

## Původní práce

### OXYGEN ANOMALIES OF OXIDE GLASSES PART II

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*In silicate glasses the boundary of anomalous changes is represented by trisilicate where the cross linked structure changes into a chain-linked one. An inversion occurs in the chemical resistance to water and acids, a deflection arises in the course of electrical conductivity. Metasilicate is a boundary of inverted glasses, which show an inverse change in the thermal expansion coefficient and  $\tan \delta$  at the point of this composition. In contrast to glasses  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ , however, the coordination number remains unchanged.*

*In alkali-alumina-silica glasses the geometrical properties are changed in relation to  $R_M$  at the boundary  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1 : 1$  when  ${}^{(4)}\text{Al}$  is changed to  ${}^{(6)}\text{Al}$ . The cause of the minimum of dielectric losses and that of the aluminoborate anomaly in relation to thermal expansion are discussed.*

*With phosphate glasses, in the region of the ratio  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 1 : 1$ , the change in thermal expansion is similar to that of borates. Alkali phosphates in vitreous state differ from borates in the course of the elasticity modulus.*

#### THE ANOMALIES OF SILICATE GLASSES

With binary and ternary silicate glasses there arise three regions of anomalies the boundaries of which are constituted by trisilicate and metasilicate.

The first anomaly is encountered in binary and ternary glasses with an  $\text{SiO}_2$  content exceeding that in trisilicate, that is in „acid“ glasses. In this case the course of the property is not linear in terms of increasing content of oxides of the modifying elements. When changing continuously the  $\text{SiO}_2$  content in the ternary system  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$  at a constant  $\text{Na}_2\text{O}/\text{CaO}$  ratio, the properties (density, refractive index, thermal expansion) will change according to formally hyperbolic curves. This is explained so that property A changes with the ratio of oxides (I) of the V-phenomenon branch towards the oxides of branch (II), that is for the given system that of the ratio  $(\text{Na}_2\text{O} + \text{CaO}) : \text{SiO}_2$  [1]. As the anomalies have been defined in the introduction as all deviations from ideal linear additivity, which holds strictly for mixtures only, the hyperbolic course of properties in silicate systems in question can also be included in the anomalies. Balta [2] ascribes the anomaly to the formation of  $(\text{O}^--\text{M}^+)$  dipoles. In silicate glasses the first non-bridging  $-\text{O}$  is bound firmly to Si (IV). Its Coulombic interaction with Na (I) is therefore weaker. The partial charge of oxygen increases and the ionic bond becomes stronger proportionally with the raising number of non-bridging oxygens  $-\text{O}$  in the tetrahedron. As the electric moment of the dipole depends on the size of the partial charges and on their mutual distance, the intensity of possible Coulombic interactions increases with the number of dipoles in the tetrahedron. The bond

strength and thus also the related property therefore change with the ratio of the modifying oxides to the network-formers, that is hyperbolically.

Seddon, Tippett and Turner [3] established a deflection on the curves  $\log \rho = f(c)$  (Fig. 1). The same results have been obtained by Blank [4]. Stevels [5] noted that the deflection lies at the boundary  $Y = 3$ , i.e. at the point where the composition with 3 bridging oxygens +O passes into that with 2 bridging oxygens. The activation energy of electrical conductivity decreases continuously with increasing  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  ratio, showing three very flat minima, which can be hardly related to any

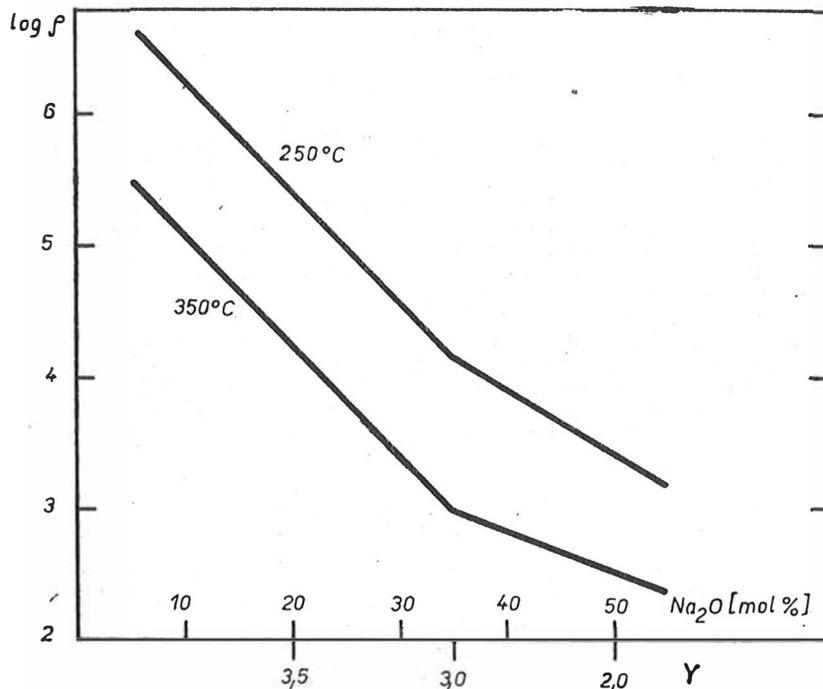


Fig. 1. The course of resistivity in the system  $\text{Na}_2\text{O}-\text{SiO}_2$  at  $Y = 3$  [3], [4], [5].

definite compositions. In the case of viscosity, the values of constants  $A$ ,  $B$ ,  $T_0$  and characteristics  $E_\eta$  and  $\Delta S_\eta$ , calculated from the values reported by Preston [6] and Eipeltauer [7], unfortunately provide an incomplete, incomparable and non-interpretible picture (Fig. 2).

