Self-organization in glass: the synergetic chemical bonding approach

E. A. CHECHETKINA
Ostrovityanova Str. 19-98, Moscow, 117437, Russia

With the use of synergetics, a theory of self-organization of the dissipative type, an original approach for understanding of glass nature and glass structure is presented. The chemical bonding instability and its collective character provide a new type of organization of non-crystalline network, which can be described as the bond wave that spreads through the sample in a direction given by information field. The bond wave model in used for explanation of both the known glass features (glass transition, first sharp diffraction peak, etc.) and the original experiments (magneto-viscous resonance, ultrasonic teatments, etc.). The synergetic approach does not contradict with the well-spread topological/network approach after *Thorpe-Phillips-Boolchand*, one reflects the dynamic (wave) and another reflects the static (network) sides of glass reality.

(Received November 05, 2015; accepted February 10, 2016)

Keywords: Glass structure, Self-organization, Bond wave, Information field

1. Introduction

Self-organization is not a rare term in contemporary theory of the glassy state. It relates usually to the topological approach, which began actually in 1932, when *Zachariasen* [1] has introduced his famous continuous random network (CRN), no matter that the term was proposed somewhat later. The 50 year jubilee of CRN was distinguished in 1982 by a special review [2], whose title "The melody lingers on" remain true now, 33 years ago. One of the most interesting themes of this "melody" is the topological approach initiating by the *Phillips's* bond constraints theory [3] and the *Thorpe's* rigidity percolation theory [4]. These interconnected theories [5] were developed further by intensive experimental study of *Boolchand* and his group, whose basic result was the discovery of intermediate phase (IP) [6], a special "rigid but unstressed" network that realizes when chemical composition ensures the average coordination number of about the predicted $<r>=2.40$. The following intensive investigations of IP in various glass-forming systems is a special theme (the reader can use review [7] for introduction). For the purpose of this article, it is essential that this self-organization is attributed to just IP while the real glasses outside IP are not the self-organized systems – these are ordinary CRN, less or more stressed, and less or more rigid [8,9].

Note, however, that classical self-organization after *Haken* [10] and *Prigogine* [11], which develops in complex far-from-equilibrium systems, bears no a relation to the above "topological self-organization", which looks like rater "self-assembling", a process that takes place in the near-of-equilibrium systems (e.g., crystallization at near/below melting point). Classical self-organization considers *dissipative patterns* [12] and *information fields* [13], which represents respectively the carriers and the directors for evolution of self-organizing systems. Just this classical/dissipation self-organization I consider here, the characteristic dissipative pattern being bond wave. This pattern arises owing to inherent instability of chemical bonding in glass-forming substances and the collective character of this instability, when elementary acts of bond exchange are in the spatio-temporal correlation (i.e., wave) with each other. The experiments that provoked bond wave model, and the experiments that was initiated by it, are considered. The glass transition and secondary relaxation, the medium-range order and the non-crystalline long-range order, all of them can be reformulated on the united basis. In conclusion, interconnection between topological and synergetic approaches is proposed for their further fruitful development.

2. Experimental precursors for the bond wave model

The first precursor is the ***alternative*** character of chemical bonding in glass. The known experimental fact of the observed *increase* of the first coordination number in glass (e.g., Z1=2.1 for Se glass instead of Z1=2.0 for crystal; Z1=2.7 for As_2Se_3 melt instead of 2.4 for crystal) became the basis for the concept of *hypervalent bonds* (HVB) as the cause of glass formation after *Dembovsky* [14-17]. These HVB are proposed to be in thermal equilibrium with ground covalent bonds (CB), so the HVB concentration is a temperature dependent value, which is maximum in melt [16]. In frames of this theory, the key property of HVB is their ability to provide *quasi-polymerisation* of glass-forming melts, when breaking of covalent bonds is compensated by bridging of covalent fragments by means of HVB. Such a quasi-polymerised melt possesses high viscosity, a feature of glass-forming melts that provides their ability to supercooling up to non-crystalline solid state.

