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Characterization of glasses based on basicity

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Basicity is defined as an electron donating ability of a material, and hence, an oxide material containing oxide ions with high electron density is regarded to be in high basicity. It has been demonstrated that basicity can be evaluated by binding energy of core level electrons, which is measured by X-ray photoelectron spectroscopy. Based on the experimental results obtained from a large number of oxide glasses, correlations among basicity, O1s binding energy, structure and properties of glasses have been investigated. In the present paper, some of the research outcomes are introduced.

Key-words : Glass, Characterization, Structure, Properties, Material design, Basicity

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1. Introduction

It has been understood that glass is a salt, which is formed by an acid–base reaction, where SiO_2 and B_2O_3 are the examples of acids, and Na_2O and CaO are classified as bases. According to an acid–base concept proposed by Lewis,[1)] acid is defined as acceptor of electrons, and base is as electron donor. Under the definition, basicity is interpreted as a measure of electron donating ability. In oxide glasses, electrons donated are excess electrons possessed by oxide ions. The excess electrons are present in outer shell levels at valence band, and hence glasses containing much oxide ions with high electron density are regarded as those in high basicity. Electron density of outer shell levels is related to various properties of materials, such as chemical reactivity and stability, optical absorption and emission, electronic and magnetic functions, and so on. Besides properties, structure of materials is also dominated by basicity.[2)] Therefore, basicity is a predominant factor for both properties and structure of glasses, and it may cover exhaustively the relation among composition, structure and properties.

Basicity can be determined by various experiments, that is, measuring activity of oxide ions, optical absorption, and electron spin resonance spectra. An optical basicity concept proposed by Duffy and Ingram[3)] is based on the optical absorption of probe ions such as Tl^+, Pb^{2+}, and Bi^{3+} with an ns^2 electron configuration. The absorption peaks of ${}^1S_0 \rightarrow {}^3P_1$ transition are observed at ultra-violet region, and the peak position is sensitive to the glass composition. The peak shift is responsible for the change in electron density of outer shell levels of probe ions, which is attributable to the change in number of electrons donated from the matrix glass, that is, the change in basicity of the matrix glass. In TeO_2 and Bi_2O_3 glasses, however, the absorption edge is present near visible light region, and hence the absorption peak of Pb^{2+} ions, for example, will be hidden in the absorption of these glasses. Thus, optical basicity is applicable to the most of conventional glasses which are transparent to UV light.

Change in the electronic states of outer shell levels, that is, change in the chemical bonding character, leads to a change in electrostatic potential inside the outer shell, resulting in the change in energy of core orbital electrons. Energy of electrons in core orbitals as well as outer shell levels is determined by X-ray photoelectron spectroscopy (XPS). It is therefore expected that XPS is used as an experimental method to evaluate basicity of a material. Then, the author's research group has measured XPS spectra for various glasses and examined the applicability of binding energy of O1s core orbital as a measure of basicity. In the present paper, the achievements in a series of investigations on basicity are introduced, where structure and properties of glasses are characterized on the basis of basicity.

2. Evaluation of basicity by XPS measurement

In theory, energy of core level electrons is measurable with XPS, and in practical, however, the measurement is quite difficult, because most of glasses are insulator and charge-up problem is unavoidable. The author's research group has revealed that metal-mesh screen was effective to remove inhomogeneous charge distribution of glass surface.[4)] By using a Ni-mesh screen, high resolution measurement has become possible; in the case of SiO_2 glass, peak width of O1s signal is broad (3.8 eV) without using any charge control, and it becomes quite sharp (1.4 eV) by combination of the Ni-mesh screen and an irradiation of low energy electron flux.

Then, XPS measurements have been carried out for various glass systems, such as B_2O_3, SiO_2, P_2O_5, GeO_2, TeO_2 and Bi_2O_3.[5)] The results of alkali binary glasses are shown in **Fig. 1**, where O1s binding energy, $E_B(O1s)$ is plotted against optical basicity, $\Lambda(\chi)$ which is calculated from the following equation.[3)]

$$\begin{cases} \Lambda(\chi) = 1 - \sum_i \frac{z_i r_i}{2}\left(1 - \frac{1}{\gamma_i}\right) \\ \gamma_i = 1.36(\chi_i - 0.26) \end{cases} \quad (1)$$

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. Equation (1) is derived empirically based on the optical basicity measurements for various multi component glasses. It is quite convenient because basicity $\Lambda(\chi)$ is calculated directly from the glass composition.

