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Low melting oxide glasses prepared at a melt temperature of 500 °C

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Transparent low-melting inorganic glass is an attractive industrial material based on its high thermal and light resistance compared with conventional engineering plastics. If the melting temperature of inorganic glass could be decreased, the doping of guest materials or compression moulding on the glass surface would be easier. Although phosphate glass is considered as a potential candidate because of its transparency in the visible region and low-melting behaviour, water durability often becomes a problem for implementation. Here, we prepared inorganic low-melting phosphate glass at a temperature of 500 °C via a melting and quenching methodology. It was found that tin-doped phosphate glasses exhibited higher thermal and light resistance properties than polycarbonates. Colourless transparent oxide glasses without organic components are capable of bringing about new possibilities for the application of inorganic glasses.

Low-melting glass represents a conventional category of glasses whose softening temperatures are below 600 °C¹. For several decades, lead-containing glasses were used as low-melting glass^{2,3} because they possessed high chemical durability, refractive index, and transparency in the visible region, as well as low-melting behaviours. However, based on recent environmental requirements, according to the Restriction of Hazardous Substances Directive, the use of lead for conventional commercial materials is strictly prohibited. Therefore, many researchers have been investigating lead-free low-melting glass alternatives^{4–8}. Notably, lead is a unique element with many advantages, as mentioned above, and it is very difficult to substitute lead cations with those of glass. Therefore, a combination of several elements is often used to satisfy these physical parameters^{8–11}. However, some characteristics of lead-containing glass are generally achieved by sacrificing several properties. For example, vanadium-containing low-melting glass has no transparent window in the visible region. Thus, it is onerous to fabricate lead-free low-melting transparent inorganic glasses.

Recently, three-dimensional printing technology has become a popular tool for the production of solid-state materials, and good formability at low melting temperatures has become a key application issue. In addition, to match the thermal properties between glass and its counterparts, the low-temperature process of glass has been comprehensively examined. Engineering plastics (EPs) have been presumed as inorganic low-melting glass alternatives. This group of plastic materials evince several advantages, such as various chemical compositions, low density, low working temperature, and better brittleness relative to inorganic glasses. Nonetheless, EPs are strictly limited based on the perspectives of thermal and light resistance. Among the many industrial applications of EPs, optical utilization through light-emitting diodes (LEDs) is envisaged to grow in importance in the near future. Recent developments in LED applications entail the fabrication of next-generation light sources with high power and shorter wavelength (high photon energies) qualities. Although several EPs have been reported for this application, the thermal and light resistance properties of organic-containing glass are inherently inferior to those of organic-free inorganic glasses. If an inorganic glass could be fabricated at a much lower temperature than that of conventional industrial glasses, a novel glass system, which could be adopted by many users without a specific electric furnace, would ensue.

Although a lower preparation temperature is industrially preferable, it often results in materials with a correspondingly low chemical durability. For example, if a low-melting inorganic oxide glass is fabricated below 400 °C, satisfying both the low preparation temperature and chemical durability requirements is expected to be very difficult. Therefore, as a target temperature herein, we choose 500 °C as the fabrication temperature for an inorganic glass that can possess both low-melting behaviour and chemical durability. Notably, the sol-gel

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ID	Chemical composition (mol%)	T_g (°C)
ID1	50SnO–50P ₂ O ₅	126
ID2	55.6SnO–44.4P ₂ O ₅ [50SnO–40P ₂ O ₅]	145
ID3	60SnO–40P ₂ O ₅	165
ID4	10K ₂ O–50SnO–40P ₂ O ₅	210

Table 1. Chemical compositions and the glass transition temperature (T_g) values of SnO–P₂O₅-based glasses.

process is suitable for glass preparation at a lower temperature than the conventional melt-quenching method^{12–14}. However, because the sol–gel process generally requires a preparation temperature above 500 °C, it is essential to examine alternative preparation methods for lower temperature synthesis. Based on a previous report, we focussed on the acid–base reaction for the preparation of organic–inorganic hybrid glasses¹⁵. A key factor entails the use of H₃PO₄ as both the reactant and the solvent of the batch, which allows for the formation of metal cation–oxygen–phosphorus bonds during the heat treatment of H₃PO₄ and metal chlorides. This concept has been previously confirmed to be adaptable for the preparation of inorganic films¹⁶. However, the spontaneous generation of HCl from the starting materials damages the reaction system, thereby constituting a challenge. Considering the less toxic leaving groups, we assumed that oxides, alkoxides, hydroxides, and phosphates could be used as starting materials. Ehrt reported the preparation of transparent SnO–P₂O₅ glasses at different melting temperatures¹⁷. It was discovered that the OH-containing SnO–P₂O₅ glass could be prepared at 450 °C, although the water durability was poor, whereas the same glass prepared at 1200 °C exhibited good durability. The water durability of phosphate glass is often problematic for practical applications^{18–20}. If we could tailor the phosphate glass network at a lower temperature range, the potential of inorganic glasses as functional industrial materials would ensue. Therefore, we focussed on the SnO–P₂O₅-based glass system as the main chemical composition of glass and set the target preparation temperature as 500 °C. Herein, we report the preparation and physical properties of lead-free inorganic glasses prepared at 500 °C via a liquid-phase reaction, and it is demonstrated that transparent phosphate glasses possess a better thermal and high-power light resistance than conventional EPs.

