COMMUNICATIONS

$PbAs_2O_6$: an example of drastic structural modifications associated with the crystal to glass transition

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Crystalline and glassy $PbAs_2O_6$ exhibit somewhat different infrared spectra: the 700–500 cm^{-1} bands characteristic of the AsO_6 octahedra in the crystal are replaced by an absorption centred near 800 cm^{-1} in the spectrum of the glass. This frequency increase is interpreted as being due to a decrease in As coordination from six to four.

In contrast to the systematic fourfold coordination of phosphorus in all phosphates, the coordination of arsenic in arsenates may be either fourfold (ortho, pyro, and a few meta arsenates) or sixfold (meta arsenates $M^{II}As_2O_6$ with M^{II} = Co, Mn, Cd, Ca, Pb, etc.).[1] In the latter case, no glass can be obtained (decomposition occurs before melting), except for the lead compound, whose melting point is relatively low (about 740°C, as determined by differential thermal analysis): rapid quenching of the melt obtained at 850°C gives a yellowish, transparent glass characterised by the lack of x-ray diffraction peaks.

The infrared spectrum of this glass is quite different from that of the crystal (Figure 1), which is very similar to that of the isotypic antimonate $PbSb_2O_6$, and the assignments proposed for this compound[2] may be applied to the arsenate: 700–500 cm^{-1} bands, As–O stretching vibrations of the AsO_6 octahedra; 400–300 cm^{-1} bands, bending vibrations; and below 150 cm^{-1}, Pb translations. In the spectrum of the glass the 700–500 cm^{-1} absorption disappears nearly completely and is replaced by a strong absorption in the 850–750 cm^{-1} region. This frequency increase strongly suggests that the As coordination decreases from six to four when going from the crystal to the glass phase. Data on the AsO_4 frequencies in meta arsenates are scarce, but strong bands in the 950–900 cm^{-1} ($K_3As_3O_9$) or 900–800 cm^{-1} ($Tl_4As_4O_{12}$) region have been assigned to As–O stretching vibrations in either As_3O_9 or As_4O_{12} rings of AsO_4 tetrahedra.[3]

In the present case, the strong absorption bands in the 800 and 350 cm^{-1} regions are assigned to the AsO_4 stretching and bending vibrations, respectively. The weak bands in the 600–500 cm^{-1} region may be assigned either to As–O–As vibrations of interlinked AsO_4 tetrahedra (the equivalent P–O–P vibrations are observed near 800–700 cm^{-1} in metaphosphates) or to residual AsO_6 groups. The low frequency absorption is assigned (as in the crystal) to Pb trans-
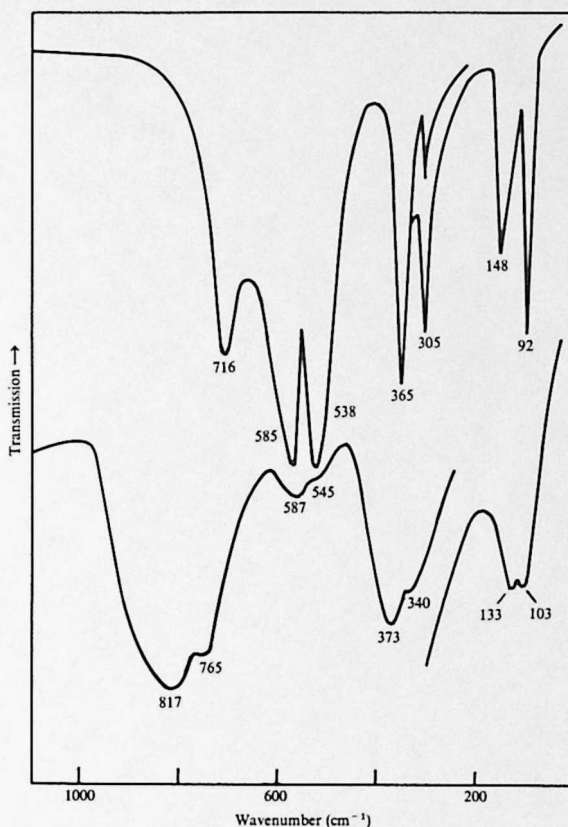

