STRUCTURE AND DEVITRIFICATION CHEMISTRY OF RE(PO₃)₃ (RE = La, Pr, Nd, Gd, Dy, Y) METAPHOSPHATE GLASSES

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Abstract The devitrification and structure of RE(PO₃)₃ (RE = La, Pr, Nd, Gd, Dy, Y) glasses are studied by infrared spectroscopy, X-ray diffraction and differential thermal analysis. The results from devitrification experiments show that RE(PO₃)₃ glasses (regardless of the size of RE³⁺) crystallize first to give monoclinic Yb(PO₃)₃ type crystals. The IR spectra of devitrified La, Pr, and Nd samples differ, however, from those of Gd, Dy and Y in the range of symmetric POP stretching frequencies. To unravel the differences demonstrated in the IR spectra of devitrified RE(PO₃)₃, we performed preliminary Rietveld refinement on the crystal structure of the "metastable" Nd(PO₃)₃ [monoclinic, P2₁/c a = 11.468(4) Å, b = 20.438(7) Å, c = 10.256(3) Å, β = 97.11(1)', Z = 12] and compared it to previously reported Yb(PO₃)₃. Comparisons between the IR spectra of the series of RE(PO₃)₃ glasses and related crystals show that νasPO2 and νasPOP stretching frequencies shift in the spectra of glasses which is explained with the alteration of chain conformation and subsequent decrease in POP bond angles in the glass network.

INTRODUCTION

Rare-earths metaphosphate glasses, RE(PO₃)₃ display a range of attractive properties at low temperatures: negative thermal expansion¹, negative pressure dependence of bulk moduli² and unprecedented magnetic, magneto-optical and opto-acoustic phenomena ³⁴. Due to the high structural complexity of glasses they were studied by a wide range of structural methods such as EXAFS⁵⁻⁹, XANES¹⁰, MAS NMR¹¹, Raman spectroscopy¹²⁻¹⁴, neutron and X-ray diffraction¹⁵⁻¹⁸. Neutron diffraction studies of Cole et al.¹⁵, Hoppe et al.¹⁸ quantified the immediate rare-earth environment and resolved the contributions of (PO₂) terminal and (POP) bridging bond separations. Rare-earths LIII-edge EXAFS studies⁵⁻⁹ confirmed these findings yielding average RE–O distances of 2.42(1)–2.23(1) Å (where RE = La–Er). K-edge EXAFS measurements extended over a 20–293 K temperature range showed that RE(PO₃)₃ glasses are extremely rigid: the Debye-Waller factors of the Re–O shell being very small and equal within experimental error.¹⁹ Reverse Monte Carlo modeling by Mountjoy et al.²⁰ showed that the structure of RE(PO₃)₃ glasses can be described as an arrangement of chains of phosphate tetrahedra with lanthanide ions six-fold coordinated to non-bridging oxygens (NBO's).

There have been a few studies, however, focused on the vibrational structure of vitreous RE(PO₃)₃ and its relation to the anomalous thermal, optical and acoustic properties of these glasses. The gap in vibrational data stems primarily from the lack of single crystal and normal coordinate studies on the crystalline RE(PO₃). Moreover, there have been a limited number of reports dealing with the spectra of polycrystalline
as well. Begun and Bamberger\textsuperscript{21} reported the Raman spectra of orthorhombic and monoclinic rare earth metaphosphates and revealed that the pattern of $\nu_{as}PO_2$ mode can be used to distinguish between the two types of structures. By means of high temperature Raman spectroscopy Balagina \textit{et al.}\textsuperscript{22} studied the phase transitions of RE(PO$_3$)$_3$ and determined the ranges of temperature stability for each phase.