The  $Y = 3$  boundary is distinct in the case of inversion of chemical resistance.

The anomalies of chemical resistance to water in ternary systems have been described by Enns [8] and those to acids by Weberbauer [9].

Enns and Weberbauer (Fig. 3) used the glass 82 ( $\text{SiO}_2 + \text{MO}[\text{M}_2\text{O}_3]) \cdot 18 \text{Na}_2\text{O}$  (%) which has been introduced by Gehlhoff and Thomas for the determination of the changes in properties in terms of changing composition, and replaced  $\text{SiO}_2$  with MO oxides ( $M = \text{Zn}, \text{Mg}, \text{Ca}, \text{Ba}, \text{Pb}$ ) or  $\text{M}_2\text{O}_3$  ( $M = \text{B}, \text{Al}$ ). Enns determined the total water extraction loss (grain size 0.5–1 mm, 100 °C, 7 hours) by weight of the evaporation residue, while Weberbauer used the classical extraction method

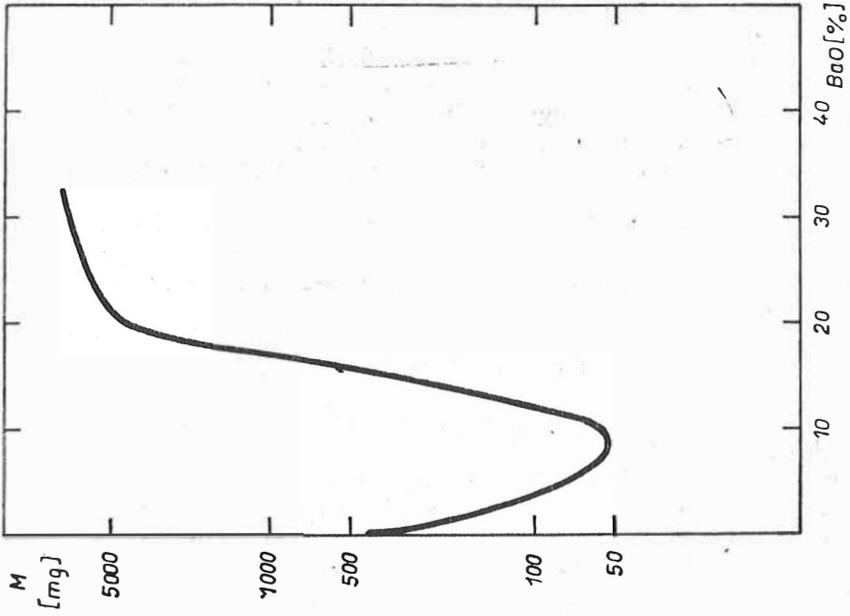


Fig. 3. Inversion of acid extraction loss in the system  $\text{Na}_2\text{O}-\text{BaO}-\text{SiO}_2$  [9].

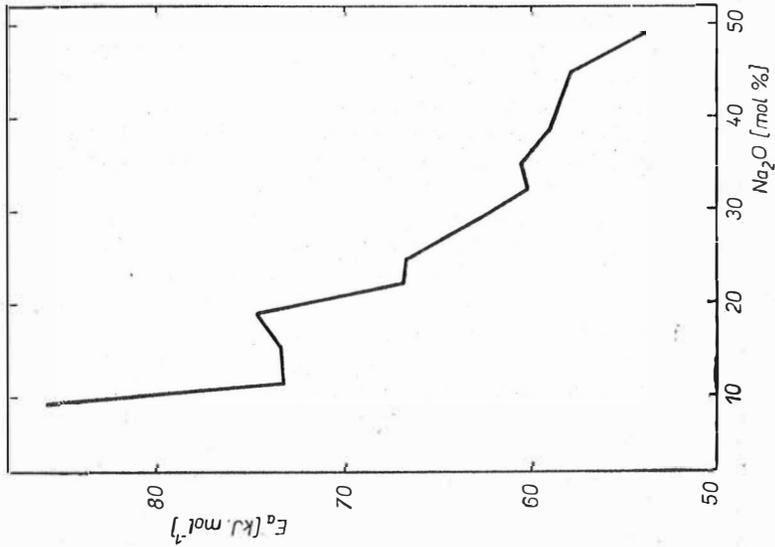


Fig. 2. The course of the chemical dependence of electrical conductivity activation energy  $E_a$  calculated from the values given in [3], in the system  $\text{Na}_2\text{O}-\text{SiO}_2$ .

(grain size 0.3—0.49 mm, 10% HCl, 100 °C, 5 hours), in which HCl was used instead of H<sub>2</sub>O and the extraction loss was also expressed in terms of dry residue weight.

Distinctly inverse changes in the course of chemical resistance have been established within the given range of concentration of MO and M<sub>2</sub>O<sub>3</sub> oxides. Enns found a parabolic course for MgO, PbO and B<sub>2</sub>O<sub>3</sub>, a hyperbolic one for CaO, ZnO, BaO and Al<sub>2</sub>O<sub>3</sub>. Weberbauer has established a parabolic course of chemical resistance to acids in relation to stepped-up content of Mg, Ca, Ba, Pb, Zn, Al and B oxides.

On introduction of the above oxides into Gehlhoff's glass Na<sub>2</sub>O . 4 SiO<sub>2</sub> (as substitution for SiO<sub>2</sub>) the extraction loss decreases steeply down to the minimum, thereafter showing a steep increase. Such a drastic change was unexpected.

The anomaly has so far eluded explanation.

For the purpose of theoretical treatment of the problem it is more convenient to express the composition of Enns' and Weberbauer's glass in mole % instead of % by weight.

