Původní práce

OXYGEN ANOMALIES OF OXIDE GLASSES

Part III

Miloš Bohuslav Volf

Sklo UNION, Kawalier Glass Works Trust, Concern Corporation, 285 06 Sázava

Received 9. 10. 1979

Anomalous courses of properties are exhibited by germanate glasses (density, refractive index, activation energy of electrical conductivity, thermal expansion coefficient, and the number of oxygen atoms per 1 cm^3 of glass).

Tellurate glasses show anomalous courses of entropy of viscous flow, of thermal expansion and dielectric losses. These changes are ascribed to inversion of rellurates to polytellurates.

A discussion is presented of the systems of anomalies involving a change in the "state" of oxygen atoms. The effect of combined ions is considered as one of conjunction of isovalent cations which is not primarily related to oxygen anomaly.

The anomalies are suppressed by introduction of elements showing a high electronegativity.

ANOMALIES OF GERMANATE GLASSES

Anomalies in the system Na_2O —GeO₂ and K_2O —GeO₂ have been described by Evstropev and Ivanov [1].

The changes in the properties exhibit a distinct relation to the invariant points in the phase diagram and to the assumed change in the co-ordination number.

Ge(IV) is usually compared with Si(IV) because of the same formal valency. However, in its crystalline compounds it is capable of existing with two co-ordination numbers as ${}^{(4)}$ Ge^{IV} and ${}^{(6)}$ Ge^{IV}.

From the binary system $Na_2O-B_2O_3$, glasses Na_2O-GeO_2 differ in that the change is indistinct in the case of density and refractive index in alkali borates, while a distinct maximum arises with glasses Na_2O-GeO_2 and K_2O-GeO_2 (Fig 2).

In the phase diagram [2] there exist 3 invariant points interesting with respect to anomalies: two eutectics and one compound:

	t °C	Na2O mole %	$N_{ m ge}$
$ \begin{array}{ll} E_1 & 2 \operatorname{Na}_2 \mathrm{O} \cdot 9 \operatorname{GeO}_2 + \operatorname{GeO}_2 \\ C & 2 \operatorname{Na}_2 \mathrm{O} \cdot 9 \operatorname{GeO}_2 \\ E_2 & \operatorname{Na}_2 \mathrm{O} \cdot \operatorname{GeO}_2 + 2 \operatorname{Na}_2 \mathrm{O} \cdot 9 \operatorname{GeO}_2 \end{array} $	950 1073 790	8.9 18.2 36.0	$\begin{array}{c} 0.477 \\ 0.450 \\ 0.390 \end{array}$



Fig. 1. Volume characteristics (0.10⁻², V_M, V₁, R_M, R₀) in the system Na₂O-GeO₂.



Fig. 2. Chemical dependence of the properties in the system Na_2O —GeO₂ (H, α , E_a , d, n_D).

In spite of a larger number of invariant points, the phase diagram of the system K_2O —GeO₂ has a similar course [3].

The top boundary of the glassy state lies between 35 to 40 mole % Na₂O [4] close to eutectic E_2 .

The volume characteristics (V_1, R_M, R_0) are plotted in Fig. 1.

The changes in properties and volume characteristics are located in the regions of 6, 10 and 16 mole % Na₂O (Fig. 2).

At 6 mole % Na₂O there are the minima of $R_{\rm M}$ and R_0 . They are situated in the region of eutectic E_1 . Close by (at 7 to 8 mole % Na₂O) there is the maximum of activation energy E_a of electrical conductivity. The chemical dependence of E_a has been calculated by the author from values published by Ivanov, Estropev and Dorochova [5]. The calculated maximum agrees well with the value found by Minami [6].

A volume minimum V_1 occurs at 10 mole % Na₂O. It appears to represent a boundary beyond which M(I) take up energetically advantageous positions in the network.

The thermal expansion coefficient α increases continuously with increasing Na₂O content, showing a mild peak at 10 mole % Na₂O.

The activation energy and entropy of viscous flow calculated according to the values of thermal dependence of viscosity reported by Nemilov [7] exhibit 4 minima and 3 maxima; however, the series of glasses measured on the penetration viscosimeter was considerably incomplete so that no explicit conclusions can be made from the set of data available.

The third distinct region of changes characteristic of binary germanate glasses lies in the region of 16 mole % Na₂O and its position approximately corresponds to the compound C 2 Na₂O . 9 GeO₂. The respective changes are as follows: maxima density [5], refractive index [5], moduls of elasticity in tension [8], microhardness [8] and the number of oxygens per 1 cm³ of glass; minimum — molar volume $V_{\rm M}$ [5].

