INFRARED SPECTRA OF PHOSPHATE MINERALS:
SYMmetry AND SUBSTITUTIONAL EFFECTS
IN THE PYROMORPHITE SERIES


ABSTRACT

Molecular site and infrared-absorption data suggest that the normally tetrahedral
$XY_r^3^-$ group in apatite- and pyromorphite-series minerals has $C_{3v}$ or lower symmetry.
Basic differences in the absorption patterns of pyromorphite, mimetite, and vanadinite
are related to differences in mass and binding energy of the functional ions, inversion of
the frequency of the $v_2$ and $v_1$ vibrations and substitution of non-periodic molecular com-
ponents such as V for P and As. Complete replacement of Ca by Pb in the apatite structure
causes a shift of the $v_3$ and $v_1$ vibrations to lower frequencies, as expected.

From inspection of absorption spectra, phosphate groups substituting in mimetite and
vanadinite can be distinguished from intergrowths of pyromorphite with mimetite or
vanadinite even at low PO$_4^{3^-}$ concentrations producing no detectable response in x-ray
spectra obtained routinely. The PO$_4^{3^-}$ molecule is apparently slightly expanded when
substituting for AsO$_4^{3^-}$ and VO$_4^{3^-}$ ions.

INTRODUCTION

The fundamental vibrations and, hence, corresponding absorptions, contributing to the infrared spectrum of a molecule are localized to a first
approximation by the mass and internal binding energy of the functional
group. In minerals, as in other solids, the vibrational and spectral
characteristics of the molecule are further altered by the environment to
which it is attached.

Because pyromorphite-series minerals enter into a wide range of substi-
tutions involving the molecular ions, they are ideal for examining in an
invariant structure the effects of solid-solution substitution on molecular
absorption spectra. In this isomorphous series, which comprises the
minerals pyromorphite, Pb$_5$(PO$_4$)$_3$Cl, mimetite, Pb$_5$(AsO$_4$)$_3$Cl, and vana-
dinite, Pb$_5$(VO$_4$)$_3$Cl, the functional ions and extramolecular cations are
compositionally variant, with Ca frequentiy substituting for Pb and with
P, As and V substituting mutually in the $XY_4$ position. Since substitu-
tion for Pb did not exceed one per cent in the specimens studied, the
molecular environment remained essentially unaltered, thus permitting
evaluation of the spectra in terms of molecular changes. For manifesta-
tions of the influence of the extramolecular environment the spectrum of
apatite, Ca$_5$(PO$_4$)$_3$(F, Cl, OH), was compared with pyromorphite. Ex-
perience already gained from studies of other mineral groups (Adler and

In this paper, the absorption spectra of apatite and the pyromorphite-
series minerals are examined in relation to the site symmetry of the func-
tional molecular group, change in mass and ionic radius of the participat-
ing atoms, and interaction between the functional ions and their external environment. Some potentially useful generalizations are offered regarding absorption trends, which provide a more complete foundation for the utilization of infrared spectra for interpretative purposes in mineralogical studies.

In addition to contributing to knowledge of the spectral changes that take place with chemical variations in mineral structures, a second gratifying aspect of this study has been the realization of an experimental result of direct mineralogical application. In investigating the pyromorphite system it was found that PO₄³⁻ ions substituting for the AsO₄³⁻ and VO₄³⁻ ions in mimetite and vanadinite can easily be distinguished on the basis of their spectral properties from phosphate ions present as intergrown pyromorphite even at concentration levels that did not produce apparent x-ray indications. The next obvious step would be to extend this application to other isomorphous systems not easily evaluated by x-ray or other means.

Infrared spectra shown here were obtained on a Perkin-Elmer spectrophotometer, Model 21, using finely ground sample material imbedded in KBr discs. The mineral specimens were obtained by permission of Dr. George Switzer from the collections at the U. S. National Museum. The writer is indebted to Dr. Irving Breger and the U. S. Geological Survey for the use of the recording spectrophotometer and to Dr. Howard Evans, Jr. for providing helpful comments on various aspects of this study.

**Symmetry of the PO₄³⁻ Ion in Apatite**

The free phosphate ion, PO₄³⁻, is an example of a molecular ion belonging to point group T₄d. In the ideal symmetry state only the triply degenerate vibration species, F₂, of tetrahedral molecules is infrared active and, therefore, among the fundamental bands only absorptions corresponding to the v₁ and v₄ vibrations should be observed. The two remaining fundamentals, v₀ and v₃, become apparent only when the configuration of the ion is modified to certain point groups of lower symmetry.