The other side of viscosity is its mechanism. Breaking of covalent bonds, which is meant usually in this respect, is a high-energy mechanism. By means of HVB a low-enegy *switching* of covalent bonds from some atoms to other can be reached. The hypothetical scheme of the CB switching through charged intermediates proposed by Dembovsky [14] have forced him to undertake a special experiment of viscous flow in magnetic field [18,19] for elicitation of HVB. The most wonderful result was obtained in alternative magnetic field in the form of ***magneto-viscous resonance*** shown in Fig.1. This is the second precursor for the bond wave model since the effect behavior cannot be understand from the classical point of view. First, the applied field (H≈300 Oe) is very weak in comparison with thermal energy: $\mu_B H << kT$. Second, the field is actually inactive in the temperature range investigated except a shallow region, in which viscosity can change in 2-3 times. The third feature was developed somewhat later, when trying to diminish the scattering of experimental points by advanced thermal isolation in order to avoid temperature gradients with an unexpected result: in the thermally isolated measuring cell the effect of magnetic field on viscosity vanished.

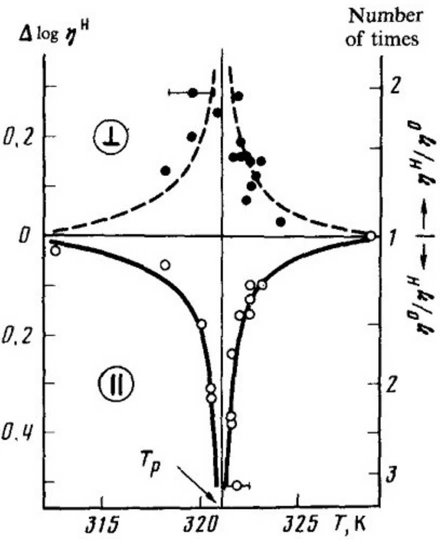

Fig.1. Change of viscosity of softening Se glass (T_g≈310K) under the action of alternating magnetic field of the 50 Hz frequency and H=280 Oe intensity after [19]. Here η^0 and η^H are the values of viscosity at the same temperature, η^H being viscosity in the field; the positive $\Delta lg\eta^H = lg\eta^H - lg\eta^0$ corresponds to transverse field, the negative $\Delta lg\eta^H$ corresponds to longitudinal field. T_P is the "resonance" temperature.

Eventually it became clear for me that when measuring viscosity we deal with the far-from-equilibrium self-organizing system, and the role of magnetic field is to give *information* for the way of this system evolution. The model for the related dissipative pattern is based on the abovemantioned alternative bonds (AB), which are probably HVB in the case of chalcogenide glasses. The bond exchange acts AB↔CB, first, have the temperature dependent frequency $f^*(T)$, and second, it is a *collective frequency* due to collective character of bond switching in the prosses of viscous flow. Resonance means that the temperature of a sample coincides with the frequency of external field (f^H=50 Hz in our case): $f^*(T_P)=f^H$. Thus, we assume that information ability of magnetic field sharply increases in resonance conditions. On the other hand, collective switching of covalent bonds means the *spatio-temporal correlation* of the bond exchange acts; corresponding dissipative pattern is ***bond wave***. The first graphical representation of bond wave is given in Fig.2.

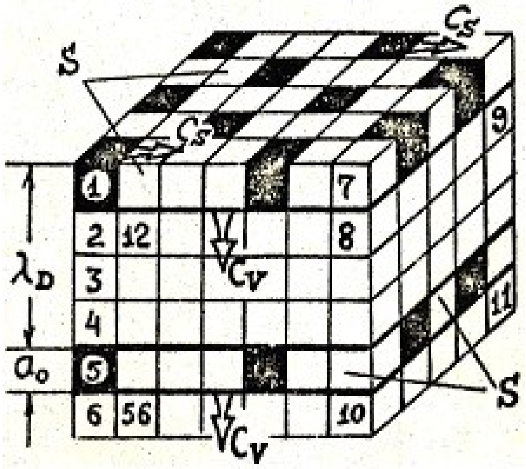

Fig.2. Snapshot of "elementary cell" of bond wave after [20]. White blocks are "normal" covalent bonds, black blocks are alternative bonds; a_0^3 is elementary volume per bond (CB or AB). Two adjacent wavefronts populated with alternative bonds are marked as S. Here $\Lambda=\lambda_D$ is wavelength and C_V is velocity for the 3D wave. The 2D bond wave spreads in the limits of S-layers with the C_S velocity.

Because bond wave is sensitive to magnetic field, the act of bond exchange should include an intermediate paramagnetic state: AB↔A*↔CB. A possible nature of the A* state is the one-electron excitation of lone-pair (intermediate harpoon), which was describe by us earlier [21]. Thus, bond wave represents also a specific *spin wave*, with which magnetic field can interact. When the field-directed bond wave runs in the same direction that needs for viscous flow, viscosity decreases, otherwise it increases (see Fig.1).

