

## Vibrational spectrum of $KM^{II}P_3O_9$ tricyclophosphates with the benitoite structure

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**Abstract**—The Raman and i.r. spectra of tricyclophosphates  $KM^{II}P_3O_9$  ( $M^{II} = Mg, Ca, Co, Mn, Zn, Cd$ ) with the benitoite structure are discussed on the basis of a factor group analysis, and by comparison with the spectrum of the structurally related  $LaP_3O_9 \cdot 3 H_2O$ . Most of the stretching frequencies have been observed and assigned, whereas the assignment of the bending modes remains more or less hypothetical. Low-frequency i.r. bands have been assigned to translations of either K or  $M^{II}$  cations on the basis of mass effects. The influence of the ring chain polymorphism is briefly discussed.

### INTRODUCTION

The benitoite structure presents an interesting case of planar  $X_3O_9$  rings ( $X = Si, Ge, P$ ) with  $C_{3h}$  symmetry (which is the highest observed local symmetry for this type of molecular group). A fairly detailed vibrational study has already been published for the silicates and the germanates [1], but such data are lacking for the phosphates  $M^I M^{II} P_3O_9$ , whose benitoite structure has been proved by X-ray diffraction [2-4]. For these compounds, the existing vibrational data are restricted to i.r. spectra, either without interpretation [5], or interpreted in the high frequency region only [6]. We present here a more systematic study of this family of compounds.

### EXPERIMENTAL

All the compounds have been synthesized by conventional techniques: stoichiometric quantities of  $NH_4H_2PO_4$ ,  $KHCO_3$  and  $M^{II}O$  (or  $M^{II}CO_3$ ) are well ground and mixed, and very progressively heated to 150-200°C to expel ammonia and water vapour. The heating is then resumed up to 600°C, and this temperature is maintained with intervening grindings until a pure phase is obtained, as checked by X-ray diffractometry. The low-temperature polymorphs are obtained at temperatures not exceeding 350°C. For all the compounds, we have checked that the measured  $d$  values of all diffraction peaks are in good agreement with the calculated ones. The Raman spectra were obtained with a CODERG double monochromator equipped with an  $Ar^+$  laser (200 mW; 5145 Å green line). The i.r. spectra have been registered with a Beckman 4250 spectrometer (2000-300  $cm^{-1}$  region, KBr discs or Nujol for the KCd phosphate), and a POLYTEC FIR 30 interferometer (350-30  $cm^{-1}$ ; polyethylene discs).

### SYMMETRY PROPERTIES AND FACTOR GROUP ANALYSIS

The hexagonal  $KM^{II}P_3O_9$  phosphates investigated in this paper are isomorphous with benitoite, space group  $P6c2-D_{3h}^2$ . The  $P_3O_9$  ring is planar, with  $C_{3h}$  symmetry. The  $M^I$  and  $M^{II}$  cations are located on different sites (2  $e$  and 2  $c$  respectively in the Wyckoff

notation), which however have the same site symmetry  $D_3$  [4].

The ring symmetry is the same in  $LaP_3O_9 \cdot 3 H_2O$ , space group  $P6-C_{3h}^1$ ,  $Z = 1$  [7, 8]. Thus, we can expect some close analogies between the spectra of the  $P_3O_9$  ring in  $KM^{II}P_3O_9$  benitoite compounds and in  $LaP_3O_9 \cdot 3 H_2O$ , but the latter presents the advantage of having one formula unit only in the crystallographic cell. A detailed factor group analysis has already been carried out [1, 6] and the results are given in Table 1. This table contains a brief description of the stretching modes, as proposed by SIMON and STEGER [9] and by LAZAREV [10].

### RESULTS AND ASSIGNMENTS

A few typical spectra are represented in Figs 1 and 2. The observed frequency values are collected in Table 2.

#### General considerations

The proposed assignments are deduced from the following bases.

