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Review
Lead in glasses

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A literature review is given on the structure, crystallization and properties of lead glasses.

1. Introduction

Lead glasses are extensively used for various purposes. In addition to the conventional industrial applications, such as crystal glass and optical glasses, low-melting glasses and glass-ceramics have been widely used during the last 20 years in the field of electronic technology. Owing to the specific properties of the lead ion, it is possible to prepare glasses containing up to 90 wt% PbO. An extensive survey of the properties and applications of lead in glass-making, including a detailed bibliography, was published in 1963 by Leiser [1].

Leiser's bibliography is very comprehensive but no longer up to date, and a more recent review is therefore needed. The present survey differs from that of Leiser in that it does not aim at being comprehensive; its purpose is to review at some length the most important publications dealing with the structure and structural properties of lead glasses. Data on specific compositions and properties rather belong in a handbook and cannot be discussed here; the reader is referred, for example, to the excellent handbook by Mazurin *et al.* [2], which contains as many as 28 pages of tables and graphs on the properties of $PbO–SiO_2$ glasses alone. Industrial production of lead glasses will not be dealt with in the present survey.

2. Constitution of lead glasses

2.1. Lead silicate glasses

The first X-ray study of lead silicate glasses, which appeared in 1936, was performed by

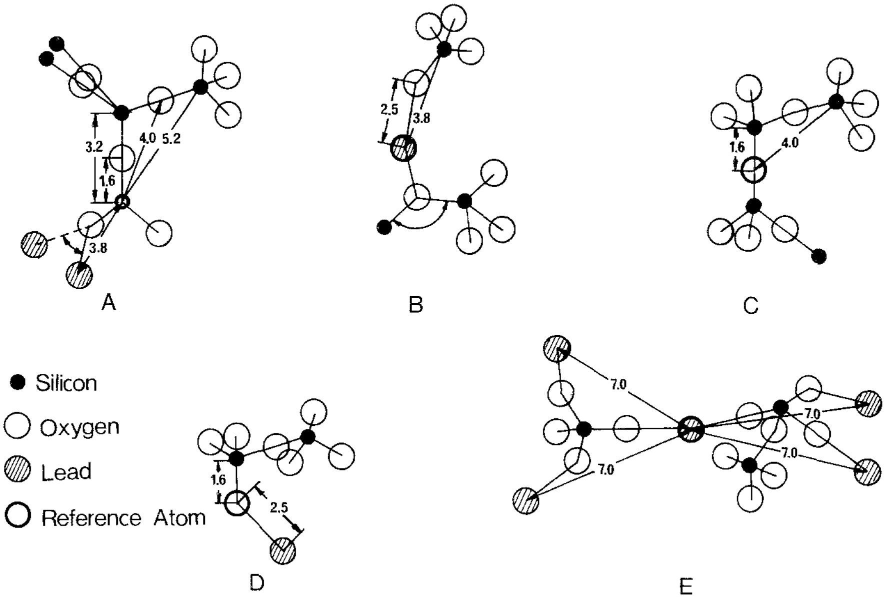

Figure 1 Atomic neighbours in lead silicate glasses (from [3]). (A) Silicon neighbours, (B) lead neighbours, (C) double-bonded oxygen neighbours, (D) single-bonded oxygen neighbours, (E) lead neighbours of lead.

Bair [3], who studied binary glasses containing 10 to 60 mol % PbO. He interpreted his results by a trial and error method. The best agreement between the observed and calculated curves was obtained for distances shown in Fig. 1. It was found that the angle Si–O–Pb is somewhat smaller than 180°, and that the length of the Pb–Si bond is 3.80 Å. Calculations based on the density data indicated that that average Pb–Pb distance varied between 4.00 and 6.50 Å depending on the composition. However, since Bair assumed that lead atoms are invariably separated from one another by the silicon–oxygen tetrahedra, he was forced to take the value 7.0 Å as the average Pb–Pb distance even for glasses containing 60 mol % PbO, and the calculated curve based on this constant value strongly deviated from the observed data. Bair concluded, accordingly, that the distance Pb–Pb was variable, and assumed that the distribution of lead atoms was of the gas type and the determination of lead-by-lead co-ordination number was impossible (the lead–lead interaction was neglected). He suggested that the structure of lead glasses was identical with that obtained by Warren and Loring [4] for soda–silica glasses, except that two sodium atoms were replaced by a lead atom. Thus, according to Bair, these glasses would consist of a continuous, randomly oriented silicon–oxygen network.

Krogh–Moe [5] contested the accuracy of Bair's results on the ground that the very strong contribution of the Pb–Pb interaction had not been allowed for. He carried out his own X-ray study of a $PbO \cdot 0.7\,SiO_2$ glass (58.8 mol % PbO), using improved experimental methods. His values for the distances Pb–O (2.27 Å) and O–O (2.65 Å) are not very different from those found by Bair (Fig. 1). The value of the distance Pb–O leads to a lead-by-oxygen co-ordination number between 6 and 10. Krogh–Moe reported the presence of a large peak at 3.90 Å, which he attributed mainly to the Pb–Pb bond and, to a minor degree, to the Pb–O and Pb–Si bonds. The experimentally found value of 6.75 for the density of the glass indicated that the average volume occupied by a lead atom was 65.3 $Å^3$. This value was utilized to calculate the Pb–Pb distance for the various lead-by-lead co-ordination numbers. The value of 4.03 Å, corresponding to the co-ordination number 6, was found to be closest to the observed value of 3.9 Å.

The lead–lead interaction can be interpreted as the ability of lead ion to form a dipole by displacement of an electron pair, i.e. as being due to the strong polarizability of the lead ion. Unlike Bair, Krogh–Moe believed that the structure of lead silicate glass with a high lead content could not be described by the random network theory. In his view, this glass consists of distorted cubes with lead ions in the corners, the edge length of the cube being 3.90 Å. Every such cube could accommodate one SiO_4 group, the shortest Pb–O distance being 2.27 Å. In a glass containing about 60 mol % PbO, about 30% of the lead cubes would be empty, which accounts for the relatively large molar volume of lead silicate glass. Krogh–Moe gave no assignation to the observed peak at 7.1 Å.

Bagdyk'yants and Alekseev [6] studied five lead silicate glasses, containing 20, 33, 40, 50 and 60% PbO, by the electron diffraction method, and they also treated the results by the trial and error method. They accepted the value of 4.2 Å for the lead-to-lead distance, rather than Krogh–Moe's [5] value of 3.9 Å, and the resulting average lead-by-lead co-ordination number was accordingly 9 rather than 6. The structure can be described in general terms as follows. In high-silica glasses Pb atoms are randomly distributed in the gaps of the three-dimensional Si–O network, each lead atom being linked with two oxygen atoms. As the lead content increases, the lead-by-oxygen co-ordination number increases to six, while the three-dimensional SiO_4 network gradually breaks down into two-dimensional and one-dimensional clusters and is eventually altogether lost.

It was shown by Brosset [7] that the position of the Pb–Pb peak at 3.9 Å is independent of the PbO content, which means that the lead groups have a definite structure (covalent Pb–Pb bonding at 3.9 Å).

Ando [8] and Hagiwara and co-workers [9, 10] published the results of their investigations of lead silicate and lead phosphate glasses by the X-ray method. An X-ray study of $PbO \cdot 2SiO_2$, $PbO \cdot SiO_2$ and $2PbO \cdot SiO_2$ glasses was also carried out by Mydler and co-workers [11–13], who also found that the stronger Pb–Pb peaks suppressed the Si–O and Pb–O peaks in these three glasses. The peak at 3.8 Å is quite sharp in $2PbO \cdot SiO_2$ and $PbO \cdot SiO_2$ glasses, which means that the distribution of the Pb atoms in these glasses cannot be altogether random. As the PbO content decreases, the peak becomes blunt. For such a

Pb–Pb interaction the best calculated values correspond to one nearest Pb atom at a distance of about 3.6 Å, two more Pb atoms at about 4.15 Å, and one more Pb atom at about 4.8 Å [13], on the assumption that other Pb–Pb peaks are present at 5.8, 6.5 and 6.8 Å.

The lead atom in the $PbO{\cdot}SiO_2$ glass is likely to be co-ordinated by two nearest oxygen atoms at about 2.2 Å and two other oxygen atoms at 2.53 and 2.8 Å; a similar bond length distribution is observed in the brown (tetragonal) PbO and in the crystalline $PbSiO_3$. A similar structure has been observed for the vitreous $2PbO{\cdot}SiO_2$. The major peak being at 3.8 Å seems to be a superposition of different Pb–Pb distances, namely the distances to the four nearest and to the four more distant atoms. Such a structure resembles that of the yellow PbO with a lead-by-oxygen co-ordination number of eight. Results of infrared [14–17] and nmr [18, 19] spectroscopy also indicate a certain resemblance between the structures of the vitreous and the crystalline lead silicates.

Kreidl and co-workers in 1948–1949 were the first to suggest that the structure of high-lead silicate glasses resembled that of lead oxide [20, 21]; these workers established an asymmetric environment of 8 oxygen ions around the lead ion in the brown PbO [20]. This suggestion for the glasses is contested by Weyl and Marboe in their fundamental work [22] which appeared 6 years before the X-ray study by Mydlar and Kreidl [11]. Weyl and Marboe repeatedly pointed out that "the lack of visible absorption of silicate, borate and phosphate glasses which contain a major concentration of lead oxide must mean that the Pb^{2+} ions participate in these glasses in the form of highly symmetrical polyhedra". In their view, lead oxides, both yellow and brown, indeed contain the Pb^{2+} ion in the form of the dipole $[Pb^{4+}(e_2^-)]^{2+}$, and this dipole is responsible for the asymmetric environment of the Pb^{2+} ion by oxygen ions and for the color of the oxides. If the Pb^{2+} ion is moved into a symmetrical environment, the colour is destroyed; thus, for example, a solid solution of PbO in SrO is colourless. Lead glasses display a similar effect. As regards the results reported in [6], Weyl and Marboe believed that "PbO_6 groups become fairly regular octahedra on cooling of the melt. Distorted polyhedra would produce visible absorption analogous to crystalline PbO. Indeed, heavy lead glasses turn brown on heating because the fluctuation of symmetry with increasing temperature shifts the absorption band into the visible region". "Colorless glass can be made which contains 90% PbO from an oxide which in itself is brown". They pointed out that, in the case of ions such as Pb^{2+}, their symmetric (glasses) or asymmetric (oxides) co-ordination was much more important than their co-ordination number. Asymmetric groups are easily formed in lead glasses, which is why these can be readily coloured by coloured oxides [22, 23].

The main result of all X-ray diffraction studies of lead silicate glasses subsequent to Bair's work is that at high lead content the three-dimensional silicon–oxygen network is no longer present, but only two-dimensional chains or isolated silicon–oxygen groups, linked together by lead ions. The interaction between lead atoms is a major structural factor in lead silicate glasses. Mydlar *et al.* [13] suggested that the Pb–O–Pb arrangement in high silicate glasses might be as shown in Fig. 2. In silicates the Pb^{2+} ion is almost as large as the O^{2-} ion, and is somewhat smaller than the edge length of the SiO_4 tetrahedron [24].

