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CONDUCTANCE OF MULTIPHASE INTERMEDIATE STATE IN $\text{Li}_2\text{O}-7\text{GeO}_2$ GLASS-CERAMICS

Conductance of the phase states, obtained on heating run at devitrification of $\text{Li}_2\text{O}-x\text{GeO}_2$ ($x = 7$) glass, is studied. Conductivity σ was measured in AC field ($f = 1$ kHz) on heating through the interval including glass crystallization temperatures. It is shown that glass crystallizes in a few stages and heat treating makes possible to turn initial glass into the intermediate state with increased conductivity. Above 904 K the composition $x=7$ is finally crystallized and σ abruptly drops in two orders of magnitude. To clear up the physical mechanisms of σ increasing in the intermediate state, impedance spectra $\rho^*(\omega)$ were measured for frequencies 10^1-10^5 Hz in the interval 600-675 K. The results are discussed on the basis of equivalent circuit approach; multiphase nature of the compounds is taken into account. Referring to previous DTA and X-Ray data, it is argued that σ increasing in the intermediate state results from nucleation of nanometer $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ordered regions. In such nano- dispersive state surface phenomena become main factor that could change the mechanisms of charge transfer. Just as for other lithium germanate oxides, it is assumed that mobile Li ions determine conductance of $\text{Li}_2\text{O}-7\text{GeO}_2$ glass-ceramics in studied frequency and temperature intervals.

Keywords: glass-ceramics, lithium heptagermanate, impedance spectroscopy.

Вивчається провідність фазових станів, отриманих при розстеклюванні складу $\text{Li}_2\text{O}-x\text{GeO}_2$ ($x=7$) в процесі нагрівання. Питома електропровідність σ вимірювалася в змінному полі ($f = 1$ кГц) при нагріванні в інтервалі, який включає температури кристалізації скла. Показано, що кристалізація відбувається поетапно і шляхом термічної обробки вихідне скло можливо перевести в проміжний стан з підвищеною електропровідністю. Вище 904 К склад $x=7$ остаточно кристалізується і σ різко падає на два порядки. Для з'ясування причин зростання σ в проміжному стані, проведено вимірювання імпедансних спектрів $\rho^*(\omega)$ в діапазоні частот 10^1-10^5 Гц і температурному інтервалі 600-675 К. Результати обговорюються на основі методу еквівалентних схем заміщення з урахуванням багатофазної природи досліджуваних сполук. Посилаючись на попередні дані ДТА та рентгенівської дифракції, припускається, що підвищення σ в проміжному стані відбувається внаслідок утворення нанометрових зародків фаз $\text{Li}_2\text{Ge}_4\text{O}_9$ і $\text{Li}_2\text{Ge}_7\text{O}_{15}$. У такому нано- дисперсному стані поверхневі явища стають домінуючим фактором, що може змінювати механізми переносу заряду. Подібно до інших літій-вогерманієвих оксидів, вважається, що мобільні іони Li визначають провідність склокераміки $\text{Li}_2\text{O}-7\text{GeO}_2$ для досліджуваних частотного і температурного інтервалів.

Ключові слова: склокераміка, гептагерманат літію, імпедансна спектроскопія.

Изучается проводимость фазовых состояний, полученных при расстекловании состава $\text{Li}_2\text{O}-x\text{GeO}_2$ ($x=7$) в процессе нагрева. Удельная электропроводность σ измерялась в переменном поле ($f=1$ кГц) при нагревании в интервале, включающем температуры кристаллизации стекла. Показано, что кристаллизация происходит поэтапно и путем термической обработки можно перевести исходное стекло в промежуточное состояние с повышенной электропроводностью. Выше температуры 904 К состав $x=7$ окончательно кристаллизуется и σ падает на два порядка. Для выяснения причин возрастания σ в промежуточном состоянии, проведены измерения импедансных спектров $\rho^*(\omega)$ в диапазоне частот 10^1-10^5 Гц и температурном интервале 600-675 К. Результаты обсуждаются на основе метода эквивалентных схем замещения с учетом многофазной природы исследуемых соединений. Ссылаясь на предыдущие данные ДТА и рентгеновской дифракции, предполагается, что повышение σ в промежуточном состоянии происходит вследствие образования нанометровых зародышей фаз $\text{Li}_2\text{Ge}_4\text{O}_9$ и $\text{Li}_2\text{Ge}_7\text{O}_{15}$. В таком нано- дисперсном состоянии поверхностные эффект становятся доминирующим фактором, что может изменить механизмы переноса заряда. Подобно другим литиево-германиевым оксидам, считается, что мобильные ионы Li определяют проводимость стеклокерамики $\text{Li}_2\text{O}-7\text{GeO}_2$ в исследуемых частотном и температурном интервалах.