The initial binary glass (SiO<sub>2</sub> 80%, Na<sub>2</sub>O 20% by wt.) corresponds to tetrasilicate Na<sub>2</sub>O . 4 SiO<sub>2</sub>.

Introduction of MO or M<sub>2</sub>O<sub>3</sub> first results in improved chemical resistance to acids (decreasing extraction loss) because the elements have a higher bond strength *F* between M and O and show a higher electronegativity *X*.

The extraction loss will decrease until the ratio

$$\psi = \frac{\text{SiO}_2}{\text{MO} + \text{M}_2\text{O}} \quad \text{or} \quad \psi = \frac{\text{SiO}_2}{\text{M}_2\text{O}_3 + \text{M}_2\text{O}} \quad (1)$$

falls below 3, that is below the trisilicate boundary.

As soon as the trisilicate boundary is exceeded, the extraction loss curve is inflected, the loss being steeply increased. According to Mackenzie [10] trisilicate represents a limit of spatial network forming which is then changed into chain-linking.

This explanation of the inversion in chemical resistance is supplemented by the values of Kühne's index  $v_n$  which has been mentioned in the introduction to Part I (cf. Silicates 1980, issue 4, p. 292, formula 11).

Kühne's formula shows that entry of an element with  $z > 1$  into binary glass Na<sub>2</sub>O . 4 SiO<sub>2</sub> changes the network forming as well as the overall relative bond strength of glass.

For bond strength *F* we may substitute into formula (11) the values of the Dietzel's electrostatic field strength  $z/\alpha^2$ , or the Magnus' number  $U_M$  (for bond energy), or electronegativity *X*, or the unit dissociation energy  $e_v$ . Values of these bonding potentials are listed in Tables I and II in [13]. The first term of Kühne's formula (1) is in a satisfactory agreement with the V-phenomenon [12], [13] as it relates the bond strengths of elements lying along the „covalent“ branch (II) to those of elements situated along the „ionic“ branch (I) of the V-phenomenon. However, the ratio of bond strengths between (NWF + NWD) : MOD in Kühne's formula does not provide a complete information. It takes into account only the bonding function of the cations, but does not consider the „state“ of oxygens which prevail by volume in the structure of oxide glasses. The relative bonding strength of glass should therefore be supplemented with another term including information on the degree of cross-linking, expressed as the ratio of non-bridging oxygens -O to the total number of oxygens



in the given glass.

Plotting of Kühne's indexes  $v_n$  for glasses of the individual ternary systems  $\text{Na}_2\text{O}-\text{MO}-\text{SiO}_2$ , where  $\text{M} = \text{Al}, \text{Mg}, \text{Ca}, \text{Zn}, \text{Ba}, \text{Pb}$  versus the respective values of the given property yields a curve the maximum of which determines the value of index  $v_n$  (inv) corresponding to the glass composition at the point of inversion. The  $v_n$  values for the compositions for the individual systems are listed in Table I.

Table I

The composition of Weberbauer's glasses (in mole %) and Kühne's index  $v_n$  at the point of inversion of chemical resistance to acids

M	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Na}_2\text{O}$	MO	$v_n$
Mg	0.220	76.341	17.162	6.276	0.773
Zn	0.515	74.283	17.911	7.911	0.953
Ca	0.283	74.157	16.953	8.606	1.038
Ba	0.281	74.204	18.939	6.576	1.1599
Pb	0.263	73.743	19.934	6.060	1.162
Al	9.458	73.846	17.145	—	0.7069

When substituting for  $f$  in Kühne's equation the bond strength  $z/a^2$ , the Kühne's index  $v_n$  (inv) for the respective composition at the point of maximum chemical resistance brought about by introduction of the elements having  $z > 1$ , is in the range 0.7 to 1.2. The value of the index in the inversion point,  $v_n$  (inv) increases parabolically with increasing ion deformability  $R_i$  as shown by Table II.

Table II

Kühne's index  $v_n$  (inv) and ionic refractivity  $R_i$  of elements

M	$v_n$ (inv)	$R_i$
Mg	0.773	6.05
Zn	0.953	9.7
Ca	1.038	10.25
Ba	1.60	16.8
Pb	1.62	27.4
Al	0.71	6.8

The above considerations allow to formulate the following conclusions:

(1) In the case of glasses  $\text{Na}_2\text{O}-\text{MO}-\text{SiO}_2$  the inversion of chemical resistance arises at the cross-linking/chain-linking boundary.

(2) Kühne's index  $v_n$  changes according to the deformability of the ion of the

entering element  $M$  which is determined quantitatively by the ionic refractivity values  $R_i$  established by Young and Finn. The higher the  $R_i$  of the entering element  $M$ , the higher the Kühne's index  $v_n$  (inv) corresponding to the glass composition at the point of inversion.

In the systems  $\text{Na}_2\text{O}-\text{MO}-\text{SiO}_2$ , Kühne [11] found similar anomalous changes in electrical conductivity expressed by the  $t_k$  100 value. The changes are characteristic in that beyond the inversion the sequence of partial properties of oxides is changed only with elements  $M$  (II) namely from  $\text{BaO} \rightarrow \text{MgO}$  to  $\text{MgO} \rightarrow \text{BaO}$ . The change in the sequence of oxides in the V-phenomenon is therefore analogous to that found for inverse glasses (see further below). Additive molar factors are shifted beyond the cross-linking/chain-linking boundary from the ionic branch to the covalent one. The change from the ionic bond of oxygen to a covalent one is considered responsible for this shift, which also arises in the case of borate glasses.

Trap and Stevels [14], [15] discovered the existence of glasses in a composition range where the network-forming elements do not form a continuous network. Inversion of certain properties occurs in these systems; the term "invert glasses" has been suggested for the respective types.

