The effect of heterovalent dopants on ionic conduction in amorphous and nanocrystalline lithium heptagermanate

Trubitsyn M.P., Bochkova T.M., Koptiev M.M., Volnianskii M.D.

E-mail: trubitsyn_m@ua.fm

Introduction

Applications of solid electrolytes in batteries, fuel cells, and supercapacitors stimulate development of solid-state ionics [1]. Design of new superionic materials includes purposeful modification of the structure on atomic, nano- and micrometer scales, formation of the morphology in multiphase composites. Doping represents an effective way to enhance ionic conduction. Heterovalent doping introduces certain electrical perturbation due to charge imbalance between impurity and substituted host. In the latter case electroneutrality of the lattice can be kept by generation of additional charged defects which compensate charge misfit of the impurity. Such defects can be vacancies or interstitials of the host ions which are the typical intrinsic defects of the crystalline media. In many cases the charge compensating defects can be mobile enough to make a considerable contribution to charge transfer.

Lithium heptagermanate $Li_2Ge_7O_{15}$ is the representative of lithium-germanium oxides family (Li_2O-GeO_2) [2] which undergoes structural phase transition to polar state below T_C=283 K and attracts attention owing to unusual features of so-called weak ferroelectricity. The lattices skeletons are formed by covalent Ge-O polyhedrons. Li ions occupy the sites within structural cavities and being loosely bound to the structural frame, demonstrate high amplitudes of thermal vibrations around the regular positions. Studies of electrical properties [3, 4] as well as ^{7}Li NMR spectra and spin-lattice relaxation [5] showed that electrical conductivity of $Li_2Ge_7O_{15}$ crystals was mainly determined by mobile lithium interstitials A_{Li}.

In this report we study the influence of doping with Cr, Mn, Cu, Al and Gd impurities on ionic conductivity in amorphous and nanocrystalline lithium heptagermanate.

Experimental results and discussion

Pure and doped with with Cr, Mn, Cu, Al and Gd lithium heptagermanate glasses were obtained by quenching the melts [2-4]. Nanocrystals were prepared by controlled glass devitrification. The samples were cut as the plane-parallel plates with 5x5 mm^2 sizes and of about 1 mm thickness. Pt electrodes were deposited on the main planes of the samples by vacuum sputtering. Electrical properties were measured in AC field ($f = 1\ kHz$) by using AC bridges E7 - 10 and Tesla BM - 507.

