INVESTIGATION OF PbO-TiO₂-P₂O₅ GLASS FORMING REGION

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ABSTRACT The glass forming range of PbO-TiO₂-P₂O₅ system has been determined at 1000°C. The bulk density was measured and the molar volume have been calculated for both binary and ternary phosphate glasses. Infrared spectroscopy has been used in 1500-400 cm⁻¹ region to assess structural changes taking place along the glass region of the lines $x \text{ PbO}-(1-x)\text{P}_2\text{O}_5$ and $x\text{PbO}-0.01\text{TiO}_2-(0.99-x)\text{P}_2\text{O}_5$ by gradual passage from $v\text{-P}_2\text{O}_5$ network to the end point of the glass forming domain ($x=0,64$). The infrared deconvolution analysis has revealed that the stretching vibration of phosphoryl group persists in all investigated glasses up to $x=0,64$. This feature has been ascribed to the fact that the P=O is not completely ruptured regardless the breakdown of the covalent phosphate glass network.

INTRODUCTION

The phosphorus pentoxide P₂O₅ was postulated as glass forming oxide along with de SiO₂ and B₂O₃¹. The later two glass-forming oxides have been extensively used as glass-ceramics containing ferroelectric phases such as PbTiO₃, BaTiO₃ and SrTiO₃²⁻⁴. However, the hygroscopic and volatile nature of P₂O₅ have hampered the use of its glassy state in this field. Moreover, because of the extreme difference in melting point between TiO₂ and P₂O₅⁵, the preparation of homogenous glasses in this system is a difficult task. For these reasons, there have been very few detailed studies on the TiO₂-P₂O₅ glasses⁶. Conversely, the bivalent phosphate glasses have received more attention, inasmuch as they are among the easiest glasses to prepare⁷⁻¹¹.

The present work is part of our investigations devoted to the identification, structural and dielectric properties of both glass and vitro-ceramic domains within the ternary systems B^{II}O-TiO₂-P₂O₅ (B^{II} = Mg, Ca, Sr, Ba, Pb)¹². The purpose of the present article is to report on the glasses isolated at 1000°C, inside the ternary diagram PbO-TiO₂-P₂O₅. The relationship between their composition, density, molar volume and the evolution of their vibrational spectra will also be discussed.

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EXPERIMENTAL PROCEDURES

Batches for glass melting were prepared by mixing appropriate amounts of metal oxides (PbO, TiO₂) and NH₄H₂PO₄. The glasses were melted in alumina crucibles at 950-1000°C (the temperature being kept constant for 30 min), poured into preheated stainless steel plate to 350-400°C, then allowed to cool normally to room temperature.

The glassy state was substantiated by the absence of the peaks in X-ray diffraction pattern. The mass densities were measured by the archimedes method using the diethylphthalate as an immersion fluid. From the density data, oxygen molar volume V(O) of each sample were calculated according to eq. 1¹³ :

$$V(O)_i = \frac{\sum_i M_i x_i}{\rho \sum_i n_i x_i} \quad [1]$$

where ρ , M_i , x_i , n_i stand for measured bulk density of the glass, atomic weight, molar fraction and the number of oxygen atom, respectively. Fourier transformed infrared FTIR spectra were recorded with FTIR spectrophotometer PERKIN ELMER 1600 within 250-1500 cm⁻¹ region, using KBr pellet technique.

RESULTS

- Glass forming region

In the present study, neither PbO-TiO₂, nor TiO₂-P₂O₅ system have yield glasses under the above described conditions. In the first diagram it is quite obvious. However, in the second one, it seems surprising as P₂O₅ is one of the four claimed glass forming oxides¹, this discrepancy may be accounted for the great difference between the P₂O₅ and TiO₂ melting points. The glass forming range was found to be extended up to $x = 0.64$, x denotes the molar fraction of PbO. Figure 1 represents the glass forming range delimited in P₂O₅-TiO₂-PbO system.