Invert glasses have been found to be formed in systems based on  $\text{SiO}_2$  [14],  $\text{B}_2\text{O}_3$  [16] as well as on  $\text{P}_2\text{O}_5$  [14].

As regards chemical composition, invert glasses are characterized by

(a) a combination of oxide couples with oxygen numbers I and II, e.g.  $\text{SiO}_2-(\text{Na}_2\text{O}, \text{K}_2\text{O})-\text{CaO}, \text{BaO}$ ;

(b) a low  $\text{SiO}_2$  content (below 50 mole %).

The existence of invert glasses has been explained by the simultaneous effect of the following two phenomena [13]:

(i) by the eci effect of combined ions of equal valency (e.g.  $\text{Na}^{\text{I}}\text{K}^{\text{I}}$  or  $\text{Ca}^{\text{II}}\text{Ba}^{\text{II}}$ ),

(ii) by the induction effect of network-forming elements.

Entropy of the system is raised by the eci effect [17]. The increase in entropy is related to the disarrangement of mass particles [18] and as the disarrangement is typical for the vitreous state, the increase in entropy resulting from the eci effect is responsible for increasing the glassiness.

The term "glassiness" has been introduced by Dietzel [19] and is equal to the inverse value of crystallization rate; it describes the ability of the system to form glass resistant to devitrification.

Glassiness is further stabilized by the induction effect of network-forming elements, i.e. by their presence even in very small amounts in such exceptional glass systems not comprising mostly network-forming elements, such as glasses containing 90%  $\text{PbO}$  + 10%  $\text{SiO}_2$  or the invert glasses mentioned above.

These exceptional glasses always comprise a group of prevailing components which are either unable to form glass alone (e.g.  $\text{PbO}$ ) or form glass with difficulty (glasses  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ). However, they are capable of forming more stable glasses in the presence of another minor component having a high bond strength  $F$ , and represented by an oxide of a network former in such a small amount that no continuous spatial network can be formed.

The presence of the minor element prevents rearrangement into a crystalline network by the induction effect.

The "induction effect" is the term suggested for the phenomenon [13] that an element with a high bond strength is capable of "inducing" in another element in the  $M-\text{O}$  bond such an increase in the share of covalent bond with

oxygen that the element acquires capabilities for polymer formation. Let us assume that the bond between the prevailing component and oxygen involves such orbit overlaps, that the share of the covalent bond is strongly increased. This effect will act against rapid shifts inside the solidifying melt and against the formation of arranged and oriented structures. The induction effect is likewise encountered in non-oxide glasses.

Inversions of properties occur in invert glasses if the mean number of non-bridging oxygen  $Y$  in the polyhedron of the network-forming element falls below 2. If in the  $(\text{SiO}_4)$  tetrahedron, the  $(\text{O}=\text{PO}_3)$  tetrahedron or in the  $(\text{BO}_3)$  triangular pyramid there are at the most 2 bridging oxygens  $+O$ , spatial cross linking cannot take place. Polymeration can only be effected by chain-linking.

Inversions in the properties of invert glasses had been established in the case of dielectric losses, viscosity and thermal expansion, but not in that of density and refractive index, that is with geometrical properties. However, a number of properties have not been investigated, so that no complete picture is available for invert glasses.

Supplementary elements show likewise anomalous effects in invert glasses.  $\text{Pb(II)}$  and  $\text{Zn(II)}$  behave as intermediate ones owing to their high ionisation energy.  $\text{Ti(IV)}$  in invert glasses reduces unexpectedly the dielectric losses and viscosity while raising permittivity.

When a modifying element is introduced into an invert glass, it usually suppresses the inversion of properties as a result of strengthening and stabilization of the glass. Inversion is also suppressed by strongly deformable elements.

Sharp deflections again arise in the case of activation energy, which supports the idea that inversion in the case of invert glasses involves a change in the "state" of oxygens similarly to the system  $\text{M}_2\text{O}-\text{B}_2\text{O}_3$ .

The thermal expansion coefficient  $\alpha$  behaves in invert glasses in a similar way as it does in alkali borates. When the content of alkali metal oxides is raised beyond the limit of around  $Y = 2$ , the  $\alpha$  coefficient shows an inverted decrease similarly to  $\tan \delta$ . In contrast to this, viscosity increases below the  $Y = 2$  boundary. As in the case of alkali borates, these changes are explained by the inversion change of ionic bonds of oxygens to covalent bonds.

The volume characteristics in the system  $\text{Na}_2\text{O}-\text{SiO}_2$  are quite monotonous, free from deflections and inversions.  $V_M$  and  $R_M$  decrease continuously with increasing  $\text{Na}_2\text{O}$  content, while  $V_1$  and  $R_0$  increase uniformly. A small minimum arises in the case of  $V_1$  between 4 to 6 mole %  $\text{Na}_2\text{O}$ .

#### ANOMALIES IN ALKALI-ALUMINA-SILICATE GLASSES

The properties which have so far been found to undergo anomalous changes in the system  $\text{M}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  include density and refractive index [20], [21], activation energy of electrical conductivity [22],  $\tan \delta$  [23] and viscosity to a limited degree. As regard volume characteristics, an anomaly was found in the case of  $R_M$ . These properties show a distinct minimum at the ratio  $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1 : 1$ . The change in properties at this ratio is not related to the  $\text{SiO}_2$  content.

In the ternary system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  [24] the boundary ratio 1 : 1 corresponds to the boundary between the regions of albite, nepheline and carneigieite (with  $y = 4$ ) and between the mullite and corundum regions (with  $y = 6$ ).