This contribution is a part of our program to explore the vibrational spectra and devitrification chemistry of metaphosphate glasses. In our previous publications \textsuperscript{23} we studied the crystallization of RPO$_3$ glasses (where R = alkali, alkali–earth cation) and showed that the kinetics of nucleation and crystal growth are strongly influenced by reconstruction process. In this work we prepared a series of RE(PO$_3$)$_3$ (Re = La, Pr, Nd, Gd, Dy, Y) glasses, recorded their IR spectra and studied the devitrification behavior of the glasses with an emphasis on the metastable Nd(PO$_3$)$_3$ and its crystal structure. Furthermore, we compared the IR spectra of glasses and crystals of relevant composition and discussed the compositional dependence of the features present in their spectra.

\textbf{EXPERIMENTAL}

RE(PO$_3$)$_3$ (RE = La, Pr, Nd, Gd, Dy, Y) glasses were prepared by mixing 25 mol\% reagent grade RE$_2$O$_3$ in the presence of 5 mol\% excess NH$_4$H$_2$PO$_4$. All samples were melted in aluminium oxide crucibles for 20 minutes in the temperature range 1280 – 1450 °C. The glass compositions were analyzed by a JEOL 733 electron probe microanalyzer and found to correspond to the metaphosphate formulae with an average deviation of ± 1 wt\% RE$_2$O$_3$.

Infrared absorption spectra were recorded on a Bruker (IFS 113 v) FT–IR spectrometer in the 4000 – 400 cm$^{-1}$ spectral region with resolution of 2 cm$^{-1}$. Samples in powder form were pressed into disks using spectroscopic KBr.

The devitrification behavior of RE(PO$_3$)$_3$ glasses was studied by differential thermal analysis (DTA). DTA curves were recorded on powdered samples at a heating rate of 10 K/min using a Perkin Elmer thermo–analyser. The XRD patterns of the devitrified specimens were collected in the 10–60° 2θ range with a step of 0.05° using CuK$_\alpha$ radiation.

The X–ray spectrum of the metastable Nd(PO$_3$)$_3$ obtained by crystallization from glass at 630 °C for 72 h was recorded on a Philips powder diffractometer in the 5 –130° (2θ) range using a step size of 0.025° (2θ) and a counting time of 40 sec per step.

\textbf{RESULTS AND DISCUSSION}

The thermal properties of RE(PO$_3$)$_3$ glasses are summarized in Table 1. The DTA curves of La, Pr, Nd, glasses show two exothermal peaks (Tc$_1$, Tc$_2$) in the 640–660 and 780–800 °C ranges. The X–ray patterns of the phases obtained at Tc$_1$ are similar to each other resembling monoclinic Yb(PO$_3$)$_3$.\textsuperscript{24} Upon increasing temperature and time these phases convert into orthorhombic RE(PO$_3$)$_3$\textsuperscript{25} metaphosphate form. Dy(PO$_3$)$_3$ and Y(PO$_3$)$_3$ glasses demonstrate single stage crystallization behavior devitrifying into Yb(PO$_3$)$_3$ type crystals. Glassy Gd(PO$_3$)$_3$ takes intermediate position between the two groups crystallizing into two phases both similar to monoclinic Yb(PO$_3$)$_3$. 

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
RE & Tc$_1$ & Tc$_2$ & Tc$_3$ & Tc$_4$ & Tc$_5$ \\
\hline
La & 640 & 780 & 900 & 1000 & 1100 \\
Pr & 650 & 790 & 920 & 1020 & 1130 \\
Nd & 660 & 800 & 940 & 1050 & 1180 \\
Gd & 670 & 820 & 960 & 1080 & 1210 \\
Dy & 680 & 830 & 980 & 1100 & 1250 \\
Y & 700 & 850 & 1000 & 1150 & 1300 \\
\hline
\end{tabular}
\caption{Thermal properties of RE(PO$_3$)$_3$ glasses.}
\end{table}
TABLE 1. Thermal properties of RE(PO₃)₃ (RE = La, Pr, Nd, Gd, Dy, Y) glasses (T_g – glass transition temperature, T_c1 – maximum of the first crystallization peak, T_c2 – maximum of the second crystallization peak on the DTA curves)

