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Polycarboxylic acids as network modifiers for water durability improvement of inorganic–organic hybrid tin-silico-phosphate low-melting glasses

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Abstract

We investigated the water durability of the inorganic–organic hybrid tin-silico-phosphate glasses Me_2SiO–SnO–P_2O_5 (Me designs the organic methyl group) doped with organic acids (salicylic acid (SA), tartaric acid (TA), citric acid (CA) and butane tetracarboxylic acid (BTCA)) containing one or more of carboxylic groups per molecule. The structure, thermal properties and durability of the final glasses obtained via a non-aqueous acid–base reaction were discussed owing to the nature and the concentration of the acid added. ^{29}Si magic angle spinning (MAS) NMR and ^{31}P MAS NMR spectra, respectively, showed clearly a modification of the network in the host glass matrix of the Me_2SiO–SnO–P_2O_5 system. The polycondensation enhancement to form –P–O–Si–O–P– linkages (PSP) and the increase of the Q^2 unit (two bridging oxygens per phosphorus atom) over the Q^3 unit (three bridging oxygens per phosphorus atom) as a function of the acid in the order $SA < TA < CA < BTCA$, suggest the formation of a chain-like structure which contrasts with the high cross-linkage in the Me_2SiO–SnO–P_2O_5 matrix. In addition, this structural change is accompanied by a decrease of the coefficient of thermal expansion and an increase of the water durability of the glasses with the acids containing a large number of carboxylic groups per molecule. The presence of carboxylic groups of the acid acting as network modifier may retard the movement of water molecules through the glasses due to the steric hindrance strengthening the PSP connections in a chain-like structure.

1. Introduction

Phosphate glasses present a considerable interest with the preparation, characterization, processing and manufacturing of new materials having low-softening temperature with interesting optical and thermal properties [1,2]. Low-melting phosphate glasses are desirable for a wide range of application especially as ionic conductors [3], photonic materials [4], hermetic seals [5,6], rare-earth ion solid-state lasers [7,8] and biomaterials [9]. Combining the low-softening temperature with high water durability

represents a tremendous potential for these glasses as good host materials for various organic compounds and their applications as active optical devices [10]. Since Sanford and Tick reported oxyfluoride glasses in the system of PbF_2–SnF_2–SnO–P_2O_5 [11], works on the synthesis and properties of low-melting glasses with similar components such as $SnCl_2$–SnO–P_2O_5 [12] were reported. Phosphate glasses are generally prepared at high temperature ($> 500\,°C$) using the conventional melt-quenching method. The glasses containing Pb showed low glass transition temperatures ranging from 85 to $150\,°C$ and high water durability comparable to that of silicate glasses. The presence of Pb, Cl or F was found to reduce the glass transition temperature. However, the preparation of environmental-friendly materials, free from lead or other

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pollutant materials exhibiting high water durability and low-softening temperature is necessary and constitutes a real challenge. Recently, Niida et al. [13,14] reported the preparation and structure of organic–inorganic hybrid low-melting glasses through a low-temperature process ($\sim$200 °C) using the non-aqueous acid–base reactions as described by the following equations:

$$P-OH + Si-Cl \rightarrow P-O-Si + HCl, \tag{1}$$

$$P-OH + Sn-Cl \rightarrow P-O-Sn + HCl. \tag{2}$$
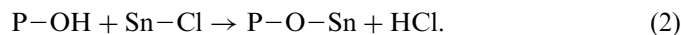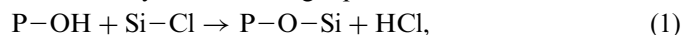
The particularity of the method employed is based on acid–base pair reaction which is driven by the Lewis acidity and/or basicity difference of the reactants. The low-melting glasses consist of –P–O–Si–O–P– network, in which some of the bridging oxygens of a SiO_4 tetrahedron are substituted by organic functional groups, and –P–O–Sn–O–P– network. The presence of terminal organic functional groups lowers the network dimension giving rise to low glass transition temperature. In that context transparent, homogeneous and colorless organically modified tin-silico-phosphate $(3-x)Me_2SiO-(x)SnO-(2)P_2O_5$ glasses $(x = 0-1.5)$ with glass transition temperature ranging from −25 to 50 °C were successfully obtained. However, it is well known that phosphate glasses have poor water durability compared to inorganic silicate ones particularly due to the electronic localization around the phosphorus. Several studies were carried out on different metal oxide phosphate glass systems to try to improve the water durability [15–17]. In our case, the low temperature process to obtain organically modified metal phosphate makes possible the addition of organic species to investigate and improve their durability. In this paper, we focused on the effects of organic acids (salicylic acid (SA), tartaric acid (TA), citric acid (CA) and butane tetracarboxylic acid (BTCA)) which contains, respectively, one to four carboxylic groups, and that are incorporated during the glasses preparation. We think that carboxylic groups could enable the delocalization around the phosphorus and improve the chemical durability of the glasses. Based on ^{29}Si and ^{31}P magic angle spinning (MAS) NMR spectra, thermal analysis (thermomechanical analysis (TMA) and differential scanning calorimetry (DSC)), we also studied the structural effects on the host matrix and the thermal properties of the glasses (softening temperature (T_s), glass transition temperature (T_g) and coefficient of thermal expansion (CTE)). The water durability of the final glasses was measured and compared to the "pure" $Me_2SiO-SnO-P_2O_5$ glass. The relations between the durability, structure and properties of the glasses are discussed owing to the addition of these acids.