Figure 1. *Infrared spectra of $PbAs_2O_6$ crystal (upper spectrum) and glass*

lations. Similarly, glassy $Pb(PO_3)_2$ exhibits a strong band at 120 cm^{-1}, and a band at 116 cm^{-1} has been reported for glassy PbB_4O_7.[4]

It is highly probable that the formation of glassy $PbAs_2O_6$ is allowed (or at least greatly favoured) by the transformation of AsO_6 groups into AsO_4 groups (no glass could be obtained with $PbSb_2O_6$, and this may be related to the fact that SbO_4 tetrahedra do not exist). Another factor is the possible formation of covalent, directional Pb–O bonds (e.g. as PbO_4 pyramids). The evidence for such bonds in various lead borates has been demonstrated by the occurrence of infrared bands in the 400–300 cm^{-1} region.[4] In the present case, however, the spectroscopic evidence is inconclusive because of the existence, in the same spectral region, of the strong bands assigned to AsO_4 bending vibrations.

We are planning a Raman study, which should present additional evidence for the proposed change in coordination.

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High resolution magic angle spinning ^{31}P nuclear magnetic resonance studies of phosphate glasses

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^{31}P nuclear magnetic resonance spectra of phosphate glasses have been recorded while spinning the sample at the magic angle. In some cases, well resolved lines are obtained which provide quantitative information about composition and structure. In other cases a link between spectral features and different types of phosphate unit can be established but we have to resort to arbitrary decomposition procedures to obtain the intensities of the spectral components. Some glasses have featureless spectra which give little qualitative information.

Solid state nuclear magnetic resonance techniques are in the process of becoming a major tool in structural studies of disordered materials. In particular, ^{29}Si and ^{27}Al investigations have recently provided new insights about silicates and aluminium compounds.[1,2] However, the ^{31}P resonance has so far found little use in studies of phosphate glasses, the reason being that the stationary spectra of solid phosphates are often dominated by a large (~ 200 ppm) chemical shift anisotropy.[3-5] Here, we will illustrate the potential of ^{31}P nuclear magnetic resonance in studies of condensed phosphates,[6] i.e. solids in which the phosphorus is surrounded by four oxygens (PO$_4$ units).

All the spectra discussed here have been collected at room temperature with a Nicolet spectrometer and a superconducting magnet with $H_0 = 3.6$ Tesla. For each sample we took both stationary and magic angle spinning spectra. Many side bands were usually observed in the latter, and these were identified by comparing spectra taken at different spinning rates. Most of the samples studied were vitreous borophos-

phates of the composition MX–M$_2$O–B$_2$O$_3$–P$_2$O$_5$ (M = Li, Ag; X = Cl, I).[7]

It is well known that different types of PO$_4$ unit exist in the binary M$_2$O–P$_2$O$_5$ phosphate system; (i) branching units, O = P – O$_3$, which have three bridging oxygens and are neutral, (ii) middle units, which have two bridging oxygens and a negative charge, (iii) end units, which have one bridging oxygen and a -2 charge, and (iv) monomeric units which constitute the orthophosphates M$_3$PO$_4$. In the binary phosphates we found that these signals were usually well separated in a magic angle spinning spectrum. An example is the spectrum of a glass of nominal composition Ag$_2$O, 0·75P$_2$O$_5$, which is known to contain middle and end units (trace (a) of Figure 1). This spectrum consists of two nearly Gaussian lines, which are assigned to middle and end units bonded to silver. The normalised intensities of these lines would correspond to Ag$_2$O, 0·71P$_2$O$_5$ and the small difference relative to the nominal composition is probably due to evaporation of P$_2$O$_5$ during the making of the glass, rather than to the uncertainty in the nuclear magnetic resonance intensities (<1% in this case). We have analysed a number of silver phosphates and have always found magic angle spinning peaks centred within few ppm from the marks at the top of Figure 1. In vitreous phosphates containing silver, each type of unit appears to have a characteristic full width, Δ, which varies from ~ 5 ppm for the monomer to ~ 12 ppm for the branching unit.

