SYNTHESES, STRUCTURES AND RAMAN SPECTRA OF LUMINESCENT GADOLINIUM PHOSPHATES

C. T. Dinh[a,b,c], P. V. Huong[b], R. Olazcuaga[c], C. Fouassier[c]

[a] Centre of Analytical Sciences and Experimentation, Hochiminh City, Vietnam,
[b] Laboratoire de Physico-Chimie Moleculaire; CNRS UMR 582, University of Bordeaux 1, 33405 Bordeaux-Talence, France.
[c] Institut de Chimie de la Matière Condensée de Bordeaux, CNRS, 33608 Pessac, France

Various phases of the (Gd_2O_3-P_2O_5) system have been synthesized and characterized by several physical methods, in particular by Raman spectrocopy. The use of the anti-symmetrical stretching frequency of the PO_2 group is revealed to be very helpful for the characterization of the structure change and of the cycling in the lengthening of the phosphate chain by polymerization. The orthorhombic phase of GdP_3O_9 is isolated and identified. A parallelism is established between gadolinium phosphates and yttrium phosphates. Correlations have been established between the stretching frequencies and the size of the cation in the orthophosphates for the derivatives belonging to monazite structure as well as for zircon structure.

1. Introduction

Several phases of the system (Gd_2O_3, P_2O_5) present interesting luminescent properties, when doped with ions such as Ce^{3+}, Nd^{3+}, Eu^{3+}, or Tb^{3+}. Up to now, six of them are known: $Gd_8P_2O_{17}$ (4 :1); Gd_3PO_7 (3:1); $GdPO_4$ (1:1); $Gd_2P_4O_{13}$ (1:2); GdP_3O_9 (1:3) and GdP_5O_{14} (1:5) [1, 2 and unpubl. results].

In 1983, Sungur et al. [3] prepared GdP_5O_{14} at 700 and 900°C and suggested that the product got at 700°C can be indexed in the monoclinic system whereas at 900°C the material belongs to the orthorhombic system. These authors mentioned besides that their infrared spectra would indicate the presence of a phosphate ring. Some years later, in 1985, Agrawal and White studied the Raman spectrum of systems (Y_2O_3 - P_2O_5) and (Gd_2O_3-P_2O_5) and found a polymerization of the PO_4 groups in the phosphorus rich materials [4]. The crystal structure types of ortho, meta and penta-phosphate are known. The structure of $GdPO_4$ has been determined by Mullica et al. [5]. The metaphosphate GdP_3O_9 has been mentioned to occur in two forms [1, 6]. The determination of the two structures was done by the Rietveld method [unpubl. results]. The orthorhombic form is isostructural with NdP_3O_9 [7], while the monoclinic one is similar to YbP_3O_9 [8]. From the indexing of the powder pattern, Sungur et al. [3] have concluded that the monoclinic form of GdP_5O_{14} is isostructural to NdP_5O_{14} [7]. Besides, the obtention of some of these materials does not follow the same process according to various authors [1, 3, 9, 10].

Oxides with wide band gaps are interesting for their eventual applications as phosphors in plasma display panels. In the investigation of luminescent characteristics of lanthanide ions in gadolinium or yttrium phosphates, it appeared necessary to make an analysis of the products issued from preparations in different conditions in order to establish the technological way to get a given compound. It was also an opportunity to study the relationship between Raman molecular spectra and the structure of various phases of the system. Only fragmentary data on the Raman spectra had been

published [4, 18]. The accent will be put on the polymerized structure of phosphates groups. The conditions of formation of the orthorhombic form of GdP_3O_9 that had not been previously characterized will be discussed.

2. Experimental

2.1. Synthesis of mixed oxide materials

The different phases of the system $(Gd_2O_3-P_2O_5)$ have been prepared by solid phase reaction at temperatures ranging from 700°C to 1480°C after dissolution of the constituents in concentrated nitric acid then evaporation to dryness.

Starting materials are $NH_4H_2PO_4$ (99% minimum) from Merck; Gd_2O_3 (99.999%) from Johnson Matthey; Y_2O_3 (99,999%) from Rhodia and Eu_2O_3 (99,99%) from ACROS.

2.2. Raman spectroscopy

The Raman spectra have been recorded on a Raman microspectrometer DILOR OMARS 89 equipped with an ion argon laser source Spectra-Physics 2016 emitting at 514.5 nm and a helium neon laser emitting at 632.8 nm operating at 400 mW and with a CCD detector. The resolution of the Raman peak is 3 cm^{-1}.