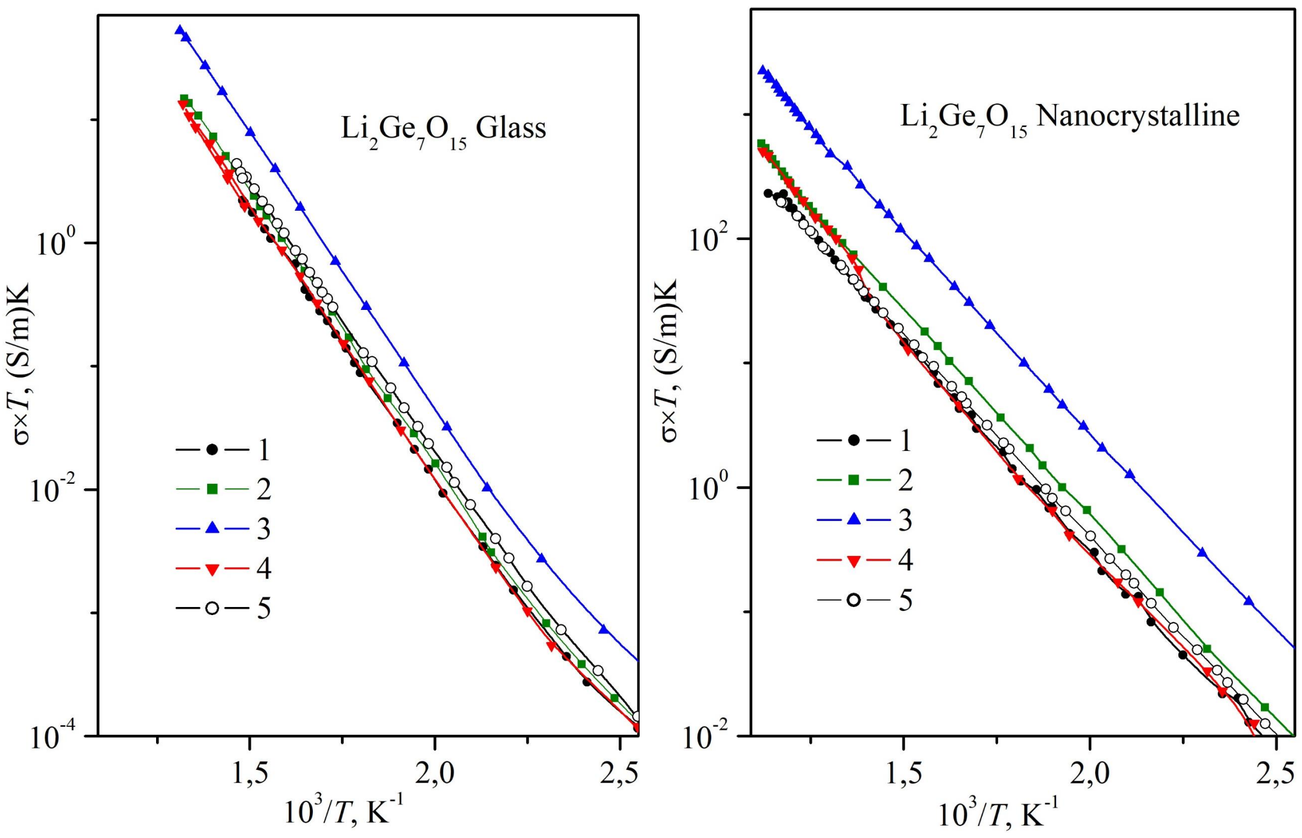

Fig. 1 The σ(1/*T*) dependencies for the glass (a) and the nanocrystalline (b) $Li_2Ge_7O_{15}$: 1 – the undoped samples and the samples doped with 2 – Cr (0.06 % wt), 3 – Mn (0.06 % wt), 4 – Cu (0.09 % wt), 5 – Al (0.3 % wt). *f* = 1 kHz.

Earlier it has been shown that ionic conductivity in $Li_2Ge_7O_{15}$ single crystals can be considerably enhanced or lowered by introducing the small amounts of heterovalent dopants.

Doping effect on conductivity in glassy and nanocrystalline $Li_2Ge_7O_{15}$ Is shown in Fig. 1 a, b. One can see that doping with small amounts of the impurities weakly affect conductivity of amorphous and nanocrystalline states. This result seems natural. In glass the concepts of regular lattice sites and of interstitials lose their sense, the number of weakly bound Li ions sufficiently increases and σ growths in about three orders of magnitude as compared with single crystal. On the other hand, the structural channels, which make possible ion migration in the single crystal, are absent in the glass. Appearance of nanometer sized nuclei with nearly ordered structure leads to a further increase in conductivity, which becomes four orders of magnitude higher relative to conductivity of the single crystal. The number of weakly bound and mobile Li ions in nanocrystalline state can be estimated as comparable to the total number of lithium ions.

Nevertheless, it is assumed, that doping effect in amorphous and nanocrystalline $Li_2Ge_7O_{15}$ can be enhanced. One can propose to use much more high concentrations of the heterovalent dopants which substitute for Ge hosts and introduce a negative charge imbalance. For the compositions with excess non-stoichiometric portion of Li_2O such additives can be expected to stabilize a great number of weakly bound lithium ions.

Conclusions

The doping effect on ionic conductivity was studied in amorphous and nanometer structured lithium heptagermanate $Li_2Ge_7O_{15}$:Cr, Mn, Cu, Al and Gd. Earlier it was shown that the small amounts of the dopants significantly affected conductivity of $Li_2Ge_7O_{15}$ single crystals. The heterovalent dopants, that induced appearance of charge compensating lithium vacancies V_{Li}, notably decreased conductivity. The impurities, generating excess lithium interstitials A_{Li}, significantly enhanced ionic conductivity. The obtained results confirmed that charge transfer in $Li_2Ge_7O_{15}$ crystal was determined by lithium interstitials moving through the structural channels. Thermal activation of the charge carrier's mobility caused temperature increase of conductivity.

In amorphous and nanocrystalline $Li_2Ge_7O_{15}$ the number of weakly bound lithium ions increased essentially. Relative to the single crystal, in these states ionic conductivity became higher in three and four orders of magnitude correspondingly. Doping with small amounts of the impurities had minor effect on ionic transport in amorphous and nanocrystalline samples. It is expected that the impurity effect on conductivity can be enhanced by introducing the certain heterovalent dopants in much more high concentration.

References

1. Maier, J. Nanoionics: ion transport and electrochemical storage in confined systems // J Nature Materials. - 2005.- Vol.4, No11.- P. 805 - 815.
2. Murthy, M.K. Studies in germanium oxide systems: I. Phase equilibria in the system $Li_2O - GeO_2$ / M.K. Murthy // J. Am. Ceram. Soc. – 1964. – Vol. 47, No. 7. – P. 328 – 331.
3. Volnianskii. M.D. , Trubitsyn M.P. , A.H. Obaidat Yahia H. Anisotropy of the electrical conductivity of lithium heptagermanate crystals // Physics of the Solid State. – 2008. – Vol. 50, No. 3. – P. 422 – 424.
4. Volnyanskii M.D. , Nesterov O.O., Trubitsyn M.P. Devitrification of the $Li_2O - xGeO_2$ // Ferroelectrics. – 2014. – Vol. 466, No. 1. – P. 126 – 130.
5. Vogel M., Petrov O., Trubitsyn M., Nesterov O., and Volnianskii M. ^{7}Li NMR spectra and spin-lattice relaxation in lithium heptagermanate single crystal // Ferroelectrics. – 2020. – V. 558, No 1. – P.46-58.