As shown in Fig. 1, a linear correlation is confirmed between $E_B(O1s)$ and $\Lambda(\chi)$ in the typical glass systems of B_2O_3, SiO_2,

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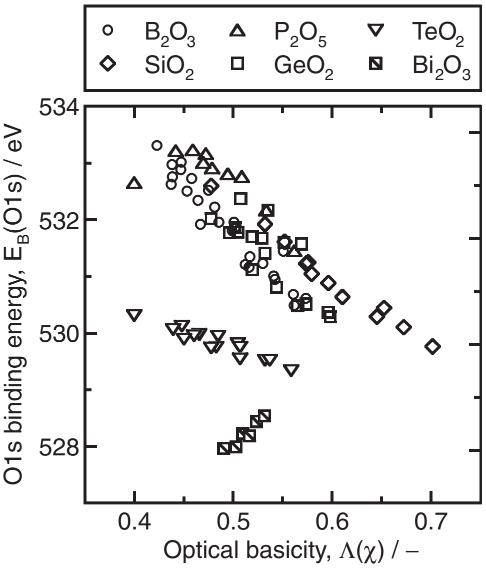

Fig. 1. Correlation between experimentally obtained O1s binding energy, E_B(O1s) and the optical basicity numerically-estimated from electronegativity, Λ(χ).[5)]

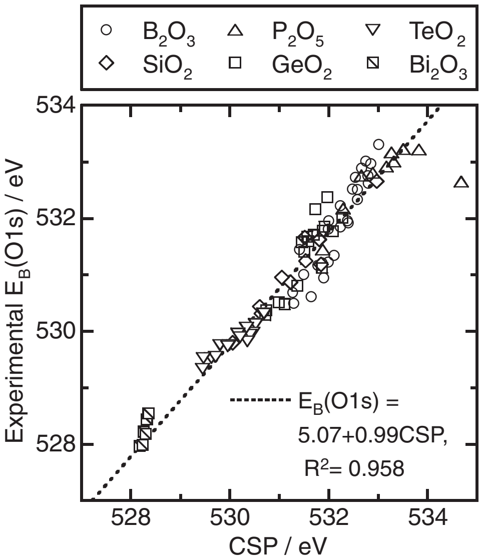

Fig. 2. Correlation between experimentally obtained O1s binding energy, E_B(O1s) and the numerically estimated chemical shift parameter, *CSP*.[5)]

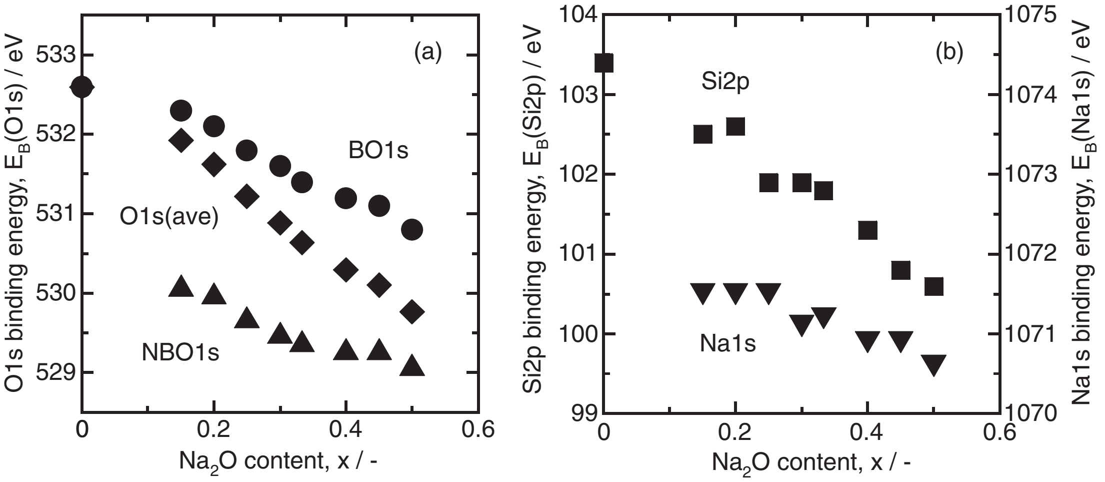

Fig. 3. XPS chemical shifts for xNa$_2$O·(1 − x)SiO$_2$ glass (molar ratio).[8)]

P_2O_5 and GeO_2, where E_B(O1s) decreases with increasing Λ(χ). The same correlation is seen in TeO_2 system, and E_B(O1s) is, however, lower than that of P_2O_5 and B_2O_3 systems at similar Λ(χ). In the case of Bi_2O_3 system, different trend is confirmed, that is, E_B(O1s) increases with increasing Λ(χ). The unique trends found in TeO_2 and Bi_2O_3 systems are probably due to the vacant d orbitals of Te and Bi ions. In the case of TeO_2 glasses, electrons are delocalized by O → Te back-donation through Te5d–O2p π orbital,[6)] and it is hence expected that wave functions of neighboring oxide ions overlap largely, resulting in higher electron density of O2p orbitals.

