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Review

Consideration on the Correlation between Basicity of Oxide Glasses and O1s Chemical Shift in XPS

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酸化物ガラスの塩基度と XPS による O1s 化学シフトの相関に関する考察

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O1s binding energy measured by X-ray photoelectron spectroscopy (XPS) is candidate as a new tool to determine a new scale of Lewis basicity of oxide ions in glass. Some mathematical expressions for the basicity or XPS chemical shift, such as charge parameter and optical basicity, were compared with the experimental O1s binding energy in binary alkali oxide glasses. The expressions so far in use needed some modification in parameters. A new empirical expression introduced in this paper gives a new concept and universal scale of basicity.

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1. Introduction

1.1 Basicity of glass

VARIOUS concepts have been proposed for acid-base behaviors. Nowadays, a definition proposed by Lewis,[1] is commonly used because of its simplicity and wide applicability, where an acid is defined as an electron accepter and a base is as an electron donor. According to the definition, basicity is interpreted as a measure of electron donating ability. Therefore, almost all properties which are concerned in electrons are closely related to basicity; for example, chemical properties such as reactivity and resistance, optical functions such as photo-emission and absorption, and electrical and magnetic properties.

The basicity of glass can be determined from the various experiments, such as activity of oxide ion, optical absorption and electron spin resonance.[2] Duffy and Ingram[3] proposed a basicity concept based on optical absorption, being named optical basicity. They noticed that a UV absorption peak of a cation such as Tl^{+}, Pb^{2+} and Bi^{3+} with an ns^2 configuration showed a chemical shift, and it was quite sensitive to the glass composition. The chemical shift is caused by the change of electron population in the outer most orbital of the probe ions, which reflects the quantitative alteration of the electrons transferred between the matrix glass and the probe ions. Based on this point of view, they defined the chemical shift of the absorption peak as an optical basicity of the matrix glass. The problem is that there are a number of glass systems in which the UV absorption peak of probe ions is not measurable; in the case of TeO_2 system, for instance, the optical absorption edge of the matrix glasses is located at the region of UV through visible lights, and hence the UV absorption peak of the probe ions cannot be measured, that is, the optical basicity cannot be determined in such glasses.

As described, the basicity of an oxide glass is expressed by the ability in electron donation of oxide ions, that is, the basicity of oxide ions. Then, what are the oxide ions with high basicity? The electrons being donated are the electrons which are excessively localized on oxide ions. The excess electrons bring about the expansion of electron cloud, and the oxide ions with expanded electron cloud should be easily polarized, that is, they should have higher polarizability. Furthermore, electrons are transferred between the probe ions and the ligand oxide ions through the molecular orbitals formed by these ions. Hence, the excess electrons being donated must be the electrons in valence band or outer-shell orbitals. It is consequently suggested that the oxide ions with higher population of outer-shell electrons and higher polarizability should have higher basicity. Dimitrov and Komatsu[4] estimated the polarizability of oxide ions in numerous oxide glass systems, being successfully related to the optical basicity.

The change in the states of outer-shell electrons, that is, the change in the chemical bonding character exerts an influence on the electrostatic interaction between nucleus and inner-shell electrons, resulting in the change of binding energy of inner-shell orbitals. The change in the binding energy can be qualitatively explained as follows; when the electron population of outer-shells is reduced, the outer-shell electrons cannot screen the positive charge of nucleus, and then the inner-electrons move toward the nucleus to screen the electrostatic field of the nucleus. As the result, the binding energies of inner-shell orbitals become larger. In the opposite case of larger electron population, the inner-shell orbitals such as O1s orbital show a chemical shift to the lower binding energy side. It is therefore expected that the basicity of oxide ions is determined by the O1s binding energy.

1.2 XPS chemical shift and basicity

X-ray photoelectron spectroscopy (XPS) can determine the binding energies of inner- and outer-shell orbitals simultaneously. Furthermore, there is no limitation in the material system. As mentioned, the optical basicity of TeO_2-based glasses is not determined because the absorption peak of the probe ions hides in the absorption of the matrix glass. XPS is therefore a promising experimental method to determine the basicity.

In principle, XPS has many advantages over the other spectrometries, and in the past, however, XPS has never been ap-

plied to the basicity determination of glasses. Many of the glasses are insulator, and hence the charge-up problem had been unavoidable. During the XPS measurement, the sample surface is positively and nonuniformly charged due to the photoelectron emission from the surface, and hence the surface potential is modulated to be difficult to obtain the correct binding energy. The dissolution of the charge-up problem has been waited for so long. Matsumoto et al.[5] developed a charge control method, where an electrically grounded Ni-metal mesh screen is mounted about 1 mm above the sample surface and a low energy electron flux is irradiated to the sample. It is quite simple but highly effective to remove the potential modulation. The charge control method allowed us to develop a novel determination method of basicity for the insulating materials such as glasses.

The accumulation of the spectral data and the compilation as a database are worth doing in themselves. Furthermore, if the basicity or chemical shift of XPS signals is estimated from some computational expressions, the application will be remarkably expanded. If basicity of a glass is evaluated from the glass composition and if basicity of a structural group or an individual atom is estimated from the local structure, we can also utilize the basicity for checking the validity of a spectrum measured or giving an assignment of a spectral component in a peak separation. Moreover, if the basicity of a novel glass can be predicted, it will also serve as a guideline in the material design.

Then, in the present study, computational expressions in describing the basicity of oxide ions have been explored. Various theoretical and empirical expressions for the XPS chemical shift and basicity have so far been proposed. The best expression was inquired by investigating the correlations between the computational quantities and the experimental O1s binding energies in various glass systems. The authors research group has applied the novel charge control method[5] to the XPS measurements for a wide variety of glass systems, accumulating highly reliable spectral data. In the present paper, alkali binary oxide glass systems, R_2O–B_2O_3,[6] R_2O–SiO_2,[7] R_2O–P_2O_5, R_2O–GeO_2,[8] R_2O–TeO_2,[9] and R_2O–Bi_2O_3 (R = Li, Na, K) were chosen to examine the correlations.

