NON-ISOTHERMAL CRYSTALLIZATION OF $LiNaGe_4O_9$ GLASS

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The glass of lithium-sodium tetragermanate $LiNaGe_4O_9$ is crystallized on heating under the control of differential scanning calorimetry and thermal gravimetric analysis. The measurements were prepared in the temperature range 300-870 K and showed the relatively weak endothermic DSC anomaly and 40-50 K above the single exothermic peak. The endothermic anomaly observed at T_g testified to softening the glass structure whereas the exothermic peak at T_C manifested crystallization of the amorphous phase. Studying of TGA demonstrated smooth nearly linear dependences without any visible anomalies. Varying the heating rate from 1.2 up to 40 K/min resulted in noticeable increase of the characteristic temperatures T_g and T_C. Lower limit of the glass transition temperature T_g^0 was estimated with the help of the existing model. The mechanism of the $LiNaGe_4O_9$ glass crystallization is discussed.

Keywords: glass crystallization, lithium-sodium tetragermanate $LiNaGe_4O_9$, differential scanning calorimetry, thermal gravimetric analysis.

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1. Introduction

Lithium-sodium tetragermanate $LiNaGe_4O_9$ (LNG) belongs to a group of complex oxide crystals with the general chemical formulae $Li(Na)_2O\text{-}GeO_2$ (see [1] and the refs therein). At room temperature LNG crystal has a non-polar orthorhombic structure of D_{2h}^8 space symmetry group [2]. The unit cell has the parameters a=9.31, b=4.68, c=15.88 Å and includes four formula units (Z=4). The structural framework is formed by covalent tetrahedral [GeO_4] and octahedral [GeO_6] complexes which are linked by the edges. Alkali metal Li and Na ions are located within the cavities formed by [Ge-O] structural skeleton. Early papers [3-5] were devoted mainly to ferroelectric phase transition occurred in LNG crystal on cooling below T_C=112.7 K. In the ferroelectric phase the symmetry of the structure reduces to the orthorhombic C_{2v}^5 space group (Z=4) [6] and spontaneous polarisation appeared along ***a*** axis. A bit later close attention was paid to studying the electrical properties of LNG crystal. In particular, it was shown that electrical conductivity σ of LNG was strongly anisotropic [7, 8] and could be significantly changed by doping [9, 10]. The data published in [7-10] gave evidence that charge transfer in LNG crystal at T>500 K was mainly determined by Li interstitials hopping through the quasi-equilibrium positions within the structural channels.

Thus, the crystal structure of LNG is suitable for relatively high ionic conduction. Besides, electrical properties of LNG could be sensitive to the technological treatments applied to increase Li charge transfer. The authors of [11-15] developed the regimes of controlled lithium heptagermanate $Li_2Ge_7O_{15}$ glass crystallisation and prepared nanometer structured glass-ceramics which conductivity was a few orders higher as compared with crystalline compounds of the same chemical composition. Of course, development of the heat treatment technology was based on the information on the mechanisms of the glass crystallization. The purpose of this paper is to study the thermal phenomena accompanying the LNG glass crystallization. The LNG glass was crystallized out on heating, the process was controlled by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2. Experimental results and discussion

The LNG glass was quenched from the melt by using the procedure described in [11, 12] for lithium heptagermanate. The samples were prepared by grinding the glass into the powder; mean linear size of the grains was 1 – 3 mm. The weight of the samples was in the range 10–30 mg. The DSC and TGA measurements were performed in the laboratory of ferroics of Krakow pedagogical university by using DSC 200F3 Maia equipment. The samples were heated from room temperature up to 870 K with the rate changed from 1.2 to 40 K/min.

Fig.1 shows the DSC curves presented as the temperature dependencies of specific heat capacity *C*(*T*). The weak endothermic anomaly observed at the temperature T_g (Fig.1 a) indicates that the amorphous structure starts to soften. Such softening signifies the beginning of the crystallization process and is accompanied by the appearance of a big number of nuclei with nearly ordered structure. The strong exothermic peak detected at T_C (Fig.1 b) evidences for a maximal growth of the ordered phase volume. The anomalies at the glass transition temperature T_g and the glass crystallization temperature T_C could be observed on the first heating run only. After heating above T_C the glass samples were crystallized and subsequent cooling and heating runs did not show any DSC anomalies. Besides, the data in [16] show that any additional DSC anomalies were absent on heating up to 1200 K. These data testify that the DSC exothermic peak in Fig.1 b manifests a final crystallization of the LNG glass.