The maxima are situated approximately where the oxygen attains the highest concentration per cm³, which agrees with minimum V_1 , i.e. the minimum of volume per 1 gramatom of oxygen.

The anomalies of binary alkali-germanate glasses have been attributed by Murthy and Kirby [28] to a change in the co-ordination number y of germanium. However, Kawiya and Sakka [29] found that the ratio of (GeO₆) increases continuously with increasing content of monovalent metal oxides, similarly to the case of (BO₄), and that it attains a maximum (about 30%) between 20 and 30 mole % Na₂O. On the other hand, the anomalies of germanate glasses are concentrated at 16 mole % Na₂O, i.e. approximately at the ratio 1 : 5 where oxygen attains its maximum concentration per cm³ and where V_1 attains a minimum. This fact sheds certain doubts on the explicit explanation that the anomalies of germanate glasses are due solely to a change in the co-ordination number. On the basis of an ESR study, Mylkin and Skalnenko[30] assume that in the case of pentagermanate, the minimum V_1 and the oxygen packing maximum are related to a reduced number of defects in the oxygen network.

In the system K_2O —GeO₂ the anomalies have a course similar to those in the system Na₂O—GeO₂, except that the density and refractive index maxima are shifted to a lower M₂O content which is in agreement with the shift of invariant points in the phase diagram.

No inverse changes in properties have been established in the system B_2O_3 —GeO₂ [4]. This is obviously due to the fact that in a binary system of oxides of two network-forming elements there are no conditions for a change in y resulting from the absence of oxygen donors. Toropov [3] does not specify any phase diagram of the system B_2O_3 —GeO₂.

ANOMALIES OF TELLURATE GLASSES

Anomalies of binary tellurate glasses are known from the studies by Stanworth [9] and from the systematic investigations by Jachkind et al. [10 through 13].

TeO₂ alone does not form any glass. However, it forms binary glasses with oxides of elements having oxidation numbers of (I) to (VI). Their survey has been published by Baynton, Rawson and Stanworth [14]. The potential glass-forming property of tellurates has been predicted by Stanworth from the high electronegativity of tellurium, X = 2.1. The potential glass-forming ability of TeO₂ is also indicated to by its relatively low melting point of 732 °C which may be considered as a measure of thermal energy required for destruction of the bonds [15]. However, the Sun's single bond strength is low (e.g. in comparison with SiO₂ where it amounts to 443.8 kJ Av⁻¹ it is only 284.7 kJ Av⁻¹, i.e. lower 1.5 times) and does not indicate to any glass-forming ability of TeO₂. Introduction of M₂O strongly reduces the melting point of TeO₂, e.g. from 732 °C for TeO₂ down to 413 °C for the eutectic Na₂O . 4 TeO₂ + Na₂O . 2 TeO₂, which is favourable for creating the glassy phase.

In the TeO₂ oxide, tellurium has the co-ordination number y = 6. The oxygens surround the central Te atom in the form of a tetragonal pyramid so that the 4 oxygens constitute an untrue tetrahedron (TeO₄) with various Te—O distances, and the 2 further oxygens are situated asymmetrically at a greater distance apart [59]. This tetragonal pyramid may also be interpreted as a deformed octahedron of the rutile type.

The tellurium polyhedron built in the glass is written by Jachkind in a simplified manner as (TeO_4) .

Because of this unusual type of structural units, the anomalies of tellurates differ in their nature from the other binary systems.

The bridging bonds between the (TeO_4) tetrahedrons are destroyed by the introduction of alkali metal oxide with the resulting change in constitution [10]

$$2 \operatorname{TeO}_{4/2} + \operatorname{Na}_2 O \rightarrow 2 [\operatorname{TeO}_{3/2} O -] \operatorname{Na}^+$$

The change takes place in the region of $Na_2O \cdot 4 TeO_2$.

The invariant points in the system Na_2O —TeO₂ are listed in Table I.

No.		Phase	<i>t</i> , °C	Na ₂ O	TeO_2
		1 1185		mole %	
1	$TeO_2 + Na_2O.4 TeO_2$	E_1	458	16.7	83.3
2	Na_2O . 4 TeO_2	C_1	470	20	80
3	$Na_2O.4 TeO_2 +$				
	+ Na ₂ O . 2 TeO ₂	E_2	413	28	72
4	Na_2O . 2 TeO_2	C_2	435	33.3	66.7
5	Na_2O . 2 TeO_2 +				
5	$+ Na_2O$. TeO ₂	E_3	420	38	62
6	Na ₂ O. TeO ₂		710	50	50
	_				

Table I Invariant points in the system Na_2O —TeO₂ [10]

The glassforming ability in the binary system Na_2O —TeO₂ begins at 10 mole % Na_2O . The volume characteristics V_1 , R_M and R_0 likewise undergo a sudden change at this concentration (Fig. 3). Beyond this deflection, however, the volume charac-



Fig. 3. Volume characteristics in the system Na_2O —TeO₂ (V₁, R_M , R_0).