2. Computational expressions for XPS chemical shift and basicity of glasses

2.1 Theoretical expressions for XPS chemical shift

Various attempts have been done to describe the chemical shifts of XPS signals. Among them, the charge potential model proposed by Siegbahn[10] has been most widely applied.

$$\Delta E_i = kq_i + V_i + l \tag{1}$$

where ΔE_i is the chemical shift of the atom i. The first term in the right side of the equation represents the inner potential of the atom i, k is the conversion constant corresponding to the repulsion between the electrons of inner- and outer-shells, and q_i is the net charge. The second term V_i represents the potential due to the atomic interactions, and the third term l is the constant corresponding to the energy criterion. Under the point charge approximation, V_i is given by

$$V_i = \sum_{j \neq i} \frac{q_j}{R_{ij}} \tag{2}$$

which is associated with a Madelung potential in the case of solids. In Eq. (2), R_{ij} is the atomic distance between the atoms, i and j. These equations suggest that the chemical shift is affected by the electronic states of atoms and molecular structures of materials.

Applying these equations, it is required to know the structure of the object substance. In the case of solids, they are applicable to the crystals of known structures and inapplicable to the non-crystalline materials, such as glasses, because it is hard to give a strict definition of their atomic arrangement. Then, several approximations have been introduced to expand the applicability. By using the electroneutrality condition,

$$q_i = -\sum_{j \neq i} q_j \tag{3}$$

Eqs. (1) and (2) can be rewritten as follows.[11]

$$\Delta E_i = -\sum_{j \neq i} \left(k - \frac{1}{R_{ij}} \right) q_j + l \tag{4}$$

In most cases, furthermore, even when the interactions from the second and farther neighbors are ignored, the chemical shifts can be roughly reproduced. Then, taking into account only the nearest neighboring atoms and assuming R_{ij} to be not so much different, the value in parentheses in Eq. (4) can be regarded as constant, obtaining a simplified equation.

$$\Delta E_i = -\text{const.} \sum_{j \neq i} q_j + l = \text{const.}\, q_i + l \tag{5}$$

Equation 5 means that the chemical shift is proportional to the charge q_i of the atom i under investigation.

What comes next is the estimation of the atomic charge q_i. Nordberg et al.[12] considered that q_i was given by the summation over the charge q_{ij} transferred between the atoms i and j, and they defined q_{ij} as an ionicity proposed by Pauling.[13]

$$\begin{cases} q_i = \sum_{j \neq i} q_{ij} \\ q_{ij} = 1 - \exp\{-0.25(\chi_i - \chi_j)^2\} \end{cases} \tag{6}$$

where χ_i is the Pauling electronegativity. The charge q_i given in this way is called charge parameter or Pauling charge, which is commonly expressed by q_p.

Jolly[14] proposed the idea that the chemical shift was expressed by the sum of parameters p_j which were specific to each bonded atom j. The atom i is unchanged under investigation, and hence χ_i in Eq. (6) is regarded as constant. In the case of C1s chemical shift, for example, $\chi_C = 2.5$, thus obtaining an approximation, $q_{ij} \approx 0.27\,\chi_j - 0.67$ for $1.0 < \chi_j < 4.0$. It was indicated that the C1s chemical shift was given by $\Delta E_C = 7.04\,q_C - 0.83$ when assuming the Pauling charge of carbon as $q_C = \Sigma(0.27\,\chi_j - 0.67)$. He has finally proposed a generalized expression, determining the parameter p_j for some atoms.

$$\Delta E_i = \Sigma p_j + l \tag{7}$$

2.2 Empirical and theoretical expressions for basicity

Duffy and Ingram[3] considered that the optical basicity of oxide ion, Λ was dependent on the sort and quantity of atoms interacting, and proposed the following equation.

$$\begin{cases} \Lambda(\chi) = \sum_i \frac{z_i r_i}{2\gamma_i} \\ \gamma_i = 1.36(\chi_i - 0.26) \end{cases} \tag{8}$$

where z_i is the oxidation number of the cation i, and r_i is the ionic ratio with respect to the total number of oxides. γ_i is the basicity moderating parameter and is empirically given by using the Pauling electronegativity χ_i.

Duffy[15] also found a relation between the optical basicity and polarizability of oxide ion, $\alpha(O)$.

$$\Lambda(\alpha) = 1.67 \left(1 - \frac{1}{\alpha(O)} \right) \tag{9}$$

Furthermore, Dimitrov and Sakka[16] derived the following equation.

$$\alpha(\mathrm{O}) = \left[\left(\frac{V_m}{2.52} \right) \frac{(n_0^2 - 1)}{(n_0^2 + 2)} - c(\mathrm{M})\alpha(\mathrm{M}) - c(\mathrm{R})\alpha(\mathrm{R}) \right] \frac{1}{c(\mathrm{O})} \quad (10)$$

where V_m is the molar volume, n_0 is the refractive index, and c is the atomic ratio in an alkali (R) metal (M) oxide, $R_{c(R)}M_{c(M)}O_{c(O)}$.

Recently, Dimitrov and Komatsu[17] introduced the interaction parameter A, which is a quantitative measure of interionic interaction and is derived from the polarizabilities of constituent ions of a material.

$$A = \{\alpha(\mathrm{O_f}) - \alpha(\mathrm{O})\}/2\{\alpha(\mathrm{M}) + \alpha(\mathrm{O_f})\}\{\alpha(\mathrm{M}) + \alpha(\mathrm{O})\} \quad (11)$$

where $\alpha(\mathrm{M})$ and $\alpha(\mathrm{O})$ are the polarizabilities of cation and oxide ion, respectively, and $\alpha(\mathrm{O_f})$ is the polarizability of free oxide ion (3.921 Å^3). A linear correlation was found between A and $\Lambda(\alpha)$ calculated from Eqs. (9) and (10) in various glass systems,[18] suggesting that the interaction parameter A was available as a measure of basicity of glass.