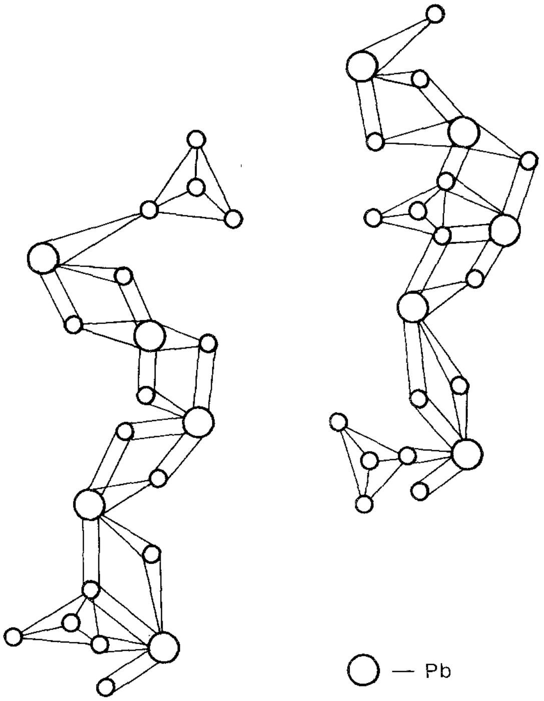

Figure 2 Possible Pb–O–Pb arrangement in lead oxide–silica glasses with high PbO content (from [13]).

It would be interesting to find out why the formation of lead glasses is not arrested by the destruction of the three-dimensional silicon–oxygen network, contrary to what is observed in the case of alkali metal cations; in fact, the vitreous lead orthosilicate and high lead glasses are fully stable commercial products, even though pure PbO does not form glasses. The effect of the high polarizability of lead ion on its glass forming capacity forms the subject of a number of studies.

If all the cations in the glass are of the noble gas type, glass formation can be explained in terms of the cation field strength [25]. It is believed that small-sized cations carrying a high charge, i.e. cations having a high field strength (B^{3+}, Si^{4+}, P^{5+}), are network-forming [20]. The so-called network modifiers carry a small charge, are large-sized, and have a high oxygen co-ordination number. Polarization of noble gas type cations by the oxygen ions can usually be neglected.

In the case of cations not having a noble gas type structure the position is different. Such cations may not be small-sized or carry a high charge, but their outer electron shells are readily polarizable and can be penetrated by the electrons of a readily polarizable anions. Thus, for instance, Mg^{2+} and Zn^{2+} ions have similar radii, but different types of electron shells [20]. As a result, in the case of the readily deformable oxygen anions, the co-ordination number of the zinc ion is smaller and distance is shorter, while in the case of the more "rigid" F^- ion the distance and the co-ordination numbers for zinc and magnesium are substantially the same. The Pb^{4+} and Zn^{2+} ions have completely filled 18-electron shells. The presence of two external electrons in the Pb^{2+} ion is at least one of the reasons for its high polarization; the molar refraction (which is a measure of polarizability) of the Pb^{2+} ion is about $9\,cm^3$ ($2.58\,cm^3$ for Sr^{2+} which has a similar ionic radius, $0.08\,cm^3$ for Li^+, $2.25\,cm^3$ for K^+, $4.73\,cm^3$ for Ba^{2+}) [20]. The molar refraction of $PbO-SiO_2$ glasses shows a practically linear increase with increasing PbO content [26].

Bobovich and Tulub [27, 28] compared the Raman spectra of silicate glasses containing lead, magnesium and boric oxides and found that the lead glass gave the most intense spectrum. This means that, in these series, it is the Pb–O bond which is the most covalent, in agreement with the modified Pauling electronegativity scale. This covalency, which is due to the strong mutual polarization of Pb^{2+} and O^{2-} ions, accounts for the tendency of the part of the Pb^{2+} ions to join silicon–oxygen groups, or in other words, to participate in the glass forming network and again impart a three-dimensional character to it. This is the explanation for the glass forming capacity of lead oxide and for the particular properties of lead glasses; but, on the other hand, Vogel [29] reported that binary lead silicate glass containing about 90 wt% PbO had an inhomogeneous structure, having separated into two phases. Lead orthosilicate has a lower meling point (740° C) than Cd_2SiO_4 (1250° C) or Ca_2SiO_4 (2150° C) [22] and PbO is an important component of low melting glasses for this reason. Owing to their high polarizability, the Pb^{2+} ions can make compatible systems which are incompatible in other conditions. Thus, for instance, lead glasses are good solvents for noble metals, chromates and sulphates [22], they also dissolve RuO_2 [30].

2.2. Lead borate glasses

Brekhoviskikh and Cheremisinov [31] studied lead borate glasses containing 39 to 90.8 wt% PbO (from $PbO \cdot 5B_2O_3$ to $3PbO \cdot B_2O_3$) by infra-red spectroscopy. All these glasses gave spectra which contained bands produced by the vibrations of boric anhydride; these bands were strongest in the spectra given by glasses containing 86.3 and 90.8% PbO. This seems to indicate that the molecular structure of B_2O_3 was retained even in the high lead glasses. The molecular type bonds were suggested to be responsible for very low viscosities and softening points of the glasses studied.

Bray and co-workers [18, 19, 32], who studied the structures of vitreous boric oxide and of lead borate glasses by the method of nuclear magnetic resonance (nmr), arrived at different conclusions. In their view, the boron atoms are situated in BO_3 triangles. If the PbO content is low, the Pb–O bond is ionic, and the Pb^{2+} ions must be considered as modifiers, while the formation of BO_4 groups proceeds at the rate of two tetrahedra for each added oxygen. Above 15 to 20 mol% PbO, the formation rate of the tetrahedra is reduced, because some of the lead atoms now participate in the network as PbO_4 pyramids, with the Pb atom forming the apex of the pyramid. These pyramids preferentially bridge to BO_3 rather than BO_4 units. The corresponding nmr spectra rapidly become similar to those of orthorhombic and tetra-

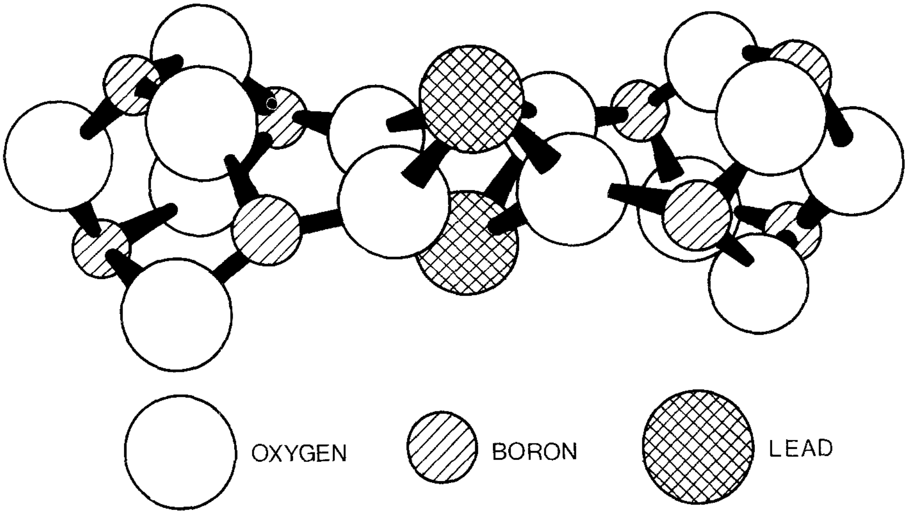

Figure 3 Bidentate ligand structure in $PbO \cdot 2B_2O_3$ glass (from [35]).

agonal PbO, the nature of the bond becoming much more strongly covalent. A similar structure of high lead silicate glasses was discussed above.

A noticeable change in the BO_3 units appears at about 30 mol% PbO. This is due to a change in the electron distribution in the B_3–O bonds, which probably results from the replacement of B_3–O–B_4 by B_3–O–Pb bonds. The fractional content of four-co-ordinated boron (B_4) attains its maximum value of about 0.5 when the PbO and B_2O_3 contents are approximately equimolar. It would seem that the content of the B_4 fraction cannot become higher, because the modified BO_3 units containing one or more B_3–O–Pb bonds are unable to accept a fourth oxygen atom.

According to Vlasov *et al.* [17], the structure of lead borate glasses is analogous to that of the corresponding crystalline borates.

Bergeron and co-workers [32–36] studied the structure of lead borate glasses and melts. Their determination of the partial molar volume of B_2O_3 in lead borates [34] showed that the concentration of BO_4 in the $PbO \cdot 2B_2O_3$ glass was constant (40%) up to 500° C, but showed a significant decrease above that temperature owing to the conversion of BO_4 to BO_3 units. In the view of these workers, BO_3 units were formed as a result of the destruction of the boron–oxygen network. The presence of both three- and four-co-ordinated boron atoms in lead borate melts can be explained by assuming the coexistence of the $(B_4O_7)^{2-}$ ion cage structure with the chain structure. These workers suggested [35] that the $PbO \cdot 2B_2O_3$ glass contained about 1/3 of the boron atoms in four-fold co-ordination in the $(B_4O_7)^{2-}$ cages with one Pb^{2+} ion associated with each cage. The remainder of the glass would be composed primarily of bidentate ligands linked together by lead atoms, each lead atom co-ordinating by four oxygen atoms (Fig. 3). Such a structure would be in agreement with the results of Bray and co-workers [18, 19, 32]. It was also suggested [35] that discrete PbO molecules were present in the glass.

The diffusion rate of lead in $PbO \cdot 2B_2O_3$ melt was also determined [33]. The auto-diffusion coefficient of lead was calculated to be 1.4×10^{-2} $cm^2 sec^{-1}$ at 479° C; it varied with the temperature according to Arrhenius, and the corresponding activation energy was 13.7 kcal mol^{-1}.

Water concentration was determined in several lead borate glasses [36]; the $PbO \cdot 2B_2O_3$ glass had the highest water content.

2.3. Lead germanate glasses

Morozov [37, 38], Evstrop'ev *et al.* [39], Vlasov *et al.* [17], and Topping and co-workers [40, 41] studied the structure and properties of glasses in the systems $PbO–GeO_2$ and $PbO–GeO_2–SiO_2$. Morozov, Evstrop'ev and Vlasov established the resemblance between the infra-red spectra of the glasses and those of crystalline germanates. Their results showed that the structure of lead germanate glasses is inhomogeneous. Germanium has an octahedral oxygen co-ordination [39]. According to Vlasov *et al.* [17], the basic structural units in binary glasses, containing 50 mol % PbO, are compounds, 50 mol % of which consist of PbO, while the other 50% consist of the glass-forming oxide; this structure is independent of the identity of the glass-forming compound (SiO_2 or GeO_2). It should be noticed that the resemblance between infra-red spectra cannot mean the full identity of structures.

According to Topping *et al.*, binary lead germanate glasses can be readily prepared from compositions containing up to 45 mol% PbO [41], while ternary glasses can be prepared from compositions containing up to 70% PbO [40]. Analysis of the molar volume data indicated that the co-ordination number of some of Ge^{4+} ions in the binary glasses changed from 4 to 6 when PbO was added. The rate of this change is slower than of that occurring in alkali germanate glasses because of the glass-forming properties of PbO; this may be compared with a similar effect on the co-ordination number of boron in lead borate glasses. The $PbO-GeO_2$ glasses were yellow, and were most intensely coloured at 20 and 25 mol% PbO. According to Weyl and Marboe [22, 23], this is due to the formation of the asymmetric groups by the highly polarizable Pb^{2+} ion [41]. A large immiscibility field was observed in the ternary system $PbO-GeO_2-SiO_2$ [40]. Measurements of the density and of the refractive index did not indicate any change in the coordination number of the Ge^{4+} ions in this system.

3. Properties of lead glasses*

3.1. Optical properties and effect of irradiation

Lead oxide is one of the main components of optical glasses, and for this reason the optical properties of lead glasses have been extensively studied [1]. Since Pb^{2+} ions are highly polarizable, lead glasses have a high refractive index and high dispersion [22]. The study of the optical properties is important to the understanding of glass structure (see Section 1 for the application of infra-red and Raman spectroscopy for this purpose). A detailed discussion of the optical properties of lead glasses would require another review solely devoted to this subject; we shall accordingly confine ourselves to a brief survey of the fundamental studies.