Silikáty č. 2, 1981

102



Fig. 4. Chemical dependence of the properties in the system $Na_2O-TeO_2[10]$ [d, n_D , ε , tan δ).

M. B. Volf:



Fig. 5. Chemical dependence of the properties in the system Na_2O —TeO₂ [10] (α , $\Delta S\eta$, $t_{10g 8}$, E_a).

teristics are not affected by further increase of the Na_2O content. New volume characteristics therefore result from the formation of a glassy phase. In the phase diagram, however, neither a compound nor an eutectic is found at this concentration. In our view, this boundary is obviously of a chemical nature and is not related to the phase diagram. Na_2O combines with TeO_2 producing tellurates and polytellurates. The significant study by Chatshaturian [22] showed that whereas tellurates oxidate readily, polytellurates are resistant to oxidation. The packing of oxygens and the volume characteristics undergo no distinct changes as soon as the glassy polytellurates have formed.

The changes in properties take place at the eutectic $TeO_2 + Na_2O \cdot 4 TeO_2$ and at the compound $Na_2O \cdot 4 TeO_2$ (Fig. 4.5).

In the eutectic region (16.7 mole % Na₂O) there arise an unexpected minimum of entropy of the viscous flow, a minimum of tan δ and a minimum of the pre-exponential term A in the Arrhenius equation for temperature dependence of log ρ .

Between 16 and 20 mole % Na₂O there is a distinct minimum of the thermal expansion coefficient. The course of V_1 is somewhat disturbed at this point. The position corresponds to the compound Na₂O. 4 TeO₂ in the phase diagram.

The course of the thermal expansion coefficient in terms of composition is similar to that of the binary system Na₂O₋₋B₂O₃. The author agrees with Jachkind [10] that the anomaly of α is due to the transition of [TeO_{4/2}] to [TeO_{3/2}O⁻] mentioned above.

Group A

[=Te-] (-O-Na+)

exhibits more covalent bonds whereas group B

[TeO₃ -O]-Na⁺ has more ionic bonds.

Group A is of mostly non-polar character, group B being markedly polar. Similarly to the system $Na_2O-B_2O_3$, also in the system Na_2O-TeO_2 in the region of polar groups with mostly ionic bonds of Na (I) the thermal expansion increases, whereas it is decreasing in the region of less polar groups or in that of non-polar Na (I) ones.

The glassy phase ceases to exist in the region of the second eutectic $Na_2O \cdot 4 \text{ TeO}_2 + Na_2O \cdot 2 \text{ TeO}_2$ at 30 mole % Na_2O .

A similar course is exhibited by the properties of glasses in the system Cs_2O —TeO₂, the phase diagram of which is similar to that of the system Na_2O —TeO₂ [10].

There arise no anomalies in the system $\text{Li}_2\text{O}-\text{TeO}_2$. The single eutectic in this system is not reflected in any change of properties. This is attributed to the fact that ⁽⁴⁾Li^I is a poor donor of oxygen as a result of small r_i and a low coordination number (y = 4). The system then behaves as a system of two network-forming elements.

DISCUSSION

The results of comparative studies of various systems allow to formulate the conclusion that anomalies are a general phenomenon in binary and some ternary glass systems containing elements that may behave as oxygen donors if their coordination number y is equal to, or larger than 6.

The anomalies are distributed throughout the entire range of the glassy state and concern both geometrical and activated properties.

The anomalous changes in properties (in \mathbf{v} ersion, local extremes, bends) are related to changes in bond.

In the majority of cases, the volume characteristics cannot be topologically connected directly with anomalies, since the change in "state" is not reflected in volume characteristics.

The change in "state" concerns for the most part changes in the "state" of oxygens. Anomalies can be divided systematically into the following five types:

Type I bond anomaly arises at the boundary between two composition differring in the "state" of oxygens. It has the nature of an isoelectric point. The property changes in an inverse manner, e.g. $\tan \delta$ with Na₂O—B₂O₃. The anomaly is related to a change in the oxygen bond from the ionic type to the covalent one during transition from a cross-linked structure to a chainlinked one. This type likewise includes property anomalies connected with separation into immiscible phases.