3. Bond wave and medium-range order

Bond wave introduces a specific “wavy” long-range order in non-crystalline network, an order that is characterized by two parameters: a_0, the length of elementary bond “jump” or the thickness of the wavefront, and $\lambda_D >> a_0$, the inter-front distance or the wavelength (see Fig.2). The first bears a relation to the so called “medium-range order”, MRO (known also as “intermediate-range order”, IRO), which we considered now. The principal sign of MRO is the so called *First Sharp Diffraction Peak* (FSDP) observed at $Q_1 \approx 1$ Å^{-1} in chalcogenide glasses and/or glass-forming liquids or at $Q_1 \approx 1.5$ Å^{-1} in oxide ones. Among the models proposed for interpretation of FSDP so far (see [22] for a critical review), the early “layer model” is less popular, just because the crystal-mimed layers are suitable for 2D networks like As_2S_3, being doubtful for 3D networks like SiO_2. Note that the considered S-layers, being wavefronts, does not appeal to the structure of crystalline counterpart or the main covalent motive in glassy network. Based on such interpretation of the reflecting layers, I have proposed the *modified layer model* [23], in which the totality of equidistant layers of the $d = a_0$ thickness gives the observed $Q_1 = 2\pi/d$ reflex. Reciprocally, one can evaluate the wavefront thickness as $a_0 = d = 2\pi/Q_1 \approx 6$Å for chalcogenide glasses and ≈4Å for oxide ones.

Since d-layers arrange in a periodical way, with the $\Lambda = \lambda_D$ regularity, their totality can form an intence and narrow (sharp) reflex. The FSDP halfwidth, $H_{1/2}$, and intensity, I, should depend on the layers concentration, which is reciprocal to Λ, and on the layer reflection ability, which depends on chemical composition, temperature and pressure. The influence of the three factors on the FSDP parameters were analyzed by me earlier [24]. Here I return to the puzzle of Se, which is the prototype glass, on the one hand, and does not demonstrate FSDP, on the other hand. When analysing the known data for the Se-Ge system, it was shown in [24] that extrapolated to Se composition FSDP is too weak, too wide, and disposes at 1.4 Å^{-1} position instead of normal $Q_1 \approx 1$ Å^{-1}. Although corresponding peak may be really extracted in the form of shoulder on the first diffuse peak in glassy selenium (this peak maximum is about 2.0 Å^{-1}), the question is would the “normal” FSDP realise in glassy Se?

Let use the bond wave model in order to answer this question. First of all, let us remember that ordinary glass is an isotropic material, in contrast to the bond wave model described above. Thus, the model must be developed by assuming a *solitonic* behavior of bond waves, which therefore can intersect each other without distortion (the reader can see such a behavior when observing ripple on the river surface). It is shown in **Fig.3**, on the top, that depending on the given directions bond waves can create of a structure of the layer (**V$_1$**), colunar (**V$_1$**+**V$_2$**), or cellural (**V$_1$**+**V$_2$**+**V$_3$**) type, and only the latter is isotropic. On the bottom of Fig.3, an example of common multiple intersection is shown.

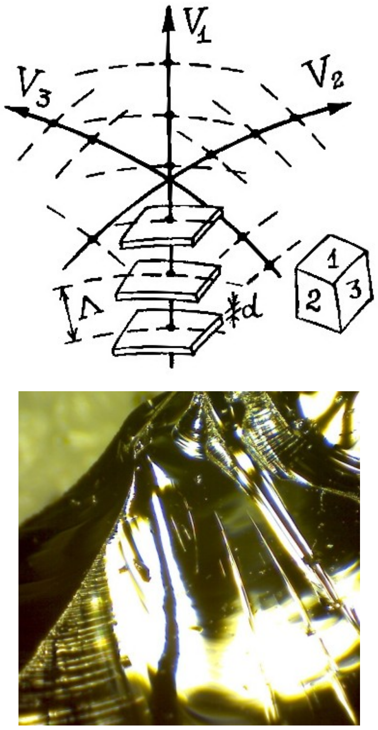

*Fig. **3**. Intersecting bond waves moving with the V_i velocities in the **V_i** directions (on the top) and real fracture observed in Se glass by optical microscope with the 150 magnification (on the bottom).*