3 Results and discussion

3.1. Influence of the phosphate enrichment on the Raman spectrum on the structure of the system

The Raman spectra of gadolinium phosphates exhibit large variations, as function of the ratio between Gd_2O_3 and P_2O_5. Some data on the shape and arrangement of PO_4 groups in gadolinium phosphates or isostructural phases are listed in Table 1 where the distances and bond angles of between atoms were obtained by Rietveld method. To facilitate the discussion, the number of apical oxygens in known phosphates is quoted in Table 2.

Table 1. Average P – O distances and O – P – O angles in ortho-, meta- and ultra-phosphates.

| COMPOUND	P – O (Å)		O – P – O (°)		References
	Apical oxygens	Bridging oxygens	Apical oxygens	Bridging oxygens	
$GdPO_4$	1.530		109.5		[5]
NdP_3O_9 Orthorhombic	1.528	1.584	117.4	102.1	[7]
YbP_3O_9 Monoclinic	1.487	1.599	119.3	102.0	[8]
GdP_3O_9 Orthorhombic	1.492	1.580	115.9	102.9	This work
NdP_5O_{14} (*) (**)	1.472 1.471	1.646 1.556	119.8	98.8 102.3	[7]
SmP_5O_{14} (*) (**)	1.474 1.471	1.605 1.556	122.4	100.2 102.5	[12]
GdP_5O_{14} (*) (**)	1;479 1.466	1.618 1.565	-	-	[21]

(*) Tetrahedra with two bridging oxygens.
(**) Tetrahedra with three bridging oxygens.

Table 2. Arrangements of PO_4 tetrahedra and number of apical oxygens per phosphorus atom in gadolinium phosphates.

Phosphates	Number O_{apex}	Arrangements of PO_4 groups	References
$Gd_8P_2O_{17}$	4	Isolated	[4]
Gd_3PO_7	4	Isolated	[4]
$GdPO_4$	4	Isolated	[5]
$Gd_2P_4O_{13}$	2.5	Probable P_4O_{13} group	[11]
GdP_3O_9	2	$(PO_3)_n$ chains	[7, 8]
GdP_5O_{14}	2 for 3/5 of P atoms 1 for 2/5 of P atoms	Ribbons made up of $2(PO_3)_n$ chains cross-linked by P atom	[7]

3.1.1 - Raman spectrum of $GdPO_4$

$GdPO_4$ possesses a monazite structure [5]. The PO_4 tetrahedra are isolated and show some slight distortions. The active vibrations in Raman scattering of a tetrahedron can be represented according to the following diagram [13].
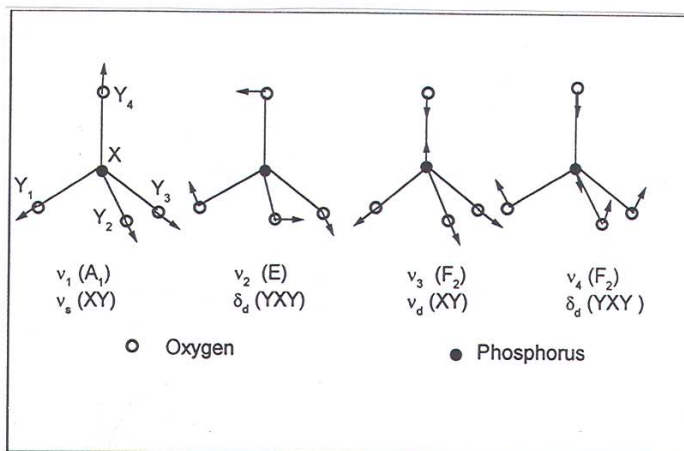
Fig. 1. The characteristic vibrations of the ion PO_4^{3-}.

For pure $GdPO_4$ as well as for $EuPO_4$, these vibrations have been determined (Fig. 2) and reported on Table 3. For $GdPO_4$, ν_3 is situated at 1070 cm^{-1} according to the correlation between the stretching frequencies and the size of the cation in the phosphate of the monazite structure family [5]. We also examined yttrium ortho-phosphates that belong to zircon structure family [14].

