

Oxidic glasses as hosts for migrating metal ions

John A. Duffy

Received: 5 October 2009 / Revised: 16 November 2009 / Accepted: 16 November 2009 / Published online: 9 January 2010
© Springer-Verlag 2009

Abstract The results of experiments where Tl^+ and Pb^{2+} ions are electrolysed into a sodium borate glass (35 mol% Na_2O and 50 °C) are brought up to date in order to take into account recent developments in the chemistry of borate glasses. It is first necessary to consider the unique chemistry of the oxide(-II) species in terms of its electronegativity, electronic polarisability and acid–base properties, and the significant relationship between these is discussed. It is described how the Lewis basicity of oxidic materials such as glasses can be expressed quantitatively on the optical basicity scale and how determinations are made by various experimental methods. These methods include optical spectroscopy of ‘probe’ ions such as Tl^+ or Pb^{2+} , measurement of electronic polarisability and far-infrared spectroscopic ‘rattling’ frequencies of constituent metal ions. When Pb^{2+} ions are electrolysed into the sodium borate glass, it is found that there is migration of Na^+ ions away from and of O^{2-} ions towards the (lead) anode with formation of PbO . There is almost complete depletion of Na_2O in the anode region so that the composition of the glass approximates to B_2O_3 . A similar process occurs to a limited degree in the case of thallium, but the Tl^+ ions are able to penetrate more deeply into the glass. Their ultraviolet $^1S_0 \rightarrow ^3P_1$ frequency indicates that the sites they occupy have much greater basicity than the bulk glass. The two-site model of Kamitsos proposes that in borate glasses, there are higher and lower basicity sites, and the measured optical basicity of Tl^+ indicates occupation of

the higher sites. Since it has been shown that BO_4 groups in the glass are weakly basic, it is unlikely that they are involved in the higher sites. It is discussed how the higher site basicity implies greater covalency in the interaction of the Tl^+ ion with the oxide(-II)s that constitute the pathway, and it is suggested that this is an important factor in the electromigration process.

Keywords Glass electrolysis · Optical basicity · Oxide ion transport · Borate glass

Introduction

About 30 years ago, experiments were conducted in Dr. Baucke's laboratory where Tl^+ and Pb^{2+} ions were electrolysed into a sodium borate glass at 50 °C, which is well below the glass transition temperature. During the intervening years, there have been several important developments in the acid–base treatment of oxidic materials and in the chemistry of borate glasses in particular. In the light of this later knowledge, it is timely to reconsider the electromigration experiments and the results to which they give rise.

Most oxidic materials contain oxygen as the oxide (-II) species, that is, where it is in the oxidation state of -2. With two electrons having been added to the neutral oxygen atom, the O^{2-} ion spontaneously loses an electron. It is stabilised to a limited extent by an environment of highly ionic cations such as K^+ or Ba^{2+} . However, there is then the tendency to form the oxide(-I) species which rapidly transforms into peroxide or superoxide. Oxygen is normally thought of as a highly electronegative element but the value, x_O , depends on the extent of negative charge that it bears (as far as this can be

Dedicated to Friedrich Baucke on the occasion of his 80th birthday.

J. A. Duffy (✉)
Department of Chemistry, University of Aberdeen,
Old Aberdeen AB24 3UE Scotland, UK
e-mail: j.a.duffy@abdn.ac.uk

estimated). This charge covers a significantly wider range compared with other elements and is responsible for the variability observed for the electronic polarisability of oxide(-II) which, in itself, is an indication of electronic charge. Many oxides, such as oxyanion glasses, can be regarded as products of an acid–base reaction, and it is significant that the polarisability of oxide(-II; that is, the electronic charge borne) is responsible for giving rise to the extremes in acidic and basic properties of oxides, for example, from the essentially covalent P_2O_5 to the mostly ionic BaO .¹

General properties of oxides

Electronegativity

The Pauling electronegativity of oxide(-II), x_O , is usually assigned a value of 3.5 [1]. A closer examination of the Pauling method of determination (using heats of formation of oxides) shows that this value applies to covalent oxides, but as the bonding becomes more ionic, there is a fall in the value of x_O [2]. This is understandable, since an increasingly negative charge on (covalently bound) oxide(-II) will cause the oxide(-II) atom to lose its tendency to acquire further negative charge. The effect is shown in Fig. 1 where the points (unlabelled) are for the oxides in Table 1. It should be noted that they are of cations with the ns^2np^6 configuration; oxides of transition metal elements do not exactly follow this trend.

