P₂O₅ DOPANT IN PbO-PbCl₂-CdCl₂ GLASSES

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ABSTRACT 3 mole% P₂O₅ were introduced in PbO-PbCl₂-CdCl₂ glasses to increase the vitrification domain. Thermal analysis indeed indicates that devitrification tendency is lowered with P₂O₅ addition. ²⁰⁷Pb NMR is in accordance with a network reticulation by P₂O₅ via P-O-Pb bond formation. However, ³¹P NMR shows that lead-cadmium orthophosphate groups are formed in the glass. These orthophosphate have a low solubility in the melt, and tend to precipitate if the quenching rate is not high enough. We conclude that P₂O₅ have not a stabilizing effect on the lead-cadmium oxychloride glasses.

INTRODUCTION

The development of anionic conducting materials is particularly interesting for sensors. Anionic conduction in glasses is less common than cationic one. However, the halide anion conductivity in lead halosilicate glasses was reported by Schultz and Mizzoni¹ and by Horton and Shelby². Sundar et al.³ have investigated ionic conduction in lead halide-lead metaphosphate glasses and have reported that the conduction was principally due to halide ions rather than to the Pb²⁺ ones. The glass forming region in the system PbO-PbCl₂-CdCl₂ has been investigated by Fu Jie et al. for optical applications⁴. The high chloride content of these glasses is of potential interest for the elaboration of chloride conducting glasses. Moreover the high polarisability of heavy metals is favourable to enable the mobility of large charge carriers. In the case of the lead atoms, the high polarizability is mainly due to the presence of a 6s² electronic lone pair in the external valence layers. This high polarisability contributes to the decrease in the strain energy term of the conduction activation energy.

The glass formation range in the PbO-PbCl₂-CdCl₂ system is narrow, as shown in figure 1⁴. Moreover, even inside the glass formation domain, it is difficult to prepare

large glass-samples, owing to the strong devitrification tendency of these glasses. Since it is known that addition of glass former oxides in heavy metal glasses enables their stabilization⁵, we added P_2O_5 in the $PbO-PbCl_2-CdCl_2$ glasses to increase the glass formation range, and to enable the casting of large glass samples. Lead phosphate are indeed known to form glasses in a wide composition range, owing to the formation of covalent $Pb-O-P$ bonds^{6,7}.

EXPERIMENTAL PROCEDURE

The glasses were prepared from reagent grade PbO , $CdCl_2$ and $PbCl_2$. They were melted in a covered vitreous carbon crucible, at a temperature ranging from 600 to 700°C. The melting temperature was limited to $\frac{1}{4}$ hour, in order to avoid volatilization from the melt. It was then poured on a water-cooled brass mould. The 2 batch compositions, (30 PbO -50 $PbCl_2$ -20 $CdCl_2$) (Glass10) and (40 PbO -40 $PbCl_2$ -20 $CdCl_2$) (Glass 40), are reported on figure 1. 3 mole % P_2O_5 were then added to each batch, and the same melting procedure was respected. It is assumed that, in the measurement precision range of the analyses reported in this paper, the volatilizations are sufficiently small to consider that the batch composition represent the actual glass composition.

^{207}Pb NMR spectra were obtained on a Bruker ASX400 spectrometer, operating at 83.71 MHz. Owing to the large electronic cloud, the shielding of lead nuclei is very large and the ^{207}Pb NMR spectra suffer from a very large chemical shift anisotropy. This is why the spectra are obtained by summing several static echos recorded at different offset (VOCS method⁶). Pulses of 60 μs followed by a 30s delay were typically employed. ^{31}P MAS-NMR spectrum was obtained on a Bruker ASX100 spectrometer, operating at 40.53 MHz. 2 μs ($\sim \pi/4$) pulses with 20s delay were used. The samples were spun at 7000Hz. $Pb(NO_3)_2$, at (-2941ppm), was used as a reference for ^{207}Pb chemical shifts, and 85% H_3PO_4 for ^{31}P .

Differential scanning calorimetry was performed on a Setaram DSC141, at a heating rate of 5°C/min. Typically 15mg of glass powder was analyzed in gold crucibles.

FIGURE 1: Glass formation range in the PbCl_2 - PbO - CdCl_2 system. The circles are the compositions of the glasses studied in this paper.

RESULTS AND DISCUSSION

Figure 2 shows the ^{207}Pb NMR spectra recorded on 2 glasses which compositions lies on a $x\text{PbCl}_2$ -(100- x) PbO - CdCl_2 line (see Figure 1). Two reference spectra of PbO and PbCl_2 are also presented. Negative chemical shifts indicate ionic bonding of oxygen or chlorine to lead atoms, as in PbCl_2 , whereas positive chemical shift indicate covalent bonding, as in PbO in which Pb atoms adopt a tetrahedral pyramidal configuration⁶.