Morinaga et al.[19] assumed that the basicity was inversely proportional to the Coulomb force between cation and oxide ion, proposing the basicity parameter B as follows.

$$\begin{cases} B_i' = \left[\dfrac{z_i \times 2}{(r_i + 1.40)^2} \right]^{-1} \\ B_i = \dfrac{B_i' - B_{\mathrm{SiO_2}}'}{B_{\mathrm{CaO}}' - B_{\mathrm{SiO_2}}'} \\ \mathrm{B} = \sum_i n_i B_i \end{cases} \quad (12)$$

where z_i is the charge of cation i, r_i is the ionic radius in Å, and n_i is the cationic ratio.

3. Results and discussion

3.1 Basicity and XPS chemical shift estimated

In the estimation of XPS chemical shift by using the equations introduced in the Section 2.1, the number of atomic pairs, that is, the structure should be given. The glass structure is inherently obscure, and hence the equations are not applicable to glass without modification. However, the properties of glass are often approximated by the linear combination of the properties of each glass constituent (additivity rule). Then, the charge of oxide ion was estimated from Eq. (6), assuming that the charge of oxide ions in an alkali binary glass was given by averaging the charge of oxide ions introduced from the alkali oxide, q_p(O in NWM) and the network-forming oxide, q_p(O in NWF). The charge q_p(O in NWF) can be estimated from Eq. (6) without modification, and in the estimation of the charge q_p(O in NWM), however, some modifications are required because the local structure around oxide ions in R_2O is far from the structure in glass. In general, the charge of alkali ions is regarded as +1, and even in the estimation of the charge parameter, it is assumed that a unit charge −1e is transferred from an alkali atom to the adjacent atom.[12] According to the XPS measurements,[7] however, the binding energies of core-orbitals of alkali ions are not invariable, and they shifts chemically as well as O1s signals, suggesting that the interactions between alkali and oxide ions are not fully ionic but partially covalent. However, the charges q_p(O in NWM) estimated from Eq. (6) assuming the crystal structures of R_2O become unrealistic values less than −2. It was therefore supposed that oxide ions in an alkali oxide possessed a fully ionic charge multiplied by the rate of ionicity. Finally, the charge of oxide ions in a glass was evaluated as follows.

$$\begin{cases} q_p(\mathrm{O}) = q_p(\mathrm{O\ in\ NWM}) + q_p(\mathrm{O\ in\ NWF}) \\ q_p(\mathrm{O\ in\ NWM}) = z_0 \times q_{ij},\ z_0 = -2 \\ q_p(\mathrm{O\ in\ NWF}) = -N \times q_{ij} \\ q_{ij} = 1 - \exp\{-0.25(\chi_i - \chi_j)^2\} \end{cases} \quad (13)$$

where NWM and NWF represent network modifier and network former, respectively. z_0 is the fully ionic charge of oxide ions, and N is the number of NWF atoms such as Si and B bound to an oxide ion. For NBO, $N=1$, and for BO and doubly-bonded oxygen such as O in P=O bond, $N=2$.

The atomic charges of oxide ions q_p(O) calculated from Eq. (13) are listed in **Table 1**, and the parameters used in the calculations are also listed in **Table 2**. The correlation between the q_p(O) determined in this way and the experimental O1s binding energy, E_B(O1s) is shown in **Fig. 1**(a). In the case of $N=2$, the data for TeO_2 and Bi_2O_3 systems are located at different regions from those for the other glass systems. However, if assuming $N=3$, that is, oxide ions are surrounded by 3 Te or Bi ions, the data shift to the region on the extension of the other data for the normal coordination number, $N=2$. The reason is unclear, but the lone-pair electrons on Te and Bi ions may be responsible for the irregular coordination number. At any rate, a roughly-linear correlation is confirmed in the systems, B_2O_3, SiO_2, P_2O_5 and GeO_2; as expected, the O1s binding energy decreases as the charge of oxide ions becomes more negative.

Next, the optical basicity derived from electronegativity, $\Lambda(\chi)$ was calculated from Eq. (8), and the correlation with E_B(O1s) is plotted in Fig. 1(b). $\Lambda(\chi)$ can be directly calculated from the glass composition, as is also the case for basicity parameter B. As similar to the case in q_p(O), the data for TeO_2 and Bi_2O_3 systems deviate from the others. In each glass system, however, a favorable linear relationship is found. Except for Bi_2O_3 system, E_B(O1s) shifts to lower side with increasing the basicity $\Lambda(\chi)$.

Figure 1(c) shows another correlation between optical basicity and O1s binding energy, where $\Lambda(\alpha)$ was estimated from Eqs. (9) and (10). According to Eq. (10), the molar volume V_m and refractive index n_0 are necessary in obtaining the polarizability of oxide ion α(O), and V_m is derived from the density d. Prior to the α(O) calculation, the values of d and n_D (Na D-line, $\lambda = 589.3$ nm) are estimated as follows. The experimental data of d and n_D were extracted from the handbooks,[20] and the data were plotted against R_2O content, performing polynomial regressions (maximum order 4). In extracting the data, the data for the glasses whose analytical compositions were specified were collected except for TeO_2 system. Moreover, the data with large deviation from the approximation curve were excluded from the regressions. The values of d and n_D listed in Table 1 were calculated by using the regressions obtained in this way. In Fig. 1(c), a decreasing tendency of E_B(O1s) with the increase in $\Lambda(\alpha)$ is commonly observed in each glass system. However, the magnitude of the change in $\Lambda(\alpha)$ in each system is quite small as compared with the difference in $\Lambda(\alpha)$ between the glass systems.