Results and discussion

Examination of the chemical composition of tin phosphate-based glasses. Firstly, we examined the chemical composition of the host phosphate glass suitable for melting at 500 °C. There is a conventional relationship between the melting point (T_m) and glass transition temperature (T_g), i.e., $T_g/T_m \sim 2/3$ ²¹. A benchmark of T_g is, therefore, approximately 243 °C to attain melting at 500 °C. In this study, we focussed on the SnO–P₂O₅ glass system because it was reported that SnO–P₂O₅ glasses generally exhibited lower T_g values below 300 °C^{4,5,17,22–24}. It is important to maintain the Sn²⁺ states during melting at 500 °C because it is reported that the oxidation reaction of Sn²⁺ starts at approximately 450 °C²⁵.

Table 1 presents the chemical compositions and T_g values of several SnO–P₂O₅-based glasses prepared at 500 °C. The differential thermal analysis (DTA) curves are shown in Fig. 1a. The error bars of these T_g values exceed 5 °C, which are marginally larger than the conventional error values estimated by extrapolating the DTA curve. An alternative composition of ID2 (50SnO–40P₂O₅) is also shown in order to understand the change in T_g with the addition of either 10 mol% of SnO (for ID3) or 10 mol% of K₂O (for ID4). This suggests that the obtained glasses are thermodynamically metastable transient states whose concentration of OH groups¹⁷ or network formation is slightly different. Because the base chemical composition is similar, it is expected that a glass possessing a higher T_g exhibits a higher chemical durability. We occasionally observed a brownish colouration of the prepared glass in the 60SnO–40P₂O₅ glass, although all starting chemicals contained no carbon species. Since remarkable diffraction peaks are not observed in the brownish-coloured sample (Fig. S1), it is expected that small amounts of Sn nanocrystallites may be formed during melting. Figure 1b shows the optical absorption spectra of the 50SnO–50P₂O₅ (ID1), 55.6SnO–44.4P₂O₅ (ID2), 60SnO–40P₂O₅ (ID3), and 10K₂O–50SnO–40P₂O₅ (ID4) glasses. The inset reveals the expanded spectra at the optical absorption edge region. If we evaluate the optical absorption edge from the extrapolation of the absorption coefficient, as shown by the dashed line in the figure, the compositional dependence can be elucidated. It was found that these optical absorption edges were located below 330 nm and that the optical absorption edges blue-shifted with decreasing T_g values, as shown in Fig. 1c. For the SnO-doped glass prepared by the conventional melt-quenching method, the optical absorption edge owing to the Sn²⁺ cation redshifts with increasing SnO fraction²⁶. However, such an edge shift depending on the SnO fraction is not observed in the present case. Considering the T_g , it is expected that the concentration of the OH group affects the blueshift of the optical absorption edge. This speculation is confirmed by the absorption spectra in the infrared (IR) region. The absorption coefficients of these glasses in the IR region increase with decreasing T_g values, thereby suggesting that a higher OH concentration induces a larger decrease in T_g . The absorption bands at 1,570 nm and 2,135 nm are assigned to the overtone of the P–OH stretching and the combination stretching–bending of the P–OH modes, respectively^{27,28}. Figure 1d shows the absorption coefficient of the 2,135 nm peak as a function of T_g . Notably, the surface of the 50SnO–50P₂O₅ glass with the highest OH concentration was rapidly damaged by water immersion at room temperature (RT). However, if the SnO fraction exceeded 60 mol%, the SnO–P₂O₅ glasses would need a melt temperature higher than 500 °C, and they sometimes exhibited opacity or a brownish colouration. The water durability of the ID1 glass was the worst, whereas ID4 was the best among these glasses. From these spectra, we concluded that ID4 (10K₂O–50SnO–40P₂O₅) was the best candidate with both low-melting behaviour and chemical durability among these compositions. As the pH of

Figure 1. Thermal and optical properties of SnO–P₂O₅-based glasses: **(a)** DTA curves of the SnO–P₂O₅-based glasses listed in Table 1. **(b)** Optical absorption spectra of 50SnO–50P₂O₅ (ID1), 55.6SnO–44.4P₂O₅ (ID2), 60SnO–40P₂O₅ (ID3), and 10K₂O–50SnO–40P₂O₅ (ID4) glasses melted at 500 °C for 30 min. Inset shows the expanded spectra at the optical absorption edge region. The dashed line indicates the ID1 extrapolation line for the optical absorption edge. **(c)** Relationship between the optical absorption edge and T_g of these glasses. **(d)** Relationship between absorption coefficient at approximately 2,135 nm and T_g .

water decreased (acidic) after the dissolution testing of these glasses, we can deduce that there is a conventional hydrolysis reaction mechanism between water and the phosphate chains¹⁸.