The electronegativity difference between two elements of a binary compound is normally taken as an indication of the degree of ionicity in the bonding, but this does not necessarily apply in the case of binary oxides. Indeed, it is possible for the electronegativity difference, $x_O - x_M$, for the oxides of two different elements (M) to be the same, yet the two oxides can have very different ionicities. For example, the electronegativity differences for Na_2O and SiO_2 are very close (1.65 and 1.67, respectively), but Na_2O is regarded as ‘ionic’ and basic, while SiO_2 is ‘covalent’ and acidic; similarly, BaO and the much less ionic Al_2O_3 have the same electronegativity difference of 1.86 (Table 1). Nevertheless, in spite of this abnormal behaviour, electronegativity has been used (in conjunction with optical basicity—see later) for estimating the percentage ionicity in several oxides, see Table 1 [3].

¹ For many oxidic compounds, it is difficult to classify the oxide(-II) species as the oxide(-II) *ion* or the oxide(-II) *atom*; for example, as for the oxide(-II) species in Al_2O_3 . In this paper, all oxygen atoms (ions) are in the oxidation state of -2 .

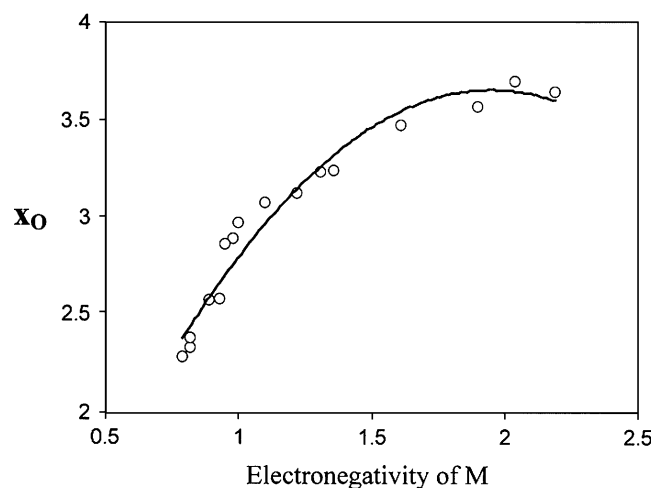


Fig. 1 Plot of oxide(-II) electronegativity, x_O , for oxides, M_aO_b (Table 1), versus electronegativity of M . Points at the bottom left-hand area are for ‘ionic’ oxides and at the top are for covalent

Electronic polarisability

The electronic polarisability of oxide(-II), $\alpha_{\text{oxide(-II)}}$, in a binary oxide, M_aO_b , can be obtained from refractivity data (density, d , in g/cm^3 , and refractive index, n) and formula weight, M , by first of all calculating the molecular polarisability, α_{mol} (in \AA^3), using the Lorentz–Lorenz relationship [4, 5]

$$\alpha_m = \frac{3M}{4\pi Nd} \frac{n^2 - 1}{n^2 + 2} \quad (1)$$

where N is Avogadro's number. The total polarisability of the cations present is subtracted from α_{mol} and the difference is divided by the number of oxide(-II) atoms or ions. Normally, polarisability is a more or less fixed parameter, e.g. for Na^+ , it is 0.179 \AA^3 and Cl^- , it is 3.66 \AA^3 [4, 5]. For oxide(-II), as mentioned above, the polarisability, $\alpha_{\text{oxide(-II)}}$, covers a wide range, e.g. in MgO , it is 1.71 \AA^3 , but with the large cation in CaO , it is 2.49 \AA^3 and in Al_2O_3 , where the oxide(-II) charge clouds are more tightly affected, $\alpha_{\text{oxide(-II)}}$ is 1.46 \AA^3 . These values and others are included in Table 1 where it can be seen that decreasing $\alpha_{\text{oxide(-II)}}$ is accompanied by decreasing basicity (increasing acidity) of the oxide.

