On the Structure of the Simplest Germanate Glasses

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Abstract

Full Text

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The properties of germanium glasses have not yet been studied sufficiently fully. Published works have been devoted mainly to elucidating the structure of glassy GeO_2. In these works, the similarity of the structures of glassy GeO_2 and SiO_2 is noted (1–3). In its position in the periodic system, germanium is the closest analogue of silicon. However, according to a number of authors (4), the difference in the ionic radii and in the structure of the electron shells of these two elements results in significant structural differences between some crystalline silicates and germanates. Thus, for example, crystalline GeO_2 and some germanates have two modifications, of which one—the high-temperature one—is isomorphous with SiO_2 and the corresponding silicon compounds, while the other—the low-temperature one, in which germanium has coordination 6—is isomorphous with rutile. The Ge^{4+} cation has an electron shell with a non-noble-gas configuration, i.e., it possesses an increased polarizing ability.

Fig. 1. Dependence of the density of germanate glasses on composition

The Ge—O bond has a more covalent character than Si—O. As our investigation has shown, the dependence of a number of properties of germanium glasses on composition has a character that differs considerably from the same dependences in silicate glasses.

The simple binary systems Na_2O—GeO_2, K_2O—GeO_2, PbO—GeO_2, and a series of glasses of the ternary silicogermanate system $20Na_2O \cdot xGeO_2(80-x)SiO_2$, in which SiO_2 was replaced by GeO_2 equimolecularly, were investigated (the coefficients preceding the oxides denote molecular percentages). The melting conditions, as well as the compositions of most of the glasses studied, were given earlier (5, 6). In the series $20Na_2O \cdot xGeO_2(80-x)SiO_2$, up to 50 mol.% GeO_2 was introduced instead of SiO_2. For the prepared glasses, the density, refractive index, specific electrical resistance were measured, and the molecular volumes, molecular refraction, average refraction of the oxygen ion, change in the volume concentration of oxygen in the glasses upon change of their composition were also calculated.

Figure 2. Dependence of the refractive index and molecular refraction of sodium- and potassium-germanate glasses on composition

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Density. As we have already noted earlier ([6]), on the density isotherms of sodium and potassium germanate glasses (see Fig. 1) there are clearly expressed maxima at 10–11 mol.% K_2O and 15 mol.% Na_2O.

Such maxima were not observed on the density isotherms of the corresponding silicate and borate glasses. The dependence of the density of lead-germanate glasses on composition has a very distinctive character. As can be seen from Fig. 1, in the region of 30 mol.% PbO there is an abrupt change in the dependence of the density of lead-germanate glasses on their PbO content. The density isotherm of glasses of the series $20Na_2O \cdot xGeO_2(80-x)SiO_2$ consists of two rectilinear segments with a point of intersection in the region of 35 mol.% GeO_2.

Fig. 2. Dependence of the refractive index and molecular refraction of sodium- and potassium-germanate glasses on composition

The **refractive index** was determined by an interferometric method on an Obreimov apparatus. Glassy GeO_2 has $n_D = 1.609$. The refractive index of alkali germanate glasses changes with composition analogously to the density (see Fig. 2). The n_D curves have maxima at 12 mol.% K_2O and 15 mol.% Na_2O. Germanate glasses have higher values of density and refractive index than analogous silicate and borate glasses. Earlier we studied the electrical conductivity of sodium-, potassium-, and lead-germanate glasses ([5],[6]). The electrical-conductivity isotherms for glasses of the above-mentioned systems also have a distinctive character and, in their external appearance, are not similar to the isotherms of the corresponding silicate systems, as should be expected, but to the isotherms of borate glasses of analogous composition.

The character of the change in the chemical durability of germanate glasses with changing composition also proves to be different from that of silicate glasses. Glassy GeO_2 is partially soluble in water. The introduction of alkali (up to 15 mol.%) leads to a considerable increase in the chemical durability of germanate glasses. The distinctive change in density, refractive index, electrical conductivity, and also the chemical durability of germanate glasses indicates significant and distinctive changes in the germanium-oxygen structure in these glasses as their composition changes.

It is known that in oxide glasses oxygen occupies the main volume of the glass, is the most polarizable constituent part, and is the most sensitive to structural changes. Since all structural transformations (for example, a change in coordination) lead to spatial changes, it may be assumed that the observed course of the property-composition curves in the germanate systems studied is connected with a change in the volume concentration of oxygen (expressed in gram-atoms

Fig. 3. Change in the volume concentration of oxygen in germanate and borate glasses with change in composition

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per milliliter). In the systems studied, as can be seen from Fig. 3, the curves of change in the volume concentration of oxygen likewise indicate profound changes in the germanium-oxygen structure at certain compositions, especially sharply expressed in the case of lead-germanate glasses. A comparison of the general course of the change in the volume concentration of oxygen in the germanate glasses studied as their composition changes with the same dependences in the corresponding borate systems shows an almost complete analogy of these dependences (see Fig. 3). In sodium-, potassium-, and lead-

In borate glasses, on the curves of the change in the volume concentration of oxygen, maxima also occur in approximately the same composition region as in the case of germanium glasses. In borate glasses, such a peculiar course of the change in the volume concentration of oxygen is associated by us with the known coordination changes of boron in the composition region under consideration. In analogous silicate systems, coordination changes of silicon are not known, and accordingly a smooth decrease in the volume concentration of oxygen is observed with change in composition (without extrema).

