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Thermal Expansion of Lead Germanate Glass

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The thermal expansion of lead germanate glass has been measured in the temperature range 310-583 K. It was established that the absolute value of the coefficient of thermal expansion increases as the temperature rises to 400 K and then it is practically held constant.

Keywords: thermal expansion, glass, lead germanate.

Introduction

Oxide compounds formed in the GeO_2-PbO system is of practical importance in view of their valuable properties and for a long time attracts considerable attention of scientists [1-3]. By now there are many works devoted to study of ferroelectric and other electrophysical properties of relevant materials. Though, their thermodynamic and thermal physical properties have not been adequately explored.

The aim of this work is to investigate the thermal expansion of $PbGeO_3$ glass.

Results and discussion

The thermal expansion of $PbGeO_3$ glass was measured by the procedure described in [4, 5]. A DIL 402 C (NETZSCH) dilatometer was used for experiments. The measuring error amounted to 3 %.

According to [6], the coefficient of thermal expansion α_T is determined by the equation

$$\alpha_T = \frac{1}{L_T}\left(\frac{\partial L}{\partial T}\right)_p , \quad (1)$$

where L_T is the length of sample at given temperature. When the extension of samples is recorded in a relatively small temperature range, the thermal expansion of homogeneous isotropic materials is noted to be characterized by the mean coefficient of linear thermal expansion:

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$$\overline{\alpha}_{TT_o} = \frac{L_T - L_o}{L_{T_o}\left(T - T_o\right)}. \qquad (2)$$

That there were complications of obtaining compounds of GeO_2-PbO system was indicated in [3, 7, 8]. In the present work the synthesis and the control of $PbGeO_3$ samples were conducted as in [9]. The obtained $PbGeO_3$ glass is shown in Fig 1.

Figure 2 gives data on thermal expansion of $PbGeO_3$ glasses.

The upper limit of measurements was bounded by the temperature 583 K beginning from which a change of behavior of the dL/L_0 curve took place. The decelerating monotonic rise of the relative length extension of the $PbGeO_3$ sample occurs at 583-630 K. As the temperature increases > 630 K, a decreasing dL/L_0 (not shown in Fig. 2) is observed. We connect this phenomenon with the softening of the glass [9]. In studies of the temperature dependences of the heat capacity of these glasses at $T > 630$ K, an anomalous growth of C_p associated also with the softening of glass was found [9].

The thermal conductivity of the $PbGeO_3$ glass has been measured in [10] to these temperatures only.

Kinetics of devitrification of $PbGeO_3$ has been studied comprehensively by C. Tomasi et al. [11]. It was established that the DSC curves of this glass at heating rate of 10 K/min were characterized by extremes at 643, 703 and 843 K. The change of heating rates from 0.1 K/min to 50 K/min resulted in shifts of the peaks to the range of higher temperatures. The first peak was related to the crystallization limit and second one to the “metastable/stable state” transition [11].

Based on the $dL/L_o = f(T)$ dependence, we obtained the temperature dependence of the coefficient of thermal expansion of $PbGeO_3$. The values of α was determined to increase as the temperature rises from 310 K to 400 K and then they are practically held constant, equal to ~ $10 \cdot 10^{-6}$ K^{-1}.

Accordingly to [10], $PbGeO_3$ glasses exhibit low values of the thermal conductivity and their weak dependence on the temperature. It can point to the presence of a structural irregularity and other centers of phonon scattering. It can be connected with the complications of obtaining lead-containing oxide compounds through a partial volatilization of PbO. Besides, PbO is characterized

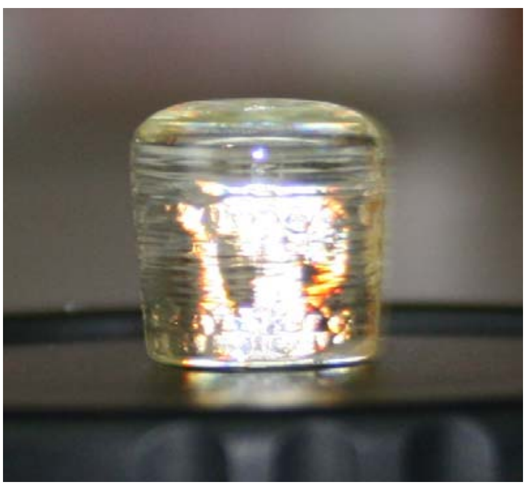

Fig.1. Image of $PbGeO_3$ glass

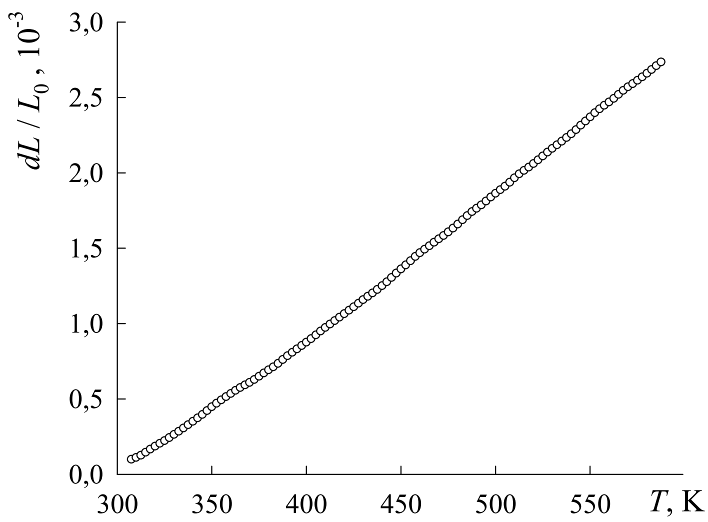

Fig. 2. Influence of the temperature on the relative length extension (dL/L_0) of the $PbGeO_3$ glass

by a positional disorder of crystal lattice [12]. The fact is that it crystallizes in the lattice identical to CaF_2 [13]: the lead occupies positions of the calcium and the oxygen takes up positions of the fluorine. In this case the capacity of vacant sites for the oxygen is two times larger than there are oxygen atoms in the lattice. There are two modifications of PbO [14]: tetragonal (low-temperature) and orthorhombic (high-temperature) ones. Within one crystal type, they can be characterized by various symmetry groups as a result of alternative positions of oxygen atoms with the invariant sublattice of lead.

It may be suggested that the aforesaid conditions the behavior of the $PbGeO_3$ glasses at high temperatures.

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Термическое расширение свинцово-германатного стекла

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Измерено термическое расширение свинцово-германатного стекла в интервале температур 310-583 К. Установлено, что значение коэффициента термического расширения растет по абсолютной величине с увеличением температуры в интервале 310-400 К.

Ключевые слова: термическое расширение, стекло, германат свинца.