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STRUCTURAL RELATIONSHIP BETWEEN VITREOUS P_2O_5 AND ITS RELEVANT CRYSTALLINE POLYMORPHS BY RAMAN SPECTROSCOPY

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Abstract Vitreous and relevant crystalline polymorphs of P_2O_5 have been synthesised and characterised by X-ray diffraction and Raman scattering spectroscopy. On the basis of the crystallographic data of single crystals of the three varieties H- P_2O_5 , O- P_2O_5 and O'- P_2O_5 , the interpretation of vitreous P_2O_5 Raman spectrum was given taking into consideration the short and intermediate range order. It is inferred that the intermediate range order in v- P_2O_5 can mainly be described in terms of a mixture of both high temperature modifications, with however predominance of O'- P_2O_5 . This hypothesis has been substantiated by in situ Raman study of v- P_2O_5 recrystallisation.

1. INTRODUCTION

During the last five decades, various crystallographic and crystal chemical studies, conducted in different Laboratories, have soundly established the existence of three crystalline forms and a vitreous variety for the diphosphorus pentoxide [1-5]. However, a closer examination of the published work, indicates that the structure of vitreous P_2O_5 has not been sufficiently studied yet. Therefore, in an attempt to find out whether there is any intimate relationship between v- P_2O_5 structure and the crystalline modifications, H- P_2O_5 [6,7], O- P_2O_5 [1,8] and O'- P_2O_5 [4,9], this question will be approached with a view toward

- synthesis and identification by X-ray analysis of the four forms.
- Raman scattering measurements.

2.- EXPERIMENTAL

2.1.- P_2O_5 glass and single crystals preparations

P_4O_{10} with quoted purity (99.999% P_2O_5 - Aldrich) was used as starting material. The sample handling was performed in a dry box. 2g of P_4O_{10} powder were loaded into a gold tube, which was inserted into another silica tube. The latter was then evacuated, sealed under vacuum and heated in a temperature gradient of 100°C, in such a way that its lower part and upper parts reside at T+100°C and at T respectively. The growth of H-form was performed at T = 260°C, with heating or cooling rates $r = 20^\circ\text{C/h}$ and heating time $t = 120\text{h}$. For O'- P_2O_5 , T = 360°C, $r = 50^\circ\text{C/h}$ and $t = 168\text{h}$. The details of the growth procedure of O- P_2O_5 form are given elsewhere [5].

In the case of the preparation of the vitreous form, the powder was loaded directly into fused silica ampoule which was sealed under vacuum, heated progressively at 50°C/hour up to 600°C, held at this temperature for 1 hour before to be quenched under ambient atmosphere. At the conclusion of each experiment, the sample were immersed in paraffin oil inside the dry box, in order to avoid their contamination by surrounding humidity.

2.2. – Raman scattering measurement

Raman spectra have been obtained using an OMARS89 spectrometer, equipped with CCD detector, cooled at liquid nitrogen temperature. Micro Raman spectra were recorded with an Olympus 100X objective in back scattering geometry. The line at 514.5 nm of a Spectra Physics Argon ion laser, has been used for the excitation. The spectral resolution was about 2 cm⁻¹.

3. – Results and discussions

3.1. – Preparation and identification of different P₂O₅ modifications

The three known crystalline modifications of the diphosphorus pentoxide have been successfully synthesised, i. e. hexagonal (rhombohedral R3c), orthorhombic (Fdd2) and orthorhombic (Pnma) corresponding to the H-form, O-form and O'-form respectively. By adjusting the heating schedules, and temperature gradient in the furnace, large and well defined crystals were relatively settled down on the cooler part of the capsule by vapour transport. The obtained single crystals were plainly distinguished by their morphology as shown in Fig.1. To dispel any ambiguity of identification, each single crystals was analysed by X-ray diffraction which allowed to select appropriate sample for Raman study.