The anomalous change in properties in the system of oxides  $\text{M}-\text{Al}-\text{Si}$  is in agreement with the hypothesis suggested by Galant [25], namely that  $\text{Al(III)}$  in conventional glasses has the co-ordination number  $y = 4$ , but at the boundary

$\text{Al}_2\text{O}_3/\text{M}_2\text{O} > 1$  also the co-ordination number  $y = 6$ . It may therefore be assumed that the anomalous changes of properties in these systems are related to the change in co-ordination number. The co-ordination change has been proved by the technique of X-ray fluorescence [26].

Molar refractivity  $R_M$ , which often allows to assess the changes in co-ordination, does not permit to formulate conclusions with respect to changes in  $y$  in the case of the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . The  $R_M$  values calculated from density and refractive index [21] agree with additively calculated refractivity  $R_M$  for  ${}^{(4)}\text{Al}^{\text{III}}$  both below and above the 1 : 1 ratio.

If Al(III) acquires co-ordination  $y = 6$ , the mass particles contribute to weight but not to volume.

Beyond the 1 : 1 boundary the isofracts take a different direction [24], [26], (Fig. 4).

Absorption in the region 13.5 to 15  $\mu\text{m}$  increases simultaneously with the change of  $n_D$  [27].

According to the conceptions by Pauling [28], sodium as donor supplements up to the 1 : 1 ratio one oxygen atom to the Al(III) atom as acceptor to produce the  $(\text{AlO}_4)$  tetrahedron. All the oxygens in  $(\text{AlO}_4)$  are of the bridging type. The non-

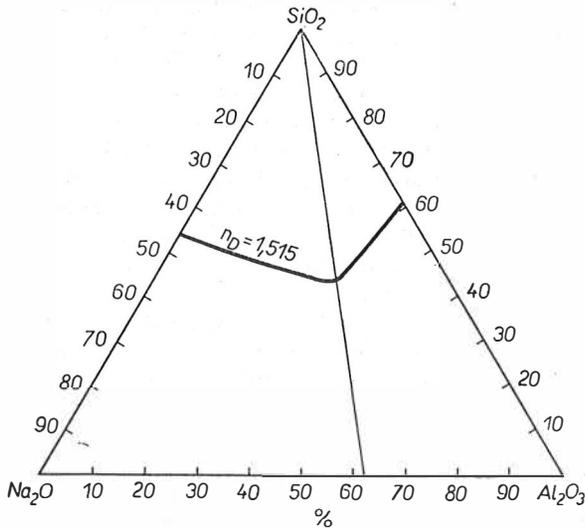


Fig. 4. The course of the isofract in the ternary system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .

bridging oxygens in  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses are therefore gradually eliminated by the introduction of Al(III). At the 1 : 1 ratio the glass contains a minimum of non-bridging oxygens and the network resembles ideally that of quartz glass. At a 1 : 1 ratio there is a lack of Na(I) as donors, and Al(III) passes partially and gradually to co-ordination 6 such as that in corundum [21].

At the 1 : 1 boundary the activation energy  $E_a$  of electrical conductivity is the lowest, increasing at both sides [21], [29]. The change of viscosity around the 1 : 1 boundary is indistinct [30]. In contrast to this, in the system  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ,

the viscosity increases distinctly towards the 1 : 1 ratio, thereafter remaining constant.

The boundary  $M_2O : Al_2O_3 = 1 : 1$  also holds for the glasses in the system  $K_2O-Al_2O_3-SiO_2$ .

A different anomaly is encountered in the system  $Na_2O-Al_2O_3-SiO_2$  in the case of dielectric losses and electrical conductivity. By entering glasses in the system  $Na_2O-SiO_2$ ,  $^{(4)}Al^{III}$  increases their electrical conductivity.  $Na(I)$  bound as a donor less strongly to  $(AlO_4)$  is more mobile in the electric field than when bound to a non-bridging oxygen. Evidence for this explanation is provided by the finding that the highest conductivity is exhibited by glass in the system of  $Na-Al-Si$  oxides just at the 1 : 1 ratio when no non-bridging oxygens are theoretically present, and all the  $Na(I)$  ions act as donors. Dielectric losses increase simultaneously with increasing electrical conductivity. However, the former show an unexpected minimum at 2 mole %  $Al_2O_3$  [31].

Aluminate glasses free from alkali metal oxides, i.e. those containing  $Al(III)$  mostly with  $y = 6$  show a high resistivity, such as the known glasses CABAL which have a higher resistivity than vitreous  $SiO_2$ .

The formation of  $(AlO_4)$  tetrahedrons by the effect of  $Na(I)$  as oxygen donors is likewise related to the anomaly of  $^{(4)}Al^{III}$  with respect to increasing chemical resistance and decreasing the tendency to crystallization, namely at a content between 1 to 4%  $Al_2O_3$ . A similar effect is exhibited by  $Mg(II)$  and  $Zn(II)$ . This anomaly is explained so that up to a content of 3 to 4%  $Al_2O_3$  there arise  $(AlO_4)$  tetrahedrons comprising a homogeneous component of the silicate network without evoking a change in the phases during crystallization, and change in the length of bonds and in the angles between the  $(SiO_4)$  tetrahedrons. The geometrical quality of the network is changed at above 4%  $Al_2O_3$  and the tendency to crystallization increases. The more alkali metal oxides the glass contains (above 17  $Na_2O$ ) the higher amount of  $Al_2O_3$  the glass can contain. This anomaly will be dealt with in Part III (discussion).