Acid–base properties

Oxides, and especially mixed oxide systems, have enormous technological application, and this has prompted efforts for establishing a quantitative scale of acidity or basicity in these systems. One scale that has been widely used is due to Lux and Flood [6]. This attempted to use the idea of $p(\text{oxide ion activity})$ analogous with pH , but its application is necessarily somewhat narrow owing to the

Table 1 Electronegativities (χ), polarisabilities (α), and optical basicity data (γ and Λ) for binary oxides

Oxide	χ_M (Pauling)	$\chi_O - \chi_M^a$	χ_O (Pauling)	% Ionicity ^b	α_M^c (\AA^3)	$\alpha_{\text{oxide(-II)}}^d$ (\AA^3)	γ_M^e	$\Lambda(\text{oxide})^e$
Cs ₂ O	0.79	1.49	2.28	80	2.42		0.66	1.52
Rb ₂ O	0.82	1.51	2.33	73	1.40		0.7	1.43
K ₂ O	0.82	1.56	2.38	66	0.83		0.76	1.32
Na ₂ O	0.93	1.65	2.58	54	0.179		0.905	1.105
Li ₂ O	0.98	1.91	2.89	45	0.029	1.58	1.23	0.81
BaO	0.89	1.86	2.57	74	1.55	3.7	0.75	1.33
SrO	0.95	1.91	2.86	59	0.86	3.07	0.95	1.05
CaO	1.00	1.97	2.97	58	0.47	2.49	1.00	1.00
MgO	1.31	1.92	3.23	34	0.094	1.71	1.10 ^f	0.91
La ₂ O ₃	1.10	1.97	3.07	67	1.32		0.85	1.18
Y ₂ O ₃	1.22	1.90	3.12	56	0.55	2.47	0.96	1.04
Sc ₂ O ₃	1.36	1.88	3.24	50	0.286	2.14	1.11	0.90
Al ₂ O ₃	1.61	1.86	3.47	21	0.052	1.46	1.65 ^f	0.61
SiO ₂	1.90	1.67	3.57	22	0.0165	1.41	2.10 ^f	0.48
B ₂ O ₃	2.04	1.66	3.70	18	0.003	1.39	2.47 ^g	0.40
P ₂ O ₅	2.19	1.45	3.64	17	0.0	1.33	2.1 ^h	0.48

^a Calculated from heats of formation [1]

^b From [3]

^c Pauling values from [4]

^d From [21]

^e From [10]

^f For fourfold coordination; for sixfold, γ_{Mg} is 1.65, γ_{Al} is 2.48 and γ_{Si} is 3.15.[21]

^g For threefold coordination; for fourfold, γ_{B} is 4.2.[27, 28]

^h γ_{P} varies in phosphate glasses [31]

flaw incurred in the assumption of a single ion (oxide, O^{2-}) activity [7]. For several applications, it has been superseded by the optical basicity concept, introduced in 1971 [5, 8–11]. Optical basicity allows comparisons to be made between molten oxidic systems regardless of the cation content thereby uniting, for example, the redox equilibria of $\text{Fe}^{2+}/\text{Fe}^{3+}$ (with air) in lithium, sodium and potassium silicate melts which otherwise show separate trends. A comparison of the optical basicity approach with the oxide ion activity method, especially to redox problems, has recently been published by Angell [12], and it is instructive to make further comparison with previous work by Baucke and Duffy concerning the striking relationship between redox equilibria in aqueous solution and in silicate melts at 1,400 °C [11]. The relationship allows basicity effects on redox equilibria, involving ion pairs such as $\text{Ti}^+/\text{Ti}^{3+}$, in the melts to be calculated from data for the ion pairs in aqueous solution.

Further examples of the application of optical basicity are as follows: to glass chemistry, references 1–20 in [13]; for slag performance in extraction metallurgy, reference [14] and references 9–25 in [3]; for catalysis, reference [15] and references 20–25 in [16].

Optical basicity measurement

The optical basicity concept was developed mainly in the context of oxidic glass chemistry. It has a fundamental reliance on molecular orbital theory and the orbital expansion experienced by certain metal ions as a result of chemical bonding (nephelauxetic effect [17]), that is, the degree of Lewis acid–base interaction between the metal ion and the coordinating oxide(-II) atoms of the glass. For optical basicity measurement, it was found that the best ions for probing oxide(-II) basicity were the $6d^{10}6s^2$ ions Tl^+ and Pb^{2+} , using the ultraviolet $^1\text{S}_0 \rightarrow ^3\text{P}_1$ (6s-6p) absorption band [5, 8, 9, 18]. These probe ions, dissolved when the glass was molten, registered a frequency maximum, ν_{medium} , which was generally found to decrease with increasing glass basicity. Crystalline calcium oxide was chosen for pragmatic reasons as representing the standard basic medium with its frequency maximum, ν_{CaO} , while the standard medium of zero basicity was taken as represented when the probe ion was in the gaseous state, with the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ frequency denoted ν_{f} . It follows that the ratio of frequency shifts, $(\nu_{\text{f}} - \nu_{\text{medium}})/(\nu_{\text{f}} - \nu_{\text{CaO}})$, represents the ratio of electron