Hagiwara and co-workers [9, 10] studied the absorption of $PbO-SiO_2$ glasses containing 40 to 70 mol% PbO in the infra-red and in the visible. They found that the dependence of wavelength of the optical absorption edge on the glass composition showed breaks at approximately 50 and 65% PbO, which they attributed to a structural changes.

The spectrum of a $1.08PbO \cdot SiO_2$ glass had a strong absorption band between 5 and 6 eV (237 to 206 nm) [42], which was attributed to the Pb^{2+} ion. A vacuum-evaporated film of this glass showed an additional band, with a peak at 7.6 eV (162 nm) and a large (3.2 eV) half-width, which was assumed to have been produced by the excitation of the oxygen ion bound to the Pb^{2+} ion.

In alkali borate and silicate glasses the band near 220 nm appeared even on the addition of very small amounts of lead (0.1 to 0.3 wt%) [43, 44]. As the basicity of the glass increased, this band showed a shift to lower energies, but its half-width remained practically unchanged. This result was interpreted as being an indication of the covalent nature of the Pb–O bond in basic glasses.

The presence of lead oxide strongly affects the colour of glass by other components. Stroud [45] studied the effect of V, Cr, Mn, Fe, Ni, Cu, Rh, Pt, Pd, Ce, and U present in impurity concentrations on the optical absorption and the colour of the following glasses: $Na_2O \cdot 3SiO_2 \cdot 2PbO$ ("oxidized" glass), the same glass with 1 wt% Sb_2O_3 ("reduced" glass), and $Na_2O \cdot 3SiO_2$. All these glasses, when free from impurities, were colourless, but the lead glasses were more readily coloured by most of the above-listed impurity elements than was the soda–silica glass. The only impurity, forming an exception to this rule, was vanadium, which coloured both the lead glasses less intensely than the soda–silica glass; manganese and copper impurities colored the "reduced" lead glass less intensely than the soda–silica glass. The arising of colour may be due to three different causes: (1) the high oxidation states of the polyvalent cations in the "oxidized" lead glass; (2) the larger absorption cross-section of the polyvalent cations in the lead glasses; (3) the lead-induced shift of the absorption maxima towards the wavelengths of the maximum eye sensitivity. As a rule, polyvalent cations in higher states of oxidation colour glass

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*Here properties of lead glasses in non-crystallized state are considered. For the effect of crystallization on properties see section 4.

more intensely, and they tend to occur in lead glasses in such states. Platinum is the only exception: unlike the other elements studied, Pt(IV) imparts a less intense colour to lead glass than does Pt(II), but the colours produced by Pt(II) and Pt(IV) are both more intense than that produced by neutral platinum in soda–silica glass.

Studies of absorption spectra showed that the presence of lead also affects the redox equilibria of polyvalent cations in glass. In the Na_2O–PbO–SiO_2 glasses, containing iron or copper, the ratio of the oxidized to the reduced form of iron was found to increase and of copper was found to decrease with increasing the PbO content [46].

Spectrophotometric investigations of binary lead borate glasses containing 0.05% CoO [47] showed that all the bands given by the glasses studied were completely overlapped by the strongly absorbing tetrahedral cobalt ions. As the lead oxide content gradually increased, a shift of the 510 and 575 nm bands towards longer wavelengths was noted. The molar extinction coefficients of the bands also increased with increasing PbO content.

Reisfeld and co-workers [48–51] studied the absorption and fluorescence of alkali germanate, borate and phosphate glasses doped with 10^{-3} to 1 wt % PbO. The position of the absorption maxima for lead varied with the matrix glass: it was found to be 234, 217 and 270 nm in borate, phosphate and germanate glass respectively [48]. These data served to calculate the nephelauxetic constant [48, 50] and it was found that the covalency of the Pb–O bond increased in the order phosphate–borate–germanate.

Bettinali and co-workers [52–54] studied the luminescence of the K_2O–PbO–SiO_2 glasses containing 5 to 60 wt % PbO. All the glasses gave luminous emissions when excited with short ultraviolet light (253.7 nm) at 120 K. As the PbO content increased, the maximum of the spectrum of the emitted luminescence shifted from 440 to 510 μm [52]. The emission is caused by Pb^{2+} ions and not by Pb^0 atoms [53]. The experimental results were explained by the Pb–Pb interaction. The shift of the maximum and the reduction of the luminous intensity with the increasing of PbO content confirm the data obtained by other methods [55]. The luminescence in the lead glasses was very close to that in $PbCl_2$.

A number of studies deal with the optical properties of irradiated glasses. An optical absorption band at about 1.5 eV (825 nm) was induced in lead borate glasses by neutron or gamma-irradiation [56]. This band assumed its maximum intensity at about 25 mol % PbO. The other band which had also been so induced (2.6 eV, 475 nm) showed maxima of intensities at about 33 and 45 mol % PbO. The addition of cerium (IV) strongly suppressed the 1.5 eV band which was attributed to an electron trap centre associated with the Pb^{2+} ions (or ions having a similar electron configuration). On this assumption the increase in the intensity of the 1.5 eV band between 18 and 25 to 30 mol % PbO would indicate that in this concentration range lead is present in the ionic form and, vice versa, the decrease in the intensity of this band which occurs at the concentrations higher than 30 mol % PbO would indicate that the Pb–O bonds become more covalent. The experimentally observed changes in infra-red absorption, molar volume [56] and esr spectra [57] also indicate that structural changes occur in glass compositions corresponding to the maxima of the intensities of the induced bands [56]. Similar bands were observed in irradiated lead-containing potassium borate glasses [58].

A study of the gamma-induced optical absorption in lead silicate glasses also revealed the presence of a band at 2.6 eV, the genesis of which is believed to be due to the formation of colour centres associated with structural defects [59]. The X-ray irradiated $K_2O \cdot 2SiO_2$ glass showed a strong absorption at about 2.0 eV (617 nm) and 2.7 eV (458 nm). The addition of a small amount of PbO resulted in a significant decrease in the intensity of the 2.0 eV band and in an increased ultraviolet-induced absorption [60]. The Pb^{2+} ions were reported [61] to reduce the optical stability of the glasses of composition $4SiO_2 \cdot Na_2O \cdot (0.25–0.5)MeO$ to gamma-irradiation. But the group of the compositions of gamma-absorbing glasses for the windows in concrete protective walls was developed in the SiO_2–R_2O–PbO system (15 to 45 wt % PbO) with added CeO_2 (0.8 to 1.8%), and, sometimes, also BaO, Al_2O_3 and B_2O_3 [62]. It is also known that the presence of PbO increases the stability of glass to ultraviolet irradiation: it prevents the solarization of most lithia and soda glasses and reduces the solarization of potash glasses [22].

3.2. Electric and magnetic properties

3.2.1. Lead silicate glasses

The nature of the electric current carriers in alkali-free lead glasses is not perfectly clear. Pb^{2+} ions [63, 64], impurity alkali metal ions [65], protons [66] and electrons [66–68] have been suggested as current carriers in $PbO–SiO_2$ glasses. A recent study on this subject by Topping and Murthy [69], examines the electric conductivity of $PbO–SiO_2$ glasses containing 30, 40, 50 and 60 mol % PbO. The resistivities and activation energies decreased with increasing PbO content. At 350° C the resistivity was about 1.6×10^{10} and $3 \times 10^7\ \Omega$ cm for glasses containing 30 and 60% PbO respectively. Fig. 4 shows activation energy data published by different workers [64, 65, 69, 70] as compiled in [69]. The individual results show large discrepancies, which were probably caused by impurities, melting atmosphere or other reasons. Topping and Murthy failed to detect electrolysis in the $PbO–SiO_2$ glasses even in the presence of 5% added Na_2O. The first alkali additions up to 10% resulted in increased resistivities. Variations in the state of oxidation were without effect on the resistivity. Hence neither alkali nor oxygen ions could be current carriers. However, the resistivities were found to vary significantly with the water content [63, 70], which means that the current may be carried by hydrogen ions [69].

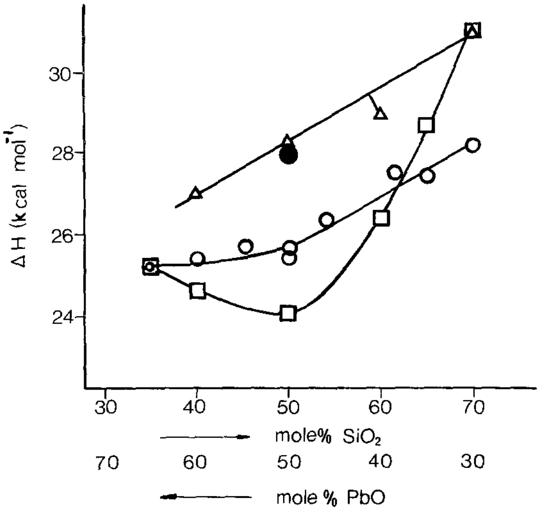

Figure 4 Published activation energies of conduction in $PbO–SiO_2$ glasses (compiled in [69]).

Hagiwara and co-workers [9, 10] studied the dielectric properties of powdered and bulk $PbO–SiO_2$ glasses. They found that the dielectric permittivity increased with increasing PbO content; in bulk glass containing about 65 mol % PbO (approximately corresponding to the composition of the orthosilicate) it was close to that for pure PbO (25.9 at 2×10^6 Hz) [10]. This fact seems to be a confirmation of the structural resemblance between PbO and high-lead silicate glass (cf. Section 2.1). The dielectric loss curve given by the bulk glasses had a large maximum at about 65 mol % PbO and a smaller one near 50% PbO. The loss was much larger at 110 Hz than at 10^5 Hz. It was suggested [9, 10] that the orthosilicate composition corresponds to a turning point of the structure, at which the silicon–oxygen network becomes distorted; above 65 mol % PbO a new network consisting of PbO_4^{6-} pyramids with the Pb atoms in the apex is predominant. Hagiwara and Oyamanda suggested [10] that between 50 and 65 mol % PbO the Pb^{2+} ion may readily jump over the potential barrier, hence the energy loss is small; but gradually a new character of the structure is developed which is densely packed at about 65 mol % PbO.

A number of studies are available on the electrical properties of lead silicate melts [71-73]. Botvinkin and Cherevkova [71] studied the electromotive force (e.m.f.) of the galvanic element $Pb|PbSiO_3|SiO_2 \cdot (PbO)_x|Pb$ in an alumina cell at 925° C; content of PbO in the melts was 35 to 100 mol %. It was found that the e.m.f. of the melt decreased while the PbO content increased and this decrease was attributed to the reduced activity of the lead ions in the melts. The curve showing the e.m.f. as a function of the melt composition had two distinct breaks, corresponding to the compositions $2PbO \cdot SiO_2$ and $PbO \cdot SiO_2$, which may indicate that these compounds preserve their stability in the melts. This interpretation parallels that of infra-red spectra of lead silicate glasses [14–17] (Section 2.1).

Contrary findings were reported by Minenko *et al.* [26], according to whom the e.m.f. at 1100° C increased with increasing the PbO content, but the former results [71] were confirmed by Ito and co-workers [72, 73]; they also found that the e.m.f. decreased with the temperature. All parameters (electric conductivity and its activation energy, density and viscosity) showed breaks at the compositions $2PbO \cdot SiO_2$ and $PbO \cdot SiO_2$, but an X-ray analysis of the crystallized glass of the stoichiometric composition $2PbO \cdot SiO_2$ indicated the presence of the anion $Si_2O_7^{6-}$ and of other anions, as well as that of SiO_4^{4-}. A new compound having the composition $3PbO{\cdot}2SiO_2$ was also discovered, but was found to decompose above 650° C to give a mixture of the compounds $2PbO{\cdot}SiO_2$ and $PbO{\cdot}SiO_2$ [72].

