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Study on attribution of laser Raman spectroscopy for hopeite crystal films

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Laser Raman spectroscopy was applied to clarify the chemical structure of hopeite crystal films. Orthophosphate [PO_4^{3-}], which is a regular tetrahedron, has four basic vibration modes, $+ \nu_1$, ν_2, ν_3 and $\nu_4 +$, of which ν_1 and ν_3 are observed at 800 to 1300 cm^{-1}. Here, the main peak corresponds to ν_1 and the other peaks correspond to ν_3 untied and split. A reference sample of 85% H_3PO_4 showed two peaks in the same region, the main peak corresponding to ν_1 and the sub-peak corresponding to ν_3 degenerated. It was found that a basic vibration mode of ν_3 appears at 1150 cm^{-1}. Raman spectra were observed for hopeite dissolved in HCl solution. Three peaks were found in the region, but the spectral pattern was quite different from that of crystalline hopeite, and was similar to that of H_3PO_4 aqueous solution. The peak intensity ratio of I_{1075}/I_{690} differed between liquid-state hopeite and H_3PO_4 aqueous solution, but the band frequencies of the three peaks were consistent with each other. It was confirmed that the three peaks correspond to the $P(OH)_3$ and PO stretching vibrations of [H_3PO_4] and the PO_2 stretching vibration of [$H_2PO_4^-$] formed by the dissociation of H_3PO_4. The PO_2 stretching vibration observed at 1075 cm^{-1} depends on the dissociation state of H_3PO_4.

1. Introduction

Phosphate treatment technology has been confirmed as a surface control of automobile steels, [1, 2]. In general, by the galvannealed steels, which improve the corrosion-resistance properties of automobile bodies, hopeite crystal films are formed by Reactions 1 and 2

$$Zn(H_2PO_4)_2 \rightarrow ZnHPO_4 + H_3PO_4 \qquad (1)$$

$$3ZnHPO_4 \underset{\langle H_2O \rangle}{\rightarrow} \underset{\text{hopeite films}}{Zn_3(PO_4)_2 \cdot 4H_2O} + H_3PO_4 \qquad (2)$$

If manganese or nickel ions are contained in the phosphating solution, modified hopeite is formed by Reaction 3 and the chemical properties (paint film adhesiveness or alkaline resistance, etc.) of the hopeite are improved [3–17].

$$3ZnHPO_4 \xrightarrow[\langle H_2O \rangle]{Mn^{2+},\ Ni^{2+}\ (Me = Mn\ \text{and/or}\ Ni)} Zn_{3-x}Me_x(PO_4)_2 \cdot 4H_2O + H_3PO_4 \qquad (3)$$

In previous reports [14, 15], we considered the relationship between the metallic components in hopeite films and laser Raman spectra. It was found that four peaks of the Raman spectrum for [PO_4^{3-}] were observed and that the Raman bands shifted according to the metallic component composition in the hopeite crystals.

In this study, conventional hopeite films not containing metal ions (system with $x = 0$ in Reaction 3) was analysed in solid and liquid states to investigate the spectral pattern of Raman spectroscopy and the attribution of Raman bands for [PO_4^{3-}] was studied.

2. Sample preparation and laser Raman spectroscopy

Films of 10 mg hopeite crystals were prepared from the powder state. The metallic component composition of hopeite crystals was determined by atomic absorption spectroscopy using a Hitachi 180-60 Zeeman instrument and the composition of the zinc component was found to be 42.6 wt %.

Because of the crystal's insolubility in water, a saturated hydrochloric acid solution of hopeite crystals was used to measure the liquid state of hopeite. If sulphuric acid was used to prepare the liquid-state hopeite, Raman spectra corresponding to [SO_4^{2-}], which has vibration modes ν_1, ν_2, ν_3 and ν_4 like [PO_4^{3-}] could be observed. As a result, spectral analysis of [PO_4^{3-}] would become complicated. Thus hydrochloric acid should be used.

The reference sample was 85 wt % H_3PO_4 (Nakaraitesuku) was used to compare the Raman spectra.

The laser Raman instrument (Jobin-Yvon Ramanor U-1000) was used with an instrument accessory (macro mode; macro sample chamber 90° or 180° scattering), a source of light (Ar^+ laser of Innova 90-5, exciting wavelength = 514.5 nm), and detector (PM:

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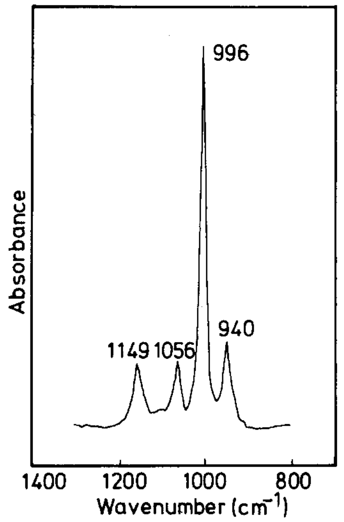


Figure 1 Raman spectrum of the powdered hopeite.

