Ionic conductivity in glassy and partially crystallized lithium-sodium tetragermanate

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Intoduction

Lithium-sodium tetragermanate LiNaGe4O9 (LNG) crystal demonstrates strong anisotropy of electrical conductivity σ contributed by interstitial Li ions moving through the channels within structural framework [1]. It is known, that under certain conditions preparation of the structures inhomogeneous in nanometer scale allows to enhance significantly ionic conduction of solid electrolytes. Earlier this assertion had been confirmed by studying single crystals, glasses and nanometer structured glass-ceramics of lithium heptagermanate Li2Ge7O15. In particular, it was shown that ionic conductance of amorhous and nanocrystalline states in about three-five orders exceeded typical σ values of the same single crystalline compound [2].

In this work we report the data on preparation of LNG glass and partially crystalized glass-ceramics.

Materials and methods

The structural content of the prepared compounds was characterized by XRD phase analysis. Electrical conductivity σ was measured in the temperature interval 300÷1000 K and in AC field frequency range 102÷106Hz.

By using the fast quenching the melt [2], we have prepared LNG samples of the two kinds. The samples of the 1-st type were prepared by melting LNG single crystals and subsequent quenching the melt. The samples of the 2-nd type were prepared by grinding of the initial reagents in stoichiometric ratio in an agate ball mill and their melting without preliminary synthesis. The samples of the both types represent optically transparent and colorless plates with the widths of about 0.5÷1.0 mm.

Results

XRD phase analysis showed that the samples of the 1-st type consist of 90÷92 % of LNG glass and contain near 8 % of the ordered regions with mean size of the crystallites of about 20 nm. Theses samples were devitrified on heating under the control of DSC. It was shown that the glass started to soften at $T_g = 780$ K whereas final crystallization happened at $T_c = 820$ K [3]. In the range included the temperatures T_g and T_c of DSC anomalies, electrical conductivity was measured on heating (Fig.1). It was shown, that conductivity of the glassy samples of the 1-st type exceeded in one-three orders σ values measured along the main axes of LNG single crystal [4]. Approaching T_g from below led to softening the glass and a more sharp increase of conductivity on heating. The final crystallisation of the glass at T_c was accompanied by the irreversible decrease of conductivity in about three orders of magnitude. An isothermal heat treatment of the samples of the 1-st type at the temperatures 10÷15 K below T_c allowed to increase the volume of the crystallized regions. Partial crystallisation of these samples was accompanied by decrease of electrical conductivity in about one order of magnitude.

XRD phase analysis evidenced that the samples of the 2-nd type practically did not contain amorphous phase and represented polycrystals with average crystallites sizes of about 40÷50 nm. Thermal treatment of these samples at 800÷815 K during a few hours resulted in σ increase in about one order of magnitude.

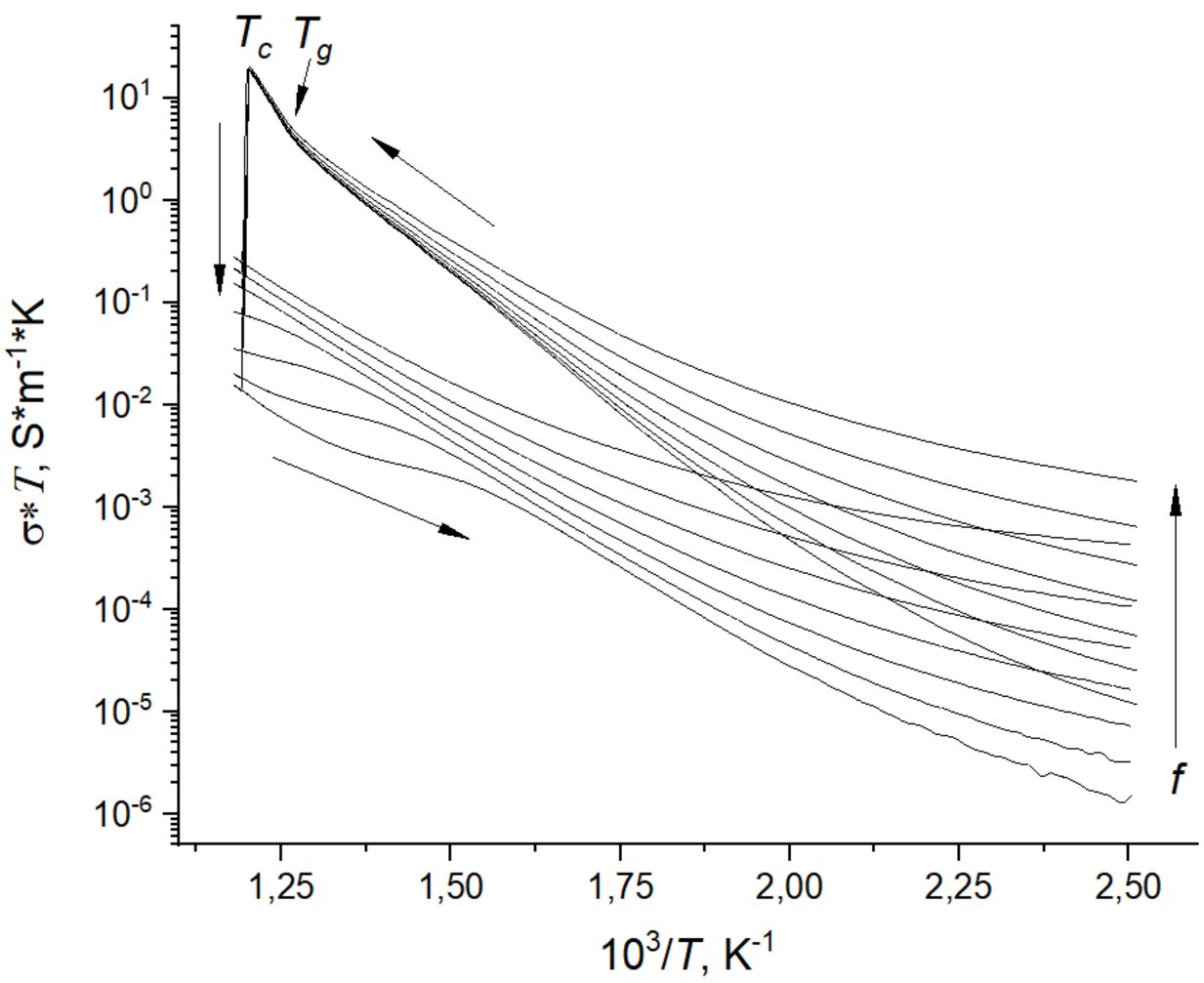

Figure 1 - The dependencies σT(1/T) for lithium-sodium tetragermanate glass, f = 1 kHz, 3,6 kHz, 11 kHz, 34 kHz, 105 kHz, 320 kHz, 1 MHz.

Conclusions

Presumably growth of electrical conductivity of these samples can be attributed to the appearance and increase in volume of nanocrystallites of highly conductive phase in Li(Na)O2 – GeO2 family.

References

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