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Vibrational spectra of double diphosphates $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Ho, Y, Er, Tm, Yb)

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Abstract

Raman and infrared absorption spectra of diphosphates $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Ho, Y, Er, Tm, Yb) have been recorded and interpreted using factor group analysis. The spectral features predicted with factor group arising from the X-ray crystallographic space group $P2_1/c$ (C^5_{2h}) for these compounds fit the observed results. Non-coincidences observed between most infrared and Raman bands confirmed that these materials possess the centrosymmetric structure. The similarities between the vibrational spectra of $CsLnP_2O_7$ suggested that they are isostructural. The shift of the frequencies ν^{as} (POP) and ν^{s} (POP) on the vibrational spectra is due to the influence of the cation Ln^{3+} on the P-O-P bridge angle. The POP angle values were estimated using the Lazarev's relationship.

Keywords: Metals; Chemical synthesis; Crystal structure and symmetry; X-ray diffraction; X-ray and *-ray spectroscopies

1. Introduction

Many investigators have reported the structures of double diphosphate compounds of the type $M^IM^{III}P_2O_7$ [1–10]. However, for the caesium derivatives, none of these studies have included their Raman and Infrared spectra.

The aim of this work is to establish and to interpret vibrational spectra of $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Ho, Y, Er, Tm, Yb) in order to check the structural relationship and the vibrational behaviour of the titled salts.

2. Experimental

2.1. Synthesis

The samples of $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Ho, Y, Er, Tm, Yb), were prepared by usual solid state reaction techniques. Stoichiometric quantities of caesium carbonate Cs_2CO_3, rare earth oxide Ln_2O_3 and the diammonium hydrogenphosphate $(NH_4)_2HPO_4$ as starting materials were well ground and mixed. They were progressively heated in platinum crucibles up to 750°C for 24 h.

2.2. X-ray diffraction powder

All X-ray diffractograms were recorded on a D5000 diffractometer calibrated with external silicon standard using the Cu Kα line.

2.3. Infrared measurements

Infrared spectra were measured using F.T.I.R 1600 spectrometer calibrated with polystyrene film and indene. Both KBr pellet and nujol mull techniques were used to obtain infrared spectra (4000–400 cm^{-1}). Wave number accuracy is within ± 2 cm^{-1} for narrow bands.

2.4. Raman measurements

Raman spectra were recorded on a homemade computer controlled spectrometer equipped with an argon laser, 200 mw on the green line, spectral slit of about 2 cm^{-1}.

3. Results and discussions

3.1. X-ray results and spectral predictions

The result analysis of X-ray diffraction of $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Ho, Y, Er, Tm, Yb), shows that the

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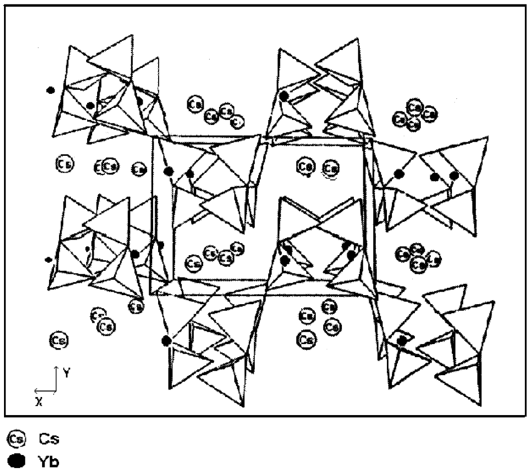

Fig. 1. The structure of $CsYbP_2O_7$ projected onto the *xy* plane.

structure of these compounds is isostructural with $KAlP_2O_7$, which crystallises in the monoclinic system (space group $P2_1/c$, $Z=4$) [11]. The structure of caesium ytterbium diphosphate $CsYbP_2O_7$ [10] projected onto the *xy* plane is given in Fig. 1.

In these compounds the $P_2O_7^{4-}$ anion consists of a pair of corner-sharing PO_4 groups in a staggered configuration [11]. Therefore the only molecular group is Cs. All the atoms are located on C_1-sites. The internal modes of the $P_2O_7^{4-}$ anions in $CsLnP_2O_7$ are given by the correlation scheme (Table 1).