The 2-15 μ infrared wavelength region scanned in this investigation includes only the v₀ and v₁ fundamentals of the phosphate ion. Herzberg (1945) places the v₀ and v₄ vibrations for the tetrahedral PO₄³⁻ ion at 1082 cm⁻¹ (9.2 μ) and 980 cm⁻¹ (10.2 μ), respectively; however, the frequencies can be expected to vary somewhat for different crystal structures. Since the v₁ mode is infrared active only for point groups compatible with a molecular dipole moment, i.e., when centers of positive and negative charges of the molecule do not coincide, its appearance in phosphate mineral spectra is indicative of a lowering of the molecular sym-
metry from $T_d$ to either $C_{3v}$, $C_{2v}$, $C_2$, $C_s$ or $C_1$. For normally tetrahedral molecules having a modified symmetry, resolution of the latent $v_1$ mode is accompanied by removal of the degeneracies of $v_3$ so that either two or three absorption bands should be apparent for the latter mode. In some cases, however, the split bands may not be resolved, and only a single $v_3$ band will appear. In apatite, the symmetry of the phosphate ion, as deduced from its absorption spectrum (Fig. 1), has evidently been lowered from $T_d$ to conform to a point group compatible with a $v_1$ dipole.

According to the site-group data for apatite (Strukturbericht II, 1928–1932), the P atom is on a $C_s$ site, thereby restricting the $PO_4^{3-}$ ion to point groups $C_{3v}$, $C_{2v}$, $C_{3v}$, $D_{2d}$ and $T_d$. $T_d$ and $D_{2d}$ symmetry are ruled out considering the molecular dipole indicated by the presence of $v_1$ at 10.35 $\mu$ (Table 1). Moreover, according to the character tables for symmetry species (Herzberg, 1945), the $F_2$ degeneracies characteristic of $T_d$ molecules are completely removed for molecular point groups $C_s$ and $C_{2v}$, and, therefore, three absorption maxima can be expected for $v_3$. The remaining point group, $C_{3v}$, has doubly degenerate and non-degenerate normal vibrations. Identification of the infrared-active modes and their state of degeneracy for a normally tetrahedral molecule modified to $C_{3v}$ symmetry was accomplished with the aid of character tables (Herzberg, 1945). This analysis indicates that the $v_3$ vibration should consist of two infrared-active modes and that $v_1$ should yield a single band (Table 1).

The spectrum for apatite (Fig. 1) conforms to the vibrational requirements of $C_{3v}$ symmetry for the phosphate ion (Table 1) and suggests that the $PO_4^{3-}$ group in apatite has or approaches this symmetry; hence, the molecule apparently has higher symmetry than the surrounding crystal field. This interpretation is supported by the data of Fischer and Ring (1957) who found absorption bands at 16.6 and 17.5 $\mu$. These correspond

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**Table 1. Possible Molecular Point Groups and Vibration Modes for the $PO_4^{3-}$ Ion Where P is on a $C_s$ Site**

<table>
<thead>
<tr>
<th>Molecular Point Group</th>
<th>Number of Infrared Active Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_d$</td>
<td>$v_2$ 0 $v_1$ 1 $v_3$ 2 $v_2$ 0</td>
</tr>
<tr>
<td>$D_{2d}$</td>
<td>$v_2$ 2 $v_1$ 0 $v_3$ 2 $v_2$ 0</td>
</tr>
<tr>
<td>$C_{3v}$</td>
<td>$v_2$ 2 $v_1$ 1 $v_3$ 2 $v_2$ 1</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$v_2$ 3 $v_1$ 1 $v_3$ 3 $v_2$ 1</td>
</tr>
<tr>
<td>$C_4$</td>
<td>$v_2$ 3 $v_1$ 1 $v_3$ 3 $v_2$ 2</td>
</tr>
</tbody>
</table>

1 Point groups to which a molecule with a dipole moment might belong.
Fig. 1. Apatite, St. Lawrence Co. N. Y., R5224; pyromorphite, Phoenixville, Pa. 12572; mimetite, Tsumeb, S. W. Africa R12415; vanadinite, Chihuahua, Mex. R8741. Specimens are identified by U. S. National Museum numbers.
to the $v_4$ fundamental and are in accord with $C_{3v}$ molecular symmetry. It presumes, however, that the observed bands correspond only to first-order fundamentals and that there are no accidental degeneracies. When consideration is given to the possibility of unrevealed degeneracies, it may be concluded that the molecule has $C_{3v}$, $C_{2v}$ or $C_{s}$, but not higher symmetry. Considering the bond-length data for the PO$_4$ group in apatite by Posner et al. (1958), $C_{s}$ molecular symmetry appears most reasonable. It is possible, therefore, that one cannot unambiguously draw a conclusion as to the exact molecular symmetry of the phosphate ion in apatite from the infrared data presented in this investigation. Nevertheless, it should be clear that the molecule would have no higher symmetry than $C_{3v}$.

