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Growth, structure and infra-red spectra of $CsRP_4O_{12}$ crystals

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$CsRP_4O_{12}$ (where R is a rare-earth ion) crystals have been grown from highly concentrated phosphoric acid solutions. X-ray and infra-red spectral studies were performed on these crystals. Structurally, the $CsRP_4O_{12}$ crystals can be divided into two types: ring-type and chain-type. The crystal chemistry of $CsRP_4O_{12}$ crystals has been briefly discussed and the absorption bands for representatives from each structural modification have been determined.

1. Introduction

The discovery of unusual spectral characteristics in rare-earth phosphates has attracted the attention of crystallographers, physcists and chemists. It is well known that these unusual spectral charactersitics are connected with a high concentration, greater than 3.5×10^{21} atoms cm^{-3}, of the active ions in the crystal structures. Among the rare-earth phosphates, ultraphosphates have been studied extenssively by number of workers. Though tetraphophates are equally important for their spectral characteristics, little work has been reported on them and, with this object, we have made an attempt to study the growth, structure and infra-red spectra of $CsRP_4O_{12}$, where R is a rare-earth ion, crystals.

2. Crystal growth

There are various methods of growing $CsRP_4O_{12}$ crystals, such as: (a) growth by evaporation of aqueous solutions; (b) flux growth; (c) melt growth, (d) hydrothermal growth; and (e) growth by chemical reactions. Our experimental method in the present work is the same as that reported in earlier work, growth by evaporation [1–3]. The growth was carried out in a four-component system $Cs_2O–R_2O_3–P_2O_5–H_2O$ by a slow heating of an homogeneous solution. The required amounts of the starting materials, phosphoric acid (85% concentration) and cesium carbonate were heated in a vitreous graphite crucible. The solution was held at room temperature till all the CO_2 was evaporated. Later, the corresponding rare-earth oxide was added to this solution and the temperature of the furnace was slowly raised up to a predetermined temperature (350 to 800° C). The $CsRP_4O_{12}$ crystals can be obtained when the starting materials are taken in the following proportions (by weight): $Cs_2O:R_2O_3:P_2O_5 =$ (27.5 to 45.0):(5 to 30):(52.5 to 70.0). A more detailed description of the growth of $CsRP_4O_{12}$ crystals is given elsewhere [4].

3. X-ray study

We have carried out X-ray analysis of $CsRP_4O_{12}$ crystals. The X-ray characteristics are given in Table I. On the basis of structure, these crystals can be divided into two major types: ring-type and chain-type.

The latter type has three totally different structural modifications, however, in all these modifications the characteristic feature is the infinite screw of PO_3 chains repeating after every eighth PO_4 tetrahedron, in contrast to the pattern of repeating every fourth PO_4 tetrahedron as seen in $LiNdP_4O_{12}$, $KNdP_4O_{12}$, $NaNdP_4O_{12}$, etc. This type of arrangement of the chains was first reported in $TlNdP_4O_{12}$ crystals [5]. The common feature in the structure of $CsRP_4O_{12}$ crystals is that the rare-earth ions are isolated from one another and are surrounded by eight oxygen atoms in its coordination to form RO_8 polyhedra, where R is

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TABLE I Results of the X-ray study of CsRP_4O_{12} crystals

Phosphate	System	Space group	Cell parameters (nm)			Axial angle, γ (°)	Axial angle, β (°)	Unit-cell volume V (nm^3)	Co-ordination number, z	Reference
			a	b	c					
$CsLaP_4O_{12}$	cubic	$I\bar{4}3d$	1.543	–	–	–		3.67365	12	[4]
$CsCeP_4O_{12}$	cubic	$I\bar{4}3d$	1.539	–	–	–		3.64515	12	[4]
$CsNdP_4O_{12}$	cubic	$I\bar{4}3d$	1.528	–	–	–		3.57175	12	[2]
$CsPrP_4O_{12}$	cubic	$I\bar{4}3d$	1.526	–	–	–		3.55356	12	[4]
$CsSmP_4O_{12}$	cubic	$I\bar{4}3d$	1.516	–	–	–		3.48415	12	[4]
$CsEuP_4O_{12}$	cubic	$I\bar{4}3d$	1.514	–	–	–		3.47038	12	[4]
$CsGd(PO_3)_4$	monoclinic	$P2_1/b$	1.0449(3)	1.3057(4)	0.8930(3)	56.13		1.01159	4	[4]
$CsLu(PO_3)_4$	monoclinic	$B2/b$	0.9955(3)	1.3961(3)	2.0023(5)	52.39		2.20450	4	[4]
α-$CsNd(PO_3)_4$	monoclinic	$P2_1/b$	1.0463	1.3008	0.9028	124.07		1.01760	4	[1]
β-$CsNd(PO_3)_4$	monoclinic	$P2_1$	0.7145	0.8809	0.9176	99.65		0.56936	2	[1]
β-$CsPr(PO_3)_4$	monoclinic	$P2_1$	0.7158	0.9184	0.8812		99.66	0.54794	2	[1]
$CsTb(PO_3)_4$	monoclinic	$P2_1$	0.7032	0.8705	0.9051	100.00		0.54568	2	[13]

