ELECTRICAL CONDUCTIVITY OF LITHIUM-SODIUM TETRAGERMANATE IN AMORPHOUS STATE

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The glass of lithium-sodium tetragermanate $LiNaGe_4O_9$ was prepared by rapid quenching the melt. The structure of the glass was characterized by X-ray phase analysis. Electrical conductivity σ was measured in AC field (f = 1 kHz÷1 MHz) in the interval T = 300÷900 K. It was shown that at T > 550 K the typical values of the glass σ were at least one–two orders of magnitude higher than in the single crystal. Ionic conductivity in disordered amorphous and ordered crystalline states was discussed by accounting the structure of lithium-sodium tetragermanate. The main contribution to conductivity in $LiNaGe_4O_9$ glass was associated with thermally activated motion of Li ions which were weakly bound to Ge-O structural framework.

Key words: lithium-sodium tetragermanate $LiNaGe_4O_9$, glass, ionic conductivity.

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1. Introduction

The interest of researchers to lithium-sodium tetragermanate $LiNaGe_4O_9$ (LNG) was associated mainly with ferroelectric phase transition, which occurred on cooling below T_C = 113 K [1, 2]. Later, it was noted that the LNG structure was promising for creating materials with high ionic electrical conductivity [3].

The structure of LNG crystal belongs to the rhombic space symmetry group D_{2h}^8, the unit cell parameters are a = 9.31, b = 4.68 and c = 15.88 Å [4]. The structural framework is formed by germanium-oxygen octahedra [GeO_6] and tetrahedra [GeO_4] linked by common octahedron-tetrahedron edges and tetrahedron-tetrahedron vertices. The skeleton of LNG structure is characterized by the presence of structural channels, in which Li and Na ions are located. The geometry of the channels connecting the sites with light mobile ions favors the high ionic conduction emergence.

Earlier, electrical properties of LNG single crystal were studied in [5]. It was shown that above 500 K electrical conductivity σ became anisotropic and was maximal along [001] axis. An increase of σ observed in the crystals of non-stoichiometric composition ($Li_{2-x}Na_xGe_4O_9$ with x = 0.2; 0.5) was attributed to a higher portion of lithium ions. Doping LNG crystal with Mn and Cr only weakly affected conductivity and did not change the anisotropy of σ [6]. Based on the available data [5], it was concluded that electrical conductivity in LNG crystals was provided by interstitial Li ions (A_{Li}) moving along the channels in the lattice. The contribution of sodium ions to conductivity was assumed as insignificant [5].

In order to meet the requirements for practically applied ionic conductors, it is of undoubted interest to find out the approaches allowing to increase ionic conductivity in lithium-sodium tetragermanate. One can expect that in amorphous phase of LNG the number of weakly bound Li ions and, consequently, σ should increase significantly. Earlier increase of conductivity in amorphous lithium heptagermanate $Li_2Ge_7O_{15}$ was reported in [7, 8]. The purpose of this work is to prepare LNG glass and to study its electrical conductivity in a wide temperature and frequency ranges.

2. Experimental results and discussion

The LNG glass was prepared by rapid quenching the melt between massive metal plates. The structure of the glass was examined by X-ray diffraction analysis (CuK_α- radiation). The samples for measurements of σ were prepared as the plane parallel plates with 5×5 mm^2 edges and about 0.5 mm widths.

The main planes of the samples were covered by Pt electrodes sputtered in Ar atmosphere. Conductivity σ was measured in AC field with frequencies $10^3 \div 10^6$ Hz by using LCR meter Keysight E4980AL. The measurements were carried out during heating from 300 K up to the temperature 820 K of the glass devitrification [9]. Heating rate was about 5 K/min.

Fig. 1 shows the X-ray diffraction pattern measured for LNG glass at room temperature. Broad halo is observed in the range of $2\theta=20 \div 40^0$ that is typical for the glasses of a similar composition (Li_2O-$x$$GeO_2$) [10]. Against the background of the halo, there are the low-intensity peaks corresponding to the LNG structure and the traces from some other phases of the (Li_2O-$x$$GeO_2$) family. The X-ray diffraction pattern analysis evidence that in the studied samples the relative volume of the amorphous phase was about 87%. The average linear size of the LNG crystallites was estimated as ~20-30 nm by using Scherrer equation.

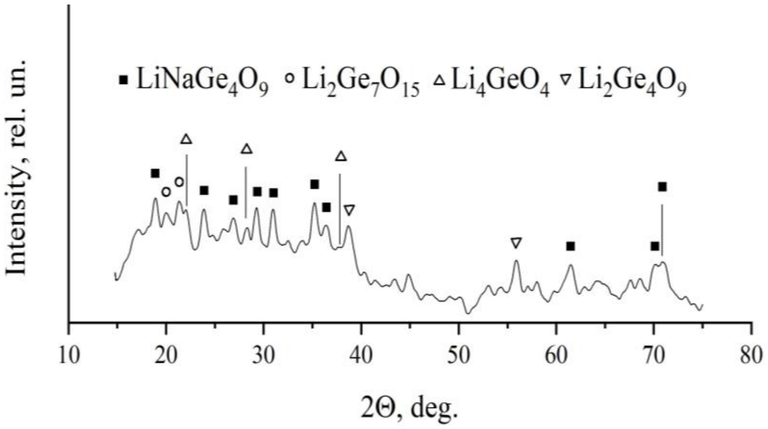

Fig.1 X-ray diffraction pattern for the LNG glass.

