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THE EFFECT OF ISOVALENT CATION SUBSTITUTION ON MECHANICAL PROPERTIES OF $(Cu_xAg_{1-x})_7SiS_5I$ SUPERIONIC MIXED SINGLE CRYSTALS

$(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals were grown by the Bridgman–Stockbarger method. The microhardness measurements are carried out at room temperature using a Vickers indenter. The compositional dependence of the microhardness is studied. The dependence of the microhardness on the depth of imprint is analyzed in the model of geometrically necessary dislocations. The indentation size effect is observed. It is established that the microhardness of $(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals decreases at the substitution of Cu atoms by Ag atoms.

Keywords: mixed crystals, mechanical properties, cation substitution, microhardness, compositional dependence.

1. Introduction

Cu_7SiS_5I and Ag_7SiS_5I crystals are the representatives of a great family of compounds with cargyrodite structure [1]. Due to the high ionic conductivity, they are of practical interest, in particular, for solid-state ionics [2, 3]. One of the main characteristics of compounds with the argyrodite structure is the capability to atomic substitution and formation of solid solution rows. It should be mentioned that the solid solutions based on phosphorous- and germanium-containing argyrodites and their physical properties are presented in Refs. [3–6]. During the growth of mixed crystals, the level of defects, as well as homogeneities, can be estimated by measuring their microhardness. Using standard indenters and measuring the microhardness at different depths of imprints give an opportunity to analyze the process of plastic deformation in these crystals. The study of the influence of a load P on the indenter on the microhardness $H(P)$ makes it possible to find an interval of loads in which the microhardness remains almost constant. This is the so-called true hardness, a value that can be used to compare with the properties of other materials or when studying the influence of various factors on the properties of the test material such as the cationic isovalent substitution. The study of the dependence of the microhardness on the indenter penetration depth can provide information on the gradient of mechanical properties with depth in the material under study, in particular, the concentration of defects and the presence of various phases and impurities. The states of the surface layer and the sample volume are not necessarily identical. Thus, the purpose of this paper was to study the dependence of microhardness for $(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals on the imprint depth, as well as on their chemical composition.

2. Experimental

$(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals grown by the Bridgman–Stokbarger method [7] were used to measure the microhardness. Samples for measurements were prepared in the form of parallelepipeds with an upper natural crystal growth face, on which the

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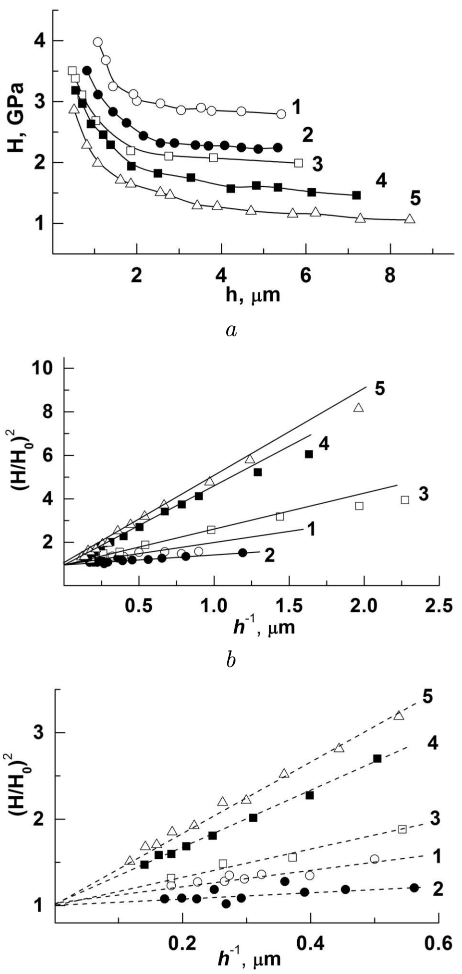

a

b

c

Fig. 1. Dependences of the microhardness of $(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals on the depth of the imprint (*a*) and their approximation in the GND model (*b, c*): Cu_7SiS_5I (*1*), $(Cu_{0.75}Ag_{0.25})_7SiS_5I$ (*2*), $(Cu_{0.5}Ag_{0.5})_7SiS_5I$ (*3*), $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ (*4*), and Ag_7SiS_5I (*5*)

microindentation by a force applied along the direction (001) was performed. Measurements of the microhardness H of these materials were carried out at room temperature using a PMT-3 microhardnessmeter, using a Vickers indenter, a diamond-shaped regular quadrangular pyramid with an angle of 136°. The microhardness H was determined by using the relation [8]

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

where $\alpha = 136°$, P is the load force on an indenter, d is the diagonal of the imprint. The load P on an indenter was changed in the interval 0.02 N – 2 N. The ratio between the diagonal of the imprint d and its depth h is 7 for the Vickers indentor ($d/h = 7$). We used the depth of the imprint h to present the measurement results.

