ANOMALOUS HEAT CAPACITY IN SiO_2-BASED MULTICOMPONENT GLASS-LIKE SYSTEMS AT LOW TEMPERATURES

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The anomaly has been observed in the course of temperature dependence C(T)/ T^3 within T 5÷30 K in glass-like and crystal SiO_2 and SiO_2- based glass-like systems given in Table 1. It is established that maximum of C(T)/T^3 function of glass-like and crystal SiO_2 is arranged at T10 K and 9 K, respectively. For the rest of systems, the maximum positions at temperature dependence C (T)/T^3 changes due to concentration and chemical composition of the second component in given systems. In these systems the anomaly of heat capacity dependence C(T)/ T^3 occurs within T 5÷30 K regardless of glass-like material composition and is related to the existence of quasi-local vibrations.

Keywords: heat capacity, anomaly, Debye theory, quasi-local vibrations.
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The study of low-energy excitations (1÷10eV) generating the observed anomaly of glass-like material thermal properties is proceeding vigorously in literature. [1-7]. By temperature dependence Cp (T) of SiO_2 heat capacity two temperature sections are observed: 1. Anomaly corresponding to the linear section of heat capacity temperature dependence is lower than the temperature ~1K(appropriate to the energy (1eV). 2. Anomaly is C(T)/T^3 function having a maximum ("peak") nearly T~ 10K. According to Debye theory for $T< \frac{\theta_D}{30}$ (where θ_D is Debye temperature) the heat capacity (C_p) of solid state lattice is defined by continuum elastic vibrations and proportional to T^3. But in helium temperature section the value of experimental specific heat capacity of amorphous substances exceeds substantially the theoretically estimated value and takes the formula:

$$C=C_1T+C_3T^3$$

Here $C_1=(1+5)\cdot10^{-6}q^{-1}K^{-2}$- and $C_3> C_D$ (the value C_3 exceeds third as great the value C_D obtained by Debye theory) is the specific heat capacity of elastic continuum at T 1K[2]. As it is mentioned the anomaly line for vitreous silica (SiO_2) is below T IK but the maximum of C (T)/T^3 function is appropriate to T~10K.

In [5] it is also shown that observed value of specific heat capacity within amorphous material temperatures (5÷10 K) exceeds significantly the estimated value. We expect that most atoms (~ 10% of the total number) in materials with disordered structure is characteristic of "soft" anharmonic potential. It generates quasilocal vibrations in glass-like materials and causes the anomaly of additional heat capacity in temperature dependence of given material heat capacity at low temperatures. According to the authors the formation of quasi-local vibrations in glass-like SiO_2 is related to the process of several interacting SiO_4 tetrahedrons.

Investigation of various amorphous materials by method of neutron scattering shows that the energy density of vibrational state in section under consideration differs essentially from Debye g_D (W): $g_D(W)\sim W^2$

Given anomaly results in additional heat capacity in all studied glass - like materials regardless of their composition (5÷30K) [7,8]. It is established that the anomaly of heat capacity temperature dependence and thermoconductivity in RS (Raman scattering) and IS (Infrared spectrum) within the frequency range 10÷100cm^{-1} and T5÷30K is associated with the material structure peculiarities of disordered structure.

For the majority of authors this peculiarity is in a great number of quasi-local vibration excitations (~10% of all vibrations) that is reflected in thermal properties [3.11]. There have been suggested several various models to account for quasi-local excitations. In paper [11] it is suggested that the formation of SiO_2 glass-like quasi-local vibrations is related to the process of several interacting SiO_4 tetrahedron rotation. Other researchers demonstrate the advent of two types of structural changes (topological and geometric) in SiO_2 grid [9]. Topological transformation is correlated with the bond changes in SiO_2 grid or breaking of chemical bonds. Geometric transformation is observed by Si-O-Si angle variations without topological transformation and occurs in passage through small energy barrier. Here the main priority is the geometric transformation and brings into the existence of anomalous properties at low temperatures [10]. It is shown that structural transformation in SiO_2 has a geometric character. [11].

Thus in spite of pursuance of intense research on SiO_2 physical properties the behavior of observed anomaly is not clearly understood.