The totally symmetrical vibration ν_1 is the most intense; it represents the P-O stretching of the PO_4 unit in a tetrahedral structure. The peak situated at 1070 cm^{-1} corresponds to the antisymmetric stretching vibration ν_3. As for ν_2 and ν_4 vibrations, they represent the angle bendings of the PO_4 group (Table 3).

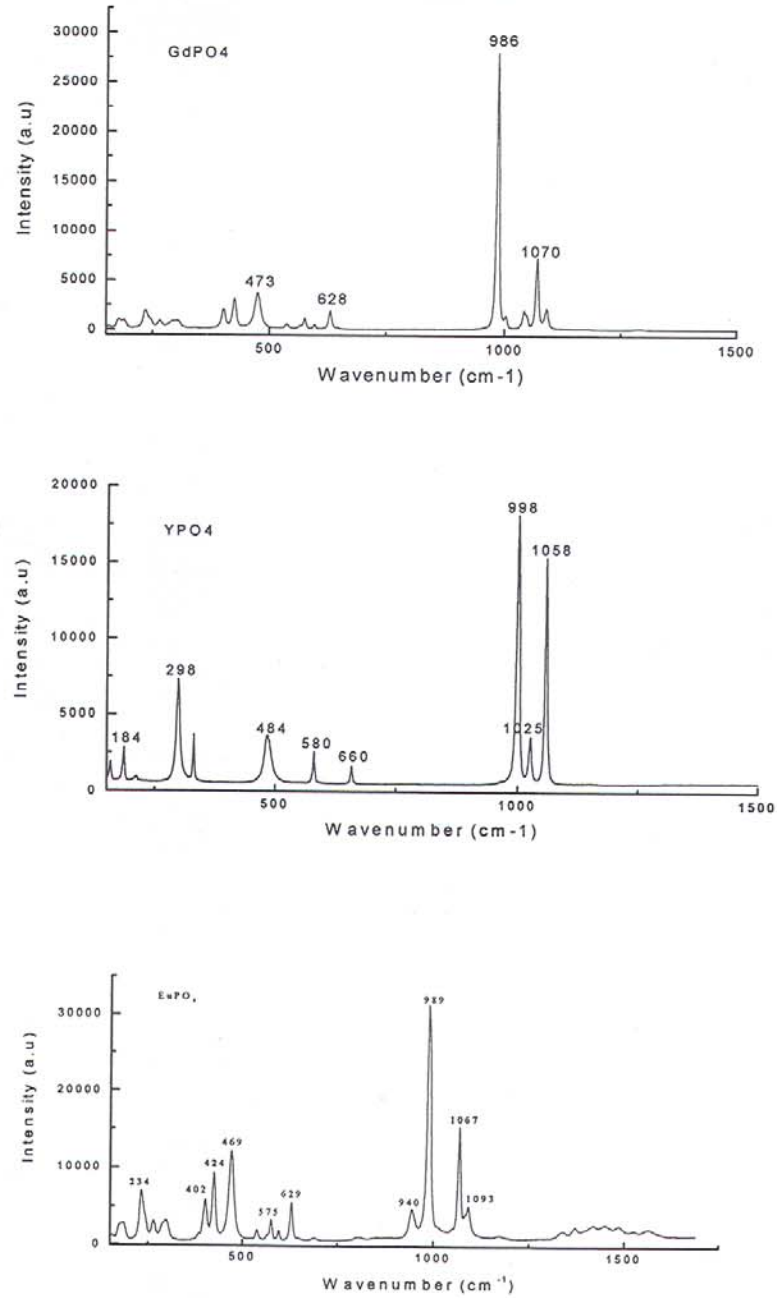On the same table, we also reported for comparison, the frequencies of other $LnPO_4$ phosphates.

Fig. 2. Raman spectrum of GdPO4, YPO$_4$, and EuPO$_4$.

Table 3. Characteristic frequencies (in cm^{-1}) of phosphates $LnPO_4$.