the rare-earth ion. This special feature in the structure of these compounds we have called "Nezoites" (after the Greek νησος meaning islands) [1]. The unusual spectral characteristics of these crystals are connected with the isolated nature of the rare-earth polyhedra and ligands often having tetrahedral ions. A more complete description of these "Nezoites" given in [6].

The representatives from each of the structural modifications I to IV of $CsRP_4O_{12}$ crystals are as follows: (I) $CsNd\,P_4O_{12}$; (II) α-$CsNd(PO_3)_4$; (III) β-$CsNd(PO_3)_4$; and (IV) $CsLu(PO_3)_4$.

The $CsRP_4O_{12}$, where R = La to Nd, crystals were obtained in the temperature range of 350 to 520° C and they are cyclic tetraphosphates. The structure of $CsNd[P_4O_{12}]$ was reported in the work [7]. In the structure of this crystal, the isolated Nd polyhedra (of average Nd–O bond length of 0.2468 nm and shortest Nd–Nd bond length of 0.7125 nm) are connected with four P_4O_{12} rings along the edges. The irregular CsO_9 polyhedra are joined along the edges and corners of the infinite chains. Each NdO_8 polyhedron is surrounded by six CsO_6 polyhedra. The P_4O_{12} rings have $\bar{4}$ symmetry. The interatomic distances and the inter-tetrahedral angles do not vary from the normal values: P–P–P = 89.63°, O–P–O (corner oxygen) = 119.71°, O–P–O (bridging oxgyen) = 101.46°, P–O (corner) = 0.1484 to 0.1493 nm and P–O (bridging) = 0.1621 to 0.1624 nm.

The second structural modification includes $CsR(PO_3)_4$, where R = La to Nd, obtained in the temperature range of 520 to 670° C. In this modification only the structure of α-$CsNd(PO_3)_4$ has so far been reported [8]. The basic structural unit consists of an infinite chain of PO_4 tetrahedra connected by bridging oxygen atoms. The crystal lattice consists of two centro-symmetric chains running along the b-axis. We have confirmed this structure using our experimental set-up. A view of the structure projected along the b-axis is shown in Fig. 1. The P–O–P angles in the given structure have been found to lie within the range 125.0 to 135.0° C and this observation does not support the conclusions of the earlier workers [9] who reported that the angles between neighbouring groups of PO_4 tetrahedra in the chain-type of tetraphosphates $MNdP_4O_{12}$, where M = Li, Na, K, Rb, increase with increase in the ionic radii

