

## The infrared spectrum of $\text{NaV}_3\text{P}_3\text{O}_{12}$

E. J. BARAN, I. L. BOTTO

*Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calles 47 y 115, 1900 La Plata, Argentina*

N. KINOMURA, N. KUMADA

*Institute of Inorganic Synthesis, Faculty of Engineering, Yamanashi University, Miyamae-cho 4, Kofu, 400 Japan*

Materials belonging to the  $\alpha\text{-CrPO}_4$  structural type are rather uncommon. Only two simple compounds, apart from  $\alpha\text{-CrPO}_4$  itself [1, 2], are known to adopt this structure, namely  $\text{CrAsO}_4$  [3] and  $\text{RhPO}_4$  [4].

A phase of composition  $\text{NaV}_3\text{P}_3\text{O}_{12}$  (with chemical formula  $\text{NaV}^{\text{II}}\text{V}_2^{\text{III}}\text{P}_3\text{O}_{12}$ ) has recently been prepared [5]. It possesses a packed structure of  $\alpha\text{-CrPO}_4$ , with the  $\text{Na}^+$  cations located in the tunnels of the  $\alpha\text{-CrPO}_4$  framework. It seems, therefore, interesting to characterize this new material by means of infrared (IR) spectroscopy in order to obtain an insight into the vibrational behaviour of this complex and unusual mixed-valence compound. The investigated samples were obtained as described in [5]. The IR spectra were recorded with a Perkin-Elmer 580 B spectrophotometer, using the KBr pellet technique.

$\text{NaV}_3\text{P}_3\text{O}_{12}$  crystallizes in the orthorhombic space group  $\text{Imma} (D_{2h}^{28} - \text{Nr } 74)$  with  $Z = 4$ . The structure is composed of two building units, which are parallel to the  $b$ -axis of the unit cell. One is an  $-\text{O}-\text{P}-\text{O}-\text{V}-\text{O}-\text{P}-$  zig-zag chain constituted by  $\text{PO}_4$  tetrahedra and  $\text{VO}_6$  octahedra linked alternately by corner sharing. The second unit is a rigid shaped  $\text{V}_2\text{P}_2\text{O}_{14}$  block consisting of two  $\text{VO}_6$  octahedra and two  $\text{PO}_4$  tetrahedra; each  $\text{VO}_6$  unit shares opposite edges with a  $\text{VO}_6$  octahedron and a  $\text{PO}_4$  tetrahedron [5].

The complexity of the structure suggests that the factor group method should be the best method for vibrational analysis of this material. This analysis was performed using the tables of Adams and Newton [6] (see also [7]), together with the known structural information [5]. The results are shown in Table I.

A more detailed analysis of the 54 internal vibrations corresponding to the six  $\text{PO}_4$ -vibrators can be obtained correlating the point group of the "free ion" ( $T_d$ ) with its site groups ( $C_2$  and  $C_{2v}$ ) and its factor group ( $D_{2h}$ ), as done formerly for the case of  $\alpha\text{-CrPO}_4$  [8]. The results are summarized in Table II.

The IR spectrum obtained is shown in Fig 1 and the measured band positions are presented in Table III. In order to propose a rough assignment of this very complex spectral pattern, it seems reasonable to analyse the higher- and lower-frequency regions independently. Relatively "pure" P-O stretching vibrations can be expected in the first region, whereas at lower frequencies an important mixing between  $\text{PO}_4$  bendings,  $\text{MO}_6$  vibrations and lattice modes is expected.

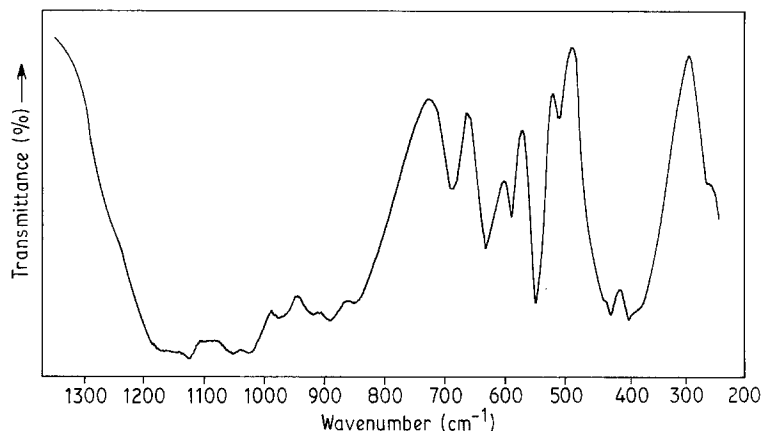
According to the information given in Table II, 10 IR-active bands can be expected in the stretching region and 11 in the bending region. The 10 expected stretching modes are clearly seen in the spectrum. They cover an unusually wide frequency range, between 1200 and  $800\text{ cm}^{-1}$ , in agreement with the very different P-O bond types present in the material. The range covered and general spectral features are similar to those found in  $\alpha\text{-CrPO}_4$  and  $\text{RhPO}_4$  [8].