donation by the oxide(-II) atoms of the medium to that in CaO. This has been defined as the optical basicity, Λ , of the medium, and it is apparent that CaO has unit optical basicity. With appropriate substitution of the $^1S_0 \rightarrow ^3P_1$ frequencies for the probe ions, the optical basicities are given by:

$$\Lambda = \frac{55,300 - \nu_{\text{medium}}}{18,300} \quad (2)$$

for Tl^+ and for Pb^{2+} :

$$\Lambda = \frac{60,700 - \nu_{\text{medium}}}{31,000} \quad (3)$$

It has been found that the values of Λ determined by Tl^+ or Pb^{2+} (and other probe ions) are normally in agreement [8]. Over the years, other methods have been developed for obtaining optical basicity. These include measurement of oxide(-II) 1s binding energies [19], of far-infrared ‘rattling’ frequencies of constituent alkali ions [20] and of electronic polarisabilities [10].

Analysis of accumulated data has shown that the optical basicity of an oxidic medium, composed of oxides A, B..., can be calculated from its chemical formula by considering two factors: (1) the concentration of each of the cations in terms of their equivalent fractions, $X(\text{oxide A})$, $X(\text{oxide B})$... and (2) the effect that each cation, A, B..., has in attenuating the electron donor power (basicity) of the constituent oxide(-II)s, expressed as the ‘basicity moderating parameter’, γ_A , γ_B ... The optical basicity is given by:

$$\Lambda = \frac{X(\text{oxideA})}{\gamma_A} + \frac{X(\text{oxideB})}{\gamma_B} + \dots \quad (4)$$

which can also be written with the substitution of $\Lambda(\text{oxideA})$ in place of $1/\gamma_A$, $\Lambda(\text{oxideB})$ in place of $1/\gamma_B$, etc. Later work suggested that the γ values represented polarising power of the cations [10].

With Λ defined as unity for CaO (see above), Eq. 4 shows that γ_{Ca} is also unity. Equation 4 allows calculation of γ values of other elements from experimentally measured optical basicities using glasses of appropriate composition. For example, measurements show that the glass of formula CaSi_2O_5 has Λ equal to 0.58; hence, by Eq. 4, $1/5\gamma_{\text{Ca}} + 4/5\gamma_{\text{Si}} = 0.58$ and γ_{Si} is 2.1. Values of γ for other cations are in Table 1. Again, the relationship, Eq. 4, makes it possible for Λ to be calculated for any oxidic glass simply from its chemical composition, provided that the relevant γ values (Table 1) are known.

Use of this facility (Eq. 4) has allowed investigation into the relationship between optical basicity and oxide(-II) polarisability, $\alpha_{\text{oxide(-II)}}$, for glasses over a very wide acid–base range [10]. The results, involving approximately 450

alkali and alkaline earth silicate glasses, have indicated the closeness of the relationship between Λ and $\alpha_{\text{oxide(-II)}}$ (details are in [10] and [21]). From $\Lambda=0.7$ downwards, the relationship is almost linear (Fig. 2) and extrapolates into an interesting region showing the effect of coordination number on the basicity of certain oxides [21]. For example, sixfold coordinated Al^{3+} , as in $\alpha\text{-Al}_2\text{O}_3$, has $\gamma=2.48$ and $\Lambda=0.403$, but with fourfold coordination, often found in glass chemistry, γ is 1.65. In $\gamma\text{-Al}_2\text{O}_3$ where two thirds of the Al^{3+} ions are in sixfold coordination and one third in fourfold, the application of these two γ values indicates an optical basicity of 0.454, close to the observed value of 0.47 [21]. Further examples are in the footnotes to Table 1. This variation in γ values complicates the simple relationship between γ and electronegativity ($\gamma_{\text{M}} = 1.33(x_{\text{M}} - 0.25)$) previously proposed [22].

Optical basicity represents the electron donor power of oxide(-II), that is, the extent of negative charge borne by oxygen. This means that in an oxyanion system, the greater the optical basicity, the more covalent is the oxide(-II)-metal ion interaction. This seeming paradox is resolved by considering the isoelectronic series of oxyanions, ClO_4^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} , where, in this order of increasing negative charge, their salts *decrease* in ionic character. Furthermore, their interaction with protons, as indicated by the dissociation constants of the acids, also becomes more covalent. Thus, for a glass, low basicity means that there is a small negative charge on oxide(-II), and therefore high ionicity/low covalency in the interaction with cations, while increasing basicity implies greater negative charge and decreasing ionicity, increasing covalency. This concept is relevant to problems of electromigration of cations through oxidic media.