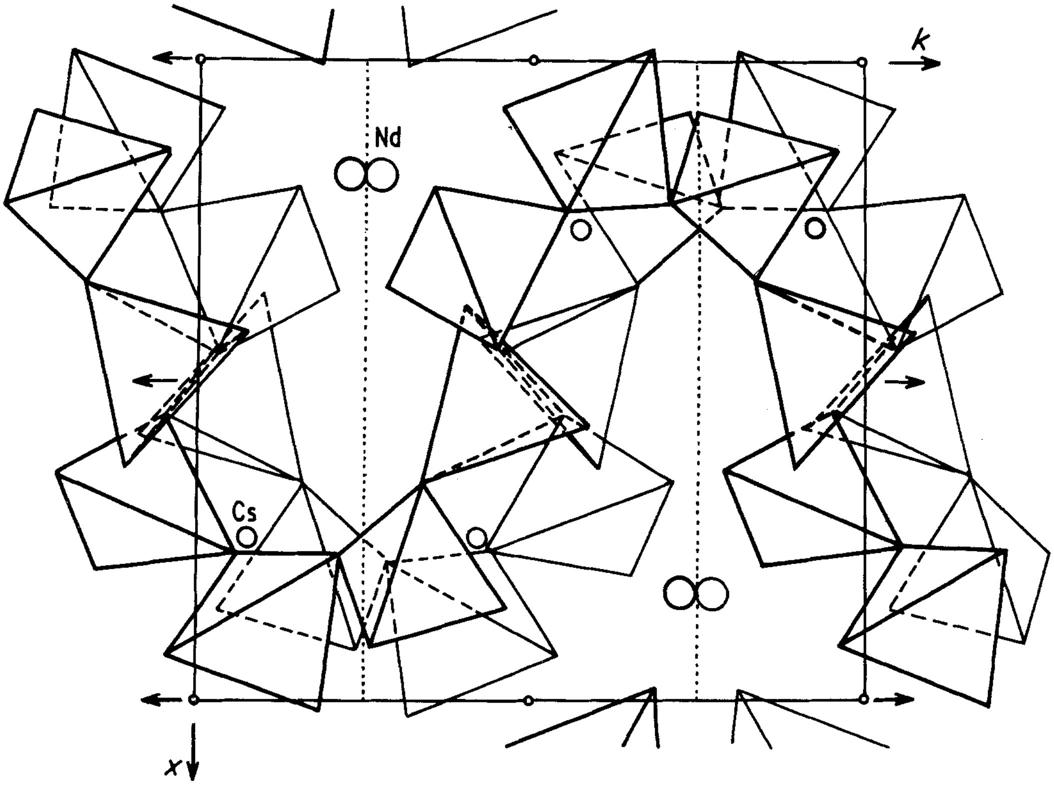

Figure 1 The α-$CsNd(PO_3)_4$ structure projected along the b-axis.

and co-ordination number of M. The average values of bond lengths (P–O (terminal) = 0.1484 nm and P–O (bridging) = 0.1612 nm) do not vary from the normal values (P–O (terminal) = 0.148 nm and P–O (bridging) = 0.161 nm). The inter tetrahedral angles are slightly less than the average values. All the eight terminal oxygen atoms of PO_4 tetrahedra form a co-ordintion with Nd and the co-ordination polyhedron is irregular. The co-ordination number of the Cs atom is 11. The shortest Nd–Nd distance is 0.577 nm. Each Nd atom is surrounded by four Cs atoms at distances in the range 0.4128 to 0.5126 nm, such that the Nd polyhedron and three nearest Cs polyhedra are linked along the common faces, edges and summits, forming a ribbon-like structure running along the b-axis. The shortest Cs–Cs length is 0.4355 nm between the pairs linked with an inversion centre ($\frac{1}{2}$00).

The third structural modification includes CsR(PO$_3$)$_4$, where R = La to Er, crystals obtained in the temperature range of 350 to 750° C. The structure of CsTb(PO$_3$)$_4$ crystals was first reported among the CsR(PO$_3$)$_4$ crystals belonging to this structural modification [10]. Later, two more structures were reported: CsPr(PO$_3$)$_4$ [11] and CsNd(PO$_3$)$_4$ [12, 13]. Let us briefly consider the structure of CsNd(PO$_3$)$_4$ crystals (in the present work this is named as β-CsNd(PO$_3$)$_4$ for convenience). The structure is made up of helical $(PO_3)_\infty$ chains connected by isolated NdO$_8$ dodecahedra and irregularly-shaped Cs polyhedra, repeating after every eighth PO$_4$ tetrahedron along the b-axis. Fig. 2 represents the projection of the β-CsNd(PO$_3$)$_4$ structure along the b-axis [10]. In the co-ordination of Nd only the corner atoms of oxgyen take part, whereas in the co-ordination of Cs both corner and bridging oxygen atoms take part. The shortest Nd–Nd is length 0.6668 nm and the average Nd–O distance is 0.2436 nm. The distances P–O (corner) and P–O (bridging) do not vary from the normal values. However, towards the Er end of the series (with a decrease in the ionic radii of the rare-earth ions) the P–O distances vary considerably from the normal values: for example, in CdTb(PO$_3$)$_4$ the valence distances