The correlations of E_B(O1s) and the other expressions of basicity were also examined.[5)] However, expression applicable to all the glass systems was not found. Then, a novel expression for the O1s chemical shift was proposed.[5)] As shown in **Fig. 2**, O1s chemical shifts of TeO_2 and Bi_2O_3 systems are in a linear correlation with other glass systems of B_2O_3, SiO_2, P_2O_5 and GeO_2.

3. Relation between basicity and glass structure

3.1 Glass structure and XPS chemical shift

Before the establishment of surface charge control method, it was also difficult to determine absolute value of binding energy in XPS measurements. In the case of silicate glass, for example, O1s binding energy has been corrected as reference to Si2p signal, assuming that Si2p binding energy was constant and insensitive to glass composition.[7)] After the establishment of binding energy correction method, it was revealed that Si2p peak also shifted chemically as well as O1s peak.[8)] As shown in **Fig. 3**, it is worth noting that not only E_B(O1s) but also E_B(Si2p) and E_B(Na1s) decrease with increasing Na_2O content. If ionicity of chemical bonds increases along with Na_2O addition, oxygen atoms get more electrons from neighboring Si and Na atoms, resulting in the negative shift of O1s and positive shifts of Si2p and Na1s. In practice, however, all the core orbitals show the negative shifts in binding energy, indicating the increase of

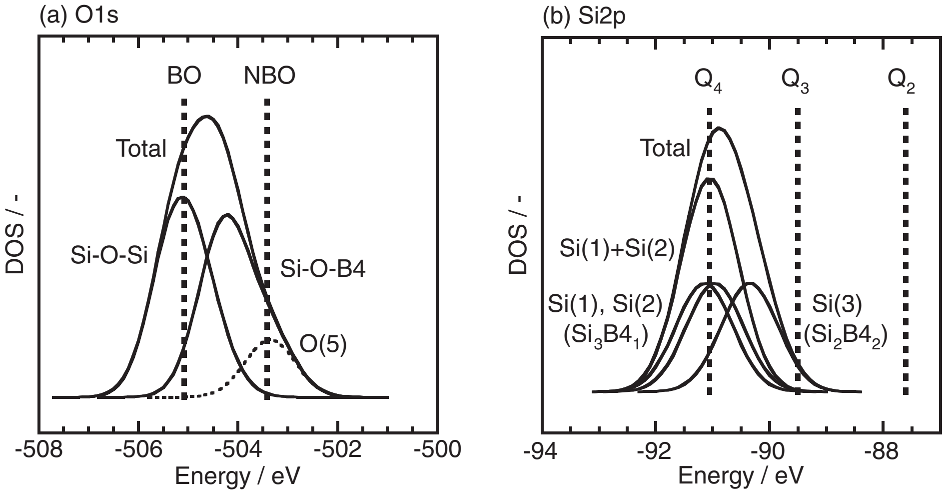

Fig. 4. Density of states (DOS) of the atomic orbitals obtained from the MO calculations.[13)] The vertical lines are the energy levels in sodium silicates.[9)] The numbers in the parentheses indicate the site number of the structural model used for the MO calculation. The notation, Si_mB4_n in the parentheses means the objective Si atom in SiO_4 unit having the neighboring units of $m$$SiO_4$ and $n$$BO_4$.

electron density, that is, the increase in covalency of the glass constituents. Molecular orbital (MO) calculations were performed,[9)] where the XPS chemical shifts were successfully reproduced. It was also revealed that the XPS chemical shifts were explainable not only by a conventional point charge model based on ionicity[10)] but also by a charge sharing model based on covalency.

In Fig. 3, binding energies are plotted against Na_2O content. If the graphs are redrawn against basicity $\Lambda(\chi)$, relations similar to Fig. 3 are obtained, suggesting that Si2p and Na1s binding energies are also expressed by $\Lambda(\chi)$. It means that basicity can be estimated from Si2p or Na1s binding energy even in non-oxides, such as SiC and Si_3N_4.