Phosphates	ν_1	ν_2	ν_3	ν_4	References
$LaPO_4$	967	465	991; 1025	572; 619	[18]
	955	-	1000-1100	540; 565; 580; 615	[15]
$CePO_4$	970	467	990; 1024	571; 618	[18]
	955	-	1000-1100	540; 565; 580 ;615	[15]
$PrPO_4$	974	469	994; 1028	572; 623	[18]
$NdPO_4$	977	470	997; 1032	574; 625	[18]
$SmPO_4$	982	473	999; 1035	575; 627	[18]
$EuPO_4$	989	471		597; 629	[18]
	989	470	1067	629	this work
$GdPO_4$	987	480	1004;1043	599; 632	[18]
	986	473	1070	628	this work
$TbPO_4$	995	484	1014; *1049*	576; 649	[18]
$DyPO_4$	998	485	1019; *1054*	578; 654	[18]
$HoPO_4$	1001	486	1021; *1055*	578; 656	[18]
YPO_4	1001	484	1027; *1058*	581; 660	[18]
	998	484	*1058*	660	this work
$ErPO_4$	1004	477	1024; *1061*	580; 659	[18]
$TmPO_4$	1006	488	1027; *1064*	580; 660	[18]
$YbPO_4$	1009	491	1030; *1068*	582; 663	[18]
$LuPO_4$	1011	493	1032; *1069*	587; 670	[18]

3.1.2. Raman spectrum of $Gd_2P_4O_{13}$

The crystal structure of $Gd_2P_4O_{13}$ is not yet known. Its Raman spectrum is shown in Fig. 3. Because of the difficulty in the preparation of this compound [1], a small amount of $GdPO_4$ is present in the product as revealed by the peaks at 985 and 1071 cm^{-1}. In our sample one remarks the *appearance* of new and intense peaks at 1182, 1231, 1242 and 689 cm^{-1} (Fig. 3).
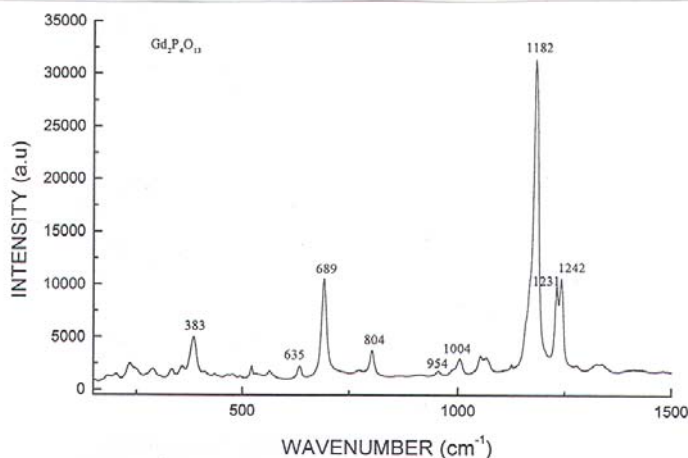
Fig. 3. Raman spectrum of $Gd_2P_4O_{13}$.

Because of the breakdown of the tetrahedral symmetry, the denomination of the above vibrations ν_1 and ν_3 in PO_4 ion is no longer valid and new vibrations appear that could be assimilated to ν_s and ν_a of the P-O-P bridges and to ν_s and ν_a of the PO_2 groups [19, 20] in the chain. The positions of the Raman peaks correspond to 1182 and 1231 cm^{-1} for PO_2 vibrations and to 689 and 1004 cm^{-1}

for P-O-P vibrations, respectively. In the chain of phosphates, PO_2 groups and P-O-P bridges can be represented with the following schema:
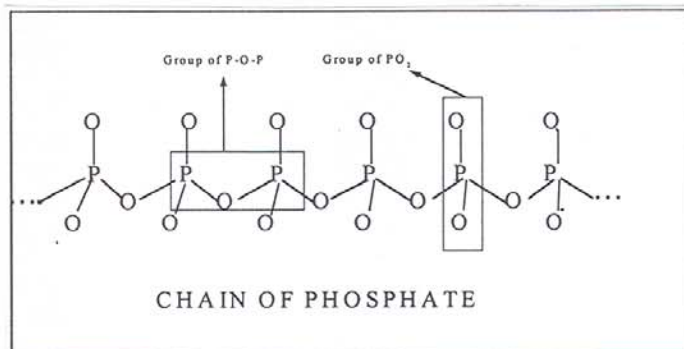
3.1.3. Raman spectrum of the monoclinic form of GdP_3O_9

