Molecular origin of the giant conductivity enhancement in \((\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}\) glasses\(^1\) CHAD HOLBROOK, P. BOOLCHAND, University of Cincinnati — The solid electrolyte additive Ag\(_2\)S is found to homogeneously alloy with base As\(_2\)S\(_3\) glass at low concentrations (\(x < 6\%\), single: \(T_g = T_{g}^{\text{high}} \sim 210\text{C}\)), but it rapidly segregates as a Ag-rich glass phase at medium concentrations (\(6\% < x < 20\%\), bimodal: \(T_{g}^{\text{high}}\) and \(T_{g}^{\text{low}} \sim 170\text{C}\)), and becomes the principal glass phase populated at higher \(x > 35\%\) (single: \(T_{g}^{\text{low}}\)) as revealed by modulated calorimetric measurements. The stoichiometry of the Ag-rich (\(T_{g}^{\text{low}}\) phase) is suggested to be near Ag\(_x\)As\(_{3x}\)S\(_{7-3x}\) at \(x \sim 25\%\) but becomes closer to that of Smithite (AgAsS\(_2\)) at \(x > 40\%\), as revealed by Raman scattering. In the \(9\% < x < 14\%\) composition range, one observes, in calorimetric experiments, the opening of a reversibility window, and a pronounced increase in the fractional population, \(R(x)\) of the Ag-rich glass phase, both of which correlate well with the 5-orders of magnitude increase in electrical conductivity\(^1,2\) across this compositional interval. In the same interval molar volumes on our samples show a local plateau. These observations suggest a new interpretation of the giant electrical conductivity enhancement observed at \(x > 15\%\) in the present electrolyte glass system. \(^1\) E.A. Kazakova and Z.U. Borisova, Fiz. Khim. Stekla 6, 424(1980).

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