The infrared spectra of TiPO$_4$ and VPO$_4$

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Examples of compounds belonging to the CrVO$_4$ structural-type (often referred to as β-CrPO$_4$-type) are very scarce. These include some divalent cation sulphates and chromates, the orthovanadates of trivalent indium and thallium and some trivalent metal orthophosphates [1–5].

The vibrational spectra of most of these substances have been recorded and discussed in the last years [6–10]. A definitive vibrational assignment for CrVO$_4$ itself has been recently given and also an interpretation of the vibrational behaviour of β-CrPO$_4$ has been advanced.

In order to extend our knowledge on the spectroscopic behaviour of material of this type we present now an analysis of the IR spectra of TiPO$_4$ and VPO$_4$, because the available information on phosphates of this type is practically restricted to the above mentioned β-CrPO$_4$ spectrum [11] and to brief comment on InPO$_4$ and TlPO$_4$ [8].

The two investigated compounds were obtained by solid state reactions. Powders of (NH$_4$)$_2$HPO$_4$ and TiO$_2$ or NH$_4$VO$_3$ were mixed in a molar ratio of 1.1:1.0 and heated at 950°C under reducing conditions in argon gas. Iron wires and porous titanium metal were used to reduce the oxygen partial pressure. Their purity was checked by X-ray diffractometry. Although the titanium orthophosphate was reported to contain a generally small amount of metal vacancies in the crystal, the formula of TiPO$_4$ is given to it here for simplicity. Details of the preparation were described earlier [5].

The IR spectra were recorded with a Perkin Elmer 580 B spectrophotometer using the KBr pellet technique. Measurements with suspensions of the samples in Nujol gave identical results.

Fig. 1 shows the spectrum obtained for TiPO$_4$. That of VPO$_4$ is practically identical. Both spectra are also very similar to that reported for β-CrPO$_4$.

As the PO$_4$ groups occupy sites of C_{2v} symmetry in the crystal lattices [11], the following changes in selection rules may be expected: the triply degenerate F_2 tetrahedral modes (antisymmetric stretching vibration v_3 and antisymmetric bending vibration v_4) are split into the three IR-active components $A_1 + B_1 + B_2$, the doubly degenerate E mode (symmetric bending vibration v_2) is split into $A_1 + A_2$ but only A_1 is IR-active, and the non-degenerated A_1 mode (symmetric stretching vibration v_1) remains unchanged.

The proposed assignment for the two investigated spectra is given in Table I. As can be seen, the stretching region shows only three of the four expected components. But the intensity of the lowest frequency band (948 cm^{-1} in TiPO$_4$ and 950 cm^{-1} in VPO$_4$) suggests that the symmetric stretching mode v_1 coincides accidentally with one of the three v_3 components. The large splitting in this region is one of the characteristic features of this type of materials and is clearly related to the great distortion of the tetrahedral moieties in this structural type, which generates PO$_4$ units presenting two groups of quite different P–O distances [6, 7, 11].

Also the three v_4 components appear strongly split. The shoulder present in one of the bands (which was also observed for β-CrPO$_4$ [11]) suggests the presence of weak correlation field effects.

The assignment is not easy to make below 500 cm^{-1} because coupling effects between PO$_4$ and $M^{III}O_6$ vibrators are expected to be especially important in this region. Notwithstanding, it is probable that the band observed immediately below the last v_4-component would be the expected v_2-bending mode. The remaining four bands can be assigned surely to $M^{III}O_6$ modes.

It is also interesting to remark that most of the VPO$_4$ bands lie at slightly higher frequencies than the corresponding TiPO$_4$ vibrations, in agreement with the smaller dimensions of the unit cell in the case of the

TABLE I Assignment of the IR spectra of TiPO$_4$ and VPO$_4$ (values in cm^{-1})

TiPO$_4$	VPO$_4$	Assignment
1078	1081	v_{3a}
1015	1020	v_{3b}
948	951	$v_{3c} + v_1$
677	677	v_{4a}
~574 sh* / 559	~583 sh / 560	v_{4b}
530	530	v_{4c}
467	468	v_2 (?)
420	426	
397	405	
350	~385 sh / 350 sh	$M^{III}O_6$ modes
285	288	

*sh = shoulder.

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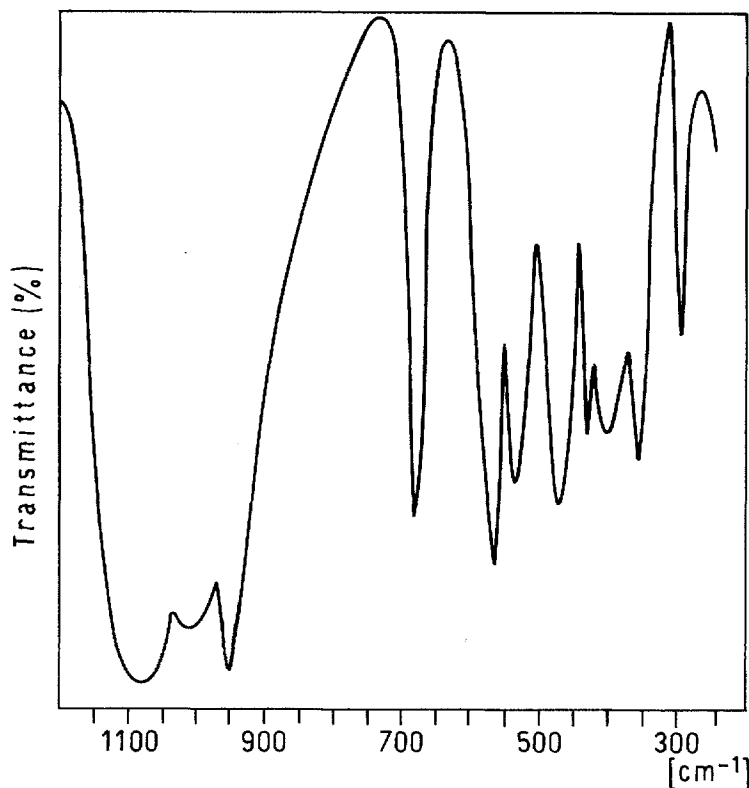
vanadium compound: the orthorhombic lattice constants are $a = 0.5230$, $b = 0.7772$ and $c = 0.6284$ nm for VPO$_4$, and $a = 0.5299$, $b = 0.7910$ and $c = 0.6368$ nm for TiPO$_4$, respectively [5]. Such a behaviour has often been observed in isostructural series of compounds, for example [12, 13], and is related to a reinforcement of the anionic bonding as the volume of the unit cell diminishes.

The present results show that the phosphates belonging to the β-CrPO$_4$ structural type possess a very characteristic IR spectral pattern which is totally different to that found for materials adopting the α-CrPO$_4$ structural type. In this last case, in agreement with a more complex and condensed structure [14, 15], the IR spectra are also more complicated [16].

Acknowledgement

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