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Pr</th>
<th>Nd</th>
<th>Gd</th>
<th>Dy</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_g</td>
<td>620</td>
<td>610</td>
<td>630</td>
<td>540</td>
<td>725</td>
<td>795</td>
</tr>
<tr>
<td>T_c1</td>
<td>640</td>
<td>640</td>
<td>660</td>
<td>620</td>
<td>860</td>
<td>945</td>
</tr>
<tr>
<td>T_c2</td>
<td>780</td>
<td>795</td>
<td>800</td>
<td>660</td>
<td>–</td>
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</tr>
</tbody>
</table>

The IR spectra of RE(PO₃)₃ (RE = La, Nd, Pr, Gd, Dy, Y) glasses are presented in Fig. 1. Fig. 2 shows the IR spectra of crystalline RE(PO₃)₃ obtained by devitrification at T_c1. In this work we shall not discuss the spectra of the orthorhombic RE(PO₃)₃ since these have been published previously. The experimental IR frequencies observed for the spectra of glassy and crystalline RE(PO₃)₃ along with suggested assignments are summarized in Table 2.

FIGURE 1. IR spectra of RE(PO₃)₃ glasses

FIGURE 2. IR spectra of crystalline RE(PO₃)₃ obtained by devitrification at T_c1
The IR spectra of glasses show five major bands at ~1266-1250, 1190-1070, 934-912, 780-720 and 535-464 cm\(^{-1}\) which fall in characteristic ranges separated from each other by minima. The bands in these ranges can be associated with \(\nu_{as}PO_2\), \(\nu_{ss}PO_2\), \(\nu_{as}POP\), \(\nu_{ss}POP\) and \(\delta PO_2\) chain modes in agreement with normal coordinate analysis of Ba(PO\(_3\))\(_2\). 27 Decreasing the radius of RE\(^+\) within the series of RE(PO\(_3\))\(_3\) glasses shifts gradually the \(\nu_{as}PO_2\) band from 1266 cm\(^{-1}\) for La(PO\(_3\))\(_3\) to 1250 cm\(^{-1}\) for Y(PO\(_3\))\(_3\) glass. Simultaneously, the bands due to \(\nu_{as}POP\) move in opposite direction increasing in frequency from 913 to 728,709,682 cm\(^{-1}\).

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### Table 2. Experimental IR frequencies observed in the spectra of RE(PO\(_3\))\(_3\) (RE = La, Pr, Nd, Gd, Dy, Y) glasses and crystals obtained by devitrification at Tc\(_1\)