Ключевые слова: стеклокерамика, гептагерманат лития, импедансная спектроскопия.

1. Introduction

Ionic conductance in spatially inhomogeneous, multiphase materials depends on a number of factors, such as structure, relative volume and size of grains and interfacial regions, type of phase spatial distribution [1]. Among dielectrics with high ionic conductivity, the crystalline and glass-ceramic compounds of lithium germanate family $\text{Li}_2\text{O}-x\text{GeO}_2$ are actively investigated. Quenching of $\text{Li}_2\text{O}-x\text{GeO}_2$ glasses and their stage-by-stage crystallization on heating were published earlier in [2]. In [3] the glass samples with $x=7, 11.5$ were heat treated and turned into the intermediate state with increased conductivity σ . In this paper we study conductance of such intermediate state in $\text{Li}_2\text{O}-7\text{GeO}_2$ composition.

2. Experimental results

$\text{Li}_2\text{O}-7\text{GeO}_2$ glass was prepared by fast quenching of the melts, more details on technology were given in [2, 3]. The samples in the initial glass state were cut as the plane-parallel plates, Pt electrodes were deposited by vacuum sputtering.

The glass samples were heated in the range 300–950 K, including the crystallization temperatures of $x=7$ composition [2, 3]. Simultaneously conductivity σ was measured in AC field ($f=1$ kHz) by bridge method. The data are presented in Arrhenius scale in Fig. 1. For comparison differential thermal analysis (DTA) curve [2] is given in the insert to Fig. 1. Joint DTA and X-ray phase analysis, performed in [2, 3], shows that devitrification of $\text{Li}_2\text{O}-7\text{GeO}_2$ glass occurs at $T_g=780$ K. DTA anomaly at $T_1=837$ K is presumably attributed to appearance of lithium tetragermanate $\text{Li}_2\text{Ge}_4\text{O}_9$ ($x=4$) nuclei which are nonequilibrium and on heating transform into thermodynamically stable regions with lithium heptagermanate $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ($x=7$) structure. Above $T_2=904$ K the samples of $x=7$ composition become $\text{Li}_2\text{Ge}_7\text{O}_{15}$ polycrystals [2].

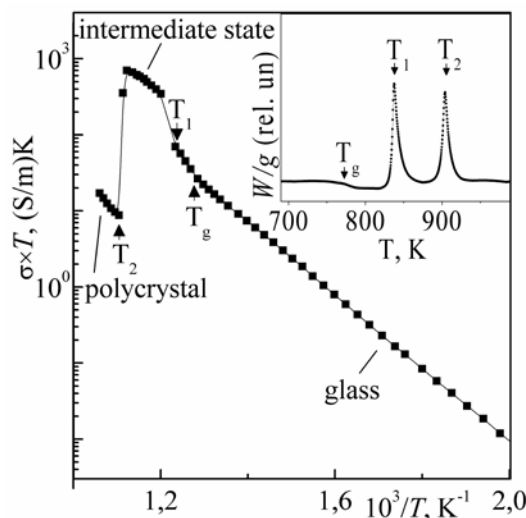


Fig. 1. $\sigma(1/T)$ dependence measured on heating of initial $\text{Li}_2\text{O}-7\text{GeO}_2$ glass in AC field ($f=1$ kHz). In the insert – DTA curve registered on the first heating run of $\text{Li}_2\text{O}-7\text{GeO}_2$ glass (the data from [2])

Comparison of $\sigma(1/T)$ dependence with DTA curve (Fig. 1) demonstrates that devitrification near T_g leads to more steep temperature growth of σ and visible deviation from linear dependence observed below T_g . Nucleation of the ordered regions at T_1 indicates transition to the intermediate state and is accompanied by σ increasing approximately in one order as compared with conductivity of glass. On heating in the range between T_1 and

T_2 the sample is in the intermediate state with increased conductivity. Above T_2 Li₂Ge₇O₁₅ phase is finally crystallized [2] and σ abruptly drops approximately in two orders of magnitude (Fig.1).

