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Introduction

Inorganic glasses have been studied for decades as solid electrolytes because of their electrochemical stability and chemical durability, and various cationic conduction, such as Li^+ , Ag^+ and H^+ conduction, in oxide glass has been investigated extensively.¹⁻³ Recent demands for highly proton conducting electrolytes in the temperature range between 250 and 500 °C that is operating temperatures of intermediate temperature fuel cells accelerate to explore proton conducting glasses.⁴⁻⁹ Our group developed a technique termed as alkali-proton substitution (APS) that injects high concentration of proton carriers, >10²¹ cm⁻³, into phosphate glasses¹⁰ and fabricated many proton conducting glasses that influence on proton conductivity, such as polymerization level of phosphate framework (ratio of the number of oxygen to phosphorous atoms; O/P ratio)¹⁵ and kinds of glass

Understanding the effect of oxide components on proton mobility in phosphate glasses using a statical analysis approach[†]

Takahisa Omata, 🝺 *ª Issei Suzuki, 🝺 ª Aman Sharma, ២ ª Tomohiro Ishiyama, 🝺 ^b Junji Nishii, ២ ^c Toshiharu Yamashita^d and Hiroshi Kawazoe^d

The models to describe the proton mobility (μ_{H}) together with the glass transition temperature (T_g) of proton conducting phosphate glasses employing the glass composition as descriptors have been developed using a statical analysis approach. According to the models, the effects of additional HO_{1/2}, MgO, BaO, LaO_{3/2}, WO₃, NbO_{5/2}, BO_{3/2} and GeO₂ as alternative to PO_{5/2} were found as following. μ_{H} at T_g is determined first by concentrations of HO_{1/2} and PO_{5/2}, and μ_{H} at T_g increases with increasing HO_{1/2} concentration and decreasing PO_{5/2}. The component oxides are categorized into three groups according to the effects on μ_{H} at T_g and T_g . The group 1 oxides increase μ_{H} at T_g and decrease T_g , and HO_{1/2}, MgO, BaO and LaO_{3/2} and BO_{3/2} are involved in this group. The group 2 oxides increase both μ_{H} at T_g and T_g , and WO₃ and GeO₂ are involved in this group. The group 3 oxides increase T_g but do not vary μ_{H} at T_g . Only NbO_{5/2} falls into the group 3 among the oxides examined in this study. The origin of the effect of respective oxide groups on μ_{H} at T_g and T_g were discussed.

> network modifier,16 and the effect of additional glass-network formers, such as GeO₂, on the thermal stability.¹⁷ As a result, $2~\times~10^{-3}~S~cm^{-1}$ of proton conductivity at 300 $^\circ C$ has been achieved by 34HO_{1/2}-2NaO_{1/2}-4NbO_{5/2}-2BaO-4LaO_{3/2}-4GeO₂-1BO_{3/2}-49PO_{5/2} glass (36H-glass) up to now.¹⁸ Based on the electromotive force and electrochemical hydrogen pump experiments, the phosphate glass electrolyte is confirmed that the mean transport number of proton is unity even under the oxidation atmosphere like an air electrode atmosphere in the fuel cell,¹⁹ suggesting that highly efficient operation of fuel cells and steam electrolysis cells is achievable owing to its no electronic leakage.20 In addition, fabrication of ultra-thin glass electrolytes with a thickness of 16 µm was recently demonstrated by the press forming.²¹ This will be a great advantage of the glass electrolyte in order to reduce electrolyte resistance (ohmic resistance) of the electrochemical cells. However, further increase of their proton conductivity $>1 \times 10^{-2}$ S cm⁻¹ at the operating temperature is still required for practical applications.

> Very recently, we have found that the mobility of proton carriers ($\mu_{\rm H}$) at the glass transition temperature ($T_{\rm g}$) in phosphate glasses converges in a small range between 2 × 10⁻⁹ and 2 × 10⁻⁷ cm² V⁻¹ s⁻¹, whereas $T_{\rm g}$ of the glasses is in the wide range of 150 to 650 °C, proton conductivity at 200 °C is also wide range of 10⁻¹⁰ to 10⁻⁴ S cm⁻¹, and proton carrier concentration is in the range of 10¹⁹ to 10²² cm⁻³.²² Because the $\mu_{\rm H}$ at $T_{\rm g}$ of the 36H-glass is 5.4 × 10⁻⁸ cm² V⁻¹ s⁻¹ that is the middle in the $\mu_{\rm H}$ at $T_{\rm g}$ range from 2 × 10⁻⁹ to 2 × 10⁻⁷ cm² V⁻¹ s⁻¹, it is suggested that its proton conductivity can be further increased by