In monoclinic metaphosphates GdP_3O_9, the PO_4 tetrahedra form $(PO_3)_n$ chains by sharing oxygens. The tetrahedra are strongly distorted. The bond lengths between phosphorus and bridging oxygens are longer than those between phosphorus and apical oxygens O_{ap} (Table 1). The angles O_{ap}-P-O_{ap} are considerably greater than the angles O_{br}-P-O_{br}.
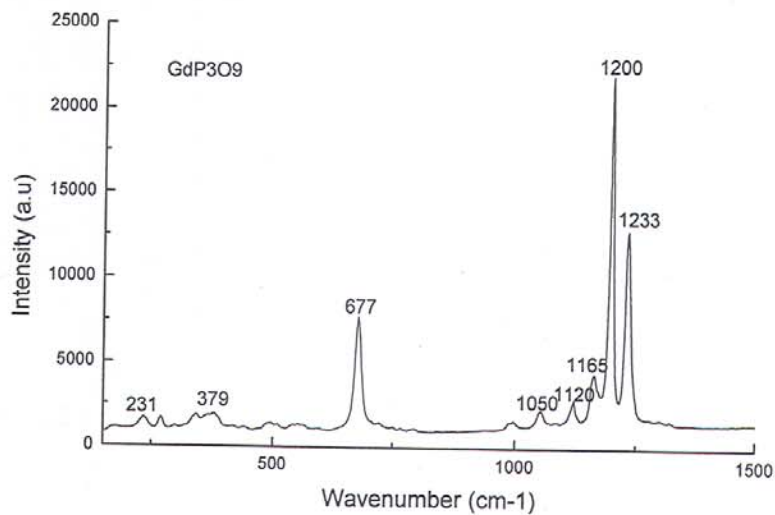

Fig. 4. Raman spectrum of GdP_3O_9.

In the Raman spectrum of GdP_3O_9 (Fig. 4), the vibrations corresponding to ν_s and ν_a of the PO_2 groups and the ν_s and ν_a vibrations of the POP bridges remain nearly unchanged compared to those of $Gd_2P_4O_{13}$. That is not surprising if we admit that in both structures, the PO_4 tetrahedra are all doubly connected with the neighbors.

3.1.4. Raman spectrum of GdP$_5$O$_{14}$

In GdP$_5$O$_{14}$ the PO$_4$ tetrahedra form ribbons made up of two chains (PO$_3$)$_n$ cross -linked by P atoms; The atomic arrangement can also be described as a monodimensional assembly of rings of eight PO$_4$ tetrahedra [7, 9]. The Raman spectrum of GdP$_5$O$_{14}$ shows a difference compared to those of GdPO$_4$ and Gd$_2$P$_4$O$_{13}$ (Fig. 5).
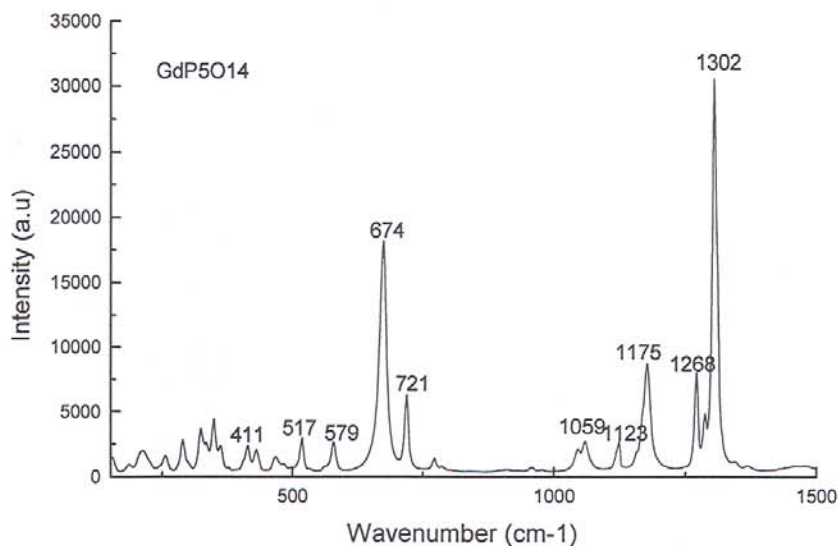
Fig. 5. Raman spectrum of GdP$_5$O$_{14}$.

With GdP$_5$O$_{14}$, the ν_s and ν_a vibrations of the PO$_2$ group are shifted distinctly toward higher frequencies and are located respectively at 1268 and 1302 cm^{-1} while the ν_s and ν_a vibrations of the P-O-P groups in the chain are nearly unchanged. This behaviour can be explained by the fact that PO$_2$ groups are much more exposed to the deformation of the structure in the cycling and to ion-ion interactions [16-17] than the P-O-P groups that are situated inside the chain and are therefore more protected. Table 1 shows that in ultra-phosphates the tetrahedra with two non-bridging oxygens are more distorted than in meta-phosphate.