We assumed that the water resistance of K₂O–SnO–P₂O₅ glasses might depend on the structural change in the P₂O₅ region. To examine the structural changes based on the chemical composition, the ³¹P magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were measured. Figure 2a shows the ³¹P MAS NMR spectra of the SnO–P₂O₅-based glasses, which are listed in Table 2. The different phosphate units, Qⁱ, in the ³¹P NMR spectra are identifiable from the chemical shift, which is attributed the number of bridging oxygen atoms^{11,31–33}. The peaks due to Q², Q¹, and Q⁰ in tin–phosphate-based glasses are located at –33 ppm, –19 ppm, and –9 ppm, respectively³⁴. It is evident from the NMR spectra that the dimer structure, Q¹, whose chemical shift is approximately –19 ppm, is the main phosphate unit in these glasses. The calculated fractions of Qⁿ units are shown in Table S1. In all the samples, a small amount of the Q⁰ unit was observed. It is previously proposed that the Q⁰ and Q¹ units, which are highly electron-delocalized units, affect the chemical (water) durability compared to the Q² unit. Put differently, if the fractions of such highly electron-delocalized units are large, the glass would exhibit excellent water durability³³. However, contrary to our expectations, there was no remarkable difference between these glasses. In addition, although the fractions of (Q⁰ + Q¹) exceed 80% in all the systems, these glasses have low water durability. Thus, we assume that the residual OH groups affect the water durability of these glasses because of the low melt temperature.

Since this preparation was conducted under ambient or reduced pressure conditions at 500 °C, which was comparable to the conventional temperature for Sn²⁺ oxidation, it was envisaged that most of the tin species were divalent²⁵. Since Sn²⁺ is more preferable for low-melting relative to Sn⁴⁺, experimental confirmation is important²⁹. To confirm the valence state of tin, we measured the Sn L-edge X-ray absorption near-edge structure (XANES) spectra according to a previous paper²⁹. Figure 2b shows the Sn L₂-edge of the ID2 and ID4 glasses, along with that of SnO. Compared with the reference (SnO), it is evident that approximately all Sn species are divalent, and the local coordination state of SnO does not drastically change with K₂O addition. Because it was also envisaged that SnO connectivity would be affected by the chemical composition, we also measured the Sn K-edge X-ray absorption fine structure (XAFS) spectra. Figure 2c shows the Sn K-edge XAFS spectra of the ID2 and ID4 glasses with SnO as a reference. Because the XANES spectra shapes are similar, the result is consistent with valence estimation from the L₂-edge. Figure 2d shows the Fourier transform (FT) of the extended XAFS (EXAFS) region of the Sn K-edge XAFS. The FT was performed with the *k* region from 3.4 to 12 Å^{–1}. The addition of K₂O changes the SnO structure, i.e., the Sn–O distance becomes longer, and the coordination number

Figure 2. Structural analysis of SnO–P₂O₅-based glasses melted at 500 °C for 1 h. **(a)** ³¹P MAS NMR spectra of SnO–P₂O₅-based glasses. Dotted lines indicate Q⁰, Q¹, and Q² components after peak deconvolution. **(b)** Sn L₂-edge XANES spectra of SnO–P₂O₅-based glasses along with that of SnO. **(c)** Sn K-edge XANES spectra of SnO–P₂O₅-based glasses. **(d)** FT of EXAFS of Sn K-edge XAFS. The *k* region for FT is from 3.4 to 12 Å^{−1}.

Additive component (mol%)	Starting chemical	Weight loss (10 ^{−6} g/mm ²)
–	–	22
0.5La ₂ O ₃	La ₂ O ₃	1.5
1.0La ₂ O ₃	La ₂ O ₃	–
0.5SiO ₂	Si(OC ₂ H ₅) ₄	27
1.0SiO ₂	Colloidal silica	26
0.5Al ₂ O ₃	Al(OH) ₃	45
1.0Al ₂ O ₃	Al(OH) ₃	38
0.5B ₂ O ₃	B(OH) ₃	23
1.0B ₂ O ₃	B(OH) ₃	12