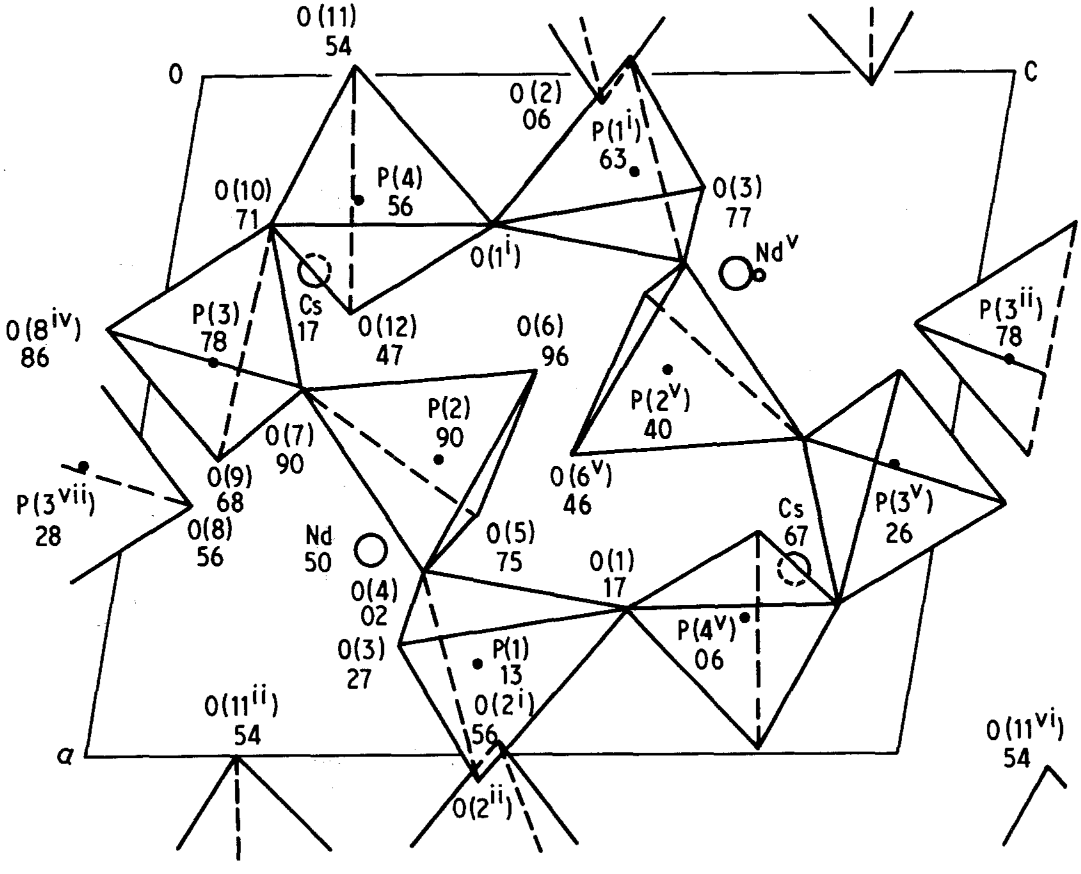

Figure 2 The β-CsNd(PO$_3$)$_4$ structure projected along the b-axis.

P–O (corner) range from 0.135 to 0.167 nm and P–O (bridging) range from 0.141 to 0.175 nm. The reason for such a variation is not yet known.

The fourth structural modification is not reported in the literature. A preliminary X-ray study shows that the $CsRP_4O_{12}$, where R = Yb, Tm and Lu, crystals also belong to the chain-type. These crystals were obtained in the temperature range of 350 to 520° C. A systematic study of the structure of $CsLu(PO_3)_4$ is in progress in our laboratory.

4. Infra-red spectra

The infra-red (i.r.) spectra of $CsRP_4O_{12}$ crystals were registered in the range of 1800 to 400 cm^{-1} and 3800 to 3000 cm^{-1} using an i.r.-spectrophotometer model UR-10W (GDR). The i.r.-spectra of rare-earth phosphates were taken in order to understand in greater detail the structure of the PO_4 chains and rings. Since, these compounds contain heavy atoms as cations, routine X-ray analysis is in some cases cumbersome; furthermore, the routine X-ray technique gives an image of the ideal structure, and it is not possible to look at just some molecules, for example, (OH) molecule. Therefore, one of the main objects of this work is to investigate the PO_4 anions in the chains and rings with the aid of i.r. spectra. For comparison of the results and the better understanding of the nature of the phosphoro-oxygen anions, we have also taken i.r.-spectra for ultraphosphates (NdP_5O_{14} and BiP_5O_{14}) and other tetraphosphates ($RbNd(PO_3)_4$ and $CsNd(PO_3)_4$, an unknown phase). The absorption spectra of rare-earth phosphates are shown in Fig. 3.

