PHOSPHATE DOPANTS IN $\text{SiO}_2\text{-Na}_2\text{O-TiO}_2$ GLASSES

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ABSTRACT 1.3 to 2.7 mole % P_2O_5 was introduced in $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses. Na^+ ions are added with P_2O_5 as charge compensating cations for the phosphate units, and ^{29}Si MAS-NMR confirms that there is no modification of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glass network polymerization. ^{31}P MAS-NMR shows the presence of ortho- and pyrophosphate units in $57\text{SiO}_2\text{-}33\text{Na}_2\text{O-}10\text{TiO}_2$ and $70\text{SiO}_2\text{-}20\text{Na}_2\text{O-}10\text{TiO}_2$ glasses, with the same chemical shift than in $67\text{SiO}_2\text{-}33\text{Na}_2\text{O}$ glasses. Two discrete resonances are observed, they are attributed to phosphate units bonded to Ti^{4+} ions. The presence of these discrete resonances is attributed to the formation of covalent Ti-O-P bonds.

INTRODUCTION

Several authors have studied the structural modifications induced in silicate glasses by the addition of small amounts of P_2O_5 ¹⁻³. RAMAN, ^{31}P and ^{29}Si NMR spectroscopies have been used to characterize the structure of alkali silicate glasses bearing small amounts of P_2O_5 ¹⁻³. The phosphates are not connected to the silicate network, and two kinds of phosphate units are present in these glasses : orthophosphate (PO_4^{3-}) and pyrophosphate ($\text{P}_2\text{O}_7^{4-}$). Furthermore, when P_2O_5 is added in the formulation of an alkali silicate glass, the formation of those alkali phosphate complexes induces the polymerization of the silicate network because the alkali ions are scavenged by the phosphate units as charge compensating cations.

We have prepared P_2O_5 bearing $\text{SiO}_2\text{-Na}_2\text{O}$ and $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ glasses in an original way^{4,5} : P_2O_5 is introduced with Na_2O and CaO to compensate the charge on ortho- and pyrophosphate groups. In such a way, the silicate network polymerization

does not change, and thus we can observe the effect of the phosphate units introduction into a silicate network with a constant polymerization degree.

This paper reports the structural characterization with ^{31}P and ^{29}Si MAS-NMR spectroscopies of $\text{SiO}_2\text{-TiO}_2\text{-Na}_2\text{O}$ glasses bearing small amounts of P_2O_5 , introduced with its charge compensating sodium ions. Since P_2O_5 is present as ortho- and pyrophosphate units, the glasses will be labelled in the following text as $\text{SiO}_2\text{-TiO}_2\text{-Na}_2\text{O} + \text{PO}_4^{x-}$, where PO_4^{x-} represents both ortho and pyrophosphates.

EXPERIMENTAL PROCEDURE

The glasses were prepared from reagent grade Na_2CO_3 , SiO_2 , TiO_2 and NaPO_3 . The raw materials were mixed during $\frac{1}{2}$ h before being introduced into a Pt/Rh crucible. The melting temperature was adjusted to a melt viscosity of approximately 10^2P ($=10\text{ Pa.s.}$). The melt was then stirred $\frac{1}{2}$ h, kept 2 h at the melting temperature before being poured into a steel mould at room temperature. 300g of glass were prepared at a time. The glasses were analysed by X-ray Fluorescence.

^{29}Si and ^{31}P MAS-NMR spectra were respectively obtained on Bruker ASX100 and ASX400 spectrometers, operating at 19,89 MHz and 40,53MHz. Pulses of $1,5\mu\text{s}$ ($\sim\pi/5$) followed by a 20s delay were typically employed for the ^{29}Si nucleus, $2\mu\text{s}$ ($\sim\pi/4$) with 20s delay for ^{31}P . We have checked that both relaxation times were sufficient to obtain quantitative spectra. The ^{29}Si spectra were obtained with 1000 to 2000 scans and ^{31}P ones with 128 to 256 scans. The samples were spun at 5000Hz for ^{29}Si and at 7000Hz for ^{31}P . TMS was used as a reference for ^{29}Si and 85% H_3PO_4 for ^{31}P . Exponential broadenings of respectively 30Hz and 10Hz were applied during the processing of the spectra. The ^{31}P spectra were deconvoluted with gaussian lines.

