X-RAY STUDY OF GLASSY, GLASS-CERAMIC, AND POLYCRYSTALLINE $LiNaGe_4O_9$

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X-ray diffraction was used to study the phase compositions of lithium tetragermanate $LiNaGe_4O_9$ glass and states obtained through its heating and crystallization. $LiNaGe_4O_9$ glass was obtained by quenching the melt. The amorphous-crystalline samples were prepared by isothermal heat treating at the temperatures chosen between the glass transition T_g = 783 K and devitrification T_C = 829 K points. The polycrystalline samples were obtained by heating the glass well above T_C. It was shown that in the glassy samples amorphous phase occupied about 92% of the whole volume, whereas the rest (~8%) fell on regions with ordered structure. In the amorphous-crystalline samples, disordered and ordered regions each occupied about half of the volume. In the polycrystalline samples, ordered regions occupied near 96% of the sample volume. The average size of ordered regions in the glass and amorphous-crystalline samples was estimated about 35 nm. In the polycrystalline samples, crystallites notably grew and had linear size near 120 nm. The obtained data demonstrate that controlled glass crystallization represents an effective way to prepare nanometer size structured solids.

Keywords: lithium tetragermanate $LiNaGe_4O_9$, glass crystallization, X-ray phase analysis.

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1. Introduction

Improvements in the performance of modern gadgets and energy storage systems, as well as the growing popularity of electric vehicles over the past few years, create a need for improved battery efficiency and stability. As is known, the solid electrolytes with mobile lithium ions are actively studied to create more efficient autonomous power supplies. As a rule, electrolytes based on organic polymers are used in lithium ions batteries and accumulators. Despite its widespread use, this type of electrolytes demonstrates tendency to aging, fatigue and has low electrical strength. Besides, the disposal of these materials has an impact on environment [1]. Therefore, recently the focus of attention of scientists and engineers has been shifted to inorganic solid electrolytes. The efforts are aimed to design new inorganic electrolytes that can withstand a greater number of recharge cycles, are less susceptible to aging, have greater electrical strength and are more environmentally friendly.

Solid electrolytes based on lithium/sodium germano-germanates $Li(Na)_2O$-GeO_2 are among the promising lithium ions conductors. The crystal structure of germano-germanates is of framework type [2] and fully satisfies lithium ion mobility requirements. In the crystal lattice, there is a large number of vacant positions available for Li ions, these positions are separated by not too high energy barriers and connected by a network of channels that are necessary for ion movement.

Study of conductivity in lithium-sodium tetragermanate $LiNaGe_4O_9$ (LNG) crystal and solid solutions $Li_{2-x}Na_xGe_4O_9$ ($L_{2-x}N_xG$) demonstrated that σ was strongly anisotropic and depended on chemical composition increasing in compounds with higher fraction of Li_2O [3, 4]. These data allowed to suppose that charge transfer in LNG was provided by mobile lithium interstitials. It is known that nanometer size structuring is actively used to increase ionic conductivity in solid electrolytes. This approach was successfully applied to lithium heptagermanate $Li_2Ge_7O_{15}$, which was another representative of germano-germanates family and had a crystal structure like LNG. It was shown (see [5, 6] and the refs therein) that amorphization and preparation of nanometer scaled glass-ceramics allowed to increase Li ion conductivity in three-five orders of magnitude. We used the same approach for LNG composition. We quenched the melt and obtained LNG glass, and then, using the data of differential scanning calorimetry (DSC) we heat treated amorphous-crystalline and polycrystalline LNG [7-9]. For the following study, it is necessary to obtain as complete information as possible on phase composition and morphology of the samples prepared. The purpose of this paper is to perform the structural characterization of the obtained compounds by using X-ray phase analysis.

2. The samples and details of experiment

LNG glass was prepared by rapid quenching the melt between two massive copper plates. The obtained samples were colorless and had no inclusions. The partially crystallized amorphous-crystalline samples were prepared by isothermal heat treatment at T = 794 K for 20 minutes. This temperature was chosen within the interval between the glass transition temperature T_g = 783 K and the point T_C = 829 K, above which complete crystallization was detected in DSC experiment [7-9]. After the heat treatment the partially crystallized sample became a bit cloudy. The totally crystallized samples were prepared by heating the glass to the temperatures notably above T_C (~900 K). The obtained samples were opaque and white in color and sometimes tended to crack.

X-ray phase analysis was carried out on X-ray diffractometer DRON-2 operating with monochromatized Co-K_α radiation (λ = 1.7902 Å). The identification of ordered phases and compounds was carried out by comparing the interplanar distances and relative intensities of the reflexes in the experimental diffractograms with the data from the PCPDFWIN electronic card-file.

3. Experimental results and discussion

Fig. 1 shows diffractograms for glassy, amorphous-crystalline, and polycrystalline LNG samples. The results of the X-ray data analysis are summarized in Table 1. One can see that in glassy samples amorphous phase occupy about 0.92 of the sample volume. The rest of the sample volume is occupied by the ordered regions with the structures of LNG (0.045), $Na_6Ge_2O_7$ (0.018), Na_4GeO_4 (0.016) and Li_4GeO_4 (0.001). In the amorphous-crystalline samples the volumes occupied by disordered (0.45) and ordered (0.55) structures are close to each other (Table 1). About 0.96 of the polycrystalline sample volume is occupied by the ordered phases. Again, in addition to the crystallites with LNG structure, there are the traces of the phases of sodium-germanium oxides. This fact indicates that sodium ions arrange their surrounding more effectively than lithium ions. Of course, this property can be attributed to higher atomic weight and lower speed of thermal motion for sodium atoms as compared to lithium ones.