2. Experimental procedure

2.1. Samples preparation

Glass samples were prepared from anhydrous (99.9%) orthophosphoric acid H_3PO_4 (Merck, Germany), dimethyl-
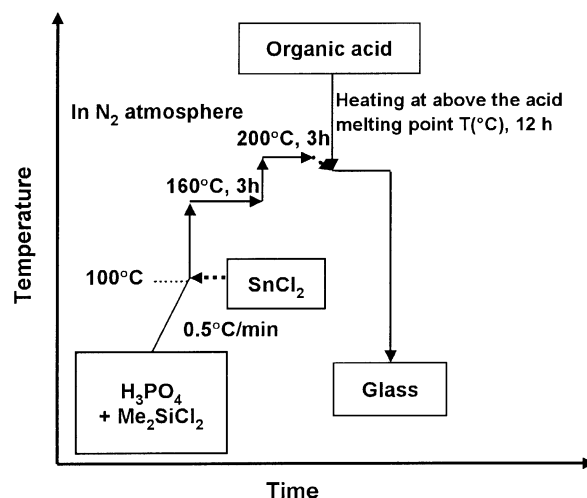

Fig. 1. Experimental process for the preparation of inorganic–organic tin-silico-phosphate hybrid low-melting glasses doped with carboxylic acids. The final step heat-treatment temperature, T, depends on the nature of acid being added (Table 1).

Table 1
Melting point of the carboxylic acid and heating temperature at the final step of the glass preparation after addition of the acid

Carboxylic acid	Melting point (°C)	Heating temperature T (°C)
SA	159	160
TA	170	180
CA	153	157
BTCA	195	200

dichlorosilane Me_2SiCl_2 (ShinEtsu Silicon Chemical, Japan) and tin(II) chloride $SnCl_2$ (Waco Pure Chemical, Japan). The final step of the process consists in the addition of polycarboxylic acids: SA, TA, CA (Nacalai Tesque, Japan) and 1,2,3,4-BTCA (Aldrich, USA). The molar compositions used were $H_3PO_4:Me_2SiCl_2:SnCl_2: R(COOH)_n = 2:2:1:y$ ($y = 0.1$, 0.2 and 0.3). $R(COOH)_n$ designs the carboxylic acids, $R = C_6H_5O$, $n = 1$ for SA; $R = C_2H_4O_2$, $n = 2$ for TA; $R = C_3H_5O$, $n = 3$ for CA; $R = C_4H_4$, $n = 4$ for BTCA. All samples were prepared under inert atmosphere (N_2 gas). The use of pure (anhydrous) orthophosphoric acid is very important. The experimental process is described in Fig. 1. The heat-treatment temperature (Table 1) applied at the end of the process is different from glass to glass as it has to be set just above the melting point and below the decomposition temperature of the acid being used. Yellowish and transparent glasses were obtained.

2.2. Samples characterization

The structure of the glasses doped and non-doped with the organic acids were characterized by ^{29}Si NMR and ^{31}P MAS NMR spectra recorded on an NMR spectrometer (CMX 400, JEOL, Japan) using a 7.5 and 4 mm resonance

probe, respectively. For ^{29}Si MAS NMR, a pulse delay acquisition was used with a pulse delay of 120 s, a spinning frequency of 3000 Hz. The chemical shifts are estimated in ppm and referenced to polydimethylsilane (−34 ppm). For ^{31}P MAS NMR, one pulse sequence was used with a pulse delay of 15 s, a spinning frequency of 12 KHz. The spectra are referenced to phosphoric acid (85% per weight) at 0 ppm. The peaks fittings (using Igor Fitting Program software, Igor Pro, Version 3.1) were made on the basis of the signals observed in ^{29}Si MAS NMR and ^{31}P MAS NMR in order to determine the percentage content of the different units composing the glasses. The signals attributed to the –P–O–Si–OH linkage (named as PS) and the –P–O–Si–O–P– linkage (named as PSP) were determined from ^{29}Si MAS NMR spectra. Q^m units ($m = 0, 1, 2, 3$, with m representing the number of bridging oxygens per phosphorus atom) were determined from ^{31}P MAS NMR. PSP/PS ratio for each glass composition was calculated from the determination of the percentage surface area (the surface area was given by the fitting program software referenced above) of the fitted PSP signal and PS signal using the following relations: $PSP (\%) = (S_{PSP}/(S_{PSP} + S_{PS})) \times 100$ and $PS (\%) = (S_{PS}/(S_{PSP} + S_{PS})) \times 100$, where S_{PSP} and S_{PS} are the surface area of the Gaussian peaks attributed to PSP and PS, respectively. PSP/PS ratio = PSP (%)/PS (%). The determination of the Q^2/Q^3 was carried out in the same manner from $Q^2 (\%)$ and $Q^3 (\%)$ with $Q^2 (\%) = (S_{Q^2}/\sum_{m=0,1,2,3} S_{Q^m}) \times 100$ and $Q^3 (\%) = (S_{Q^3}/\sum_{m=0,1,2,3} S_{Q^m}) \times 100$, where S_Q^m are the surface area of the Gaussian peaks attributed to the Q^m units.

