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Structure and properties of x SnO–(100 – x) P$_2$O$_5$ glasses

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Abstract

x SnO–(100 – x) P$_2$O$_5$ glasses ($0.30 \leq x \leq 0.75$) were prepared under argon atmosphere. The Sn^{2+}/Sn$_{total}$ ratio, determined by wet chemical analysis, varies from 90 to 99% depending on glass composition. Glass transition temperatures are very low, and no effect of Sn^{4+} could be detected. Glass structure was characterised with ^{31}P and ^{119}Sn NMR. There is no evidence for a specific Q^n site bonded to Sn^{4+}, but taking into account the amount of Sn^{4+} enabled to obtain Q^n distribution close to calculated values for binary site distribution. ^{119}Sn NMR spectra were recorded in static conditions. Chemical shift anisotropy (CSA) of glasses were compared to crystalline reference compounds. Tin(II) local environment in glasses is close to a trigonal pyramid, and Sn^{4+} NMR parameters are in accordance with a local environment similar to SnP$_2$O$_7$. ***To cite this article: É. Bekaert et al., C. R. Chimie 7 (2004).***

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Résumé

Des verres x SnO–(100 – x) P$_2$O$_5$ ($0,30 \leq x \leq 0.75$) ont été préparés sous atmosphère d'argon. Le rapport Sn^{2+}/Sn$_{total}$, mesuré par analyse chimique en solution, varie de 90 à 99%, en fonction de la composition du verre. Les températures de transition vitreuse sont très basses, et aucun effet de Sn^{4+} n'a pu être détecté. La structure des verres a été caractérisée par RMN du ^{31}P et ^{119}Sn. Il n'y a pas d'évidence pour qu'un site Q^n soit spécifiquement lié à Sn^{4+}, mais la prise en compte de la quantité de Sn^{4+} a permis d'obtenir une distribution de sites Q^n proche des valeurs calculées pour une distribution binaire. L'anisotropie de déplacement chimique des verres a été comparée à celle de références cristallisées. L'environnement local de Sn(II) dans les verres est proche d'une pyramide trigonale, et les paramètres RMN de Sn^{4+} sont en accord avec un environnement local similaire à SnP$_2$O$_7$. ***Pour citer cet article : É. Bekaert et al., C. R. Chimie 7 (2004).***

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1. Introduction

During fly ash vitrification processes, heavy metals volatilise and are recovered into chlorinate salts, called secondary ashes [1]. The secondary ashes contain large amounts of chlorinated salts rich in highly soluble and volatile heavy metal chlorides, like lead and cadmium chloride. This is why the treatment of these toxic compounds must involve, in a first step, the conversion of the heavy metals into a thermally stable form [2]. Several processes have been proposed for this conversion. One involves dissolving chlorides in water followed by a precipitate of hydroxides in alkaline medium. The drawback is the handling of brine and energetic cost for eliminating water [3]. Ikeda et al. [4] have studied the thermal conversion reactions of metal chlorides into oxides with boric acid to develop a method for vitrification of radioactive molten salt wastes. But the melting occurred at 1100 °C and volatilisation still occurred at this temperature. We proposed an alternative way using a solid-state conversion of chlorides into phosphates, using ammonium hydrogenphosphate [2]. The reaction leads to the recovery of chlorides as ammonium chloride which sublimates around 300 °C [4], and heavy metals are transformed into non-volatile phosphates that can be vitrified at 900 °C. Tin chlorides are difficult to convert because they are much more volatile than lead and cadmium. Furthermore, Sn^{2+} can oxidise into Sn^{4+}, which has a low solubility in glasses. It has been reported [5] that stannous chloride ($SnCl_2$) reacts with ammonium dihydrogenphosphates to form glasses in the SnO–$SnCl_2$–P_2O_5 system. The conversion of tin chlorides into phosphate using an ammonium phosphate process is efficient [6]. Tin is known to decrease glass transition temperatures of phosphate glasses [7]. However, very little is known about the structure of tin phosphate glasses. Holland et al. reported a NMR study of x SnO–$(100 - x)$ P_2O_5 glasses [8], but did not considered the presence of Sn(IV), since its quantity was expected to be low. Contrary to Holland et al. [8], we paid a special attention to the effect of the redox ratio $R = Sn^{2+}/Sn_{total}$, on the structure and properties of tin phosphate glasses, because oxidation of Sn^{2+} into Sn^{4+} is expected during vitrification of fly ashes. In order to investigate this effect on the structure of phosphate glasses, a series of x SnO–$(100 - x)$ P_2O_5 glasses was synthesised and characterised with ^{31}P and ^{119}Sn NMR.