The effect of oxide additions on the properties of the binary melts was also studied [73]. It was shown that the conductivity increased with decreasing value of the ionic radius of the alkali metal added, since a small-sized cation (such as Li^+) was more mobile than a large-sized one (such as Cs^+). However, when alkali-earth oxides were added, the conductivity decreased with decreasing ionic radius; according to the authors, this effect is due to the mechanism of bond between the cation and the oxygen ion, becoming more covalent as the ionic radius of the cation decreases from Ba^{2+} to Be^{2+}.

Saringyulyan and Kostanyan [74] studied the viscosities and electric conductivities of 28 glasses of the K_2O–PbO–SiO_2 system at temperatures up to 1000° C. They suggested that the reason for the very low resistivity of high lead glasses of this system was the indirect effect of the low viscosity, caused by the presence of PbO, on the mobility of K^+ ions. When glasses having equal viscositiies were compared, it was found that the resistivity showed a significant increase if SiO_2 was replaced by PbO. Rao [75] studied the effect of TiO_2 on the various parameters, including electric parameters, of the same system. He suggested that the ionic character of the system becomes weaker in the presence of the Ti^{4+} ions, while being enhanced by the Pb^{2+} ions. This suggestion is in contradiction with the structural representations found for simpler glasses (e.g., see Bray's results [19, 32] obtained for lead borate glasses in Section 2.2). Electrical conductivities of solid Na_2O–PbO–SiO_2 glasses were determined by Grechanik *et al.* [64].

Stoicheva [76] studied the electrical conductivity, dielectric loss and permittivity of multicomponent industrial glasses containing 2.5 to 25 wt % PbO.

Schultz and Mizzoni [77] studied the properties of halogen-containing lead silicate glasses. The original glass contained 68.6 mol% PbO and 31.4 mol% SiO_2; the other glasses studied contained the same PbO:SiO_2 ratio (48.5% PbO and 22.2% SiO_2) and, in addition, 29.2 mol% of F, Cl, Br or I (in fact, the true content of F was only 23.1%, because of volatilization). It was found that as the anion size increased, (1) the loss tangent decreased; (2) the dielectric permittivity decreased; (3) the d.c. volume resistivity increased. It was confirmed, with the aid of Tubandt tests and electron microprobe analysis, that the conduction in these glasses was of the anionic type, and that the anion was liberated from the glass as a gas at the anode surface.

Milnes and Izard [63] studied the electrical conductivity of lead silicate glasses, containing water in the form of OH groups, and found that the resistivity decreased with increasing water content.

Anderson and MacCrone [78] determined a.c. and d.c. conductivities in PbO–SiO_2–Fe_2O_3 glasses containing equimolar amounts of PbO and SiO_2 and 0 to 10 mol % Fe_2O_3, in the temperature range 77 to 700 K. As could be expected, the electric conductivity increased with increasing concentration of the transition metal ion. At concentrations above 2 mol % Fe_2O_3 the conductivity is undoubtedly of the electronic type. The increase of the conductivity with the concentration was much more rapid than would be in the case if random hopping were involved. For the explanation the structural model of chains of the transition metals ions in a tree-like arrangement was proposed.

Vargin *et al.* [79, 80] studied the magnetic properties of glasses in the same system. They showed that the binary lead silicate glass was diamagnetic. The glasses containing up to 11 mol % Fe_2O_3 were paramagnetic, in agreement with the results of Anderson and MacCrone [78]. At higher Fe_2O_3 concentrations, which depended on the PbO content, the appearance of ferromagnetism was observed. The molecular magnetic susceptibility is determined only by the Fe_2O_3 content and not by the other components of the glass [79]. When a glass containing 15 mol % Fe_2O_3 was crystallized, its ferromagnetic properties were intensified as a result of precipitation of hexagonal ferrite [79, 80]. The magnetic moment of the Co^{2+} ion in lead silicate glasses depends on its co-ordination number, which varies with a composition [80]. Magnetic properties of high lead silicate and borate glasses containing vanadium were described in [81].

Hirashima and Yoshida [82] studied the electrical conductivity of PbO–SiO_2–Fe_2O_3 melts, containing 0 to 25 mol % Fe_2O_3. The values of the apparent activation energy of conduction were 10 to 25 kcal mol^{-1}, which are almost equal to those for PbO–SiO$_2$ glasses. The electrical conductivity increased with increasing PbO or Fe$_2$O$_3$ content. These results, which could have been expected, were attributed to the ionic character of the conductivity with the Pb^{2+} and Fe^{3+} ions as the current carriers, but it was seen above that the increase of the conductivity with Fe$_2$O$_3$ content can also be attributed to the electronic type conductivity. In the view of the authors, the Fe^{3+} ion interacts more strongly with a silicate anion than does the Pb^{2+} ion. The existence of an unknown ternary compound in the system has been suggested.

The electrical conductivity of Na$_2$O–PbO–SiO$_2$ glasses containing 0 to 10 mol % Fe$_2$O$_3$ was studied by Grechanik, Fainberg and Zertsalova [83]. It was found that if PbO is replaced by Fe$_2$O$_3$, the resistivity and the activation energy of the glasses show a sharp decrease, which is much larger than that observed when PbO is substituted by Na$_2$O. The conductivity of glasses containing both Na$_2$O and Fe$_2$O$_3$ seems to show the coexistence of the ionic and electronic types of conductivity.

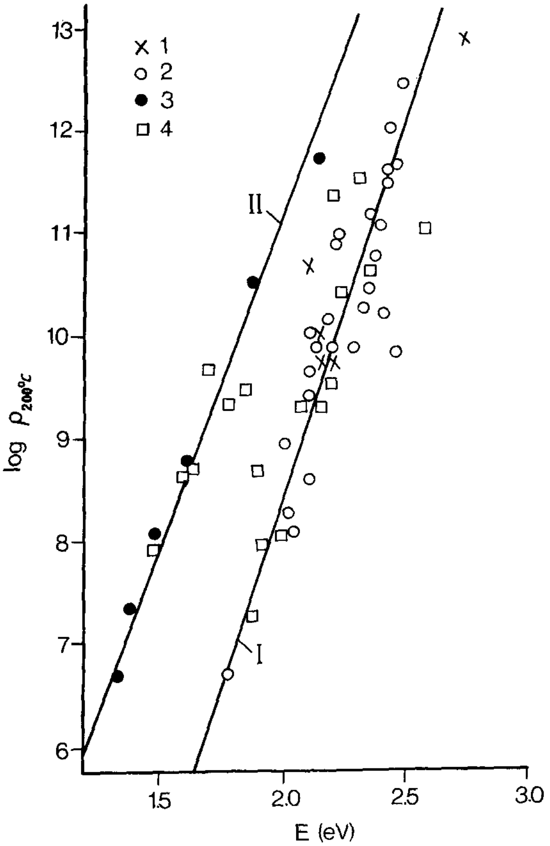

Figure 5 Interrelation of activation energy and volume resistivity of glasses in systems: (1) PbO–SiO$_2$, (2) Na$_2$O–PbO–SiO$_2$, (3) Fe$_2$O$_3$–PbO–SiO$_2$, (4) Na$_2$O–Fe$_2$O$_3$–PbO–SiO$_2$ (from [83]).

The most interesting result of [83] is the discovery of the relationship between resistivities and activation energies (Fig. 5). The points below line I on the graph refer to glasses with ionic conductivity, while the points referring to glasses with electronic conductivity are situated above line II. Points situated between lines I and II refer to glasses with conductivities of both ionic and electronic types. Fig. 5 shows results obtained for lead glasses only, but the authors have indicated that this relationship has been examined for a number of other systems and is, therefore, general. It is seen from Fig. 5 that the points given by the binary PbO–SiO$_2$ glasses gravitate towards line I, which is an indirect indication of the ionic character of their conductivity.

The secondary electronic emission coefficient (SEEC) of various glasses, including lead silicate, lead borate and lead germanate glasses, was studied by Ul'ko and Fainberg [84]. These workers found that if PbO was substituted by Fe$_2$O$_3$ (up to 10 mol %) in a glass containing 60 mol % SiO$_2$, 15% Na$_2$O and 25% PbO, the maximum SEEC (about 2.8) remained practically unaffected, whereas a similar substitution in an alkali-free glass (60% SiO$_2$, 40% PbO) resulted in a decrease of SEEC, probably owing to the character of the electrical conductivity in these glasses.

3.2.2. Lead borate and borosilicate glasses

The electrical properties of lead borate and borosilicate glasses were described in [35, 85–92]. De Luca and Bergeron [35] studied the electrical conductivity, dielectric permittivity and dielectric loss of the PbO•2B$_2$O$_3$ glass (solid and melt) between 300 and 850° C. The experimental activation energy of conduction was 37 ± 4 kcal mol^{-1} between 300 and 450° C and 89 ± 10 kcal mol^{-1} between 450 and 650° C, and gradually decreased to 34 ± 4 kcal mol^{-1} as the temperature was further increased. These workers assumed that lead ions are current carriers and proposed possible mechanisms of ion transport for lead. Hirashima and Yoshida [91] established the sharp increase in the conductivity of PbO–B$_2$O$_3$ melts as the PbO content increased from 0 to 30 mol %, but when the PbO content increased beyond 30%, the increase in conductivity was slow, which depends on the structure of the complex borate anion.

Gough *et al.* [85] studied the properties of $RO–Al_2O_3–B_2O_3$ glasses, where R = Ca, Sr, Ba or Pb, and of $PbO–Bi_2O_3–B_2O_3$ glasses, and found significant differences between the behavior of PbO and that of the other oxides. The activation energy of d.c. conductivity in alkali earth oxide glasses depended only on the molecular formula, but not on the identity of the cation, whereas it was lower in the case of the readily polarizable lead ion, which is of the non-noble gas type. The conductivity of $PbO–B_2O_3$ glasses was found to be independent of trace impurities. The substitution of Bi_2O_3 for PbO lowered the activation energy and resistivity. The permittivities of the glasses showed a nearly linear increase with the concentration of the cation. The mechanism of the dielectric loss and its variation with temperature and frequency were also studied.

Ershov and co-workers investigated the conductivities of lead borosilicate glasses [86, 87]. They found that the conductivity increased with the PbO content, as had been found for lead silicate glasses. When SiO_2 was substituted by B_2O_3, the conductivity decreased and the activation energy increased. The dielectric permittivity of $PbO–B_2O_3$ glasses increased with the PbO content, but when the PbO content was kept constant, it did not change with the changing SiO_2/B_2O_3 ratio [90]. When SiO_2 in $Na_2O–B_2O_3–SiO_2$ glasses was replaced by PbO, the conductivity showed only a slight increase [88].

In $PbO–Al_2O_3–B_2O_3–SiO_2$ system the glasses with high resistivities and activation energies has been found [89]. Their dielectric permittivities can be high or low, depending on the PbO content [89, 92]. Small amounts of Al_2O_3 or B_2O_3 have been found to be very effective in altering the electrical properties of the glasses.

3.2.3. Lead germanate glasses

$PbO–GeO_2$ and $PbO–GeO_2–SiO_2$ glasses were studied by Topping and co-workers [41, 69]. The resistivities of the binary glasses [41] were found to vary between 10^9 and $10^{10}\,\Omega$cm at 350° C, with a very broad flat maximum around 80 mol% GeO_2. The activation energies lie between 30 and 40 kcal mol^{-1} with a plateau between 70 and 90 mol% GeO_2.