The factor group analysis predicts the distribution of irreducible representation of the internal modes of $P_2O_7^{4-}$ ions in $CsLnP_2O_7$:

$P_2O_7^{4-}$

$$\Gamma_{\mathrm{vib}}\,(C_{2h}) = 21\,A_g(\mathrm{Ra}) + 21\,B_g(\mathrm{Ra}) + 21\,A_u(\mathrm{IR}) + 21\,B_u(\mathrm{IR}).$$

The A_g and B_g species are Raman active, while the A_u and B_u species are infrared active. According to the C_s symmetry all 21 vibrations are both infrared and Raman active, only 13 lines are polarised, the normal coordinate analysis of $P_2O_7^{4-}$ ion exhibits more difficulties in computation and the large number of force constants which would need to be estimated. Owing to the difficulties to interpret the vibrational spectra, a D_{3d} model was considered for the following reasons:

- The normal coordinates analysis of $P_2O_7^{4-}$ with D_{3d} symmetry were performed and all vibrations modes of $P_2O_7^{4-}$ were interpreted [12].
- The correlation between D_{3d}, C_s, and C_{2h} allows us to calculate the contribution in the different frequency ranges in $CsLnP_2O_7$

The internal modes of the $P_2O_7^{4-}$ anions in $CsLnP_2O_7$ are given by the correlation scheme Table 2.

In order to interpret the vibrational spectra it is useful to give the distribution of the vibrational modes of the $P_2O_7^{4-}$ anion among the symmetry species of D_{3d} [13]:

P–O–P bridge stretching: $A_{1g}+A_{2u}$
P–O–P bridge deformation: E_u
PO_3 terminal stretching: $A_{1g}+E_g+A_{2u}+E_u$
PO_3 terminal deformation: $A_{1g}+E_g+A_{2u}+E_u$
PO_3 rocking modes: E_g+E_u
Torsion modes: A_{1u}

3.2. Vibrational spectra of $CsLnP_2O_7$

The infrared and Raman spectra of these compounds are illustrated in Figs. 2 and 3 respectively. Band assignments for the fundamental modes of $P_2O_7^{4-}$anions of $CsLnP_2O_7$ are tabulated in Table 3. Two factors were considered in order to make a reasonable set of empirical band assignments: first, the wave numbers of bands resulting from factor group splitting of the same site group mode should

Table 1
Correlation scheme for the internal modes of $P_2O_7^{4-}$ ions in $CsLnP_2O_7$[a]

Free ion group symmetry (C_s)	Site group symmetry (C_1)	Factor group symmetry (C_{2h})
		21 A_g (Ra)
13 A′ (IR, Ra) $\searrow$		$\nearrow$ 21 B_g (Ra)
	21 A (IR, Ra)	
		$\searrow$ 21 A_u (IR)
8 A″ (IR, Ra) $\nearrow$		$\searrow$ 21 B_u (IR)

Activities	G_M	G_S	G_F
Raman	21	21	42
Infrared	21	21	42
Coincidences	21	21	0

[a] G_M: Molecular group, G_s: Site group, G_F: Factor group.

Table 2
Correlation scheme for the internal modes of $P_2O_7^{4-}$ ions in $CsLnP_2O_7$[a]

Free ion group symmetry (D_{3d})	Site group symmetry (C_1)	Factor group symmetry (C_{2h})
3A_{1g} (Ra) $\searrow$		21 A_g (Ra)
3 E_g (Ra) $\searrow$		$\nearrow$ 21 B_g (Ra)
A_{1u} (In) $\rightarrow$	21 A (IR, Ra)	
3 A_{2u} (IR) $\nearrow$		$\searrow$ 21 A_u (IR)
4 E_u (IR) $\nearrow$		$\searrow$ 21 B_u (IR)

Activities	G_M	G_S	G_F
Raman	09	21	42
Infrared	11	21	42
Coincidences	0	21	0

[a] $P_2O_7^{4-}$

$$\Gamma_{\mathrm{vib}}(D_{3d}) = 3A_{1g}(\mathrm{Ra}) + 3E_g(\mathrm{Ra}) + 1A_u(In) + 3A_{2u}(IR) + 4E_u(IR).$$