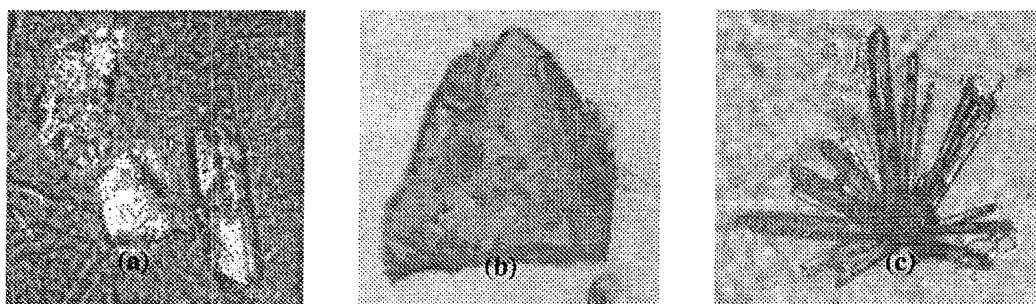


Fig.1. – Morphology of different crystalline modifications (a) : H-P₂O₅, (b) : O-P₂O₅, (c) : O'-P₂O₅.

3.2. – Raman study

Typical features of the Raman spectrum of anhydrous P₂O₅ glass are three band complexes (figure 2) :

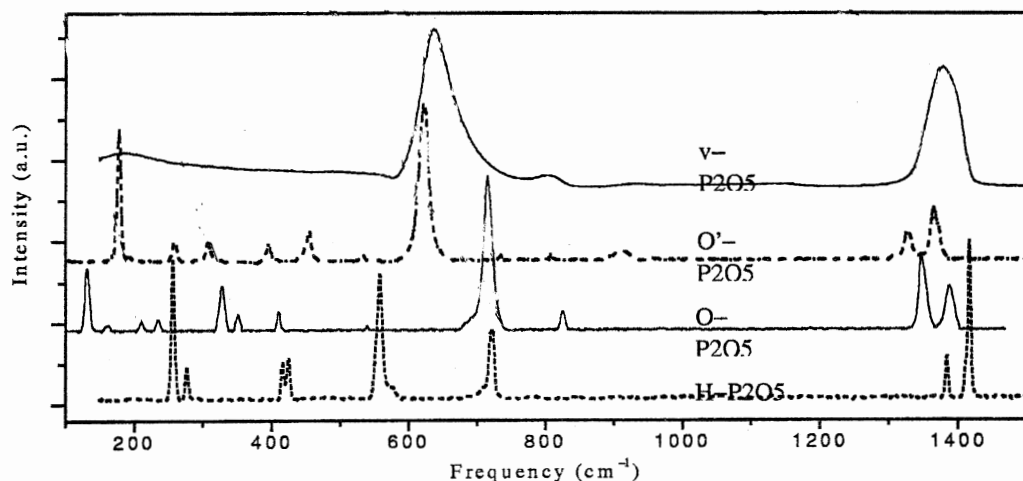
- the symmetric phosphoryl stretch ν_s (P=O) band complex I, whose maximum is at 1379 cm⁻¹
- the symmetric stretch of bridging oxygen ν_s P–O–P band complex II at 635 cm⁻¹,
- the P–O–P bending mode δ P–O band complex III appearing at a lower frequency range 300–500 cm⁻¹.

It seems interesting to note that no feature in the range of 1350–1100 cm⁻¹, which is generally associated with the formation of Q² tetrahedra, has been observed. Our room temperature Raman spectrum of vitreous P₂O₅ is found to be similar to those reported in the literature [10–13]. In addition to the intense bands at 1379 and 635 cm⁻¹ those spectra present weaker bands at 193, 802 and 932 cm⁻¹.