<table>
<thead>
<tr>
<th>Composition</th>
<th>(\nu_{as}PO_2)</th>
<th>(\nu_{ss}PO_2)</th>
<th>(\nu_{as}POP)</th>
<th>(\nu_{ss}POP)</th>
<th>(\delta PO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(PO(_3))(_3) crystal</td>
<td>1246</td>
<td>1177,1150</td>
<td>986,915</td>
<td>725,708,678</td>
<td>418</td>
</tr>
<tr>
<td>La(PO(_3))(_3) glass</td>
<td>1263</td>
<td>1170,1069</td>
<td>771,724</td>
<td>532,470</td>
<td></td>
</tr>
<tr>
<td>Pr(PO(_3))(_3) crystal</td>
<td>1246</td>
<td>1178,1150</td>
<td>987,916</td>
<td>788,768,754</td>
<td></td>
</tr>
<tr>
<td>Pr(PO(_3))(_3) glass</td>
<td>1261</td>
<td>1165,1073</td>
<td>774,724</td>
<td>528,464</td>
<td></td>
</tr>
<tr>
<td>Nd(PO(_3))(_3) crystal</td>
<td>1247</td>
<td>1180,1150</td>
<td>994,925</td>
<td>768,750,727</td>
<td></td>
</tr>
<tr>
<td>Nd(PO(_3))(_3) glass</td>
<td>1259</td>
<td>1078</td>
<td>779</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Gd(PO(_3))(_3) crystal (I)</td>
<td>1249</td>
<td>1189,1160</td>
<td>1018,1000</td>
<td>787,771,752</td>
<td></td>
</tr>
<tr>
<td>Gd(PO(_3))(_3) crystal (II)</td>
<td>495,447,422</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd(PO(_3))(_3) glass</td>
<td>1249</td>
<td>1089</td>
<td>730,708,680</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td>Dy(PO(_3))(_3) crystal</td>
<td>1252</td>
<td>1175,1168</td>
<td>1014,942</td>
<td>785,770,746</td>
<td>592</td>
</tr>
<tr>
<td>Dy(PO(_3))(_3) glass</td>
<td>1250</td>
<td>1184,1082</td>
<td>771,720</td>
<td>535,473</td>
<td></td>
</tr>
<tr>
<td>Y(PO(_3))(_3) crystal</td>
<td>1254</td>
<td>1179,1171</td>
<td>1023,944</td>
<td>789,772,748</td>
<td></td>
</tr>
<tr>
<td>Y(PO(_3))(_3) glass</td>
<td>1235</td>
<td>1096</td>
<td>713,685</td>
<td>483,416</td>
<td></td>
</tr>
</tbody>
</table>
934 cm\(^{-1}\). The frequency shifts of the bands associated with \(v_\text{PO}_2\) and \(\delta\text{PO}_2\) are on a smaller scale (±5 cm\(^{-1}\)). The bands observable in the spectra of crystalline RE(PO\(_3\))\(_3\) also fit into five characteristic ranges corresponding to \(v_\text{as} \text{PO}_2\), \(v_\text{s} \text{PO}_2\), \(v_\text{as} \text{POP}\), \(v_\text{s} \text{POP}\) and \(\delta\text{PO}_2\) modes. It is worth noticing that the effect of the lanthanide contraction shifts all bands in the spectra of the series of iso-structural RE(PO\(_3\))\(_3\) crystals into higher energies thus a clear discrepancy in the behavior of \(v_\text{as} \text{PO}_2\) mode in the spectra of RE(PO\(_3\))\(_3\) glasses and crystals is observed. Furthermore, comparisons of the spectra of crystalline RE(PO\(_3\))\(_3\) show that the nature of the \(v_\text{POP}\) bands in the spectra of La, Pr, Nd, and Gd(I) (group I) differs from those of Gd(II), Dy, and Y (group II) samples. As can be seen in Fig. 2 the components of the \(v_\text{POP}\) mode in the IR spectra of group (I) rare-earth metaphosphates possess lower relative intensities compared to their counterparts in the spectra of group (II).

Rare earth metaphosphates occur in five different structural forms: an orthorhombic, characteristic for lanthanides from La to Gd \(^{28}\) two monoclinic forms spanning Sm–Lu (P\(_2_1/c\))^\(^{28}\) and Tb–Lu (Pm)^\(^{29}\), a cubic tetrametaphosphate (Yb–Lu)^\(^{29}\) and a trigonal Yb(PO\(_3\))\(_3\)^\(^{30}\). From a structural point of view the chain structures may be characterized by the periodicity of the chain \([\text{PO}_3\text{O}]_{n}\) with \(n = 2, 3, 4\)? The majority of the rare-earth metaphosphates have a structure based on \([\text{PO}_3\text{O}]_{n}\) chains whose configuration is governed by the set of symmetry operations of the space group (cf. Fig. 3). The trigonal Yb(PO\(_3\))\(_3\) (\(R\bar{3}\) space group)^\(^{30}\) is an exception comprising chains with 12 tetrahedra per period.