^aInstitute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan. E-mail: takahisa.omata.c2@tohoku.ac.jp; Fax: +81-22-217-5832; Tel: +81-22-217-5832

^bFuel Cell Materials Group, Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

^cResearch Institute for Electronic Science, Hokkaido University, Kita 21 Nishi 10, Kitaku, Sapporo 001-0021, Japan

^dKawazoe Frontier Technologies Corporation, Kuden-cho 931-113, Sakae-ku, Yokohama 247-0014, Japan

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improving the $\mu_{\rm H}$ at $T_{\rm g}$. Because the determining factor of $\mu_{\rm H}$ at $T_{\rm g}$ of proton conducting phosphate glasses has yet to be cleared, we unfortunately still do not understand how to improve $\mu_{\rm H}$ at $T_{\rm g}$.

The composition of glasses is continuatively controllable unlike the crystalline materials; therefore, various properties of glasses, have been empirically expressed by the mole fraction weighting mean of the respective components.23-26 Whereas to understand the effects of fundamental properties of glasses, such as O-H bonding, local structure surrounding protons and short range atomic structure of the glass framework, on $\mu_{\rm H}$ at $T_{\rm g}$ are of course important to understand the proton conduction in phosphate glasses from the physical aspect, understanding the relationship between the glass composition and $\mu_{\rm H}$ at $T_{\rm g}$ is also valuable in order to improve the electrolyte performance of proton conducting phosphate glasses. When the proton conductivity is successfully described by the glass composition, the proton conductivity of phosphate glasses will be easy to improve based on the obtained relationship between the glass composition and $\mu_{\rm H}$ at $T_{\rm g}$, and that will have a major impact on the electrochemical cells such as fuel cells and steam electrolysis cells working at intermediate temperatures. The proton conducting phosphate glasses prepared by using APS previously reported consists of many oxide components;²² for example, 36H-glass involves 8 oxides as HO_{1/2}, NaO_{1/2}, BaO, LaO_{3/2}, NbO_{5/2}, GeO₂, BO_{3/2} and PO_{5/2}; therefore, it is not easy to understand the role of the respective component oxides on $\mu_{\rm H}$ at $T_{\rm g}$ and the relationship between the composition and $\mu_{\rm H}$ at $T_{\rm g}$.

Here, we have developed a model, using a statical analysis approach, to describe $\mu_{\rm H}$ at $T_{\rm g}$ of phosphate glasses according to the glass composition, *i.e.*, the mol% of respective component oxides were employed as descriptors. We also developed a model to describe $T_{\rm g}$ because the thermal stability of proton conducting glasses is another key property taking the working temperature of the electrochemical devices involving the glasses into account. The effect of respective component oxides on $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$ were discussed based on the model obtained.

Methodology

Dataset details

The dataset for $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$ of proton conducting phosphate glasses used as training data in this study is referenced from previous report (Table 1 in ref. 16). The dataset has originally 32 records, but for the 13 records in the original dataset, the proton carrier concentrations are smaller than 1 mol% because the proton carrier in those 13 glasses are originated from the residual water. Therefore, we used a dataset that consists of remaining 19 records as summarized in Table 1. Each record contains glass composition in mol% and experimentally determined $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$.

Regression models and method

A linear combination model, in which mol% of respective oxides are used as predictors, is employed for both $log(\mu_H \text{ at } T_g)$

and T_g in this study. The regression algorithm used in this study is based on the linear regression as implemented in MATLAB (MathWorks, USA). When the general linear regression was preliminary performed for $\log(\mu_{\rm H}$ at $T_{\rm g})$, the overtraining occurred maybe because of small number of training data; the predicted $\mu_{\rm H}$ at $T_{\rm g}$ for the 55 296 glass compositions described later was unreasonable values in the range of 10^{-29} to 10^{17} cm² V⁻¹ s⁻¹ (Fig. S1 and S2 in ESI[†]), although the range of the experimentally observed values is in the range of 2×10^{-9} to 2×10^{-7} cm² V⁻¹ s⁻¹.²² Therefore, we employed the principal components analysis to fit a linear regression in order to avoid overtraining. Five principal components were employed to explain 95% of variance of original data. The mathematical model can be written as

$$\log(\mu_{\rm H} \text{ at } T_{\rm g}/{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}) = a_0 + \sum_{n=1}^5 a_n {\rm PC}_n$$
 (1)

$$T_{g}/^{\circ}C = b_{0} + \sum_{n=1}^{5} b_{n}PC'_{n}$$
 (2)

$$PC_n = \sum_i c_i x_i \tag{3}$$

where PC_n and PC'_n are *n*th principal component explaining the variance of experimentally observed $log(\mu_H \text{ at } T_g)$ and T_g , respectively, a_0 and b_0 are intercepts, a_n and b_n are coefficients of *n*th principal component, x_i is the mol% of the oxide *i*, and c_i is its coefficient.