In spite of the analysis of Infrared [14–20] and Raman spectra [10–13, 19, 20] of ν -P₂O₅, its structural approach is yet a difficult task, inasmuch as there is no direct method

for determining the structure of an amorphous solid, like X-ray or neutron diffraction techniques which allow a precise resolution of crystalline structures. Some insights into the $v\text{-P}_2\text{O}_5$ glass structure are however possible by comparing its Raman spectrum with those of related crystalline polymorphs. The Raman spectrum of the low temperature modification labelled $\text{H-P}_2\text{O}_5$ is presented together with those of the high temperature modification $\text{O-P}_2\text{O}_5$, $\text{O}'\text{-P}_2\text{O}_5$ and $v\text{-P}_2\text{O}_5$ in figure 2. From the synthesis procedure, it is thought that the low temperature form is not relevant to glass structure, because the temperature program of melting process guaranties that the glass is derived from high temperature modification of P_2O_5 [21]. At first sight, none of the three modifications seems to yield a Raman spectrum with close similarities with that of $v\text{-P}_2\text{O}_5$. Nevertheless, a closer analysis of all recorded spectra, has allowed to relate the vitreous skeleton to the crystalline forms of this compound.

For example, concerning the band positions, the $\nu_s \text{P=O}$ of $\text{O-P}_2\text{O}_5$ and $\text{O}'\text{-P}_2\text{O}_5$ are located inside $\nu_s \text{P=O}$ $v\text{-P}_2\text{O}_5$ envelop. Conversely, in $\text{H-P}_2\text{O}_5$, the intense band at 1415 cm^{-1} appears at the onset of the band complex I of vitreous P_2O_5 , whilst the less intense band at



1384 cm^{-1} is very close to that (1386 cm^{-1}) of $v\text{-P}_2\text{O}_5$ (figure 2).

Fig. 2.— Raman spectra of vitreous and crystalline P_2O_5 polymorphs

In spite of the described differences, the largest deviation from the maximum peak position of the band complex II is yet smaller than half width. Thus far, no definite conclusion can be stated. Nevertheless, the deviation from the maximum peak position of the band complex II assigned to symmetric stretching vibration $\nu_s \text{P-O-P}$ in $v\text{-P}_2\text{O}_5$ is remarkably larger in the case of $\text{H-P}_2\text{O}_5$ form as compared with that of the high temperature modification $\text{O}'\text{-P}_2\text{O}_5$. Moreover, the very intense peak appearing at 558 cm^{-1} on the Raman spectrum of $\text{H-P}_2\text{O}_5$ is missing in the $v\text{-P}_2\text{O}_5$ Raman spectrum. However, the peak position at 715 cm^{-1} observed in $\text{O-P}_2\text{O}_5$ spectrum seems to fit in with the band complex II of $v\text{-P}_2\text{O}_5$ but its intensity ratio should be taken into consideration. Even though the peak appearing in $\text{O-P}_2\text{O}_5$ at frequency range $804\text{--}825 \text{ cm}^{-1}$ is very weak, it does persist in $v\text{-P}_2\text{O}_5$ Raman spectrum. Accordingly, it follows that the two high temperature P_2O_5 modifications ($\text{O-P}_2\text{O}_5$ and $\text{O}'\text{-P}_2\text{O}_5$) and $v\text{-P}_2\text{O}_5$ are to some extent structurally similar in the intermediate range order. This hypothesis is in a good agreement with that postulated by Hoppe et al. [22]. On the basis of the data of the P-O bond lengths in vitreous P_2O_5 and the three crystalline modifications probed by neutron diffraction with high real space resolution, Hoppe et al. suggested that the network structure of $v\text{-P}_2\text{O}_5$ possesses open non bridging

oxygen environment like those in P_4O_{10} but P–O–P angle are rather similar to those of O and O'– P_2O_5 modifications. At this point, it is as yet difficult to say which of the two crystalline form is the most structurally similar with vitreous P_2O_5 . As its Raman spectrum (Fig. 2) is composed of relatively broad peaks (FWHM = 60 cm^{-1}), the breadth reflects the structural disorder of different PO_4 units. These units are probably inter-joined in several ways increasing the number of allowed vibrational modes and therefore the peaks become broad.