Type II phase anomalies are similar to type I. These arise in particular in binary systems with compounds and eutectics, in ternary systems at phase boundaries, in eutectics and at the centres of primary phase fields. In eutectics and at phase boundaries the effect involved is contact of two chemically diverse structures incompatible owing to various content of oxygens. At these points, the activation energy usually exhibits a minimum while the change in entropy attains a maximum. The maxima in the curves of chemical dependence of properties are situated at compounds or at the centres of phase fields. Formation of compounds with a stoichiometric composition has the result that the system entropy decreases while the structural arrangement improves.

In systems having similar phase diagrams (e.g. Na_2O-GeO_2 and K_2O-GeO_2) there occur similar chemical dependences of properties and a similar topology of the anomalies. On the other hand, a difference in phase diagram likewise results in a difference in the course of anomalies.

Type III co-ordination anomaly is related to the number of oxygens and to their distribution around the central ion. The change in co-ordination number brings about in particular a change in the geometrical properties. For example, in alkali-alumina-silica glasses, the geometrical properties change in relation with the established change in co-ordination number. A similar course of chemical dependence arises with alkali-germanate glasses. The dual co-ordination of boron does not bring about any anomalies in glassy alkali borates. Only shallow deflections are found in the case of d and $n_{\rm D}$. This may be due to the masking effect of structural units (BO_3) on the (BO_4) ones, or due to the continuous growth in the number of (BO_4) units showing no abrupt changes at certain compositions, or rather due to the fact that during transition from y = 3 to y = 4, both structural units retain their polymerizing ability, while transition from y = 4 to y = 6 results in depolymeration revealed by a distinct change in the course of the property. In the case of boron, a change from y = 3 to y = 4 is responsible for transforming non-polar structural units into polar ones. A change of y = 4 to y = 6 strengthens the ionic bond at the expense of the strongly covalent bond, which has a more distinct effect on the course of a property than a change in polarity. The anomalies should be ascribed to a change in co-ordination number with utmost care only, unless the change in y has been experimentally proved.

Type IV chain-linking anomalies are due to changes in the number of bridging oxygens (Stevel's symbol Y) and non-bridging ones (Stevel's symbol X). The effect of change in Y on the course of various properties has been pointed out by Stevels [16], [17] and by Ray [18]. A change in the chemical dependence of a property in terms of a change in Y has been demonstrated on permittivity [16], on resistivity [19] and on chemical resistance [20]. Type V eci-anomaly (the effect of combined ions) arises even in multicomponent systems. This distinct anomaly that lends itself to be utilized technologically, is in the author's view the single one which does not belong among the oxygen anomalies. The effect of combined ions and a survey of various theories have been described in detail by Isard [21], Day [22] and Volf [23]. For this reason we are going to deal here with its main characteristics only.

1. It occurs with glasses containing a combination of monovalent elements independently of the anionic component (in silicate, borate, phosphate, alumosilicate, germanate, tellurate glasses, in ionic crystals, in glass-ceramics). It is therefore of a general nature.

2. It occurs likewise in non-oxygen compounds (e.g. with chlorides) which casts some doubts on the various existing explanations and theories on this phenomenon. However, it has so far been studied very little in the field of non-oxygen compounds in spite of the possibility that this might be the correct basis for its future interpretation and explanation.

3. In oxide glasses the effect appears only above a certain concentration limit of alkali metal oxides (4 to 12 mole $\% M_2 \bullet$ according to the system). This boundary agrees topologically with the minima of the volume characteristics.

4. The volume characteristics are not brought to extreme values by combinations of alkali metals, so that no geometrical changes, no network reconstructions and no network densification takes place. The geometrical properties likewise remain unchanged.

5. Free energy of the system decreases as a result of the eci effect.

6. The cci effect strongly suppresses diffusion of alkali metal ions. This is related to a distinct increase in resistivity by several orders of magnitude, and an improvement of chemical resistance. The changes in α and tan δ are less distinct.

7. The eci effect occurs both below and above t_{g} .

8. The eci effect is followed by a marked new peak in the case of internal friction. Similar peaks have been found by Doremus [24] in the case of glasses containing hydrogen bonds. As it has been proved that H^+ may form with M^+ phenomena sinular to the eci effect, it is not ruled out that the new large peak is just an effect of the combined ions, similar to the combination of equivalent $M^+ - H^+$ rather than one of a shift of non-bridging oxygens.

The sum of the manifestations of the eci effect provides the impression as if the ions of two isovalent elements were conjugated into a new formation $(A^+ + B^+ \rightarrow A^+B^+)$. This conjunction is possible regardless of the anion and may arise even in nonoxide systems. Bonds between the ions of equal charges are not unknown and are frequently explained by wave mechanics resonancy. However, study of these bonds is extremely difficult and it would be premature to consider them as an explicit cause of the eci effect. The existing knowledge of the eci effect seems rather to justify the assumption that the eci anomaly *does not belong* among explicitly oxygen anomalies and that it should be generally designated as an effect of conjunction from the point of view of phenomenology.