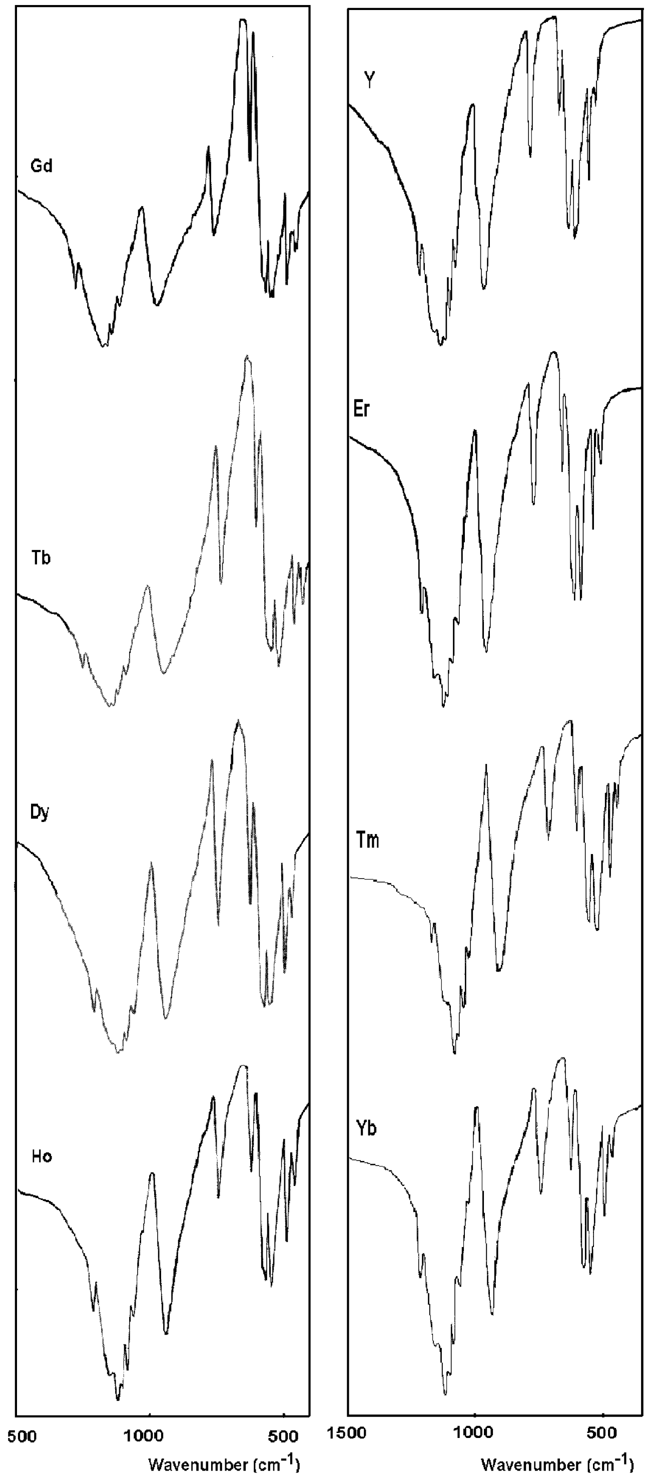

Fig. 2. Infrared spectra of $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Ho, Y, Er, Tm, Yb).