![Diagram](image)

**FIGURE 3.** Configurations of infinitive chains of PO\(_4\) tetrahedra in crystalline RE(PO\(_3\))\(_3\)

The structure of the metastable RE(PO\(_3\))\(_3\) crystallizing from La, Pr and Nd metaphosphate glasses at temperatures near \(T_g\) was apparently unknown prior to this report. This structure is of crucial importance understanding the network arrangement of glassy RE(PO\(_3\))\(_3\) since i) it bears genetic relation to the structural motif in glass and ii) none of the structural probes used so far has succeeded in resolving the nearest RE–RE
correlation in the glasses. Powder X-ray diffraction patterns of the metastable Nd(PO₃)₃ can be indexed according to the monoclinic P2₁/c, space group with unit cell parameters: a = 11.469(4) Å, b = 20.438(7) Å, c = 10.256(3) Å, β = 97.11(1)°, Z = 12. Preliminary Rietveld refinement has shown that the phase is isostructural with previously reported monoclinic Yb(PO₃)₃. The unit cell contains two distinct types of [(PO₃)₆]²⁻ chains oriented along the C₂ screw axis. The Nd–O polyhedra are isolated octahedra, each linking four neighboring [(PO₃)₆]²⁻ chains into a three-dimensional lattice. Detailed description on the crystal structure including the atomic coordinates, temperature factors, bond distances and angles will be published elsewhere. Although the chain arrangement remains the same in both structures, the small differences in the configuration of REO₆ octahedra (NdO₆ octahedra possess greater distortion) influence the corresponding IR spectra. The differences between the IR spectra of group (I) and group (II) RE(PO₃)₃ may be thus related to the level of distortion of REO₆ octahedra within the series of isostructural P2₁/c crystals.

Comparisons between the IR spectra of RE(PO₃)₃ glasses and their crystalline counterparts reveal three principal tendencies. First, the crystal-to-glass transition is accompanied by changes in the positions of the stretching bridge frequencies. In the spectra of glasses v₃PO bands are shifted into lower wavenumbers as compared to their initial positions in the spectra of the crystals. Second, the effect of the lanthanide contraction shifts v₅PO₂ bands to lower frequencies in the spectra of glasses (1266 cm⁻¹ for La(PO₃)₃ → 1250 cm⁻¹ for Y(PO₃)₃) and to higher wave-numbers in the spectra of the crystals (1246 cm⁻¹ for La(PO₃)₃ → 1256 cm⁻¹ for Y(PO₃)₃). Third, decreasing the size of RE³⁺ minimizes the differences in vibrational frequencies between crystal and glass of identical composition: e.g. the spectral shift of v₅PO₂ mode is nearly 20 cm⁻¹ for the couple of La(PO₃)₃ metaphosphates and 4 cm⁻¹ for the pair of glassy and crystalline Y(PO₃)₃.

The shifts in POP stretching frequencies are generally considered to reflect changes in POP bond angles. Normal coordinate analyses of condensed silicate and phosphate structures showed that decreasing v₃-­v₅ frequency separation corresponds to a decrease in the POP (SiOSi) bond angle. Frequency shifts of v₅PO and v₃PO in the spectra of other vitreous phosphates such as Ga(PO₃)₃, Cu(PO₃)₃, M₁M₂P₂O₇ (M₁ = alkali cation, M₂ = Al, Ga, Fe), Nd ultraphosphate glasses and interpreted in terms of decreasing POP angles in the glass network. The change in POP bond angles suggests that i) the metaphosphate chains adopt different conformation in the glass and ii) the "symmetry" of the field around the RE³⁺ differ from that in the corresponding crystals. In terms of the fact that the POP angles in monoclinic (P2₁/c) type RE(PO₃)₃ fall in the range 157–128° and accounting for the decrease in the v₅PO–v₃PO frequency difference in the spectra of glasses, it is reasonable to assume that glassy RE(PO₃)₃ consist of chains with smaller POP angles very probably in the 135–109° range. In our previous publications we showed that the alteration of the chain conformation in the glass may result from the small energy for deformation and rotation of POP bond angles. Normal coordinate analyses on crystalline phosphates showed that POP force constants are very small especially those involving out-of-plane motion of bridging oxygen atoms. The energy of the low frequency modes is comparable with thermal
energy ($kT = 200 \text{ cm}^{-1}$ at ambient temperature) suggesting that the changes in the configuration of the polyphosphate chains may stem from the increased thermal population of low-frequency modes (deformation, rotation and torsion of bridging oxygen atoms) near $T_g$. The marked non-linear elastic behavior\textsuperscript{2,36} and negative thermal expansion\textsuperscript{1} of RE(PO$_3$)$_3$ glasses (i.e. properties governed by thermal motion) present evidence for the level of vibrational anharmonicity and the role of the low frequency modes in the vibrational dynamics of these materials. According to Angell \textsuperscript{37} the generation of low frequency modes suffices to explain the sharp increases in both low frequency light scattering and mean square displacement, seen for some super-cooled liquids as $T > T_g$.