The spectrum shown in trace (b) of Figure 1 consists of partially overlapping Gaussian lines (dotted curves) and refers to a silver borophosphate. The small peak on the left side (intensity 1·3%) is due to monomeric units and its small width ($\Delta = 1$ kHz, independent of H_0) is characteristic of crystalline Ag$_3$PO$_4$, although no Bragg peaks were observed in this sample by x-ray

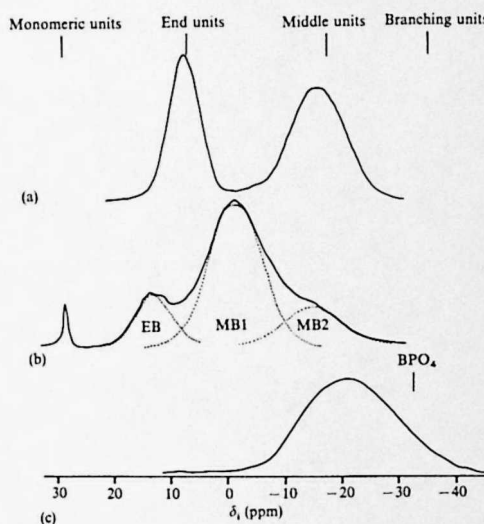**Figure 1.** ^{31}P *magic angle spinning nuclear magnetic resonance spectra of vitreous phosphates*
(a) glass with the nominal composition Ag$_2$O, 0·75P$_2$O$_5$: the marks give the average isotropic shifts of the units determined in a number of silver phosphates
(b) Ag$_2$O, 1·6B$_2$O$_3$, 0·4P$_2$O$_5$ glass
(c) Li$_2$O, 0·8B$_2$O$_3$, 1·2P$_2$O$_5$ glass: the crystalline BPO$_4$ shift is indicated

diffraction. The other peaks in trace (b) of Figure 1 have been associated with an end unit with an oxygen bridging to a boron (EB), a middle unit connected to two borons (MB2), and a middle unit connected to one boron and one phosphorus (MB1). The evidence supporting these assignments comes from analyses of nuclear magnetic resonance and Raman spectra of many silver borophosphates, which will be described in a full article. Here, we will mention only that discrimination between the signal of the MB1 and middle units requires a correlative use of stationary and spinning nuclear magnetic resonance spectra. In fact, while the magic angle spinning signals of these units nearly overlap, the anisotropic chemical shift, δ_a, is about -150 ppm for a middle unit and about -100 ppm for a MB1 unit. The chemical shift tensors of these units also differ in the average asymmetry parameter, η, which is ~0.55 for middle units and ~0.85 for MB1 units.

While we have identified the spectral ranges characteristic of several borophosphate units, we have been unable, so far, to estimate how accurately the intensities of the decomposed peaks in trace (b) of Figure 1 reproduce the population of the units. These intensities may depend upon the decomposition procedure (number of peaks allowed, strategy for parameter optimisation, etc.). For example, within a root mean square deviation of 9%, the magic angle spinning spectrum of trace (c) of Figure 1 can be described by a single Gaussian line. However, in this lithium borophosphate glass there are probably branching, middle, MB1, and 'BPO$_4$' units; the last type of unit is found in the silica like crystalline BPO$_4$, in which the PO$_4$ units have four bridging oxygens and a nominal $+e$ charge.

It should be noted that the position of the BPO$_4$ signal does not agree with the simple correlation between δ_i and the PO$_4$ charge, which is implied by the marks above trace (a) of Figure 1. Furthermore, we found that the isotropic shift of the same unit depends upon the cation, and apparently correlates with the radius of the cation rather than with its electronegativity. Extensive studies of phosphate esters in solution have given evidence of empirical correlations between the ^{31}P nuclear magic resonance chemical shifts and the distortion of the phosphorus environment from the tetrahedral symmetry.[8] The above observations suggest the relevance of geometrical effects in determining the δ_i of the units found in inorganic phosphates.

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