### Table 2. Absorption Wavelengths for Mineral Spectra in Fig. 1

<table>
<thead>
<tr>
<th>Mineral</th>
<th>PO$_4^{3-}$</th>
<th>AsO$_4^{3-}$</th>
<th>VO$_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_3$</td>
<td>$v_1$</td>
<td>$v_3$</td>
</tr>
<tr>
<td>Apatite</td>
<td>R5224$^a$</td>
<td>9.16, 10.35</td>
<td>12.25, 12.75, 12.75</td>
</tr>
<tr>
<td>Pyromorphite</td>
<td>12572</td>
<td>9.78, 10.8</td>
<td>12.75</td>
</tr>
<tr>
<td>Mimetite</td>
<td>R12415</td>
<td>n.d.</td>
<td>12.75</td>
</tr>
</tbody>
</table>

n.d. Not detectable.

$^1$ Assignment based on Siebert's (1954) analysis of the Raman spectrum of Na$_3$VO$_4$, made certain by the polarization of the Raman line for Na$_3$VO$_4$ and confirmed by its intensity and sharpness.

$^a$ U. S. National Museum number.

Spectral Relations in the Pyromorphite Series

A knowledge of the site population in the apatite lattice is obtainable from structure data available in Strukturbericht II (1928–1932) which gives reference to the original data. As previously indicated, the P atoms are located on $C_s$ sites, thus allowing considerable choice of molecular point groups. The apparent symmetry of the PO$_4^{3-}$ ion, which in this case may only approximate the true symmetry, emerges from inspection of the infrared spectrum of the fundamental vibration modes.

The acceptable molecular sites for pyromorphite may be identified according to the method of Halford (1946) using data on space-group symmetry and the unit-cell content. However, this approach was unnecessary
since the structures of pyromorphite and apatite are evidently analogous.

Although pyromorphite, mimetite and vanadinite are isomorphous, their spectra (Fig. 1) show certain basic differences. The absence of absorption corresponding to the \( v_1 \) vibration for arsenate ions in mimetite is caused by the proximity of the \( v_1 \) and \( v_3 \) modes so that \( v_1 \) cannot be resolved from the stronger \( v_3 \) absorption. This is in accord with Siebert's (1954) observation of the coincidence of Raman lines for \( v_3 \) and \( v_1 \) at 813 cm\(^{-1}\) (12.30 \( \mu \)). For vanadinite, the \( v_1 \) vibration of vanadate ions occurs at a higher frequency than \( v_3 \), according to Siebert's (1954) assignment of the observed Raman line at 870 cm\(^{-1}\); hence, the absorption at 11.48 \( \mu \) for vanadinite specimen R8741 (Fig. 1) is presumably \( v_1 \). Because of its low amplitude, this band appears not to have been resolved sufficiently to be detectable in the spectrum of specimen R9320 (Fig. 3). The absorption patterns of mimetite and vanadinite are otherwise in accord with the molecular symmetry suggested for pyromorphite.

No detailed interpretation is offered to account for the apparent dissimilarity between the physical configurations of AsO\(_4^{3-}\) and VO\(_4^{3-}\) absorptions, which contrasts with the striking resemblance between the AsO\(_4^{3-}\) and PO\(_4^{3-}\) spectra (exclusive of \( v_1 \)) of the pyromorphite series. There is, however, a suggestion of a dependency on atomic periodicity. Whereas the electronic arrangement is maintained for the P and As ions, it does not hold for the V ion which in its ground state has a different con-
Fig. 3. 1. Mimetite, Durango, Mex. 95576; 2. mimetite, Zacatecas, Mex. R12470; 3. mimetite, Cumberland, Eng. C4130; 4. 80% mimetite, Chihuahua, Mex. C5879; 20% pyromorphite, Phoenixville, Pa. 12572; 5. pyromorphite, Phoenixville, Pa. 12572; 6. vanadinite, Durango, Mex. R9320. Specimens are identified by U. S. National Museum numbers.
configuration of valence electrons and a different orbital population. A somewhat similar though not strictly analogous relation has been observed for carbonate minerals (Adler and Kerr, 1963) which yield aberrant spectra on substitution of non-periodic cations adjoining vibrating CO$_3^{2-}$ molecules, e.g., Pb or Fe, Mn and Zn in place of Group II elements in the aragonite-type and calcite-type lattices.