2. Experimental procedures

x SnO–$(100 - x)$ P_2O_5 glasses were prepared from batches of reagent-grade SnO (Aldrich) and $(NH_4)_2HPO_4$ (Fisher). Each batch was calcined in an alumina crucible at 200 °C to drive off NH_3 and H_2O and was then melted in a carbon crucible at 1000 °C for 2 h under argon.

The glasses were analysed by inductively coupled plasma atomic emission spectrometer (ICP–AES). The $[Sn^{2+}]$ concentration was analysed by polarography. The redox R is then calculated as $R = Sn^{2+}/Sn_{total}$. The redox was also checked with tin Mössbauer on some glass compositions, and found in good agreement with solution measurements.

The glass transition temperature (T_g) was determined using a differential scanning calorimeter. The samples were heated at 5 K min^{-1} up to 450 °C. The reported T_g values are reproducible within ±5 K.

The ^{31}P MAS-NMR spectra were recorded on a Bruker ASX100 spectrometer operating at 2.34 T, with a 1.5-µs pulse (45°), and a 60-s delay between each accumulation to enable full relaxation. A 7-mm MAS probe was used. The MAS–NMR spectra were decomposed with the DM-FIT software [9]. Gaussian lines were used since ^{31}P resonances in glasses are dominated by chemical shift distribution. However, a small Lorentzian contribution (ca 5%) was used to optimise the fits. ^{31}P NMR chemical shifts are referenced to an 85% H_3PO_4 solution.

The ^{119}Sn NMR spectra were recorded at 9.4 T on a Bruker AV-400 spectrometer (Larmor frequency 149.1 MHz), with a 2-µs pulse (45°) and a 60-s delay between each accumulation. A 4-mm MAS probe was used, but the spectra were recorded in static condition, since the large CSA of tin, due to its large electronic shielding, cannot be removed by MAS. ^{119}Sn NMR chemical shifts are referenced to liquid $Sn(CH_3)_4$ (TMT).

3. Results and discussion

Table 1 reports the batch and analysed compositions of x SnO–$(100 - x)$ P_2O_5 glasses. The analysed compositions are very close to the batch ones, meaning that only few losses occurred during melting (excepted for the composition $x = 42$). In the following text, x always

Table 1
Chemical and redox compositions of x SnO–$(100 - x)$ P$_2$O$_5$ glasses

SnO batch (%mol)	P$_2$O$_5$ batch (%mol)	SnO$_{tot}$ = SnO+SnO$_2$ (%mol) ± 2	P$_2$O$_5$ analysed (%mol) ± 2	Redox Sn^{2+}/Sn$_{tot}$
75	25	74	26	0.99
72.5	27.5	73	27	0.98
70	30	71	29	0.99
68	32	69	31	0.97
65	35	64	36	0.98
60	40	60	40	0.95
55	45	57	43	0.95
50	50	49	51	0.93
45	55	46	54	0.94
30	70	42	58	0.9

refers to the analysed compositions and to the total Sn content (x = SnO + SnO$_2$). Table 1 also reports Sn^{2+}/Sn$_{total}$ ratios. Owing to the melting under neutral argon atmosphere, the amount of Sn^{4+} is always low. It decreases from 10% for low x values to 1% for the highest Sn content. The solubility of Sn^{4+} is known to be very low in glasses [10], but no opacity was detected in the glasses for these Sn^{4+} contents.

Fig. 1 shows the glass-transition temperatures of x SnO–$(100 - x)$ P$_2$O$_5$ glasses. Increasing x does not influence T_g before 60 mol% SnO, and only a small increase in T_g is observed above 60 mol% SnO. This is in accordance with the previously reported effect of SnO on phosphate glass properties [5]. Indeed, tin phosphate glasses are known to exhibit very low T_g values and the reticulating effect on the depolymerised phosphate network is found to be low. This effect is more evident when compared with x ZnO–$(100 - x)$ P$_2$O$_5$ and x PbO–$(100 - x)$ P$_2$O$_5$ glasses (Fig. 1): for
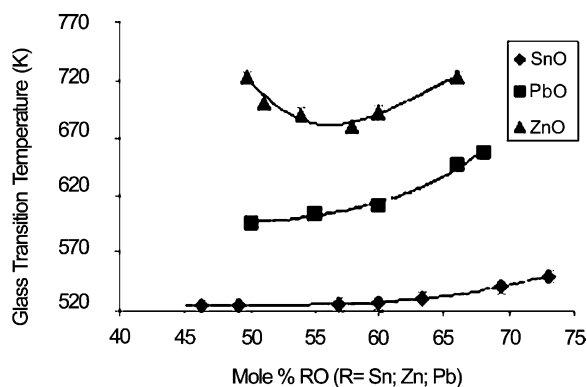

