

# Nanocrystalline $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$ solid solutions devitrified from glass

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## Introduction

Lithium-sodium tetragermanate  $\text{LiNaGe}_4\text{O}_9$  crystal undergoes a phase transition from the nonpolar phase (space symmetry group  $D_{2h}^8$ ) to the ferroelectric one (group  $C_{2v}^5$ ) on cooling below  $T_c = 113$  K [1]. Changing  $x$  from 1 to 0.2 in the series of  $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$  crystalline solutions is accompanied by an increase in the phase transition temperature  $T_c$  from 113 K ( $x = 1$ ) to 330 K ( $x = 0.2$ ). In addition, the typical values of electrical conductivity and the character of its anisotropy in  $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$  change significantly [2]. In accord with the data in [2], charge transfer in  $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$  crystals can be mainly associated with Li ions interstitials moving along the channels within the structural framework. In amorphous and nanocrystalline states, electrical conductivity of  $\text{LiNaGe}_4\text{O}_9$  increases by approximately two and three orders of magnitude correspondingly as compared to the single crystal [3]. It is of interest to study the crystallization processes and ionic conductivity in glasses and nanocrystalline state of lithium-sodium tetragermanate solid solutions. Here we report the thermal analysis data on  $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$  glasses ( $x = 1, 0.6, 0.45, 0.2$ ) devitrification performed on heating. Also, we discuss electrical properties of  $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$  in amorphous and partially crystallized nanocrystalline states.

## Experimental results

The LNG glass was prepared by rapid quenching the melt between massive metal plates. The glasses were crystallized by heating the samples in the temperature range of  $300 \div 1200$  K. The heating and cooling rates were 10 and 20 K/min. Thermal analysis of devitrification processes was performed by differential scanning calorimetry (DSC). The phase states of amorphous and polycrystalline  $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$  were controlled by X-ray diffraction analysis ( $\text{CuK}_\alpha$ -radiation). The samples for measurements of  $\sigma$  were prepared as the plane parallel plates with  $5 \times 5$  mm<sup>2</sup> edges and about 0.5 mm widths. The main planes of the samples were covered by Pt electrodes sputtered in Ar atmosphere. Conductivity  $\sigma$  was measured in AC field with frequencies  $10^3 \div 10^6$  Hz by using LCR meter Keysight E4980AL. The measurements were performed on heating from 300 K up to the temperature 820 K of the glass devitrification [3]. Heating rate was about 5 K/min.

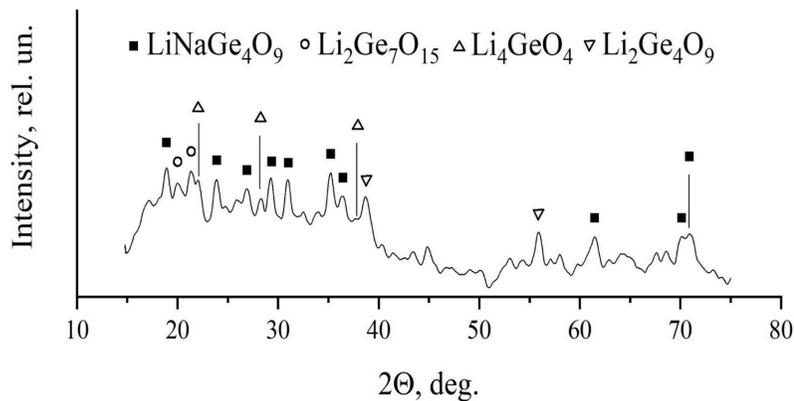


Fig.1 X-ray diffraction pattern for the LNG glass

## Discussion

Fig. 1 shows the X-ray diffraction pattern measured for LNG glass at room temperature. Broad halo is observed in the range of  $2\theta = 20 \div 400$  that is typical for the glasses of a similar composition ( $\text{Li}_2\text{O}-x\text{GeO}_2$ ) [4]. 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 ( $\text{Li}_2\text{O}-x\text{GeO}_2$ ) family. Analysis of the X-ray diffraction pattern 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  $\sim 20 \div 30$  nm by using Scherrer equation.