Table 2. Chemical compositions and weight loss of KSP glasses after the immersion test at 50 °C for 72 h. However, the 1.0La₂O₃-doped KSP glass was not obtained because of strong bubbling during the heat treatment at 500 °C.

increases through K₂O addition. It seems rather peculiar that the Sn–O distance of K₂O-substituted SnO–P₂O₅ glasses is closer to SnO than that of the SnO-rich SnO–P₂O₅ glass. It has been reported that SnO has a tetragonal unit cell with a litharge structure³⁰. However, it is speculated that the P=O bond of the P₂O₅ unit in the SnO–P₂O₅ structure can expand the interatomic distance of Sn²⁺ owing to the repulsion of electrons. It is, therefore, expected that potassium cations will be located near the phosphate chains for preferential charge compensation, and the residual Sn²⁺ cations will exist in a higher coordination state, similar to the SnO structure. Since the ³¹P NMR and Sn L₂ edge XANES spectra are similar, the change in Sn cation coordination by the addition of K₂O is one of the reasons for obtaining better water durability. Based on the results of the compositional survey, we selected 10K₂O–50SnO–40P₂O₅ glass, which is hereafter denoted as KSP glass and possesses the lowest OH concentration and the highest *T_g* among these glasses, as the tin phosphate-based glass composition.

Figure 3. Transparency of alkaline-substituted KSP glasses. **(a)** Photographs of $x\text{Li}_2\text{O}-(10-x)\text{KSP}$ and **(b)** $x\text{Na}_2\text{O}-(10-x)\text{KSP}$ glasses melted at 500 °C for 10 min. The substitution fractions are 0, 5, and 10. **(c)** XRD patterns of KSP, $10\text{Na}_2\text{O-SP}$, and $10\text{Li}_2\text{O-SP}$ glasses along with JCPDS patterns of Sn (#00-004-0673), SnO (#01-072-1012), and $\text{Sn}_2\text{P}_2\text{O}_7$ (#00-056-0358).

Improvement of water durability of KSP-based glasses. Although we select KSP glass as the main host composition, its water durability property is insufficient. Therefore, additional material design under a melting condition of 500 °C is needed. The dissolution behaviours of phosphate glasses are often discussed based on the nature of the glass surface and the P–O–P hydrolysis rates. It is natural that the composition and structure of glasses affect the dissolution behaviour. Alkali oxides and Q^2 and Q^3 phosphate units increase their dissolution rates, whereas high field strength cations, such as Al_2O_3 and Fe_2O_3 , decrease the dissolution rates. It has occasionally been reported that the mixing of alkaline metal oxides, i.e., the mixed alkali effect of oxide glasses, improves the water durability of glasses^{35,36}. Recently, Onodera et al. proposed that the correlated pair arrangement of Na and K was the intrinsic origin of the mixed alkali effect. Based on previous reports, several glasses containing two alkaline metal oxides were prepared. Figure 3a shows a photograph of $x\text{Li}_2\text{O}-(10-x)\text{KSP}$ glasses prepared at 500 °C. The transparency decreases with increasing Li_2O concentration, and, in particular, the K_2O -free glass is opaque, which is unsuitable for optical applications (see Fig. S2). A similar result was also confirmed in the Na_2O -substituted $x\text{Na}_2\text{O}-(10-x)\text{KSP}$ system (Fig. 3b). In the Na-substituted system, KSP glass also exhibited the best transparency among them. The crystallization behaviours are evaluated by acquiring XRD patterns. Figure 3c shows XRD patterns of KSP, $10\text{Na}_2\text{O-SP}$, and $10\text{Li}_2\text{O-SP}$ glasses along with the Joint Committee on Powder Diffraction Standards (JCPDS) patterns of Sn (#00-004-0673), SnO (#01-072-1012), and $\text{Sn}_2\text{P}_2\text{O}_7$ (#00-056-0358). In these glasses remarkable precipitation of crystallites was not observed. Therefore, it is envisaged that 500 °C is too low to make homogeneous glass melt to exhibit the mixed alkali effect, and only phase separation occurs during the melting. Although the reason K_2O introduction presents the best outcome among the alkaline metal oxides remains unclear, it is presumed that the cationic radius of K_2O is suitable for transparency and low-melting behaviour.

To improve the water durability of the low-melting KSP glass, we tried to add a fourth component. Table 2 shows the chemical compositions and weight loss of KSP glasses after the water immersion test at 50 °C for 72 h. The data in Table 2 show that the additive concentration seems to be less effective relative to the elements. Among several metal oxides, we discovered that La_2O_3 could effectively improve the water durability of the materials. An improvement of water durability through the addition of La_2O_3 has been reported in several glass systems prepared via the melt-quenching method^{37,38}. In the present glass system, improved water durability through La_2O_3 addition is also confirmed, even with a melt temperature of 500 °C, which is much lower than the conventional melt temperature. It is also notable that the addition of La_2O_3 induces no degradation on the transparency of KSP glass. We assume that La cations connect to phosphate units to prevent phase separation.