At this point it seems desirable to comment concerning the implication of the alteration in pattern of the XO$_3^{2-}$ absorption for the pyromorphite series when X ions have similar valence but different electron configurations. First, it might erroneously be concluded in the absence of knowledge of the structure of the minerals being examined, that such spectral difference denotes structural non-conformity. A number of recent papers could be cited in which similar conclusions have been drawn. Such a conclusion would have to be based on the assumption that isostructural minerals will yield absorptions that may differ in wavelength but are otherwise essentially alike. Accepting the evidence presented here as a contraindication of this condition, we should be alert to a possible change in absorption pattern when functional components having similar chemical binding properties but different electronic structures are substituted in isomorphous systems.

**Vibration Frequency, Mass and Ionic Radius Dependencies**

The frequency of a molecular vibration is dependent first of all on the molecular parameters and to a lesser degree on the forces exerted on the molecule by the crystal field. For apatite and pyromorphite, the reduced masses of the molecular ions are identical, therefore the frequencies of the PO$_4^{3-}$ oscillations are governed primarily by the molecular force constants, which for both minerals are dependent on the equilibrium internuclear distances between the P and O atoms in these structures. This distance is undoubtedly sensitive to variations in lattice characteristics that exert variable forces on the molecular ions. For example, it has been established for both calcite- and aragonite-type carbonates, in which divalent cations are coordinated to molecular oxygen atoms, that the frequencies of stretching and bending vibrations of the CO$_3^{2-}$ ion are generally lowered with increasing cation size (Adler and Kerr, 1963). The relationship apparently is further dependent on the electronic arrangement of the cations, since frequency-cation-radius trends for series of cations belonging to different periodic groups have been found to be non-collinear. The displacement of the $v_3$ and $v_1$ fundamentals to lower frequencies (Fig. 1) on substitution of Pb for Ca in the apatite-type structure is consistent with these observations on carbonates.

For the pyromorphite series, the equilibrium internuclear X–Y dis-
stance in XY$_4$ molecules such as PO$_4^{3-}$, AsO$_4^{3-}$ and VO$_4^{3-}$ is primarily a function of the ionic radius of the variable X atom. Since Pb, in this case, is always the dominant externally coordinated cation, there is for the various members no significant change in the interaction between the molecular vibrations and the external environment. Badger's (1934) equation,

$$k_0 = 1.86 \times 10^5/(R - d)^3,$$

although specifically applicable to diatomic molecules, reflects generally the inverse relationship between the force constant, $k_0$, and the internuclear distance, $R$. The molecular vibration frequency, $v$, is dependent on the restoring forces, measured in terms of $k_0$, between the participating atoms as well as the masses of these atoms. The relationship may be expressed approximately by

$$v = \frac{1}{2\pi c} \sqrt{\frac{k}{u}},$$

where the vibration frequency, $v$, is a function of the force constant, $k$, and the reduced mass, $u$, of the vibrating atoms, all other terms being invariant.

The spectral frequency differences between pyromorphite, mimetite and vanadinite are explicable and to a considerable degree predictable in terms of these parameters. On complete substitution of As or V for P the effect of diminished force constants is reinforced by the increases in mass, thereby shifting $v_3$ and $v_1$ to lower frequencies. Because of opposing mass and force-constant effects and perhaps also because of dissimilarities in orbital configuration, the relative positions of absorption bands are less predictable for mimetite and vanadinite than for pyromorphite and mimetite. The theoretical frequency trends are depicted in Fig. 2, and the actual displacements are shown in the mineral spectra (Fig. 1).