The softening temperature and CTE of the glasses were measured using a thermomechanical analyzer (TMA 8310, Rigaku Co. Ltd., Japan) which could enable the measurements from −50 °C. The TMA curves were recorded from −50 °C under 1 g loaded condition at a heating rate of 10 K min^{-1}. The glass transition temperature was measured by a differential scanning calorimeter (diamond DSC, Perkin-Elmer, USA) with a heating rate of 10 °C min^{-1}. Infrared absorption spectra were recorded by KBr pellets method (sample: KBr = 1:100 in weight) using an FT-IR spectrometer (AVATAR 360, Thermo Nicolet, USA). The water durability was estimated from the weight gain of the glass due to the hydrolysis of –P–O–Si– linkage. The glass samples prepared in glass beakers (Pyrex) of 1.25×10^{-3} m^2 surface area were placed in a chamber with saturated water vapor atmosphere at 25 °C. The weight gain per unit area is expressed in (g m^{-2}): $w = m/\pi r^2$, where m is the weight gain of the sample divided per the surface area of the glass. The change of the sample weight was measured at different time intervals.

3. Results and discussion

3.1. Structure of the glasses

The structure of Me$_2$SiO–SnO–P$_2$O$_5$ (Me designs the methyl organic group) low-melting glasses (Fig. 2(a)) has been established from ab initio calculations from ^{29}Si and ^{31}P MAS NMR spectra [13]. Two types of connections are discernable around Si and are ascribed as PS and PSP models (Fig. 2(b)). One consisting in –P–O–Si–OH linkage (PS) is characterized by a terminal silanol group and the other –P–O–Si–O–P– linkage (PSP) results in the polycondensation during the reaction. The PS connections for the whole glasses (doped and non-doped with the acids) present a signal at −2.9 to −3.1 ppm, while PSP connections present a signal at −9.9 to −10.1 ppm observed in the ^{29}Si NMR spectra shown in Fig. 3. The structure of the
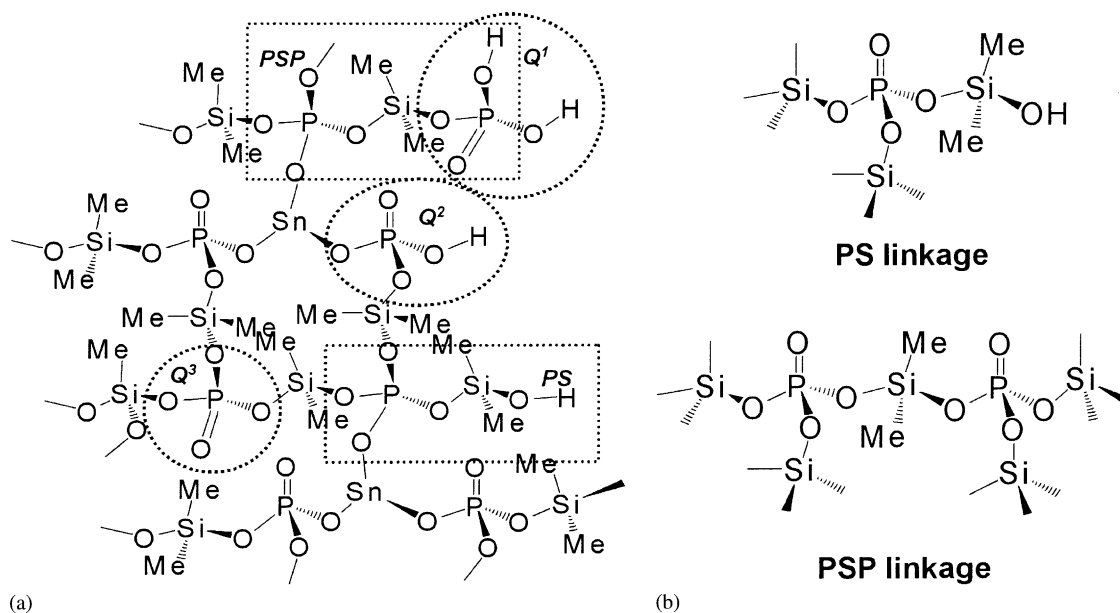

Fig. 2. (a) Model of the structure for the Me$_2$SiO–SnO–P$_2$O$_5$ glass determined from ab initio calculations [13] and (b) PS and PSP linkages models resulting from the polycondensation.