In order to check the validity of the models and to understand the effect of respective component oxides on $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$, we performed to predict $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$ for 55 296 glass compositions containing 30, 33 and 36 mol% of HO_{1/2}, 0, 2 and 4 mol% of WO₃, 0, 2, 4 and 6 mol% of NbO_{5/2}, 0, 2, 4 and 6 mol% of MgO, 0, 2, 4 and 6 mol% of BaO, 0, 2, 4 and 6 mol% of LaO_{3/2}, 0, 1, 2, 3, 4 and 5 mol% of GeO₂, 0, 1, 2 and 3 mol% of BO_{3/2} and 28–70 mol% of PO_{5/2}. In this prediction, all the compositions were assumed to form homogeneous glasses.

Results and discussion

Linear regression models for $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$

The following relationships of $log(\mu_H \text{ at } T_g)$ and T_g against the five principal components of glass composition were obtained after regression:

$$log(\mu_{\rm H} \text{ at } T_{\rm g}) = -7.8549 + 0.022233 \times PC_{1} - 0.01167 \times PC_{2} + 0.26874 \times PC_{3} - 0.01727 \times PC_{4} + 0.160456 \times PC_{5},$$
(4)
$$T_{\rm g} = 204.368 - 1.622 \times PC'_{1} + 1.282 \times PC'_{2} - 2.350 \times PC'_{3} + 7.897 \times PC'_{4} + 5.630 \times PC'_{5},$$
(5)

The principal components are summarized in Tables 2 and 3 for $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$, respectively. Fig. 1(a) and (b) show comparison of experimentally observed and predicted values of $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$, respectively, for the 19 training data. The root mean square error (RMSE) was 0.2775 for $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and was

Table 1 Training dataset of the relationship between the glass compositions and the proton mobility (μ_{H}) at the glass transition temperature (T_{g}) and T_{g}

	Mol% of component oxide															
No.	$\mathrm{HO}_{1/2}$	NaO _{1/2}	WO_3	NbO _{5/2}	TaO _{5/2}	MgO	BaO	LaO _{3/2}	AlO _{3/2}	YO _{3/2}	GdO _{3/2}	GeO ₂	BO _{3/2}	PO _{5/2}	$\mu_{\rm H}$ at $T_{\rm g} \left({\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1} \right)$	$T_{\rm g}$ (°C)
1	25	3	1	8	0	0	0	5	0	0	0	0	0	58	$2.1 imes 10^{-9}$	200
2	24	8	1	8	0	0	0	5	0	0	0	0	0	54	$5.5 imes10^{-9}$	177
3	25	10	1	8	0	0	0	5	0	0	0	0	0	51	$3.7 imes10^{-8}$	190
4	32	6	1	8	0	0	0	5	0	0	0	0	0	48	$3.7 imes10^{-8}$	170
5	32	8	1	8	0	0	0	5	0	0	0	0	0	46	$1.2 imes 10^{-8}$	167
6	28	2	1	8	0	0	0	5	3	3	0	0	0	50	$2.0 imes 10^{-8}$	281
7	29	6	1	8	0	0	0	5	3	0	0	0	0	48	$7.6 imes10^{-9}$	224
8	30	5	1	8	0	0	0	5	0	3	0	0	0	48	$4.1 imes 10^{-9}$	228
9	35	0	0	3	0	5	0	3	0	0	0	2	2	50	$1.3 imes 10^{-8}$	192
10	32	3	0	3	0	0	5	3	0	0	0	2	2	50	$6.8 imes10^{-9}$	163
11	34	2	0	4	0	0	2	4	0	0	0	4	1	49	$5.4 imes10^{-8}$	180
12	38	2	0	0	4	2	0	4	0	0	0	2	1	47	$2.7 imes10^{-8}$	165
13	17	8	0	0	0	0	0	8	0	0	0	1	0	66	$2.6 imes 10^{-9}$	227
14	12	13	0	0	0	0	0	6	0	0	0	6	0	63	$1.3 imes 10^{-8}$	243
15	33	2	0	0	0	2	0	5	0	0	0	5	0	53	$4.0 imes10^{-8}$	182
16	31	4	0	0	0	2	0	0	0	0	5	5	0	53	$1.2 imes 10^{-8}$	178
17	20	5	0	0	0	0	0	6	0	0	0	6	0	63	$1.5 imes 10^{-8}$	252
18	28	7	0	0	0	2	0	0	0	0	5	5	0	53	$1.4 imes 10^{-8}$	233
19	34	1	8	8	0	0	0	5	0	0	0	0	0	44	$1.1 imes 10^{-7}$	231
19	34	T	0	0	U	U	U	5	U	U	0	U	U	44	1.1 ^ 10	4

