ISSN 1560-8034, 1605-6582 (On-line), SPQEO, 2020. V. 23, N 1. P. 37-40.

Influence of cation substitution on mechanical properties of $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals and composites on their base

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Abstract. Microhardness of $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals and composites on their base was investigated using the Vickers indenter at room temperature. $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals were obtained using the Bridgman–Stockbarger method. Composites on their base were prepared as a pressed mixture of $(Cu_{1-x}Ag_x)_7GeSe_5I$ micropowder and ethylene-vinyl acetate polymer in 90:10 concentration ratio, respectively. Dependences of microhardness versus the indenter penetration depth have been analyzed. Influence of $Cu^+ \rightarrow Ag^+$ isovalent cation substitution on the microhardness of $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals and composites on their base have been studied.

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

https://doi.org/10.15407/spqeo23.01.37
PACS 78.40.Ha, 77.80.Bh

Manuscript received 10.11.19; revised version received 14.01.20; accepted for publication 18.03.20; published online 23.03.20.

1. Introduction

Cu_7GeSe_5I and Ag_7GeSe_5I crystals belong to a large family of compounds with argyrodite structure [1]. They are characterized by high values of ionic conductivity and well-known as the superionic conductors [2, 3]. This makes them interesting materials to create modern energy sources. It is important task to study the mechanical properties of $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals as well as the composites on their base, to perform a comparison between crystals and composites and to explain an influence of cation substitution on hardness of these materials.

It should be noted that microhardness measurements give opportunity to estimate material homogeneity. Analysis of microhardness dependence versus the indenter penetration depth can explain the process of plastic deformation occurrence in the investigated material. Moreover, study of these dependences allows obtaining information about material defects, impurities, and presence of various phases.

Thus, this paper is devoted to study the microhardness compositional dependences in $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals as well as the composites on their base and to provide a comparative analysis between them.

2. Experimental

$(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals obtained using the Bridgman–Stockbarger method were used for microhardness measurements [4]. The measurements were carried out using the samples with the natural upper plane. Thereby, an indentation was performed in the (001) direction of applying force. Composites were prepared as a pressed mixture of $(Cu_{1-x}Ag_x)_7GeSe_5I$ micropowder and ethylene-vinyl acetate polymer in 90:10 concentration ratio. Surfaces of composites and crystals were polished for measurements clarity.

Microindentation tests were carried out using the microhardness meter machine PMT-3 at room temperature. The indenter was a Vickers pyramid (a diamond-shaped regular quadrangular pyramid with 136° angle at vertex). Numeric values of microhardness H were calculated using the equation [5]:

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

where $\alpha = 136°$, P is the load on the indenter, d – diagonal of the imprint. The range of applied forces was 0.1…2 N.

3. Results and discussion

The dependences of microhardness H versus the penetration depth of indenter h are presented in Fig. 1. It can be seen that with the indenter depth increasing, the microhardness H decreases. This behavior can be represented as the direct dimensional effect [6].

It should be mentioned that sample deformation under indenter consists of elastic, plastic and relaxation components [7], and deformation distribution has a complex character [8]. As follows, the imprint depth can be represented by the sum of elastic component h_e, relaxation component h_r, and plastic component h_p:

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

where $h_e = P/k$, k is the stiffness of the material under indenter, $h_r = h_{r0} - h_0 \exp(-t/\tau)$, t – time of applying the load onto the imprint ($h_{r0} = h_r$ at $h \to \infty$), τ – relaxation time, $h_p = (-\Delta h_p/\Delta t)t$, $\Delta h_p/\Delta t$ – velocity of the viscous flow.

Formation of deformation zones is a consequence of structural defects migration and changes in the deformation mechanisms with increasing the indenter penetration depth. There are four following deformation regions observed under indenter in solids: hydrostatic zone, gradient zone, elastoplastic zone and elastic zone [9]. The volume of these zones grows with increasing the load P, and they extend over the total thickness of the sample. Contribution of different deformation mechanisms to overall process of imprint formation changes. Consequently, complex microhardness behavior is observed.

