Influence of glassy backbone on the photoformation and properties of solid electrolytes Ag : As-S-Ge

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The work is conducted to clarify the effect of the glassy backbone on the process of fabrication and some properties of solid electrolytes obtained via photodissolution (PD) of Ag. For this purpose the ternary chalcogenide glasses (ChG) As-S-Ge have been synthesized by the melt-quenching method in vacuum. The compositional line $(GeS_4)_x\ (AsS_3)_{1-x}$ $(0 \le x \le 1)$ has been chosen to realize the monotonic transition of the structural units of glassy backbone from trigonal to tetragonal configuration. XRD and far IR spectroscopy have been applied for microstructural investigation. Thin films have been prepared by thermal evaporation of synthesized materials in vacuum onto Pyrex glass or Si/SiO_2 substrates, while the silver layers were deposited on top of the ChG films, using the same method. Fabrication of solid electrolytes was performed at room temperature, by PD of silver onto ChG films, using the light of a halogen lamp focused by a quartz lens. The power incident at the sample surface was estimated as ~ 250 mW/cm^2. The obtained results have shown that the process of solid electrolyte formation occurs in three steps [1], but the last two steps, as well as the electrical properties of the finally fabricated electrolyte, are strongly influenced by chemical composition and microstructure of the used ChG backbone. The rate of light – induced solid state reaction between Ag and ChG films increases to a maximum around composition $(GeS_4)_{0.33}(AsS_3)_{0.67}$ and then falls down. The maximum and minimum rate of reaction for different compositions differs by 20 times. On the other hand, the resistivity of the final obtained solid electrolytes decreases with GeS_4 increase, reaching the minimum value at the same $(GeS_4)_{0.33}(AsS_3)_{0.67}$ composition. At the same time, IR transmission spectra shows that for AsS_3, this spectrum comprises only one main oscillation mode at 310 cm^{-1}, characteristic for As –S bond. Introduction of about 7 at.% Ge, that is alloy $(GeS_4)_{0.33}(AsS_3)_{0.67}$, results in appearance of an additional oscillation mode, at 374 cm^{-1}, characteristic for Ge –S bond. We assume that these peculiarities of solid electrolyte formation as well as the lowest electrical resistivity of electrolytes based on backbone of glassy $(GeS_4)_{0.33}\ (AsS_3)_{0.67}$ may be due to its homogenization, that is to building in this alloy of an amalgamation of tetrahedral and trigonal structural units connected in a random network, without clustering. Such homogenization promotes the transport of both electrons and ions involved in photoreaction [2] because of lack of phase boundaries and additional defects.

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References

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