When SiO_2 was replaced by GeO_2 in a glass containing 50 mol% PbO and 50% SiO_2 [69] the resistivity and activation energy changed very little up to 30 mol% GeO_2, but at higher GeO_2 content the activation energy was lowered.

3.3. Thermal properties and viscosity

3.3.1. Thermal expansion

It was found by Karkhanavala and Hummel [93] that the thermal expansion of glasses in the low temperature region was independent of the electron shell type of cation, but was only dependent on its size. Thus, the linear coefficient of thermal expansion (CTE) did not change when Mg^{2+} was replaced by Cu^{2+}, or when Sr^{2+} was replaced by Pb^{2+}. This is additional evidence that cations having non-noble gas electron configuration participate in the glass structure as highly symmetrical polyhedra similarly to Mg^{2+} and Sr^{2+} ions [22]. But a significant difference was observed with respect to formation of defects. Glasses containing non-noble gas type ions show a rapid increase of their configurational and vibrational entropy at lower temperatures than the glasses containing noble gas type ions of a similar size. As a result of the increase of concentration of defects, at elevated temperatures the CTE of glasses, containing CuO and PbO, is higher, and increases more rapidly than that of MgO and SrO glasses [22].

The thermal expansion of alkaline lead silicate glasses was studied by Appen [94] and other workers [22]. These glasses can have very high CTE values, for instance, $Cs_2O–PbO–B_2O_3$ glasses with CTE = $288 \times 10^{-7}\,{}^\circ C^{-1}$ have been obtained [22]. Glassy lead orthosilicate has a CTE of $112 \times 10^{-7}\,{}^\circ C^{-1}$; this value decreases to $90 \times 10^{-7}\,{}^\circ C^{-1}$ (0 to 100° C) when the PbO content has decreased to the metasilicate composition. A partial replacement of the $(SiO_4)^{4-}$ groups by the $(SO_4)^{2-}$ groups in lead silicate glasses introduces an asymmetry and results in a sharp increase in CTE [22].

The detailed CTE data of binary lead silicate glasses are collected in [2].

3.3.2. Heat conductivity

Thermal conductivities of $PbO–Bi_2O_3–Al_2O_3–SiO_2$ and $BaO–PbO–SiO_2$ glasses at 40 and 120° C were studied by van Velden [95]. Partial factors at 40° C were calculated for each oxide. The results clearly indicate that the thermal conductivity factor for silica markedly decreases when the glass structure changes from the conventional to the so-called "invert" type, unlike the thermal conductivity factor of alumina, which increases. The factor of Bi_2O_3 was found to be about 1.5 times that of PbO. The thermal conductivity factor of PbO ($\sim 0.9 \times 10^{-5}$ cal °C^{-1} $cm^{-1} sec^{-1}$) was one-third that of SiO_2, 4.5 times lower than that of Al_2O_3, and 1.5 to 2 times higher than that of BaO.

3.3.3. Viscosity

The viscosities of lead silicate melts were studied by Ito and co-workers [72, 73]. In binary melts the viscosity seemed to vary with the temperature in accordance with the equation

$$\log \eta = a + b/T^2,$$

where η is the viscosity, T is the absolute temperature, and a and b are constants, but breaks were observed on some of the curves [72]. The higher the SiO_2 content, the higher was the viscosity. The activation energy of viscous flow also increased with the SiO_2 content and curve displayed breaks corresponding to the compositions $PbO \cdot SiO_2$ and $2PbO \cdot SiO_2$. The effect of the additions of oxides on the viscosity of lead silicate melts was also studied [73].

Nemilov and Romanova [96] studied the viscosity of lead borate glasses in the region of the softening point and in the annealing zone. Isocomes, free energies and entropies of activation of viscous flow showed breaks or extreme points corresponding to the compositions $PbO \cdot 2B_2O_3$ and $2PbO \cdot B_2O_3$. The formation of four-co-ordination of boron in this system was accompanied by an increase in the entropy of activation. The compositional curves were very similar to those given by PbO–SiO_2 glasses, but the activation entropies were larger (more 200 cal mol^{-1} °C^{-1}), indicating that the Pb–O bonds were more strongly polarized.

Substitution of PbO by R_2O in PbO–SiO_2 glasses reduces their softening point; if PbO is substituted by MgO or CaO, the softening point increases [97].

3.3.4. Thermochemical characteristics

The thermochemical characteristics (enthalpy, heat capacity) of PbO–Na_2O–SiO_2 melts were studied by Toporisev *et al.* [98].

3.4. Mechanical properties

3.4.1. Density and molar volume

The density and molar volume of various lead glasses were studied in [26, 99, 100]. It was found that the variation of density with composition is a fairly sensitive indicator of phase separation in PbO–B_2O_3 glasses. In K_2O–PbO–SiO_2 glasses structural compacting was observed when the Si:O ratio was 0.445 [55]; this composition corresponded to the maximum microhardness and the minimum volatility of PbO.

3.4.2. Tensile strength, Vickers microhardness and Young's modulus

These parameters of binary lead borate glasses were studied by Imaoka *et al.* [101]. They showed that the tensile strength of B_2O_3 glass fibres was 60 kg mm^{-2}, which is very low if compared to the tensile strength of silica glass fibres. This strength increased somewhat when the PbO content increased to about 35 mol %, but markedly decreased thereafter. Maxima of microhardness and Young's modulus also corresponded to this composition. These results were correlated with the increase in concentration of (BO_4) groups, but nmr measurements showed that the maximum concentration of these groups occurs at 50% PbO, in agreement with the results of Bray and co-workers [18, 32].

The elastic properties of PbO–B_2O_3 and PbO–SiO_2 glasses were studied by Shaw and Uhlmann [99]. As the PbO content increased, the elastic modulus of PbO–B_2O_3 glasses showed a significant increase, while decreasing somewhat in PbO–SiO_2 glasses. If phase separation occurred, the values of the elastic modulus could be calculated as for ordinary composite materials. The sonic velocity reduced with increase in the PbO content in PbO–SiO_2 [99] and PbO–Na_2O–SiO_2 [102] glasses, mainly owing to the increase in their density.

In PbO–GeO_2 glasses the room temperature Young's and shear moduli show maxima at 70 to 75 mol % GeO_2 [103]. The positions of these maxima showed good correlation with the minimum deviation of molar volumes from ideality, indicating that a change had taken place in the co-ordination number of Ge^{4+} ions in the system. The Poisson's ratios μ were within the range typical for glasses: if the PbO content was low, $\mu < 0.25$; if it was high, $\mu > 0.25$ (up to 0.3).

3.5. Chemical durability

Lead glasses usually have a better resistance to water than to acid and alkaline solutions [1].

Abou El-Asm and Hussein [104] studied the resistance to acid of binary and ternary high lead silicate and borate glasses with additions of R_2O, RO, R_2O_3 and RO_2. The chemical durability of the glasses was determined by the powder method, using 0.1 N HCl at 100° C for 3 h. It was found that the substitution of SiO_2 by PbO in the binary glasses reduced the durability: the weight loss increased from 0.34 to 30.31 mg per 10 cm^2 when the PbO content increased from 60 to 85 wt %, while the PbO content in the filtrates decreased from 100 to 95.8%, the remainder consisting of silica, the first traces of which appeared when the glass contained 70% PbO.

When the PbO in a glass consisting of 75% PbO and 25% SiO_2 was partly replaced by Li_2O, Na_2O or K_2O (cation for cation), the durability of the glass increased, particularly when lithia was used. When PbO was partly replaced by MgO, ZnO, CaO or BaO, the durability also increased; it decreased when 1 to 2 parts of lead oxide were replaced by SrO, but increased again when 5 to 10 parts of it were so replaced.

When the silica in this glass was replaced by B_2O_3 or Al_2O_3, the durability decreased. Glasses with small contents of alumina were more durable than glasses containing B_2O_3, but when 5 to 10 parts of SiO_2 had been replaced by R_2O_3, borosilicate glasses were more durable than alumosilicate glasses. The durability increased if SiO_2 was replaced by TiO_2, and, in particular, by ZrO_2.

The resistance of lead borate glasses to the acid decreased with increasing the B_2O_3 content, and increased when B_2O_3 was replaced by alumina or titania.

It was found that the increase in the field strength of the added cation resulted in increased durability, owing to the strengthening of the glass structure [104].

Kudashev [105] studied the water resistance of the surface layer of lead borate glasses containing 0 to 75 mol % PbO and found that the durability was highest at 36.2% PbO.

El-Shamy and Taki-Eldin [106] investigated the resistance of lead silicate glasses (molar ratio $PbO:SiO_2 = 0.5 - 2$) to water, acid and alkaline solutions. The lowest amounts of PbO were extracted by water and by feebly alkaline solutions (pH 7 to 12). The extraction of silica was nearly zero at $pH < 11$, but increased rapidly thereafter. The plot of the extracted PbO as a function of the composition of the glass had a maximum at $PbO:SiO_2 = 1$. This maximum can be attributed to a change in the nature of the lead–oxygen bond in the glass structure. These results were in good agreement with the results obtained by the other methods described above. The appearance of silica in the filtrates from glasses containing 65 to 70 wt % PbO (approximate composition $PbO \cdot 2SiO_2$) or more [104, 106] is the result of the appearance of isolated silicon–oxygen groups containing not more than two tetrahedra, which cannot form a continuous network. These groups are interlinked through lead atoms.

When an alkali lead silicate glass was treated with ethylene diamine tetraacetic acid (EDTA) a thin film developed on the glass surface, owing to the fact that a smaller amount of SiO_2 than of PbO and R_2O had been extracted from the glass [107].

3.6. Reduction of lead glasses by hydrogen

Lead glasses darken as a result of heat-treatment in a reducing atmosphere [108]. Electro-conducting films, formed on the glass surface, has practical importance [109]. It was found by Fainberg [109], who used X-ray diffraction, DTA and softening point determinations, that when high lead glass was heat-treated in a hydrogen atmosphere, the surface layers consisted of crystalline aggregates of metallic lead dispersed in a silica-rich glass. These layers had increased electrical conductivity; acid etching reduced the surface conductivity [110]. The effects of the different ions [111] and of previous chemical treatment [112] on the reduction process in lead glasses and on the surface conductivity were studied. The most compact structure (e.g. at Si:O ratio of 0.445 in K_2O–PbO–SiO_2 system) showed the minimum reduction of lead by hydrogen [55].

Owing to the strong polarizability of Pb^{2+} ions, the electron density distribution in lead glass in contact with metal surface can be highly asymmetric. In such glasses the Pb^{2+} ion may resemble the Pb^{4+} ion in one direction and the metallic lead atom in the other. The process can be considered as "an internal redox reaction"; $Pb^{2+} = \frac{1}{2}Pb^{4+} + \frac{1}{2}Pb^0$. It is a bridge between the structure of lead glass and the metallic structure, which provides the good adhesion between the glass and the metallic surface [113].

4. Phase separation and crystallization in lead glasses

Although lead oxide is a component which usually reduces the tendency of glasses to crystallization, it can enter into glass-ceramics of various types. As a rule, the process of fine crystallization of glass in the bulk is preceded by liquid–liquid phase separation [114–116]. The separation in the $PbO-B_2O_3$ [117–121] and the $PbO-B_2O_3-Al_2O_3$ [120, 122] systems forms the subject of several studies. These systems can be conveniently studied by small-angle X-ray scattering, since the high atomic number of lead ensures a high contrast between the separated phases. Fig. 6 shows the coexistence curve of two liquids in the binary $PbO-B_2O_3$ system [119]. Electron micrographs showed clear liquid–liquid phase separation in a glass containing 2 wt% PbO at 415° C. After 16h the droplet size was about 0.1 μm [119]. The kinetics of the separation were studied in detail; like crystallization, so the liquation process consists of two main stages – nucleation and coalescence of particles. The dimensions of the particles, their number and their statistical distribution were calculated. The dependence of the particle size on the heat-treatment schedule for a glass containing 1% PbO is shown in Fig. 7. The activation energy of the diffusion constant was estimated as $E = 75\,\text{kcal mol}^{-1}$ and the diffusion constant in this glass was found to be $D = 4.32 \times 10^{-13}\,\text{cm}^2\,\text{sec}^{-1}$ [119].