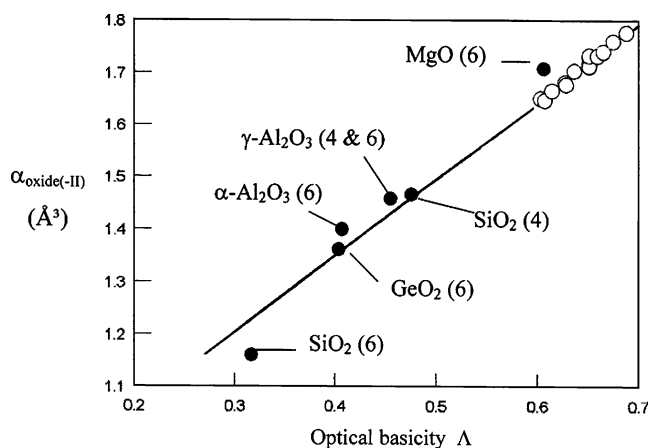


Fig. 2 Plot of oxide(-II) polarisability, $\alpha_{\text{oxide(-II)}}$, versus optical basicity showing binary oxides (labelled) close to the linear extension of the relationship established for alkali and alkaline earth silicate glasses (top right-hand corner)

Electrolysis of borate glass

Silicate, borate and phosphate glasses at ordinary temperatures are poor ionic conductors, except when they contain certain ions such as Ag⁺ or Γ⁻. Usually, the oxide network remains intact, but several years ago, Baucke and the present author investigated the possibility of electrically disrupting the glass network by experimenting with borate glasses.

The choice of these glasses was based on the well-known facility that boron has for readily interchanging its stereochemistry between trigonal and tetrahedral. In alkali borate glasses, both these forms (as BO₃ and BO₄) are present (see below), and the intention was to exploit the bond rupture of the interconversion in order to effect ionic conduction. At the same time, there was the hope that by using thallium or lead as anode, Tl⁺ or Pb²⁺ ions would enter the glass and signal, through their ¹S₀→³P₁ frequency, the nature of the site occupied during electromigration. For practical reasons, the glass samples had the Na₂O:B₂O₃ composition of 35:65 and electrolysis took place at well below the glass transition temperature at 50 °C; further experimental details are in [23–25]. Ion ablation of the electrolysed glasses from the surface inwards indicated that with lead as anode, only a small number of Pb²⁺ ions had entered the glass. The sodium ions in the glass had migrated to the (mercury) cathode, with simultaneous migration of oxide(-II) to the anode and the formation of PbO so that the glass composition in the anode region, with the depletion of Na⁺ and O²⁻ ions, approximated to B₂O₃ (Fig. 3). When thallium amalgam was the anode, there was again evidence for the formation of oxide (Tl₂O), but the migration of Na⁺ ions was less clear-cut and indicated a lesser degree of oxide(-II) ion migration. The combination of ion ablation and ultraviolet absorption spectroscopy showed that Tl⁺ ions had entered to a depth greater than 150 nm. The absorption band had a frequency maximum of 43,100–43,300 cm⁻¹, corresponding (by Eq. 2) to an optical basicity of 0.66–0.67.

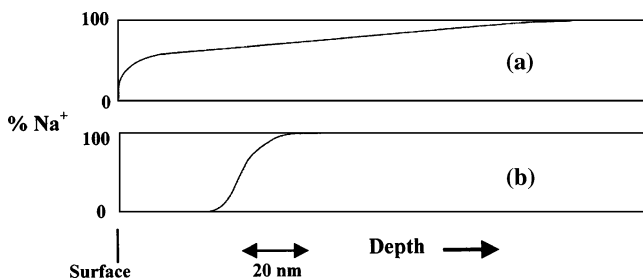
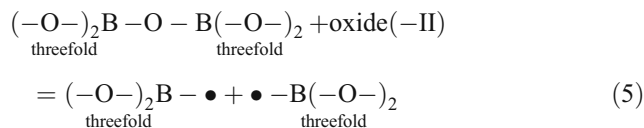
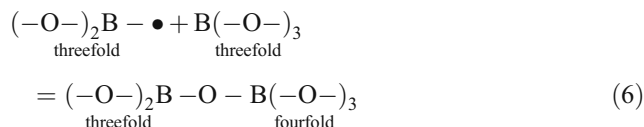