Table 2 Five principal components obtained from the analysis of $\mu_{\rm H}$ at $T_{\rm g}$

Principal component	S	PC_1	PC_2	PC_3	PC_4	PC_5
Proportion of variance	e	0.659	0.183	0.061	0.026	0.021
Cumulative proportio	on	0.659	0.842	0.903	0.929	0.950
Factor loading	$x(HO_{1/2})$	0.69239	-0.32693	-0.07750	-0.19571	-0.15439
	$x(NaO_{1/2})$	-0.24549	0.28854	0.71623	-0.35865	-0.03489
	$x(WO_3)$	0.06837	0.15986	-0.11444	0.32222	0.77387
	$x(NbO_{5/2})$	0.16670	0.68417	-0.16598	0.28247	-0.30664
	$x(TaO_{5/2})$	0.02694	-0.05991	0.00355	-0.24336	0.04874
	x(MgO)	0.03954	-0.18457	0.01768	0.06160	-0.13778
	x(BaO)	0.02319	-0.04547	-0.02005	-0.12335	-0.09325
	$x(LaO_{3/2})$	-0.08309	0.19943	-0.33952	-0.50726	0.26128
	$x(AlO_{3/2})$	0.01281	0.06277	-0.04134	0.08739	-0.09090
	$x(\mathrm{YO}_{3/2})$	0.01467	0.05828	-0.05950	0.09692	-0.09979
	$x(GdO_{3/2})$	-0.00319	-0.15212	0.31784	0.52266	-0.11954
	$x(\text{GeO}_2)$	-0.10164	-0.37370	0.21746	0.08717	0.28694
	$x(BO_{3/2})$	0.02654	-0.05917	-0.04343	-0.10435	-0.08555
	$x(PO_{5/2})$	-0.63774	-0.25119	-0.41100	0.07224	-0.24811

23.6 °C for $T_{\rm g}$. No systematic error was observed and the fitting were reasonably good for both $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$. Fig. 2(a) and (b) respectively show the predicted values of $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ for the 55 296 phosphate glass compositions. The predicted values are ranging between 8.1×10^{-10} and 7.7×10^{-7} cm² V⁻¹ s⁻¹ for $\mu_{\rm H}$ at $T_{\rm g}$ and between 152 and 256 °C for $T_{\rm g}$. As compared with experimentally determined $\mu_{\rm H}$ at $T_{\rm g}$,²² the range of the predicted values are very close to the range of the experimentally observed values from 2×10^{-9} to 2×10^{-7} cm² V⁻¹ s⁻¹. These results indicate that the models obtained are quite reasonable and available to discuss the effects of respective component oxides on $\mu_{\rm H}$ at $T_{\rm g}$.

As seen in Table 2, absolute values of the factor loading of $\rm HO_{1/2}$ and $\rm PO_{5/2}$ components are particularly larger than those

of the other components, indicating that $\mu_{\rm H}$ at $T_{\rm g}$ is first determined by the concentration of HO_{1/2} and PO_{5/2}. Taking into account that the coefficient of PC₁ in eqn (4) is positive, $\mu_{\rm H}$ at $T_{\rm g}$ increases with the increasing HO_{1/2} concentration, and it reduces with the increasing PO_{5/2} concentration. In this respect, the experimental observation that the $\mu_{\rm H}$ increases with the decreasing polymerization level of phosphate glass-network is reproduced well by the present model. $\mu_{\rm H}$ turns into decrease at O/P ratio (ratio of the number of oxygen to phosphorous atoms) higher than 3.5–3.6;¹⁵ however, such a behavior cannot be reproduced using linear regression model. Consequently, applicable composition range of the present model is limited in a O/P ratio smaller than 3.5–3.6.