The author's research group has studied the structure of borosilicate glasses, where structural changes, such as change in coordination number of boron and formation of non-bridging oxygen (NBO), were successfully explained on the basis of basicity,[11)] and an apparent conflict was, however, found among the experimental results of ^{11}B and ^{29}Si MAS-NMR and XPS.[12)] In low alkali content glasses, ^{11}B MAS-NMR indicates absence of NBOs, and ^{29}Si MAS-NMR and XPS suggest presence of NBOs. MO calculations were carried out to understand the inconsistency.[13),14)] As shown in **Fig. 4**, a bridging oxygen (BO) bound to Si and four-fold coordinated B (B4) is in an electronic state similar to NBO, and an Si atom in SiO_4 unit having two B4 as neighbors (Si_2B4_2 in Fig. 4) is in an electronic state similar to an Si atom in Q_3 unit consisting of three BOs and one NBO. It tells us that careful analysis is required for the glasses containing B4 atoms.

3.2 Basicity and structure of glass

As mentioned, the presence of B4 leads to the anomaly in electronic states of glasses. Hence, if the amount of B4 in a glass can be predicted, it will be quite helpful for the material design, particular in commercial glasses consisting of a number of components. In alkali borosilicate glasses, a model proposed by Dell et al.[15)] has been widely used for the prediction of B4 fraction. In practice, however, it is difficult to predict B4 fraction due to the compositional change in a component other than R_2O, B_2O_3 and SiO_2. As mentioned, glass structure is dependent on basicity,[2)] and it is therefore expected that B4 fraction is expressed as a function of basicity. Then, the relation between B4 fraction and basicity was examined in alkali and alkaline-earth borosilicate glasses.[16),17)]

Figure 5(a) shows the relations between conventional notation of B4 fraction, N_4 and basicity,[16)] where N_4 is given by the proportion of B4 to total boron content, B4/B. At constant SiO_2/B_2O_3 ratios, maxima in N_4 are seen commonly at around $\Lambda(\chi) = 0.55$, and N_4 values at maxima are different between SiO_2/B_2O_3 ratios. N_4 value is dependent on SiO_2/B_2O_3 ratio, and hence the proportion of B4 to total content of network forming atoms, B4/(B + Si) is examined.[16)] As shown in Fig. 5(b), the higher the SiO_2/B_2O_3 ratio, the smaller the B4/(B + Si) value, which is opposite to Fig. 5(a). From **Figs. 6**(a) and 6(b), SiO_2 seems to contribute surely but partly the formation of B4. Then, introducing a coefficient f, B4 fraction is expressed by $B4/(B + Si \times f)$.[16)] As shown in Fig. 5(c), $B4/(B + Si \times f)$ value is seemingly independent to SiO_2/B_2O_3 ratio and is expressed by a polynomial function of $\Lambda(\chi)$. The coefficients f for various alkali and alkaline-earth oxides are given in Fig. 6. Except for Li_2O, a linear correlation between f and field strength, Z/r is confirmed, where Z and r are the charge and radius of a cation, respectively. The f values given in Fig. 6 are applicable to the mixed alkali and alkaline-earth glasses,[17)] indicating that the prediction of B4 fraction is possible even in the multi component glasses.

4. Material and process design based on basicity

4.1 Compositional design in optical function

Optical absorption and emission of Er^{3+} ions change significantly according to glass composition. As shown in **Fig. 7**, optical absorption, σ_a at around 1.5 µm consists of broad magnetic dipole (MD) and sharp electric dipole (ED) transitions.[18)] In particular, relative intensity of these transitions changes considerably in borate glass. In the usage as amplifier, glasses with broad absorption and emission peaks are desirable. When O^{2-} ions neighboring to Er^{3+} ions have less electron donating ability, that is, small basicity, probability of ED transition increases, resulting in wider line width.[19)] Then, relation between the line width and basicity was examined.[18)]