Figure 4. Effect of La_2O_3 addition on KSP glasses. **(a)** DTA curves of KSP glass and La_2O_3 -doped KSP (LKSP) glass. **(b)** Optical absorption spectra of KSP and LKSP glasses. Inset shows the expanded absorption spectra at the absorption edge region. **(c)** Optical absorption edge and the absorption coefficient around 2,135 nm as a function of T_g . **(d)** ^{31}P MAS NMR spectra of KSP and LKSP glasses. **(e)** Sn K-edge XANES spectra of KSP and LKSP glasses along with SnO. **(f)** FT of EXAFS of Sn K-edge XAFS spectra of KSP and LKSP glasses along with SnO.

Physical properties of La_2O_3 -doped KSP (LKSP) glasses. Previous data suggest that $0.5\text{La}_2\text{O}_3$ -doped KSP (LKSP) glass is a promising candidate for inorganic low-melting glasses. Over a course of three years, we confirmed that the LKSP glass is stable under ambient conditions (25 °C, ~60% humidity) despite the considerable amount of K_2O , because La_2O_3 and SnO prevent the hydrolysis reaction. Therefore, we examined the structure and physical properties of the LKSP glass. Figure 4 presents a comparison between the KSP and the LKSP glasses. An increase in T_g upon La_2O_3 addition is observed, as shown in Fig. 4a, and simultaneously, a decrease in the OH concentration is apparent in the optical absorption spectra (Fig. 4b). Therefore, the decrease of OH groups by the addition of La_2O_3 is one of the origins of increasing T_g . The effect of La_2O_3 addition is also observable at the optical absorption edge. Although the molar fraction of SnO slightly decreases with the addition of La_2O_3 , the absorption edge redshifts, as shown in the inset of Fig. 4b. The relationship between T_g and these absorption properties was also confirmed in the La-doped sample, as shown in Fig. 4c. It is notable that the Q^n fractions in the ^{31}P MAS NMR spectra are slightly changed by La_2O_3 addition (Fig. 4d), and the fraction of Q^2 increases by addition of La_2O_3 (Table S1). In the case of iron-containing glass, it is proposed that added Fe cations connected to phosphate chains to improve the chemical durability^{39,40}. From the results of Q^2 ratio, it is expected that La cations work the similar role to the previous report on the phosphate network³⁹. Since a remarkable difference is not observed in the Sn L_2 -edge XANES (Fig. 4e) and Sn K-edge XAFS spectra (Fig. 4f), it is suggested that La cations mainly interact with phosphate units to decrease OH concentration at 500 °C heating, thereby improving the water durability of the LKSP glass.

Figure S3 shows the viscosity curve of an LKSP glass. The experimental data can be fitted using the Vogel–Fulcher–Tamman (VFT) equation^{41–43}. From the viscosity curve, we can determine several thermal parameters, which are listed in Table 3. The thermal expansion coefficient and elastic parameters are also shown therein. From the thermal parameters, we can understand that the obtained glass can exhibit a low-melting behaviour, whose T_g is comparable to that of conventional low-melting glass^{2–10}. The T_g of 235 °C is close to the expected T_g value (243 °C), based on the relationship: $T_g/T_m \sim 2/3$ ²¹. Based on the fragility of glass-forming liquid defined by Novikov et al.⁴⁴, the ratio of longitudinal and transversal sound velocity v_L/v_T is approximately 1.76, indicating that the glass is strong rather than fragile. It is expected that surface tailoring via the nanoprinting method can be adapted to this glass below 400 °C, which is an advantage not only for decreasing temperature but also for the possibility of applying other types of moulds for superficial nanoprinting at the surface. Nonetheless, the refractive index at 633 nm of the LKSP glass is 1.65, which is higher than that of conventional EPs, thereby presenting another advantage of this low-melting inorganic glass.

It is notable that the LKSP glass is hard to be prepared by conventional melting using Pt crucibles. As shown in Fig. S4, significant damage of surface of Pt crucible was detected after melting at 800 °C in Ar atmosphere. Therefore, the low-melting process at 500 °C using aqueous H_3PO_4 has additional advantage that damage of crucibles due to strong reduction reaction is prevented.