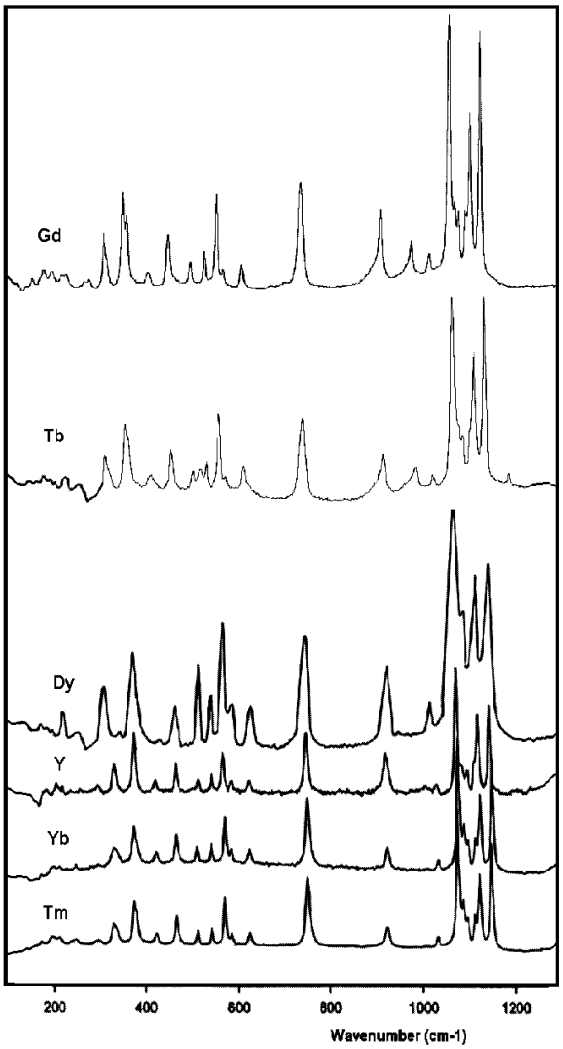

Fig. 3. Raman spectra of $CsLnP_2O_7$ (Ln=Gd, Tb, Dy, Y, Yb, Tm).

be close together. Second, the relative intensities of bands should relate to the symmetry of the vibrational modes involved. For instance, a mode belonging to the A_g species usually has a polarizability change that is greater than that for a related B_g species; the former mode is usually more intense in Raman spectra.

3.2.1. The PO_3 stretching modes

The terminal stretching modes of $P_2O_7^{4-}$ anions usually occur in the region 1250–975 cm^{-1} [14]. The Raman spectra show more than six peaks in this internal mode region. The most intense band in the Raman spectra around 1070 cm^{-1} is assigned to the symmetric terminal P–O stretching vibrations of A_g symmetry species and it is possible to assign the weak infrared band around 1061 cm^{-1} to the A_u symmetry species [15]. The other bands are the asymmetric terminal P–O stretches.

3.2.2. The POP bridge stretching vibrations

All previous assignments of the POP stretching modes in $P_2O_7^{4-}$ have agreed that such modes lie at lower wave numbers than the terminal stretches [13,15]. So two

Table 3
Band assignments for $CsLnP_2O_7$ (cm^{-1})[a]