As mentioned earlier, decreasing the size of RE exerts non-uniform influence on the behavior of $v_{\text{as}}$PO$_2$ mode in the spectra of RE(PO$_3$)$_3$ glasses and relevant crystals. This result suggests that the effect of the lanthanide contraction exerts a smaller influence on the P–O– force constants in the spectra of the RE(PO$_3$)$_3$ glasses than it does in the spectra of their crystalline counterparts. Diffraction\textsuperscript{15-18} and EXAFS\textsuperscript{5-9} measurements performed on vitreous RE(PO$_3$)$_3$ showed that the RE–O coordination numbers decrease from 6.6 at La(PO$_3$)$_3$ to 6.0 at Er(PO$_3$)$_3$ and most authors explained these findings by possible RE–RE clustering in the glass network. The increase in $v_{\text{as}}$PO$_2$ mode frequency in the spectra of La, Pr and Nd metaphosphate glasses over the corresponding values in the spectra of the crystals observed here also favors this interpretation. On the other hand, the possible clustering of RE ions in RE(PO$_3$)$_3$ (RE = La–Nd) glasses does not conform to the observed linear dependence of the macroscopic density of rare-earth metaphosphate glasses as a function of the radius of RE$^{3+}$: the density linearly increases from 3.30 g/cm$^3$ for La(PO$_3$)$_3$ to 3.63 g/cm$^3$ for Yb(PO$_3$)$_3$ glass.\textsuperscript{38} Furthermore, the relationship between an optical property such as the refractive index ($n_0$) and the radius of RE$^{3+}$ also linearly changes across the series of RE(PO$_3$)$_3$ glasses.\textsuperscript{38} If RE(PO$_3$)$_3$ glasses fell into two distinct structures: the first based on clusters of RE polyhedra (La–Nd) and second containing isolated REO$_6$ octahedra (Gd–Y) then the structure/property relationships would display a crossover at the Gd(PO$_3$)$_3$ composition. Furthermore, clustering of RE ions would increase the average P–O$_{\text{ab}}$ bond distance as found in the orthorhombic Nd(PO$_3$)$_3$ where the bond distance between the P atom and three-fold oxygen reaches 1.571(9) Å.\textsuperscript{25} Neutron diffraction studies performed on glassy Nd(PO$_3$)$_3$ resolved the contributions of P–O$_{\text{ab}}$ and P–O$_b$ separations yielding an average P–O$_{\text{ab}}$ distance of 1.49(5) Å which suggests that the fraction of three-fold oxygens is negligibly small. The asymmetry of the peak associated with the RE–O separation in a T(r) correlation function of La and Nd metaphosphate glasses may result from the great anisotropy of RE–O distances present in the glass. Within the series of iso-structural RE(PO$_3$)$_3$ (RE = La,\textsuperscript{39} Ce,\textsuperscript{40} Nd) the level of distortion of the REO$_6$ polyhedra appears to decrease with increasing atomic number, presumably because the rare-earth ion becomes more accommodating as it decreases in size. The same trend has been observed for the $P2_1/c$ type REP$_5$O$_{14}$ (RE = La, Eu, Gd) ultraphosphates.\textsuperscript{41} If we correlate the asymmetry of the RE–O peak in a T(r) function of Nd(PO$_3$)$_3$ glass with the anisotropy of the Nd–O bond lengths in the NdO$_6$ octahedra and take account of the fact that the P–O$_{\text{ab}}$ distances are almost equal in the glass and $P2_1/c$ crystals then the change in $v_{\text{as}}$PO$_2$ force constants may stem from the alteration in the “O–P–O” bond angles. At this stage, it cannot be stated definitely if the increase in
nPO₂ mode frequency in the IR spectra of RE(PO₃)₃ (RE = La–Nd) glasses is due to clustering of RE or is due to alteration in the "O–P–O" bond angles. However, this issue can be resolved by calculating the coordinates of normal modes of the C222₁ RE(PO₃)₃ structure (containing three-fold oxygen atoms), which is a subject of our forthcoming report.⁴²