Nonetheless, with special attention to the validity of using the band deconvolution analysis of spectra [23] and by careful examination of the shoulders and the maximum of the peak positions, it has been found that the deconvolution yields quite acceptable results. Figure 3 depicts the results of the deconvolution analysis of band complex II of ν - P_2O_5 Raman spectrum. The deconvolution data reveal the existence of a number of Raman peaks which may be related to different P–O–P and P=O vibrational modes, resulting in a vibrational density of states [24]. A more detailed study and the discussion of these results are summarised elsewhere [24].

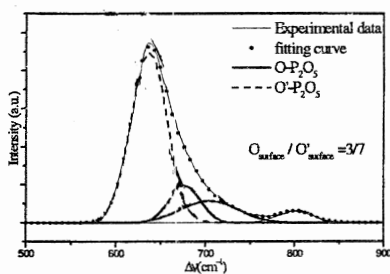


Fig.3.– Deconvolution analysis of band complex II $\nu_{S(P-O-P)}$ of ν - P_2O_5 Raman spectrum

As a result of the present Raman investigation, it therefore appears that the ν - P_2O_5 network structure may be best described by a mixture of the high temperature modifications O- P_2O_5 and O'- P_2O_5 but their proportions should be taken into consideration. The deconvolution analysis indicates that O'- P_2O_5 (form III) is more likely to predominate within the glass network structure. As a matter of fact, this form (O'- P_2O_5) could be estimated at 70% of the vitreous matrix against about 30% for O- P_2O_5 (form II). The predominance of O'- P_2O_5 is corroborated by the trends of the in situ Raman spectra recorded for ν - P_2O_5 tempered at different temperatures, 350, 400 and 450°C ; as illustrated by figure 4, from which it can be seen that the O- P_2O_5 is the predominant form in the Raman spectra of ν - P_2O_5 tempered at 350°C. An increase in temperature up to 450°C gives rise to an identical O'- P_2O_5 Raman spectrum (not presented here). This apparent discrepancy might be accounted for the slow kinetic of the crystallisation of O'- P_2O_5 and / or its metastability.

4. Conclusion

It has been shown that the interpretation of Raman spectra of the three P_2O_5 crystalline polymorphs, proves to be useful to extract structural information from ν - P_2O_5 Raman spectrum. The intermediate range order in ν - P_2O_5 can be described in term of a combined orthorhombic structures, with, however, predominance of O'- P_2O_5 (form III). This hypothesis

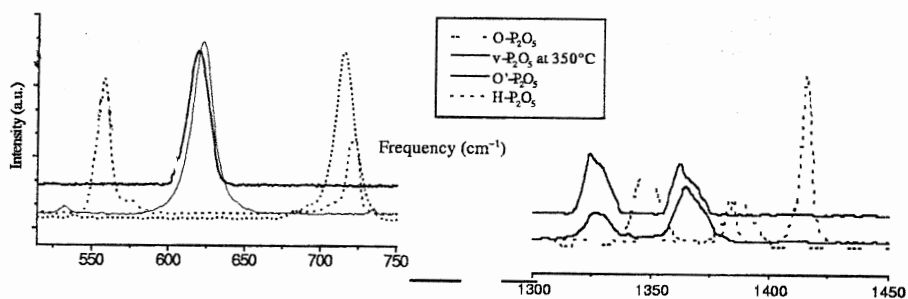


Fig. 4.– Comparison of Raman spectra of $v\text{-P}_2\text{O}_5$ at 350°C and related crystalline forms

has been substantiated by the in situ Raman spectrum of tempered $v\text{-P}_2\text{O}_5$ at 350°C . In spite its metastability and its more effectively oriented terminal oxygen atoms engaged in the $\text{P}=\text{O}$ bond and thus higher packing density than the glass, $\text{O}\text{-P}_2\text{O}_5$ represents almost 30% of $v\text{-P}_2\text{O}_5$ network structure. The $\text{H}\text{-P}_2\text{O}_5$ was excluded from this model because its $\nu_{\text{S}(\text{P}-\text{O}-\text{P})}$ vibration mode lies out of the frequency range of that of $v\text{-P}_2\text{O}_5$.

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