

Supplementary Information

Proton transport properties of proton-conducting phosphate glasses at their glass transition temperatures

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S1. Determination of T_g from the thermal expansion of the glasses

T_g of the glasses after APS was determined from the thermal expansion of the glasses. Typical example of the thermal expansion curve of $38\text{HO}_{1/2}-2\text{NaO}_{1/2}-2\text{MgO}-4\text{TaO}_{5/2}-4\text{LaO}_{3/2}-2\text{GeO}_2-1\text{BO}_{3/2}-47\text{PO}_{5/2}$ (No. 13 in Table 1) is shown in Fig. S1.

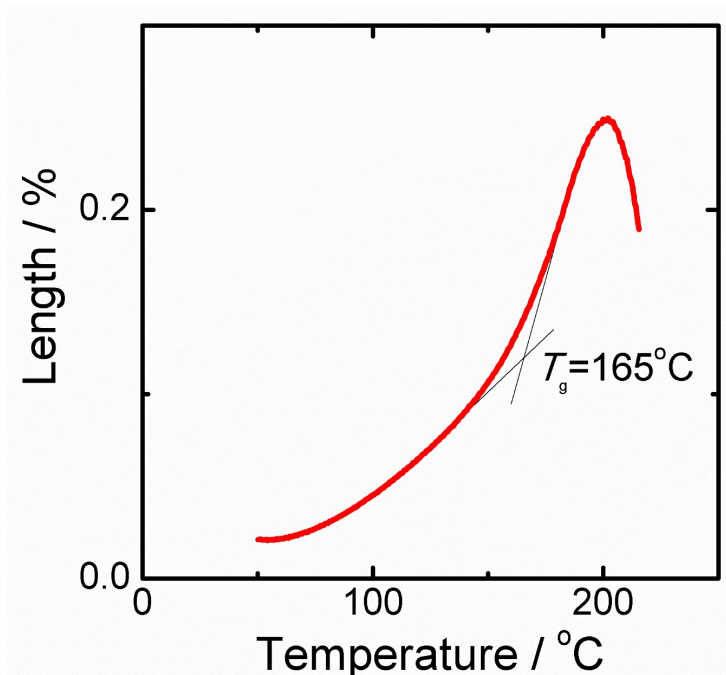


Figure S1. Thermal expansion curve of $38\text{HO}_{1/2}-2\text{NaO}_{1/2}-2\text{MgO}-4\text{TaO}_{5/2}-4\text{LaO}_{3/2}-2\text{GeO}_2-1\text{BO}_{3/2}-47\text{PO}_{5/2}$ glass (No. 13 in Table 1).

S2. Calculation of the diffusion coefficient of protons in the phosphate glasses at T_g

For general ionic liquids, the diffusion coefficient D can be evaluated using the following Stokes–Einstein equation,^{S1}

$$D = \frac{kT}{6\pi r\eta}, \quad (S1)$$

where r denotes the radius of the mobile particle and η is the viscosity of the liquid. In the case of proton conduction in liquids, because the actual radius of a proton, i.e., the root-mean-square charge radius of a proton, is extremely small (~ 1 fm),^{S2} the migration of protons is generally explained using an effective radius of 20–30 pm^{S3} taking the interaction with the surrounding media, like solvation, into account. In the case of proton migration in phosphate glasses, the protons are of course not solvated, but the local atomic distortion accompanied with proton migration similar to polarons should be considered, because the proton is strongly attracted by surrounding bridging and non-bridging oxygen atoms owing to its high charge density. Assuming that the effective radius of a proton in a phosphate glass is similar to that in liquid, i.e., 25 pm, D at T_g , where η is 10^{12} Pa s, is calculated to be $\sim 8 \times 10^{-20}$ cm² s⁻¹ for $T_g = 200$ – 500 °C using Eq. S1. This value is ten orders of magnitude smaller than the experimentally obtained D of 4×10^{-10} cm² s⁻¹. This discrepancy indicates that proton diffusion is not related to the motion of the surrounding media; i.e., the motion of the glass framework is frozen at T_g whereas that of the protons is not frozen at T_g . Such a phenomenon is usually observed in the diffusion of silver ions (Ag^+) in common superionic conducting glasses^{S4} and is considered as decoupling of the ionic diffusion from the motion of glass framework.

S3. Attempt to explain the constant mobility and diffusion coefficient at T_g based on the excess-free-volume theory

According to the excess-free-volume theory^{S4} that is used to explain the migration of mobile ions in superionic conducting glasses,^{S5,S6} D of the mobile species is expressed by the following equation:

$$D = D^0 \exp\{-v^*/(v_{eq} + v_{ex})\}, \quad (S2)$$

where v_{eq} is the equilibrium free volume, v_{ex} is the excess free volume, and v^* is the critical volume for migration of the mobile species. We tried to explain the constant D at T_g based on this theory; however, the excess-free-volume theory cannot be applied to proton-

conducting phosphate glasses according to the following logic.

In this theory, the temperature dependence of D is described by the temperature dependence of $(v_{eq} + v_{ex})$ arising from thermal expansion, because v^* is independent of temperature. In the proton-conducting phosphate glasses, v^* is assumed to be $6 \times 10^4 \text{ pm}^3$, which is the volume of a sphere with a radius corresponding to the effective radius of a proton of 25 pm, and v_{eq} corresponds to the space of the site occupied by the proton, which should be at least larger than the open space for the closest packing of oxygen ions and is assumed to be $1 \times 10^6 \text{ pm}^3$ at smallest based on the ionic radius of oxygen of 140 pm. v_{ex} in the present glasses is not clear; however, it should be of the same order of magnitude as v_{eq} , which is $\sim 10^6 \text{ pm}^3$. Under these conditions, the exponential term in Eq. S2 is almost unity, because of the small $-v^*/(v_{eq}+v_{ex})$ (0.1 at most) and the variation of the exponential term with the change of $(v_{eq}+v_{ex})$ is very small. For example, $\exp\{-v^*/(v_{eq}+v_{ex})\}$ increases by only 5% when $(v_{eq}+v_{ex})$ is doubled. Considering that the linear thermal expansion coefficient of the present glasses and supercooled liquids is of the order of 10^{-5} K^{-1} , the diffusion coefficient, i.e., mobility, exhibits almost no temperature dependence when the excess-free-volume theory is applied to the proton-conducting phosphate glasses. However, the proton conductivity, i.e., the mobility of proton carriers, is considerably temperature dependent in practice, as shown in Fig. 1, with an activation energy of 0.8–1.2 eV (Table 1). This clearly indicates that the excess-free-volume theory is not applicable to the proton-conducting glasses because of the very small size of a proton. In contrast, this theory readily explains the Ag^+ migration in common superionic conducting glasses, which is because v^* of Ag^+ is of the same order of magnitude as $(v_{eq}+v_{ex})$.

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