Gradient of plastic deformation, which is formed during indentation can be represented in the model of geometrically necessary dislocation (GND) [10-14]. To find correlation between the mechanism of sample deformation and the experimental data, based on strain gradient plasticity (SGP) and to determine the parameters of investigated material using GND model, the microhardness dependences versus the indenter penetration depth need to be analyzed.

According to GNP model, formation of circular loops of geometrically necessary dislocations with Burgers vectors normal to the plane surface takes place during indentation of the crystals. The dependence $H(h)$ should be described by equation [12]:

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

where H is the hardness at a given depth of imprint h, H_0 – hardness when the deformation gradient under the indenter does not affect on the hardness value (at $h >> h^*$), ρ_G – geometrically necessary dislocations density, ρ_S – statistically accumulated dislocations density, h^* – characteristic depth of the imprint that depends on the indenter shape, hardness and displacement module.

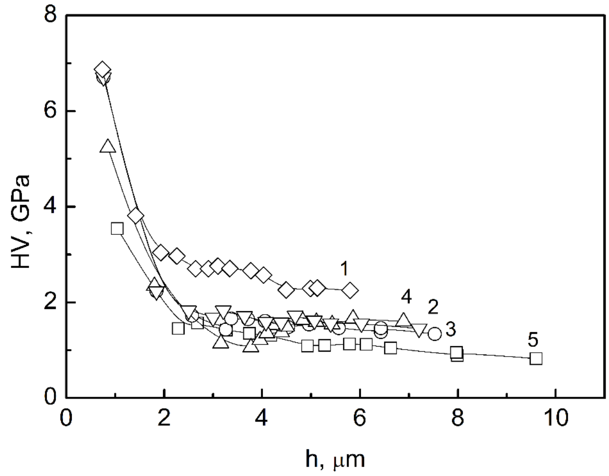

Fig. 1. Dependences of microhardness H versus penetration depth h for Cu_7GeSe_5I (*1*), $(Cu_{0.75}Ag_{0.25})_7GeSe_5I$ (*2*), $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ (*3*), $(Cu_{0.25}Ag_{0.75})_7GeSe_5I$ (*4*), and Ag_7GeSe_5I (*5*) crystals.

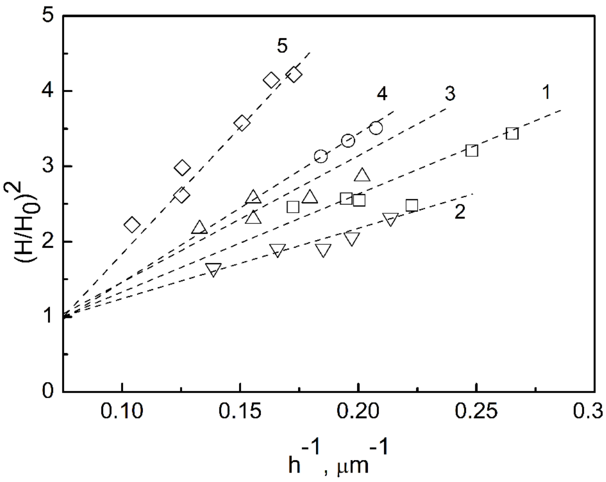

Fig. 2. Dependences $(H/H_0)^2$ versus h^{-1} for Cu_7GeSe_5I (*1*), $(Cu_{0.75}Ag_{0.25})_7GeSe_5I$ (*2*), $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ (*3*), $(Cu_{0.25}Ag_{0.75})_7GeSe_5I$ (*4*), and Ag_7GeSe_5I (*5*) crystals.

It can be deduced from Eq. (3) that H^2 linearly depends on h^{-1}, and dependences $(H/H_0)^2$ on h^{-1} should be extrapolated to unity (if $h \to \infty$ and $H \to H_0$). Eq. (3) was tested for $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals. The experimental dependences $H(h)$ were constructed in $H^2 - h^{-1}$ coordinates. The intersection point of the indicated line with the ordinate H_0 axis was determined from the linear approximation by the equation

$$H^2 = H_0^2 + \frac{H_0^2 \cdot h^*}{h} . \quad (4)$$

From the slope angle tangent value of this line to the abscissa axis, which was divided by H_0^2, h^* values were calculated.