(i) According to previous papers [1, 9-12], the stretching X-O modes of a  $X_3O_9$  ring ( $X = S, P, Si$ ) will be found in the following sequence:  $\nu_{as}(O^- - X - O^-) > \nu_s(O^- - X - O^-) > \nu_{as}(X - O - X) > \nu_s(X - O - X)$ . This is easily justified by the fact that the X-O<sup>-</sup> (external) bond is significantly shorter than the X-O (internal) bond.

(ii) Frequencies appearing in both i.r. and Raman spectra should be assigned to  $E'$  modes.

(iii) The modes which belong to either  $E'$  (i.r. + Ra) or  $E''$  (Ra) species in  $LaP_3O_9 \cdot 3 H_2O$  should split into doublets in the spectrum of crystals with the benitoite structure, whereas the modes which belong to  $A'$  (Ra) or  $A''$  (i.r.) species remain single.

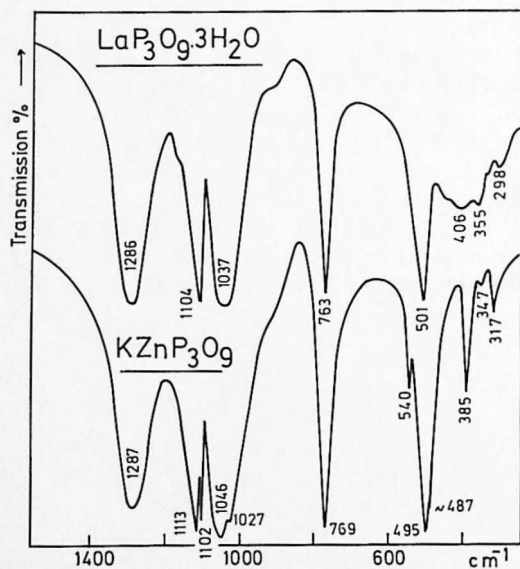
(iv) The frequencies of the P-O<sup>-</sup> bonds should be more sensitive to the nature of the cations than the frequencies of the P-O bonds.

These rules should not be applied too strictly for evident reasons: some i.r.-Ra coincidences may be

Table 1. Factor group analysis of  $\text{LaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  and benitoite-type  $\text{KM}^{\text{II}}\text{P}_3\text{O}_9$ 

Internal modes of the $\text{P}_3\text{O}_9$ ring, stretching vibrations	
$\text{LaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ ( $C_{3h}^1, Z = 1$ )	$\rightarrow \text{KM}^{\text{II}}\text{P}_3\text{O}_9$ ( $D_{3h}^2, Z = 2$ )
$3 A'(\text{Ra}) \nu_s(\text{O}^- - \text{P} - \text{O}^-) + \nu_{\text{as}}(\text{P} - \text{O} - \text{P}) + \nu_s(\text{P} - \text{O} - \text{P})$	$\rightarrow 3 A'_1(\text{Ra}) + 3 A'_2(\text{i})$
$1 A''(\text{i.r.}) \nu_{\text{as}}(\text{O}^- - \text{P} - \text{O}^-)$	$\rightarrow 1 A'_1(\text{i}) + 1 A'_2(\text{i.r.})$
$3 E'(\text{Ra, i.r.}) \nu_s(\text{O}^- - \text{P} - \text{O}^-) + \nu_{\text{as}}(\text{P} - \text{O} - \text{P}) + \nu_s(\text{P} - \text{O} - \text{P})$	$\rightarrow 6 E'(\text{Ra, i.r.})$
$1 E''(\text{Ra}) \nu_{\text{as}}(\text{O}^- - \text{P} - \text{O}^-)$	$\rightarrow 2 E''(\text{Ra})$
Bending vibrations	$\rightarrow 3 A'_1(\text{Ra}) + 3 A'_2(\text{i})$
	$\rightarrow 3 A'_1(\text{i}) + 3 A'_2(\text{i.r.})$
	$\rightarrow 6 E'(\text{Ra, i.r.})$
	$\rightarrow 6 E''(\text{Ra})$
External modes (for benitoite only)	
Cation translations:	
$\Gamma_{\text{M}^{\text{II}}} = \Gamma_{\text{M}^{\text{II}}} = 1 A'_2(\text{i}) + 1 A'_2(\text{i.r.}) + 1 E'(\text{Ra, i.r.}) + 1 E''(\text{Ra})$	Ring translations: $\Gamma_{\text{T}} = 1 A'_1(\text{i}) + 1 A'_2(\text{i.r.}) + 2 E'(\text{Ra, i.r.})$
	Ring librations: $\Gamma_{\text{Lib}} = 1 A'_1(\text{Ra}) + 1 A'_2(\text{i}) + 2 E''(\text{Ra})$