3. Results and Discussion

Figure 1, *a* presents the dependences of the microhardness H on the depth h of the imprint for $(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals at room temperature. These dependences were obtained by a variation of the load on an indenter from 2 g to 200 g. It can be seen that, with increasing P and the imprint depth h, the microhardness H decreases. Thus, the direct dimensional effect is observed for $(Cu_xAg_{1-x})_7SiS_5I$ mixed crystals [9]. During the formation of an imprint in the region of contact with the indenter, various deformation zones are formed. They determine the elastic, plastic, and relaxation components of the deformation of the sample [10], and the distribution of deformation under the indenter has a complex character [11]. Therefore, the depth of the imprint can be represented by the sum of components that are determined by the different mechanisms of deformation of the sample under the indenter:

$$h = h_e + h_r + h_p, \qquad (2)$$

where h_e, h_r, and h_p are the elastic, relaxation, and plastic component, respectively. The formation of deformation zones is associated with the migration of structural defects and, as a consequence, a change in the mechanisms of deformation of the crystal, as the indenter is deepened. In particular, under a sharp indenter, the following deformation regions appear in solids: the hydrostatic, gradient, elastoplastic, and elastic zones [12]. With an increase in the load P on the indenter and its deepening, these zones extend to the depth of the investigated sample, and their volumes grow. The contributions of individual mechanisms to the overall process of forming the imprint change, which leads to a change in the hardness of the crystal. With a decrease of the microcontact zone at low loads on the indenter, the contribution of the elastic component of a deformation of solids will increase. An increase in the Young modulus E and the hardness H and the approach of the mechanical stress σ to the theoretical limit of ideal crystal lattice strength ($\sigma \approx 0.1E$) are observed. It is known that the dimensional effect is a consequence of the induced, i.e. created during the indentation, gradient of a plastic deformation in the microcontact zone, which can be interpreted in the model of geometrically necessary dislocations (GND) [14–18]. The analysis of the microhardness dependence on the depth of the indenter immersion provides an opportunity to establish a correspondence between the experimental data and the mechanism of deformation of a sample based on the theory of strain gradient plasticity (SGP) and to determine the parameters of the GND model for the investigated material. The plastic deformation of a material during the indentation can be described in Brown's model [19]. In this model, the plastic flow is regarded as a displacement along semicircular sliding surfaces with a center at the indenter vertex. With such a deformation mechanism, geometrically necessary dislocations appear to change the shape of the sample in the course of plastic deformation, and the dimensional effect is caused by an increase in the density of dislocations in connection with a decrease of the imprint size and the movement of dislocations in a smaller sliding circle. The change in the microhardness of the investigated $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ mixed crystals, depending on the depth of the imprint, can be interpreted within the framework of the GND model [14–16].

According to this model, the indentation of crystals is accompanied by the formation of circular loops of geometrically necessary dislocations with Burgers vectors perpendicular to the plane surface of the crystal. In this case, the dependence $H(h)$ should be described by the relation [16]:

$$\frac{H}{H_0} = \sqrt{1 + \frac{\rho_G}{\rho_S}} = \sqrt{1 + \frac{h^*}{h}}, \tag{3}$$