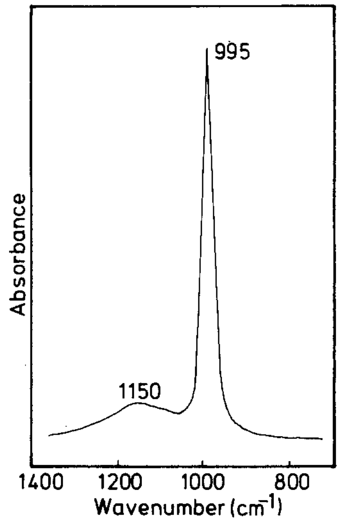


Figure 3 Raman spectrum of 85% H_3PO_4 solution.

RCA31034/photon counting system, Hamamatsu C1230). Measurements were made with a beam size of 0.3 to 0.5 mm, PM supply of 1650 V, a gate time of 1.0 sec, and a scan speed of 60 cm min^{-1}.

3. Results and discussion

Raman spectrum for hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, in the solid state is shown in Fig. 1. Four peaks were observed in the region 800 to 1300 cm^{-1} [14, 15]. This spectrum corresponds to [PO_4^{3-}] in hopeite films and is attributable to stretching vibration.

In general, [PO_4^{3-}] forms a regular tetrahedron as shown in Fig. 2 [18]. ν_1, ν_2, ν_3, and ν_4 are the symmetrical stretching vibration, A_1, the double degeneracy vibration, E, with deformation, the triple degeneracy vibration, F_2, of stretching type, the triple degeneracy vibration, F_2, with deformation, respectively. At 800 to 1300 cm^{-1}, only ν_1 and ν_3 are observed [18]. However, in the case of a solid crystal such as hopeite, the symmetry will become distorted by interaction with the surrounding crystalline structure. As a result, it is thought that the degeneracy of the vibration modes shown in Fig. 2 will be untied and split. Because the number of the degeneracy of ν_3 is triple, four peaks were thought to be observed with one peak for ν_1 and three peaks for ν_3. This was consistent with the results given by Sommer and Leidheiser [19].

[PO_4^{3-}] in liquid-state material exists as a free molecule and there is no interaction, so it is predicted that the degeneracy state will be different from the solid state. Phosphoric acid, H_3PO_4, which is a simple liquid with [PO_4^{3-}], was investigated. The Raman spectrum for 85% H_3PO_4 is shown in Fig. 3. A sharp peak at 995 cm^{-1} and a broad beak at 1150 cm^{-1} were observed. The former corresponds to 996 cm^{-1} solid hopeite in Fig. 1 and the latter to 1149 cm^{-1}. The 995 cm^{-1} peak also implies the symmetrical stretching vibration mode, ν_1, in Fig. 2. On the other hand, the 1150 cm^{-1} peak corresponds to the triple degeneracy, ν_3. That is, the intrinsic vibration mode of ν_3 exists in 1149 to 1150 cm^{-1}. If the degeneracy becomes untied, the basic mode will split into three peaks.

A sample of hopeite was dissolved in HCl by preparing a concentration 0.47 mol l^{-1} HCl and adding excess hopeite films to it. This reaction is expressed as

$$Zn_3(PO_4)_2 \cdot 4H_2O + 6HCl \rightarrow 2H_3PO_4 + 3ZnCl_2 + 4H_2O \qquad (4)$$

The concentration of the hopeite solution was 7.8 × 10^{-2} mol l^{-1} and that of H_3PO_4 is 0.16 mol l^{-1}. The Raman spectrum for this sample is shown in Fig. 4.

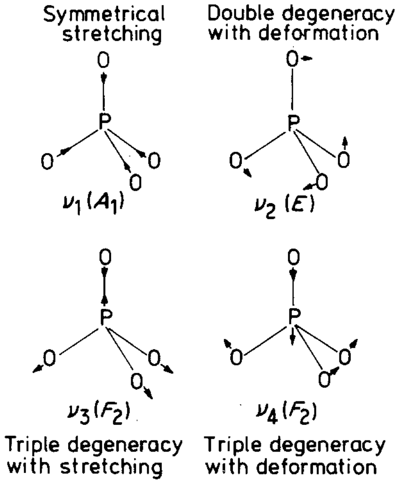


Figure 2 Structural model of basic vibration for [PO_4^{3-}].