As usual,  $\text{O}^- - \text{P} - \text{O}^-$  stands for exocyclic,  $\text{P} - \text{O} - \text{P}$  for endocyclic, oxygen atoms.

Fig. 1. Compared i.r. spectra of  $\text{LaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  and  $\text{KZnP}_3\text{O}_9$ .

accidental; or the splitting of some modes may not be evident because, either the splitting is too small, or one of the split components is too weak to be observed. Nevertheless, the systematic study of a whole family of compounds greatly reduces the possibility of accidental features and thus of misinterpretations.

The assignments proposed for the stretching vibrations (Table 2) are consistent with these rules and do not need detailed comments. We will just point out the behaviour of the  $E'$  ( $\text{P} - \text{O} - \text{P}$ ) band near  $770 \text{ cm}^{-1}$ : by its nearly constant frequency and its very strong infrared absorption, it is characteristic of a planar  $\text{P}_3\text{O}_9$  ring. However, it is very weak or missing in the Raman spectrum, and its expected splitting has never been observed. The corresponding  $A'_1$  ( $\text{P} - \text{O} - \text{P}$ ) mode can be assigned to either the  $650$ , or the  $625 \text{ cm}^{-1}$

Raman band, but a definite choice does not seem possible. It should be noted that, for these medium-frequency vibrations, the labelling "stretching modes" is not strictly appropriate, since these vibrations have certainly some bending character.

Most of the assignments proposed for the bending vibrations are only tentative; nevertheless, the strong and sharp Raman peak observed between  $355$  and  $370 \text{ cm}^{-1}$  (Fig. 2) is probably the totally symmetric, ring breathing vibration.

#### External modes

The low-frequency ( $< 150 \text{ cm}^{-1}$ ) Raman spectrum is generally of poor quality and will not be discussed. On the contrary, most of the compounds investigated give a very characteristic far i.r. pattern, with one strong, but asymmetric band in the  $250$ – $150 \text{ cm}^{-1}$  region, and a sharp doublet at still lower frequencies (Fig. 3).

The strong band (and the associated asymmetry or shoulder) is displaced from  $250$  to  $150 \text{ cm}^{-1}$  when going from the Ca to the Cd compound; it exhibits significant  $^{24}\text{Mg}$ – $^{26}\text{Mg}$  and  $^{40}\text{Ca}$ – $^{44}\text{Ca}$  isotopic shifts, and the relationship between the frequency and the square root of the atomic mass is nearly linear (Fig. 4). The assignment to a  $\text{M}^{\text{II}}$  translation is thus straightforward. The shoulder is possibly the second translational mode of  $\text{M}^{\text{II}}$  predicted by the factor group analysis. Apart from the Cd compound, the very low frequency pattern is nearly the same for all the  $\text{KM}^{\text{II}}$  compounds, with 2 sharp bands near  $135$  and  $110 \text{ cm}^{-1}$ . These are probably the 2 predicted i.r. active translations of the  $\text{K}^+$  cation.

The pattern given by the Cd compound is somewhat different, probably because the low-frequency translation of the heavy Cd cation allows a mixing with the  $\text{K}^+$  translations (the site symmetry of both cations is the same).