3.1.5. Raman spectrum of orthorhombic GdP$_3$O$_9$

In orthorhombic GdP$_3$O$_9$ the PO$_4$ tetrahedra build helical (PO$_3$)$_n$ chains [7]. The obtained product presents a distinct Raman spectrum compared to those of monoclinic GdP$_3$O$_9$ and GdP$_5$O$_{14}$ (Fig. 6). In our spectra, the ν_s and ν_a vibrations of the PO$_2$ groups are located at 1200 and 1275 cm^{-1}. These frequencies are in between those of GdP$_3$O$_9$ and GdP$_5$O$_{14}$ (Table 4). Remind that by quantitative analysis of elements, its structure is found very closed to (1:3) and corresponds to the formula GdP$_3$O$_9$.

We note that for Gd$_2$P$_4$O$_{13}$ and monoclinic GdP$_3$O$_9$, no noticeable change was observed when the length of the phosphate chains changed. With the new phase that we found as orthorhombic GdP$_3$O$_9$, the strong increase of its frequency ν_a (PO$_2$) can be explained by a stronger constraint of the PO$_x$ group in a chain in comparison to more relaxed PO$_x$ groups in the monoclinic variety GdP$_3$O$_9$.
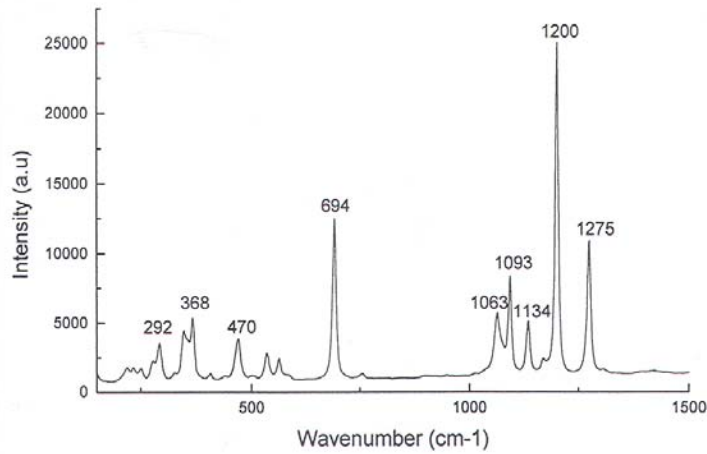
Fig. 6. Raman spectrum of orthorhombic GdP$_3$O$_9$.

Table 4. Frequencies $\nu_{P\text{-}O\text{-}P}$ and ν_{PO2} of gadolinium phosphate polymers.

Phosphates	Group P-O-P		Group PO$_2$		Structure	References
	ν_s	ν_a	ν_s	ν_a		
Gd$_2$P$_4$O$_{13}$	689	1004	1182	1231	Probable P$_4$O$_{13}$ group	This work
GdP$_3$O$_9$ monoclinic	677	1000	1200	1233	helical chain	This work
GdP$_3$O$_9$ orthorhombic	694	1063	1200	1275	helical chain	This work
GdP$_5$O$_{14}$	674	1059	1268	1302	ring	This work

3.1.6. Correlation between frequency, bond length and structure

In Table 3 we report the Raman frequencies of GdPO$_4$ and YPO$_4$. The values are in agreement with those already presented by Begun et al. [18] except for the antisymmetric stretching ν_3 of the GdPO$_4$ which we have localized at 1070 cm^{-1} due to correlation between the frequency and the size of the cation: for Gd an Eu that are of similar sizes with the same monazite structure family from La to Gd phosphates, their ν_3 vibrations should be close. As for yttrium orthophosphates, its ν_3 frequency follows the same correlation but in the ortho-phosphates of zircon structure family from Tb to Lu.

By chain lengthening only above the trimer configuration stage, when strong structural change occurs, such as the appearance of orthorhombic symmetry or cycling, we note that longer the chain is, higher is the antisymmetric vibration frequency ν_a of the PO$_2$ groups (Table 4). We interpret this fact by a shortening of the P-O bond (Table 1) in the slightly distorted motives by polymerization or by cyclization with regard to tetrahedral symmetry of the "monomer" [16, 17].