Dimitrov et al. have examined the correlations among the polarizability, basicity, interaction parameter, and XPS chemical shift for a number of glass systems (see references in Ref. 18). A linear correlation was observed between the interaction parameter A and the optical basicity $\Lambda(\alpha)$.[17),18),21] When A is

Table 1. Glass Composition, Estimated Density d and Refractive Index n_D, Experimental O1s Binding Energy $E_B(O1s)$, Pauling Charge of Oxide Ion $q_p(O)$ and Optical Basicity $\Lambda(\chi)$ Calculated from Electronegativity χ, Polarizability of Oxide Ion $\alpha(O)$, Optical Basicity $\Lambda(\alpha)$ Calculated from $\alpha(O)$, Basicity Parameter B Calculated from Atomic Charge z, and Chemical Shift Parameter CSP, Where $q_p(O)$, $\Lambda(\chi)$, $\alpha(O)$, B, and CSP are Calculated from the Parameters Listed in Table 2

(a) $xR_2O\cdot(100-x)B_2O_3$

R	x* (mol%)	d (g/cm³)	n_D	E_B(O1s) (eV)	q_p(O) from χ	q_p(O) from χ_1	$\Lambda(\chi)$	$\Lambda(\chi_2)$	α(O) (Å³)	α_1(O) (Å³)	$\Lambda(\alpha)$	$\Lambda(\alpha_1)$	B from z	B from z_1	CSP (eV)
	0	1.837	1.459	533.31	-0.860	-0.901	0.423	0.433	1.369	0.424	0.450	-2.266	0.026	1.086	533.01
Li	8	1.950	1.486	532.97	-0.880	-0.916	0.438	0.450	1.363	0.445	0.445	-2.081	0.156	1.342	532.84
	12	2.010	1.500	533.02	-0.892	-0.925	0.447	0.460	1.360	0.459	0.442	-1.972	0.229	1.484	532.75
	19	2.109	1.521	532.34	-0.913	-0.941	0.464	0.478	1.353	0.481	0.436	-1.805	0.348	1.712	532.58
	23	2.168	1.534	532.52	-0.927	-0.952	0.475	0.490	1.350	0.496	0.433	-1.695	0.420	1.850	532.47
	27	2.216	1.545	531.96	-0.940	-0.962	0.486	0.502	1.349	0.514	0.432	-1.579	0.485	1.970	532.38
	33	2.270	1.560	531.85	-0.960	-0.977	0.502	0.519	1.357	0.550	0.440	-1.367	0.576	2.139	532.23
	37	2.291	1.573	531.35	-0.979	-0.992	0.517	0.536	1.379	0.598	0.459	-1.122	0.656	2.284	532.10
	41	2.282	1.583	531.23	-0.995	-1.004	0.530	0.550	1.412	0.654	0.487	-0.885	0.718	2.396	531.99
	44	2.247	1.592	530.95	-1.011	-1.017	0.542	0.564	1.460	0.724	0.526	-0.638	0.776	2.497	531.89
	52			530.62	-1.051	-1.047	0.574	0.599					0.905	2.717	531.65
Na	6	1.977	1.484	532.62	-0.876	-0.914	0.437	0.447	1.366	0.450	0.447	-2.043	0.161	1.322	532.80
	10	2.041	1.491	532.89	-0.886	-0.923	0.447	0.457	1.364	0.467	0.446	-1.903	0.247	1.471	532.66
	12	2.073	1.494	532.51	-0.893	-0.928	0.453	0.463	1.363	0.478	0.445	-1.824	0.295	1.555	532.58
	16	2.142	1.499	531.92	-0.908	-0.940	0.467	0.477	1.362	0.504	0.443	-1.642	0.407	1.745	532.39
	26	2.285	1.511	531.81	-0.941	-0.968	0.499	0.508	1.368	0.572	0.449	-1.249	0.630	2.116	531.99
	31	2.346	1.517	531.17	-0.960	-0.983	0.516	0.525	1.379	0.617	0.459	-1.036	0.739	2.292	531.78
	37	2.380	1.515	531.01	-0.986	-1.005	0.541	0.549	1.405	0.692	0.481	-0.744	0.881	2.516	531.49
	41	2.339	1.500	530.69	-1.007	-1.022	0.561	0.569	1.434	0.760	0.505	-0.528	0.985	2.677	531.27
K	5	1.976	1.482	532.76	-0.874	-0.916	0.438	0.449	1.362	0.448	0.444	-2.062	0.190	1.310	532.79
	11	2.054	1.488	532.73	-0.891	-0.935	0.458	0.469	1.364	0.487	0.446	-1.758	0.378	1.561	532.53
	17	2.112	1.488	532.23	-0.911	-0.956	0.481	0.492	1.369	0.536	0.450	-1.448	0.583	1.826	532.24
	21	2.167	1.489	531.96	-0.928	-0.975	0.501	0.512	1.372	0.576	0.453	-1.227	0.744	2.028	531.99
	24	2.202	1.492	531.21	-0.938	-0.986	0.512	0.523	1.375	0.601	0.455	-1.109	0.831	2.135	531.86
	32	2.299	1.502	531.45	-0.972	-1.022	0.550	0.562	1.400	0.700	0.477	-0.717	1.103	2.456	531.41
	34	2.308	1.502	530.50	-0.981	-1.032	0.562	0.574	1.415	0.736	0.490	-0.598	1.177	2.540	531.29