In borosilicate glasses,  $Na(I)$  as a donor transmits oxygen preferentially to  $Al^{III}$ , in other words, the  $(AlO_4)$  tetrahedrons are formed in the melt preferentially with respect to  $(BO_4)$  tetrahedrons. This is the cause of the aluminoborate anomaly, which was first described by Appen [32]. The simultaneous presence of  $B_2O_3$  and  $Al_2O_3$  brings about changes of  $d$ ,  $n_D$  and  $\epsilon$  in certain composition regions. The  $(BO_4)$  tetrahedrons are formed only from the oxygens of residual sodium atoms. The increase of co-ordination number of  $Al(III)$  and  $B(III)$  results in an increase of  $n_D$ ,  $\epsilon$ ,  $H$  and in a decrease of  $V_M$ . The properties do not change proportionally with the ratio  $\psi = Na_2O : B_2O_3$ , but proportionally to the ratio

$$\psi = \frac{Na_2O + K_2O - Al_2O_3}{B_2O_3} \quad (3)$$

where the oxides are given in mole %.

The effect of the aluminoborate anomaly on the change in additivity has been more recently treated in detail by Tykachinskij [33].

The aluminoborate anomaly is further related to an interesting empirical relationship found by Volf who studied a large number of commercial technical borosilicate glasses. The  $Al_2O_3$  content decreases proportionally with the decrease of thermal expansion coefficient  $\alpha$  according to the equation

$$Al_2O_3 (\%) = \alpha \times 10^6 - 0.8 \quad (4)$$

In view of the above considerations, interpretation of equation [4] is obvious. Particular types of glasses are characterized by particular thermal expansion, which depends above all on the content of alkali metal oxides and alkali earth oxides. The content of  $\text{Al}_2\text{O}_3$  is then advantageous in amounts improving chemical resistance and suppressing the tendency to devitrification and separation, and in amounts capable of providing oxygens from Na(I) as donors for the formation of  $(\text{BO}_4)$  which are necessary for the creation of the three-dimensional network.

This is why for  $\alpha = 3.2 \times 10^{-6} \text{ K}^{-1}$  (Simax) the  $\text{Al}_2\text{O}_3$  content is 2.4%, and for  $\alpha = 5 \times 10^{-6} \text{ K}^{-1}$  (Sial, G 20) the  $\text{Al}_2\text{O}_3$  content is 4.2%.

#### THE ANOMALY OF PHOSPHATE GLASSES

The  $(\text{PO}_4)$  tetrahedron differs substantially from the  $(\text{BO}_4)$  and  $(\text{SiO}_4)$  ones. Phosphorus P(V) is usually surrounded by 4 oxygens ( $y = 4$ ), among which, however, only three are of the bridging type, the fourth being attached to the central ion by a double bond. In contrast to B(III), P(V) does not behave as an oxygen acceptor, so that tetrahedrons with 4 bridging oxygens cannot be formed.

The invariant points in the phase diagram of phosphate glasses  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  [34] and their compositions are listed in Table III.

Table III  
Invariant points in the system  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  [129]

No.	Phase	$t$ °C	mole %		$N_P$	$\frac{\text{P}_2\text{O}_5}{\text{Na}_2\text{O}}$	
			$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$			
1	$\alpha\text{-}3 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$C_1$	1 583	43.3	56.7	0.247	1.3
2	$\alpha\text{-}3 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 + \beta\text{-}3 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	MD	1 474	44.5	55.5	0.345	1.25
3	$\alpha\text{-}3 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 + 2 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$E_1$	944	49.84	50.16	0.334	1.0
4	$2 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$C_2$	978	53.4	46.6	0.925	0.9
5	$2 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 + \text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$E_2$	546	63.3	36.7	0.297	
6	$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$C_3$	588	69.6	38.4	0.274	

$\text{P}_2\text{O}_5$  is capable of forming chains with alkali metal oxides if the  $(\text{O}=\text{PO}_3)$  tetrahedron contains at least 2 bridging oxygens.

The glassiness boundary lies between 52—60 mole %  $\text{Na}_2\text{O}$ , i.e. between compound  $C_2$  and eutectic  $E_2$  [35].

The volume characteristics  $V_1$  and  $R_M$  increase continuously without any changes with increasing  $\text{Na}_2\text{O}$  content (Fig. 5).

Fanderlik and Paleček [36] found a change in certain properties in the region of the ratio  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 1 : 1$ . This boundary is explained by the authors by the mean numerical length of chains given by the Stevel's formula:

$$\bar{n} = \frac{2}{\psi - 1} \quad (5)$$

where  $\psi$  is the ratio  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ .

The following values are obtained for the three boundary binary compounds:

$\text{Na}_2\text{O} \cdot 2 \text{P}_2\text{O}_5$	$\psi = 0.5$	$\bar{n} = 2 : -0.5$
$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$\psi = 1$	$\bar{n} = \infty$
$2 \text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	$\psi = 2$	$\bar{n} = 2$

If  $\text{Na}_2\text{O}$  decreases down to  $\psi = 1$ , the chain length increases up to a numerically infinite value at a ratio  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 1 : 1$ . At a still lower  $\text{Na}_2\text{O}$  content (so that  $\psi < 1$ ) the chain length will cease to grow ( $\bar{n}$  becomes a numerically negative value), the formation of chains will reach a limit, the structure of phosphate glasses will change and spatial crosslinking will arise.

