Structure of lead vanadophosphate glasses.

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$PbO-V_2O_5-P_2O_5$ glasses were prepared by additions of V_2O_5 to $PbO-P_2O_5$ phosphate glasses. The melts were equilibrated under air, then quenched. The $V^{(V)}/V^{(IV)}$ redox ratio was determined by a wet electrochemical method. The relative amount of $V^{(IV)}$ decreases with increasing total vanadium in the glasses, or with increasing PbO content. This is explained by the variation of the glass basicity, that influences the redox ratio. ^{31}P MAS-NMR shows that the introduction of V_2O_5 depolymerizes the phosphate chains up to isolated PO_4 tetrahedra.

introduction

Semi-conducting properties of transition metals were discovered by De Boer and Verwey in 1937. Using those elements in their glass compositions, Denton, Stanworth and Rawson[1] could prepare the first semi-conducting glasses in 1954. In such glasses, transition metals exist under several oxidation states, and electronic conductivity is due to electronic jumps or polaron hopping. $P_2O_5-V_2O_5$ semi-conducting glass system is one of the most studied[234], but semi-conduction was also detected in ternary glass systems like $Ag_2O-V_2O_5-P_2O_5$[5] or $Na_2O-V_2O_5-P_2O_5$[6].

Our aim is to study conductivity- structure relationships in semi-conducting glasses. The $PbO-V_2O_5-P_2O_5$ is interesting since lead oxide can occupy both glass forming and modifying sites, moreover both ^{31}P, ^{51}V and ^{207}Pb nuclei are observable with solid-state NMR. ^{17}O needs an isotopic enrichment because its natural abundance is 0.04%.

One of the main troubles when preparing semi-conducting glasses is the control of the glass redox, i.e. the ratio of oxidation states of the transition metal. Hirashima et al.[7] reported the conductivity data for $PbO-V_2O_5-P_2O_5$ glasses, but no systematic control of the redox was undertaken. In these glasses, the conductivity increases with the V_2O_5 content[7], as also observed in $P_2O_5-V_2O_5$ glasses[2].

We report here some factors influencing the redox of $PbO-V_2O_5-P_2O_5$ glasses: the melting time, the atmosphere control, and the glass composition.

Experimental procedure.

$PbO-V_2O_5-P_2O_5$ glasses were prepared from PbO, V_2O_5 and $(NH_4)_2HPO_4$. The batch was heated first slowly to remove ammonia and water, then up to 800°C, under air, excepted when specified in the text. The melting time was typically 0.5h, excepted when the effect of melting time was evaluated. Alumina crucibles were used, but no contamination from the crucible was detected, probably owing to the low melting temperature.

The V^{4+}/Vtotal ratio (the glass redox) was measured by a potentiometric method[8]. The glass conductivity was measured by the complex impedance method.

The ^{31}P NMR experiments were carried out at Bo= 2.3 T using a Bruker ASX100 spectrometer. The ^{31}P Larmor frequency is 40.53 MHz at this magnetic field. A 7 mm MAS probe was used at a MAS frequency of 7 kHz. 32 scans have been accumulated. The pulse length for the 1D experiment was 1.5 μs (π/4).

Results and discussion.

Redox vs. Melting time.

Figure 1 shows that the melting time has no influence on the redox ratio of a 60PbO-$24V_2O_5$-$16P_2O_5$ glass. This means that an equilibrium state is reached even for shorter melting times. The very low viscosity of the melts can contribute to this observation.

Redox vs. V/P ratio.

We prepared xV_2O_5-(100-x)(60PbO-$40P_2O_5$) glasses. Figure 2 shows that the redox is high at small V_2O_5 addition, but decreases to a constant value for high V_2O_5 content. This behaviour is attributed to the effect of glass basicity on redox, according to the following reaction :

$$V^{4+} + 1/4O_2 + 1/2O^{2-} \square VO^{3+}$$

Notice that the stoechiometry of this reaction has here only an indicative character, but is not supported by experimental evidence.

P_2O_5-rich phosphate glasses are acidic glasses (acceptors of O^{2-}), and then have a reducing character[9]. Increasing the V_2O_5 content decreases the glass acidity[10], and also changes the composition from a phosphate into a vanadate solvent. The Redox value is then governed by the V^{4+}/V^{5+} equilibrium in a vanadate matrix. The V^{4+}/Vtotal ratio in pure V_2O_5 heated in air at 800°C is indeed close to the value in Figure 2 (2-3%).

Redox vs. Pb/(P+V) ratio.

Figure 3 shows the effect of PbO addition in a $20P_2O_5$-$80V_2O_5$ glass. The more basic lead oxide[10] decreases the glass acidity, leading to a reduced redox for increasing PbO content.