Each of the systems studied has its own chemical model. However, the systems have some common characteristics.

The thermal expansion anomaly has been established in all the binary systems studied and in invert glasses.

The dielectric loss anomaly has been described for binary systems of elements B (III) and Te (IV) and for invert glasses.

Among the geometrical properties, distinct anomalies are exhibited by density,

refractive index and V_1 with alkali-alumina-silica glasses and with alkali-germanate glasses. These anomalies are linked up to changes in permittivity, the Poisson's ratio and the moduli of elasticity. However, the number of measurements performed has so far been inadequate.

Viscosity, with respect to constant B in the VFT equation for Na₂O—B₂O₃, shows maxima at invariant points of compositions 1:3 and 1:4, and minima at relative compositions where E_n is small and ΔS_n is high.

Electrical conductivity (log ϱ and E_a) does not show any sharp local changes. However, the sequence of partial molar additive factors for M (II) changes with changing Y. In all the systems involved, M (I) maintain their ability to transmit electric current even in the course of changes in co-ordination, even when the type of bonds is changed or when the co-ordination oxygen is transferred from the donor to the acceptor.

The amonalous changes in the individual systems have not a common single cause. At a certain proportion to the flat triangular pyramids of (BO₃) the tetrahedron (BO₄) provides conditions for numerous diverse linking up of structural units into chains, rings and spatial cross-linking corresponding to variously complicated borate compounds. The most significant changes in the chemical dependence of properties are situated at the ratio Na₂O : B₂O₃ = 1 : 5 and according to the present author, can be explained by a change in the oxygen bond.

In glasses with a spatial network the oxygen bonds to electropositive elements are mostly ionic in nature even when the element does not form separate ions. In the case of crosslinked glasses we are therefore justified to consider oxygen or molybdenum or silicon as ions and to designate them by symbols O^{2-} , Mo^{6+} or Si^{4+} , as well as to take for granted central ions of polyhedrons.

The relationship between the bond type and the chemical dependence of a property can be better understood when one considers the following two hypothetical rules:

(a) The bond type has its influence on the entire polyhedron, which is in agreement with the conception suggested by Sanderson [25] in that the electronegativity of the molecule is a geometrical mean of electronegativities of all the atoms constituting the molecule. According to this conception, in both cross-linking and chain-linking regions of borate glasses these co-exist in polyhedrons with a covalent bond with polyhedrons showing an ionic bond. The property then changes continuously (in the form of open V), as in the case of the thermal expansion coefficient, or sharply locally, as is the case of the contact between two structures, in each of which one bond type is prevailing, as is e.g. the case of dielectric losses in the system $Na_2O-B_2O_3$ (the isoelectric effect type).

(b) Elements with $y \ge 6$ may be donors of one oxygen only. The bond of the other remaining oxygens is strengthened by the loss of oxygen from the co-ordinating oxygen envelope of the cation.

In the case of the V-phenomenon, the elements situated along the two branches were distinguished according to the degree of their ionicity and covalency. During transition from crosslinking to chain-linking the distribution of elements along the two branches is changed in a mirror-like way. Elements with prevailing ionic bonds are shifted from the "ionic" branch (I) to the "covalent" branch (II). The change in the bond is related to the change in the bond type of oxygen, as has been explained in connection with borate anomalies.

The anomalies are suppressed by introduction of elements showing higher electronegativity X.

Alkali metal ions are bound in binary glasses mostly by Coulombic forces. As soon as an element with a higher electronegativity is introduced, more complex formations arise and the details of the bonds are changed (in an imperceptible manner in the case of multicomponent glasses). The equilibria between the components depend mainly on the field strength z/a^2 , and on the ability of the donor to provide oxygen. Gan Fusi [46] expresses the ability of an element as a donor by the ratio of its electronegativity $X_{\rm M}$ to that of sodium $X_{\rm Na}$.

The total capability of donors ΣD in a given glass is then expressed by the sum

$$\Sigma D = \Sigma \left[\frac{X_{\text{Na}}}{X_i} \cdot (m_i) \right]$$
(17)

For Na (I), $\Sigma D = \Sigma(0.9:0.9)$ $(m_i) = 1$ (m_i) , for Mg (II), $\Sigma D = (0.9:1.2)$ $(m_i) = 0.75$ (m_i) .

The electronegativity values reported by Gordy and Orville-Thomas [26] can be conveniently used for the respective calculations.

Introduction of elements with a higher electronegativity thus suppresses the overall effect of donors on anomalies, and in particular, introduction of acceptors (Al, Ga, B) to multicomponent glasses reduces the proportion of ionic bonds, so that those anomalies which depend on donorship or polarity of mass particles are suppressed.