In the glass spectra (Figure 2), two large resonances are detected, they are centered on 600ppm and -1300ppm. The very large width of these resonances is attributed to a chemical shift distribution, that reflects a distribution of ionic-covalent bonds around the lead nuclei, as shown by Fayon⁶. In the case of $x\text{PbCl}_2$ -(100- x) PbO - CdCl_2 glasses, we attribute these distribution to a variation of the average number of oxygens and chlorine atoms in the lead coordination sphere, and of the mean Pb-O and Pb-Cl bonds distances. The presence of two resonances means that there are two distinct environments of the lead atoms in the glasses : according to our above hypothesis, the average number of oxygens should be higher for the resonance located at 600ppm. This attribution is supported by the spectra evolution versus the glass composition : when the glass composition moves toward the PbO corner, i.e. with a chloride substitution by oxygen, the relative amplitude of the resonance at 600ppm increases compared to the other resonance.

FIGURE 2 : ^{207}Pb NMR spectra of PbO , PbCl_2 , Glass10 and Glass40

Figure 3 compares the spectra of the $50\text{PbCl}_2\text{-}30\text{PbO-}20\text{CdCl}_2$ glass and of the same glass with 3 mole% P_2O_5 . The amplitude of the resonance at 600ppm is smaller in the P_2O_5 -containing glass spectrum. It is attributed to the formation of lead-phosphate bonds, because these latter reported at a more negative chemical shift, (-2500ppm^6) in lead phosphate compounds. Thus the introduction of P_2O_5 results in the decrease of the number of covalent Pb-O(Pb) bonds in the lead coordination sphere, that is in accordance with the network former character of P_2O_5 .

FIGURE 3 : Effect of 3 mole% P_2O_5 on ^{207}Pb NMR spectrum of $50\text{PbCl}_2\text{-}30\text{PbO-}20\text{CdCl}_2$ glass.

The ^{31}P MAS-NMR spectrum of $50\text{PbCl}_2\text{-}30\text{PbO-}20\text{CdCl}_2 + 3\%$ mole P_2O_5 glass shows a single resonance at 0ppm (Figure 4). The ^{31}P chemical shifts are dependant on the phosphate condensation level, and on the second neighbour electrostatic field strength. The value of the chemical shift measured on Figure 4 is consistent with an average bonding of an orthophosphate unit with lead and cadmium, because lead orthophosphate resonates at 0ppm⁶, and cadmium orthophosphate at 5ppm. (This last value was estimated from the cadmium electrostatic field strength, because no data is available for the cadmium orthophosphate chemical shift). Thus the assumption of the formation of lead-phosphate bonds is confirmed by ^{31}P MAS-NMR.

FIGURE 4 : ^{31}P MAS-NMR spectrum of $50\text{PbCl}_2\text{-}30\text{PbO-}20\text{CdCl}_2$ glass + 3 mole% P_2O_5 .

The effect of P_2O_5 on the glass stability can be observed on the DSC thermograms on Figure 5. The glass transition and crystallization temperatures increase ($\Delta T_g = +5^\circ\text{C}$, $\Delta T_c = +16^\circ\text{C}$). This effect can be attributed to the glass former character of P_2O_5 , that results in a network reticulation, in accordance with the above structural analyses.

FIGURE 5 : Effect of 3 mole% P_2O_5 on the DSC thermogram of 50PbCl₂-30PbO-20CdCl₂ glass.

CONCLUSION

The structural characterization of PbO-PbCl₂-CdCl₂ glasses with ^{207}Pb and ^{31}P NMR is consistent with the network former character of P_2O_5 . Lead-phosphate bonds are formed, and the average number of Pb-O-(Pb) bonds decreases. These latter bonds can be indeed assumed to reticulate the glass network in the absence of a conventional network former. DSC data are also in accordance with this structural scheme because the T_g and T_c increase with P_2O_5 addition. However, we can not conclude that P_2O_5 has a stabilizing effect on the PbO-PbCl₂-CdCl₂ glasses because the glass formation range is not larger, and we observed that the P_2O_5 -containing glasses have a higher tendency to devitrification during the quenching. This is probably due to the precipitation of lead orthophosphate during the cooling. Lead-phosphate bonds were indeed detected by the structural analyses, and although they reticulate the glass network, they also increase the crystallization tendency, probably owing to the large free energy of crystallization of these lead orthophosphates.

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