Fig. 3. ^{29}Si MAS NMR spectra for (a) the non-doped glass ($y = 0$) and the doped glass with citric acid (CA) (b) $y = 0.1$, (c) $y = 0.2$ and (d) $y = 0.3$ as a function of the acid content, y.
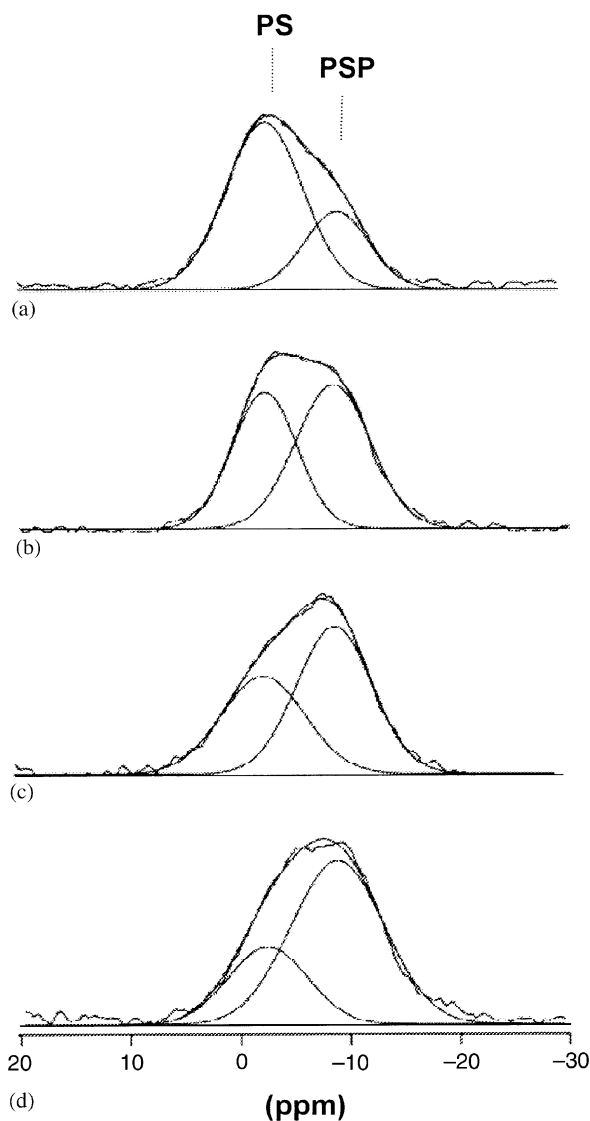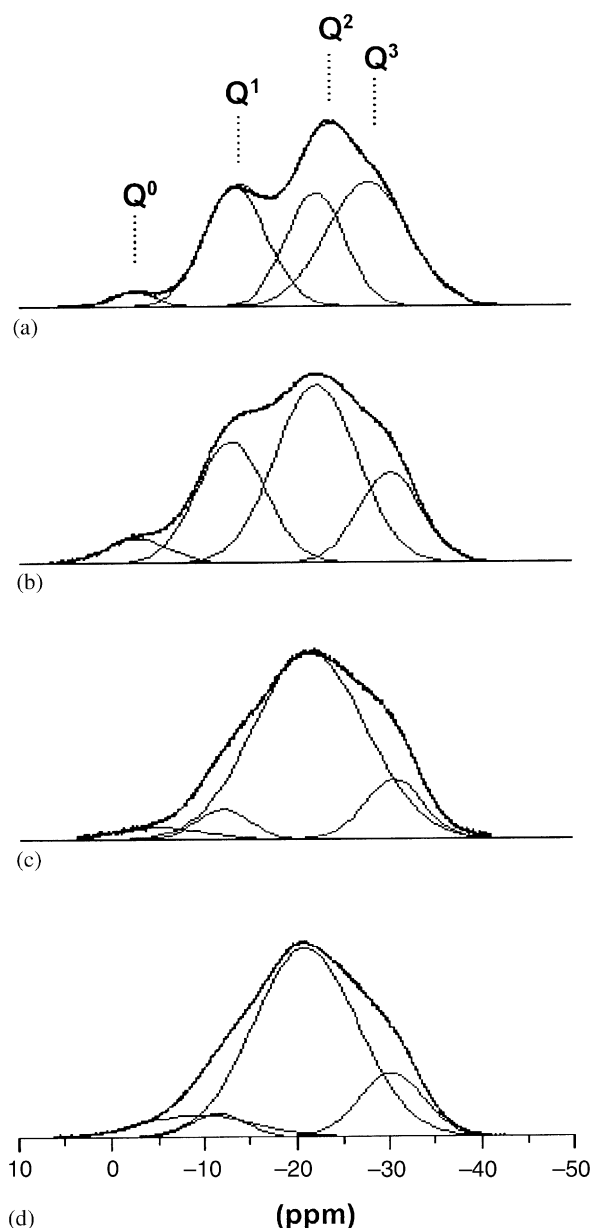

Fig. 4. ^{31}P MAS NMR spectra for (a) the non-doped glass ($y = 0$) and the doped glass with citric acid (CA) (b) $y = 0.1$, (c) $y = 0.2$ and (d) $y = 0.3$ as a function of the acid content, y.

glasses matrix is also characterized around the phosphorus by the presence of Q^1 (two terminals –OH groups and one bridging oxygen), Q^2 (one –OH terminal group and two bridging oxygens) and Q^3 (three bridging oxygens) units determined from the ^{31}P NMR signals at the respective chemical shifts: -13.1 to -14.1, -22.8 to -23.5, and -28.7 to -29.1 ppm (Fig. 4). A signal at -1.8 to -2 ppm is attributed to the Q^0 unit corresponding to orthophosphate groups. Although the chemical shifts showed slight difference from sample to sample, the major difference between Me$_2$SiO–SnO–P$_2$O$_5$ glasses doped with carboxylic acids and the non-doped ones concerns with the change in the degree of polycondensation and the degree of cross-linkage when the acid was added. Fig. 3 shows the ^{29}Si NMR spectra of the non-doped and CA-doped glasses as a function of the CA content y ($y = 0, 0.1, 0.2$ and 0.3). The spectra of the acid-doped glasses (Fig. 3(b,c,d)) show