FIGURE 1 : Glass forming region in the PbO - TiO₂ - P₂O₅ system at 1000° C

FIGURE 2 : Bulk density and molar volume of (1-x)P₂O₅-xPbO (a,a') and (0.99-x)P₂O₅-0.01TiO₂-xPbO (b,b') glass versus PbO contents

- bulk density and molar volume

Figure 2 shows a linear increase in bulk density with the PbO content of both binary and ternary phosphate glasses. However, their corresponding calculated molar volume for one atom of oxygen of ternary phosphate glasses exhibits a different behaviour. It can be seen that the addition of 1 mole % of TiO_2 (Fig. 2) to lead phosphate glasses with $x = 0.3$ yields a molar volume of 13.25 cm^3 , instead of 12.24 cm^3 calculated for titanium free lead phosphate glass. Therefore, within the composition range $0.3 \leq x \leq 0.5$, $V(\text{O})$ remains constant regardless the PbO content. Thereafter, it augments with further addition of PbO. These results suggest that firstly, the atomic weight of lead is the bulk density controlling factor and secondly, the $v\text{-P}_2\text{O}_5$ structure is built with excess of structural volume with regard to its crystalline varieties. The calculated molar volumes from density data found in the literature for $v\text{-P}_2\text{O}_5$ and its related crystalline forms α and α' , have shown that $V(\text{O})_{v\text{-P}_2\text{O}_5}^{14} > V(\text{O})_{\alpha\text{-P}_2\text{O}_5}^{15} > V(\text{O})_{\alpha'\text{-P}_2\text{O}_5}^{16}$. This excess could not assist the Pb^{2+} and Ti^{4+} incorporations, because their size are larger than the voids available within the glass network. Furthermore, in principle, the variation of physical properties, such as density and molar volume of a glass, seems to be closely related to its structural variation as discussed below.

- Infrared spectra

The vibrational spectroscopy has been used in the $400\text{-}1500 \text{ cm}^{-1}$ region to identify the anionic species present in both series of glasses $x \text{ PbO}-(1-x)\text{P}_2\text{O}_5$ and $x\text{PbO}-0.01\text{TiO}_2-(0.99-x)\text{P}_2\text{O}_5$. Typical examples of spectra of the first series are presented in figure 3. The infrared spectrum of vitreous P_2O_5 is taken as a starting point and that of $x = 0.64$ as end point of this series. This representation ought to facilitate the comparisons related to noticeable changes taking place in the lead phosphate glass structures. Before investigating the evolution of infrared spectra of this series, a careful re-examination of the reflectance calculated infrared absorption spectrum of vitreous P_2O_5 ¹⁷ was felt necessary. Unfortunately, in this case the band emerging from the region $1250\text{-}1150 \text{ cm}^{-1}$ is found rather too intense. This band is likely resulting from the effect of humidity (due to the synthesis procedure¹⁷), giving rise to P-O-H group. Indeed, Meyer et al.¹⁸ have successfully recorded a better reflectance infrared spectrum of an almost anhydrous P_2O_5 glass with no such intense band. The band positions, in

FIGURE 3 : Infrared absorption spectra of $(1-x)\text{P}_2\text{O}_5\text{-}x\text{PbO}$ glasses Compared with that of $v\text{-P}_2\text{O}_5$ ¹⁸

both calculated absorbance from reflectance spectrum¹⁸ and absorbance spectrum performed in KBr pellet¹⁹ of P_2O_5 glass, were found at about 1380, 960, 800-630 cm^{-1} and 500-300 cm^{-1} corresponding respectively to, the symmetric phosphoryl stretch $\nu_s P=O$, asymmetric stretching vibration of P-O-P bridges $\nu_{as} P-O-P$, symmetric stretching vibration of P-O-P and the phosphate skeleton deformation. These results are highly consistent with our formerly $\nu-P_2O_5$ recorded Raman spectra²⁰.