* analytical compositions determined by an inductively coupled plasma method

(b) $xR_2O\cdot(100-x)SiO_2$

R	x* (mol%)	d (g/cm³)	n_D	E_B(O1s) (eV)	q_p(O) from χ	q_p(O) from χ_1	$\Lambda(\chi)$	$\Lambda(\chi_2)$	α(O) (Å³)	α_1(O) (Å³)	$\Lambda(\alpha)$	$\Lambda(\alpha_1)$	B from z	B from z_1	CSP (eV)
	0	2.203	1.456	532.66	-1.029	-0.910	0.477	0.464	1.455	0.435	0.522	-2.171	0.000	1.035	532.97
Li	33	2.343	1.534	531.19	-1.138	-1.017	0.579	0.582	1.557	0.748	0.597	-0.562	0.853	2.723	531.84
Na	20	2.387	1.490	531.63	-1.096	-0.980	0.552	0.540	1.547	0.694	0.591	-0.736	0.783	2.441	531.80
	25	2.429	1.497	531.67	-1.115	-1.000	0.573	0.562							531.51
	30	2.468	1.502	530.87	-1.135	-1.021	0.596	0.585	1.596	0.841	0.624	-0.316	1.084	2.932	531.22
	33	2.489	1.505	530.96	-1.148	-1.034	0.610	0.599	1.612	0.889	0.634	-0.209	1.166	3.058	531.05
	40	2.530	1.511	530.32	-1.179	-1.067	0.645	0.635	1.656	1.011	0.661	0.018	1.342	3.318	530.64
	45	2.551	1.514	529.93	-1.204	-1.092	0.672	0.663							530.35
	50	2.563	1.517	529.80	-1.230	-1.119	0.701	0.692	1.734	1.214	0.707	0.295	1.566	3.615	530.05
K	20	2.391	1.494	531.25	-1.101	-1.007	0.576	0.566	1.560	0.748	0.599	-0.563	1.127	2.577	531.53
	33	2.473	1.508	530.44	-1.157	-1.083	0.652	0.652	1.635	0.985	0.649	-0.025	1.678	3.207	530.60

* nominal compositions

(c) $xR_2O\cdot(100-x)P_2O_5$

R	x* (mol%)	d (g/cm³)	n_D	E_B(O1s) (eV)	q_p(O) from χ	q_p(O) from χ_1	$\Lambda(\chi)$	$\Lambda(\chi_2)$	α(O) (Å³)	α_1(O) (Å³)	$\Lambda(\alpha)$	$\Lambda(\alpha_1)$	B from z	B from z_1	CSP (eV)
	0			532.65	-0.775	-0.698	0.400	0.350					-0.103	0.185	534.68
Na	30			533.24	-0.926	-0.846	0.459	0.413					0.633	0.974	533.51
	23			533.22	-0.886	-0.807	0.442	0.395					0.461	0.785	533.82
	35			533.17	-0.956	-0.876	0.472	0.428					0.755	1.111	533.26
	34			533.01	-0.950	-0.870	0.470	0.425					0.731	1.084	533.31
	37			532.92	-0.969	-0.889	0.478	0.434					0.804	1.167	533.16
	42			532.81	-1.002	-0.921	0.494	0.451					0.927	1.309	532.89
	46			532.76	-1.030	-0.949	0.509	0.466					1.025	1.424	532.66
	52			532.17	-1.076	-0.993	0.533	0.492					1.172	1.603	532.29
	58			531.45	-1.124	-1.041	0.562	0.523					1.319	1.790	531.87

* analytical compositions determined by XPS

(d) $xR_2O\cdot(100-x)GeO_2$

R	x* (mol%)	d (g/cm³)	n_D	E_B(O1s) (eV)	q_p(O) from χ	q_p(O) from χ_1	$\Lambda(\chi)$	$\Lambda(\chi_2)$	α(O) (Å³)	α_1(O) (Å³)	$\Lambda(\alpha)$	$\Lambda(\alpha_1)$	B from z	B from z_1	CSP (eV)
	0	3.646	1.608	532.02	-1.029	-0.964	0.477	0.516	1.900	0.534	0.791	-1.456	0.045	1.575	532.27
Li	7	3.908	1.663	531.77	-1.049	-0.982	0.496	0.535	1.870	0.555	0.777	-1.337	0.264	2.046	532.08
	11	4.021	1.687	532.38	-1.061	-0.992	0.508	0.547	1.851	0.567	0.768	-1.274	0.377	2.280	531.97
	15	4.088	1.705	531.12	-1.074	-1.003	0.519	0.560	1.837	0.586	0.761	-1.179	0.482	2.490	531.86
	20	4.084	1.716	532.17	-1.090	-1.018	0.535	0.576	1.837	0.629	0.761	-0.987	0.603	2.724	531.72
	25	3.955	1.714	531.60	-1.108	-1.033	0.551	0.594	1.867	0.703	0.775	-0.706	0.715	2.929	531.59
	30	3.673	1.696	531.58	-1.126	-1.050	0.569	0.612	1.945	0.829	0.811	-0.345	0.818	3.108	531.45
Na	7	3.960	1.663	531.86	-1.051	-0.985	0.502	0.539	1.872	0.573	0.778	-1.245	0.346	2.159	531.91
	15	4.043	1.683	531.41	-1.078	-1.010	0.532	0.567	1.874	0.658	0.779	-0.869	0.646	2.705	531.50
	25	3.862	1.662	530.52	-1.115	-1.046	0.573	0.606	1.915	0.813	0.798	-0.385	0.967	3.238	530.98
	30	3.702	1.641	530.37	-1.135	-1.065	0.596	0.627	1.946	0.906	0.812	-0.173	1.108	3.452	530.73
K	6	3.848	1.651	531.78	-1.049	-0.989	0.505	0.543	1.890	0.592	0.786	-1.149	0.423	2.145	531.88
	9	3.885	1.659	531.71	-1.059	-1.003	0.519	0.557	1.885	0.624	0.784	-1.007	0.596	2.394	531.68
	11	3.890	1.661	531.68	-1.067	-1.012	0.529	0.566	1.883	0.647	0.783	-0.912	0.706	2.547	531.55
	14	3.870	1.659	530.81	-1.078	-1.026	0.544	0.581	1.884	0.685	0.784	-0.767	0.864	2.759	531.36
	18	3.798	1.650	530.49	-1.093	-1.045	0.565	0.602	1.893	0.746	0.788	-0.568	1.063	3.013	531.10
	24	3.615	1.629	530.29	-1.117	-1.076	0.598	0.634	1.931	0.867	0.805	-0.255	1.336	3.335	530.71