It is well known that the orthophosphates PO_4^{3-} with tetragonal symmetry have four fundamental vibrations. The basic vibrations frequencies (cm^{-1}) of the PO_4 tetrahedra are given in Table II [14]. The vibration $\nu_1(A_1)$ activates the irregularity in the tetragonal symmetry of the PO_4 tetrahedra. With a fall of this symmetry up to C_s (obeying the selection rule) in the region $\nu_3(F_2)$ we find the multiplication of absorption bands. This activated the former inactive vibration and gives some additional bands in the spectra. Another reason for the multiplication of absorption bands in the spectra may be due to the distortion of the PO_4 tetrahedra. On the basis of a uniform distribution of multiple bonds in PO_4 tetrahedra in orthophosphates, one can expect quite similar P–O distances; in practice, however, the distance varies from 0.143 to 0.161 nm [15]. From the crystal chemistry of phosphates, it is evident that the variation in the P–O distances is quite large and it is difficult to find an analogue to PO_4 tetrahedra among the inorganic compounds. In this respect the PO_4 tetrahedra is highly distorted and, therefore, we can expect highly complex spectra for these compounds.

In pyro-, poly- and meta-phosphates it is observed that with an increase in the ionic bonding of M–O, the P–O bond lengths decrease due to the reduction in the positive charge on P atoms and, alternatively, with an increase in the covalent bonding of M–O, the P–O bond lengths increase. In the chain-type polyphosphates it is observed that the P–O stretching, for example in $Yb(PO_3)_3$ (the difference function of the structure factors, R, in the work is 0.076), varied as follows [16]:

P–O (terminal) : 0.135 to 0.167 nm

and

P–O (bridging) : 0.141 to 0.175 nm.

According to the crystal chemistry of phosphates, it is well established that the symmetry of the PO_4 tetrahedra is always strongly dependent upon the nature and degree of condensation. The spectra of orthophosphates consist primarily of two intense bands for ν_s and ν_I valence vibrations in the range 1100 to 1000 cm^{-1} and for ν_4 in the range 600 to 500 cm^{-1} (see Fig. 4). The spectra of mixed orthophosphates consist of absorption bands in the range 1150 to 1100, 980 and 600 to 500 cm^{-1} (see Fig. 5). In comparison with these spectra, the tetraphosphates have diverse spectra consisting of five groups of absorption bands (see Fig. 3).

The representative of the cyclic tetraphosphates, $CsNd[P_4O_{12}]$ has the following absorption bands in its spectrum: intense bands in the ranges 1300, 1120, 980 to 960 and 550 to 530 cm^{-1}; medium strong bands in the range of 850 to 750 cm^{-1} and a number of weaker bands (Fig. 3). An analogous picture has been found for $RbNd[P_4O_{12}]$ (see Fig. 3).

The spectrum of $CsGd(PO_3)_4$* has the following absorption bands in its spectrum bands: intense bands in the range 1310 to 1260 cm^{-1}, slightly less intense and medium strong bands in the ranges

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*$CsGd(PO_3)_4$ is isostructural with α-$CsNd(PO_3)_4$.