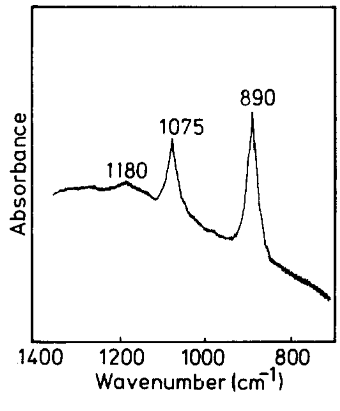


Figure 4 Raman spectrum of the hopeite dissolved in HCl at a concentration of 0.16 mol l^{-1}.

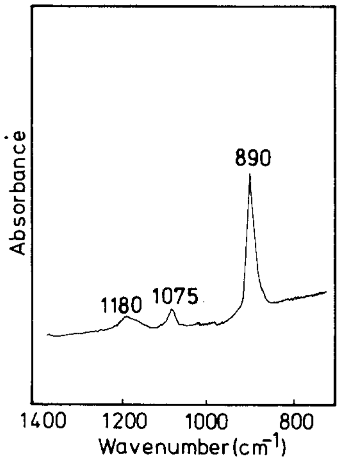


Figure 5 Raman spectrum of H_3PO_4 diluted with pure water at a concentration of 0.16 mol l^{-1}.

There were three peaks at 800 to 1300 cm^{-1}, but the Raman bands of each peak differed from those for solid state hopeite in Fig. 1 or those for H_3PO_4 in Fig. 3. If the chemical state of the hopeite dissolved in HCl formed by Reaction 4 is similar to H_3PO_4, Raman bands will be consistent with each other. The reference samples of 0.16 mol l^{-1} H_3PO_4 (the same concentration as that of hopeite dissolved in HCl) and 1.6 mol l^{-1} H_3PO_4 were provided to investigate the Raman spectra. These results are shown in Figs 5 and 6. Raman spectra for these two H_3PO_4 aqueous solutions showed three peaks, and the Raman bands were consistent with those for hopeite dissolved in HCl. This supported the fact that the chemical state of hopeite dissolved in HCl was similar to that of diluted H_3PO_4.

H_3PO_4 may be dissociated as shown in Reactions 5 to 7

$$H_3PO_4 + H_2O \overset{K_1}{\rightleftharpoons} H_2PO_4^- + H_3O^+ \qquad (5)$$

$$H_2PO_4^- + H_2O \overset{K_2}{\rightleftharpoons} HPO_4^{2-} + H_3O^+ \qquad (6)$$

$$HPO_4^{2-} + H_2O \overset{K_3}{\rightleftharpoons} PO_4^{3-} + H_3O^+ \qquad (7)$$

where K_1, K_2 and K_3 are the dissociation constants, and the values of pK_1, pK_2 and pK_3 are 2.1, 7.26 and 12.67, respectively. Hence, it is considered that Raman spectrum varies according to the dissociation level. The peak intensities of 890, 1075 and 1175 to 1180 cm^{-1} are expressed as I_{890}, I_{1075} and $I_{1175\text{ to }1180}$, respectively. Table I gives a summary of the relative intensity ratios. The Raman bands for each peak were consistent, but I_{1075}/I_{890} for hopeite dissolved in HCl showed a large value compared to those for diluted H_3PO_4 aqueous solutions. The big difference between these samples was thought to be caused by the dissociation level, even if the H_3PO_4 concentrations for hopeite dissolved in HCl and 0.16 mol l^{-1} H_3PO_4 solution were the same.

TABLE I Intensity ratios of Raman peaks

Specimens	Intensity ratio	
	I_{1075}/I_{890}	$I_{1175\text{ to }1180}/I_{890}$
Dissolved hopeite in HCl solution	0.50	0.11
0.16 mol l^{-1} H_3PO_4	0.14	0.08
1.6 mol l^{-1} H_3PO_4	0.05	0.09

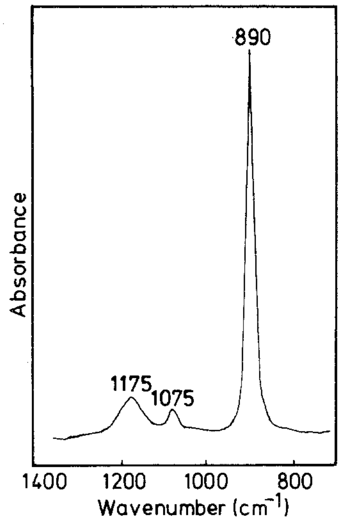


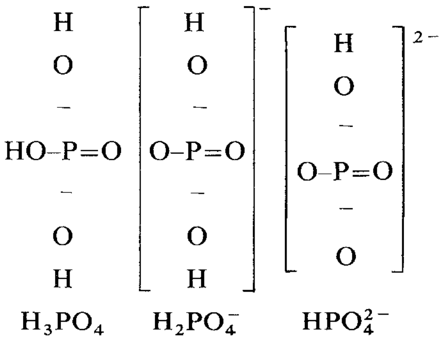
Figure 6 Raman spectrum of H_3PO_4 diluted with pure water at a concentration of 1.6 mol l^{-1}.