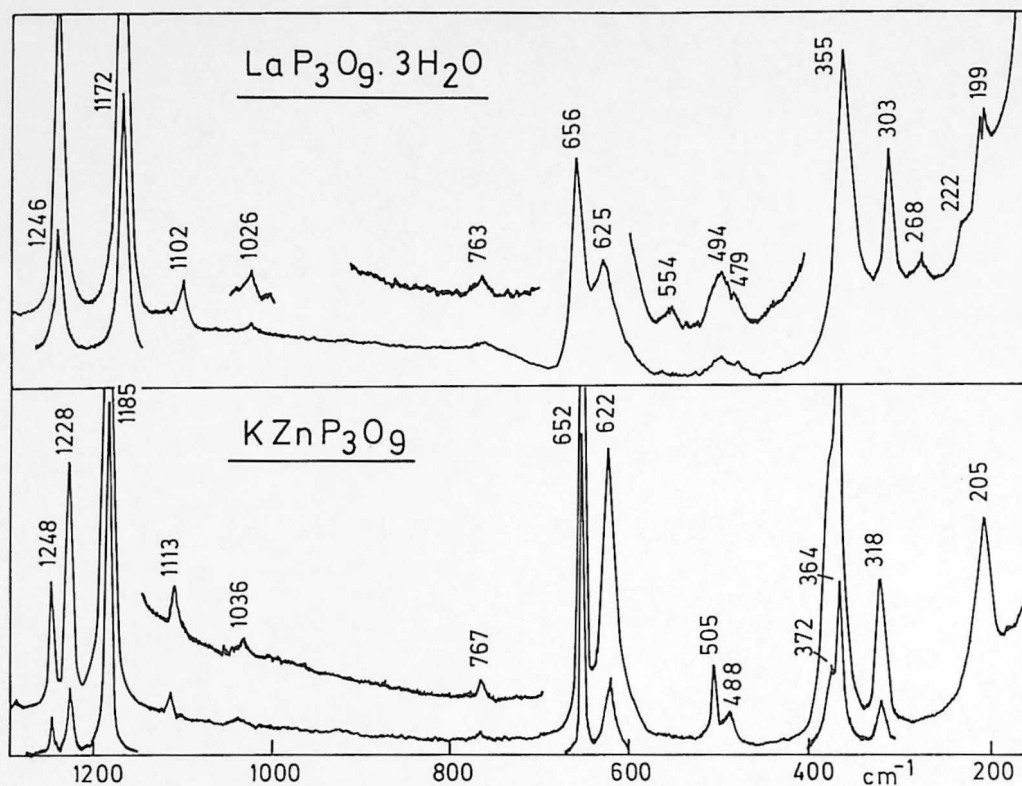


Fig. 2. Compared Raman spectra of  $\text{LaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  and  $\text{KZnP}_3\text{O}_9$ .

#### Influence of the ring-chain polymorphism

Some of the investigated compounds ( $\text{M}^{\text{II}} = \text{Mg}, \text{Co}, \text{Zn}$ ) may also be obtained as a low temperature polymorph with a chain structure [13], and we shall discuss very briefly the essential similarities or differences between the spectra of the two polymorphs. The comparison will be restricted to the Co and Zn compounds (we have been unable to obtain the low temperature Mg polymorph in a pure and well-crystallized state) with, in addition, the Ni compound (chain structure only).

*i.r. Spectra* (Fig. 5). For both structures, strong absorption bands are found in the  $1300\text{--}1000\text{ cm}^{-1}$  region, and near  $500\text{ cm}^{-1}$ , most of these bands are assigned to  $\text{O}^- \text{--} \text{P} \text{--} \text{O}^-$  vibrations. Striking differences appear in the  $900\text{--}700\text{ cm}^{-1}$  region, which corresponds to  $\text{P} \text{--} \text{O} \text{--} \text{P}$  vibrations. The chain structure exhibits near  $900\text{ cm}^{-1}$  a strong band which is missing in the ring structure; conversely, the ring structure is characterized by a strong band near  $770\text{ cm}^{-1}$  (its peak intensity is nearly the same as that of the  $1300\text{--}1000\text{ cm}^{-1}$  bands), whereas the chain structure has 2 weaker bands in the same region.