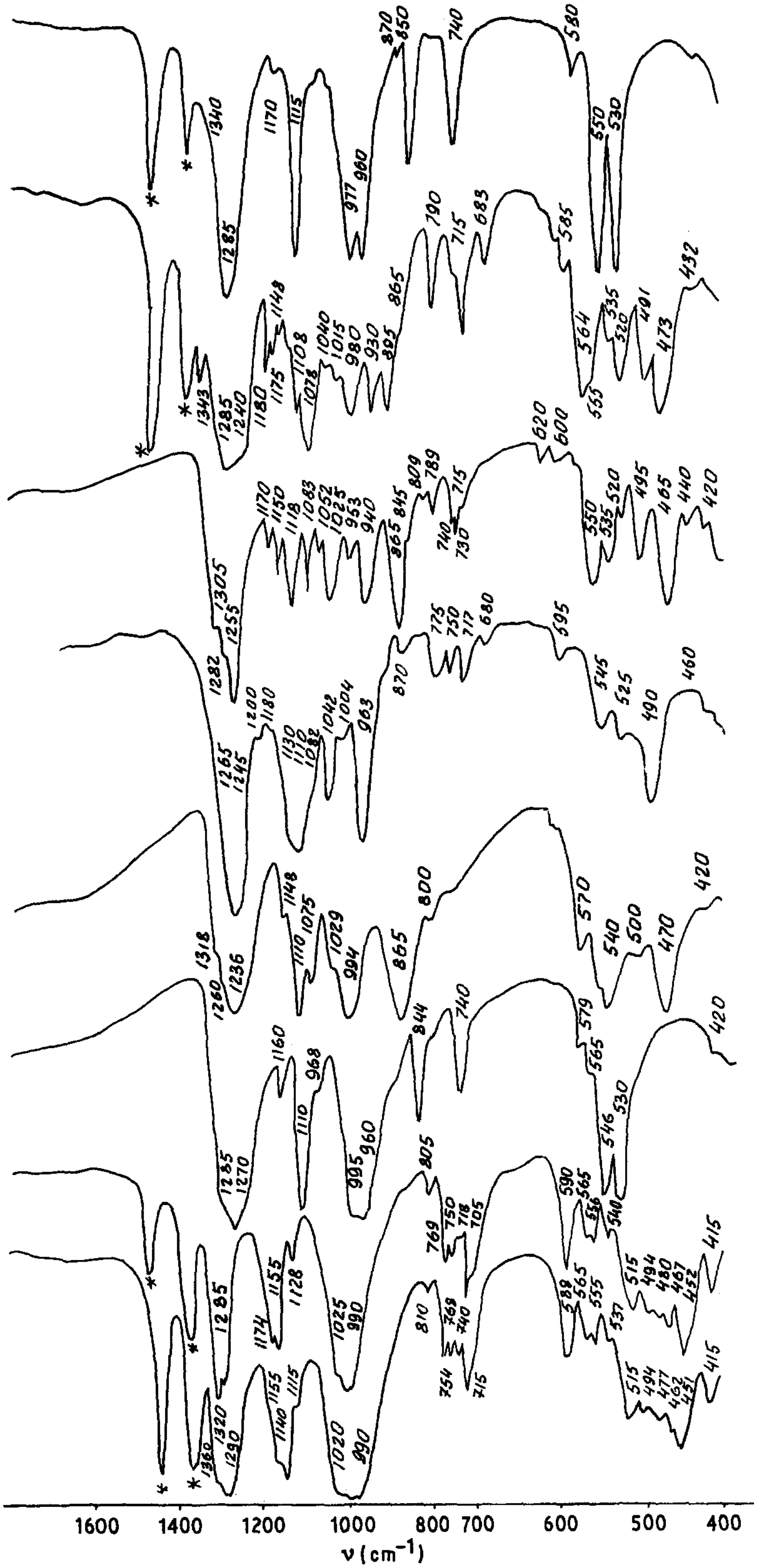

Figure 3 Infra-red spectra of rare-earth phosphates: (a) CsNd[P_4O_{12}] (ring type); (b) β-$CsNd(PO_3)_4$; (c) $CsGd(PO_3)_4$; (d) $CsLu(PO_3)_4$; (e) $Cs_3NdP_6O_{18} \cdot nH_2O$; (f) RbNd[$P_4O_{12}$] (ring type); (g) NdP_5O_{14}; and (h) BiP_5O_{14}.

TABLE II Fundamental vibration frequency of the orthophosphate PO_4 tetrahedra

Orthophosphate	Frequency (cm^{-1})			
	$\nu_1 (A_1)$	$\nu_2 (E)$	$\nu_3 (F_2)$	$\nu_4 (F_2)$
$Ba_3[PO_4]_2$	980	363	1082	515
	970	358	1080	500
	988	420	1017	567

1030 to 870 cm^{-1} and 560 to 460 cm^{-1}, and a number of weaker bands in the range 1180 to 1100 cm^{-1} (see Fig. 3).

β-$CsNd(PO_3)_4$ has the following absorption bands in its spectrum: intense bands in the range 1300 to 1260 cm^{-1} and a series of medium strong bands in the range of 1100 to 900 cm^{-1}. The difference between the $CsGd(PO_3)_4$ and β-$CsNd(PO_3)_4$ spectra is that the $CsGd(PO_3)_4$ spectrum has a highly complex and fine structure, particularly in the range 1200 to 1100 cm^{-1}. This is connected with differences in the geometrical orientation of the PO_4 chains in the crystal structure.