In order to clear up the physical mechanisms of σ increase in the intermediate state, we studied spectra of complex impedance $\rho^*(\omega)=(\sigma^*(\omega))^{-1}$ in frequency range 10^1 - 10^5 Hz and for temperature interval 600-675 K. Li₂O-7GeO₂ samples in the intermediate state were prepared by heating of glass to the temperatures between T_1 and T_2 and subsequent cooling to room temperature. In accordance with [3], such treating makes possible to stabilize the intermediate phase for temperatures well below T_g . The experimental data are presented in Fig. 2 as the diagrams in $(\rho''-\rho')$ complex plane. One can see that the experimental hodographs consist of arcs from two semicircles which are well separated in frequency scale. Such hodographs can be simulated by impedance of serially connected two parallel R_1C_1 and R_2C_2 circuits [4]. The dispersion of relaxation times $\tau_i=R_iC_i$ ($i=1, 2$), which is usually observed for real systems, results in shift of the semicircles centers downwards from abscissa axis ρ' . Such behavior is described by substituting of usual capacities C_i by constant phase elements (CPE) $C_n^*=A \cdot (i\omega)^{n-1}$ (ω – external field frequency, $0 \leq n \leq 1$) [4]. The experimental spectra $\rho^*(\omega)$ were described with a help of the equivalent circuit (the insert to Fig. 2), which impedance is given by:

$$\rho^*(\omega) = (S/d) \cdot \left[\left(R_1^{-1} + A_1 (i\omega)^{n_1} \right)^{-1} + \left(R_2^{-1} + A_2 (i\omega)^{n_2} \right)^{-1} \right], \quad (1)$$

where S, d – the electrodes area and the sample thickness correspondingly. The results of calculation are plotted by solid lines in Fig. 2. The dependences of the relaxation times $\tau(1/T)$, determined for high- and low-frequency arcs (Fig. 2), are shown in Fig. 3.

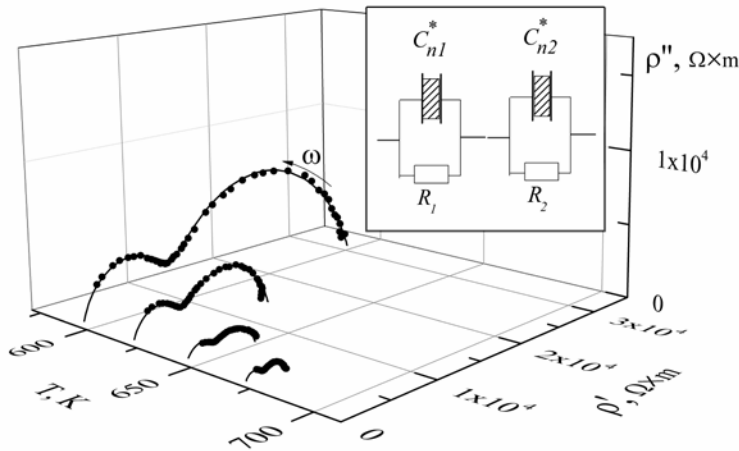


Fig. 2. $(\rho''-\rho')$ diagrams for Li₂O-7GeO₂ samples in the intermediate state. Circles represent experimental data; solid lines are calculated using the impedance of the equivalent circuit in the insert

3. Discussion

It is known, that presence of two or more semicircles in the hodographs is typical for heterogeneous, multiphase systems [4]. According to X-Ray phase analysis [2], the intermediate state of Li₂O-7GeO₂ composition contains nuclei with Li₂Ge₄O₉ ($x=4$) and Li₂Ge₇O₁₅ ($x=7$) structures, which are surrounded by amorphous medium. Therefore spe-

cific conductivity σ and impedance ρ , plotted in Figs. 1, 2, are the quantities averaged over the existing phases. X-Ray diffraction shows [2] that for composition with $x=7$ relative volumes of $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ordered regions are comparable with each other. Since $\text{Li}_2\text{O}-7\text{GeO}_2 \rightleftharpoons \text{Li}_2\text{O}-4\text{GeO}_2+3\text{GeO}_2$, one can see that nucleation of $\text{Li}_2\text{Ge}_4\text{O}_9$ metastable regions slightly depletes with Li the surrounding glass matrix relative to $x=7$ stoichiometry.