There has been investigated dependence of heat capacity on the temperature (5÷300 K) and

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composition [12-16]. This paper deals with the temperature dependence $C(T)/T^{-3}$ within T 5÷30K of heat capacity of mentioned materials and the temperature appropriate to anomalies is determined (see Table 1). Maximum("peak") of function $C(T)\ T^{-3}$ of glass-like and crystal SiO_2 is at T 10 K and 9 K, respectively (Fig.1). I suppose that the first anomaly in low-temperature behavior of SiO_2 glass-like and crystal heat capacity is associated with the presence of anharmonic vibrations and the second anomaly is associated with more high-frequency vibrations. Based on simple calculation by Einstein's theory (approximation) the values $60cm^{-1}$ and $77cm^{-1}$ for specific frequency of lattice vibrations appropriate to the maxima of dependences of $C\ (T)/T^{-3}$ for glass-like and crystal SiO_2 have been obtained.

But for systems in Table 1 it is shown that position and amplitude of maxima on dependence $C(T)/T^{-3}$ are different due to the concentration and chemical composition of other components in these systems relating to SiO_2 vitreous composition: for SiO_2- B_2O_3 system (Fig.2), for SiO_2-GeO_2 system (Fig.3), for SiO_2- Al_2O_3 system (Fig.4), for SiO_2-TiO_2 system (Fig.5), for SiO_2-B_2O_3-Na_2O system (Fig.6), for SiO_2-PBO-B_2O_3-K_2O-Na_2O system (Fig.7)

As it is seen from figures as the maximum position on the dependence $C(T)/T^3$ do not differ, greatly their amplitude mainly depends on the concentration of the second components in systems like this. As it is shown that in [12] the anomalous behaviour of heat capacity isotherm depending on B and Ye cations in the composition of (Fig.2,3) SiO_2-B_2O_3, SiO_2-GeO_2 systems is due to the bonds formed among SiO_4 tetrahedrons and BO_3 octahedrons glass-like and GeO_4 tetrahedrons (Si-O-Si, Si-O-B, Si-O Ge) are based on geometric lines (Fig.2,3). While doping glass-like SiO_4 by B_2O_3 oxide up to the concentration 20 mol% Si atom is substituted by B(Si-O-B) [17].

As a result of infrared (IR) spectroscopic study of glass-like SiO_2 doped by germanium dioxide (GeO_2) the isomorphous substitution of Si by Ge (Si-O-Ge) up to GeO_2 concentration 50mol% [18] has been determined. Atoms B and Ge cause geometrically the change in Si-O-Si angle and increase the mobility of anion frame bonds in SiO_2 and initiate heat capacity in going from $C(T)/T^3$.

As it is shown [13] in SiO_2-Al_2O_3 and SiO_2-TiO_2 glass-like systems according to Al and Ti atoms in composition the anomalous behavior of heat capacity isotherm is due to the bonds formed among SiO_4 tetrahedrons, Al_3O_3 octahedrons and TiO_4 tetrahedrons (Si-O-Si, Si-O-Al, Si-O-Ti) based on geometric lines. That is to say in systems like this Al and Ti atoms included in SiO_2 lattice produce geometrically the change in its Si-O-Si angle and increases the mobility of anion frame in SiO_2 (Fig.4,5).

According to author's own SiO_2-B_2O_3-Na_2O and SiO_2-Al_2O_3-Na_2O glass-like systems [19,20] we attribute the dependence of heat capacity on the concentration by the change in coordination number of B and Al atoms in terms of property dependence on the composition [14,15].

It is shown that the presence of Na_2O small amount in sodium borosilicate (SBS) and sodium aluminum silicate (SAS) tends to the reconstruction of borooxygenous and alumooxygenous frames in these material structures. Hence the part of B and Al atoms in tetrahedral position substitutes isomorphically Si atom in them, the rest of B and Al atoms remains in octahedral position that is in a good agreement with the idea set forth in [10,20].