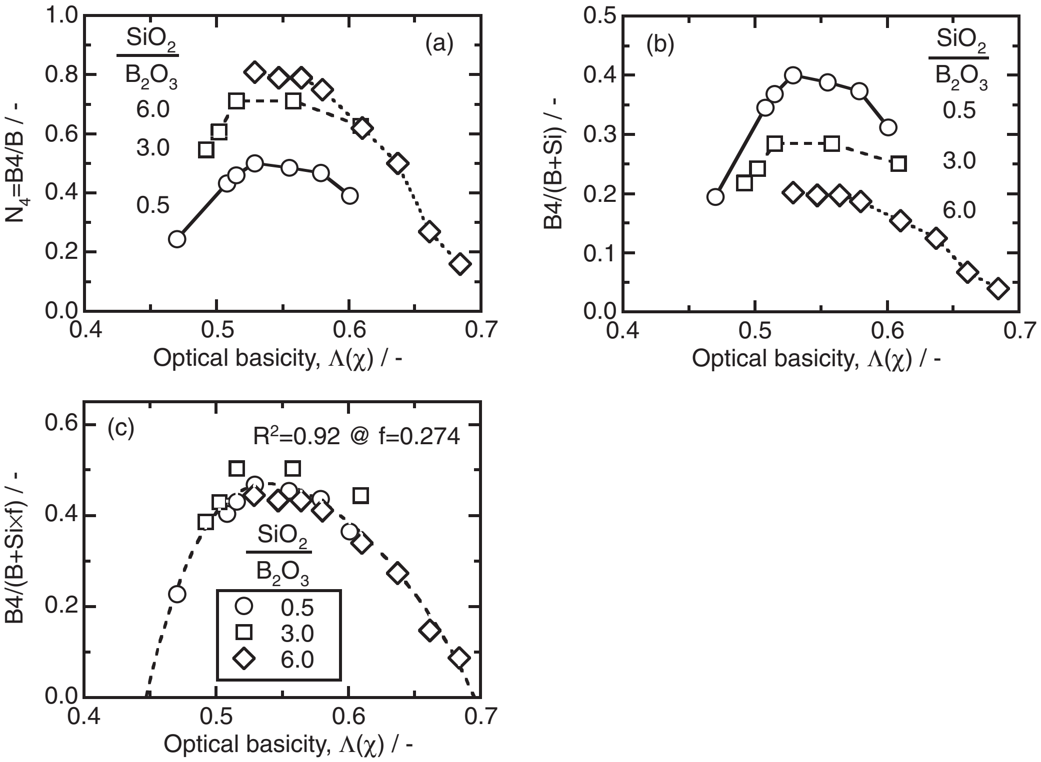

Fig. 5. Fraction of four-fold coordinated boron atoms given by (a) $N_4 = B4/B$, (b) $B4/(B + Si)$ and (c) $B4/(B + Si \times f)$ in Na_2O–CaO–B_2O_3–SiO_2 system.[16)]

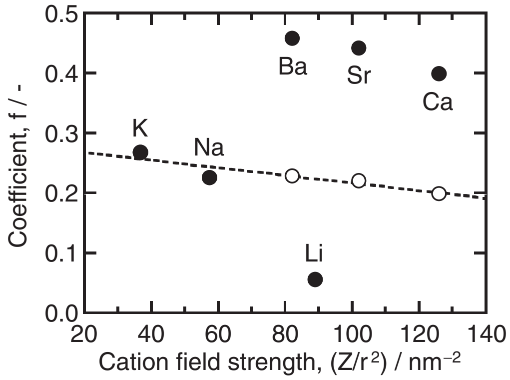

Fig. 6. Field strength, Z/r^2 and the optimal coefficient f in $B4/(B + Si \times f)$ for the ternary borosilicate glasses.[16)] Z and r indicate ionic charge and radius, respectively. Open circle: $f/2$ for alkaline-earth oxides.

In **Fig. 8**(a), the absorption line width, $\Delta\lambda_a$ of Er^{3+} ions in various glasses is plotted against basicity, $\Lambda(\chi)$. As a general trend, $\Delta\lambda_a$ decreases with increasing $\Lambda(\chi)$, and as for TeO_2 and Bi_2O_3 glasses, however, $\Lambda(\chi)$ is small but $\Delta\lambda_a$ is not so large. Er^{3+} ions are highly selective for the neighbors. For example, in NBO-containing glasses, such as alkali silicates, NBOs are preferentially coordinated to Er^{3+} ions.[18)] $\Lambda(\chi)$ indicates the average basicity of overall O^{2-} ions in a glass, and the basicity of O^{2-} ions surrounding Er^{3+} ions is different from $\Lambda(\chi)$.