*Raman spectra* (Fig. 6). Out of the strong bands observed near  $1180, 650$  and  $360\text{ cm}^{-1}$  in the ring structure, two only are still present near  $1170$  and  $700\text{ cm}^{-1}$  in the chain structure. Thus, the strong

intensity of the peak(s) observed in the  $370\text{--}350\text{ cm}^{-1}$  region is apparently characteristic of the ring structure. It should be recalled that we have assigned one of these peaks to the "breathing" vibration of the ring. Other distinguishing features are less striking, and a general comparison of the existing results suggests that the most characteristic feature of the chain structure is the strong i.r. band near  $900\text{ cm}^{-1}$ .

#### DISCUSSION

On the basis of the reported frequencies of  $\text{Na}_3\text{P}_3\text{O}_9$ , IGNATEV and LAZAREV have calculated the vibrational frequencies of a  $\text{P}_3\text{O}_9$  ring with  $C_{3v}$  symmetry [14]. Taking into account the approximate character of these calculations and of the comparison, the agreement between these calculated frequencies and our own results and assignments is satisfactory, at least for the stretching modes (Table 3). The agreement has been consistently considered as a typical vibration of the  $\text{P}_3\text{O}_9$  ring.

Some of the assignments proposed by GRIFFITH [12] are open to discussion. Thus, the highest-frequency i.r. band near  $1290\text{ cm}^{-1}$  is assigned to an *E* vibration, whereas it is clearly of the *A* type. Likewise, the frequency assigned to the ring mode labeled  $\nu_{15}$  is



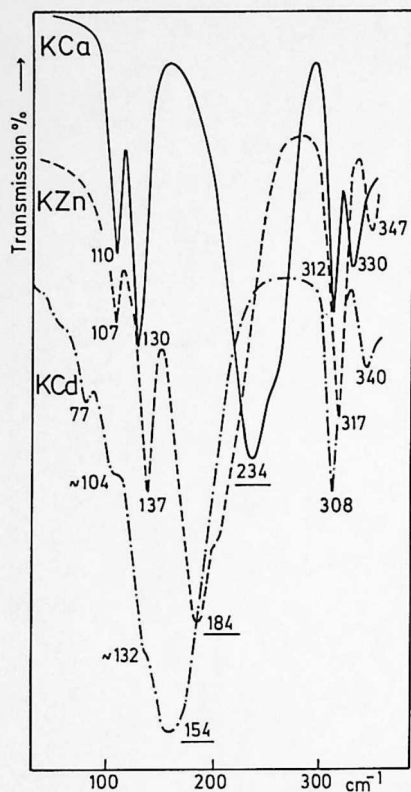


Fig. 3. Far i.r. spectra of  $KM^{II}P_3O_9$  ( $M^{II} = Ca, Zn, Cd$ ) showing the  $M^{II}$  mass effect on the strong band in the  $250\text{--}150\text{ cm}^{-1}$  region.

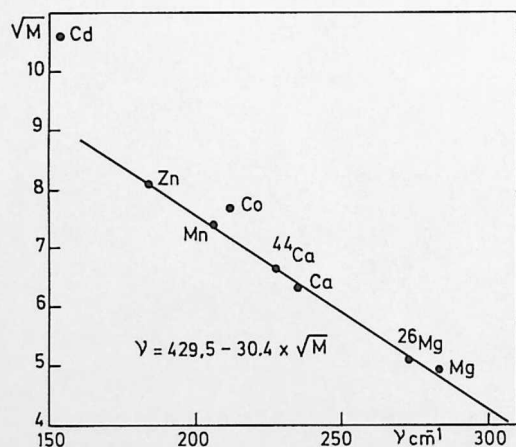


Fig. 4. Relationship between the frequency of the strongest far i.r. band and the square root of the mass of the bivalent cation  $M^{II}$ . The straight line has been obtained by a regression analysis neglecting the points of the Co and Cd compounds.

