Mechanical properties of superionic ceramics based on $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions

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Superionic conductors Ag_7SiS_5I and Ag_7GeS_5I belong to a wide family of compounds with an argyrodite structure [1]. Due to the high ionic conductivity of $Ag_7(Si_{1-x}Ge_x)S_5I$ crystals they are promising materials for creation an efficient electrode materials, photoanodes, supercapacitors, etc. [2]. Recently, increasing attention is observed to the preparation and investigation of superionic conductors in the form of ceramics due to their greater manufacturability.

Ceramic samples of $Ag_7(Si_{1-x}Ge_x)S_5I$ (x = 0.2; 0.4; 0.6; 0.8) solid solutions were prepared by sintering of pressed micro- and nanocrystalline powders. Nanocrystalline powders were obtained by grinding in a planetary ball mill PQ-N04 for 30 and 60 min, and microcrystalline powders were ground in an agate mortar. Annealing of the pressed samples was performed in evacuated quartz ampoules at 973 K for 36 h. Thus, ceramics were obtained in the form of disks with a diameter of 8 mm and a thickness of 3-4 mm (Fig.1).

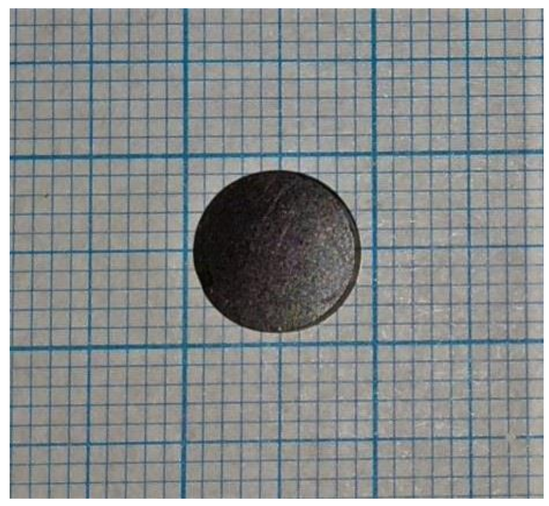

Fig. 1. View of $Ag_7(Si_{0.5}Ge_{0.5})S_5I$-based ceramics.

Measurements of microhardness was performed by indentation of the Vickers pyramid in the load range of 0.05-1.5 N. The depth of penetration of the indenter was 1-10 μm.

It has been established that the microhardness of $Ag_7(Si_{1-x}Ge_x)S_5I$-based ceramics decreases with increasing the depth of penetration. This is explained by the dimensional effect of indentation during microindentation of ceramics. The decrease in microhardness with decreasing of Si content during the $Si^{4+} \rightarrow Ge^{4+}$ substitution is observed both for the studied ceramics and single crystals. The decrease in the values of microhardness for ceramic samples compared to the single crystals is established. This is due to the porosity and presence of intercrystalline areas (with a large number of structural defects) and, as a consequence, “free” volume in the ceramics (Fig.2).

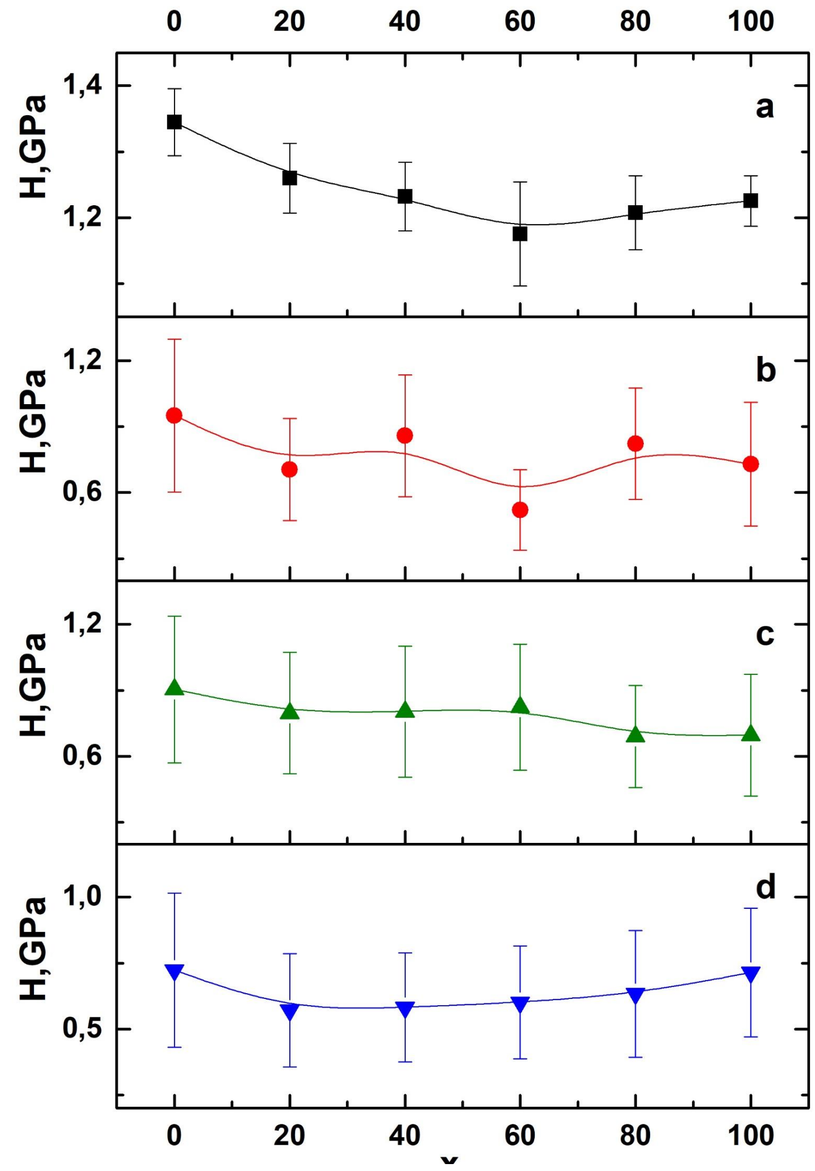

Fig. 2. Compositional dependences of microhardness H ($P = 0.5N$) of the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions in single crystalline (a) and ceramics obtained by the grinding in agate mortar (b), and a planetary ball mill for 30 min (c) and 60 min (d)

1. *W.F. Kuhs, R. Nitsche, K. Scheunemann,* The argyrodites – A new family of the tetrahedrally close-packed structures // Mater. Res. Bull.-1979. Vol.14, pp. 241-248.
2. *M. Laqibi, B. Cros, S. Peytavin, M. Ribes*, New silver superionic conductors Ag_7XY_5Z (X = Si, Ge, Sn; Y = S, Se; Z = Cl, Br, I) – synthesis and electrical studies // Solid State Ionics.-1987.- Vol. 23, pp. 21-26.