RESULTS AND DISCUSSION

Figure 1 shows the ^{29}Si MAS-NMR spectra recorded in a $67\text{SiO}_2\text{-}33\text{Na}_2\text{O}$ glass, and in the glasses derived from the former by substitution of 5 and 10 mole% TiO_2 for SiO_2 . In $67\text{SiO}_2\text{-}33\text{Na}_2\text{O}$ glass spectrum, 3 resonances at -78 , -88 and -98ppm are

attributed to Q^2 , Q^3 and Q^4 sites, respectively⁶. These lines broaden with the addition of TiO_2 . This can be related to a modification of the bond length and angles between Q^n units, or to the presence of Ti^{4+} cations as second neighbours of silicon nuclei. No significative modification of the ^{29}Si MAS-NMR spectra (not shown) was observed after addition of 1.3 mole% Na_3PO_4 in these glasses. We conclude, as we have reported in our previous studies on soda silicate and soda-lime silicate glasses^{4,5}, that it is possible to introduce a small amount of P_2O_5 in Na_2O - TiO_2 - SiO_2 glasses without any significant modification of the silicate network condensation.

FIGURE 1 : ^{29}Si MAS-NMR spectra of $67SiO_2$ - $33Na_2O$ glass, and in the glasses derived from the former by substitution of 5 and 10 mole% TiO_2 for SiO_2 .

The ^{31}P MAS-NMR spectra, obtained for $57SiO_2$ - $33Na_2O$ - $10TiO_2$ and $70SiO_2$ - $20Na_2O$ - $10TiO_2$ glasses to which 2.7 mole% PO_4^{x-} were added, are presented on Figures 2 and 3. These spectra were decomposed into gaussian lines, in accordance with a chemical shift distribution due to the amorphous state. The spectrum of $57SiO_2$ - $33Na_2O$ - $10TiO_2$ + 2.7 mole% PO_4^{x-} (Figure 2) contains 3 resonances at 15.8, 10.3 and 3 ppm. Four resonances are observed on the spectrum of $70SiO_2$ - $20Na_2O$ - $10TiO_2$ +2.7 mole% PO_4^{x-} (Figure 3). They are located at 15.8, 10.4, 2.8 and -4.2 ppm.

FIGURE 2 : ^{31}P MAS-NMR spectrum of $57\text{SiO}_2\text{-}33\text{Na}_2\text{O-}10\text{TiO}_2 + 2.7$ mole% $\text{PO}_4^{\text{x-}}$

FIGURE 3 : ^{31}P MAS-NMR spectrum of $70\text{SiO}_2\text{-}20\text{Na}_2\text{O-}10\text{TiO}_2 + 2.7$ mole% $\text{PO}_4^{\text{x-}}$

The lines at 15.8 and 3ppm are attributed to sodium orthophosphate units and pyrophosphate units, respectively, in accordance with the resonances observed on Na₂O-SiO₂-P₂O₅ glasses²⁻⁵.

We notice that the short range order near the ortho- and pyrophosphate units is not modified by the presence of TiO₂, since the same chemical shifts are observed for these units in Na₂O-SiO₂-P₂O₅ and Na₂O-TiO₂-SiO₂-P₂O₅ glasses. Although the spectra are not reported here, we also note that TiO₂ substitution for SiO₂ does not change the relative amount of ortho- and pyrophosphate units in the glasses. Increasing the phosphate quantity from 1.3 to 2.7 mole% does not change the ³¹P NMR spectra of ortho- and pyrophosphate units any more. Two discrete resonances appear in TiO₂ bearing glasses, located at 10.3 and -4.2 ppm. These resonances may be attributed to Q¹ and Q² sites of sodium tripolyphosphate, respectively⁷. The resonance at 10.3ppm is however observed alone on the spectrum of Figure 2, which eliminates this attribution. Hence these resonances must be associated to phosphate units bonded to Ti⁴⁺ cations, since the bonding to Si⁴⁺ should lead to resonances near -45ppm⁸. These phosphate units are not bonded only to Ti⁴⁺, because they would resonate at ca. -20 to -30 ppm⁹. Hence we attribute these resonances to phosphate units bonded to both sodium and titanium ions. Ti⁴⁺ are more electronegative¹⁰ than Na⁺, so their presence induce a shift of phosphorus resonance toward higher field (more negative chemical shifts). On this basis, the resonance at 10.3ppm is attributed to orthophosphates units bonded to Ti⁴⁺, whereas the resonance at -4.2ppm can be due either to pyrophosphate units bonded to Ti⁴⁺ ions, or to orthophosphate units bonded to a larger number of Ti⁴⁺ ions than those which resonante at 10.3ppm.

CONCLUSION

The introduction of phosphate units in Na₂O-TiO₂-SiO₂ glasses leads to the formation of discrete phosphate units bonded to titanium ions. This is contrary to what was observed in Na₂O-CaO-SiO₂ glasses, in which the phosphate units are surrounded by an averaged number of Na⁺ and Ca²⁺, and no discrete resonance was observed. This behavior can be attributed to the high electrostatic field strength¹⁰ (z/a^2) of Ti⁴⁺ ions, that lead to the formation of covalent bonds between the phosphate units and Ti⁴⁺ ions.

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