The spectrum of $CsLu(PO_3)_4$ has intense bands in the range 1300 to 1200 cm^{-1}, in common with the other chain phosphates, β-$CsNd(PO_3)_4$ and $CsGd(PO_3)_4$. However, in the range of 700 to 1200 cm^{-1}, the multiplication of the bands is less than in the other chain phosphates. This can be explained due to the decrease in the element of repetition of PO_4 tetrahedra in the chain. On the whole, the spectrum of $CsLu(PO_3)_4$ is nearer to the spectrum of β-$CsNd(PO_3)_4$.

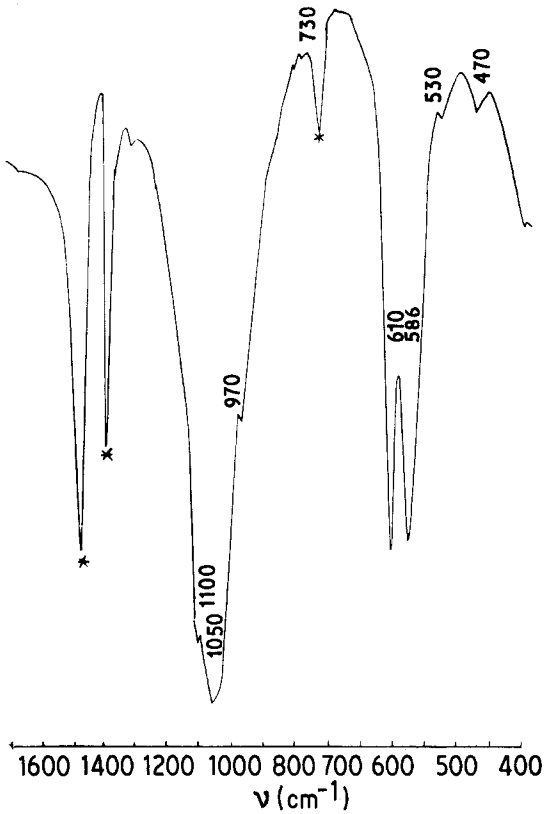

Figure 4 Infra-red spectra of apatite.

The spectra of NdP_5O_{14} and BiP_5O_{14} are similar. They belong to the ribbon-type of phosphates. The spectra taken by us correspond with those of earlier workers [17, 18]. In comparison with the spectra of cyclic and chain phosphates, the ultraphosphates have a more complicated spectra and the P–O absorption bands are confined to the shorter wavelength region of the spectra. This is connected with an increase in the degree of polymerization of phosphoro-oxygen anions.

It is well known that the spectra of minerals are exclusively determined by the arrangement and character of the anionic group in the structure. In a fine structure, the absorption bands depend upon the symmetry of polyhedra and a relatively slight displacement of bands in the frequency scale determines large variations in the degree of condensation of the anionic group. Thus, orthophosphates made up of PO_4 tetrahedra retain one or another tetrahedral symmetry and have basic absorption bands in the range of 1170 to 110 cm^{-1} and 600 to 500 cm^{-1}. During condensation

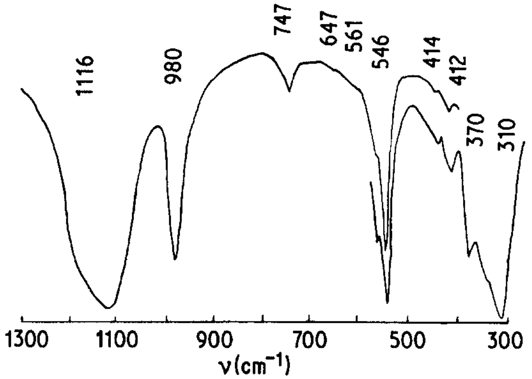

Figure 5 Infra-red spectra of $Ba_3(PO_4)_3$.