* analytical compositions determined by an inductively coupled plasma method

(e) $xR_2O\cdot(100-x)TeO_2$

R	x* (mol%)	d (g/cm³)	n_D	E_B(O1s) (eV)	q_p(O) from χ	q_p(O) from χ_1	$\Lambda(\chi)$	$\Lambda(\chi_2)$	α(O) (Å³)	α_1(O) (Å³)	$\Lambda(\alpha)$	$\Lambda(\alpha_1)$	B from z	B from z_1	CSP (eV)
	0	5.604	2.187	530.32	-1.162	-1.056	0.400	0.609	2.354	1.004	0.961	0.006	0.078	3.154	530.69
Li	15	5.178	2.078	530.13	-1.196	-1.088	0.448	0.646	2.313	1.076	0.948	0.118	0.506	3.759	530.52
	20	5.017	2.041	529.98	-1.209	-1.100	0.466	0.659	2.301	1.106	0.944	0.160	0.625	3.898	530.46
	25	4.847	2.002	529.95	-1.222	-1.113	0.484	0.673	2.289	1.139	0.941	0.203	0.734	4.011	530.40
	30	4.667	1.964	529.82	-1.236	-1.126	0.504	0.689	2.278	1.175	0.937	0.248	0.835	4.101	530.34
Na	10	5.258	2.095	530.07	-1.187	-1.082	0.439	0.637	2.377	1.123	0.967	0.183	0.491	3.760	530.33
	15	5.074	2.044	529.96	-1.200	-1.095	0.460	0.653	2.381	1.179	0.969	0.254	0.670	3.991	530.15
	20	4.883	1.990	529.76	-1.214	-1.110	0.483	0.669	2.378	1.231	0.968	0.313	0.835	4.183	529.98
	25	4.685	1.932	529.76	-1.229	-1.125	0.507	0.686	2.366	1.278	0.964	0.363	0.986	4.340	529.80
	30	4.480	1.870	529.53	-1.245	-1.141	0.532	0.704	2.344	1.316	0.957	0.401	1.126	4.465	529.62
	35	4.267	1.805	529.34	-1.262	-1.158	0.559	0.724	2.307	1.344	0.946	0.428	1.256	4.562	529.44
K	10	5.062	2.064	529.9	-1.189	-1.095	0.450	0.650	2.428	1.194	0.982	0.271	0.679	3.843	530.20
	15	4.810	2.002	529.74	-1.204	-1.115	0.478	0.672	2.450	1.278	0.988	0.363	0.940	4.096	529.95
	20	4.572	1.940	529.55	-1.219	-1.137	0.507	0.695	2.458	1.352	0.991	0.435	1.179	4.298	529.71
	25	4.347	1.878	529.53	-1.236	-1.160	0.537	0.720	2.449	1.413	0.988	0.488	1.399	4.456	529.46

* nominal compositions

(f) $xR_2O\cdot(100-x)Bi_2O_3$

R	x* (mol%)	d (g/cm³)	n_D	E_B(O1s) (eV)	q_p(O) from χ	q_p(O) from χ_1	$\Lambda(\chi)$	$\Lambda(\chi_2)$	α(O) (Å³)	α_1(O) (Å³)	$\Lambda(\alpha)$	$\Lambda(\alpha_1)$	B from z	B from z_1	CSP (eV)
Li	20			527.97	-1.436	-1.218	0.490	0.784					0.753	5.496	528.17
	25			528.00	-1.441	-1.227	0.503	0.791					0.814	5.465	528.23
	27.5			528.23	-1.444	-1.231	0.510	0.795					0.844	5.446	528.26
	30			528.19	-1.447	-1.235	0.517	0.799					0.874	5.426	528.29
	32.5			528.44	-1.450	-1.240	0.524	0.803					0.904	5.403	528.32
	35			528.55	-1.453	-1.245	0.531	0.807					0.934	5.379	528.35

* nominal compositions

Table 2. Original and Optimum Parameters Used in the Calculations; Electronegativity χ, Polarizability α, Ionic Charge z, and Chemical Shift Parameter p. The Parameters, χ_1, χ_2, α_1 and z_1 are Optimized for the Charge Parameter $q_p(O)$, the Optical Basicities $\Lambda(\chi)$ and $\Lambda(\alpha)$, and the Basicity Parameter B, respectively

	χ / –	χ_1 / –	χ_2 / –	α / Å^3	α_1 / Å^3	z / –	z_1 / –	$z\times q_{ij}$ / –	p / eV
B	2.0	1.95	1.96	0.002	1.419	3	1.96	1.29	517.40
Si	1.8	1.94	1.85	0.033	2.073	4	2.50	2.06	512.08
P	2.1	2.19	2.36			5	6.35	1.94	513.79
Ge	1.8	1.88	1.69	0.137	2.869	4	2.17	2.06	509.97
Te	2.1	2.18	1.47	1.595	4.296	4	1.89	1.55	505.24
Bi	1.9	2.08	1.23			3	1.23	1.42	504.79
Li	1.0	1.23	0.95	0.024	0.000	1	0.79	0.79	522.61
Na	0.9	1.08	0.90	0.240	0.000	1	0.84	0.82	519.19
K	0.8	0.51	0.79	1.000	0.574	1	1.00	0.84	517.07
O	3.5								543.41
Const.									0.0