The overall bond energy is affected by the introduction of an element with higher electronegativity X in dependence on the basic composition of the glass, the glass properties being changed at the same time.

It has been proved that the length of bonds and the angles between the polyhedrons are changed by the entry of cations into monooxide glasses, and that the bonding energy becomes more diverse and complex [27]. The partial molar additive factor g_i , which holds exactly only for chemically close compositions, also includes the bond length and the angles between the polyhedrons. When this structural characteristics are changed by changing the sum of electronegativities and by cross-linking, this necessarily results in changes in partial molar additive factors g_i ; however, all substantial anomalous changes in properties are suppressed at the same time, so that additivity can be applied while obtaining relatively small deviations from experimental values.

Introduction of a second oxide into a monooxide glass will therefore change the bond length as well as angles between the polyhedrons, but only when the concentration of the entering oxide has exceeded a certain threshold limit. This limit lies between 4 to 6 mole % of the oxide. Various anomalies are found at this concentration in binary glasses. This is the case of oxides of Al, Ti, Sn, Zn combined with an oxide of a network forming element. Below the threshold concentration, alumina does not affect the monooxide network, exhibiting solely its favourable effect on devitrification. Above the threshold concentration, Al₂O₃ brings about a change in the primary phase and suppresses devitrification in contrast to the former case.

The present study had the aim of pointing out some more recent aspects and a new complex approach which may bring about a revision of the existing ideas of anomalies, in particular those of borate glasses, with respect to a unified method of glass preparation and measurement aimed at reducing to a minimum the differences in the results of measurements obtained in various laboratories.

The phenomenological chemical model based on existing tabellated data will have to be further verified.

M. B. Volf:

SUMMARY

1. Anomalies represent deviations from ideal linear additivity.

2. Anomalies occur in binary and ternary systems, when the system contains, apart from a network-forming element, an oxide of a modifying element with co-ordination number $y \geq 6$. Anomalies have been found in alkali systems containing oxides of elements B, Si, P, Ge and Te.

3. Anomalies arise throughout the entire range of the glassy state.

4. Anomalies have in common a change in the "state" of oxygens which is ascribed to a change in the bond type from the ionic to a covalent one.

5. Anomalies are classified systematically into the following 5 groups:

(1) the bond type at the point of contact between compositions differring in the "state" of oxygen (anomaly of alkali borates, phosphate glasses and invert glasses);

(2) the phase type related to invariant points in phase diagrams (the course of viscosity of glassy alkali borates, the anomaly of tellurate glasses);

(3) the co-ordination type related to a change in the co-ordination number. The anomalous changes arise in particular in connection with properties related to geometrical arrangement of mass particles. It has been established in alkali-alumina-silica glasses and in germanate glasses;

(4) the cross-linking type related to the number of bridging oxygens in the polyhedron (inversion change in chemical resistance with silicate glasses);

(5) the type of combined isovalent ions (changes in resistivity and chemical resistance).

6. Distinct changes in properties arise when a cross-linked polymer is transformed to a chain-linked one. The change is revealed by inversion of the thermal expansion coefficient.

7. The course of activation energy usually differs from that of the chemical dependence of the respective property.

8. Anomalies are suppressed by the entry into the system of an element with a high electronegativity.

References

- [1] Evstropev K. S., Ivanov A. O.: Advances in Glass-Technology (II). VIth Intern. Congress on Glass, New York 1962, p. 79.
- [2] Murthy M. K., Aguayo J.: J. Amer. Cer. Soc. 47, 444 (1964).
- [3] Toropov N. A. et al.: Composition Diagrams of Silicate Systems (in Russian), Izd. Nauka, Leningrad 1969 (I).
- [4] Mazurin O. V.: The Properties of Glasses and Glass-Forming Melts (in Russian), Izd. Nauka, Leningrad (I) 1973; (II) 1975; (IIIa) 1977; (IIIb) 1978.
- [5] Ivanov A. O., Evstropev K. S., Dorochova M. L.: Optiko-mech. prom. 31 (1962).
- [6] Minami T., Fujikawa N., Tanaka M.: J. Cer. Assoc. Japan 85, 384 (1977).
 [7] Nemilov S. V.: Sh. prikl. chim. 43, 2602 (1970).
- [8] Shaw R. R.: J. Amer. Cer. Soc. 54, 170 (1971).
- [9] Stanworth J. E.: J. Soc. Glass Techn. 36, 217 (1952); 38, 425 (1954).
- [10] Jachkind A. K.: Collection The Structure and Physico-Chemical Properties of Inorganic Glasses (in Russian), Ed. A. G. Vlasov and V. A. Florinskaya. Izd. Chimia, Leningrad 1974. Part VIII, p. 285-352.
- [11] Jachkind A. K.: Glass-Forming Compositions 1964 (in Russian), Ed. 4, Minsk 1964, p. 50; Glass-Forming Compositions 1974, M-L, p. 100; J. Amer. Cer. Soc. 49, 670 (1966); Physico-Chemical Properties of Tellurate Glasses and Composition of New Optical Glasses on their Basis (in Russian), (Thesis 1973).
- [12] Jachkind A. K., Martychenko N. S.: Neorg. Mater. 6, 1459 (1970).
- [13] Jachkind A. K., Tatarnicev B. V., Makarova T. M.: Neorg. Mater. 8, 1654 (1972).