where H is the hardness for a given depth of imprint h; H_0 is hardness in the absence of geometrically necessary dislocations (i.e., for $h \gg h^*$, when the deformation gradient under the indenter imprint does not affect the hardness value), ρ_G is the density of geometrically necessary dislocations, ρ_S is the density of statistically accumulated dislocations, h^* is the characteristic depth of the imprint, which depends on the form of the indenter, displacement module, and hardness. It can be seen from Eq. (3) that H^2 should be linearly dependent on h^{-1}. The normalized dependences $(H/H_0)^2$ from h^{-1}, as $h \to \infty$, should extrapolate to 1 (if $h \to \infty$, then $H \to H_0$). To test Eq. (3) for $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ mixed crystals, the experimental dependences $H(h)$ were constructed in the $\langle\langle H^2 - h^{-1}\rangle\rangle$ coordinates. The point of intersection of the indicated line with the ordinate axis H_0 was found from the linear approximation of the dependence $H(h)$ by the formula $H^2 = H_0^2 + \frac{H_0^2 h^*}{h}$ in the region $h > h_M$. The value h^* was found from the value of the tangent of the angle of inclination of this straight line to the abscissa axis and taking H_0 into account. The normalized dependences $\langle\langle (H/H_0)^2 - h^{-1}\rangle\rangle$ are shown in Fig. 1, *b*. The compositional dependences of the H_0 and h^* parameters are presented in Fig. 2. Figure 2 shows that the indicated dependences are satisfactorily approximated by straight lines, that is, the dimensional effect of $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ mixed crystals indentation has a dislocation mechanism of plastic deformation and can be explained in the theory of strain gradient plasticity [16]. Figure 1, *a* shows that, with increasing $h > 3\mu$ m, the microhardness of crystals remains almost unchanged. The H values in this interval of h can be assumed to be the true hardness of $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ mixed crystals and might be used as the physical parameters of these materials. Figure 2 shows that, at the Cu → Ag isovalent substitution, the hardness H of crystals and the limiting hardness H_0 decrease. This indicates a decrease in the hardness of the crystalline structure of these materials. The decrease in the HV values for the investigated crystals with increasing the Ag content correlates with a decrease in their melting temperature [7]. These features may be caused by an increase in the ionic radius R_I of a cation at the

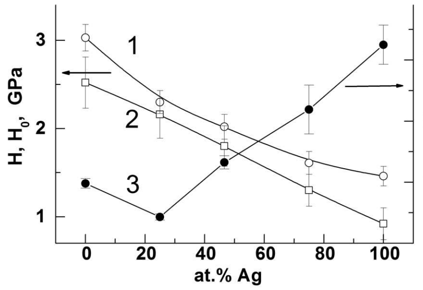

Fig. 2. Compositional dependences of the microhardness H (curve *1*) (at $P = 0.5N$) and parameters of the model of geometrically necessary dislocations (GND) H_0 (curve *2*) and h^* (curve *3*) for $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ mixed crystals

$Cu^+ \rightarrow Ag^+$ substitution, (R_I (Cu^+) $= 0.095$ nm, R_I (Ag^+) $= 0.115$ nm), resulting in an increase of the elementary cell volume. So, the hardness of the crystal lattice somewhat decreases [7, 20]. The parameter h^* of the GND model does not change monotonously (h^* has a minimal value for $x = 25$). This parameter h^* is uniquely associated with the density of statistically distributed dislocations ρ_S: $h^* \approx (\rho_S)^{-1}$ [21]. When the density of such dislocations increases, the parameter h^* decreases. In other words, as can be seen from Fig. 2, the maximum density of statistically distributed dislocations is in $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ mixed crystal, and the minimal one is in Ag_7SiS_5I.

4. Conclusions

The dependences of the microhardness for $(Cu_xAg_{1-x})_7SiS_5I$ crystals on the composition and the depth of immersion of a Vickers indenter are investigated. The revealed indentation size effects in these crystals are interpreted within the framework of the theory of strain gradient plasticity and are caused by the formation of circular loops of geometrically necessary dislocations with Burgers vectors perpendicular to the plane surface of the crystal. It is established that, at the isomorphic substitution of Cu atoms by Ag atoms, the microhardness of the investigated mixed crystals decreases, which may be caused by the growth of the ionic radius of the cation. The minimal density of statistically distributed dislocations is revealed in Ag_7SiS_5I crystal.

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ВПЛИВ ІЗОВАЛЕНТНОГО КАТІОННОГО ЗАМІЩЕННЯ НА МЕХАНІЧНІ ВЛАСТИВОСТІ СУПЕРІОННИХ КРИСТАЛІВ $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$

Резюме

Кристали твердих розчинів $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ вирощували методами Бріджмена–Стокбаргера. Вимірювання мікротвердості проводили при кімнатній температурі за допомогою індентора Віккерса. Досліджено композиційну залежність мікротвердості кристалів $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$ у залежності від глибини занурення індентора Віккерса. Залежності мікротвердості від глибини відбитка були проаналізовані в рамках моделі градієнта пластичної деформації. Виявлено розмірні ефекти при мікроіндентуванні кристалів $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$. Встановлено, що при заміщенні атомів Cu атомами Ag проходить зниження мікротвердості кристалів $(\mathrm{Cu}_x\mathrm{Ag}_{1-x})_7\mathrm{SiS}_5\mathrm{I}$.