31P MAS-NMR

On the ^{31}P MAS-MR spectrum of the 50PbO-$5V_2O_5$-$45P_2O_5$ glass, two resonances are observed at -10 and -25ppm. They are attributed to Q^1 and Q^2 phosphate sites, respectively. The Q^1 sites are assumed to originate from the bonding of vanadium polyhedra to the phosphate groups, since the intensity of this resonance increases with the V_2O_5 content. Above 15 mol% V_2O_5, a third resonance appears at 0 ppm (Figure 4). Since its intensity becomes independent of the V_2O_5 content above 25 mol% V_2O_5, it is attributed to isolated Q^0 sites.

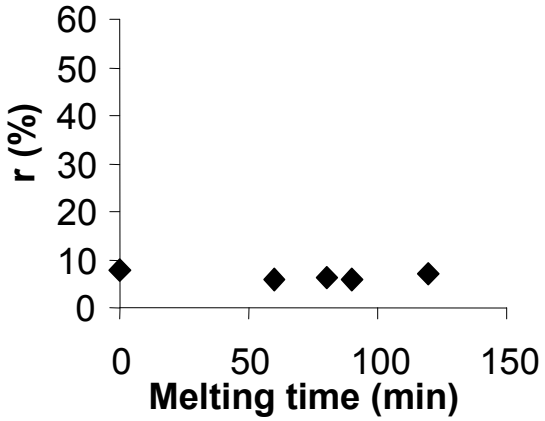

Figure 1 :Redox ratio r (V^{4+}/Vtotal) versus melting time of 60PbO-24V_2O_5-16P_2O_5 glass.

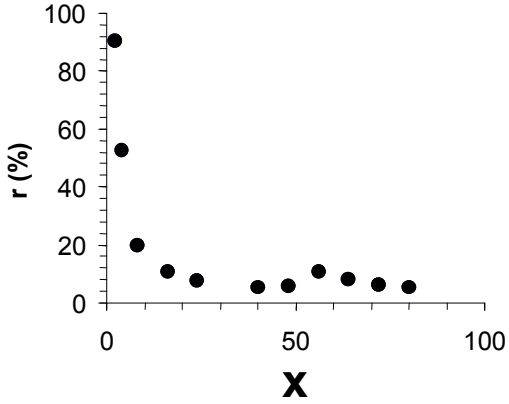

Figure 2 : Redox versus x of xV_2O_5- (100-x)(60PbO-40P_2O_5) glasses.

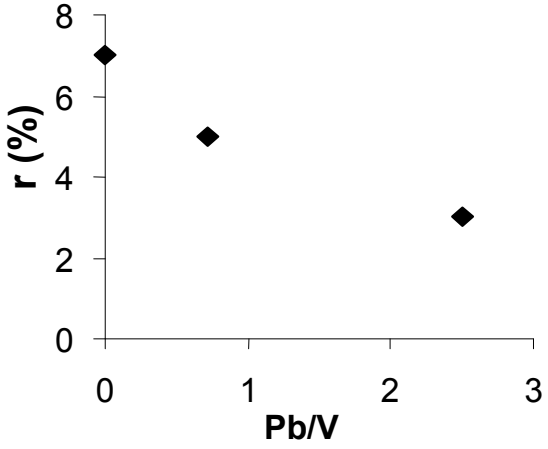

Figure 3 : Redox versus Pb/V of xPbO-(1-x)[80V_2O_5-20P_2O_5] glasses.

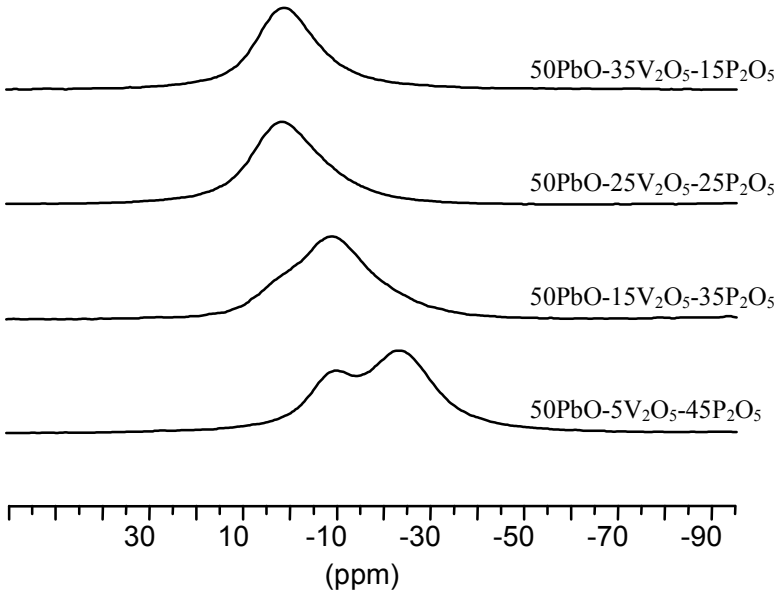

Figure 4 : ^{31}P MAS-NMR spectra of $PbO-V_2O_5-P_2O_5$ glasses.

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