conductivity and is realized through unfilled vacancies in the cationic sublattice [3–5]. Purposeful variation of ion transport parameters in superionic materials can be effectively carried out by creating a structural disorder in the cationic sublattice, which increases the number of vacancies. In addition to formation of superionic solid solutions, the degree of structural disordering can be increased by forming ceramic samples on their basis, in particular, by using the method of solid-phase sintering.

A sensitive method of studying the effects of this disordering is the method of microindentation [6]. Its effectiveness is caused by the fact that the external mechanical field actively influences various structural subsystems, defects, areas with different structural rigidity. This enables to study the effects associated with both the mobility of individual atoms, structural defects, and collective effects in the cationic sublattice, which are manifested in the field of internal mechanical stresses. Application of the microindentation method makes it possible to study the effects associated with the presence of areas with different structural rigidity, particularly, in ceramic and composite materials.

The aim of this research was to measure and study changes in microhardness of $(Cu_{1-x}Ag_x)_7GeSe_5I$ super-ionic ceramics during isovalent substitution in the catio-nic sublattice and variation in the size of microcrystalline grains, as well as to analyze indentation size effects within the framework of the dislocation model.

2. Experimental

$(Cu_{1-x}Ag_x)_7GeSe_5I$ ($x = 0$, 0.25, 0.50, 0.75, 1) ceramics were prepared on the basis of micropowders of pre-grown crystals with similar compositions [7]. Micropowders of different sizes were obtained by mechanical dispersion in an agate mortar and grinding in a planetary ball mill PQ-N04 for 30 and 60 minutes.

Then the powders were pressed under the pressure close to 400 MPa. The obtained samples were annealed in evacuated down to 0.13 Pa silica ampoules during 36 hours at 973 K. Using the method of microstructural analysis by means of a METAM R1 metallographic microscope, it was found out that the average size of crystallites in ceramics as a result of recrystallization (solid phase sintering) was 12 µm (K1), 5 µm (K2) and 3 µm (K3), respectively. Cylindrical samples with the diameter 8 mm and height 4 mm were made for microhardness measurements. The ceramic samples for microindentation measurements were polished (<0.5 µm).

To measure the microhardness, we used the device PMT-3 with the Vickers indenter (correct quadrangular pyramid with the angle 136° at its apex). The range of loads on the indenter was approximately 0.005–2 N ($m = 0.5…200$ g). Usually the microhardness measured with the Vickers indenter is denoted as HV. In what follows, for convenience, we will denote this parameter as H. The measurements were carried out at room temperature. Numerical values of microhardness were calculated using the formula [8]:

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

where P is the load on the indenter, d – diagonal of the imprint. For each P-value, five measurements were performed, then followed by averaging the results. During the measurements, the depth of the indenter imprints constituted $0.3…10$ µm. The diagonal of indenter imprints on the polished surface of the ceramic samples varied within the range of 2 to 70 µm with a change in the load force from 0.005 up to 2 N. Fig. 1 shows the microstructure images of ceramic samples depending on the Cu-Ag compositional ratio. It is seen that with increasing the silver content, the size of dark zones formed by intercrystalline defect regions increases. The light zones are formed by regions, in which the solid-phase sintering of the original microcrystals has occurred in a high quality mode. Indentation of ceramic samples was subsequently performed in light areas of the polished surface. Indentation of dark zones showed a large scatter of numerical H-values, and sometimes it was impossible to determine their hardness.