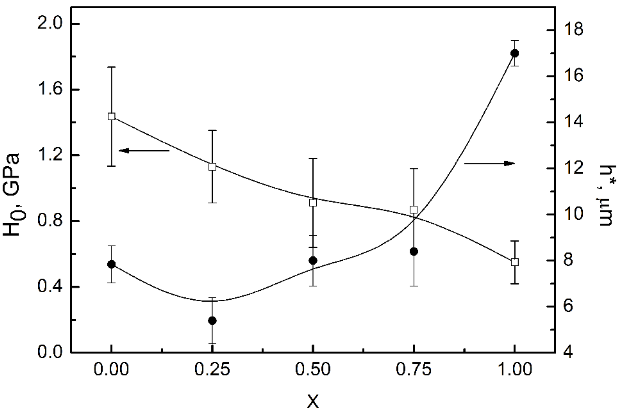

Fig. 3. Compositional dependences of GNP model parameters H_0 and h^* for $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals.

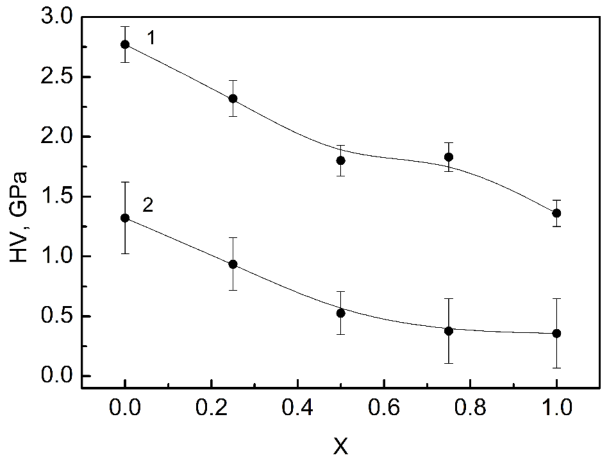

Fig. 4. Compositional dependences of the microhardness *H* for $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals (*1*) and composites on their base (*2*).

Fig. 2 presents the enlarged image of $(H/H_0)^2$ versus h^{-1} dependences (at small h^{-1} values). It can be seen that the intersection point of extrapolated straight lines with the ordinate axis corresponds to unity. It follows that the dimensional effect for $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals has a dislocation mechanism of plastic deformation and can be explained within the strain gradient plasticity (SGP) theory [12].

Fig. 3 shows the compositional dependences of calculated H_0 and h^* values. The density of statistically distributed dislocations ρ_S and parameter h^* is associated as $h^* \sim (\rho_S)^{-1}$ [15]. It can be seen that the parameter h^* has a minimal value at $x = 0.25$ (Fig. 2). It follows that the maximum density of statistically distributed dislocations is inherent to $(Cu_{0.25}Ag_{0.75})_7GeSe_5I$ mixed crystal, and the minimum one – to Ag_7GeSe_5I crystal.

The compositional dependence of hardness for $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals is shown in Fig. 4. It can be seen the nonlinear microhardness decrease at $Cu^+ \rightarrow Ag^+$ isovalent cation substitution. It can be explained by the lattice parameter increase and ionic radii difference ($R_i(Cu^+) = 0.095$ nm, $R_i(Ag^+) = 0.115$ nm) [4, 16]. For composites based on $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals, the same hardness behavior is observed at $Cu^+ \rightarrow Ag^+$ isovalent cation substitution. But due to the soft EVA polymer content (10%) they are more than 2 times softer.

4. Conclusions

Mechanical properties of $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals have been investigated. The dependences of microhardness *H* on the penetration depth of the indenter *h* have been obtained and analyzed. The indentation size effect in the investigated mixed crystals has been revealed and interpreted within the framework of strain gradient plasticity theory. It has been ascertained that the minimum of statistically distributed dislocation density is observed in the Ag_7GeSe_5I crystal. Compositional dependences of $(Cu_{1-x}Ag_x)_7GeSe_5I$ mixed crystals have been analyzed. The microhardness decrease at $Cu^+ \rightarrow Ag^+$ isovalent cation substitution has been shown and explained. Compositional dependences of $(Cu_{1-x}Ag_x)_7GeSe_5I$-based composites have been analyzed and compared to mixed crystals.

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