Reflexes from d-layers belonging to different bond waves should weaken each other (as well as diffraction picture of monocrystal is much more intensive than that from polycrystal of the same substance), thus, in order to intensify FSDP we must perform solidification in the conditions that favor for one direction, so preparing glass of a preferably layer substracture. Fortunately, such a sample remains after our experiments on measuring of viscosity of softening Se glass by penetration method (see insertion in Fig.4). Really, after removing of deformed surface layer, as it is (see green line in the insertion), the sample displays a peak at “normal” position of $Q_1 \approx 1$ Å^{-1}.

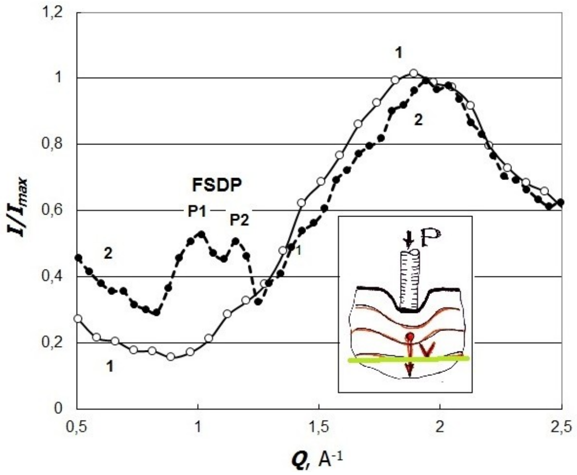

Fig.4. X-ray diffraction from Se glass; (1) prepared as usual and (2) after the measuring of viscosity by penetration method (see the insertion).

But the question is why this peak is splitted? Let me refer to the quantum-chemical investigation [25], in which the lowest-energy alternative bonding state in the form of Se_4^0 was discovered. In this state two pair of Se-Se bonds around the central four-coordinated Se atom exist: two “short” bonds Se-Se of 2.4Å (2.3 Å for “normal” covalent bond) arranged at about 90°, and two “long” bonds of the 2,8Å arranged linearly. Therefore, two types of d-layers are possible, when “short” bonds hold the $d(P2)=2\pi/1.15=5.5$Å layers and when “long” bonds hold the $d(P1)=2\pi/1.05=6,0$Å layers. This is not an exact coincidence; however, one cannot expect it just because of a limited cluster with one Se_4^0 in it [25]. The calculated energies and distances should change when expanding the region under consideration. Really, when two Se_4^0 were introduced, the cluster energy decreases up to the *negative* values for definite arrangements of alternative bonds [26]. The same fall of energy when association of alternative bonds was observed also in the Se-Cl [27] and Se-Te [28] cases. This is a result in favor of the bond wave model, which needs grouping of AB in the limits of wavefronts, which therefore represent the low-energy formations in a “normal” continuous random network existing between the layers/wavefronts.

4. Bond wave and long-range order

Bond wave, being an ordered macroscopic formation, is characterized by two parameters: vector **V** (velocity), and scalar Λ (wavelength). In the previous section we have seen how by means of elastic information field, which was untroduced by penetrating indentor (see insertion in Fig.4), one can manage the **V** vector (s), thus creating a layered substructure with the following intensification of FSDP, the sign of medium-range order. The question is how one can manage Λ?

Wavelength Λ is the distance between *d*-layers (or S-layers in Fig.2), which are populated by alternative bonds (black blocks in Fig.2). Thus, Λ depends on the AB concentration and the AB population of d-layers. Using a simple one-barrier scheme for the act of bond exchange CB↔AB and geometric image in Fig.2, one obtains

$$N = N_0 \cdot \exp(-\Delta\varepsilon/kT) \qquad \text{and}$$

$$\Lambda = (N_S/N_0) \cdot \exp(\Delta\varepsilon/kT) = \Lambda_0 \cdot \exp(\Delta\varepsilon/kT)$$

where N is the averaged per volume concentration of AB, $\Delta\varepsilon$ is the AB energy as compared with the CB energy (the levels difference), N_S is the AB population of the *d*-layer, and N_0 and $\Lambda_0= N_S/N_0$ are formal pre-exponents.