Fig. 3. Change in the volume concentration of oxygen in germanate and borate glasses with change in composition

Analysis of the experimental data obtained in the study of germanium glasses leads us to the conviction that the peculiar change observed by us in a number of properties of germanium glasses with change in their composition is connected with a change in the coordination state of germanium in the glasses. The following points indicate the possibility of such transformations of germanium in glasses: the limiting value of the ratio of ionic radii

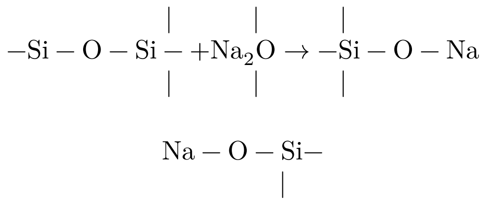
$$r_{\mathrm{Ge}^{4+}} : r_{\mathrm{O}^{2-}} = 0.40$$

$$(r_{\mathrm{Ge}^{4+}} = 0.53\ \text{Å});$$

the presence of different coordinations of germanium in crystalline compounds; the character of the change in density, refractive index, electrical conductivity, chemical durability, and also the volume concentration of oxygen in germanium glasses with change in their composition.

In our opinion, in glasses of the systems Na_2O-GeO_2, K_2O-GeO_2, and PbO $-GeO_2$, with increasing concentration of Me_2O or PbO, a transition of part of the germanium from fourfold coordination to sixfold coordination is possible, with the formation of germanium-oxygen octahedra. In a partial transition of germanium to sixfold coordination, the most probable, apparently, will be a uniform distribution of the octahedra formed among tetrahedra, similar to the way in which, in boron-alkali glasses, the boron-oxygen tetrahedra $[BO_{4/2}]$ are surrounded by nonpolar trigonal nodes $[BO_{3/2}]$. In this case each of the six oxygen vertices of the germanium-oxygen octahedron may be common to a neighboring tetrahedron. According to the proposed scheme of joining octahedra with the surrounding tetrahedra, the structural octahedral unit has the following formula $[Ge^{-2}O_{6/3}]$; in this case the octahedron receives a double negative charge. The indicated process of transition of germanium to sixfold coordination requires an excess of oxygen, whose donor in the present case is the alkali. At the same time, densification of the structure and an increase in the volume concentration of oxygen should occur, which is in fact observed (see Fig. 3).

As is known, when alkali is introduced into silicate glasses, the alkali ions break the silicon-oxygen network:



$$\begin{array}{c} \begin{array}{ccccccc} & & & | & & | & & | & \\ -\mathrm{Si} & - & \mathrm{O} - \mathrm{Si} & - & +\mathrm{Na_2O} & \rightarrow & -\mathrm{Si} & - \mathrm{O} - \mathrm{Na} \\ & & & | & & | & & | & \end{array} \\ \\ \begin{array}{r} \mathrm{Na} - \mathrm{O} - \mathrm{Si}- \\ | \end{array} \end{array}$$

leading to a general loosening of the structure and weakening of the strength of the lattice, which becomes more pronounced as the alkali concentration increases.

In borate and, according to our assumption, germanate glasses, the introduction of alkali leads to the formation of negatively charged structural units, i.e., to the appearance of additional bonds in the structural unit and to a general strengthening of the germanium-oxygen lattice of the glass, manifested in a number of properties. The alkali ions in borate and germanate glasses are located in the interstices of the negatively charged units, without causing bond rupture. In electrical conductivity this is manifested in the fact that, in borate and germanate glasses, the introduction of small amounts of alkali produces some decrease in the equivalent electrical conductivity and a slight increase in the dissociation energy; only at an alkali concentration at which contact between polar structural units becomes possible does a significant increase in electrical conductivity begin. In the case of alkali silicate glasses, the introduction of the first portions of alkali immediately leads to a significant increase in conductivity as a result of loosening and a decrease in the strength of the glass lattice. A further consequence of the differing influence of alkalis on the structure of germanate and silicate glasses is that, although glassy GeO_2 has a higher electrical conductivity than quartz glass, in the concentration range from 2 to 25-30 mol.% Me_2O the germanate glasses have a lower conductivity than the silicate glasses.

The transition of germanium to sixfold coordination probably occurs in a limited concentration region of Me_2O (up to 15 mol.%), after which the previously formed octahedra are destroyed; this is manifested in the curves of the change in the volume concentration of oxygen, density, and refractive index (see Figs. 1–3). In glassy sodium and potassium germanates, apparently, direct linkage of charged octahedra through shared vertices is impossible; this is probably due to repulsion of the negatively charged octahedra when they approach one another (as also in the case of boron–oxygen tetrahedra). This is also indicated by our calculations, which showed that the extrema on the isotherms of density and refractive index of sodium and potassium germanate glasses correspond to those alkali concentrations at which direct contact of charged germanium–oxygen octahedra becomes possible: approximately 15 mol.% Me_2O. In the case of lead germanate glasses, judging from the character of the change in volume concentration of oxygen, density, and electrical conductivity with composition, the transition of germanium to sixfold coordination occurs in the range from 0 to 30 mol.% PbO. In this case, when direct contact of charged units becomes possible, linkage of the latter may occur through Pb cations. At PbO concentrations of 30–33 mol.%, judging from the abrupt and step-like change in properties in this region with an insignificant change in composition, destruction of the greater part of the octahedra occurs.

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