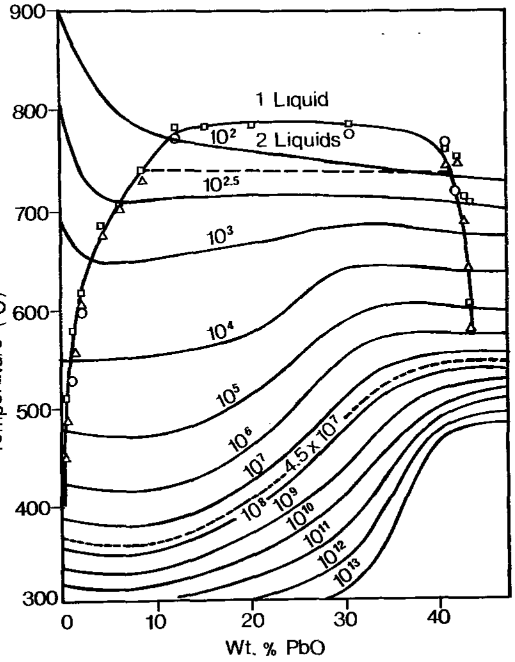

Figure 6 Coexistence curve in $PbO-B_2O_3$ system showing curves of equal viscosity in poises (from [119]).

It was found by Liedberg *et al.* [118] that $PbO-B_2O_3$ glasses containing 15 to 35 mol% PbO contained heterogeneties 2000 to 3000 Å in size. The infra-red study of the $PbO \cdot B_2O_3$ glass showed that various modifications of lead metaborate precipitated out during crystallization at 420 to 600° C for 6 to 260h [123].

If alumina is added to the binary system, the diffusional mobility decreases [122]. The liquation surface has a rather flattened shape, with a

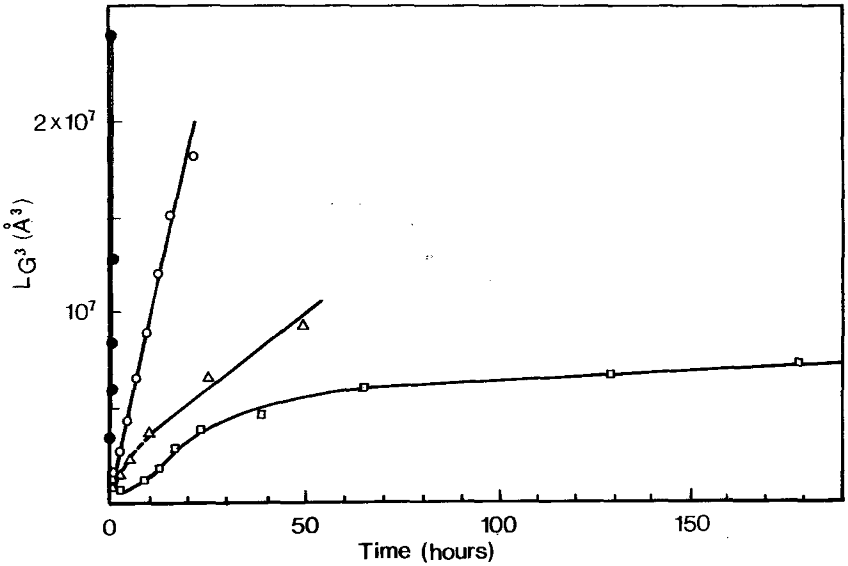

Figure 7 Plots of L_g^3 against time for a specimen containing 1 wt% PbO and 99% B_2O_3 heat-trained at 415° (●), 375° (○), 365° (△) and 340° C (□). $L_g = 1.17L$, where L is the average diameter of the particles (from [119]).

long valley and a saddle point near the composition of 80 wt % B_2O_3, 15% PbO and 5% Al_2O_3. One of the separating phases consists of the almost pure B_2O_3. The spinodal decomposition of the ternary glasses shows that Cahn's theory [124] is approximately obeyed in the initial stages [122].

Samdani *et al.* [125] studied the crystallization of the $PbO \cdot Al_2O_3 \cdot 2SiO_2$ and the $PbO \cdot Al_2O_3 \cdot 6SiO_2$ glasses. The first crystalline phase to precipitate out of these glasses at 1000° C (10 h) was $PbO \cdot Al_2O_3 \cdot 2SiO_2$. The tendency to crystallization of the high silica glass was much weaker than that of the $PbO \cdot Al_2O_3 \cdot 2SiO_2$ glass. When SiO_2 in the high silica glass was partly substituted by B_2O_3, the degree and the temperature of the crystallization reduced.

Differential thermal analysis (DTA) of two lead borate glasses during crystallization was carried out by Bergeron *et al.* [126]. The DTA curves contained two endotherms which preceded the crystal growth exotherm. Micrographs of the crystallization products showed spherulitic lead borate crystals. The first endotherm was attributed to the glass transformation range and the reversible nature of the process was shown. The reversibility of the second large endotherm was not established and the authors believe it to be connected with the coalescence of the glass particles. We cannot agree with this view, since coalescence is accompanied by a decrease in the surface area of the glass and by a decrease in the surface energy, which would be evolved and be evidenced by an exothermal peak.

A number of studies deal with the crystallization process in different lead glasses which can be converted into glass-ceramics. The two most important properties of lead glass-ceramics are the low melting temperature and high dielectric permittivity, especially as regards lead oxide–titania compositions, in which the perovskite type lead titanate ($PbTiO_3$) can be precipitated [127].

The precipitation of the lead titanate from glasses was studied by several workers. Russel and Bergeron [128, 129] investigated the structure of the appropriate glasses and initial stages of the nucleation and the growth of the lead titanate in these glasses. The rate of growth of the $PbTiO_3$ crystals from a glass containing 48.5 mol % PbO, 36.5 % B_2O_3 and 15% TiO_2 was determined as a function of temperature. This temperature dependence is very well described by the Brown–Ginell equation [130] and the constants of the equation were determined experimentally. The resulting equation is:

$$g = \frac{4.394 \times 10^6 T e^{-18190/T} \left[1 - e^{-30(T_L/T - 1)}\right]}{1 + 2.484 \times 10^{44} e^{-1.0627 \times 10^5 / T}}$$

where g is growth rate of the $PbTiO_3$ crystals (in μm min^{-1}) at temperature T (in K) and T_L is liquidus temperature (in K) [128]. The activation energy of the $PbTiO_3$ crystal growth was determined to be 34 kcal mol^{-1}. The activation energy of the viscous flow was 75 kcal mol^{-1}. It was found that the crystallization exotherm on the DTA curve was situated 100 to 150° C below the temperature of the maximum rate of the crystal growth (at 750° C, $g_{max} = 70$ μm min^{-1}) [128].

Processes which precede crystallization were studied for the composition (mol %): 37.1 SiO_2, 10.9 Al_2O_3, 17.3 TiO_2 and 34.7 PbO [129]. X-ray and electron micrographic observations showed the presence of immiscible liquid droplets 100 to 300 Å in size; the droplets were present in the annealed glass and increased in size as the duration of the thermal treatment at 620° C was extended. The relatively high small-angle scattering intensities indicated that the droplet phase had an electron density which was significantly different from that of the matrix glass; hence it could be concluded that the droplet phase had a very high lead content (the electron density of the annealed glass was 1.29 electrons/$Å^3$, that of PbO was 2.11 electrons/$Å^3$).

The DTA curve of this glass showed three exotherms at 680, 735 and 880° C. At 680° C a large number of irregularly shaped particles, 2000 to 4000 Å in size, were formed; the X-ray analysis did not show any diffraction maxima. The apparent size of the discrete phase particles increased at 735° C, and a small number of lath-like particles appeared; the X-ray analysis showed the presence of several weak maxima, which could not be identified. The phase which appeared at 880° C was readily identified as $PbTiO_3$, while the phase which appeared at 735° C was not revealed at 880° C. The size of the individual $PbTiO_3$ crystallites was found to be of the same order of magnitude as that of the individual discrete liquid droplets formed at the lower temperatures. It was, therefore, suggested that the lead titanate crystals had formed in the particulate discrete phase.

TABLE I Lead titanate glass-ceramic compositions in mol % (wt % in parentheses)

No.	PbO	BaO	ZnO	TiO_2	B_2O_3	TeO_2	SiO_2	Al_2O_3	Na_2O	Reference
1	46.0(72)	–	–	26.8(15)	8.2(4)	–	19.0(8)	–	–	[131]
2	41.7(69)	–	–	33.75(20)	–	–	20.2(9)	–	4.35(2)	
3	25.0	22.0	–	23.8	25.0	3.0	–	–	–	[136]
4	23.8	20.0	–	23.8	25.0	1.5	3.0	3.0	–	
5	19.0	20.0	4.8	25.0	25.0	1.5	3.0	3.0	–	
6	16.8	20.0	7.0	23.8	25.0	1.5	3.0	3.0	–	
7	15.3	20.0	8.5	23.8	25.0	1.5	3.0	3.0	–	
8	13.0	20.0	10.8	23.8	25.0	1.5	3.0	3.0	–	

The dissolution of the crystals was indicated by an endotherm at about 1050° C.

The unidentified metastable low-temperature phase, described in [129], may have been identical with a metastable cubic phase, discovered by Martin [131]. He studied the crystallization of compositions 1 and 2 (Table I; we recalculated the compositions to mol % for the sake of a more convenient comparison with other compositions). Heat-treatment at 620 ° C for 30 min resulted in the precipitation of the tetragonal (cubic above 480° C) perovskite lead titanate alone from composition 1, but a second cubic phase was found to be present at lower temperatures. The maximum precipitation of this phase was observed after heat-treatment at 560° C for 30 min. The X-ray powder diffractometric data for the new phase are shown in Table II. Its cell length is about 10.4 Å. An electron micrograph of the cubic phase obtained by direct transmission through thin sections is shown in Fig. 8. The development of the cubic face can be distinctly seen on the micrograph. It was suggested that the new phase had a pyrochlore structure. An increase in the contents of SiO_2, TiO_2 and a decrease in the content of B_2O_3, resulted in the cubic phase becoming more persistent; it was also stabilized by sodium ions, so this phase was much more persistent in composition 2. The phase is much less soluble in dilute nitric acid than the residual vitreous phase, so that it was possible to extract and analyse the crystals. The approximate composition (the sum of the components is less than 100%) is: 71.9 wt % PbO, 19.3 wt % TiO_2, 9.4 wt % SiO_2, which means that silica enters into the metastable titanate. The average CTE of the metastable titanate crystals was determined by measuring the X-ray diffraction lines at elevated temperatures and was found to be $96 \times 10^{-7} \,°C^{-1}$ (25 to 330° C). The CTE of the crystallized glass 1, determined by dilatometer, had the same value; this could be due to a chance coincidence between the expansion of the crystals and the residual vitreous phase.