Glass transition temperature	235 °C
Density	3.40 g/cm ³
Yield point	260 °C
Softening point (10 ^{7.65} poise)	320 °C
Working point (10 ⁴ poise)	420 °C
Thermal expansion coefficient (50–150 °C)	1.70 × 10 ⁻⁵ /°C
Longitudinal sound velocity v_L	3.48 km/s
Transverse sound velocity v_T	1.98 km/s
Shear modulus	13.4 GPa
Poisson ratio	0.26
Young modulus	33.7 GPa
Bulk modulus	23.4 GPa

Table 3. Thermal and elastic properties of the LKSP glass. **Figure 5.** Transmittance of LKSP glass accelerated durability test by comparison with polycarbonates (PCs). **(a)** Transmittance spectra of LKSP glass and PCs after UV irradiation and heat treatment at 200 °C for 1000 h. **(b)** Photographs of PCs before and after durability tests. Remarkable transmittance degradation is observed in PCs, while no change is observed in the LKSP glass.

As mentioned in the Introduction, we assume that the counterpart of low-melting inorganic glass is EPs. Here, we compare the thermal and light resistance of the LKSP glass with those of conventional EPs and polycarbonates (PCs). Figure 5a shows the transmittance spectra of La₂O₃-doped KSP glass, as well as those of PCs after the accelerated durability test. For comparison, the thicknesses of PCs and glass were normalised to 1 mm. To check the properties, two accelerated tests were performed: (1) ultraviolet (UV) exposure at RT for 700 h and (2) heat treatment at 200 °C for 1000 h in an ambient atmosphere. The transparency of the inorganic glass remained unchanged after both durability tests, while a large degradation in PC transparency was observed after both tests. Figure 5b shows photographs of PCs before and after the UV exposure and thermal treatment durability tests. The transmittance of the PCs deteriorates drastically after both durability tests. Conversely, the transparency of the glass was unchanged after both accelerated durability tests. The results herein demonstrate that the present inorganic glass can be used in some application regions of EPs. Recently, inorganic glasses have been substituted by organic resins or EPs owing to their density, preparation cost, and preparation temperatures. However, from the viewpoint of thermal and high-power light resistance, advantages exist in employing inorganic glasses. By decreasing the preparation temperature, we have emphasised that several application windows are now open to inorganic glasses.

Summarily, we fabricated low-melting phosphate glass with a melt temperature of 500 °C. By selecting the chemical composition and the starting materials, colourless, transparent glasses can be obtained. The T_g is below 250 °C, which is a great advantage for melting and shaping at low temperatures. Although water durability occasionally constitutes a major problem for low-melting phosphate glass, this property can be improved by the composition and preparation process. Because this low-melting glass is durable against thermal and strong light conditions, it is considered as a novel colourless solid-state matter candidate that can partially function as a substitute for conventional EPs.

Experimental

The starting materials for the low-melting glasses were H_3PO_4 (85%), SnO , as well as metal phosphate, such as KPO_3 , K_2HPO_4 , and other metal oxides. These chemicals were mixed in a 60 mL cylindrical borosilicate glass beaker (inner diameter: $\phi 50$ mm, height: 55 mm, wall thickness: 1.3 mm, supplied by the Maruemu Corporation, Japan) at room temperature (RT). The mixture in the glass beaker was initially preheated to reduce residual concentrations of OH groups and H_2O at approximately 400 °C. After the pre-heat treatment, the obtained solid was melted at 500 °C for 15–30 min in an ambient or reduced atmosphere. If the generation of bubbles was significant during melting, the pressure was manually reduced in the pressure range from 0.1 MPa to 1 kPa. The temperature whereat the inorganic glass is held in a molten state is referred to as the ‘melt temperature’ herein. The obtained glass was gradually cooled down to RT without temperature control or quenched at RT.

The glass transition temperature was determined through differential thermal analysis at a heating rate of 10 °C/min. To examine the crystalline phases in the prepared glass, we performed X-ray diffraction measurements using a RINT2100 (Rigaku, Japan) with Cu K α radiation. The densities of the glasses were determined according to Archimedes’ method using distilled water as an immersion liquid. The refractive index was measured with a prism coupling method using a prism coupler with 473-, 633-, and 1,319-nm light sources (Metricron, USA). The elastic properties were measured by means of the ultrasonic pulse echo method using a DPR-300 (JSR ultrasonics, USA). The frequencies of the longitudinal and transverse waves were 10 MHz and 5 MHz, respectively. The viscosity curve was obtained through a viscometer with 10 mm ϕ parallel plates using PRVM-1100 (Motoyama, Japan). Optical transmission spectra were measured using a UH4150 spectrophotometer (Hitachi High-Tech Science, Japan).

Furthermore, ^{31}P MAS nuclear magnetic resonance (NMR) spectra of the glasses were acquired on a DELTA 600 spectrometer (JEOL, Japan) and a CMX-400 NMR spectrometer (JEOL, Japan) at a frequency of 161.80 MHz (CMX-400) and 242.95 MHz (DELTA 600), as well as a spin rate and relaxation delay of 10 kHz and 5 s, respectively. The chemical shifts were estimated with respect to an 85% H_3PO_4 aqueous solution (0 ppm).

