

THERMAL ANALYSIS OF $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$ GLASSES CRYSTALLIZATION

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The glasses of lithium-sodium tetragermanate $\text{LiNaGe}_4\text{O}_9$ and solid solution $\text{Li}_{1.8}\text{Na}_{0.2}\text{Ge}_4\text{O}_9$ were prepared by quenching the melt and crystallized on heating. The glass crystallization was controlled by differential scanning calorimetry and thermal gravimetric analysis. The DSC measurements performed in the range 300–1200 K show that the crystallization of the glasses occurs through a single stage. There are no anomalies on TGA dependences. It is assumed that $\text{LiNaGe}_4\text{O}_9$ and $\text{Li}_{1.8}\text{Na}_{0.2}\text{Ge}_4\text{O}_9$ glasses crystallize in accordance with a polymorphic mechanism.

Keywords: glass crystallization, lithium-sodium tetragermanate $\text{LiNaGe}_4\text{O}_9$, differential scanning calorimetry, thermal gravimetric analysis.

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1. Introduction

Ionic conductivity in solids is actively studied due to wide applications of electrolytes in autonomic sources of power such as batteries, accumulators, fuel cells etc [1]. Design of new perspective ionic conductors is the current problem of modern solid state physics and material science. A few specific features are typical for the structures of superionic conductors and the most important are the following: i) a large number of vacant quasi-stable positions which can be occupied by mobile ions; ii) adjacent vacant positions should be separated by not too high energy barriers as compared with thermal excitation energy kT ; iii) quasi-stable positions should be linked by a network of structural channels that is necessary to provide the ions movement. Just these features are necessary to provide high mobility of ions (see [2] and the references therein). The compounds of lithium-germanium oxide $\text{Li}_2\text{O}-x\text{GeO}_2$ represent the promising inorganic solid electrolytes since their structures are of framework type and thus satisfy all above requirements [3].

It was repeatedly shown that nanometer sized structuring was an effective approach to enhance ionic conduction [4]. Thus, the authors of [5-9] by using the technology of controlled glass crystallization prepared the nanometer structured $\text{Li}_2\text{O}-x\text{GeO}_2$ glass-ceramics with significantly increased ionic conduction as compared with crystalline as well as amorphous compounds. The effect was attributed to an increase of a number of weakly bound lithium ions as well as unoccupied positions accessible for light ions. Just these structural features were peculiar to near surface regions of the crystal nuclei in glass-ceramics. Increased partial volume of nuclei shells as compared with the volume of ordered nuclei cores and amorphous inter-nuclei surroundings caused high conductivity of the partially crystallized materials.

The crystals of lithium-sodium tetragermanate $\text{LiNaGe}_4\text{O}_9$ (LNG) and solid solutions $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$ ($\text{L}_{2-x}\text{N}_x\text{G}$) ($0.2 \leq x \leq 1$) are studied intensively mainly due to ferroelectric phase transition and specific (x - T) phase diagram [10, 11]. In addition, the electrical properties of LNG single crystal were the subject of a few studies. Earlier a strong anisotropy of LNG electrical conductivity σ at high temperatures ($T > 500$ K) was reported in [12]. Besides σ was found to be significantly dependent on the $\text{L}_{2-x}\text{N}_x\text{G}$ solid solutions stoichiometry [13]. It was concluded that charge transfer in LNG and $\text{L}_{2-x}\text{N}_x\text{G}$ crystals was mainly contributed by Li ionic conduction.

It is of interest to apply the technology of structuring on nanometer level developed in [5-9] to LNG and $\text{L}_{2-x}\text{N}_x\text{G}$ solid solutions. One may expect that the size of nanometer crystal nuclei should strongly influence ionic conduction in composite glass-ceramic compounds.

This paper is devoted to studying the crystallization of the LNG and $L_{2-x}N_xG$ glasses carried out on heating. The processes accompanying glass crystallization were controlled by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2. Experimental results and discussion

The glasses of LNG and $L_{2-x}N_xG$ ($x = 0.2$) were prepared from the melt by rapid quenching between massive metal plates. For DSC and TGA measurements the samples of the glasses were grinded in an agate mortar. By using a fine sieve, the resulting powders were divided into granules with the diameters ranged from 0.1 mm to 1 mm. The masses of the LNG and $Li_{1.8}N_{0.2}G$ samples were 40 mg and 60 mg, respectively.

The DSC and TGA dependences were measured with the help of DSC 200F3 Maia and STA6000 instruments. The samples were heated in the range from 100 to 1200 K with the rate 10 K/min. Fig. 1 shows the DSC curves measured on the first heating run.