Fig. 1. Glass-transition temperatures of RO-phosphate glasses (incertitude is within the size of symbols).
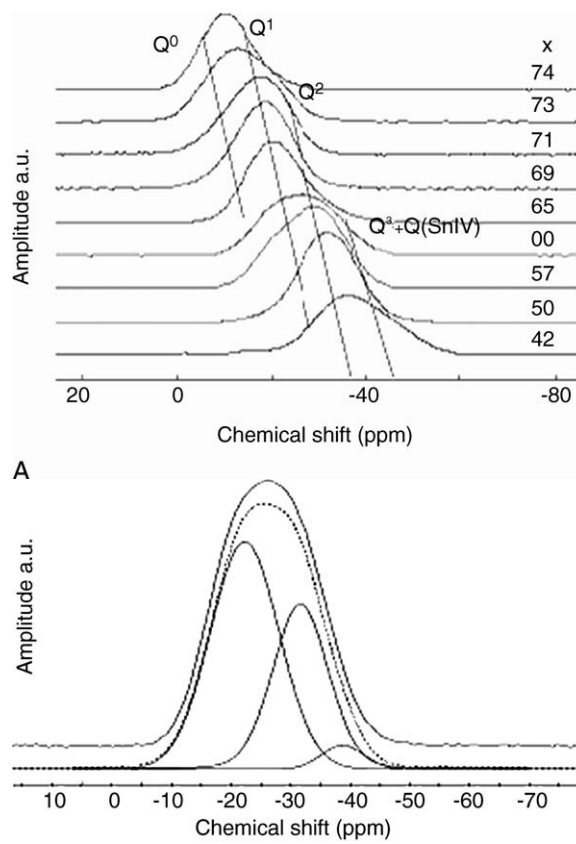

Fig. 2. (**A**) ^{31}P MAS NMR spectra of x SnO–$(100 - x)$ P$_2$O$_5$. (**B**) Typical fit of ^{31}P MAS NMR spectrum of 60 SnO–40 P$_2$O$_5$ glass. Continuous line: experimental spectrum, dotted line: calculated spectrum.

both glass systems, T_g values are much larger (up to 200 K for x ZnO–$(100 - x)$ P$_2$O$_5$. Surprisingly, no effect of Sn^{4+} is visible on T_g, whereas even small amounts of tetravalent ion like Ti^{4+} have a large influence of T_g [11].

The ^{31}P MAS-NMR spectra of x SnO–$(100 - x)$ P$_2$O$_5$ glasses are shown in Fig. 2. Broad resonances are observed, in accordance with the chemical shift distribution expected for glasses. However, several resonances, attributed to different Q^n sites (n = 3, 2, 1, 0), can be distinguished. The Q^n assignment, shown in Fig. 2, is obtained by comparison with spectra of similar glass systems: x ZnO–$(100 - x)$ P$_2$O$_5$ [12], x CaO–$(100 - x)$ P$_2$O$_5$ [13], and x PbO–$(100 - x)$ P$_2$O$_5$ [14]. Q^3 sites are located at –43 ppm. Q^2 and Q^1 sites resonate between –30 and –38 ppm and between –20 and –22 ppm, respectively. The observed shifts with glass

composition are attributed to a modification of the bond angle and distance distributions with SnO content in glasses [15]. Indeed, the average chain length decreases when the amount of SnO increases, which influences the bond characteristics. We notice that no specific line can be attributed to Q^n sites bonded to Sn^{4+}. Due to the higher electrostatic field strength of Sn^{4+} compared to Sn^{2+} ($z/a^2 = 96$ and 38 nm^{-2}, respectively), Q^n sites bonded to Sn^{4+} are expected to resonate at higher field than those bonded to Sn^{2+} [11]. This absence of specific resonance may be due either to the small amount of Sn^{4+} (signal not detectable), or to an averaged bonding of Q^n sites to both Sn^{2+} and Sn^{4+} (meaning no specific Q^n site for each tin valence). This point will be discussed below.

The relative amount of Q^n sites can be measured by spectral decomposition with Gaussian lines, representative of chemical shift distribution encountered on glass spectra. In a first attempt for quantifying Q^n sites, we neglected the contribution of Sn^{4+}, since its effect is not visible on ^{31}P NMR spectra. The fraction of Q^n sites was calculated with the assumption of a binary Q^n distribution, as generally reported in binary phosphate glasses [11–13].