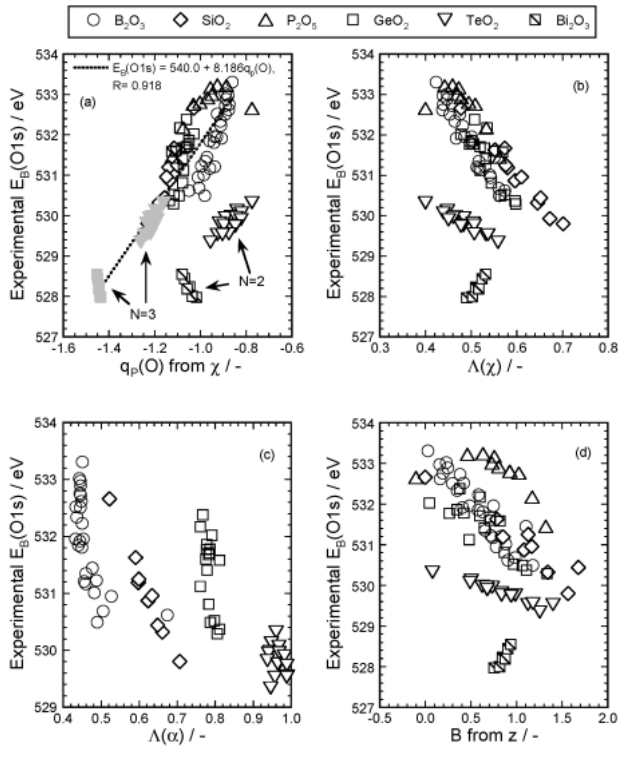

Fig. 1. Correlation between experimentally obtained O1s binding energy E_B(O1s) and the quantities numerically estimated; (a) charge parameter, q_p(O), (b) optical basicity estimated from electronegativity $\Lambda(\chi)$, (c) optical basicity estimated from polarizability $\Lambda(\alpha)$, and (d) basicity parameter B.

plotted against $1/\alpha$(O) at constant α(M), almost linear relationship is obtained, and especially at small α(M), such as B, Si, Li, and Na, the contribution of α(M) is neglected and the regression becomes a straight line. As is obvious from Eq. (9), $\Lambda(\alpha)$ is also proportional to $1/\alpha$(O), and hence $\Lambda(\alpha)$ and A should be proportional to each other if calculated from the same α(O). It is therefore expected that the similar correlations shown in Fig. 1(c) would be obtained if E_B(O1s) were plotted against A.

Figure 1(d) shows the correlation between the basicity parameter B and E_B(O1s). A similar correlation is seen between Figs. 1(b) and 1(d), and the data in Fig. 1(d) are more widely scattered as compared with Fig. 1(b).

Bi_2O_3 system shows the opposite correlation to the other glass systems; excepting Bi_2O_3 system, O1s binding energy commonly decreases with increasing the basicity. It is also the case in the O1s chemical shift against the glass composition; except for Bi_2O_3 system, O1s binding energy commonly decreases with increasing R_2O content. The positive electron holes in bismuthate glass[22] may be responsible for the anomalous O1s chemical shift.

Among Figs. 1(a)–(d), a linear correlation is seen only between the charge parameter q_p(O) and O1s binding energy E_B(O1s), while an unusual assumption is required in the local structure around oxide ions in TeO_2 and Bi_2O_3 systems. Excluding these systems, the basicity estimated from electronegativity $\Lambda(\chi)$ gives the smallest deviation.

3.2 Optimization of parameters in computational expressions

It is well known and is clearly seen from Eq. (6) that the effective charge on oxide ions varies according to the chemical environment. It is naturally expected that cations also vary in charge as well as oxide ions. As shown in Eq. (12), the basicity parameter B includes the charge of cations z, where fully-ionic charges are used in the calculation of the basicity parameter. It is expected that the better correlation with O1s binding energy is obtained when modifying the charge into a realistic value. It is also known that electronegativity χ differs according to the chemical bonding states.[23] Te and Bi ions might have possessed different electronegativities in the glasses. Moreover, different values have been reported for the polarizability α of cations, and hence there is no reason not to modify the cation polarizabilities. Then, the parameters, charge z, electronegativity χ and polarizability α for the cations were optimized by a non-linear least square method so as to establish linear correlations with O1s binding energy.

The parameters before and after the optimization are listed in Table 2, and the resultant quantities and correlations are shown in Table 1 and **Figs. 2**(a)–(d). In the optimization, the data for pure P_2O_5 glass and part of the glasses in Li_2O–GeO_2 system were excluded, otherwise optimum solutions could not be obtained. As seen from Fig. 2, the better correlations are achieved after the optimization. However, only the basicity parameter B successfully reproduces the inverse O1s chemical shift in Bi_2O_3 system. Among the parameters, the optimal electronegativity χ_1 used in the calculation of q_p(O) shows the smallest difference from the original value. The optical basicity $\Lambda(\chi)$ is also derived from electronegativity, and the optimal parameters χ_2 of Te and Bi are significantly reduced from the original values, suggesting that the chemical bonding character of Te–O and Bi–O bonds is not so covalent but more ionic as compared with B–O and Si–O bonds. As for polarizability α, it is unexpected that the network forming cations have changed drastically as compared with modifiers. As for the cation charge z in basicity parameter B, the optimal charge of P, z_1(P) is 6.35, which exceeds the full charge, z(P) = 5+. The electronegativity χ(P) is 2.1, which is highest among the conventional network formers, suggesting the highest covalency of P–O bond. In practice, the apparent charge z(P) × q_{PO} (= full charge × ionicity) is 1.94, in which the difference from z_1(P) is largest among the investigated cations.