$CsGdP_2O_7$		$CsTbP_2O_7$		$CsDyP_2O_7$		$CsHoP_2O_7$	$CsYP_2O_7$		$CsErP_2O_7$	$CsTmP_2O_7$		$CsYbP_2O_7$		Assignments
IR	Ra	IR	Ra	IR	Ra	IR	IR	Ra	IR	IR	Ra	IR	Ra	
1200 s		1206 s	1188 w	1212 s		1210 s	1211 s		1211 s	1212 s		1215 s		
–	1134 s	–	1135 s	1161 s	1134 s	1157 s	1159 s	1146 s	1159 s	1161 s	1149s	1161 s	1151 s	
1115 vs	1121 s	1112 vs	–	1120 vs	–	1117 vs	1119 vs	1121 s	1119 vs	1120 vs	1123 s	1122 vs	1125 s	
1098 vs	1110 w	1100 vs	1114 s	1102 vs	1111 s	1102 vs	1108 vs	1115 w	1108 vs	1102 vs	1112 w	1109 vs	1116 w	ν^{as} PO_3
–	1096 w	–	1097 w	1098 w	–	–	–	1097 w	–	–	1096 w		1098 w	
1080 s	1083 w	1080 s	1085 w	1084 s	1087 w	1085 s	1086 s	1089 w	1086 s	1084 s	1087 w	1085 s	1090 w	
1064 s	1067 s	1058 s	1068 vs	1067 s	1067 vs	1061 s	1067 s	1074 vs	1067 s	1067 s	1076 vs	1061 s	1077 vs	ν^{s} PO_3
–	1023 w	–	1024 w	–	1023 w	1022 w	–	1030 w	–	–	1032 w	–	1034 w	ν^{as} PO_3
	984 w		986 w		989 w			1007 w			–			
936 s	917 m	940 s	918 m	941 s	916 m	942 s	942 s	923 m	942 s	943 s	924 m	944 s	925 m	ν^{as} POP
737 m	743 s	742 m	745 s	743 m	744 s	744 m	744 m	749 s	745 m	746 m	751 m	747 m	751 s	ν^{s} POP
618 m	618 w	619 m	620 m	622 m	620 m	621 m	622 m	626 m	622 m	622 m	626 m	623 m	626 m	
563 s	577 w	568 s	580 w	572 s	582 w	570 s	582 s	586 w	582 s	572 s	586 w	573 s	586 w	
542 s	564 m	542 s	566 s	555 vs	565 s	552 vs	552 vs	569 m	552 vs	555 vs	572 m	556 vs	573 m	
493 s	538 w	492 s	540 w	494 s	539 w	495 s	495 s	545 m	495 s	494 s	544 m	494 s	544 m	δ PO_3 and
464 m	509 w	460 m	528 m	466 m	517 s	467 m	468 m	516 m	468 m	466 m	514 m	468 m	514 m	ρ PO_3
	461 w		511 m		463 m			469 m			468 m		469 m	
	417 w		464 m		419 w			423 w			424 w		424 w	
	376 w		420 w		367 s			377 s			376 s		376 s	
	362 m		367 s		323 w			333 m			332 m		333 m	
	320 w		323 w		288 m			298 w			298 w		–	External modes
	235 w				267 w			–			249 w		249 w	
	203 w		267 w		–			219 w			–		–	δ POP
	185 w		–		205 w			107 w			211 w		–	
					188 w			185 w			197 w			ι P_2O_7
	161 w													

[a] s = strong, v = very, ρ = rocking, m = medium, ν = stretching, w = weak, δ = bending, ι = torsional, s = symmetric; as = asymmetric.

stretching modes are assigned in all infrared and Raman spectra between 950 and 700 cm^{-1}.

The peaks observed around 924 and 750 cm^{-1} in the Raman spectra are assigned to the B_g asymmetry specie and to the A_g symmetry specie of POP stretching respectively.

The bands observed around 940 and 744 cm^{-1} in the infrared spectra are attributed to the B_u asymmetry mode and to the A_u symmetry mode of POP stretching respectively.

3.2.3. The PO_3 deformation modes

These are spread over a large spectral range in the Raman spectra. Thirteen Raman modes should lie between 300 and 700 cm^{-1}. In this case, the modes lying between 320 and 150 cm^{-1} in the Raman spectra can be corresponded to the external, torsional and the POP deformation modes. The deformation frequency of the P–O–P bridge occurs around 320 cm^{-1} [16–18], while the rocking and the PO_3 deformation modes are seen in the region 330–626 cm^{-1}.

A comparison of the Raman and infrared bands shows that the majority of them are not coincident. This fact confirms that $CsLnP_2O_7$ (Ln = Gd, Tb, Dy, Ho, Y, Er, Tm, Yb) have a centrosymmetric structure.

3.3. Correlation between the POP bridge stretching frequencies and the bridge angle value

One of the most interesting aspects of this study is the possibility of obtaining direct information about the configuration of P–O–P bridges from spectroscopic data.

The presence of the symmetric and antisymmetric POP band stretching vibration in all infrared and Raman spectra of $CsLnP_2O_7$, points to a bent $P\hat{O}P$ bridge in $CsLnP_2O_7$ (Ln = Gd, Tb, Dy, Ho, Y, Er, Tm, Yb). This result is in good agreement with the X-ray diffraction study [9,10].