Table 3 Five principal components obtained from the analysis of T_g

Principal component	ts	$\mathbf{PC'}_1$	$\mathbf{PC'}_2$	PC'_3	$\mathbf{PC'}_4$	PC'5
Proportion of varian	ce	0.659	0.183	0.061	0.026	0.021
Cumulative proportion	on	0.659	0.842	0.903	0.929	0.950
Factor loading	$x(HO_{1/2})$	0.69239	-0.32693	-0.0775	-0.19571	-0.15439
	$x(NaO_{1/2})$	-0.24549	0.28854	0.71623	-0.35865	-0.03489
	$x(WO_3)$	0.06837	0.15986	-0.11444	0.32222	0.77387
	$x(NbO_{5/2})$	0.1667	0.68417	-0.16598	0.28247	-0.30664
	$x(TaO_{5/2})$	0.02694	-0.05991	0.00355	-0.24336	0.04874
	x(MgO)	0.03954	-0.18457	0.01768	0.0616	-0.13778
	x(BaO)	0.02319	-0.04547	-0.02005	-0.12335	-0.09325
	$x(LaO_{3/2})$	-0.08309	0.19943	-0.33952	-0.50726	0.26128
	$x(AlO_{3/2})$	0.01281	0.06277	-0.04134	0.08739	-0.0909
	$x(YO_{3/2})$	0.01467	0.05828	-0.0595	0.09692	-0.09979
	$x(GdO_{3/2})$	-0.00319	-0.15212	0.31784	0.52266	-0.11954
	$x(\text{GeO}_2)$	-0.10164	-0.3737	0.21746	0.08717	0.28694
	$x(BO_{3/2})$	0.02654	-0.05917	-0.04343	-0.10435	-0.08555
	$x(PO_{5/2})$	-0.63774	-0.25119	-0.411	0.07224	-0.24811



Fig. 1 Comparison of experimentally observed and predicted values of (a) μ_{H} at T_{g} and (b) T_{g} .

From comparison of the models of $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$ as summarized in Tables 2 and 3, the factor loadings of respective principal components for $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ are surprisingly found to be the same each other, *i.e.*, the variance in both $\log(\mu_{\rm H}$ at $T_{\rm g})$ and $T_{\rm g}$ are explained by the same principal components, clearly indicating that there should be some kind of relationship between $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$. This is quite consistent with our previously reported estimation that the motion of protons (proton diffusion or mobility) determines the motion of glass framework (T_g) in the proton conducting phosphate glasses.²² Fig. 3 shows log($\mu_{\rm H}$ at T_g) as a function of T_g of 55 296 predicted values (black dots) together with the experimentally observed 19 values (red dots). A trend that log($\mu_{\rm H}$ at T_g) decreases linearly with the increasing T_g was clearly observed for the predicted



Fig. 2 Predicted values of (a) $log(\mu_H \text{ at } T_g)$ and (b) T_g for the 55 296 phosphate glass compositions.



Fig. 3 Plot of $\log(\mu_{\text{H}} \text{ at } T_{\text{g}})$ as a function of T_{g} of 55 296 predicted values (open black dots) together with the experimentally observed 19 values (closed red dots).

values in Fig. 3. The observed relationship between $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ may be a key to understand physical factor to determine $\mu_{\rm H}$ at $T_{\rm g}$; however, we need additional information in order to go further this problem. Therefore, the origin of the relationship between $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ remains as an open question, and we do not discuss further in this paper.

Effects of respective component oxides on $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$

As mentioned in the previous section, there is a clear relationship between $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$; therefore, the effect of each component oxide was studied in this regard. Fig. 4 shows the distribution of relationship between $log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ depending on the concentration of respective component oxides. All data plotted in Fig. 4 are predicted values. In Fig. 4(a), 55 296 predicted values are distinguished into three parts depending on the concentration of $HO_{1/2}$. In Fig. 4(b), 18 432 predicted values for the glasses with 30 mol% of $HO_{1/2}$ are plotted and they are distinguished into three parts depending on the concentration of WO_3 . In Fig. 4(c), 6144 predicted values for the glasses with 30 mol% of $HO_{1/2}$ and 0 mol% of WO_3 are plotted and they are distinguished into four parts depending on the concentration of $LaO_{3/2}$. In Fig. 4(d), (e), (f), (g) and (h), 1536 predicted values for the glasses with 30 mol% of HO_{1/2}, 0 mol% of WO3 and 0 mol% of LaO3/2 are plotted and they are distinguished into four or six parts depending on the concentration of the oxide of interest (MgO, BaO, NbO_{5/2}, BO_{3/2} and GeO₂). The situation observed, when the component oxide of interest adds into the glass as alternative to $PO_{5/2}$, is described as follows.