clearly a structural change compared to the non-doped tin-silico-phosphate glass ($y = 0$, Fig. 3(a)). Indeed, an increase of the polycondensation was observed as a function of the addition of the acid and the concentration of the acid added. This enhancement of the polycondensation by addition of organic acids to form a PSP linkage is also confirmed when SA, TA and BTCA were added (Fig. 5). The degree of polycondensation was characterized by the PSP/PS ratio. The PS and PSP contents in the structure were determined from the percentage surface area of the Gaussian peaks (see Section 2.1). For comparative study of the properties between doped and non-doped glasses, the same heat treatment has been applied to the non-doped glasses owing to the difference in the heat
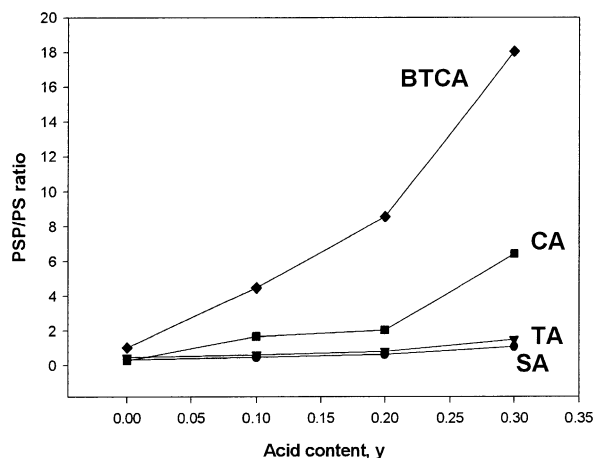
Fig. 5. PSP/PS ratio characterizing the degree of polycondensation of the glass network as a function of the different polycarboxylic acids content y. $y = 0$ for the non-doped glasses (for which the variation depends only on the final heat-treatment temperature at the final step of the experimental process), and $y = 0.1$, 0.2 and 0.3 for the acid-doped glasses (SA, TA, CA and BTCA) for which the degree of polycondensation is enhanced by the amount the acid added.

treatment applied at the end of the experimental process for the doped glasses with the respective carboxylic acids. This difference in heat treatment at this end of the experimental process was necessary taking in account the different decomposition temperature of each acid. The graph in Fig. 5 shows that a slight increase of PSP connection is observable for the pure organically modified tin-silico-phosphate glasses ($y = 0$) and the polycondensation increase is due to the heat treatment (Table 1). However, the addition of a large amount of acid enhances highly the polycondensation, the degree of which depends on the nature of carboxylic acids, especially the number of carboxylic groups, n. The PSP connections increase in the order of $SA(n = 1) < TA(n = 2) < CA(n = 3) < BTCA(n = 4)$. It is worth noting that the incorporation of 1,2,3,4-BTCA increases the PSP connections from 51% (when no acid was added, but only a heat treatment at 200 °C for 12 h was applied) to 94% (Table 2). A drastically change is also observable in the cross-linkage. Indeed, Fig. 4 shows the ^{31}P MAS NMR spectra as a function of the CA content (y) in the $Me_2SiO–SnO–P_2O_5$ glass to illustrate the variation of Q^1, Q^2 and Q^3 unit content present in the glass when we add the acid. While Q^1 decreases, we observe from the Gaussian fit, that Q^2 increases and Q^3 decreases. This behavior is observed for the whole doped glasses and is characterized in Fig. 6 showing the variation of Q^2/Q^3 ratio as a function of the carboxylic acids and their content in the glasses. The effect is also found to be strengthened by the number of carboxylic groups of the acid used. In fact, compared to the value of the non-doped glass, Q^2/Q^3 shows a higher increase when we add BTCA (increase of 3.69) than when we add SA in the glass (increase of 0.52). Taking in account the formation of PSP together with the increase of Q^2 unit,

Table 2
PS% and PSP% content in the glass as a function of the acid content, y, and the heating temperature applied at the final step of the glass preparation process

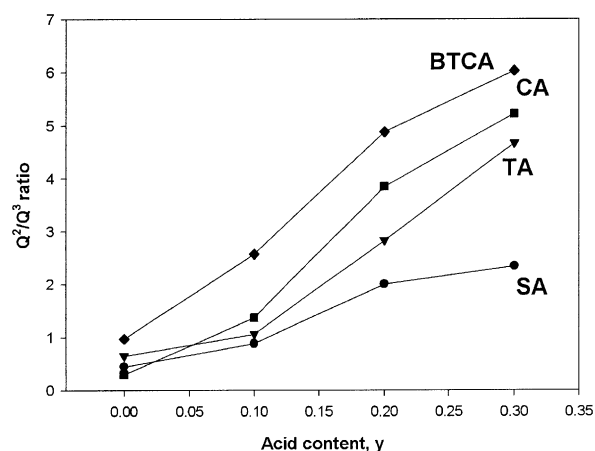| Glasses obtained with final heat-treatment temperature	Heat-treatment temperature (°C)	PS (%)	PSP (%)
Non-doped glasses ($y = 0$)	160	73.21	26.77
	180	67.46	32.54
	157	77.26	22.74
	200	48.92	51.07
SA-doped glasses	160		
$y = 0.1$		67.82	32.18
$y = 0.2$		60.95	39.05
$y = 0.3$		47.78	52.22
TA-doped glasses	180		
$y = 0.1$		61.45	38.55
$y = 0.2$		54.88	45.12
$y = 0.3$		40	60
CA-doped glasses	157		
$y = 0.1$		37.48	62.52
$y = 0.2$		32.88	67.12
$y = 0.3$		13.42	86.58
BTCA-doped glasses	200		
$y = 0.1$		18.27	81.73
$y = 0.2$		10.47	89.54
$y = 0.3$		5.25	94.75

Fig. 6. Graph showing the diminution of the cross-linkage with the Q^2/Q^3 ratio increasing as a function of the acid carboxylic added and its content y.