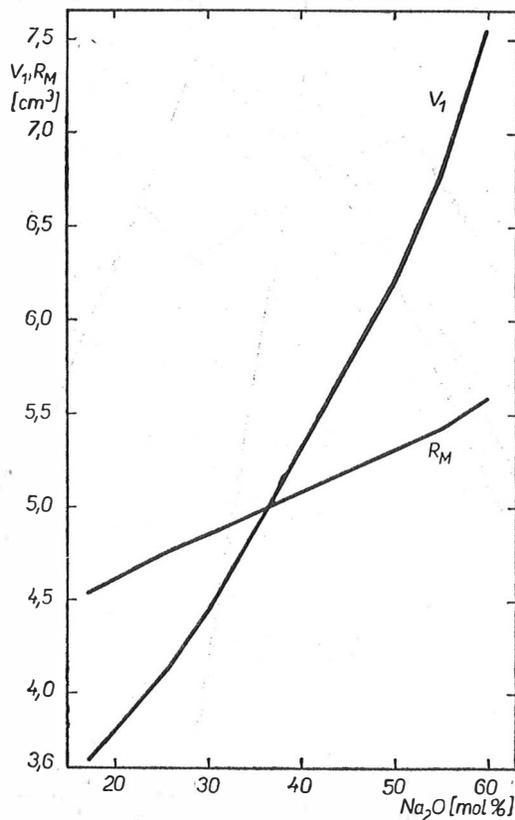


Fig. 5. The volume characteristics  $V_1$  and  $R_M$  in the system  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ .

The fact that has so far eluded attention is that in the region where chain-linking is considered to take place, an increase in  $\text{Na}_2\text{O}$  content brings about a decrease of thermal expansion coefficient similarly to the region of chain-linking in the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ . In the region of assumed cross-linking,  $\alpha$  increases in both systems with increasing  $\text{Na}_2\text{O}$  content. The  $\alpha$ -anomaly described so far as a singular case in the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ , holds likewise for the  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  glasses, as well

as for invert glasses. In both systems it may be ascribed to the different "state" of oxygen in the chain-linked and cross-linked structure.

The modulus of elasticity in tension decreases with increasing  $\text{Na}_2\text{O}$  content in the chain-linking region, increasing in the cross-linking one. Phosphate glasses differ from the borate ones in the inversion-type course of the modulus.

Inversion is likewise exhibited by the course of transformation temperature  $t_g$ .

The points of changes in  $\alpha$ ,  $t_g$  and  $E$  do not coincide (Fig. 6).

The change of  $\alpha$  does not lie precisely at the 1 : 1 ratio which corresponds by its position to eutectic  $E_1$ , where  $\psi$  is equal to unity, but is shifted somewhat higher, at  $\psi = 1.2$  to 1.3, i.e. closer to the compound  $C_1$ .

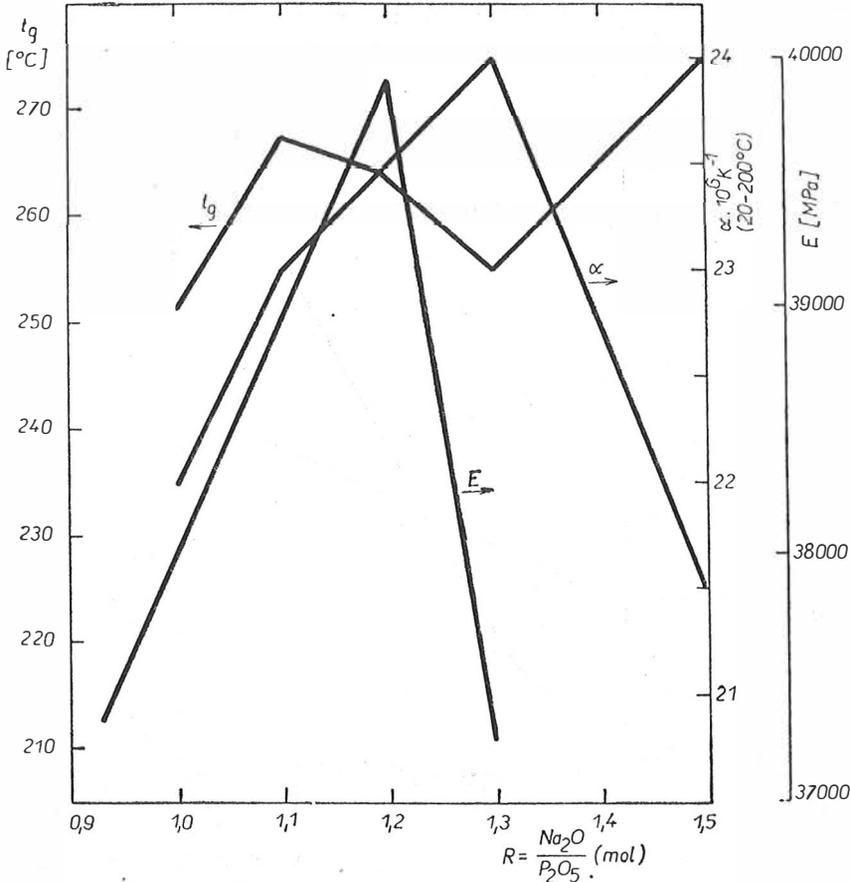


Fig. 6. Chemical dependence of the properties ( $\alpha$ ,  $E$ ,  $t_g$ ) in the system  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  (according to [35]).

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## КИСЛОРОДНЫЕ АНОМАЛИИ ОКИСНЫХ СТЕКОЛ ЧАСТЬ II

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В системах  $\text{Na}_2\text{O}—\text{MO}—\text{SiO}_2$  появляется резкая аномалия у химической стойкости к воде и кислотам. Заменом окислов MO (где M = Mg, Zn, Ca, Ba, Pb; Al) за  $\text{SiO}_2$  в стекле  $\text{Na}_2\text{O} \cdot 4 \text{SiO}_2$  вытяжка резко понижается, химическая стойкость улучшается. За пределами трисиликата ( $V = 3$ ) химическая стойкость резко ухудшается. У стекол с  $V > 3$  вытяжка понижается в результате большой прочности химической связи входящих элементов с кислородом. Величина  $V = 3$  является нижним пределом пространственного структурирования. У стекол с  $V > 3$  вызывает изменение сетчатой структуры в линейную структуру резкое ухудшение химической стойкости и повышение вытяжки.