The spectral range below  $800\text{ cm}^{-1}$  is more difficult to analyse. However, as shown in Table III, the first group of bands can be assigned to factor group components of the antisymmetric bending of the  $\text{PO}_4$  groups (i.e. we can identify five of the eight expected bands). All of the remaining bands, in the range below  $500\text{ cm}^{-1}$ , are certainly strongly mixed modes.

Especially interesting to remark is the strong shift to

TABLE I Factor group analysis of the  $\text{NaV}_3\text{P}_3\text{O}_{12}$  lattice (space group  $\text{Imma}-D_{2h}^{28}$ ;  $Z = 4/2 = 2$ )

Atom	Number and position	$A_g$	$B_{1g}$	$B_{2g}$	$B_{3g}$	$A_u$	$B_{1u}$	$B_{2u}$	$B_{3u}$
Na	2c	1	0	1	1	0	1	1	1
V(1)	2a	0	0	0	0	1	2	2	1
V(2)	4g	1	2	1	2	1	2	1	2
P(1)	2e	1	0	1	1	0	1	1	1
P(2)	4g	1	2	1	2	1	2	1	2
O(1)	4h	2	1	1	2	1	2	2	1
O(2)	4i	2	1	2	1	1	2	1	2
O(3)	8j	3	3	3	3	3	3	3	3
O(4)	8j	3	3	3	3	3	3	3	3
Total (= $3N = 114$ )		14	12	13	15	11	18	15	16
Acust. (= 3)							1	1	1
$T_{\text{total}}$ (= $14 \times 3 = 42$ )		4	4	4	6	3	8	6	7
Rot. (= $6 \times 3 = 18$ )		1	3	2	3	2	2	2	3
$N_{\text{int}}$ (= $6 \times 9 = 54$ )		9	5	7	6	6	8	7	6

TABLE II Expected factor group components for the internal  $\text{PO}_4$  vibrations

Symmetric stretching	$2A_g + B_{2g} + A_u + B_{1u} + B_{2u}$
Antisymmetric stretching	$2A_g + 2B_{1g} + 2B_{2g} + 3B_{3g} + A_u + 3B_{1u} + 2B_{2u} + 3B_{3u}$
Symmetric bending	$3A_g + B_{1g} + 2B_{2g} + 3A_u + B_{1u} + 2B_{2u}$
Antisymmetric bending	$2A_g + 2B_{1g} + 2B_{2g} + 3B_{3g} + A_u + 3B_{1u} + 2B_{2u} + 3B_{3u}$

Activity:  $A_g$ ,  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$  Raman;  $B_{1u}$ ,  $B_{2u}$  and  $B_{3u}$ , IR;  $A_u$ , inactive.

higher wavenumbers of all of the internal phosphate modes, when compared with those usually found in crystalline phosphates and in phosphate solutions ( $\nu_s = 938$ ,  $\nu_{as} = 1017$ ,  $\delta_s = 420$  and  $\delta_{as} = 567 \text{ cm}^{-1}$ ), [9]. These shifts are a direct consequence of the highly condensed nature of this structural type.

In conclusion, the  $\text{NaV}_3\text{P}_3\text{O}_{12}$  investigated presents a very complex IR spectral pattern, in agreement with its highly condensed structure and the very different building units that constitute it. Its vibrational behav-

our resembles closely that of the other materials belonging to the same structural type [8].

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TABLE III IR spectrum of  $\text{NaV}_3\text{P}_3\text{O}_{12}$  (band positions in  $\text{cm}^{-1}$ )

1175	688	
~ 1150 sh	630	Principally
1125	589	$\sigma_{as}(\text{PO}_4)$ modes
~ 1095 sh	548	
1050	511	$\text{PO}_4$ stretching
1022		
975	~ 435 sh	
920	392	Strongly mixed
890	377	$\text{PO}_4$ bendings, $\text{VO}_6$
850	~ 263 sh	and external modes

sh, Shoulder.

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