**Effects of Limited Molecular Substitution**

Phosphate was detected in the spectra of several specimens of mimetite and vanadinite, and its presence in concentration of the order of 1 to 10 per cent P was confirmed by spectrographic analysis. The positions of the phosphate bands suggest that the ion is not present as an admixture, i.e., in intergrown pyromorphite, nor are sufficient amounts of other cations present (none exceeds 1 per cent) to suggest the presence of another phosphate component. It is also very unlikely that the bands are contributed by another lead-phosphate mineral inasmuch as the few known natural compounds of this kind are fairly rare and ordinarily contain additional cationic components which would reveal the presence
of such compounds. It may reasonably be concluded, therefore, that the phosphate in these specimens is a substitutional component replacing arsenate and vanadate ions in the mimetite and vanadinite lattices.

The spectra of the specimens under discussion are shown in Fig. 3 and the absorption data appear in Table 3. Pyromorphite (curve 5) characteristically has its two $v_3$ absorptions at about 9.78 and 10.34 μ and its single $v_1$ band at about 10.8 μ. These values are also observed for pyromorphite in an artificial mixture of 20% pyromorphite and 80% mimetite by weight (curve 4). For natural phosphatian mimetite (curves 1, 2 and 3) and phosphatian vanadinite (curve 6) the corresponding phosphate absorptions are shifted to about 10.0 and 10.50 μ ($v_3$) and 10.9μ ($v_1$). This displacement to lower frequencies appears to be diagnostic of substituted phosphate groups. It indicates an expansion of unknown but probably very low magnitude of the P to O distance when PO$_4^{3-}$ groups occur on AsO$_4^{3-}$ or VO$_4^{3-}$ sites in the mimetite and vanadinite lattices. No conspicuous changes were observed in the arsenate- and vanadate-band positions for phosphatian and non-phosphatian mimetite and vanadinite.

Of three specimens identified by museum label as endlichite (arsenian vanadinite) only one showed evidence of phosphate substitution (curve 6, Fig. 3). Emission spectrographic analyses indicated less than 1 per cent As in each of the three, and the P content exceeded 1 per cent only in the

### Table 3. Absorption Wavelengths for Mineral Spectra in Fig. 3

<table>
<thead>
<tr>
<th>Mineral</th>
<th>PO$_4^{3-}$</th>
<th>AsO$_4^{3-}$</th>
<th>VO$_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_3$</td>
<td>$v_1$</td>
<td>$v_3$</td>
</tr>
<tr>
<td>Mimetite 95576</td>
<td>10.0</td>
<td>n.d.</td>
<td>12.2--4.4</td>
</tr>
<tr>
<td>Mimetite R12470</td>
<td>10.48</td>
<td></td>
<td>12.73</td>
</tr>
<tr>
<td>Mimetite C4130</td>
<td>10.50</td>
<td>v.w.</td>
<td>12.45</td>
</tr>
<tr>
<td>80:20 mixture Mi/Py</td>
<td>10.05, 10.9</td>
<td>10.74</td>
<td>12.74</td>
</tr>
<tr>
<td>Pyromorphite 12572</td>
<td>10.34</td>
<td></td>
<td>12.75</td>
</tr>
<tr>
<td>Vanadinite R9320</td>
<td>10.05, v.w.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d. not detectable.

v.w. very weak.

1 U. S. National Museum number.
specimen represented by curve 6. The phosphate bands for vanadinite in curve 6 are identical in frequency to those for phosphate-substituted mimetite and are, also, indicative of solid-solution substitution.

There is more to be learned about substitutional effects. For instance, if Ca were to substitute partially for Pb in the phosphatian mimetite or vanadinite lattice, the vibrations of the phosphate ion would probably be shifted to higher frequencies. This shift could possibly cause coincidence with the frequencies for pyromorphite. In this circumstance, the spectrum could be misinterpreted. However, inasmuch as the vibration frequencies of arsenate and vanadate ions should also increase with Ca substitution, this problem may be circumvented by a close inspection of the position of arsenate and vanadate bands. Moreover, a spectrographic analysis will readily confirm the presence of significant amounts of Ca if there is any doubt concerning the interpretation.

**X-ray Spectra**

X-ray spectra were obtained on all samples for which infrared patterns are shown. End members can be identified readily on the basis of distinct 2θ values.