Table 5. Frequencies ν(P-O-P) and ν(PO$_2$) of yttrium phosphate polymers.

Phosphates	Group P-O-P		Group PO$_2$		Reference
	ν_s	ν_a	ν_s	ν_a	
Y$_2$P$_4$O$_{13}$	688	1004	1187	1235;1246	This work
YP$_3$O$_9$	680	1000	1205	1241	This work
YP$_5$O$_{14}$	690	1045	1157;1179	1304;1326	This work

A parallelism is observed with yttrium phosphates although the vibrational frequencies of the latters are somewhat more sensitive to the chain lengthening (Table 5) and the Raman analysis can reveal the presence of more than one PO_x groups with different environments.

3.2. Influence of the preparation conditions on the GdP_3O_9 phase

Bagieu-Beucher and Tranqui [6] mentioned that there would be two forms for the compound GdP_3O_9, one around 800°C and isostructural with the metaphosphates of La to Eu, and the other, at around 850°C, isostructural with the metaphosphates of Tb to Lu. Both were obtained by decomposition of GdP_5O_{14} with volatilization of P_2O_5.

We have investigated the conditions of formation by direct synthesis. The experiments were performed in air. In some experiments a vapor pressure of P_2O_5 was maintained by placing a crucible filled with $NH_4H_2PO_4$ besides the crucible containing the starting product.

In the first case, a treatment at 800°C during 2 hours for the atomic ratio Gd/P = 1/3 leads to the monoclinic form of GdP_3O_9. Its Raman spectrum is represented in Fig. 4. When firing this product at 900°C during 20 hours, no change in its Raman spectrum is observed, except for some weak bands perhaps that could come from a slight decomposition of GdP_3O_9 leading to $GdPO_4$ Fig. 7 b.

In reducing the annealing temperature during 20 hours at 800°C, its Raman spectrum doesn't change but, GdP_3O_9 is still present. We must then conclude, contrarily to Bagieu-Beucher and Tranqui. [6] that there isn't phase transition in GdP_3O_9.

In presence of P_2O_5 deposited on the tube of the oven during a previous synthesis or in presence of P_2O_5 intentionally added with a crucible containing $NH_4H_2PO_4$ at 900°C during 15 hours, we get the orthorhombic variety, Fig. 7a. The same variety can also be got at 760°C, in an atmosphere rich in P_2O_5 from initial proportions Gd/P of 1:3; 1:4; 1:5. With initial ratio Gd/P =1:4 its Raman spectrum as well as its X-ray diffraction pattern show that the product is pure, Fig. 7c.

When we submit the orthorhombic variety got at 900°C to a new thermal treatment during 20 hours in 800°C in air, the Raman spectrum of the resulting product shows a transformation into the monoclinic form.

In conclusion, in all the experiments where vapour of P_2O_5 was maintained in the furnace, the orthorhombic form of GdP_3O_9 has been obtained. This seems to indicate that the composition slightly deviates from stoichiometry. By quantitative analysis of elements, its structure is found very close to (1:3) with formula GdP_3O_9, but indicates a slight excess of P_2O_5.

Fig. 7. Raman spectrum of GdP_3O_9.
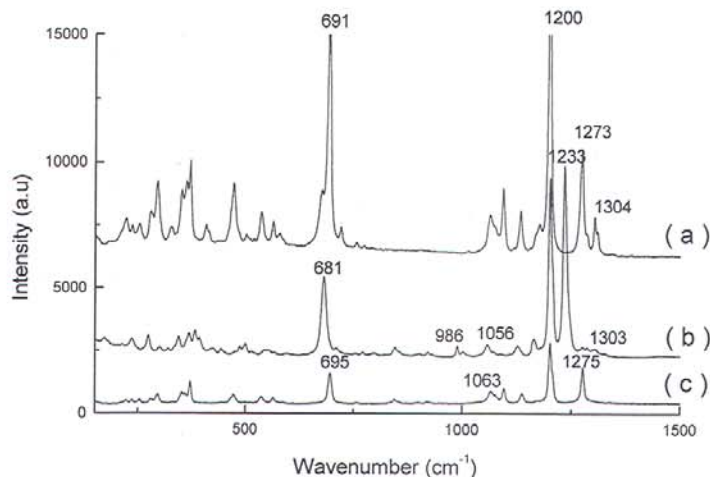(a) at 900°C/15h/O_2/oven contaminated by P_2O_5.
(b) at 800°C /2h-900°C /20h (monoclinic GdP_3O_9; $GdPO_4$).
(c) at 760°C/15h/ vapour pressure of P_2O_5 (orthorhombic).