3. Results and discussion

The changing of imprint diagonal d from 2 to 70 µm enabled to study the size effects of indentation when measuring the microhardness of $(Cu_{1-x}Ag_x)_7GeSe_5I$ ceramics. Some of the reasons for these effects in the studied ceramic materials may be as follows: 1) movement of their own and formation of new dislocations in the crystalline regions (microcrystals) with increasing the imprint depth; 2) change between the imprint size and the average microcrystal size (d/d_0), which causes an increase in the contribution of intercrystalline regions with increasing d.
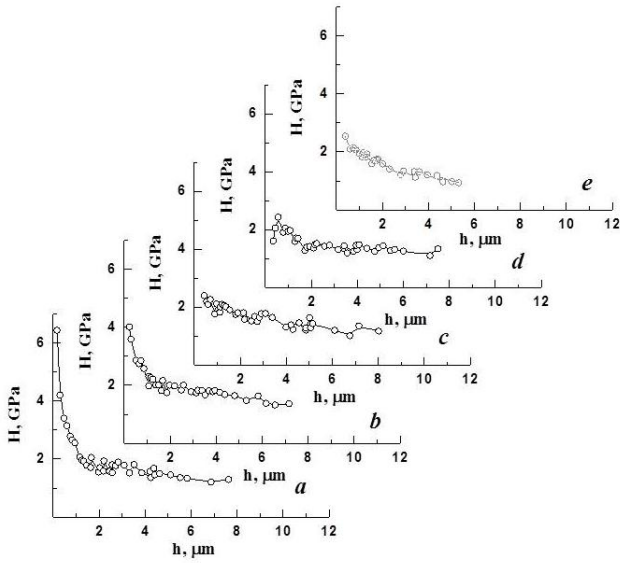
In Fig. 2, the dependences of microhardness in $(Cu_{1-x}Ag_x)_7GeSe_5I$ (K2) ceramics on the depth of imprint are presented. It was shown that the dependences of $H(h)$ reveal the rapid decrease of microhardness in the region where $h < 2$ µm and a slow decrease of H with increasing $h > 2$ µm.

The change in microhardness, when changing the depth of the imprint, indicates the presence of dimensional effect of indentation due to the peculiarities of local deformation of the material under the indenter [9, 10]. Since the formed superionic ceramics can be considered as a set of chaotically sintered microcrystals, interpretation of size effects can be carried out within the framework of gradient theory of plasticity used for crystals [11, 12]. According to this theory, the size effects of microhardness are caused by plastic deformation related with formation and motion of two types of dislocations in the crystals. The first type is statistically distributed dislocations that are formed in crystals during their growth. Motion of these dislocations causes plastic deformation of crystals in the region of h-small values.
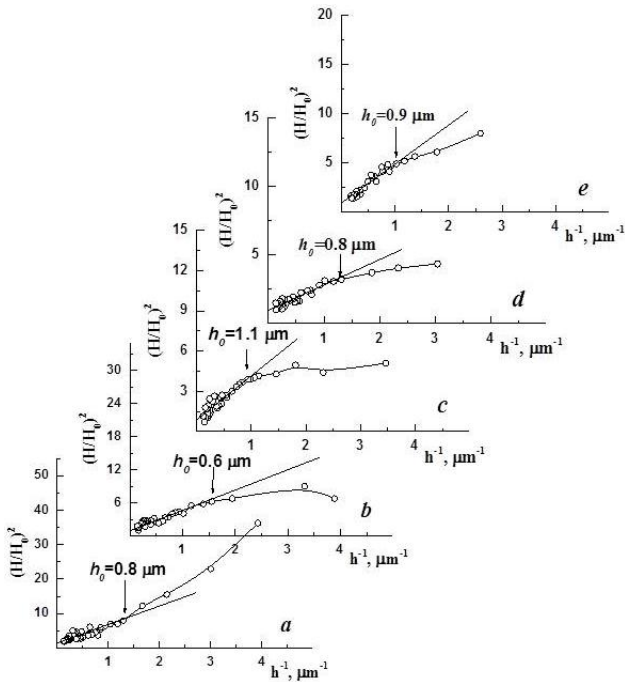
The second type is geometrically necessary dislocations generated when statistically distributed dislocations are not enough for the plastic deformation of the crystal under the indenter, and internal mechanical stresses in the microcontact area exceed the limit of plasticity. The Burgers vector of these dislocations is normal to the plane of the crystal surface, while for statistically distributed dislocations it can have an arbitrary direction. To form the geometrically necessary dislocations in the near-contact area, it is important for the internal mechanical stresses in the crystal to exceed
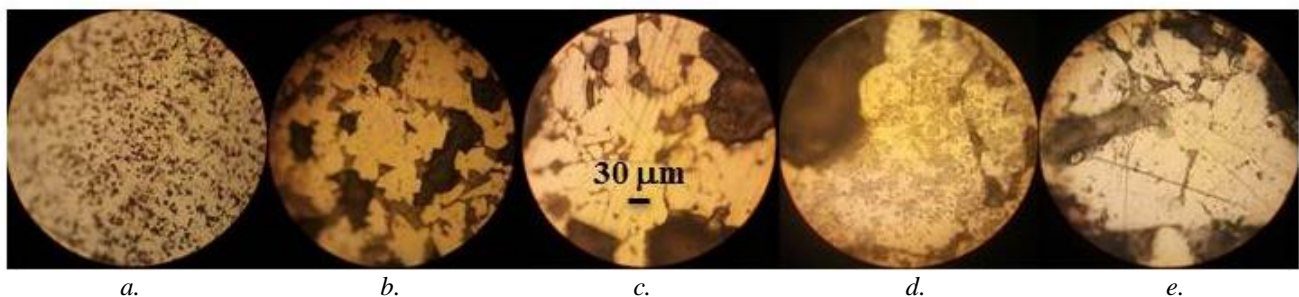
Fig. 1. The microstructure images for ceramic samples (K2) prepared on the basis of $(Cu_{1-x}Ag_x)_7GeSe_5I$ solid solutions: (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1$ (scale in µm is the same for all samples).