- [14] Baynton P. L., Rawson H., Stanworth J. E.: IVe Congrès International du Verre, Paris 1956. I-5.
- [15] Rawson H.: IVe Congrès International du Verre, Paris 1956, I-6.
- [16] Stevels J. M.: Glass Ind. 35, 657 (1954); Verres Réfract. 7, 91 (1953).
- [17] Stevels J. M.: Progress in the Theory of Physical Properties of Glass. Elsevier, Amsterdam 1948.
- [18] Ray N. H.: J. Non-Cryst. Solids 15, 423 (1974).
- [19] Stevels J. M.: Glass Ind. 35, 69, 100, 102, 135, 160 (1954).
- [20] Weberbauer A.: Glast. Ber. 10, 361, 426 (1932).
- [21] Isard J. O.: J. Soc. Glass Techn. 43, 113 (1959).
- [22] Day D. E.: J. Non. Cryst. Solids 21, 343 (1976).
- [23] Volf M. B.: Chemistry of Glass (in Czech) SNTL, Prague 1978.
- [24] Doremus R. H.: Glass Science. John Wiley and Sons, New York 1 1973.
- [25] Sanderson R. T.: J. Chem. Educ. (I) 29, 539 (1952); (II) 31, 2 (1954); (III) 31, 238 (1954).
- [26] Gordy W., Orville-Thomas W. J.: J. Chem. Phys. 24, 436 (1956).
- [27] Balta P., Balta E.: Introduction to the Physical Chemistry of the Vitreous State. Editura Academiei, Bucarest 1971 — Abacus Press, Tunbridge Welles 1976.
- [28] Murthy W. K., Kirby P. L.: Phys. Chem. Glasses 5, 1964, 144.
- [29] Kawiya K., Sakka S.: Phys. Chem. Glasses 20, 1979, (3), 60.
- [30] Mylkin V. A., Skelnenko N. J.: Inorg. Mater. Consultants Bur. Transl. 7, 1971, 1959.

KYSLIKOVÉ ANOMÁLIE OXIDOVÝCH SKEL, ČÁST III

Miloš Bohuslav Volf

Sklo UNION k. p. Sklárny Kavalier, Sázava

V germaničitanových sklech probíhají anomálně geometrické vlastnosti (hustota, index lomu, dále aktivační energie elektrické vodivosti, koeficient teplotní roztažnosti a počet kyslíků na l cm³ skla).

- U telluričitanových skel probíhají anomálně entropie viskozního toku, teplotní roztažnost a dielektrické ztráty. Objemové charakteristiky se ohybově mění při 10 mol. % Na₂O. Změna
- je přičítána přechodu telluričitanů na polytelluričitany.
- 1. Anomálie představují odchylky od ideální lineární aditivity.
- 2. Anomálie se vyskytují v binárních a ternárních systémech, obsahuje-li systém vedle oxidu síťotvorného prvku oxid prvku modifikujícího, s koordinačním číslem $y \ge 6$. Anomálie byly nalezeny u alkalických systémů s oxidem prvku B, Si, P, Ge a Te.
- 3. Anomálie se vyskytují v celém rozsahu skelného stavu.
- Společné anomáliím je změna ,,stavu" kyslíků, kterou přisuzujeme změně typu vazby z iontové na kovalentní.
- 5. Anomálie se systematicky třídí do 5 skupin:
 - typ vazebný na styku složení lišících se "stavem" kyslíku (anomálie alkalických boritanů, fosforečnanových skel a skel invertních);
 - (2) typ fázový vztažený k invariantním bodům ve fázových diagramech (průběh viskosity u skelných alkalických boritanů, anomálie telluričitanových skel);
 - (3) typ koordinační související se změnou koordinačního čísla. Anomální změny se projevují zejména u vlastností, souvisejících s geometrickým uspořádáním hmotových částic. Byl nalezen u skel alkalicko-hlinito-křemičitých a u skel germaničitanových;
 - (4) typ zesítění vztažený k počtu můstkových kyslíků v polyedru (inverzní změna chemické odolnosti u křemičitanových skel);
 - (5) typ kombinovaných stejnomocných iontů (změny měrného odporu a chemické odolnosti).
- K výrazným změnám vlastností dochází při přechodu ze zesítěného polymeru na polymer zřetězený. Změna se projeví v inverzi koeficientu teplotní roztažnosti.
- 7. Aktivační energie nemívají stejný průběh jako chemická závislost příslušné vlastnosti.
- 8. Vstupem oxidů prvků s vysokou elektronegativitou se anomálie potlačují.