Fig. 3 Sodium concentration profiles in the anode region of 35 mol% Na₂O sodium borate glass after electrolysis at 50 °C using (a) thallium amalgam anode and (b) lead anode. Total charge transported: 0.03 °C; current density ca. 4 μA cm⁻²

As mentioned earlier, in alkali borate glasses, increasing addition of alkali oxide to B₂O₃ results in the conversion of the threefold coordination of boron to fourfold. Denoting bridging oxides (bos) as –O– and nonbridging (nbos) as –● and conveniently ignoring anionic charge, the reaction can be viewed as follows:



simultaneously followed by:



The reactions, which occur up to an alkali oxide content of approximately 30 mol%, favour the predominance of fourfold coordinated B(-O)₄ groups over threefold (-O)₂-B-● groups, although this tendency is modified for the alkali glasses from lithium to caesium [26]. To account for oxide(-II) ion migration during electrolysis, a mechanism relying on the reverse of Eq. 6, and of Eq. 5, was proposed [23].

The optical basicity of 0.66–0.67 which was observed for Tl⁺ electrolysed into the glass was much greater than expected for the 35 mol% Na₂O glass and presented a problem that is still not fully resolved. The determination of optical basicity in borate glasses by probe ions is not straightforward owing to the tendency for the probe ions to distribute themselves between two sites of different basicity. Nevertheless, the trend in these two sites (upper basicity and lower basicity) in the sodium borate glass system has been determined using the far-infrared ‘rattling’ frequencies of the Na⁺ ions [20]. From Fig. 4, it is apparent that in the 35 mol% Na₂O glass that was used in the electrolysis experiment, the Tl⁺ ions occupy the upper basicity sites similar to those signalled by the infrared spectra of the Na⁺ ions.

Turning to the lower basicity sites shown in Fig. 4, it is seen that there is almost no increase in optical basicity with Na₂O content until beyond ca. 20 mol%. This is also revealed when the optical basicity trend is determined from refractivity data (Fig. 5, which, of course, shows only a single trend). The reason for this early lack of increase arises because of the much greater γ value that has been found for fourfold coordinated boron compared with threefold (values are 4.2 and 2.47, respectively; compare Al³⁺, above) [27]. This means that the oxide(-II) atoms attached to the fourfold coordinated boron atoms are of much lower basicity than those attached to the threefold. The BO₄ units (Eq. 6) are much less basic than the BO₃ units and tend

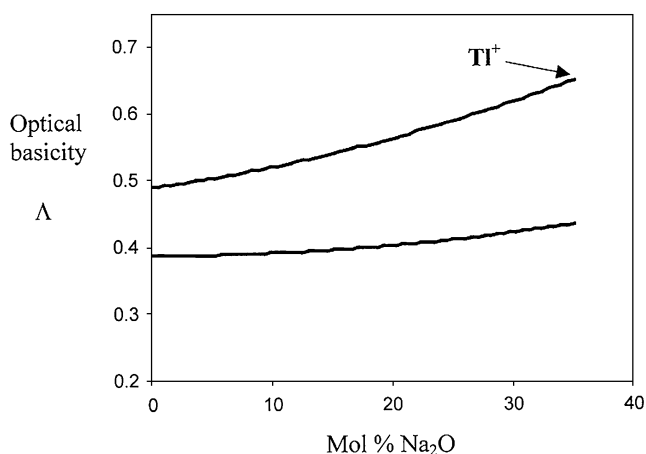


Fig. 4 Trends in optical basicity for sodium borate glass system, as determined using far-infrared ‘rattling’ frequencies of Na^+ ions, showing the higher and lower basicity sites. The point for TI^+ electrolysed into the glass is denoted

to cancel the increased basicity of the $(-\text{O}-)_2\text{B}-\bullet$ which are simultaneously produced, though in small quantity (Eqs. 5 and 6). Indeed, for the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glass system, increasing Li_2O content causes, initially, a decrease in basicity, as seen in the unexpected redox behaviour of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Cr}^{6+}/\text{Cr}^{3+}$ pairs [28]. The important conclusion follows that the chemical composition of the upper basicity sites (Fig. 4) excludes BO_4 units and must rely solely on the small number of BO_3 units (containing nonbridging oxide(-II) atoms) that are produced. Until the discovery of the exceptionally large γ value for fourfold coordinated boron, it was generally assumed that the basicity of BO_4 units was relatively high.