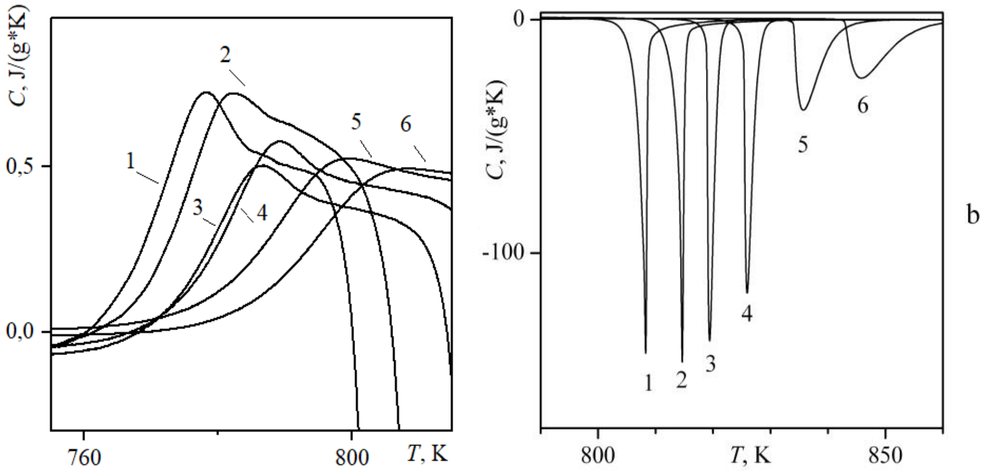

Figure 1. The temperature dependences of specific heat capacity for LNG glass heated on the first run with the following rates α: 1 – 1.2; 2 – 2.5; 3 – 5; 4 – 10; 5 – 20; 6 – 40 K/min. a) The subtle endothermic anomaly at T_g; b) the intense exothermic peak at T_C manifesting glass crystallization.

TGA measurements were carried out simultaneously with DSC studies. TGA curves demonstrated nearly linear dependences without any visible anomalies. It can be concluded that chemical composition of the samples in the temperature range studied was unchanged and the DSC anomalies (Fig.1 a, b) were resulted from the structural ordering.

One can see that the subtle endothermic (Fig.1a) and the strong exothermic (Fig.1b) DSC anomalies noticeably shift to high temperature side as the heating rate $\alpha = dT/dt$ increases. The values of T_g and T_C for different rates α are given in Table 1. Fig.2 illustrates determination of T_g as the middle point between characteristic temperatures T_e and T_f which are defined by crossing the tangent lines as described in [17]. The glass crystallization temperature T_C was determined as the positions of the corresponding exothermic peaks (Fig.1b). Specific heat *Q* released at glass crystallization is also presented in the last column of Table 1. The values of *Q* were determined from the areas under *C*(*T*) exothermic peaks.

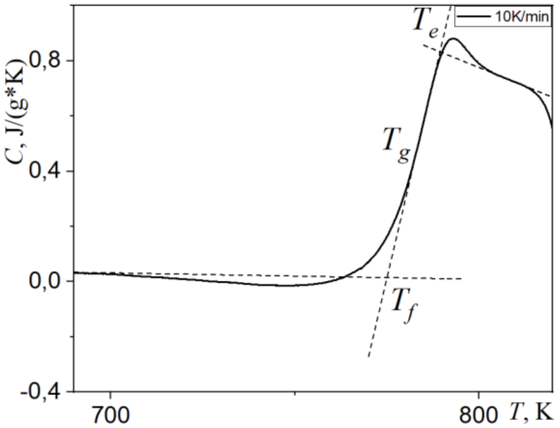

Figure 2. Determination of the glass transition temperature T_g [17].

The shifts of T_g and T_C with an increase of the heating rate α reflect the kinetics of the crystallization process. Within the model proposed in [18] the dependence of T_g on α can be used to estimate the limiting devitrification temperature T_g^0 below which softening the structure of the glass becomes infinitely slow. By using the empirical expression $T_g^0(\alpha) - T_g^0 \sim ln\alpha$ we have obtained the value $T_g^0 = (767 \pm 3)$ K which can be considered as a low limit of the glass transition temperature.

Table 1

The values of T_g and T_C for the different heating rates α. The specific heat Q released at the glass crystallization is also presented.

α, K/min	T_g, K	T_C, K	Q, J/g
1.2	769	808	208
2.5	774	815	194
5	777	819	205
10	782	826	215
20	787	836	206
40	793	846	221

3. Conclusion

The glass of lithium-sodium tetragermanate was prepared by quenching the melt and crystallized on heating. DSC studies show the subtle endothermic anomaly at the glass transition temperature T_g and the intense exothermic peak at the crystallization temperature T_C. It was shown that LNG glass crystallized through a single stage. Such behavior is typical for polymorphic mechanism when disordered amorphous structure transforms into ordered crystalline phase of the same chemical composition.

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