lower for  $P_3O_9$  than for  $As_3O_9$ , which is in contradiction with the fact that the P (or As) atom is moving during this vibration. Finally, the totally symmetric ring breathing is assigned to a band located at

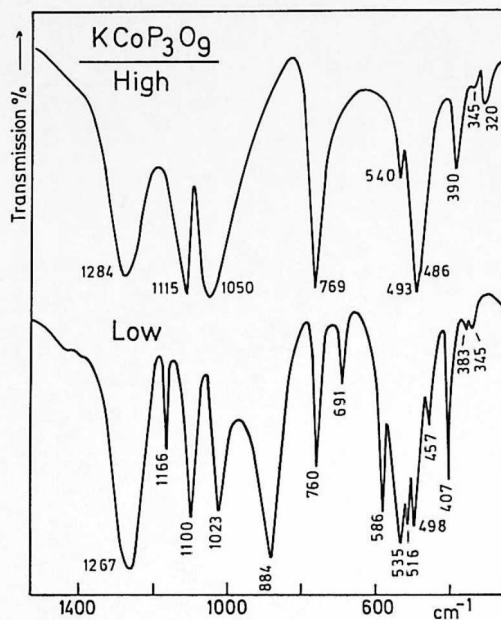


Fig. 5. i.r. spectra of the high ( $600^\circ\text{C}$ ) and low ( $350^\circ\text{C}$ ) temperature polymorphs of  $KCoP_3O_9$  (ring and chain structure, respectively).

$695\text{ cm}^{-1}$  in  $Na_3P_3O_9 \cdot 6H_2O$ . This assignment is contestable for the following reasons.

—The ring breathing frequency is observed at  $802\text{ cm}^{-1}$  for cyclohexane  $C_6H_{12}$ . Since the  $P_3O_9$  ring is much heavier than  $C_6H_{12}$ , the corresponding vibration is expected at much lower frequencies.

—According to GRIFFITH, the equivalent vibration is observed at  $676\text{ cm}^{-1}$  for the  $P_4O_{12}$  ring in  $Na_4P_4O_{12}$ . This is hardly lower than the frequency assigned to the  $P_3O_9$  ring, despite the increase in size and mass.

—A frequency of  $368\text{ cm}^{-1}$  is proposed by GILLESPIE and ROBINSON for the breathing mode of  $S_3O_9$  [11]. This seems more reasonable and a similar figure is expected for  $P_3O_9$ : we have assigned to this vibration the strong Raman peak observed near  $360\text{ cm}^{-1}$  in the Raman spectrum of the benitoite-like phosphates.

#### Comparison with the silicates

We have included in Table 3 the frequency values reported for benitoite itself, the  $^{28}\text{Si}\text{--}^{30}\text{Si}$  isotopic shifts [1], and the  $\nu_{PO}/\nu_{SiO}$  ratio for the different stretching modes. This ratio is significantly higher for most of the  $X\text{--}O_{\text{ext}}$  vibrations than for the  $X\text{--}O_{\text{int}}$  ones, but this correlates very well with the relative values of the P–O or Si–O distances:

$$\text{for } KMgP_3O_9: r_{P\text{--}O_{\text{ext}}} = 1.43 \text{ \AA} \quad r_{P\text{--}O_{\text{int}}} = 1.57 \text{ \AA} \quad [4]$$

$$\text{for benitoite: } r_{Si\text{--}O_{\text{ext}}} = 1.605 \text{ \AA} \quad r_{Si\text{--}O_{\text{int}}} = 1.648 \text{ and } 1.630 \text{ \AA} \quad [15]$$