If only Sn^{2+} is taken into account, the fractions f of the Q^n species for ultraphosphate glasses ($x < 0.50$) is:

$$fQ^2 = \frac{x}{1-x}$$

$$fQ^3 = \frac{(1-2x)}{1-x}$$

The fraction f of the Q^n sites for polyphosphate glasses $0.50 \leq x \leq 0.67$:

$$fQ^1 = \frac{(2x-1)}{1-x}$$

$$fQ^2 = \frac{2-3x}{1-x}$$

For glasses with $0.67 \leq x \leq 0.75$:

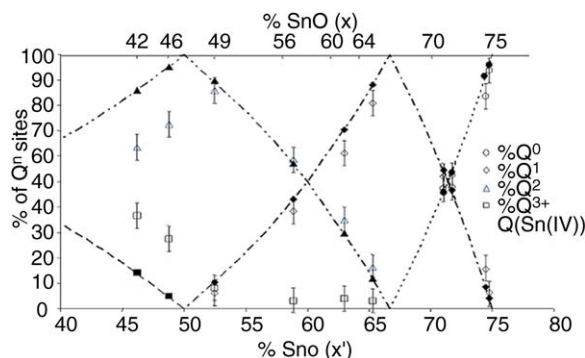$$fQ^0 = \frac{3x-2}{1-x}$$

$$fQ^1 = \frac{(3-4x)}{(1-x)}$$

Fig. 3. Q^n fractions of x SnO–$(100 - x)$ P$_2$O$_5$ glasses versus x (top scale), or versus $x' = $ SnO $+ 2 \times$ SnO$_2$ (bottom scale). Dotted lines: calculated values. Open symbols: experimental values obtained from fitting of NMR spectra, without contribution of Sn^{4+}. Closed symbols: experimental values obtained from fitting NMR spectra with contribution of Q^n sites bonded to $Sn^{4+}(Q(Sn(IV))$.

If $R = Sn^{2+}/Sn_{total}$ is taken into account, the total Q^n_{Sn} species for ultraphosphate glasses ($x < 0.50$) is:

$$Q^n_{Sn} = fQ^3(Sn^{4+}) + fQ^3(Sn^{2+}) + fQ^2(Sn^{4+}) + fQ^2(Sn^{2+})$$

The fraction (f) of the Q^3 sites for ultraphosphate glasses:

$$Q^3_{Sn} = fQ^3(Sn^{4+}) + fQ^3(Sn^{2+})$$

$$fQ^3(Sn^{4+}) = \frac{(1-2(1-R))}{1-(1-R)}$$

$$fQ^3(Sn^{2+}) = \frac{(1-2R)}{1-R}$$

The calculation is the same for polyphosphate compositions.

Fig. 3 shows that there is a large discrepancy between calculated and experimental values, meaning that Sn^{4+} actually has a large influence on the proportion of Q^n distribution. In a second step, the amount of Q^n sites bonded to Sn^{4+} was included in the Q^n site proportion, and the experimental Q^n proportions were thus corrected. A further contribution was indeed included in the fits (Fig. 2b), at a chemical shift close to those of Q^3 sites (ca. -38 ppm). This small resonance was neglected in the first attempt for quantifying Q^n sites, but its presence enables to obtain a better fit, and its small intensity is actually in accordance with the small amount of Sn^{4+} in the glasses (Table 1). Fig. 3 shows that the corrected Q^n proportions are in very good accordance with the calculated values.
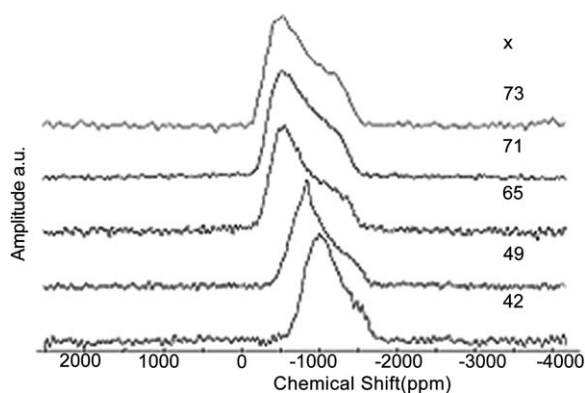
Fig. 4. Static ^{119}Sn spectra of x SnO – $(100 – x)$ P_2O_5 glasses.

We notice that further information on Q^n sites connectivity may have been obtained with double-quantum filtered ^{31}P MAS–NMR [12,16], or even better with the recently reported INADEQUATE filter which probes scalar couplings [17]. However, the resolution of Q^n sites on our ^{31}P MAS–NMR spectra is not enough to obtain separate cross peaks.