In this case all non-bridging oxygen atoms enter into BO_4 and AlO_4 tetrahedrons but each Na ion is arranged in BO_4 and AlO_4 tetrahedrons. It brings about chemical bonds reinforcement in glassy frame and confirm the existence of isomorphism between sites $[SiO_{4/2}\ [BO_{4/2})^-Na^+$ and $[AlO_{4/2}]^-\ Na^+$ in glassy frame. In doing so the energy of ordinary bonds B-O and Al-O in tetrahedrons BO_4 and AlO_4 of anion structure of glass like this is 80÷100kkal/mol [21] that is about for ~ 15% lower than binding energy of Si-O in SiO_4 tetrahedrons. As a result, SiO_2 anion generates the increase of frame bond mobility that is manifested in the course of dependence $C(T)T^3$ for given materials (Fig.6).

There has been studied heat capacity $C(T)\ T^3$ in SiO_2-PbO-B_2O_3-K_2O-Na_2O glass-like and crystal systems within T 5÷30K and the anomaly is found out. Maximum ("peak") of $C(T)T^3$ function of these systems is at T13K and 11K, respectively (Fig.7).

Thus while entering B, Ye, Al and Ti atoms into SiO_2 frame and replacing Si atoms that results in Si-O-B, Si-O-Ge, Si-O-Al and Si-O-Ti bond formation, Si-O-Si increases the bond mobility of SiO_2 atomic frame at the expense of its change in angles. It is likely that it brings about the creation of quasi-local vibrations and heat capacity system anomaly within T 5÷30K presented in Table 1.

OBTAINED RESULTS

The presence of "peak" on dependence $C(T)T^3$ within T~(5÷30K) in vitreous systems is related to the structural peculiarities of disordered structure materials that is the excitation of quasi-local vibrations originated in them. As it is seen from Table 1 the given anomaly is observed within T 5 ÷30K in all glass-like materials under investigation regardless of their composition. It is established that maximum position on the dependence $C(T)T^3$ for materials under investigation shifts to the high-temperature range due to the concentration of the second components in systems like this.

Temperatures of dependence $C(T)/T^3$ appropriate to "peak" in SiO_2-based vitreous multicomponent glass-like systems

№	Substance	Temperature K
1.	SiO_2-vitreous solid	10
2.	SiO_2-crystal	9
3.	98,81mol%SiO_2+1,19 mol%B_2O_3	17
4.	95,65mol%SiO_2+4,35mol%B_2O_3	18
5.	92,22mol%SiO_2+7,78mol%B_2O_3	12
6.	84mol%SiO_2+16mol% B_2O_3	9
7.	96mol%SiO_2+4mol%GeO_2	14
8.	94mol%SiO_2+6mol%GeO_2	14
9.	89,80mol%SiO_2+10,20mol%GeO_2	15
10.	97,00mol%SiO_2+3,00mol%Al_2O_3	12
11.	95,00mol%SiO_2+5,00mol%Al_2O_3	10
12.	90,60mol%SiO_2+9,40mol%Al_2O_3	11
13.	96,12mol%SiO_2+3,88mol%TiO_2	11
14.	89,75mol%SiO_2+10,25mol%mol%TiO_2	13
15.	97,00mol%SiO_2+2,50mol%B_2O_3+0,50mol%Na_2O	9,6
16.	97,00mol%SiO_2+1,00mol%B_2O_3+2,00mol%Na_2O	8,5
17.	97,00mol%SiO_2+0,50mol%B_2O_3+2,50mol%Na_2O	8
18.	93,90mol%SiO_2+1,00mol%Al_2O_3+5,10mol%Na_2O	8,4
19.	93,90mol%SiO_2+3,00mol%Al_2O_3+3,10mol%Na_2O	9
20.	93,90mol%SiO_2+5,00mol%Al_2O_3+1,10mol%Na_2O	11
21.1*	71,84mol%SiO_2+14,19mol%PbO+2,50mol%B_2O_3+10,34mol%K_2O+1,12mol%Na_2O	13
22.2*	71,84mol%SiO_2+14,19mol%PbO=2,50mol%B_2O_3+10,34mol%K_2O+1,13mol%Na_2O	15

1.∗- vitreous solid
2.∗ -crystal

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