If we consider a borate glass where BO_4 units are discounted, then we are dealing with a hypothetical glass which consists only of BO_3 units, and where the boron-oxide(-II) network will be a mixture of bridging and nonbridging oxygen atoms. To some extent, the greater

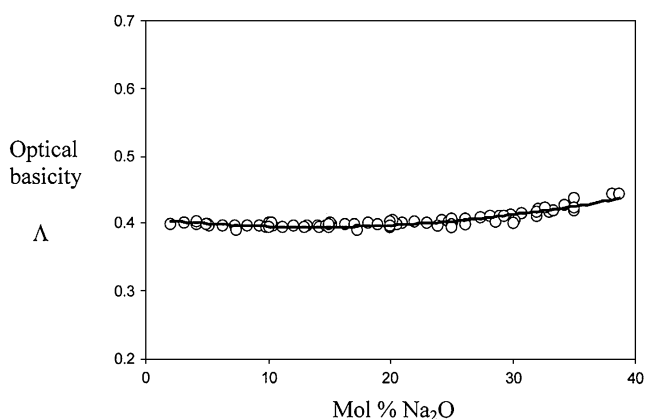


Fig. 5 Trend in optical basicity in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glass system as determined using refractivity data. The scale of the axes is the same as in Fig. 4

electron density of the nbos is modified by spreading on to the bos through π -bonding. Thus, for a set of glasses with increasing nbo:bo ratio, there would be an overall increase in the basicity of all the oxygen atoms. For the (hypothetical) sodium borate glass, $x\text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3$, it is possible to calculate the nbo:bo ratio for various borate species together with their optical basicities. It is worthwhile noting that since the optical basicity of the glass is given by Eq. 4 as: $\Lambda = [x/\gamma_{\text{Na}} + (300 - 3x)/\gamma_{\text{B}}]/(300 - 2x)$, and the proportion of nbos to total oxygen, r , equals $2x/(300 - 2x)$, it follows that:

$$r = \frac{\Lambda - 1/\gamma_{\text{B}}}{1/\gamma_{\text{Na}} - 1/\gamma_{\text{B}}} \quad (7)$$

where γ_{B} is the value for threefold coordination (2.47—see Table 1). Results are in Table 2.

With the aid of Table 2, it can be seen that the electrolysed TI^+ ions, with their optical basicity registering 0.66–0.67 (corresponding to $r=73$ –76% by Eq. 7), suggest a local environment corresponding to a sodium borate glass approximating to the composition $2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$. Such a glass is known to exist (30) and, moreover, the boron atoms are all threefold coordinated. This suggests that in the 35 mol% Na_2O glass, clusters approximating to composition $2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ exist for the TI^+ ions. Possibly the formation of these, or similar clusters, is favoured by the migration of oxide(-II) atoms towards the anode (Fig. 3). At this stage, it is not possible to comment with certainty on the local environment of the Na^+ ions (upper line in Fig. 4), and this problem is presently being considered [30]. Nevertheless, for the migrating TI^+ ions, and possibly also the Na^+ ions, it is apparent that the pathway is of significantly greater basicity than the average for the glass. There is a greater degree of electron donation to the TI^+ ion and, as discussed earlier, this means that there is a more

Table 2 Nonbridging oxide(-II) (nbo) content and optical basicity values for sodium borate glasses hypothetically devoid of fourfold coordinated boron

$\text{Na}_2\text{O}:\text{B}_2\text{O}_3$	mol% Na_2O	Borate unit	nbo:bo	% nbo (r)	Λ
1:3	25.0	$\text{B}_6\text{O}_{10}^{2-}$	1:4	20.0	0.475
1:2	33.3	$\text{B}_4\text{O}_7^{2-}$	2:5	29.6	0.505
1:1	50.0	$\text{B}_2\text{O}_4^{2-}$	1:1	50.0	0.580
3:2	60.0	$\text{B}_4\text{O}_9^{6-}$	2:1	66.7	0.638
2:1	66.7	$\text{B}_2\text{O}_5^{4-}$	4:1	80.0	0.685
5:2	71.4	$\text{B}_4\text{O}_{11}^{10-}$	10:1	90.9	0.723
3:1	75.0	BO_3^{3-}	All nbo	100	0.755

covalent, less ionic, interaction between the cation and the oxygen atoms constituting its pathway.