we can say that the incorporation of polycarboxylic acids modify sensibly the tin-silico-phosphate glass network and lead to the formation of chain-like structure. We can imagine the structure (Fig. 7) in which the acid, due to consequent number of carboxylic groups per molecule, occupy the vacant space within the rearranged glass structure and contribute to stabilize the inorganic network in the following order: $SA < TA < CA < BTCA$. The network dimension of phosphate glasses is generally determined by the [O]/[P] ratio for most of the phosphate glasses
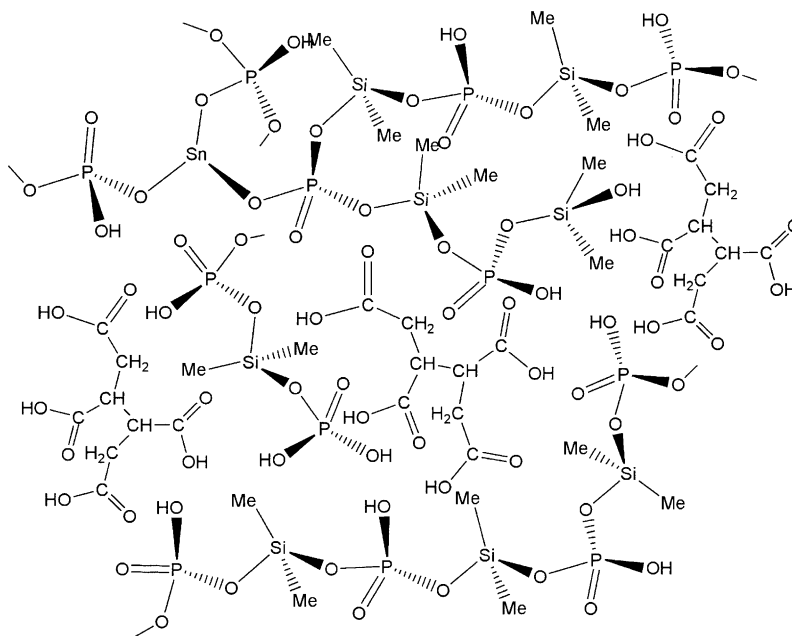
Fig. 7. Representation of the possible structure formed with the enhancement of the polycondensation and the chain-like structure formation after addition of acid (butane tetracarboxylic acid is shown as an example in the figure).

prepared by melt-quenching method at high temperature using metal oxides and/or metal halides, and P_2O_5 (generally generated from $NH_4H_2PO_4$) as precursors [1,12]. The particularity of the method we employed is based on acid–base pair reaction which is driven by the Lewis acidity and/or basicity difference of the reactants (Me_2SiCl_2 is considered to act as a Lewis acid while H_3PO_4 (although is acid), acts as a Lewis base). One possible reason that could explain the preferential formation of Q^2 rather than Q^3 is based on the acid–base reaction of the H_3PO_4–Me_2SiCl_2 pair considering the proton dissociation constants (K_a) of orthophosphoric acid in water: $pK_1 = 2.15$, $pK_2 = 7.1$, $pK_3 = 12.4$ ($pK_a = -\text{Log} K_a$). The large pK_a of the third proton indicates that it tends to be hardly dissociated. The acidic condition that is imposed by incorporation of polycarboxylic acids during the glass network formation makes more difficult the reaction of –PO–H to form the Q^3 unit compared to that in the pure Me_2SiO–SnO–P_2O_5 glass. The acid incorporation inhibits the formation of Q^3 and we observe consequently a predominant presence of Q^2 in the glass network and a decrease of Q^3 in the acid-doped glasses compared to the non-doped one. However, it was difficult to measure and compare the different pH when the respective acids were added due to the high viscosity of the reaction mixture and the high temperature process, but it is clear that Q^2/Q^3 ratio increase of the doped glasses was found associated with to the increasing number of the carboxylic groups of the respective acid being incorporated ($SA(n = 1) < TA(n = 2) < CA(n = 3) < BTCA(n = 4)$).

FTIR spectra (Fig. 8), for the non-doped ($y = 0$) and doped glasses with CA ($y = 0.1$, 0.2 and 0.3)), show that the acid is just embedded in the glass. Absorption band at $1715 \, \text{cm}^{-1}$ is attributed to the free carbonyl (C=O) of the carboxylic groups. The oxygen of the carbonyl is not coordinated to the metals as no related peak occurs at $1595 \, \text{cm}^{-1}$. From ^{29}Si NMR, no Si–C=O bonds are evidenced suggesting that no reaction occurred between Me_2SiCl_2 and the carboxylic acids during the reaction. These results confirm that the change in the network may then arise from interactions between the polycarboxylic groups incorporated and the forming hybrid glass network. The measured FTIR spectra normalized with respect to the amount of H_3PO_4 are characterized by the main typical absorption bands found for the Me_2SiO–SnO–P_2O_5 glass system. The absorption bands in the 1260–$1270 \, \text{cm}^{-1}$ range are due to CH_3 symmetric deformation mode and an absorption band at 800–$840 \, \text{cm}^{-1}$ is due to methyl rocking and Si–C stretching vibrations. The absorption band near $1100 \, \text{cm}^{-1}$ is attributed to P–O stretching vibration in P–O–Si linkages, whereas an absorption band near $1023 \, \text{cm}^{-1}$ is assigned to Si–O stretching vibration in P–O–Si linkages. An absorption band near $1090 \, \text{cm}^{-1}$ is due to P–O stretching vibration in Sn–O–P linkage.