TABLE II X-ray powder diffractometer data for metastable cubic lead titanate [131]

hkl	*d* (Å)	I/I_0	*hkl*	*d* (Å)	I/I_0
1 1 1	6.06	24.6	5 3 1	1.758	21.6
3 1 1	3.153	48.6	5 3 3	1.588	7.8
2 2 2	3.020	100	6 2 2	1.570	46.5
4 0 0	2.610	54.7	4 4 4	1.501	13.7
3 3 1	2.390	41.0	7 1 1	1.457	6.1
5 1 1	2.006	22.4	7 3 1	1.356	8.2
4 4 0	1.840	54.7			

The DTA curves of glasses 1 and 2 show a crystallization exotherm and an endotherm occurring at higher temperatures (at 620° C for glass 1, at 730° C for glass 2); this endotherm was attributed to the conversion to the stable tetragonal

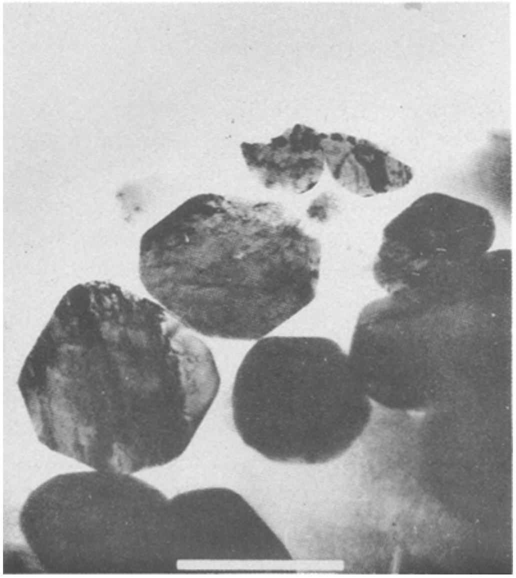

Figure 8 Transmission electron micrograph of thin section of composition 1 (Table I) heat-treated at 560° C for 0.5 h (from [131]). Bar represents 1 μm.

phase [131]. This interpretation cannot be regarded as final, since it is known [132] that in most cases the conversion of a metastable phase to a stable phase is accompanied by evolution rather than by absorption of heat. Exceptions may occur if the metastable phase is denser than the stable phase [132], but this is not the case here: the calculated density of the pyrochlore phase at room temperature is 7.16 as against 8.00 for the perovskite type lead titanate [131].

Phase separation, crystallization and dielectric properties of crystallized $PbO-TiO_2-Al_2O_3-SiO_2$ glasses were also studied by Kokubo and co-workers [133–135]. The glass formation region in this system is shown in Fig. 9 [133]. It varies only to a minor extent with the Al_2O_3/SiO_2 ratio, which was explained by the network-forming effect of lead in glass structure. Some of the glasses became opaque during the heat-treatment, most probably due to liquid–liquid phase separation, since they were found to contian no crystals. Fig. 10 is a graphic summary of the results of heat-treatments of the different glasses. It was found that the pyrochlore type lead titanate precipitated out at the lower temperatures, for example, in a glass of group (a) with a low Al_2O_3 content which is close to the composition of Russel and Bergeron [129]. The ferroelectric perovskite type lead titanate was detected in compositions with the higher Al_2O_3 content [133].

The dielectric properties of the glasses were determined at 1 MHz at room temperature. Both the dielectric permittivity (ϵ) and the dielectric loss ($\tan \delta$) increased as a result of crystallization: in the glasses ϵ was 23 to 36, $\tan \delta$ was 15×10^{-4} to 37×10^{-4}; in the crystallized products ϵ was 35 to 70 and $\tan \delta$ was 41×10^{-4} to 172×10^{-4}. The most interesting case was presented by composition no. 19, containing 40 mol % PbO, 25% TiO_2, 10% Al_2O_3, and 25% SiO_2, in which the cubic perovskite type $PbTiO_3$ ($c/a = 1.0$) precipitated out at 650° C (Fig. 10), giving a resulting high value of $\epsilon = 70$. A detailed study was made of dependence of the dielectric properties of this glass in the crystallized state on heat-treatment schedule, temperature of measurement and frequency. It was found that the content of $PbTiO_3$ increased at 650° C from 16 wt % after 10 min to 34 wt % after 9 h. The dielectric permittivity varied approximately linearly with the $PbTiO_3$ content (Fig. 11). The crystallization of glass no. 19 involved the following stages: (1) separation into two glassy phases (630° C); (2) precipitation of the $PbTiO_3$ crystals in the dispersed glassy phase (650° C); (3) formation of lead aluminium silicate on the surface of the specimen (800° C); (4) formation of the $PbTiO_3$ crystal aggregates (850° C);

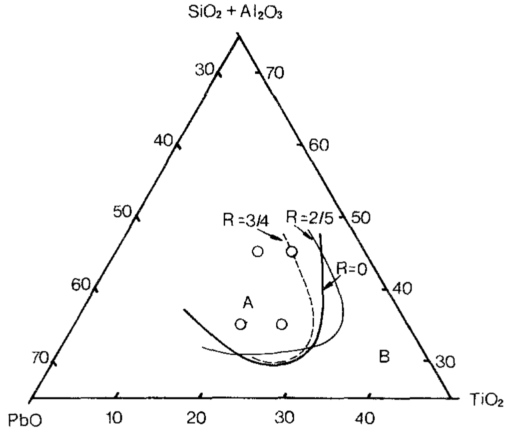

Figure 9 Glass formation (A) and devitrification (B) regions in $PbO-TiO_2-(SiO_2 + Al_2O_3)$ system; $R = Al_2O_3/SiO_2$ (from [133]).

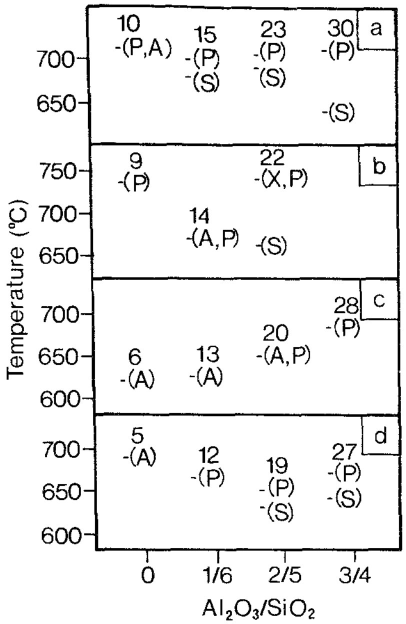

Figure 10 Crystallization process of glasses in $PbO-TiO_2-(SiO_2 + Al_2O_3)$ system (from [133]). P: Precipitation of perovskite type $PbTiO_3$; A: Precipitation of pyrochlore type lead titanate; X: Precipitation of unidentified crystals; S: Separation into two glassy phases. Glass compositions (mol %): (a) 38.0 PbO, 17.0 TiO_2, 45.0 (Al_2O_3 + SiO_2); (b) 33.8 PbO, 21.2 TiO_2, 45.0 (Al_2O_3 + SiO_2); (c) 45.0 PbO, 20.0 TiO_2, 35.0 (Al_2O_3 + SiO_2); (d) 40.0 PbO, 25.0 TiO_2, 35.0 (Al_2O_3 + SiO_2).

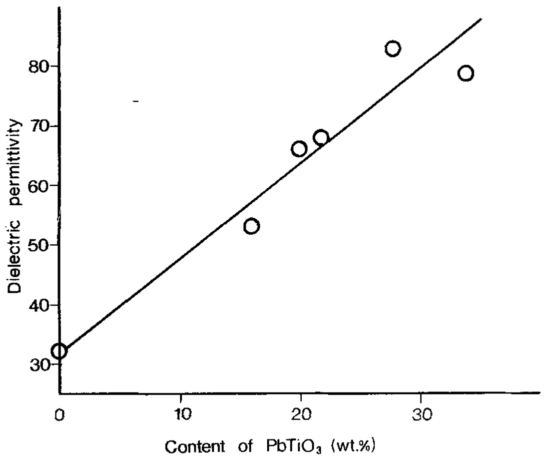

Figure 11 Dielectric permittivity as a function of $PbTiO_3$ content (from [133]).

and (5) spread of the aggregates (950° C) [133]. The replacing of SiO_2 by Al_2O_3 promoted the $PbTiO_3$ precipitation out of the PbO- and TiO_2-rich glassy phase which had formed as a result of phase separation. In high silica glasses without Al_2O_3 the pyrochlore type lead titanate containing SiO_2 in solid solution precipitated out without previous phase separation; it was transformed to the stable perovskite type $PbTiO_3$ crystals at elevated temperatures [135].

The results of these studies found practical application in the development of thick-film capacitors made of the $PbO–TiO_2–Al_2O_3–SiO_2$ glass-ceramics with added B_2O_3, PbF_2, ZnO, and K_2O [134]. A capacitor with a dielectric permittivity of 94 and $\tan\delta = 130 \times 10^{-4}$ (at 1 MHz) was obtained by firing powdered glass containing 45 mol % PbO. 25 mol % TiO_2, 12 mol % SiO_2, 10 mol % Al_2O_3, and 8 mol % B_2O_3 on an alumina substrate to about 600° C. The temperature coefficient of dielectric permittivity was $830 \times 10^{-6}\,°C^{-1}$ in the range from room temperature to 270° C.

The glasses for the capacitors have to soften before crystallization. It was found that there was a significant difference between the properties of the powdered and the bulk glass-ceramics: the dielectric permittivity of the latter was higher but $\tan\delta$ was lower than those of the thick-film powdered material. No information was given in [134] on the CTE of the thick-film dielectrics, but it was indicated that they tended to develop numerous cracks, which resulted in the reduction of dielectric permittivity.

Grossman and Isard [136] prepared compositions of the $PbO–BaO–TiO_2–B_2O_3$ glass-ceramins containing various additions; their compositions no. 3–8 are listed in Table I. The glasses were melted at 1100° C, poured into transparent glass discs, annealed at 500° C for 15 to 30 min and crystallized at 520 to 610° C. The glasses melted in platinum crucibles had a higher nucleation rate than those melted in refractory pots.

It was found that added SiO_2, Al_2O_3 and Na_2O reduced the nucleation of $PbTiO_3$, but small amounts of alumina were required to prevent the formation of voids and cracks during crystallization. In the presence of ZnO and CaO the overall number of the $PbTiO_3$ crystals was reduced. In spite of the high BaO content, precipitation of $BaTiO_3$ was not observed. The highest content of the $PbTiO_3$ crystals was 44 vol %. During the crystallization a small amount of PbO precipitated in the surface layers and was removed before the dielectric measurements. As the $PbTiO_3$ content increased, the dielectric permittivity at 10^3 Hz and 100° C increased from 45 to about 125, while the resistivity decreased from 10^{10} to $10^{7.5}$ Ωcm under these conditions. Glass-ceramics with a high nucleation rate showed a smoother variation of the properties with the crystal content; their resistivities were higher and their permittivities were lower than those of materials containing the same volume fraction of crystals in the form of large crystal clusters [136].

Freidenfel'd *et al.* [137] studied glasses and glass-ceramics in the above system and in the $PbO–BaO–B_2O_3–Bi_2O_3–TiO_2$ system with MnO_2 as the nucleating agent. They showed that glasses containing 45 to 50 mol % (BaO + PbO) had the highest dielectric permittivity, which increased in the presence of Bi_2O_3. The permittivity of crystallized glasses at 10^3 Hz was in certain cases as high as 130 at room temperature and as high as 400 at 300° C.

Glass-ceramics in $B_2O_3–Al_2O_3–PbO–TiO_2$ system with a low dielectric loss factor and a negative temperature coefficient of dielectric permittivity are described in [138].

Glass-ceramics based on lead metaniobate have been prepared [139]. Their dielectric permittivity can vary from 25 for the non-crystallized glass to 1000 to 2000 for the glass-ceramics. The temperature coefficient of dielectric permittivity varies from + (90 to 140) × 10^{-6} to − (2000 to 3000) × $10^{-6}\,°C^{-1}$. These properties depend on a heat-treatment schedule which determines the crystallization of the rhombic or the tetragonal lead metaniobate. The precipitation of the lead metaniobate is preceded by the precipitation of the pyrochlore type phase. The compositions of the glasses are not given in [139].