With the increasing HO_{1/2} concentration (Fig. 4(a)), the T_g decreases by 5 °C per 1 mol% HO_{1/2} and log(μ_H at T_g) increases by 0.06 per 1 mol% of HO_{1/2}. In contrast to the dependence of HO_{1/2} concentration, both T_g and log(μ_H at T_g) increases with the increasing WO₃ concentration by 6.5 °C and 0.08 per 1 mol% of WO₃, respectively (Fig. 4(b)). In the case of LaO_{3/2} shown in Fig. 4(c), T_g decreases with the increasing LaO_{3/2} concentration by 2.2 °C per 1 mol% of LaO_{3/2}, and log(μ_H at T_g) increases with the increasing LaO_{3/2}. In the cases for MgO, BaO and BO_{3/2} shown in Fig. 4(d), (e) and (f), respectively, the dependence are similar to

the case of HO_{1/2} and LaO_{3/2}; $T_{\rm g}$ decreases and log($\mu_{\rm H}$ at $T_{\rm g}$) increases with the increasing concentration of the additional oxide. The variation in $T_{\rm g}$ and $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ are respectively -1.5 °C and 0.05 per 1 mol% of MgO, -2.4 °C and 0.05 per 1 mol% of BaO and -2.2 °C and 0.05 per 1 mol% of BO_{3/2}. For $NbO_{5/2}$, as clearly seen in Fig. 4(g), the relationship between $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ is little dependent on the NbO_{5/2} concentration, i.e., Tg increases by 0.7 °C per 1 mol% of NbO_{5/2} and $\log(\mu_{\rm H}~{\rm at}~T_{\rm g})$ does not change regardless $\rm NbO_{5/2}$ concentration. In the case of GeO₂ shown in Fig. 4(h), both T_g and $\log(\mu_H \text{ at } T_g)$ increases with the increasing GeO₂ concentration similar to the case of WO₃; however, increase in T_{g} , 0.6 °C per 1 mol% of GeO₂, is much smaller than that of WO₃ (6.5 $^{\circ}$ C per 1 mol% of WO₃), while increase in $\log(\mu_{\rm H} \text{ at } T_{\rm g})$, 0.12 per 1 mol% of GeO₂, is slightly larger than that of WO₃ (0.08 per 1 mol% of WO₃). These situations are summarized in Table 4.

It is noticed that the component oxides are categorized into three groups in terms of the effect on the $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$. The group 1 consists of HO_{1/2}, MgO, BaO, LaO_{3/2} and BO_{3/2}. They increase $\mu_{\rm H}$ at $T_{\rm g}$ but decrease $T_{\rm g}$, when their concentrations increase. The group 2 involves WO₃ and GeO₂ that increase both $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$, when their concentrations increase. The group 3 consists of NbO_{5/2} only in the present study, and it increases $T_{\rm g}$ but does not changes $\mu_{\rm H}$ at $T_{\rm g}$, when its concentration increases. Such effects categorized into three groups could not be found in the experimentally observed data, *i.e.*, 19 glass compositions that used as training data in this study. The information of the three groups is useful to obtain purposedesigned glasses.

The effect on $T_{\rm g}$ of respective group oxides is quite reasonable and explained according to the glass structural chemistry as following. The group 1 consists of the glass-modifiers except for $BO_{3/2}$; therefore, the reduction of T_g with the increasing concentration of the group 1 oxide is reasonably understood as a result of breaking of the phosphate glass-network by introduction of the glass-modifier oxides. BO3/2 is a glass-former oxide, and it may exist in the glass as the trigonal planer BO3 in addition to the BO4 tetrahedron in the phosphate glasses assumed in the present study.²⁷⁻²⁹ When the trigonal planer BO₃ is introduced into the glass as alternative to PO₄ tetrahedra, the number of the bridging oxygens in the glass-network reduces as the concentration of the trigonal planer BO3 increases. Consequently, BO_{3/2} acts as almost glass-modifier, and its effect on T_{g} is similar to the other group 1 oxides that are glass-modifier oxides. The groups 2 and 3 consist of the oxides exhibiting high glass forming ability, *i.e.*, GeO₂ is a glass-former and WO₃ and NbO_{5/2} are conditional glass-formers.³⁰ When the groups 2 and 3 oxides are introduced into the glass as alternative to $PO_{5/2}$, GeO_2 tetrahedra and WO_6 and NbO_6 octahedra strengthen the phosphate glass-network, resulting in increasing T_{g} .