As the stretching modes of the phosphate tetrahedra labelled Q^1 , Q^2 with one and two bridging oxygen respectively, all emerge²¹ in the region 1000-1150 cm^{-1} . These bands exist in all the spectra except for P_2O_5 , either as distinct or a shoulder-like feature at this region. There is another band complex appearing in 1200-1350 cm^{-1} region. This band complex consists of stretching vibration of phosphoryl group $\nu P=O$ and asymmetric stretching vibration of Q^2 tetrahedra $\nu_a PO_2$, both of which are not observed as separate and well defined bands, whose peak is located near 1272 cm^{-1} for ultraphosphates and its amplitude is smaller than that of $\approx 1150 cm^{-1}$ band, observed for $x = 0.64$, which is associated with the symmetric stretching of Q^1 ($\nu_{as} PO_3$). The decrease of the maximum amplitude of the band at 1272 cm^{-1} is accompanied by a shift towards lower frequencies. There is also emergence and growth of bands in 960-1100 cm^{-1} region. This region is attributed to the stretching vibration of Q^1 tetrahedra possessing three unshared oxygen corners. The frequency range assigned to the asymmetric stretching vibration of P-O-P ($\nu_a P-O-P$) shows a large and diffuse band whose peak is located around 900 cm^{-1} . Whereas, the one attributed to the symmetric band stretching vibration of P-O-P linkages, exhibits two peaks whose maximum amplitudes are observed at $\approx 770 cm^{-1}$ and $\approx 690 cm^{-1}$ which are presumably due to the presence of several type of bridges P-O-P units²². The first one can be attributed to $\nu_s P-O-P$ of Q^2 tetrahedra and the second band to $\nu_s P-O-P$ of Q^3 tetrahedra, because the relative intensity of the band at 770 cm^{-1} is constantly increasing to the detriment of that at 690 cm^{-1} as the PbO content increases. According to Bruni et al.²³, such bridges should have a bent configuration. Because, in the case of linear configuration, $\nu_s P-O-P$ is only Raman active. As matter of fact, in $[Pb(PO_3)_2]_x$ crystallising in space group $P2_1/c$, all the P-O-P angles are lower than 180° : i. e. 147, 143 and 138° ²⁴.

As the infrared band complexes are large and diffuse, it is difficult to have a deeper insight into a glass structure, thus deconvolution analysis was felt necessary. The patterns of deconvolution analysis of IR active modes of $xPbO-(1-x)P_2O_5$ glasses (figure 4), turned out to be even more complicated than that seen from the raw IR spectra. A minimum of seven bands were found, thus showing that the spectra comprise no less than ten active vibrational modes in the 600-1350 cm^{-1} range. According to Meyer et al.²², the interpretation of infrared spectra of P_2O_5 complicated structures essentially based on the number of PO_4 per unit cell as well as the type of their connection and symmetry. Each PO_4 with three shared oxygen Q^3 correspond to one $\nu_s P=O$, one $\nu_s P-O-P$ and two $\nu_{as} P-O-P$ of the three bridging groups, as the number of non equivalent tetrahedra in $(P_2O_5)_\infty$ are two, one should expect, more than one infrared active mode for each group. As matter of fact, the deconvolution analysis meet theoretical expectation in both cases: $\nu-P_2O_5$ and lead metaphosphate glasses. For $Pb(PO_3)_2$ four stretching vibrations of each of the four mode: $\nu_{as} PO_2$, $\nu_s PO_2$, $\nu_{as} P-O-P$ and $\nu_s P-O-P$ are expected, because its crystalline structure consists of meandering chains of four PO_4 tetrahedra²⁴. It seems instructive to point out that the structure of lead metaphosphate glass cannot be described in term of Q^2 only. As the band appearing

at $\approx 1130\text{--}1050\text{ cm}^{-1}$ region is predominant in the infrared spectrum of the composition $0.36\text{P}_2\text{O}_5\text{--}0.64\text{PbO}$. This band is ascribed to $\nu_{\text{as}}\text{PO}_3$ or $\nu_{\text{as}}\text{P-O}^- (\text{Q}^1)$. These results suggest that the chain length is shorter than that of the corresponding crystalline form.