The three phosphatian mimetite and one phosphatian vanadinite specimens studied show no obvious indication in their x-ray spectrograms of the presence of phosphate. No peak deviation greater than 0.2 2θ was observed. Since these minor shifts were not unidirectional, they do not appear to be structurally significant. The x-ray spectrum of a mixture comprising 10% pyromorphite and 90% mimetite by weight yielded no obvious indication of the presence of pyromorphite; however, phosphate as pyromorphite was readily detectable in the infrared spectrum. When the ratio is increased to 20:80, however, the three most intense x-ray “lines” of pyromorphite are observed (Fig. 4). Hence, routine x-ray determination does not seem to provide an indication of phosphate in these specimens. Since substitution of PO₄ for AsO₄ may possibly be detected by careful and rigorous x-ray determination of axis dimensions as a function of composition, infrared spectra do not provide a unique manifestation of this phenomenon. However, it may be concluded as a result of this study that infrared spectroscopy is much more sensitive and rapid than x-ray diffraction, used routinely, in recognizing pyromorphite mimetite and pyromorphite-vanadinite intergrowths and in distinguishing such aggregates from phosphate-substituted mimetite and vanadinite. It seems less likely, however, because of overlapping absorptions, that arsenate substitution or mimetite intergrowth in vanadinite will be discernible by this method. These results appear to provide some justification for
Fig. 4. X-ray diffractometer powder patterns of pyromorphite and mimetite. Mimetite from Tsumeb yields an infrared spectrum containing no phosphate bands; mimetites from Durango, Zacatecas and Cumberland yield infrared spectra that contain phosphate bands.
making greater use of infrared spectroscopy in investigating molecular substitution in mineral structures.

**V₃-V₁ Inversion**

It is of some interest that υ₃ is at a lower frequency than υ₁ for the vanadate ion, whereas for the phosphate and arsenate ions υ₃ is higher than υ₁. Woodward and Roberts (1956) have pointed out that according to the simple valence force field, υ₃ should always be greater than υ₁ in tetrahedral molecules, the two approaching equality as mₓ/mᵧ increases, i.e., as the mass of X in XY₄ increases with respect to Y. In a number of cases with high values of mₓ/mᵧ, υ₃ is observed to be slightly less than υ₁ so that one is apt to infer that this reversal of position can be correlated with a high value of mₓ/mᵧ. However, examination of mₓ/mᵧ relationships for the pyromorphite series indicates no such dependency, inasmuch as the υ₃-υ₁ reversal is prominent for VO₄³⁻ but not for AsO₄³⁻ in spite of the much larger mass of As.

This frequency inversion might also be examined from the standpoint of a possible relationship to the repulsion forces between nearest oxygen atoms in contiguous tetrahedra. One is encouraged to believe that the repulsion between oxygen atoms linked through a mutual Pb atom has a real effect on the molecular vibration frequencies, for if Ca substitutes for the larger Pb ion, the oxygen atoms in adjoining tetrahedra are brought closer together resulting in a shortening of the P–O distances and a corresponding increase in the vibration frequencies of the PO₄³⁻ ion. However, for all pyromorphite-series minerals, the distance between nearest oxygen atoms in adjacent tetrahedra should be relatively constant since the size of the extramolecular cation is invariant and the increase in size of the X ion, when, for example, As substitutes for P, is compensated structurally by expansion of the lattice. It appears, therefore, that the υ₁-υ₃ frequency inversion may be more closely related to an internal, non-mass-dependent property of the XY⁺ ion, such as its possible distortion and expansion along certain symmetry directions. It is interesting to note in this connection that tetrahedrally coordinated ions with υ₁ higher than υ₃, namely ReO₄⁻, VO₄³⁻, MoO₄²⁻, and WO₄²⁻, also have large four-fold radii, whereas those with υ₃ higher than υ₁, such as SO₄²⁻, SeO₄²⁻, PO₄³⁻, SiO₄⁴⁻, CrO₄²⁻, MnO₄⁻, ClO₄⁻ and IO₄⁻, have relatively small four-fold radii.

**Conclusions**

As far as its application to mineralogy is concerned, the present work has demonstrated that infrared spectra can distinguish phosphatian mimetite and vanadinite rapidly and easily from pyromorphite-mimetite
and pyromorphite-vanadinite intergrowths at phosphate concentrations producing no readily detectable response in routine x-ray spectra. It is likely that other mineral systems will also lend themselves to this approach.

The results obtained here also lead to the conclusion that dissimilarities in the spectra of isostructural minerals may result from substitutions of electronically dissimilar components and from $v_3-v_1$ inversions. This consideration becomes especially important when using infrared spectra as a basis for demonstrating or confirming the structural equivalence or non-equivalence of two mineral substances. There is also sufficient grounds for suggesting that absorption spectra obtained on powdered samples may not always reflect the true symmetry of the functional molecule because of insufficient spectral resolution; nevertheless, they are useful in restricting consideration to specific point groups.

References


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