Now let us evaluate a possible $N(T)$ and $\Lambda(T)$ behavior using the following assumptions and the known parameters for Se. Since CB is the ground state, the AB concentration cannot exceed the CB concentration. The critical point at which $N(AB)=N(CB)=0.5$ is the boiling point (T_b=958K for Se), above which the network distroyed completely with escaping of covalent fragments into the gaseous phase. The second particular temperature is the glass transition temperature, below which supercooled liquid freeses into a solid glass ($T_g\approx310$ for Se). Concentration of AB in this point is unknown, but one can suppose that it is not exceed 10% (1) and not smaller than 1% (2). Then from the first equation one obtains the following AB energies: $\Delta\varepsilon(1)=0.0636$ eV and $\Delta\varepsilon(2)=0.1539$ eV, and, using the above assumptions concerning AB concentrations at critical temperatures, one can construct two temperature dependencies for concentration of alternative bonds in liquid selenium – see Fig. 5.

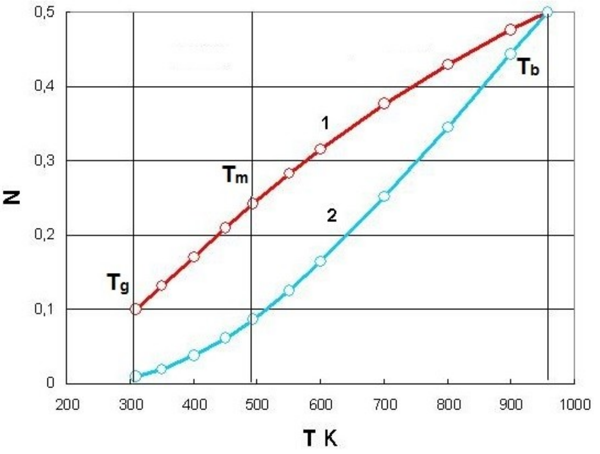

Fig.5. Concentration of alternative bonds in amorphous Se in dependence of temperature. Curve 1 for 10% AB, and curve 2 for 1% AB at T_g (see text for details).

Then, using the second equation in the assumption that wavefronts come into contact at boiling point, i.e., $\Lambda(T_b)=a_0$ and a_0=5.6Å (two “long” bonds – see the previous section), one obtains the temperature dependence for wavelength – Fig.6, again in two varians in concord with Fig.5. When cooling a melt and then supercooled liquid (SQL) Λ decreases, and it is clear that the process must abrupt when the distance between the layers becomes so high that the layers cannot “feel” each other in order to proceed their collective movement, i.e. bond wave. It is proposed that such a “collective catastrophe” occurs at the glass transition temperature, which separate the mobile (liquid-like) region from the immobile (solid-like) region. Below T_g the layers stop their propagation in the network, however, they are not destroyed, as it is confirmed by the presence of FSDP in glass. Moreover, the mobility within the stopped layers remains because alternative bonds concentrated there and so can “feel” each other and create 2D bond waves in the limits of the stopped *d*-layers. The wavefronts of 2D bond waves are equidistant strips populated with alternative bonds.

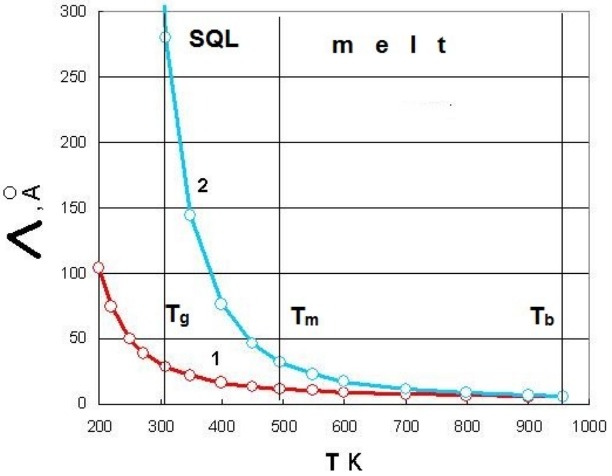

Fig. 6. Calculated temperature dependencies for the 3D bond wave. Curves 1 and 2 corresponds to concentration curves 1 and 2 in Fig.5.