In contrast to the effect on T_g , the origin of the effect on μ_H at T_g is still an open question as already mentioned. However, the effect of the group 2 oxides, *i.e.*, they increase μ_H at T_g with the increasing their concentration, may be explained phenomenologically as following. For the effect of WO₃, we refer to the heteropoly acid of WO₃ combined with PO_{5/2}. It is well known

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O 18,432 data

x(WO_)=0

• x(WO3)=2

• x(WO3)=4

250

O 1,536 data

x(MgO)=2
 x(MgO)=4

x(MgO)=6

230

O 1,536 data

• x(BO))=1

x(BO_{3/2})=2

x(BO_{3/2})=3

230

O 1,536 data

x(GeO_)=0

• x(GeO2)=1

x(GeO)=2

x(GeO_)=3

x(GeO) x(GeO_)

230

x(BO3/2)=0

x(MgO)=0

270

240

240

240

230

220

220

220

°C

°C

°C

°C



Fig. 4 Distribution of the relationship between predicted values of $log(\mu_H \text{ at } T_g)$ and T_g depending on the concentration of respective component oxides. (a) 55 296 predicted values distinguished by the HO_{1/2} concentration (red dots = 30 mol% HO_{1/2}, blue dots = 33 mol% HO_{1/2} and green dots = 36 mol% HO_{1/2}), (b) 18 432 predicted values for the glasses with 30 mol% of HO_{1/2} distinguished by the WO₃ concentration (red dots = 0 mol% WO₃, blue dots = 2 mol% WO₃ and green dots = 4 mol% WO₃), (c) 6144 predicted values for the glasses with 30 mol% of HO_{1/2} and 0 mol% of WO₃ distinguished by the LaO_{3/2} concentration (red dots = 0 mol% LaO_{3/2}, blue dots = 2 mol% LaO_{3/2}, green dots = 4 mol% LaO_{3/2} and orange dots = $6 \text{ mol}\% \text{ LaO}_{3/2}$. (d), (e), (f), (g) and (h) 1536 predicted values for the glasses with 30 mol% of HO_{1/2}, 0 mol% of WO₃ and 0 mol% of LaO_{3/2} respectively distinguished by the concentration of MgO, BaO, BO_{3/2}, NbO_{5/2} and GeO₂.

Table 4	Variation of $\log(u_{\rm H})$ at T) and T_{x} with	the increasing	component	oxide by 1 mol%
		g/anu /g with	the increasing	component	Ovide by THIOU

		Group 1			Group 2		Group 3	
Component oxide	MgO	BaO	LaO _{3/2}	BO _{3/2}	WO ₃	GeO_2	NbO _{5/2}	
Variation per 1 mol% of oxide	$\log(\mu_{ m H} ext{ at } T_{ m g}) \ T_{ m g}/^{\circ} { m C}$	$\begin{array}{c} 0.05 \\ -1.5 \end{array}$	$\begin{array}{c} 0.05 \\ -2.4 \end{array}$	$\begin{array}{c} 0.10 \\ -2.2 \end{array}$	$\begin{array}{c} 0.05 \\ -2.2 \end{array}$	0.08 6.5	0.12 0.6	0.00 0.7

that WO₃ and PO_{5/2} form heteropoly acid, H₃PW₁₂O₄₀·6H₂O, and it exhibits strong acidity much stronger than H₂SO₄.^{31,32} The strong acidity, *i.e.*, easy proton formation, is explained by dispersion of the negative charge over many atoms of the polyanion, PW₁₂O₄₀³⁻, and the polarization of the outer W=O bond.³² Of course, the molar ratio of WO₃ over against PO_{5/2} is much smaller (4 mol% of WO₃ is the highest, while 28 mol% of PO_{5/2} is the lowest) than that of PW₁₂O₄₀³⁻; therefore, formation of PW₁₂O₄₀³⁻-like polyanion should be excluded. However, the WO₃ coexisting with PO_{5/2} may have an effect to enhance acidity of \equiv P-O-H units. In this case, protons are easy to dissociate from \equiv P-O-H units; as a result, $\mu_{\rm H}$ would be increased by the addition of WO₃ into phosphate glasses.