3.2. Thermal properties of the glasses

Thermal analysis (TMA and DSC) showed an increase of the glass transition temperature (T_g) and the glass softening temperature (T_s) of the glasses as a function of the polycarboxylic acids content (Figs. 9(a) and (b), respectively). The variation of T_g and T_s for $y = 0$, as for the previous characterizations, is due to the different heating temperature applied at the final step of the experimental process for the doped-glass preparation (temperature that is different from acid to acid). We
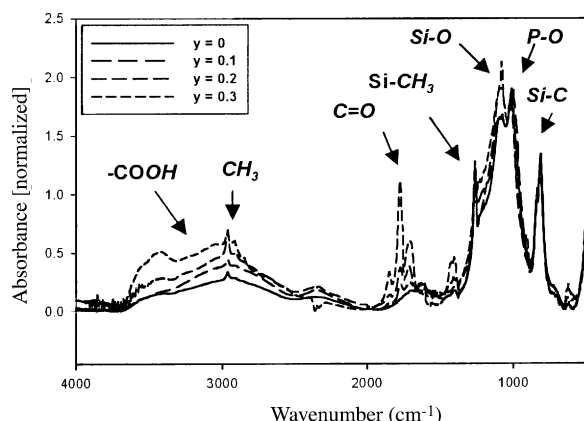
Fig. 8. Infrared spectra for the non-doped glass ($y = 0$) and the glasses doped with citric acid ($y = 0.1, 0.2$ and 0.3).
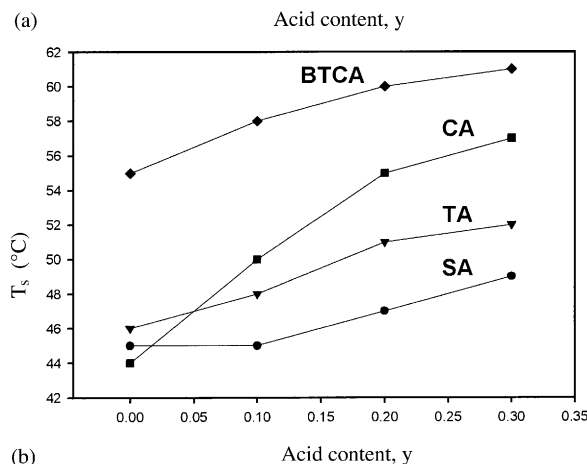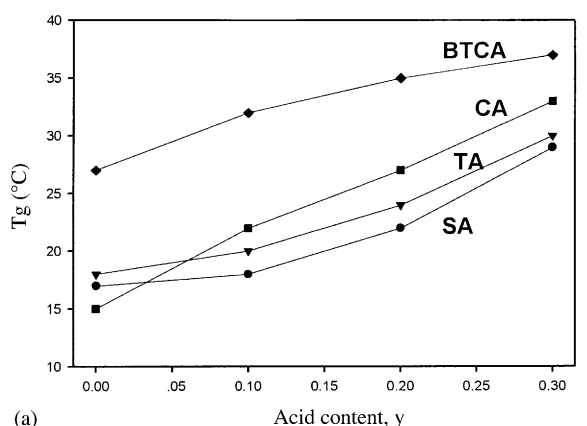

Fig. 9. (a) Variation of the glass transition temperature (T_g) and (b) variation of the glass softening temperature (T_s) as a function of the acid content y. $y = 0$, for the non-doped glass and $y = 0.1, 0.2$ and 0.3 for the acid-doped glasses. The variation of T_g and T_s for $y = 0$ is only due to the different final heat-treatment temperatures applied at the final step of the experimental process for the preparation of the respective acid-doped glasses.

applied then the same heat-treatment temperature for the non-doped glass as for the respective acid-doped ones to check the effect of the acid on T_g and T_s. The increase of T_g and T_s is then due to the enhanced polycondensation and the strengthening –P–O–Si– bonds of the glass matrix with

addition of the acid content again in the order SA < TA < CA < BTCA. However, the glass transition temperature comprised between 17 and 37 °C as well as the glass softening temperatures comprised between 44 and 61 °C remains low. The values for the glass transition and softening temperatures are lower than in oxyfluoride low-melting glasses such as PbO–SnF$_2$–SnO–P$_2$O$_5$ with T_g about 137–140 °C and T_s about 150–160 °C, respectively. In such system, the glass transition and softening temperature are reduced with the presence of the fluorine and tin content [18]. The organically modified tin-silico-phosphate glasses doped with polycarboxylic acids preserve thus the low-softening temperature of the glasses without addition of non-environmental-friendly elements such as F or Pb.