Obr. 1. Objemové charakteristiky (0.10⁻². V_M, V₁, R_M, R₀) v systému Na₂O-GeO₂.

- Obr. 2. Chemická závislost vlastností v systému Na_2O-GeO_2 (H, α , E_a , d, n_D).
- Obr. 3. Objemové charakteristiky v systému Na₂O-TeO₂ (V₁, R_M, R₀).
- Obr. 4. Chemická závislost vlastností v systému Na_2O — TeO_2 [10] (d, n_D , ε , tang δ).
- Obr. 5. Chemická závislost vlastností v systému Na₂O—TeO₂ [10] (α , ΔS_{η} , $t_{\log 8}$, E_{α}).

M. B. Volf:

КИСЛОРОДНЫЕ АНОМАЛИИ ОКСИДНЫХ СТЕКОЛ III

Милош Богуслав Вольф

Скло УНИОН, конц. предпр. Скларны Кавалиер, Сазава

В германатных стеклах протекают аномально свойства (плотность, показатель преломления), далее энергия активации электропроводности, коэффициент термического расширения и количество кислородов на 1 см³ стекла. Изменение геомстрических свойств вызывается изменением координационного числа Ge (IV) с y = 4 на y = 6.

У теллуритных стекол протекают аномально энтропия вязкого течения, коэффициент термического расширения и диэлектрические потери. Объемные характеристики изгибом изменяются при 10 мол. % Na2O. Изменение вызывается переходом теллуритов в полителлуриты.

- 1. Аномалий представляют собой отклонения от идеальной линейной аддитивности.
- 2. Аномалии встречаются в бинарных и тернарных системах, когда в них содержится кроме окисла структурирующего элемента окисел модифицирующего элемента с координационным числом $y \ge 6$. Аномалии были найдены у щелочных систем с окислом элемента B, Si, P, Ge и Те.
- 3. Аномални встречаются в общих пределах стеклообразного состояния.
- 4. Общим признаком аномалий является изменение "состояния" кислородов, вызываемое изменением типа ионной связи в ковалентную связь.
- 5. Аномалии систематически подразделяют в 5 групи:
 - (1) связывающий тип на пределе состава, отличающийся "состоянием кислорода" (аномалии щелочных боратов, фосфатных стекол и инвертных стекол);
 - (2) фазовый тип соотносящийся с инвариантными точками в фазовых диаграммах (ход вязности у стеклообразных щелочных боратов, аномални теллуритных стекол);
 - (3) координационный тип, связанный с изменением координационного числа. Аномальные изменения проявляются именно у свойств, связанных с геометрическим упорядочением массовых частиц. Он был найден у щелочноалюмо-силикатных и германатных стекоп;
 - (4) тип структурирования, соотносящийся с количеством кислородных мостиков в полиэдре (инверсионное изменение в химической устойчивости у силикатных стекол);
 - (5) тип комбинированных изовалентных ионов (изменення удельного сопротивления и химической устойчивости).
- 6. Резкие изменения свойств наступают при переходе из сипитого полимера в ценеобразный полимер. Изменение проявляется в инверсии коэффициента температурного
- расширения. 7. Энергии активации не имеют, как правило, ход, совпадающий с ходом химической зависимости соответствующего свойства.
- 8. Присутствием окислов элементов с высокой электроотрицательностью аномалии подавляются.
- Рис. 1. Объемные характеристики (О. 10⁻², V_M, V₁, R_M, R₀) в системе Na₂O-GeO₂.
- Рис. 2. Химическая зависимость свойств в системе Na_2O —GeO₂ (H, α , E_a , d, n_D).
- Рис. 3. Объемные характеристики в системе $Na_2O TeO_2$ (V_1, R_M, R_0). Рис. 4. Химическая зависимость свойств е системе $Na_2O TeO_2$ [10] (d, n_D , ε , tang δ).
- Puc. 5. Химическая зависимость свойств в системе Na_2O —TeO₂ [IO] ($\alpha, \Delta S\eta, the s, E_a$).