3.3 Chemical shift parameter —a novel expression

As mentioned, Jolly[14] proposed Eq. (7) based on the idea that the XPS chemical shift was expressed by the sum of the parameters p_j which were characteristic of each atom j bonded to a specific atom under investigation. As also described, it is hard to determine the sort and number of atoms adjacent to a specific atom in glass. It is therefore convenient for glass to

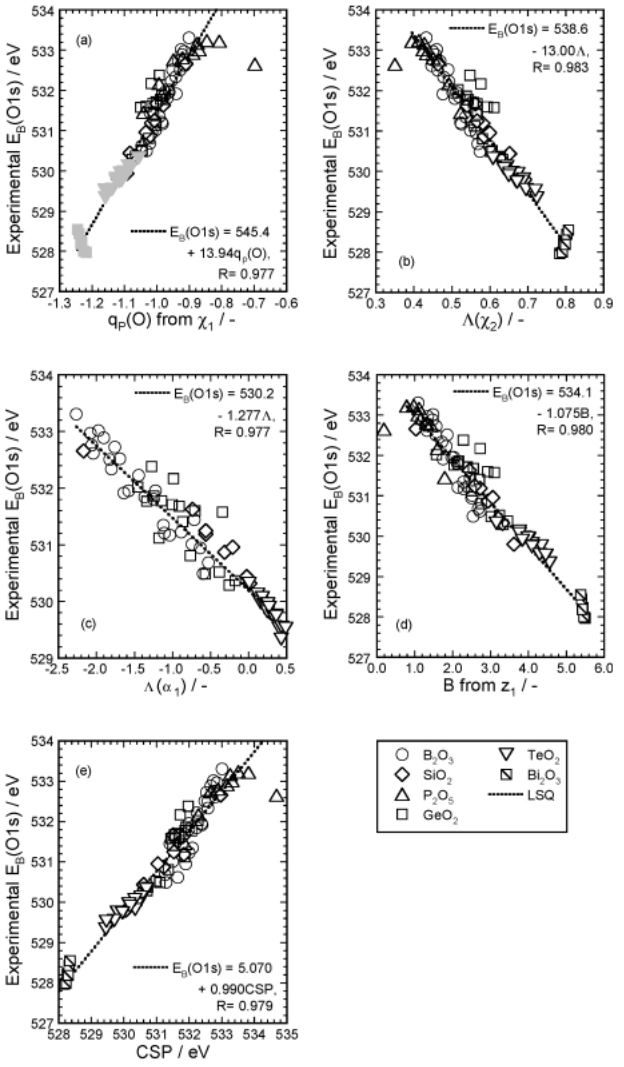

Fig. 2. Correlation between experimentally obtained O1s binding energy E_B(O1s) and the quantities numerically estimated from the optimal parameters; (a) charge parameter q_p(O), (b) optical basicity estimated from electronegativity $\Lambda(\chi)$, (c) optical basicity estimated from polarizability $\Lambda(\alpha)$, (d) basicity parameter B, and (e) chemical shift parameter CSP.

adopt a quantity which directly reflects the chemical composition of a material rather than the structure. Then, we modified the Jolly's idea as O1s binding energy was expressed by the sum of the parameters p_j which were characteristic of each atom j constituent of a material, and we devised the following equation.

$$E_B(\text{O1s}) = \Sigma c_j p_j + \text{const.} \equiv CSP \qquad (14)$$

where c_j is the atomic ratio of the constituent atom j. We did not adopt p_j for the constituent compound j, because if doing so, the chemical shift of a structural group would not be estimated. Defining a p_j for each atom j, it is able to estimate the XPS chemical shift for the individual structural fragments, such as BO, NBO, SiO_4 tetrahedron, BO_3 triangle, and so on. We will name the parameter p_j including the sum of p_j "chemical shift parameter, CSP."

Then, the parameters p_j were empirically determined so as to achieve a linear correlation between CSP and the experimental E_B(O1s). The resultant correlation and the optimal parameter p_j are shown in Fig. 2(e) and Table 2, respectively. It is noted that the chemical shift parameter for oxygen is ca. 543 eV, which is approximately consistent with the actual observation for oxygen molecule.[24] The parameters in CSP should be determined empirically according to the actual observations, and CSP however has great advantage as compared with the other empirical expressions. In the present paper, the O1s chemical shift has been discussed. In XPS spectra, however, the signals for cations, such as B1s, Si2p, Na1s, and so on, also shift chemically. Little has been proposed for the computational expression of the XPS chemical shifts of cation signals. It is quite easy for CSP to express the chemical shifts of cation signals. Accumulating the spectral data, CSP will be the best expression for the XPS chemical shifts as well as the basicity of glasses.

4. Conclusion

It has so far been expected that O1s binding energy determined from XPS measurements was applicable as a measure of basicity of oxide glasses. Correlations between O1s binding energy and the quantities estimated from various computational expressions were examined to explore the best expression for the O1s chemical shift and the basicity of oxide glasses. The obtained results are summarized as follows.

(1) In the glasses of TeO_2 and Bi_2O_3 systems, the correlations different from the other conventional glasses in the systems, B_2O_3, SiO_2, P_2O_5 and GeO_2, were found. In the conventional glasses, however, the correlations with linear and small deviations were confirmed in the expressions for the Pauling charge q_p(O) and the electronegativity-derived optical basicity $\Lambda(\chi)$.

(2) Linear correlations covering the whole glasses could not be obtained without the modification of the parameters required in the computations, such as electronegativity and polarizability of cations.

(3) A novel expression named chemical shift parameter, CSP was devised. Despite the simple expression, a linear correlation covering the whole glasses could be successfully obtained. It was expected that CSP became the best expression for the XPS chemical shifts as well as the basicity of glasses by accumulating the experimental data.

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