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Fig. 2. The dependences of the microhardness on the depth of the imprint for $(Cu_{1-x}Ag_x)_7GeSe_5I$ (K2) ceramics: (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1$.

Fig. 3. The standardized dependences of microhardness $(H/H_0)^2 = F(h^{-1})$ in K2 ceramics for different compositional ratios of Cu:Ag at approximation of size effects in the model of geometrically necessary dislocations: (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1$.

the plasticity limit. The change interval of h, which separates the two regions of size effects, is defined by the ratio between the densities of these two types of dislocations in the microcontact area. In our case, in addition to these two types of dislocations in microcrystalline grains, intercrystalline sintering areas also contribute to plastic deformation.

Shown in Fig. 2 $H(h)$ dependences were approximated within the framework of gradient theory of plasticity in the model of geometrically necessary dislocations based on the relationship between the microhardness and imprint depth by the formula [12]:

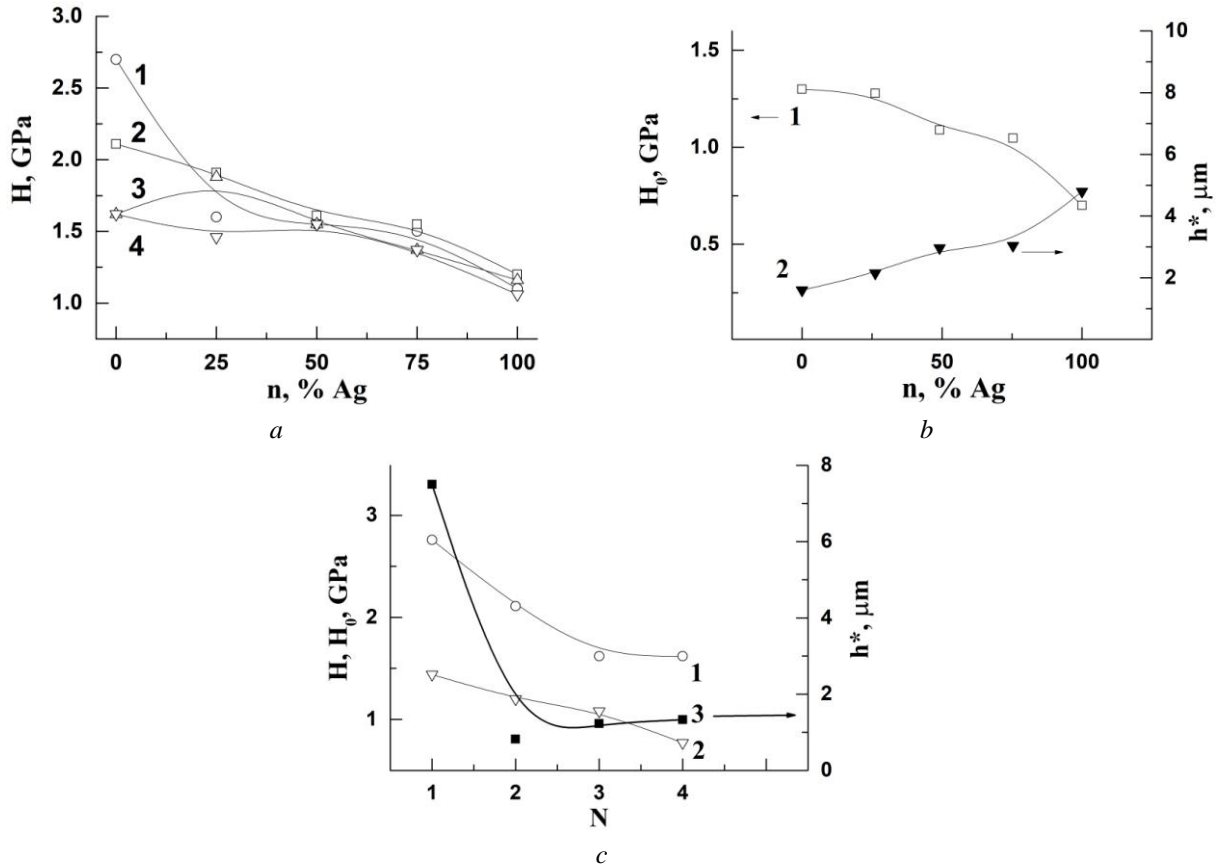$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} \; , \qquad (2)$$