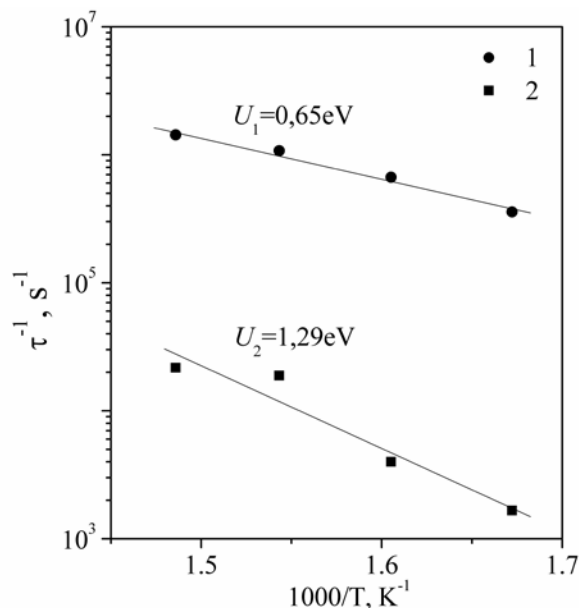


Fig. 3. Dependences $\tau(1/T)$, determined for high-frequency (1) and low-frequency (2) arcs in the hodographs in Fig. 2

Thus, the intermediate state of $\text{Li}_2\text{O}-7\text{GeO}_2$ samples consists of three phases, namely nuclei of $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{Li}_2\text{Ge}_7\text{O}_{15}$ and glass surroundings [2]. Nevertheless, the experimental hodographs demonstrate only two semicircles. As it was pointed out in [5], the crystal structures of $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{Li}_2\text{Ge}_7\text{O}_{15}$ are similar to each other. Authors of [5] emphasized that formation of lithium heptagermanate ($x=7$) crystallites occurs through nucleation of $\text{Li}_2\text{Ge}_4\text{O}_9$ metastable clusters which subsequently turn into $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ordered regions. Similarity of $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{Li}_2\text{Ge}_7\text{O}_{15}$ structures allows to think that relaxation times τ and corresponding rates of charge transfer are close for nuclei of both $x=4$ and 7 phases. Analysis of $\rho^*(\omega)$ spectra and the data in Fig. 3 shows that relaxation times for two observed arcs differ in two orders of magnitude. Therefore one can assume that one arc in the hodographs (Fig. 2) reflects charge transfer within nuclei of both $x=4$ and 7 ordered phases, whereas another arc corresponds to conduction in amorphous surroundings.

According to [6, 7], conductance in $\text{Li}_2\text{Ge}_7\text{O}_{15}$ single crystals is determined by interstitial Li ions hopping along the channels of the framework structure. It is natural to suppose that conductivity of the materials, studied in this work, is contributed by mobile Li ions too. In that case high-frequency arc with less diameter (Fig. 2) can be associated with Li ions moving within nuclei of the ordered phases. Then low-frequency arc can be attributed to Li ions motion through the amorphous surrounding matrix. Since relaxation times τ for high- and low-frequency arcs (Figs. 2, 3) differ in two orders of magnitude, one can conclude that mobility of Li ions is essentially higher within nuclei in comparison with amorphous interfacial space.

4. Conclusion

In summary we notice that recrystallization of $\text{Li}_2\text{Ge}_4\text{O}_9$ metastable nuclei and growth in size of $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ordered regions lead to abrupt conductivity fall observed for polycrystal above T_2 (Fig. 1). Since initial glass, intermediate state and polycrystal correspond to the same chemical composition ($x=7$), the observed changes of conductivity (Fig.1) should be attributed to the structural features. Apparently, σ increasing in the intermediate state can be connected with high spatial dispersity. High conductivity is observed when mean size of the nuclei is less than certain value, typical for the compound studied. In that case surface phenomena are expected to play a key role and determine charge transfer of the intermediate state.

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