Hence, relation between $\Delta\lambda_a$ and O1s binding energy, E_B(O1s) was examined. As shown in Fig. 8(b), $\Delta\lambda_a$ is plotted against E_B(O1s), where E_B(O1s) of NBO is chosen for the glasses in which NBO components are confirmed in O1s spectra. Except for TeO_2 and Bi_2O_3 glasses, in Fig. 8(b), a correlation higher than Fig. 8(a) is recognized for the typical glass systems. TeO_2 and Bi_2O_3 glasses seem to be highly basic in the basicity scale of O1s binding energy, and despite the small E_B(O1s), $\Delta\lambda_a$ is relatively large as compared with SiO_2 glasses. Figures 8(a) and 8(b) suggest that TeO_2 and Bi_2O_3 glasses have basicity dependencies different from the typical glasses, and different material design is required for TeO_2 and Bi_2O_3 glasses. In addition, it may be necessary to look for another measure of basicity other than $\Lambda(\chi)$ and E_B(O1s).

4.2 Development of chemical recycling process of wastes

Inorganic wastes, such as municipal waste slags, include transition metal ions, such as Fe^{3+}, Cr^{3+} and Mn^{2+}, from which wastes are generally colored in visible region. Most of transition metal ions have high polarizability,[20)] and they are expected to prefer an environment in high basicity. Glass phases formed by phase separation have different compositions, that is, different basicities. It was thought that if inorganic wastes could be phase-separated and transition metal ions were selectively concentrated in a basic glass phase, another acidic glass phase not containing transition metal ions should be recovered by immersing the phase-separated wastes into aqueous acids, such as hydrochloric acid. Akai et al.[21)] have applied phase separation to a recycling process of waste glasses. Then, the author's research group have tried to apply the process to inorganic wastes, such as granulated blast furnace slag[22)] and municipal waste slag.[23)] The results for a municipal waste slag are shown in **Figs. 9** and **10**. As shown in Fig. 9, the recovered solids are colorless and transparent in visible region. As shown in Fig. 10, SiO_2 content in the recovered solids is higher than 80 mass%, and coloring agents of Fe_2O_3 and S are almost completely removed. Boron is not detectable with the X-ray fluorescence apparatus used in the present study, and thereby B_2O_3 is not listed in Fig. 10.

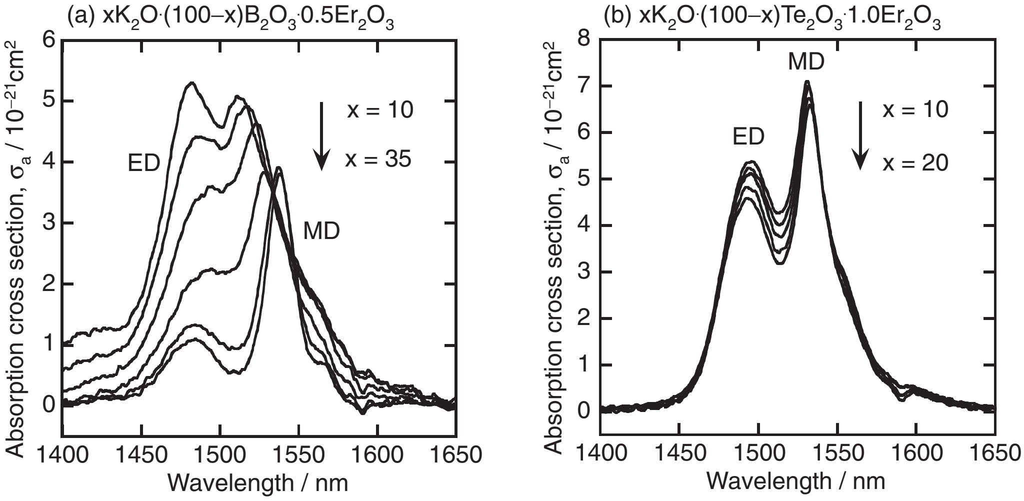

Fig. 7. Absorption cross section, σ_a at 1.5 µm band of Er^{3+} ion.[18)]