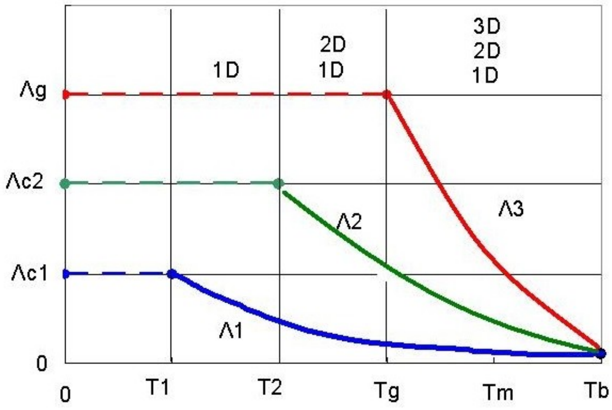

Fig. 7. Temperature intervals for existing of bond waves of different dimensionality. T_1, T_2 and T_g are the "collective catastrophe" temperatures.

In the same manner, when further cooling of glass, AB concentration becomes too low for the critically distant strips can "feel" each other, and at T_2 the second "collective catastrophe" occurs (fig.**7**). Again, alternative bonds within the strips remains near enough to carry the 1D bond wave in the limits of the stopped strips – up to the third catastrophe at T_3, below which alternative bonds freeze completely, being fixed in their positions. The completely immobile structure is a "dead" one. Fortunately, this "death" is reversible: when heating AB concentration increases, and the bond waves of the increased dimensionality come on successively: 1D, 1D+2D, 1D+2D+3D. In such a way one can understand not only the glass transition and softening of glass, the processes of freezing/defreezing of 3D bond waves, but also the so-called "second relaxation" processes and their different behavior in three different regions (0-T_1, T_1-T_2, T_2-T_g), which can be attributed to the δ-, γ- and β-relaxation processes.

5. Bond wave and continuous random network

It is obvious that for the collective behavior of alternative bonds they should be informed about their mutual presence, a property that was named above as "feeling". It seems reasonable that just CRN, in which bond wave spreads, ensures such an information by means of elastic stress arising in the network of conjugated bonds. Thus, CRN cannot move and even exist (remember the old problem of "soft" relaxing units for a mechanically stable glass) without bond wave, but also bond wave cannot exist and even be imaged without CRN, in which it is spreads.

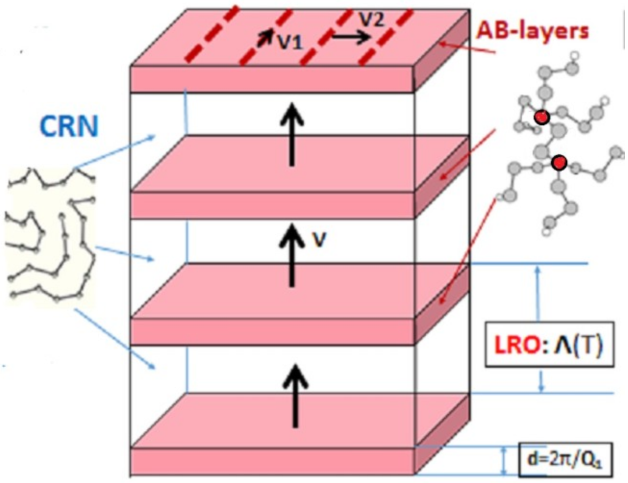

Fig. 8. Interrelation of CRN and bond wave (with Se as an example).

6. Conclusion

Is was argued that glass can be considered as a self-organizing system not only from the convenient "topological" point of view, which seems to be rather a self-assembling of "normal" covalent bonds, but also from the synergetic point of view, taking into account intrinsic chemical-bonding instability and the collective character of this instability. In contrast to topological "intermediate phase", this self-organization of the dissipative type is an intrinsic property of every glass irrespectively of its composition.

On the other hand, interaction of self-assembled CRN and self-organized bond wave (Fig.8) seems to be a fruitful tool for understanding of real glass with their obvious and hidden peculiarities. Moreover, a new way for managing of glass structure/properties by means of external information fields is possible; we have demonstrated such a possibility by means of special experiments in magnetic (Fig.3), elastic (Fig.4) and ultrasonic [29-32] fields.

Acknowledgements

I am grateful to *Prof. S.A. Dembovsky* (1932-2010) for providing me the chemical-bond fundament of this work and for his continuous support during my stay in the *Institute of General and Inorganic Chemistry* of Russian Academy of Sciences (1980-2011). The financial support of *Russian Foundation for Basic Research* (Grants Nos.00-03-32646, 05-03-33047, 09-03-01158) is also acknowledged.