The Sn K-edge X-ray absorption near edge structure (XANES) spectra were measured using the transmittance method, whereas the Sn L_{2-3} -edge XANES spectra were evaluated via the fluorescent method. These measurements were performed at the BL14B2 beamline of SPring-8. The operated storage ring energy was 8 GeV with a conventional current of 100 mA. For the transmittance method, the samples were mixed with boron nitride and pelletised.

The water durability of the samples was tested through weight loss. The samples prepared via melt-quenching were cast into a stainless-steel cell. These glasses were then re-melted in a 25 mL cylindrical borosilicate glass beaker (inner diameter: $\phi 35$ mm, height: 45 mm, wall thickness: 1.3 mm, supplied by the Maruemu Corporation, Japan) to obtain the free surface. For the dissolution experiment, 10 mL of ultrapure water was added to the beaker. After heat treatment at 50 °C for 72 h, the samples were dried at 80 °C for 3 h under vacuum conditions. By comparing the sample weight before and after water immersion, the weight losses of each samples were calculated. The error bars of the weight loss were estimated to be ± 10 wt%.

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References

1. Yamane, M. *et al.* (eds) *Glass Kogaku Handbook* (Asakura Shoten, Tokyo (in Japanese), 2010).
2. Tick, P. A. Water durable glasses with ultra low melting temperatures. *Phys. Chem. Glasses* **25**, 149 (1984).
3. Cheng, J. & Jin, Z. New lead-halide-based glass-forming systems. *J. Non Cryst. Solids* **184**, 213 (1995).
4. Liu, H. S., Shih, P. Y. & Chin, T. S. Low melting PbO – ZnO – P_2O_5 glasses. *Phys. Chem. Glasses* **37**, 227 (1996).
5. Morena, R. Phosphate glasses as alternatives to Pb-based sealing frits. *J. Non Cryst. Solids* **263–264**, 382–387 (2000).
6. Cha, J., Kubo, T., Takebe, H. & Kuwabara, M. Compositional dependence of properties of SnO – P_2O_5 glasses. *J. Ceram. Soc. Jpn.* **116**, 915–919 (2008).
7. Brow, R. K. & Tallant, D. R. Structural design of sealing glasses. *J. Non Cryst. Solids* **222**, 396–406 (1997).
8. Masai, H., Takahashi, M., Tokuda, Y. & Yoko, T. Gel-melting method for preparation of organically-modified siloxane low-melting glasses. *J. Mater. Res.* **20**, 1234–1241 (2005).
9. <https://www.hitachi.co.jp/New/cnews/month/2012/11/1126a.html>
10. https://www.neg.co.jp/uploads/news_20191203_jp
11. Brow, R. K. Review: the structure of simple phosphate glasses. *J. Non Cryst. Solids* **263**, 1–28 (2000).
12. Dislich, H. New routes to multicomponent oxide glasses. *Angew. Chem. Int. Ed.* **10**, 363–370 (1971).
13. Yoldas, B. E. Preparation of glasses and ceramics from metal-organic compounds. *J. Mater. Sci.* **12**, 1203–1208 (1977).
14. Sakka, S. & Kamiya, K. Glasses from metal alcoholates. *J. Non Cryst. Solids* **42**, 403–442 (1980).
15. Niida, H., Takahashi, M., Uchino, T. & Yoko, T. Preparation and structure of organic-inorganic hybrid precursors for new type low-melting glasses. *J. Non Cryst. Solids* **306**, 292–299 (2002).
16. Masai, H. *et al.* Tin-doped inorganic amorphous films for use as transparent monolithic phosphors. *Sci. Rep.* **5**, 11224 (2015).
17. Ehrh, D. Effect of OH-content on thermal and chemical properties of SnO – P_2O_5 glasses. *J. Non Cryst. Solids* **354**, 546–552 (2008).
18. Douglas, R. W. & Elshamy, T. M. Reactions of glasses with aqueous solutions. *J. Am. Ceram. Soc.* **50**, 1 (1967).
19. Minami, T. & Mackenzie, J. D. Thermal-expansion and chemical durability of phosphate glasses. *J. Am. Ceram. Soc.* **60**, 232–235 (1977).
20. Paul, A. Chemical durability of glasses-thermodynamic approach. *J. Mater. Sci.* **12**, 2246–2268 (1977).
21. Sakka, S. & Mackenzie, J. D. Relation between apparent glass transition temperature and liquids temperature for inorganic glasses. *J. Non Cryst. Solids* **6**, 145–162 (1971).
22. Takebe, H. *et al.* Imprinted optical pattern of low-softening phosphate glass. *Opt. Lett.* **32**, 2750–2752 (2007).
23. Cha, J., Kubo, T., Takebe, H. & Kuwabara, M. Compo compositional dependence of properties of SnO – P_2O_5 glasses. *J. Ceram. Soc. Jpn.* **116**, 915–919 (2008).
24. Hayashi, A., Konishi, T., Tadanaga, K., Minami, T. & Tatsumisago, M. Preparation and characterization of SnO – P_2O_5 glasses as anode materials for lithium secondary batteries. *J. Non Cryst. Solids* **345**, 478–483 (2004).