Analysis of the X-ray diffractograms makes it possible to estimate the average size d of the crystallites by using Selyakov-Scherrer formula:

$$d = K\lambda \Big/ \left((\beta_1 - \beta_2) \cos\theta \right) \tag{1}$$

where K is a coefficient close to unity, λ is the wavelength, β_1 is the half-width of the peak at half-maximum on the experimental diffractograms (Fig 1), β_2 is the half-width of the corresponding peak in the X-ray pattern for LNG single crystals, θ determines the peak position. The estimations given in Table 1 indicate that amorphous-crystalline samples can be defined as nanocrystalline. The mean size of the ordered regions in polycrystal (Table 1) allows to classify this state rather as microcrystalline.

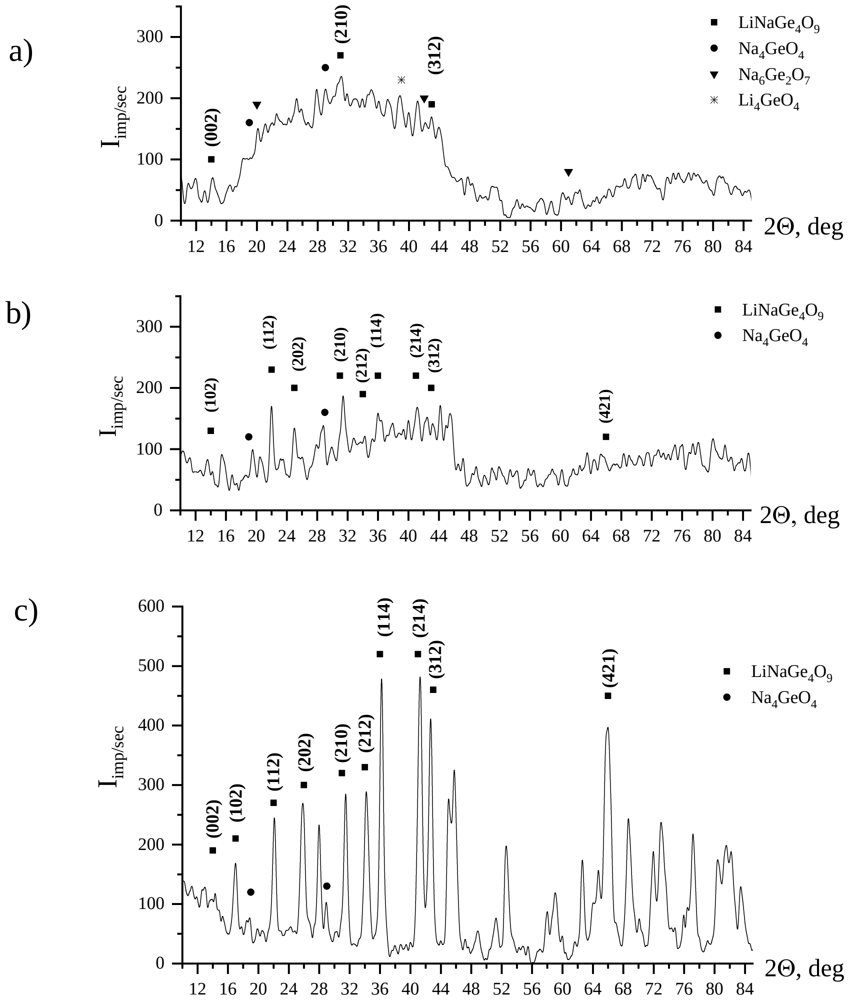

Fig. 1. Diffraction patterns measured at room temperature for the LNG glass (a), amorphous-crystalline (b) and polycrystalline (c) samples.

Table 1

The phase composition of the studied LNG samples

LNG	The relative volumes of amorphous and ordered phases	The ordered phases and their relative volume	Crystallites average size *d*, nm
Glassy	0.92/0.08	LNG (0.045) Na_4GeO_4 (0.016) $Na_6Ge_2O_7$ (0.018) Li_4GeO_4 (0.001)	35.3
Amorphous-crystalline	0.45/0.55	LNG (0.53) Na_4GeO_4 (0.016) unidentified phase (0.004)	35.4
Polycrystalline	0.04/0.96	LNG (0.92) Na_4GeO_4 (0.03) unidentified phase (0.01)	121.0

4. Conclusions

Phase composition of glassy, amorphous-crystalline and polycrystalline LNG was studied by X-ray diffraction. It was shown that in amorphous-crystalline sample the nanometer sized crystallites ($d \approx 35$ nm) were imbedded into amorphous matrix. The mean size of crystallites in LNG polycrystal ($d \approx 120$ nm) was found to be rather in micrometer scale. The analysis of the X-ray patterns showed that owing to higher atomic weight and slower thermal motion sodium atoms arranged their surroundings more effectively as compared with more light lithium atoms. The obtained data will be useful to design ionic conductors in $Li(Na)_2O – (GeO_2)$ family with optimized chemical composition and phase content.

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