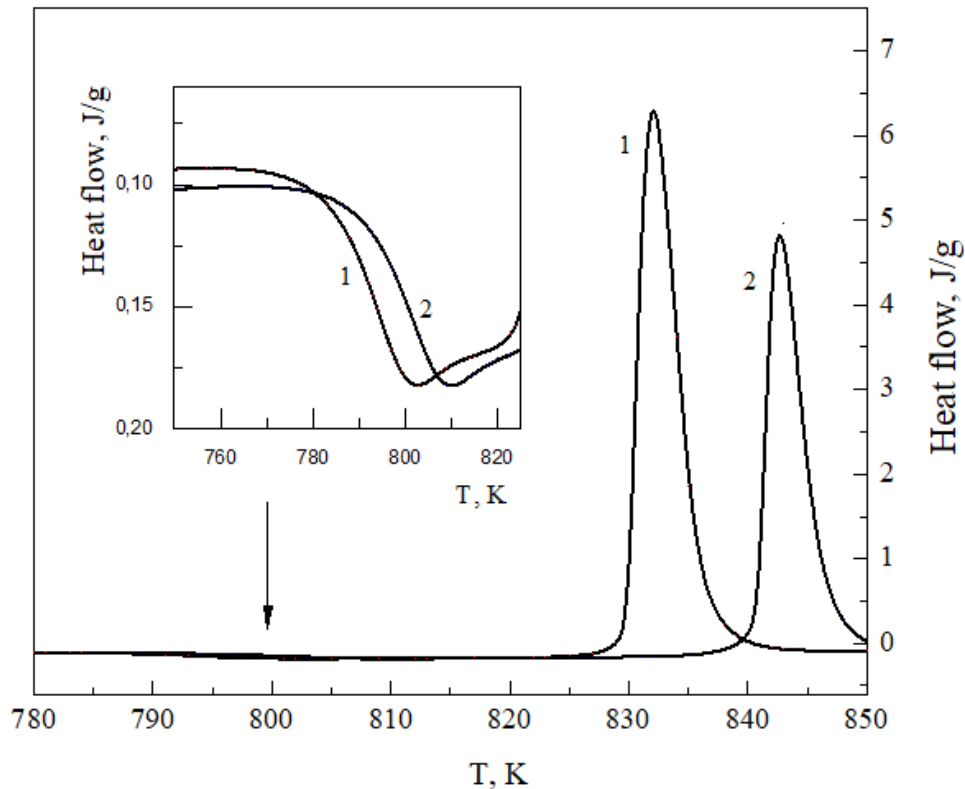


Fig. 1. DSC curves measured on the first heating run of the LNG (1) and $Li_{1.8}N_{0.2}G$ (2) samples. The insert shows the enlarged fragment around the glass transition temperature T_g . The heating rate was 10 K/min.

The subtle endothermic anomalies at T_g (the insert to Fig. 1) and the intense exothermic maxima at T_{cryst} (Fig. 1) were registered on the first heating run. The DSC anomalies (Fig. 1) indicate that LNG and $Li_{1.8}N_{0.2}G$ glasses devitrified at the temperatures T_g and further crystallized at the temperatures T_{cryst} . Subsequent cooling and heating did not show any DSC anomalies since the samples were finally crystallized after first heating above T_{cryst} . In the temperature interval studied TGA measurements showed no change in mass during the first heating run and the subsequent temperature cyclings.

Consequently, the anomalies of heat flux observed on the DSC curves (Fig. 1) manifest the changes of the sample structure.

One can see that the glass of $\text{L}_{2-x}\text{N}_x\text{G}$ ($x = 0.2$) crystallizes at somewhat higher temperature in comparison with the glass of LNG ($x = 1$). The temperatures of DSC anomalies for the glasses studied are gathered in Table 1. Besides, the values of specific heat Q released at glass crystallization are added. The values of Q were determined by measuring the area under the crystallization peaks T_{cryst} (Fig. 1).

Table 1

**Temperatures of the glass devitrification T_g and crystallization T_{cryst} .
Specific heat Q released at glass crystallization is given in the last column.**

The glass	T_g , K	T_{cryst} , K	Q , J/g
LNG ($x = 1$)	786	832	131
$\text{L}_{2-x}\text{N}_x\text{G}$ ($x = 0.2$)	794	843	105

It is important that the glasses of LNG and $\text{Li}_{1.8}\text{N}_{0.2}\text{G}$ are crystallized through a single stage. Such case is quite different from the situation observed for $\text{Li}_2\text{O}-x\text{GeO}_2$ compounds with $x=7, 11.5, 18$ [5-9] where amorphous state is ordered through the intermediate metastable phase. The intermediate phase is characterized by the appearance of the metastable lithium tetragermanate nuclei and thermodynamically stable lithium heptagermanate crystallites. Accordingly, the intermediate phase in $\text{Li}_2\text{O}-x\text{GeO}_2$ glass-ceramics [5-9] combines structural and chemical segregation.

The presence of the single DSC peak in Fig. 1 indicates that the LNG and $\text{Li}_{1.8}\text{N}_{0.2}\text{G}$ glasses crystallize through a single stage. Such situation is peculiar for the polymorphic mechanism [14] when crystallization occurs without changing the chemical composition. It means that the amorphous phase transforms into the corresponding stoichiometric crystalline phase. To confirm this assumption, we plan to carry out X-ray phase analysis of the LNG and $\text{Li}_{1.8}\text{N}_{0.2}\text{G}$ glass and crystallized samples. These experiments are now in progress.

3. Conclusions

The glasses of lithium-sodium tetragermanate LNG and solid solution $\text{L}_{2-x}\text{N}_x\text{G}$ were crystallized on heating. The process of the amorphous phases ordering was controlled by DSC and TGA measurements. It was shown that both LNG and $\text{L}_{2-x}\text{N}_x\text{G}$ glasses crystallized through a single stage. A polymorphic mechanism is assumed for the LNG and $\text{L}_{2-x}\text{N}_x\text{G}$ glasses crystallization. The obtained DSC data allow to expect that isothermal heat treating in the range between T_g and T_{cryst} can be used for preparation of the nanometer structured glass-ceramics based on lithium-sodium tetragermanates.

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