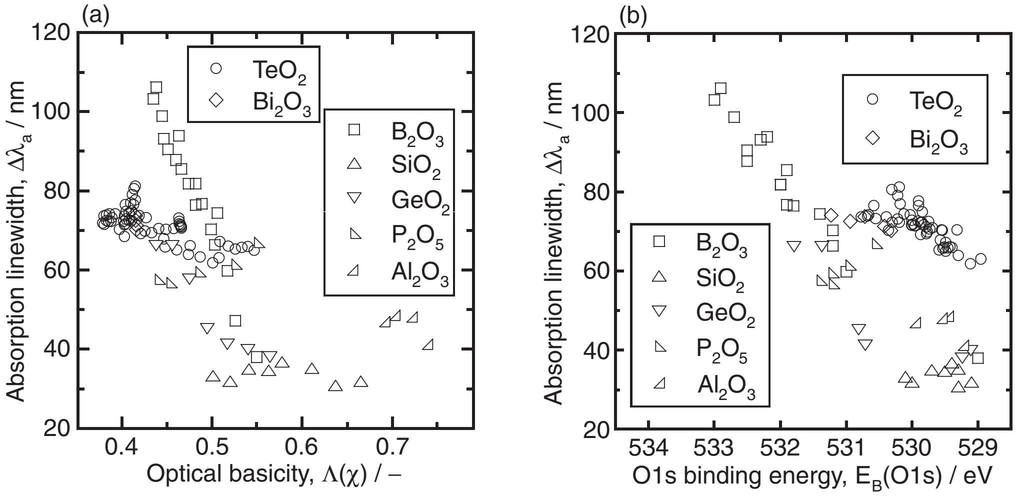

Fig. 8. Absorption linewidth, $\Delta\lambda_a$ at 1.5 µm band of Er^{3+} ion against (a) optical basicity $\Lambda(\chi)$ and (b) O1s binding energy, $E_B(O1s)$.[18)]

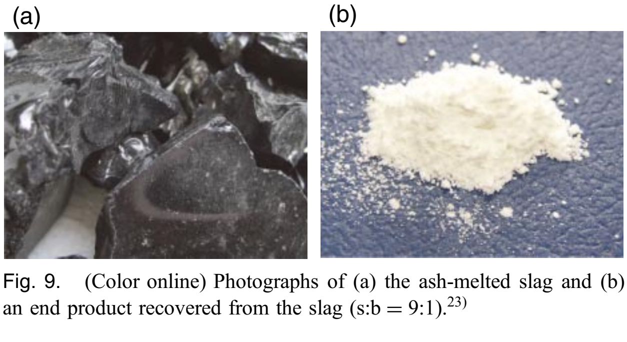

Fig. 9. (Color online) Photographs of (a) the ash-melted slag and (b) an end product recovered from the slag (s:b = 9:1).[23)]

It is also noted in Fig. 10 that comparatively large amount of P_2O_5 and TiO_2 are remaining in the recovered solids, suggesting that phase separation is available for the recycling of valuable elements, such as P and Ti. In particular, Japan completely depends on imports for phosphorous resources, and hence phase separation is expected to be used as a phosphorous recycling method. The author's research group is currently investigating the

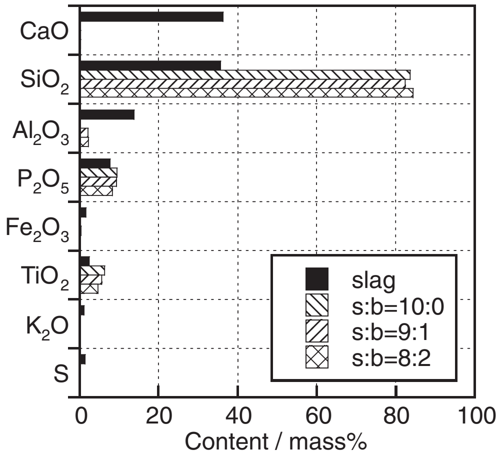

Fig. 10. X-ray fluorescence-analytical composition of the end products recovered from a municipal waste slag.[23)] The ratio s:b indicates the weight ratio between the slag and B_2O_3 in the slag glasses. The composition of the untreated slag is also shown for comparison.

distribution of phosphorous during the phase separation of borosilicate glasses, and it is revealed that phosphorous distribution is greatly influenced by Al[24] and Ti.[25] It is consequently suggested that the P, Ti and Al distributions shown in Fig. 10 are dependent on the coexisting elements. By clarifying the distribution mechanism, selective recovery of valuable elements should be possible.

5. Concluding remarks

In 1992 the XPS apparatus was installed in Okayama University, which was almost 20 years ago. After that, many findings were obtained; not only O1s but also Si2p shifts chemically, and furthermore, they shift to the same direction. BO1s and NBO1s components also shift chemically, and the magnitude of the shifts are almost the same with those of the core level components of cations with strongly-interacted with respective oxide ions. O1s binding energy can be used as a measure of basicity. Heavy metal oxides such as TeO_2 and Bi_2O_3 seem to be basic in experimental O1s binding energy but acidic in calculated optical basicity. To interpret these findings, MO calculations have been introduced, from which a number of know-how have been accumulated.