References

[1] W.H. Zachariasen , J. Am. Chem. Soc. **54**, 3841 (1932).
[2] A.R. Cooper, W.H. Zachariasen, J. Non-Cryst. Solids **49**, 1 (1982).
[3] J.C Phillips, J. Non-Cryst. Solids **49**, 1 (1982).
[4] M.F. Thorpe, J. Non-Cryst. Solids **57**, 1 (1983).
[5] J.C. Phillips, M.F. Thorpe, Solid State Commun. **53**, 699 (1985).
[6] P. Boolchand, D.G. Georgiev, B. Goodman, J. Optoelectron. Adv. M., **3**, 703 (2001).
[7] J.C. Mauro, Amer. Ceram. Soc. Bull. **90**, 31 (2011).
[8] P. Boolchand, J. Lucovsky, J.C. Phillips, Philos. Mag. **85**, 3823 (2005).
[9] M. Micoulaut M., J.C. Phillips, J. Non-Cryst. Solids **353**, 1732 (2007).
[10] H. Haken, The Science of Structure: Synergetics. (Van Nostrand Reinhold, 1981).
[11] I. Prigogine, From Being to Becoming: Science and Complexity in the Physical Sciences. (Freeman and Company, 1980).
[12] G. Nicolis, I. Progogine, Self-Organization in Nonequilibrium Systems (Wiley, 1977).
[13] H. Haken, Information and Self-Organization: A Macroscopic Approach to Complex Systems. (Springer, 2006).
[14] S.A. Dembovsky, Mater. Res. Bull. **16**, 1331 (1981).
[15] S.A. Dembovsky, E.A. Chechetkina, J. Optoelectron. Adv. M., **3**, 3 (2001).
[16] S.A. Dembovsky, J. Non-Crystalline Solids **353**, 2944 (2007).
[17] E.A. Chechetkina, J. Optoelectron. Adv. M. **13**, 1385 (2011).
[18] S.A. Dembovsky, S.A. Kozyukhin, E.A. Chechetkina, Mater. Res. Bull. **17**, 801 (1982).
[19] S.A. Dembovsky, E.A. Chechetkina, S.A. Kozyukhin, JETP Lett. **41**, 88 (1985).
[20] E.A. Chechetkina, One-dimention and two-dimention continua in glasses. In: New ideas in glass physics. Proc. of Seminar in memory of V.V. Tarasov (in Russ.). Moscow, Chem.-Tech. Institute, p.149, 1987.
[21] S.A. Dembovsky, E.A. Chechetkina, Philos. Mag. **B53**, 367 (1986).
[22] C. Massobrio, A. Pasquarello, J. Chem. Phys. **114**, 7976 (2001).
[23] E.A. Chechetkina, Solid State Commun. **91**, 101 (1994).
[24] E.A. Chechetkina, J.Phys: Condens. Matt. **7**, 3099 (1991).
[25] A.S. Zyubin, F.V. Grigoriev, S.A. Dembovskii, J. Inorg. Chem. (Russ) **46**, 1350 (2001).
[26] A.S. Zyubin, S.A. Dembovskii, J. Inorg. Chem. **54**, 455 (2009).
[27] A.S. Zyubin, S.A. Dembovskii, J. Inorg. Chem. **56**, 395 (2011).
[28] A.S. Zyubin, E.A. Chechetkina, S.A. Dembovskii, J. Inorg. Chem. **57**, 843 (2012).
[29] E.A. Chechetkina, E.V. Kisterev, E.B. Kryukova, A.I. Vargunin, J. Optoelectron. Adv. M. **11**, 2034 (2009).
[30] E.A. Chechetkina, E.V. Kisterev, E.B. Kryukova, A.I. Vargunin, Inorg. Mater.: Appl. Res. **2**, 360 (2011).
[31] E.A. Chechetkina, E.V. Kisterev, E.B. Kryukova, A.I. Vargunin, Materialovedenie (Russ.) No.12, 3 (2012).
[32] E.A. Chechetkina**.** Crystallization in glass-forming substances: The chemical bond approach. In: Crystallization – Science and Technology (Ed. M.R.D. Andreeta), InTech, p.3, 2012. http://intechopen.com/books/crystallization-science-and-technology/crystallization-in-glass-forming-substances-the-chemical-bond-approach.DOI: 10.5772/50539.

---

*Coresponding author: eche2010@yandex.ru