where H is the hardness for a given imprint depth h; H_0 – hardness at an infinite depth of the imprint, when the deformation gradient under the imprint does not affect the value of hardness; h^* – characteristic depth of the imprint.

As can be seen from Eq. (2), the value of H^2 should depend linearly on h^{-1}. Standartized values $(H/H_0)^2$ depending on h^{-1} for $h \to \infty$ should be extrapolated to unity (if $h \to \infty$ then $H \to H_0$). Therefore, the experimental dependences of $H(h)$ were plotted in the coordinates "H^2–h^{-1}" (Fig. 3). As can be seen from this figure, on the dependences $(H/H_0)^2 = F(h^{-1})$ we can distinguish two regions with a characteristic point h_0. The first one is observed within the region of small values $h^{-1}(h > h_0)$, which can be approximated by a straight line (Eq. (2) is fulfilled). The second is realized within the region of large values of $h^{-1}(h < h_0)$, which deviates from the rectilinear dependence. From the linear approximation of $H^2 = F(h^{-1})$ dependence by the formula

$H^2 = H_0^2 + \dfrac{H_0^2 \cdot h^*}{h}$ in the region $h^{-1} \to 0$ the point H_0^2

was found at the interception of the specified line with the y-axis. The value h^* was found from the value of the tangent of the angle for inclination of this straight line to the abscissa axis and taking into account H_0^2. The obtained parameters of approximation of dependences $H = F(h)$ in the model of geometrically necessary dislocations reflect processes of deformation of samples under the indenter and can be the characteristics of materials at the given structural level of deformation. In particular, H_0 is the ultimate microhardness of the crystal during its plastic deformation due to geometrically necessary dislocations, as well as h^* is the correlation size in the ensemble of geometrically necessary dislocations. The form of dependences $H^2 = F(h^{-1})$ indicates that at $h < h_0$ these dependences are not described by Eq. (2), and plastic deformation of the sample is mainly caused by motion of statistically distributed dislocations (h_0 is the depth of the imprint that separates the linear and nonlinear sections on the curve $H = F(h)$).

At $h > h_0$, the dependence $H^2 = F(h^{-1})$ is approximated by a straight line, so we can assume that geometrically necessary dislocations are formed for the growth of plastic deformation. Obviously, both the microhardness H and parameters of the model of geometrically necessary dislocations H_0 and h^* are sensitive to the structural features and mechanisms of material deformation.

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Fig. 4. (a) The compositional dependences of microhardness H at the load force 0.5 N for single crystals (*1*) and ceramics $(Cu_{1-x}Ag_x)_7GeSe_5I$ (2 – K1, 3 – K2, 4 – K3). (b) The compositional dependences of parameters of GND model for K2 ceramics. (c) The dependences of H (at $P = 0.5$ N), H_0 and h^* parameters for Cu_7GeSe_5I single crystal (N = 1) and ceramics based on them N = 2 (K1), N = 3 (K2), N = 4 (K3): curve *1* – H (at $P = 0.5$ N), curve *2* – H_0, curve *3* – h^*.