The CTE determined in the temperature range comprised between $-50\,°C-T_g$ and T_g-T_s for the whole glasses was found to be in the range of $\sim 10^{-5}$–$10^{-6}\,K^{-1}$. A significant decrease of the CTE of almost one order (from $\sim 10^{-5}$ (without acid) to $\sim 10^{-6}\,K^{-1}$ (with acid)) was observed in the case of the glass incorporated with CA. In the range $-50\,°C-T_g$, the CTE decrease from $2.85 \times 10^{-5}\,K^{-1}$ ($y = 0$, $T_g = 15\,°C$) to $2.78 \times 10^{-6}\,K^{-1}$ ($y = 0.1$, $T_g = 22\,°C$), $3.05 \times 10^{-6}\,K^{-1}$ ($y = 0.2$, $T_g = 27\,°C$), $6.32 \times 10^{-6}\,K^{-1}$ ($y = 0.3$, $T_g = 33\,°C$). The CTE value of $2.85 \times 10^{-5}\,K^{-1}$ for the non-doped hybrid glass is comparable to that for PbO–SnF$_2$–SnO–P$_2$O$_5$ ($2.87 \times 10^{-5}\,K^{-1}$) with PbO = 0.99 mol%, SnF$_2$ = 49.50 mol%, SnO = 9.90 mol% and P$_2$O$_5$ = 36.60 mol% [18]. It was found that the increase of Pb content according to the molar composition of the glass with PbO = 16.67 mol%, SnF$_2$ = 41.67 mol%, SnO = 8.33 mol% and P$_2$O$_5$ = 33.33 mol% decreases slightly the CTE to $2.20 \times 10^{-5}\,K^{-1}$. However, the effect of CA incorporation on the decrease of the CTE of about one order (10^{-5}–$10^{-6}\,K^{-1}$) is new. It is not known yet if this decrease is the related to the structure change in the glass matrix; however, we think that further study on the rheology of the glasses may be helpful. These results constitute an important property of the glasses as we can possibly decrease the CTE by incorporating organic molecules in hybrid glasses. The low CTE for phosphate represents also an important potential for sealing applications [5,6].

3.3. Water durability of the glasses

The water durability is characterized by the hydrolysis rate when the glasses are exposed in humid atmosphere. The following equation illustrates the collapse of the inorganic network when the glass is exposed for several hours:
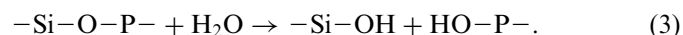
$$-Si-O-P- + H_2O \rightarrow -Si-OH + HO-P-. \qquad (3)$$

The water durability was estimated from the weight gain of the glass due to the hydrolysis of P–O–Si bonds. The change of the sample weight was measured at different time intervals (Fig. 10). We observed that the water durability increased with the addition of a small amount of acid ($y=0.1$) in
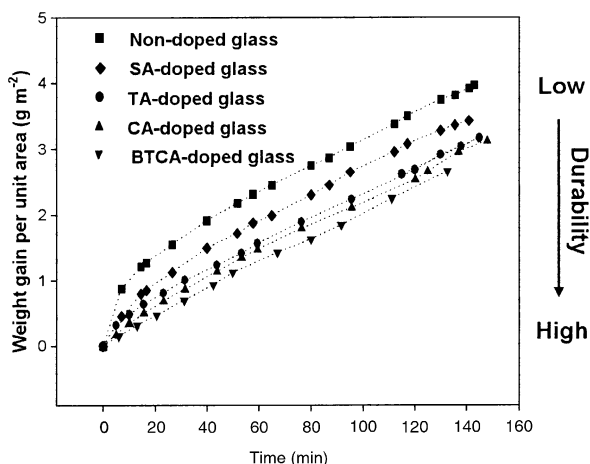
Fig. 10. Chemical durability of the glasses (non-doped, $y = 0$ and acid doped for $y = 0.1$) determined from the samples weight gain due to the hydrolysis of the P–O–Si bonds when the glass samples were placed in a saturated water vapor chamber at 25 °C.

the order $SA(n=1) < TA(n=2) < CA(n=3) < BTCA(n=4)$. The low polycondensation and the electronic localization around the phosphorus contribute to the low chemical durability of the phosphate glasses. The presence of polycarboxylic groups modifies the structure of tin-silico-phosphate host matrix with the formation of chain-like structure and the polycondensation effect with a large content of PSP connections may strongly affect the durability of the doped glasses. The acids which occupy the vacant space in that chain-like structure tend to stabilize the organic–inorganic hybrid structure and strengthen the O–Si–O–P bonds (Fig. 7). O–Si–O–P bonds are generally weak and sensitive to hydrolysis. In addition, the water durability seems to be associated to the number of carboxylic groups n per molecule. After the addition of the polycarboxylic acid, the steric hindrance due to the number of carboxylic groups could also retard the movement of the water molecules and simultaneously enhance the polycondensation reaction to form the PSP connections. One another reason may be the possible interactions between the carboxylic groups and phosphate groups in a short-range distance to each other. Strong hydrogen bondings could favor the increase of the water durability and influence the electronic delocalization around the phosphorus. Ab initio calculations are under way for the determination of any possible interactions, which will be helpful to the optimization of the model structure.

4. Conclusions

We incorporated different carboxylic acids during the preparation of tin-silico-phosphate low-melting glass system $Me_2SiO–SnO–P_2O_5$ to improve the chemical durability of the glass. The glasses were characterized by a series of techniques that show several interesting properties that are related to the improvement of the chemical durability when carboxylic acids were added. ^{29}Si and ^{31}P MAS NMR showed that the acids embedded in the glass acts as network modifiers with an increasing polycondensation effect and a diminution of the cross-linkage to form a chain-like structure. The effects are enhanced with increasing number of carboxylic groups per molecule. The durability increasing in the order of $SA < TA < CA < BTCA$ suggests that the carboxylic groups may retard the movement of water molecules through the glasses due to the steric hindrance and simultaneously enhance the polycondensation reaction to form the PSP connections. The thermal analysis showed also an important decrease of the CTE ($\sim 10^{-6} K^{-1}$). This thermal behavior is the object of further investigation. The possible improvement of the chemical durability and the decrease of the CTE by incorporating organic species in organic–inorganic hybrid glasses were only possible due to the low-melting temperature properties of the materials. Thus, these results represent tremendous potential particularly for sealing applications to a wide range of materials such as liquid crystal display.

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