Ниже предела  $V = 3$ , где прекращается образование пространственной структуры, понижается также удельное сопротивление приводимых стекол.

Инверсия некоторых свойств наступает также у инвертных стекол с  $V < 2$ . Инвертные стекла отличаются комбинацией ионов (Na, K—Ca, Ba) с низким содержанием

структурообразующего элемента. Существование стекол, у которых  $\text{SiO}_2$  не образует сплошной решетки, объясняется (а) эффектом смешанных ионов еси, (б) индукционным эффектом структурообразующих элементов, когда элемент с высокой прочностью связи индуцирует уже при небольшом содержании своей среде такое повышение доли ковалентных связей с кислородом, что возникает предположение для образования полимера.

Инверсионные изменения некоторых свойств ( $\alpha$ ,  $\text{tang } \delta$ ,  $\eta$ ) объясняются изменением ионных связей кислородов в ковалентные связи, по которому инвертные стекла похожи на аномалии боратных стекол.

В системе  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  изменение свойств ( $d$ ,  $n_D$ ,  $E_a$ ,  $\text{tang } \delta$ ) связывается с изменением координационного числа Al.

У фосфатных стекол в системе  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  были найдены инверсионные изменения некоторых свойств ( $\alpha$ ,  $E$ ,  $t_g$ ) опять на разделе пространственной и линейной структур подобного характера, как в случае боратных стекол.

*Рис. 1. Изменение удельного сопротивления в системе  $\text{Na}_2\text{O}-\text{SiO}_2$  при  $Y = 3$  [3], [4], [5].*

*Рис. 2. Ход химической зависимости активационной энергии электропроводности  $E_a$  (расчитана из величин согласно [3]) в системе  $\text{Na}_2\text{O}-\text{SiO}_2$ .*

*Рис. 3. Инверсия вытяжки кислотой в системе  $\text{Na}_2\text{O}-\text{BaO}-\text{SiO}_2$  [9].*

*Рис. 4. Ход изофракты в тернарной системе  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .*

*Рис. 5. Объемные характеристики  $V_1$  и  $R_M$  в системе  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ .*

*Рис. 6. Химическая зависимость свойства ( $\alpha$ ,  $E$ ,  $t_g$ ) в системе  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ . (Согласно [35]).*

## KYSLÍKOVÉ ANOMÁLIE OXIDOVÝCH SKEL. ČÁST II

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1. V systémech  $\text{Na}_2\text{O}-\text{MO}-\text{SiO}_2$  dochází k výrazné anomálii u chemické odolnosti k vodě a ke kyselinám. Vstupem oxidů MO (kde  $M = \text{Mg, Zn, Ca, Ba, Pb; Al}$ ) místo  $\text{SiO}_2$  do skla  $\text{Na}_2\text{O}$ . 4  $\text{SiO}_2$  výluh silně klesá a chemická odolnost se zlepšuje. Za hranicí trisilikátu ( $Y = 3$ ) se chemická odolnost strmě zhoršuje. U skel s  $Y > 3$  výluh klesá v důsledku velké vazebné pevnosti vstupujících prvků ke kyslíku. Hranice  $Y = 3$  je spodní hranicí prostorového zesílení. U skel s  $Y < 3$  vede změna struktury zesílené na zřetězenou k prudkému zhoršení chemické odolnosti a zvýšení výluhu.

2. Podkročením hranice  $Y = 3$ , kde přestává prostorové zesílení, klesá také měrný odpor uvedených skel.

3. K inverzi některých vlastností dochází u invertních skel, s  $Y < 2$ . Invertní skla se vyznačují kombinací iontů (Na, K — Ca, Ba) a malým obsahem síťotvorného prvku. Existence skel, u nichž  $\text{SiO}_2$  netvoří souvislou síť, je vysvětlována:

(a) efektem smíšených iontů eci, (b) indukčním efektem síťotvorných prvků, kdy prvek s vysokou vazebnou pevností indukuje již při malém množství svému okolí takové zvýšení podílu kovalentních vazeb s kyslíkem, že se vytváří předpoklad pro tvorbu polymeru.

Inverzní změny některých vlastností ( $\alpha$ ,  $\text{tang } \delta$ ,  $\eta$ ) jsou vykládány změnou iontových vazeb kyslíků na vazby kovalentní, kterou se podobají invertní skla anomáliím boritanových skel.

4. V systému  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  je změna vlastností ( $d$ ,  $n_D$ ,  $E_a$ ,  $\text{tang } \delta$ ) uváděna ve spojitost se změnou koordinačního čísla Al.

5. U fosforečnanových skel v systému  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  byly nalezeny inverzní změny některých vlastností ( $\alpha$ ,  $E$ ,  $t_g$ ) opět na hranici mezi strukturou zesílenou a zřetězenou podobné povahy jako u skel boritanových.

*Obr. 1. Změna měrného odporu v systému  $\text{Na}_2\text{O}-\text{SiO}_2$  při  $Y = 3$  [3], [4], [5].*

*Obr. 2. Průběh chemické závislosti aktivační energie elektrické vodivosti  $E_a$  (počítáno z hodnot podle [3]) v systému  $\text{Na}_2\text{O}-\text{SiO}_2$ .*

*Obr. 3. Inverze výluhu kyselinou v systému  $\text{Na}_2\text{O}-\text{BaO}-\text{SiO}_2$  [9].*

*Obr. 4. Průběh izofrakty v ternárním systému  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .*

*Obr. 5. Objemové charakteristiky  $V_1$  a  $R_M$  v systému  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ .*

*Obr. 6. Chemická závislost vlastností ( $\alpha$ ,  $E$ ,  $t_g$ ) v systému  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$  (podle [35]).*