The P–O–P bridge of $P_2O_7^{4-}$ group may be considered as an independently vibrating unit and within the limits of this approximation, its stretching frequencies (which are those of a three-body system) depend on the value of the P–O–P angle, but also on the value of the force constant of P–O bond of the bridge:

Table 4
The values of the POP angle in $CsLnP_2O_7$

Compounds	ν^{as} POP (IR-in cm^{-1})	ν^{s} POP (IR-in cm^{-1})	100 Δ	POP angle value from [21]
$CsGdP_2O_7$	936	737	11.89	130.8
$CsTbP_2O_7$	940	742	11.77	130
$CsDyP_2O_7$	941	743	11.75	129.9
$CsHoP_2O_7$	942	744	11.74	129.7
$CsYP_2O_7$	942	744	11.74	129.7
$CsErP_2O_7$	942	745	11.67	129.3
$CsTmP_2O_7$	943	746	11.66	129.2
$CsYbP_2O_7$	944	747	11.65	128.9

$$\nu^{s}\,(\mathrm{POP}) = 1/2\pi c\sqrt{}k(1/m_{\mathrm{p}} + (1+\cos\alpha)/\mathrm{m_O});$$

k: force constant, m_{p}: mass of phosphorus atom.

$$\nu^{as}\,(\mathrm{POP}) = 1/2\pi c\sqrt{}k(1/m_{\mathrm{p}} + (1-\cos\alpha)/m_{\mathrm{O}});$$

m_{O}: mass of oxygen atom, α: POP angle, ν^{as} POP (the antisymmetric bridge POP stretching mode), ν^{s} POP (the symmetric bridge POP stretching mode).

This approximation leads to Lazarev's relationship:

$$\Delta = (\nu^{as}\mathrm{POP} - \nu^{s}\mathrm{POP})/(\nu^{as}\mathrm{POP} + \nu^{s}\mathrm{POP}) = f(\alpha)$$

[19] which eliminates the contribution of the force constant. The vibrational study of a number of pyrosilicates, pyrogermanates and pyrophosphates [13,20] shows that the Lazarev's relationship is satisfactorily obeyed for a number of compounds.

In order to estimate the POP angle values in $CsLnP_2O_7$ (Ln = Gd, Tb, Dy, Ho, Y, Er, Tm, Yb) we applied the Lazarev's relationship and the plot given by Rulmont et all [21]. The numerical values are presented in Table 4.

The shift of the frequencies ν^{as} (POP) and ν^{s} (POP) (Table 4) is due to the influence of the cation Ln^{3+} on the P–O–P bridge angle, this result is confirmed by the plot (Fig. 4) showing the linear evolution of the POP angle versus the rare earth ionic radii.

It can be seen from Fig. 4 that an increase in the P–O–P angle is indeed correlated with an increase in the ionic radii of Ln^{3+}. Cruickshank [22] attributed this opening of the P–O–P bridge angle to the acquirement of P–O bonds some π-character from the orbitals in the P–O–P plane as well.

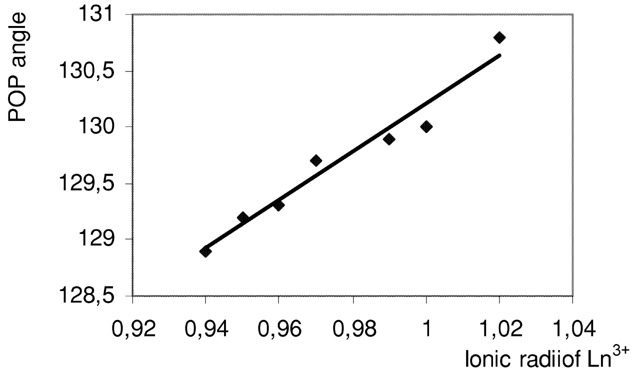

Fig. 4. Evolution of the POP angle versus the rare earth ionic radii in $CsLnP_2O_7$.

4. Conclusion

The spectroscopic data point to a bent P–O–P bridge conformation in $CsLnP_2O_7$ (Ln = Gd, Tb, Dy, Ho,Y, Er, Tm, Yb). The POP bridge angle values are estimated for titled compounds.

The non-coincidence of the majority of the Raman and the IR spectra bands confirms a centrosymmetic structure of these compounds.

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