In the case of GeO₂, we refer to the silicophosphate gel that is prepared by reacting SiCl₄ with anhydrous phosphoric acid (H₃PO₄).³³ The silicophosphate gel that involves Si–O–P bondings exhibits evidently higher proton conductivity than H_3PO_4 ,^{33,34} although the increase in conductivity is not so large. Taking into account that the polymerization occurs in silicophosphate gel, the concentration of proton carriers in silicophosphate is smaller than that in phosphoric acid, indicating that the SiO₂ addition enhances $\mu_{\rm H}$. Although the reason why SiO₂ addition enhance proton conductivity has not been fully understood yet, the octahedrally coordinated SiO₆ that appears in silicophosphate gel is pointed out as a key feature to explain the effect of SiO₂ addition into phosphoric acid.³³ While GeO₂ exhibits similar feature to SiO₂, *i.e.*, both GeO₂ and SiO₂ are group 4 oxides and exhibit as glass-formers, preference of sixfold coordination of Ge⁴⁺ ion is higher than Si⁴⁺ ion. These imply that GeO_2 would enhance μ_{H} , when it is added into the phosphoric acid. In this case, increase in $\mu_{\rm H}$ by the addition of GeO₂ to phosphate glass would be understood by the analogous to silicophosphate gel.

Conclusion

In summary, we developed a linear regression models for the compositional dependence of $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ and $T_{\rm g}$ for the proton conducting phosphate glass based on the approach of principal component analysis, and $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$ were predicted for 55 296 of phosphate glasses involving 9 component oxide of HO_{1/2}, MgO, BaO, LaO_{3/2}, WO₃, NbO_{5/2}, BO_{3/2}, GeO₂ and PO_{5/2}. The models themselves do not have any physical meaning of course, but they provide the following information about the effects of respective component oxides on $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$: (i) the $\mu_{\rm H}$ at $T_{\rm g}$ is determined first by concentrations of HO_{1/2} and $PO_{5/2}$; μ_H at T_g increases with increasing $HO_{1/2}$ concentration and decreasing PO_{5/2}. (ii) There is a trend for $\log(\mu_{\rm H} \text{ at } T_{\rm g})$ to increase linearly as T_{g} decreases. This is quite consistent with our estimation previously reported that the motion of protons determines the motion of glass framework in the proton conducting phosphate glasses. (iii) The component oxides are categorized into three groups according to the effects on $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$. The group 1 oxides that behave as glass-modifiers increase $\mu_{\rm H}$ at $T_{\rm g}$ and decrease $T_{\rm g}$, and HO_{1/2}, MgO, BaO and $LaO_{3/2}$ and $BO_{3/2}$ are involved in this group. The group 2 oxides increase both $\mu_{\rm H}$ at $T_{\rm g}$ and $T_{\rm g}$, and WO₃ and GeO₂ are involved

in this group. The group 3 oxides increase $T_{\rm g}$ but do not vary $\mu_{\rm H}$ at $T_{\rm g}$. Only NbO_{5/2} falls into the group 3 among the oxides examined in this study. These information are very useful to obtain purpose-designed glasses; therefore, they will be applied to the future development of proton-conducting phosphate glasses. Especially, the effects of the additional glass-formers, such as GeO₂ and WO₃, are very important to design highly proton conducting phosphate glass at intermediate temperatures.

The enhance of $\mu_{\rm H}$ at $T_{\rm g}$ by WO₃ and GeO₂ of group 2 oxide is phenomenologically understood by referring to the strong acidity of PW₁₂O₄₀³⁻ heteropoly acid and the enhancing $\mu_{\rm H}$ of phosphoric acid by SiO₂ addition, respectively. In contrast, the origin of the effect of groups 1 and 3 oxides on $\mu_{\rm H}$ at $T_{\rm g}$ and the relationship between log($\mu_{\rm H}$ at $T_{\rm g}$) and $T_{\rm g}$ still remain as open questions.

Author contributions

Takahisa Omata: conceptualization, methodology, formal analysis, software, writing – original draft and visualization, Issei Suzuki: validation, visualization and writing – review & editing, Aman Sharma: formal analysis and data curation, Tomohiro Ishiyama: writing – review & editing, Junji Nishii: conceptualization, funding acquisition and writing – review & editing, Toshiharu Yamashita: supervision and writing – review & editing, Hiroshi Kawazoe: supervision and writing – review & editing.

Conflicts of interest

The authors declare no competing interests.

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