Fig. 4 presents the compositional dependences of the mechanical parameters of K2 ceramics, which are defined by the results of approximation of experimental dependences. It follows from Fig. 4a that at $Cu \rightarrow Ag$ substitution, the hardness of ceramic H decreases (on average from 1.6 to 1.1 GPa). For similar crystals, it varies much more (from 2.7 to 1.1 GPa) [13]. At $x > 0.5$, the microhardness of ceramics are slightly different from each other. The decrease in the values of the mechanical parameters for the studied ceramic samples with increasing Ag content correlates with the previously detected changes in the hardness of similar crystals [14].

These peculiarities may be caused by a decrease in the rigidity of ceramic samples due to structural disordering as a result of increasing the ionic radius of the cation R_I and the volume of the elementary cell at $Cu^+ \rightarrow Ag^+$ substitution (R_I (Cu^+) is 0.095 nm, R_I (Ag^+) = 0.115 nm) [14].

The parameters of the GND model H_0 and h^* for ceramics change monotonously with the chemical composition changes (Fig. 4c). In particular, with increasing the silver content, the ultimate hardness H_0 decreases almost 2 times. It correlates with the change of this parameter in similar crystals [13]. As the silver content

increases, the parameter h^* of these ceramics increases from 1.6 up to 4.8 μm. For single crystals, a similar growth occurs from 7.5 up to 17.2 μm [13]. Thus, during the transition from single crystals to ceramics, the correlation parameter in the ensemble of dislocations decreases significantly. This may be caused by the growing defects and disordering of the ceramic structure.

Fig. 4c presents the dependences of the mechanical parameters of Cu_7GeSe_5I during the transition from single crystal to ceramics with different sizes of the microcrystalline grains. For ceramics of other compositions, these dependences are qualitatively similar. The figure shows that this transition reduces the characteristic H-values by 40%. For ceramics K2 and K3, the numerical values of microhardness are almost equal. For these ceramics, the condition $d/d_0 > 1$ is fulfilled, and therefore reducing the size of the original microcrystalline grain from 5 down to 3 μm does not lead to a change in the microhardness of the ceramic. It should be noted that the parameter h^* changes the most significantly from 7.5 μm for the crystal to 2.1 μm for ceramics, which indicates a significant decrease in the correlation parameter in motion of dislocations in the microcontact area.

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4. Conclusions

The size effects and compositional changes in the microhardness of ceramics based on $(Cu_{1-x}Ag_x)_7GeSe_5I$ solid solutions have been studied. It has been ascertained that with the silver content increase from 0 to 100 at.% the microhardness of the ceramic decreases by 35%. At $x > 0.5$, the microhardness of ceramics prepared from microcrystals of different sizes differ slightly. As the microcrystalline grains size decreases, the microhardness of the ceramics also decreases. However, for $d_0 = 3$ μm and 5 μm the microhardness of the ceramics is almost the same.

It has been shown that the size effects of microindentation, which are manifested as a function of microhardness on the depth of the imprint, can be interpreted within the framework of the gradient theory of plasticity. The determined approximation parameters H_0 and h^* change monotonously, when the silver content in ceramics changes. During the transition from crystal to ceramics, the correlation parameter in motion of dislocations decreases significantly due to structural disordering.

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Механічні властивості суперіонної кераміки на основі твердих розчинів $(Cu_{1-x}Ag_x)_7GeSe_5I$

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Анотація. Кераміку на основі мікрокристалів $(Cu_{1-x}Ag_x)_7GeSe_5I$ отримували пресуванням і спіканням з мікро- і нанопорошків. Керамічні зразки досліджували методом мікроструктурного аналізу. Мікротвердість вимірювали методом індентування з використанням піраміди Віккерса. Показано, що мікротвердість кераміки на основі $(Cu_{1-x}Ag_x)_7GeSe_5I$ зменшується зі зменшенням вмісту міді при катіонному заміщенні $Cu^+ \rightarrow Ag^+$. Проаналізовано композиційні залежності і розмірні ефекти мікротвердості кераміки на основі $(Cu_{1-x}Ag_x)_7GeSe_5I$. Розмірні ефекти мікроіндентування проінтерпретовані в рамках градієнтної теорії пластичності.

Ключові слова: тверді розчини, суперіонний провідник, катіонне заміщення, кераміка, мікротвердість.

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