25. Batzill, M. & Diebold, U. The surface and materials science of tin oxide. *Prog. Surf. Sci.* **79**, 47–154 (2005).
26. Masai, H. *et al.* Correlation between preparation conditions and the photoluminescence properties of Sn^{2+} centers in $\text{ZnO-P}_2\text{O}_5$ glasses. *J. Mater. Chem. C* **2**, 2137–2143 (2014).
27. Bartholomew, R. F., Butler, B. L., Hoover, H. L. & Wu, C. K. Infrared spectra of a water-containing glass. *J. Am. Ceram. Soc.* **63**, 481–485 (1980).
28. Efimov, A. M., Pogareva, V. G. & Shashkin, A. V. Water-related bands in the IR absorption spectra of silicate glasses. *J. Non Cryst. Solids* **332**, 93–114 (2003).
29. Masai, H., Ina, T. & Mibu, K. Validity of valence estimation of dopants in glasses using XANES analysis. *Sci. Rep.* **8**, 415 (2018).
30. Pannetier, J. & Denes, G. Tin(II) oxide: structure refinement and thermal expansion. *Acta Crystallogr. B* **36**, 2763–2765 (1980).
31. Brow, R. K., Tallant, D. R., Myers, S. T. & Phifer, C. C. The short-range structure of zinc polyphosphate glass. *J. Non Cryst. Solids* **191**, 45–55 (1995).
32. Brow, R. K. & Kirkpatrick, R. J. Nuclear magnetic resonance investigation of the structures of phosphate and phosphate-containing glasses: a review. *Solid State Nucl. Mag.* **5**, 9–21 (1995).
33. Masai, H. *et al.* ^{31}P NMR and IR study of highly water-stable $\text{SrO-BaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5$ glass and glass-ceramics. *Chem. Lett.* **42**, 1305–1307 (2013).
34. Saitoh, A., Hashida, Y., Tricot, G. & Takebe, H. Properties and structure in ternary meta-, pyro-, and ortho-zinc tin phosphate glasses with small photoelasticity. *Phys. Status Solidi B* **255**, 1800318 (2018).
35. Habasaki, J., Okada, I. & Hiwatari, Y. MD study of the mixed alkali effect in a lithium–potassium metasilicate glass. *J. Non Cryst. Solids* **183**, 12–21 (1995).
36. Onodera, Y. *et al.* Origin of the mixed alkali effect in silicate glass. *NPG Asia Mater.* **11**, 75 (2019).
37. Zhang, X. H., Yue, Y. L. & Wu, H. T. Influence of La_2O_3 additions on chemical durability and dielectric properties of boroaluminosilicate glasses. *Surf. Rev. Lett.* **19**, 1250062 (2012).
38. Shi, Q. S. *et al.* Effect of rare-earth oxides on structure and chemical resistance of calcium aluminophosphate glasses. *J. Non Cryst. Solids* **491**, 71–78 (2018).
39. Yu, X. Y., Day, D. E., Long, G. J. & Brow, R. K. Properties and structure of sodium-iron phosphate glasses. *J. Non Cryst. Solids* **215**, 21–31 (1997).
40. Ma, L., Brow, R. K. & Schlesinger, M. E. Dissolution behavior of $\text{Na}_2\text{O-FeO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses. *J. Non Cryst. Solids* **463**, 90–101 (2017).
41. Vogel, H. The temperature dependence law of the viscosity of fluids. *Phys. Z.* **22**, 645 (1921).
42. Fulcher, G. S. Analysis of recent measurements of the viscosity of glasses. *J. Am. Ceram. Soc.* **8**, 339–355 (1925).
43. Tamman, G. & Hesse, W. The dependancy of viscosity on temperature in hypothermic liquids. *Z. Anorg. Allg. Chem.* **156**, 245 (1926).
44. Novikov, V. N. & Sokolov, A. P. Poisson's ratio and the fragility of glass-forming liquid. *Nature* **431**, 961 (2004).

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Author contributions

H. M. formulated the research project. H. M. and T. N. prepared the materials. H. M., T. N., S. Y., T. A., Ta. N., and M. Y. performed the material characterization, except for elastic modulus and MAS NMR. N. K. measured elastic properties and analysed the data. T. O. measured the ^{31}P MAS NMR spectra and analysed the resulting data. H. M. wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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