It is known that temperature growth of σ due to thermally excited transfer processes can be described by the exponential function

$$\sigma(T) = \frac{A}{T} exp\left(-\frac{E_a}{k_B T} \right) \tag{1}$$

where factor A depends on carriers' concentration, E_a is activation energy for charge transfer, k_B is Boltzmann constant. Fig. 2 shows the temperature dependencies of electrical conductivity, which in accord with (1) is plotted in Arrhenius scale. The DSC curve showing the thermal anomalies accompanying LNG glass devitrification on heating [9] is presented in the inset to Fig. 2. One can see that the glass starts to soften at T_g = 780 K whereas final crystallization happens at T_c = 820 K [9].

The σ(1/T) dependencies show nearly linear behavior in the interval from ~550 K to glass transition temperature T_g [9, 10]. The slope of the σ(1/T) dependencies in the interval 550 K ÷ T_g decreases in energy units from 1,07 eV to 0,77 eV with increasing AC field frequency from 1 kHz to 1 MHz (Table 1). Disorder of the amorphous phase structure causes the dependence of activation energy on measuring field frequency. Between T_g and T_c the glass softens and σ(1/T) increases on heating faster (Fig. 2). One can note that the slope of the dependencies σ(1/T) in the interval T_g ÷ T_c is practically the same for all frequencies of AC field (~2,0 eV) and is about 2 times higher as compared with the slopes in the 550 K ÷ T_g interval (Fig. 2). This greater slope cannot be interpreted as a measure of higher potential barrier overcome by carriers (Table 1). Seemingly, it indicates that on heating not only the probability to jump over the barriers increases. For the interval $T_g \div T_c$ the structure of the glass changes, it becomes softer, and mobility of atoms increases more sharply as compared with the rigid lattice.

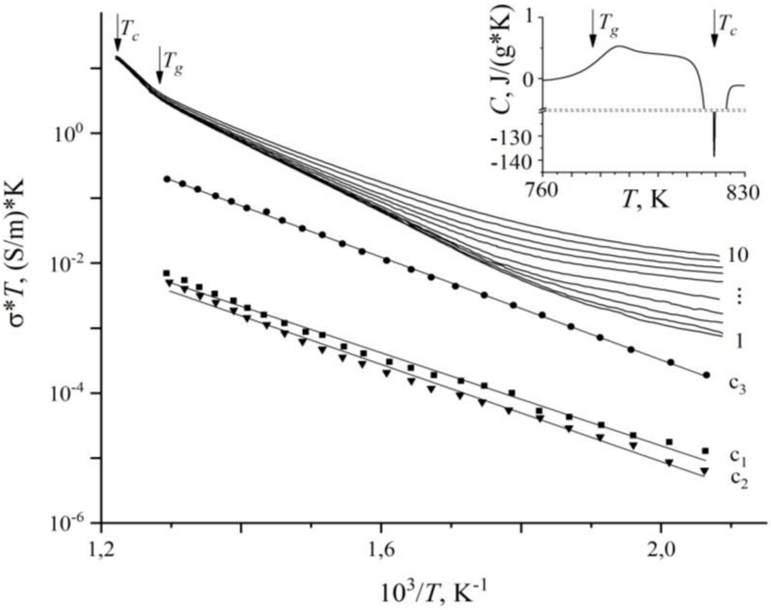

Fig. 2. σ(1/*T*) dependence measured on heating of LNG glass. AC field frequency was *f* = 10^3 (1), $2\cdot10^3$ (2), $5\cdot10^3$ (3), 10^4 (4), $2\cdot10^4$ (5), $5\cdot10^4$ (6), 10^5 (7), $2\cdot10^5$ (8), $5\cdot10^5$ (9), 10^6 (10) Hz. Curves (c_1, c_2, c_3) show σ(1/*T*) dependence for LNG single crystal measured along [100], [010] and [001] axis correspondingly [5]. In the inset: exothermic anomalies of DSC at T_g=780 K and T_c=820 K accompanying LNG glass devitrification [9].

The data in Table 1 show that electrical conductivity in the LNG glass exceeds the values of σ for a single crystal: by three orders of magnitude along [100] and [010] axes and by one order of magnitude along [001] axis.

Table 1

The values of activation energy E_a and conductivity σ
for LNG glass and single crystal (*f* = 1 kHz)

LNG	E_a, eV (550 K ÷ T_g)	σ, S/m (*T*=700 K)
Glass	1.07±0.02 (Fig. 2)	$7.3\cdot10^{-4}$
Single crystal	0.88±0.02 (**E** || [100], [010]) 0.79±0.01 (**E** || [001]) [5]	$2.3\cdot10^{-6}$ (**E** || [100]) $1.7\cdot10^{-6}$ (**E** || [010]) $9.1\cdot10^{-5}$ (**E** || [001])

As it was shown in [5], charge transfer in LNG crystal was contributed mainly by the motion of Li ions through interstitial positions. One can suppose that in LNG glass conductivity is determined by the same carriers, i.e., Li ions weakly bound to Ge-O structural framework. Thus, in the glass where the concept of lattice site has lost its sense, the number of weakly bound Li^+ ions increases. The difference between activation energies E_a in NBT glass and single crystal reflects this fact.

3. Conclusions

LNG glass was prepared by quenching the melt. In accord with the X-ray diffraction data the relative volume of the amorphous phase was estimated as 87%. AC conductivity of LNG glass was measured in the interval from room temperature up to the point T_c=820 K of the glass devitrification. It was shown that on heating above ~600 K conductivity was contributed mainly by thermally activated charge transfer. The latter was associated with Li^+ ions hopping through quasi-equilibrium positions in amorphous medium. The conductivity of LNG glass was found to be by one–three orders of magnitude higher as compared to a single crystal. This fact was caused by an increase in the number of Li^+ ions, which in amorphous phase were weakly bound to (Ge-O) structural framework.

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