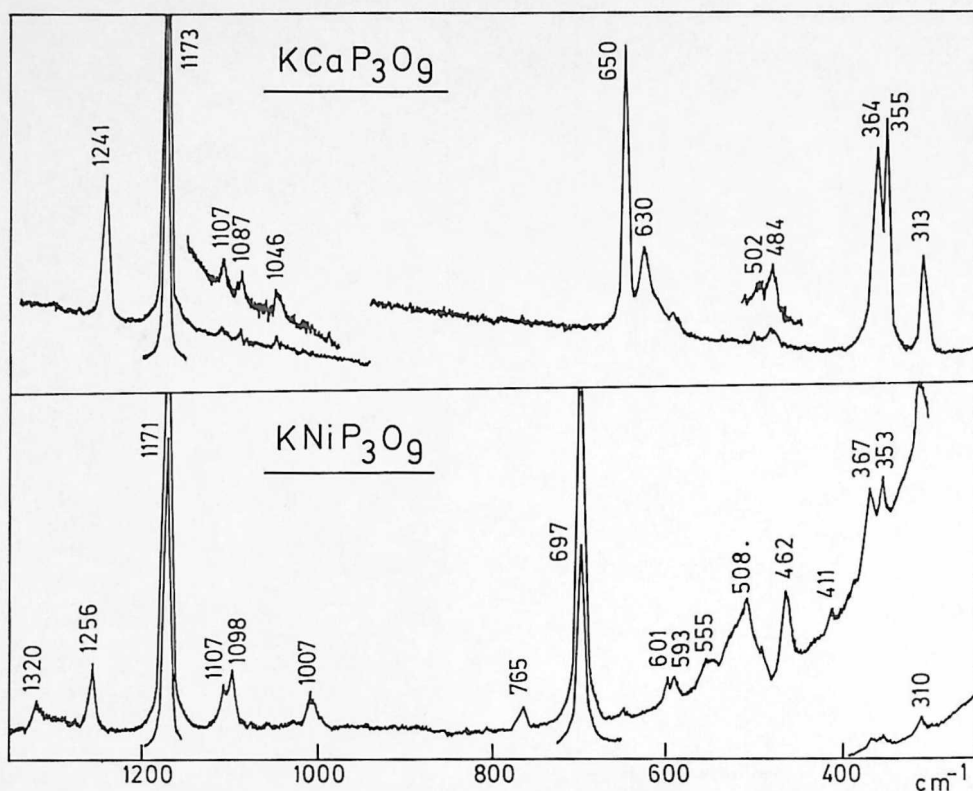


Fig. 6. Raman spectra of  $\text{KCaP}_3\text{O}_9$  (ring structure) and  $\text{KNiP}_3\text{O}_9$  (chain structure).

Table 3. Compared stretching frequencies of  $\text{X}_3\text{O}_9$  rings in the benitoite structure

Observed benitoite-like phosphates		Calculated for $\text{Na}_3\text{P}_3\text{O}_9$ [14]		$\nu$	Silicate	
Average	Assignment		Assignment		$28_{\text{Si}}-30_{\text{Si}}$	$\nu_{\text{PO}}/\nu_{\text{SiO}}$
1283	$A_2''(\text{O}^- - \text{P} - \text{O}^-)_{\text{as}}$	1280	$A_1(\text{O}^- - \text{P} - \text{O}^-)_{\text{as}}$	1030	4	1.25
1244	$E''(\text{O}^- - \text{P} - \text{O}^-)_{\text{as}}$	1267	$E(\text{O}^- - \text{P} - \text{O}^-)_{\text{as}}$	951	?	1.30
1233						
1180	$A_1'(\text{O}^- - \text{P} - \text{O}^-)_s$	1137	$A_1(\text{O}^- - \text{P} - \text{O}^-)_s$	939	10	1.26
1113	$E'(\text{O}^- - \text{P} - \text{O}^-)_s$	1131	$E(\text{O}^- - \text{P} - \text{O}^-)_s$	990	7	1.12
1100						
1049	$E'(\text{P} - \text{O} - \text{P})_{\text{as}}$	992	$E(\text{P} - \text{O} - \text{P})_{\text{as}}$	930	7	1.13
1040	$A_1'(\text{P} - \text{O} - \text{P})_{\text{as}}$	990	$A_2(\text{P} - \text{O} - \text{P})_{\text{as}}$	917	0	1.13
770	$E'(\text{P} - \text{O} - \text{P})_s$	773	$E(\text{P} - \text{O} - \text{P})_{\text{as}}$	760	14	1.01
650	$A_1'(\text{P} - \text{O} - \text{P})_s$	697	$A_1(\text{P} - \text{O} - \text{P})_s$	577	3	1.13