The comparison between the IR spectra of the RE(PO₃)₃ glasses and their crystalline counterparts indicates that the structure of RE(PO₃)₃ glasses is very similar but not identical to that of the monoclinic (P2₁/c) metaphosphate crystal form (cf. Fig.4). The larger spectral (structural) differences between RE(PO₃)₃ (RE = La–Nd) glasses and corresponding crystals may be related primarily to the difficulties which the largest RE ions find whilst accommodating themselves in the P2₁/c structural framework. Since the P2₁/c structural form is uncommon for group (I) crystalline RE(PO₃)₃ compounds the vitrifying liquids of such composition avoid crystallization by transforming themselves into maximum volume structures modifying more substantially the basic framework of the P2₁/c structural type.

CONCLUSIONS
RE(PO₃)₃ (RE = La, Pr, Nd, Gd, Dy, Y) glasses crystallize first to give monoclinic Yb(PO₃)₃ type crystals. The differences observed in the range of νPO₂ mode in the spectra of group (I – La, Pr, Nd, Gd(II)) and group (II – Gd(II), Dy, Y) crystalline RE(PO₃)₃ can be related to the level of distortion of REO₆ octahedra. The close correspondence between the IR spectra of glassy RE(PO₃)₃ and their crystalline counterparts suggests that the structure of glasses is broadly similar but not identical to that of the P2₁/c crystalline RE(PO₃)₃ type. The shifts of stretching bridge frequencies in the spectra of glasses may be explained by the

FIGURE 4. IR spectra of vitreous, monoclinic and orthorhombic Nd(PO₃)₃, obtained by devitrification at Tc₁ and Tc₂.

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CONCLUSIONS
RE(PO₃)₃ (RE = La, Pr, Nd, Gd, Dy, Y) glasses crystallize first to give monoclinic Yb(PO₃)₃ type crystals. The differences observed in the range of νPO₂ mode in the spectra of group (I – La, Pr, Nd, Gd(II)) and group (II – Gd(II), Dy, Y) crystalline RE(PO₃)₃ can be related to the level of distortion of REO₆ octahedra. The close correspondence between the IR spectra of glassy RE(PO₃)₃ and their crystalline counterparts suggests that the structure of glasses is broadly similar but not identical to that of the P2₁/c crystalline RE(PO₃)₃ type. The shifts of stretching bridge frequencies in the spectra of glasses may be explained by the
small energy for deformation and rotation of POP bond angles. The larger deviation of vibrational frequencies in the IR spectra of RE(PO₃)₃ glasses (where RE = La–Nd) from those in the corresponding crystals can be associated with difficulties which the largest RE ions face whilst trying to accommodate themselves in a liquid of "pseudo-monoclinic" type. The non-uniform behavior of ν₄PO₂ mode in the spectra of vitreous and crystalline RE(PO₃)₃ indicates that the effect of the lanthanide contraction exerts smaller influence on the P–O– force constants in the spectra of the glasses than it does in the spectra of the crystals.

REFERENCES

42. D. Ilieva et al. *J. Raman Spectrosc.* (to be published)