Conclusions

Oxidic materials such as oxyanion glasses owe much of their chemistry to the variability in the properties of the oxide(-II) species. Depending on the cations present, oxide (-II) can vary in the degree of electronic polarisability (i.e. $\alpha_{\text{oxide(-II)}}$) or, in other words, the extent of the negative electronic charge that it bears. This effect is intimately related to the acid–base properties of the material which is quantified as the optical basicity, Λ . Experimentally, there is a simple quantitative relationship between Λ and $\alpha_{\text{oxide(-II)}}$ (Fig. 2).

These considerations are useful for discussing the results of past experiments that attempted to electrolyse Tl^+ and Pb^{2+} ions into a sodium borate glass. Using thallium amalgam and lead films as anodes, there is migration of Na^+ ions towards the cathode in both cases. For the lead anode, the simultaneous oxide(-II) migration towards the anode results in a growing region where the depletion of Na_2O leads to conversion of the glass to B_2O_3 . For thallium, there is evidence that Tl^+ ions enter more deeply into the glass than the Pb^{2+} ions, and the ultraviolet $^1\text{S}_0 \rightarrow ^3\text{P}_1$ spectrum indicates an environment with $\Lambda=0.66\text{--}0.67$, which is significantly greater than the expected optical basicity of the glass. This is evidence that there is a greater degree of covalency in the interaction between the Tl^+ ion and oxide(-II) during the migration process. Generally, for electromigration of ions through solids, ionic-covalent interactions between the migrating metal ion and the anionic pathway should be regarded as an important factor.

References

- Pauling L (1948) The nature of the chemical bond. Chapter II. Cornell University Press, Ithaca
- Duffy JA (1977) *J Chem Phys* 67:2930
- Duffy JA (2006) *J Phys Chem A* 110:13245
- Tessman JR, Kahn AH, Shockley W (1953) *Phys Rev* 92:890
- Duffy JA (1990) Bonding, energy levels and bands in inorganic solids, chapters 3, 6 and 8. Longmans, UK
- Flood, Förland T (1947) *Acta Chem Scand* 1:592
- Guggenheim EA (1929) *J Phys Chem* 33:842
- Duffy JA, Ingram MD (1971) *J Am Chem Soc* 93:6448
- Duffy JA, Ingram MD (1976) *J Non-Cryst Solids* 21:373
- Duffy JA (2002) *J Non-Cryst Solids* 297:275
- Duffy JA, Baucke FGK (1995) *J Phys Chem* 99:9189
- Angell CA (2009) *J Solid State Electrochem* 13:981
- Duffy JA (2005) *Phys Chem Glasses* 46:1
- Yang Y, Sommerville ID (2002) *Phys Chem Glasses (Proc XIX Int Congr Glass)* 43C:362
- Bordes-Richard E, Courtine P (2006) In: Fierro JLG (ed) *Metal oxides, chemistry and applications*, chapter 10. CRC Taylor and Francis, London, pp 319–352
- Duffy JA, Macphee DE (2007) *J Phys Chem B* 111:8740
- Jørgensen CK (1969) *Oxidation numbers and oxidation states*, chapter 4. Springer-Verlag, Berlin
- Duffy JA, Ingram MD (1971) *J Chem Phys* 54:443
- Dimitrov V, Komatsu T, Sato R (1999) *J Ceram Soc Jpn* 107:21
- Duffy JA, Kamitsos EI, Chryssikos GD, Patsis AP (1993) *Phys Chem Glasses* 34:153
- Duffy JA (2004) *J Phys Chem B* 108:14137
- Duffy JA, Ingram MD (1973) *J Chem Soc Chem Commun* 17:635
- Baucke FGK, Duffy JA (1980) *J Electrochem Soc* 127:2230
- Baucke FGK, Duffy JA (1983) *J Chem Soc Faraday Trans I* 79:661
- Baucke FGK (2000) In: Bach H, Baucke FGK, Krause D (eds) *Electrochemistry of glasses and glass melts, including glass electrodes*. Springer-Verlag, Berlin, pp 275–301
- Kamitsos EI, Karakassides MA, Chryssikos GD (1987) *J Phys Chem* 91:5807
- Duffy JA (2008) *Phys Chem Glasses* 49:317
- Duffy JA (2008) *Phys Chem Glasses* 49:202
- Duffy JA (1975) *Phys Chem Glasses* 16:22
- Kamitsos EI, Ingram MD Personal communication
- Duffy JA (2004) *Phys Chem Glasses* 45:322