Fig. 2 shows the temperature dependencies of electrical conductivity which is plotted in Arrhenius scale. DSC curve showing the thermal anomalies accompanying LNG glass devitrification on heating [3] 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 [3]. The  $\sigma(1/T)$  dependencies show nearly linear behavior in the interval from  $\sim 550$  K to glass transition temperature  $T_g$  [3, 4]. The slope of the  $\sigma(1/T)$  dependencies in the interval  $550 \text{ K} \div T_g$  decreases in energy units from 1,07 eV to 0,77 eV with increasing AC field frequency from 1 kHz to 1 MHz. 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  $\sigma(1/T)$  increases on heating faster (Fig.2). One can note that the slope of the dependencies  $\sigma(1/T)$  in the interval  $T_g \div T_c$  is practically the same for all frequencies of AC field ( $\sim 2,0$  eV) and is about 2 times higher as compared with the slopes in the  $550 \text{ K} \div T_g$  interval (Fig.2). This greater slope cannot be interpreted as a measure of higher potential barrier overcome by carriers. 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.

The obtained data show that electrical conductivity in the LNG glass exceeds the values of  $\sigma$  for the single crystal: by three orders of magnitude along [100] and [010] axes, and by one order of magnitude along [001] axis. As it was shown in [5], charge transfer in LNG crystal was contributed mainly by Li ions motion 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  $\text{Li}^+$  ions increases. The difference between activation energies  $E_a$  in LNG glass and single crystal reflects this fact.

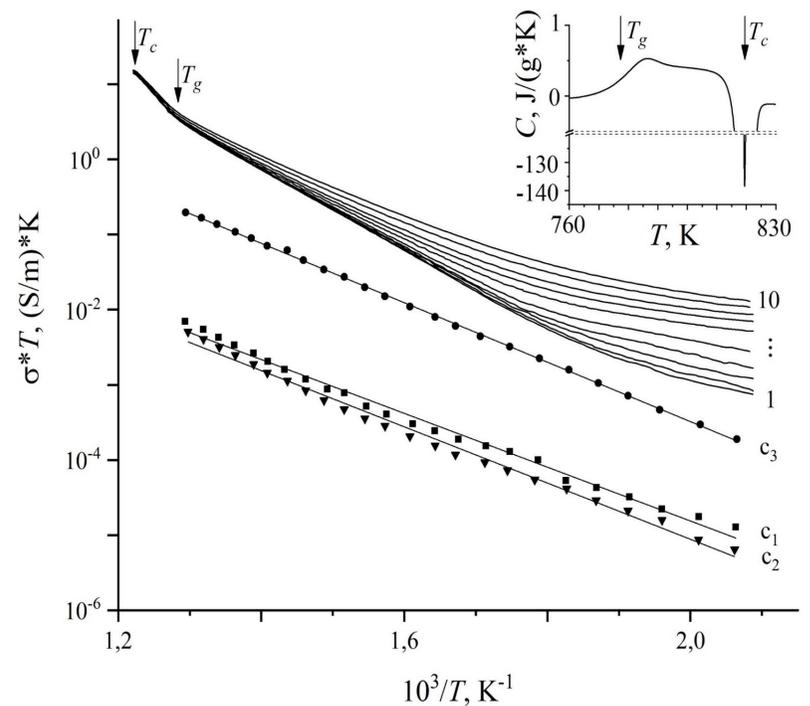


Fig. 2.  $\sigma(1/T)$  dependence measured on heating of LNG glass. AC field frequency was  $f = 10^3$  (1),  $2 \cdot 10^3$  (2),  $5 \cdot 10^3$  (3),  $10^4$  (4),  $2 \cdot 10^4$  (5),  $5 \cdot 10^4$  (6),  $10^5$  (7),  $2 \cdot 10^5$  (8),  $5 \cdot 10^5$  (9),  $10^6$  (10) Hz. Curves ( $c_1, c_2, c_3$ ) show  $\sigma(1/T)$  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 [3].

## References

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