Much knowledge was also obtained from borosilicate glasses. Structural changes in borosilicate glasses are quite complicated; coordination change in boron and NBO formation. However, the changes are successfully explained on the basis of basicity. BO that looks like NBO was also found in borosilicate glasses. MO calculations were helpful to understand unique electronic states of borosilicate glasses. The knowledge obtained from borosilicate glasses and basicity has been applied to interpret the distribution of elements during phase separation of borosilicate glasses and vitrified wastes. There remain a number of unclear phenomena in borosilicate glasses and phase separation, and hence the author will pursue the unsolved issues further.

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References

1) G. N. Lewis, “Valence and structure of atoms and molecules”, ACS monograph, Chemical Catalog Co. (1923).
2) H. Kawazoe, *J. Non-Cryst. Solids*, 42, 281–285 (1980).
3) J. A. Duffy and M. D. Ingram, *J. Non-Cryst. Solids*, 21, 373–410 (1976).
4) S. Matsumoto, T. Nanba and Y. Miura, *J. Surf. Sci. Soc. Japan (Hyomen Kagaku)*, 18, 466–472 (1997).
5) T. Nanba, Y. Miura and S. Sakida, *J. Ceram. Soc. Japan*, 113, 44–50 (2005).
6) Y. Himei, Y. Miura, T. Nanba and A. Osaka, *J. Non-Cryst. Solids*, 211, 64–71 (1997).
7) R. Brückner, H.-U. Chun and H. Goretzki, *Glastech. Ber.*, 51, 1–7 (1978).
8) S. Matsumoto, T. Nanba and Y. Miura, *J. Ceram. Soc. Japan*, 106, 415–421 (1998).
9) T. Nanba, T. Hagiwara and Y. Miura, *Adv. Quantum Chem.*, 42, 187–198 (2003).
10) U. Gelius, P. F. Hedén, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling and K. Siegbahn, *Phys. Scr.*, 2, 70–80 (1970).
11) Y. Miura, H. Kusano, T. Nanba and S. Matsumoto, *J. Non-Cryst. Solids*, 290, 1–14 (2001).
12) T. Nanba and Y. Miura, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, 44, 244–248 (2003).
13) T. Nanba, M. Nishimura and Y. Miura, *Geochim. Cosmochim. Acta*, 68, 5103–5111 (2004).
14) T. Nanba, Y. Asano, S. Sakida, Y. Benino and Y. Miura, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, 50, 301–304 (2009).
15) W. J. Dell, P. J. Bray and S. Z. Xiao, *J. Non-Cryst. Solids*, 58, 1–16 (1983).
16) T. Nanba, S. Sakida and Y. Miura, Proceedings in Materials Science & Technology 2006, Materials and systems, Vol. 1 (2006) pp. 535–544 [CD-ROM].
17) Y. Tanaka, S. Sakida, Y. Benino, T. Nanba and Y. Miura, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, 50, 289–293 (2009).
18) Y. Tateyama, S. Sakida, T. Nanba and Y. Miura, Proceedings in Materials Science & Technology 2006, Materials and systems, Vol. 1 (2006) pp. 555–565 [CD-ROM].
19) N. Sugimoto and S. Tanabe, *J. Ceram. Soc. Japan*, 113, 120–122 (2005).
20) V. Dimitrov and S. Sakka, *J. Appl. Phys.*, 79, 1736–1740 (1996).
21) T. Akai, D. Chen, H. Masui, K. Kuraoka and T. Yazawa, “Method for recycling waste glass and recycled glass”, International Patent No. WO/2003/024879 (2003).
22) T. Nanba, S. Mikami, T. Imaoka, S. Sakida and Y. Miura, *J. Ceram. Soc. Japan*, 116, 220–223 (2008).
23) T. Nanba, Y. Kuroda, S. Sakida and Y. Benino, *J. Ceram. Soc. Japan*, 117, 1195–1198 (2009).
24) Y. Ohtsuki, S. Sakida, Y. Benino and T. Nanba, *IOP Conf. Ser.: Mater. Sci. Eng.*, **18**, 112022 (2011) (http://iopscience.iop.org/1757-899X/18/11/112022).
25) Y. Ohtsuki, S. Sakida, Y. Benino and T. Nanba, Pacrim 9: Symposium 15, Cairns, Australia (2011) (submitted to J. Am. Ceram. Soc.).

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