Kleine *et al.* [140] studied the crystallization and dielectric properties of $PbO-TiO_2-ZrO_2-SiO_2$ glass-ceramics; the most complete information is given for the compositions containing (wt%) 50 PbO, 30 SiO_2, 20 (TiO_2 + ZrO_2), with 0, 2, 4, 6 and 8% ZrO_2. It was found that the crystallization temperature increased when TiO_2 was replaced by ZrO_2. The phase composition of the glass containing 20% TiO_2 after heat-treatment at 615° C was $2PbO \cdot SiO_2$, $4PbO \cdot SiO_2$, and TiO_2, but at 800° C the precipitation of $PbTiO_3$ was observed. According to the authors, glass with 8% ZrO_2 contained 6 crystalline phases, including $PbZrO_3$ and ZrO_2, but this result cannot be accepted as conclusive because it is based on the X-ray diagram containing only 9 peaks, which cannot yield a reliable identification of 6 phases.

Fig. 12 shows the dependence of the dielectric permittivity and the dielectric loss at 10^3 Hz on temperature. It is seen that up to 200° C the values of these parameters did not change significantly, but increased rapidly beyond that point. The increase in the zirconia content was accompanied by an increase in the permittivity from 28 to 68 and of the tan δ from 120×10^{-4} to 200×10^{-4} at room temperature. The electrical conductivity curve of the glass-ceramics showed a break at 100 to 200° C, which was attributed to the different conductivities of the vitreous and the crystalline phases. The conductivity of the glass-ceramics increased with temperature from 7.1×10^{-13} to 1.8×10^{-11} Ωcm. The values of CTE given in Table III decreased with increasing in the ZrO_2 content; they also decreased with crystallization. The values of the chemical durability to water determined by the powder method are also included in Table III. It is seen that the durability was rather low in the absence of zirconia, but increased considerably in the presence of ZrO_2. The durability of the glass-ceramics was higher than that of the glasses. The density of the glass-ceramics varied from 5.6 g cm^{-3} in the absence of ZrO_2 to 6.20 g cm^{-3} in the presence of 8% ZrO_2.

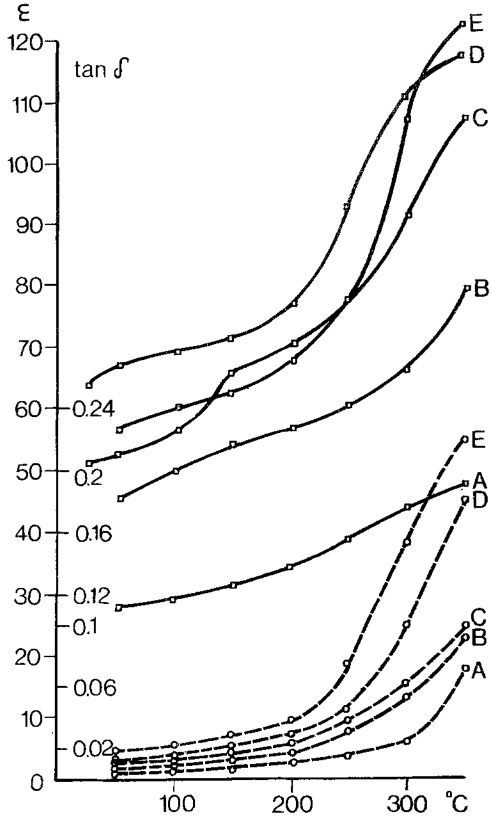

Figure 12 Temperature dependence of dielectric permittivity ϵ (solid lines) and loss tan δ (dashed lines) at 10^3 Hz for crystallized glasses, containing 30 wt% SiO_2, 50% PbO, 20% (TiO_2 + ZrO_2) and ZrO_2 content is (A) 0%, (B) 2%, (C) 4% (D), 6%, (E) 8% (from [140]).

TABLE III Linear coefficients of thermal expansion (α) and chemical stability in water of glass and glass-ceramics containing 30 wt% SiO_2, 50 wt% PbO and 20 wt% (TiO_2 + ZrO_2) [140]

Content of ZrO_2 (wt%)	$\alpha \times 10^7$ (°C^{-1}) Glass (20 to 200° C)	Glass-ceramics	Weight loss (%) Glass	Glass-ceramics
0	145	72(20–200° C)	0.28	0.22
2	96	63(20–300° C)	0.21	0.20
4	90	60(20–300° C)	0.15	0.12
6	87	56(20–300° C)	0.11	0.10
8	45	24(20–500° C)	0.09	0.08

Bogdanova *et al.* [141] studied the dielectric properties of the cordierite glass-ceramics containing lead titanate, but the compositions are not given. The frequency dependencies of the dielectric permittivity and the dielectric loss were complicated; the loss tangent was rather high at low frequencies and was low at high frequencies (at 10^8 Hz and higher). The dielectric permittivity of the glass-ceramics was 10 to 30.

Mikoda *et al.* [142] described the effect of crystallization on the electrical properties of a glass containing (wt%) 66.7 PbO, 16.4 SiO_2, 3.9

Na_2O, 2.4 K_2O, 0.3 Li_2O, 7.7 SrO, and 2.6 MgO. They found a crystallization exotherm at 610° C and a melting endotherm at 760° C on the DTA curve. The crystalline phase was identified as $PbO \cdot SiO_2$. It was established that the volume resistivity of the glass decreased, while the loss factor at 10^3 Hz increased with the crystallization; this result was attributed to the sharp increase in the concentration of alkaline ions in the residual vitreous phase: after treatment of the glass for 10 h at 610° C this concentration was about 39 wt % R_2O against 6.6% in the original glass.

Pavlushkin and co-workers [143–145] studied the crystallization of $PbO–SiO_2$ and $PbO–B_2O_3–SiO_2$ glasses containing additions. A mixture of various crystalline lead silicates ($2PbO \cdot SiO_2$, γ–$4PbO \cdot SiO_2$ and $3PbO \cdot 2SiO_2$) was precipitated at 600° C out of the galss containing 84.6 wt% PbO and 15.4 wt% SiO_2 [143]. This crystallized glass had a coarse microstructure and a low strength, from which it was concluded that it does not possess the specific structure required for the development of the glass-ceramic structures. The effects of TiO_2 (up to 10%), P_2O_5 (up to 3.5%) and F (up to 2%) added to the basic composition were studied. It was shown that only the glass containing P_2O_5 was capable of developing a fine crystalline structure with $3PbO \cdot 2SiO_2$ as a main phase. This glass was examined more in detail. It was found that the maximum CTE value ($140 \times 10^{-7}\,°C^{-1}$) and the maximum softening point (about 700° C) were reached at 550° C in 1 h. The precrystallized heat-treatment at 300 to 420° C did not affect these properties of the glass-ceramic. It was accordingly concluded that the liquation and nucleation processes were completed during the cooling after the melting of the glass. Lead titanate was formed in the glass containing 7.5% TiO_2.

The $PbO–B_2O_3–SiO_2$ glasses containing added MoO_3, TiO_2, and ZnO were studied [144, 145]. It was found that the degree of crystallization increased as the PbO content increased from 50 to 70 mol %, and decreased as the B_2O_3 and ZnO contents increased. The $PbTiO_3$ and $PbMoO_4$ crystals were formed in the respective glasses. On the other hand, no crystalline zinc compounds were detected in ZnO-containing glasses. The properties of the products of the crystallization of these glasses are not described [144, 145].

Microstructure, phase separation and reflectance of opaque glasses containing (wt%) 50 PbO, 25 B_2O_3 and 25 SiO_2 with added 15% TiO_2, 15% ZrO_2, or 7.5% SnO_2 were described [146]. It was shown that a fine droplet structure was essential to the opacity of the glasses and this structure promoted the maximum reflectance.

Suzuki and Ichimura [147] studied the thermal expansion of crystallized $PbO–B_2O_3–TiO_2$ glasses. The devitrification of these glasses was very rapid, and the vitreous specimens could only be obtained as thin films by rapid quenching. The crystallization temperature of the glasses depended mainly on the PbO content. The CTE of the crystallized specimens decreased with increase of TiO_2 content. The CTE showed a gradual decrease with the precipitation of the perovskite type $PbTiO_2$, and attained the value of $61.5 \times 10^{-7}\,°C^{-1}$ (at 100 to 300°C) in a glass containing (wt%) 70 PbO, 15 B_2O_3 and 15 TiO_2 after crystallization at 580°C for 30 min. When 2% B_2O_3 were replaced by SiO_2, the precipitation of $PbTiO_3$ was enhanced, and the CTE of the crystallized product reduced to $50 \times 10^{-7}\,°C^{-1}$. However, these CTE values were not as low as might have been expected from the negative CTE of the lead titanate. This effect seemed to be caused by the high CTE of the residual vitreous phase in the crystallized materials.

Caslavska *et al.* [148] described the crystallization of a glass containing 70% PbO, 5% Al_2O_3 and 25% SiO_2. Orthorhombic PbO precipitated out at temperatures below 500° C, while at higher temperatures the precipitate consisted of a mixture of the orthorhombic and the tetragonal modifications of PbO. The initial glass gave electron micrographs indicating a two-phase structure, while the absence of the peaks on the X-ray diagrams showed that this structure was vitreous.

Low-melting lead glasses are extensively used as non-crystallized and crystallized solder glasses, the latter being also known as "glass-ceramic cements". Many of these glasses are of the $PbO–B_2O_3$, $PbO–B_2O_3–ZnO$ and $PbO–Al_2O_3–SiO_2$ systems. Crystallized solder glasses soften and flow before crystallization, but subsequently solidify as a result of crystallization, and their working temperature in the crystallized state is close to the soldering temperature. Hence they are very valuable for vacuum tight joining of components of various reliable electronic devices (colour TV tubes, packages of integral circuits etc.), because these devices can be evacuated at rather high temperatures. The detailed survey of crystallized solder glasses was published by the author in 1971 [149], the survey of non-crystallized solders was published by Broukal [150]. Therefore, we shall not consider these subjects in detail; we shall merely mention a few publications in this field. The crystallization and the thermal expansion of the $PbO-B_2O_3-ZnO$ glasses were studied by Zhdanets and Kheifets [151]. Adding TiO_2 to glasses of this system brings the precipitation of the lead titanate which reduces the CTE of the crystallized material, obtained from the low-melting and low-softening glasses with a rather high CTE [152]. The crystallized solder glass with soldering temperature 420° C for the colour TV tubes was found by the present author and colleagues [153]. The author [154] also considered the mechanism of the crystallization of the solder glass and found it to have a surface character as in ordinary glasses which are not intended for conversion into glass-ceramics (glasses, which can be converted into glass-ceramics, crystallize in the volume). The relatively slow crystallization provides satisfactory spreading of the solder glass and joining details of the devices before the glass solidifies.

Lead oxide is often used as flux in glass-ceramic enamels [155] and glazes [156]; these glazes are intended for strengthening glass-ceramic and ceramic articles with CTE higher than that of the glazes.

Glass-ceramics containing PbO as a main component, or as addition, form the subject of a number of patents [157-160]. Glass-ceramics with stable electrical properties were obtained in the $SiO_2-PbO-RO$ system (20 to 30 mol % PbO) with added alkali fluorides and oxides [158]. Low-melting glass-ceramics in the $PbO-B_2O_3-Tl_2O_3-SiO_2$ system are described in [159]. A glass-ceramic with composition $K_2O \cdot 4PbO.8SiO_2$ was prepared; its bending strength was 1000 to 1400 kg cm^{-2} [161].

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