3.3. Effect of phosphate impoverishment on the Raman spectra of gadolinium phosphates

When the amount of Gd_2O_3 increases, one observes in the Raman spectrum of the products $Gd_8P_2O_{17}$ (4:1) and Gd_3PO_7 (3:1) the appearance of intense peaks at the low frequencies side, where the vibrations involving gadolinium are expected (Fig. 8, 9).
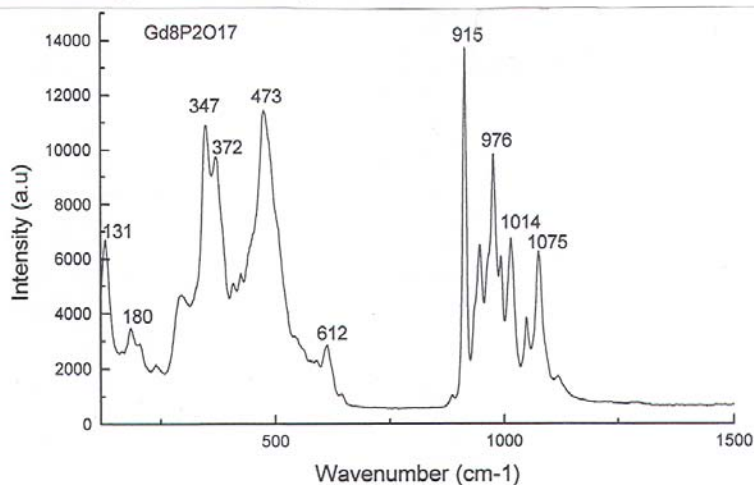

Fig. 8. Raman spectrum of $Gd_8P_2O_{17}$.

The absence of the Raman peaks around $680 \div 700$ and $1200 \div 1300$ cm^{-1} proves the absence of the PO_4 motive polymerization. Additional peaks appeared in the range $900 \div 1100$ cm^{-1} were observed. These could be due to the stretching vibrations of PO_4 motives distorted by the presence in high amount of GdO_y groups. They could also come from the overtones or combinations of phonons corresponding to GdO_y units.

One can note that the fundamental peaks corresponding to GdO_y motives are considerably broadened in $Gd_8P_2O_{17}$. We, therefore, deduce that in this phase some disorder occurs.
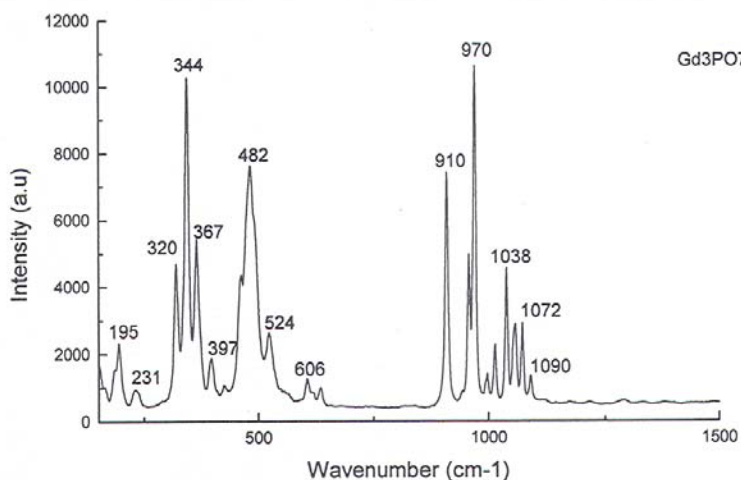

Fig. 9. Raman spectrum of Gd_3PO_7.

4. Conclusion

The phosphates of gadolinium and yttrium are synthesized and studied by X-ray diffraction and by Raman spectroscopy. The use of the frequency of the antisymmetric stretching vibration of the PO_2 group is proved to be very helpful to follow the structure change resulting from the condensation of the phosphate groups. Correlations have been established between this stretching frequencies and the size of the cation in the orthophosphates for the derivatives belonging to monazite structure as well as for zircon structure. The parameters governing the formation of the orthorhombic form of GdP_3O_9 that had not been previously characterized, have been investigated. The role of P_2O_5 in excess has been demonstrated.

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