FIGURE 4 : Deconvolution analysis of the infrared spectra of $(1-x)\text{P}_2\text{O}_5\text{--}x\text{PbO}$ and $0.49\text{PbO}\text{--}0.01\text{TiO}_2\text{--}0.5\text{P}_2\text{O}_5$ glasses
— simulated band, $\sim$ experimental and ...simulated spectrum

A close examination of the whole series of infrared deconvolution analysis spectra reveals that band ascribed to $\nu\text{P=O}$ persist in all the spectra even in those corresponding to $x > 0.5$. However, its relative intensity as well as its wave number decrease when PbO content exceeds the metaphosphate compositions. This fact was explained on the basis of Pb^{2+} position between P-O-P layers. Thereby, they have direct

interaction between Pb^{2+} and phosphoryl group^{25,26}. Therefore, the inclusion of $\text{P}=\text{O}$ bond into Pb^{2+} coordination sphere yields an elongation of $\text{P}=\text{O}$ bond and hence a drop in the wave number from 1300 cm^{-1} for metaphosphate to 1266 cm^{-1} for the oligophosphate composition of $x = 0.64\text{ PbO}$. On the other hand, the continuous presence of $\nu_s\text{P}=\text{O}$ band from the $\nu\text{-P}_2\text{O}_5$ to the highest limit of glass formation range indicates that no complete rupture of $\text{P}=\text{O}$ bond by Pb^{2+} occurs²⁷. However, the emergence and growth of the bands located in $1130\text{-}1050\text{ cm}^{-1}$ region, associated with stretching vibration of the end group PO_3 suggest a progressive break down of the covalent phosphate glass matrix as the PbO content increases.

It is worth noting that the Infrared spectra of titanium free-lead phosphates glasses are affected by the addition of TiO_2 as illustrated by the clear differences between the spectra of the samples having the same P_2O_5 concentration $x = 0.5$. Specially in the frequency region associated with the general profile of the stretching vibrations of phosphate groups PO_2 (Q^2) and PO_3 (Q^3) (figure 4). The obtained data, from the IR deconvolution analysis of both titanium free and 1% TiO_2 containing lead metaphosphate glass, on the inherent frequencies of the observed mode remain more or less unchanged. However, their intensity exhibits variable changes, mainly, in the case of those associated with symmetric and asymmetric stretching vibration of PO_3 and PO_2 groups. The intensity of the later modes increases at the expenses of the former ones. This is consistent with the fact that when PbO is replaced by TiO_2 , it tends to displace the glass forming region towards ultraphosphate domain. As a matter of fact, the latter region is more inclined to contain PO_2 entities than the terminal groups PO_3 .

In addition, the molar volume increase observed in the case of titanium-lead metaphosphate glasses does not seem to be easily explained by simple mechanisms such as a differences of masses, field strength or polarizability between substituting Ti^{4+} and Pb^{2+} ions. Unlike the case of the $(45-x)\text{B}^{\text{II}}\text{O-xNa}_2\text{O-}2,5\text{Al}_2\text{O}_3\text{-}52,5\text{P}_2\text{O}_5$ ($\text{B}^{\text{II}} = \text{Ca}, \text{Sr}, \text{Ba}$) glasses, the decrease of molar volume deriving from the B^{2+} substituting for Na^+ , was explained on the basis of the field strength²⁸. These changes could be accounted for the difference between the roles of Ti^{4+} and Pb^{2+} in the glass forming tendency. The Ti^{4+} and Pb^{2+} ions are presumably located in different sites. To determine the correlation between the molar volume and the structure, more experiments are needed.

CONCLUSION

The glass forming domain of the ternary system $\text{PbO-TiO}_2\text{-P}_2\text{O}_5$ has been determined at 1000°C . The evolution of the bulk density with PbO content is found to be controlled by the atomic weight of lead.. The infrared spectroscopy has successfully allowed to identify the anionic species present in the glass structure. its deconvolution analysis has on one hand revealed the continuous existence of $\text{P}=\text{O}$ bond beyond the metaphosphate composition ($x = 0,5$) up to $x = 0,64$ and in the other hand, the emergence and growth of the band ascribed to the end groups PO_3 . These results suggest a progressive breakdown of the covalent phosphate glass network without a complete rupture of $\text{P}=\text{O}$ bond by Pb^{2+} as the PbO content increases. The effect of titanium on lead phosphate glasses has been evidenced by the clear change in infrared spectra particularly in the region associated with the middle and the end group phosphate tetrahedra.

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