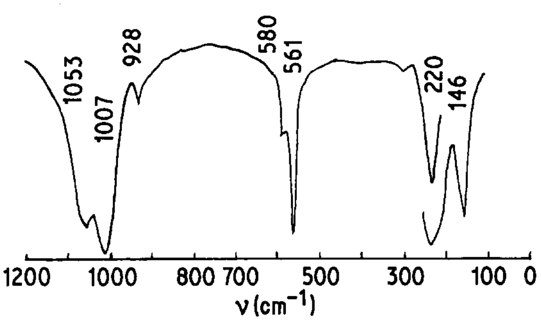

Figure 6 Infra-red spectra of ZrP_2O_7.

of PO_4 tetrahedra it appears that the P_2O_7 group is the result of an decrease in the positional symmetry of the PO_4 tetrahedra and the splitting of the PO_4 valence vibration ν_{as} (F_2), into components at 1000 cm^{-1} giving few absorption bands. The number of bands often exceeds three, which serves as a clue for the existence of the distortion of the PO_4 tetrahedra in the structure. The POP ν_s vibration appears at 980 cm^{-1} for ZrP_2O_7 (see Fig. 6) [19]. In the course of linking the PO_4 tetrahedra to form a ring or a chain or a ribbon the spectra vary, particularly with increase in the absorption bands of phosphoro-oxygen anions. Similarly, with an increase in the degree of condensation there will be an increase in the overall number of bands, particularly an increase in the number of intense bands from one to three in the spectra. It is important to note that such a sharp change in the spectra with increase in the degree of condensation of the anionic group can be seen only in phosphates.

In correspondance with the earlier works, the vibration of the chains in polyphosphates due to the differences in bond strengths can be divided into two groups. An extremely strong bond for PO_2 groups developed as a result of two σ bonds and one π bond. In the O–P–O–P–chains developed as a result of σ-bonds (that is the phosphates with linear bonds of PO_4 tetrahedra) we can expect the following vibrations ν_{as} PO_2, ν_s PO_2, δ_{as} PO_2, ν_{as} POP, ν_s POP and δ_{as} POP [20] (δ_{as} is a deformational vibration). The vibrations of the two P–O bonds in the O–P–O group strongly interact with one another and, as a result, the vibration splits into two mixed vibrations, i.e., ν_s PO_2 (the bond lengths vary in phases) and ν_{as} PO_2 (the bond lengths vary out of phases). The higher the O–P–O angle, the larger the splitting between the two components of the frequency. Therefore, our results agree with the contention that the O–P–O angle is less for cyclic phosphates than for chain phosphates. The splitting in the ν_{as} PO_2 and ν_s PO_2 vibrations is higher for chain phosphates ($\Delta\nu \approx 200$ cm^{-1}) than for cyclic phosphates ($\Delta\nu \approx 170$ cm^{-1}). The splitting in the vibrations for ultraphosphates (ribbon phosphates) is slightly less than for cyclic phosphates ($\Delta\nu \approx 150$ cm^{-1}) and, therefore, we can presume that the O–P–O angle in ultraphosphates is almost equal to or slightly less than that in cyclic phosphates (see Fig. 3 and Table III).

The valence vibration of two P–O bonds in the O–P–O–P– chain also strongly interacts and splits the vibration into ν_s POP ν_{as} POP. Apart from this, there exists an weak interaction of the O–P–O–P– chain vibration with other P–O bonds results in further splitting in ν_s POP and ν_{as} POP. Thus, in chain phosphates made up of two links, O–P–O–P, there are two symmetric vibrations, ν_{1s} POP and ν_{2s} POP, and two asymmetric vibrations, ν_{1as} POP and ν_{2as} POP. This suggestion is corroborated by the mulitplication of the absorption bands in the ν POP and ν_{as} POP region (vibrations for $CsGd(PO_3)_4$ and β-$CsNd(PO_3)_4$, respectively). Depending upon the number of bands in the ν_s POP region, we can determine the relatively period or the relative element of repetition of PO_4 tetrahedra in the

TABLE III Vibrational frequencies, ν (cm^{-1}) or rare-earth phosphates

Vibrational	Frequency (cm^{-1})		
	Cyclic	Chain	Ribbon
ν_{as} PO_2	1310–1285*	1340 1280–1260	1310–1280
ν_s PO_2	1150–1115	1180–1020–1080	1180–1170–1140
ν_{as} POP	977–960	1020–870	1020–980
ν_s POP	870–740	800–680	800–730
δ PO_2	580–430	620–580–475	590–420
δ POP	< 400	< 400	< 400

*Values underlined represent intense peaks in the spectra.

chain. The splitting is distinct for the group, where the planes are lying perpendicular to one another. In addition to this, for $CsGd(PO_3)_4$ and β-$CsNd(PO_3)_4$, from the observation of multiplication of the ν_s PO_2 bands, it is evident that, from the distinct interaction of the valence vibration of the neighbouring PO_2, it probably takes place in one plane. However, the splitting resulting from this is not great.

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