One (OPO) vibration does not fit into this scheme, namely the  $E'$  doublet located near  $1100 \text{ cm}^{-1}$  with a  $\nu_{\text{PO}}/\nu_{\text{SiO}}$  ratio of 1.12 only. This is possibly explained by some mixing with the (POP) vibration near  $1050 \text{ cm}^{-1}$ , which belong to the same  $E'$  symmetry.

#### CONCLUSIONS

A comparative study of  $\text{La}_3\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  and  $\text{KM}^{\text{II}}\text{P}_3\text{O}_9$  tricyclophosphates with benitoite structure, together with a group-theoretical approach,

allows a fairly detailed assignment of the stretching vibrations of the  $\text{P}_3\text{O}_9$  ring in the benitoite structure. Among the external modes, the  $\text{K}^+$  and  $\text{M}^{\text{II}}$  translations are assigned on the basis of mass effects. The ring-chain polymorphs may be identified by their i.r. or Raman spectra, but the most striking differences appear in the i.r. spectrum.

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## REFERENCES

- [1] J. CHOISNET, A. DESCHANVRES and P. TARTE, *Spectrochim. Acta* **31 A**, 1023 (1975); **32 A**, 57 (1976). J. CHOISNET, Thèse de Doctorat, Université de Caen (1973).
- [2] R. ANDRIEU, R. DIAMENT, A. DURIF, M. Th. POUCHOT and D. TRANQUI, *C.r. hebdomadaire Séances Acad. Sci., Paris* **262**, 718 (1966).
- [3] M. Th. POUCHOT, I. TORDJMAN and A. DURIF, *Bull. Soc. fr. Minér. Cristallogr.* **89**, 405 (1966).
- [4] R. MASSE, J. C. GRENIER, M. Th. AVERBUCH-POUCHOT, D. TRANQUI and A. DURIF, *Bull. Soc. fr. Minér. Cristallogr.* **90**, 158 (1967).
- [5] L. VAN DER MAREN, Thèse annexe de Doctorat, Université de Liège (1972).
- [6] K. SBAL, Thèse de Doctorat d'Etat, Université de Dijon (1984).
- [7] O. A. SERRA and E. GIESBRECHT, *J. inorg. nucl. Chem.* **30**, 793 (1968).
- [8] M. BAGIEU-BEUCHER, I. TORDJMAN and A. DURIF, *Revue Chim. Minér.* **8**, 753 (1971).
- [9] A. SIMON and E. STEGER, *Z. anorg. allg. Chem.* **277**, 209 (1954).
- [10] A. N. LAZAREV, *Optics Spectrosc.* **12**, 28 (1962).
- [11] R. J. GILLESPIE and E. A. ROBINSON, *Can. J. Chem.* **39**, 2194 (1961).
- [12] W. P. GRIFFITH, *J. chem. Soc. A* 905 (1967).
- [13] A. DURIF, J. C. GRENIER, M. Th. POUCHOT and D. TRANQUI, *Bull. Soc. fr. Minér. Cristallogr.* **89**, 273 (1966).
- [14] I. S. IGNATEV and A. N. LAZAREV, *Dokl. Akad. Nauk SSSR* **191**, 596 (1970) (pp. 218-221 of the English translation).
- [15] K. FISCHER, *Z. Kristallogr.* **129**, 222 (1969).