Tin NMR spectra are dominated by a very large CSA (Fig. 4), which cannot be removed by magic angle spinning (spectra width is larger than 95 kHz). This behaviour is similar to that observed for ^{207}Pb NMR, although static tin NMR spectra keep a well-defined line shape contrary to ^{207}Pb spectra. The simulation of static spectra enabled to measure the chemical shift anisotropy span (Ω) and to estimate the averaged value of isotropic chemical shift (which takes into account the chemical shift distribution). Unfortunately, there are very few chemical shift data for inorganic tin compounds and even less for tin phosphates. Only three crystalline tin phosphate compounds are known: SnP_2O_7 (Q^1, Sn^{4+}), $Sn_2P_2O_7$ (Q^1, Sn^{2+}) and $Sn_3(PO_4)_2$ (Q^0, Sn^{2+}). Curiously, no crystalline tin metaphosphate is known [18]. Moreover, the crystal structure of $Sn_2P_2O_7$ is not reported. Fig. 5 shows NMR data for these compounds. Some trends can be proposed: by similarity with lead NMR [17] and by examining data in Fig. 5, increasing the covalent character of Sn–O bonds will induce an increase in the CSA span, and a down-field shift of the static line. Fig. 5 illustrates the evolution of CSA span and δ_{iso} for ^{119}Sn spectra of x SnO–$(100 – x)$ P_2O_5 glasses. The isotropic chemical shifts (δ_{iso}) reported in Fig. 5 were obtained by recording ^{119}Sn MAS–NMR spectra at a very low field (2.34 T) and a spinning rate of 15 kHz, which enabled
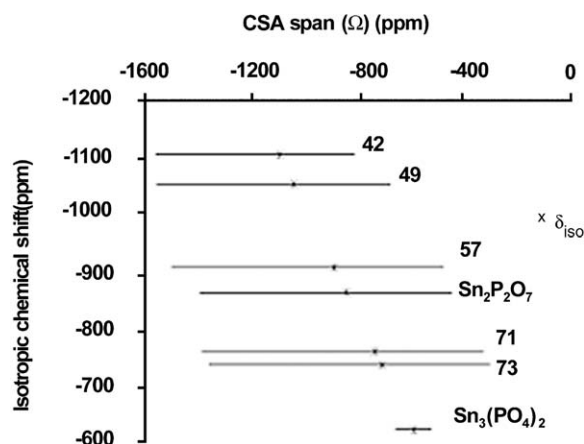

Fig. 5. Plot of ^{119}Sn NMR data for some crystalline reference compounds and x SnO–$(100 – x)P_2O_5$ glasses.

to observe isotropic lines resolved from spinning side-bands. They were also estimated by fitting the static spectra recorded at 9.4 T.

When the SnO amount increases in the glass, tin is bonded to less and less polymerised Q^n sites (Q^2 down to Q^0), meaning that Sn–O bonds become more covalent. This is in accordance with the evolution of CSA span and δ_{iso} observed in Fig. 5. Moreover, Fig. 5 shows that the spectra of $Sn_2P_2O_7$ and $Sn_3(PO_4)_2$ are close to those obtained in glasses, excepted for the lower CSA span of $Sn_3(PO_4)_2$, due to the absence of distribution. We conclude that in glasses containing a high amount of tin(II), the tin(II) environment should be close to that observed in $Sn_3(PO_4)_2$, i.e. a trigonal pyramid. The presence of Sn^{4+} is detected only on the static tin NMR spectrum of x = 49 glass, probably because of its small amount in the other glasses. Like in silicate and germanate glasses, a narrow resonance near –800 ppm indicates the presence of Sn^{4+} with a symmetric environment, generally octahedral in crystalline tin(IV) compounds. We notice that the chemical shift and CSA are close to those obtained in crystalline SnP_2O_7, suggesting that Sn^{4+} in the glasses has an octahedral environment similar to that in crystalline SnP_2O_7.

4. Conclusion

Although even small quantities of tetravalent ions have large effects on glass structure and properties, the presence of Sn^{4+} in x SnO–$(100 – x)$ P_2O_5 is difficult to

detect on ^{31}P and ^{119}Sn spectra, as well as on glass transition temperatures. The influence of Sn^{4+} becomes visible only for the most oxidised glasses in which the Sn^{4+} local environment is close to SnP$_2$O$_7$. This suggests that Sn^{4+} may segregate as SnP$_2$O$_7$ even in non-oxidised tin phosphate glasses.

Acknowledgements

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