Incidentally, the basic vibration models for [PO_4^{3-}] shown in Fig. 2 are indicated as the point group, T_d [21], but [HPO_4^{2-}] and [$H_2PO_4^{2-}$] are expressed as point group, C_{3v} and point group C_{2v}, respectively [22]. For T_d, Γ_{vib}, the number of degrees of freedom of the vibration, corresponds to

$$\Gamma_{vib} = A_1 + E + 2F_2 \qquad (8)$$

Because A_1, E and F_2 are Raman active, they provide four Raman bands. However, only A_1 and F_2 are involved in the region 800 to 1300 cm^{-1} in this study. In general, the degrees of freedom of the vibration for a non-linear molecule which is constituted by N atoms is $3N - 6$. Because [PO_4^{3-}] consists of five atoms, six atoms for [HPO_4^{2-}] and seven atoms for [$H_2PO_4^{2-}$], the degrees of freedom of vibration are 9, 12 and 15, respectively. These differences produce the different Γ_{vib} and will alter the Raman spectrum pattern.

Attribution of Raman bands shown in Figs 4 to 6 was carried out, and compared to the attribution given by Steger and Herzog [22] and Adams *et al.* [23]. The Raman bands at 890, 1075 and 1175 to 1180 cm^{-1} could correspond to the symmetrical stretching vibration for $P(OH)_3$ in [H_3PO_4], the symmetrical stretching vibration for PO_2 in [$H_2PO_4^-$] and to the stretching vibration for PO in [H_3PO_4], respectively. Here the chemical structures of H_3PO_4, $H_2PO_4^-$ and HPO_4^- are expressed as



$$\begin{array}{c}H\\O\\-\\HO-P=O\\-\\O\\H\end{array}\quad\left[\begin{array}{c}H\\O\\-\\O-P=O\\-\\O\\H\end{array}\right]^{-}\quad\left[\begin{array}{c}H\\O\\-\\O-P=O\\-\\O\end{array}\right]^{2-}$$

H_3PO_4 $\quad$ $H_2PO_4^-$ $\quad$ HPO_4^{2-}

The dissociation constants of H_3PO_4 are:

$$K_1 = 7.94 \times 10^{-3} \quad \text{for } H_2PO_4^-$$

$$K_1 \times K_2 = 4.90 \times 10^{-10} \quad \text{for } HPO_4^{2-}$$

The concentration of HPO_4^{2-} is negligible compared to that of $H_2PO_4^-$, thus $[H_2PO_4^-]$ and undissociated $[H_3PO_4]$ were thought to be responsible. The fact that the relative intensity of the symmetrical stretching vibration for PO_2 in $[H_2PO_4^-]$ appearing at 1075 cm^{-1} was larger than those of other samples, supports the dominant dissociation of Reaction 5.

There is clear difference in the basic vibration between the Raman spectrum of hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, with a crystalline state, and that of hopeite dissolved in HCl. Although ν_1 and ν_3 modes were observed for the former, the Raman spectra of undissociated $[H_3PO_4]$ and dissociated $[H_2PO_4^-]$ were observed for the latter.

Analysis of 85% H_3PO_4 elucidated the splitting of the degeneracy about the ν_3 mode for solid state hopeite, and analysis of diluted H_3PO_4 solution provided the dissociation state of liquid state hopeite. Therefore, analysis of solid state hopeite is suitable for characterization of hopeite itself, and it was found that the analysis of liquid state hopeite became complicated because of new Raman spectra accompanying the dissociation. The analysis for hopeite dissolved in HCl also provided useful information for clarifying the degeneracy state of $[PO_4^{3-}]$ in hopeite films.

4. Conclusions

1. The Raman spectra for hopeite films with a solid state exhibited four peaks showing ν_1, the symmetrical stretching vibration and ν_3, the triple degeneracy stretching vibration split.

2. 85% H_3PO_4, which forms a regular tetrahedron, showed a ν_3 peak only at 1150 cm^{-1}. Thus it was found that this band corresponded to the intrinsic ν_3 band.

3. The Raman spectrum for hopeite films dissolved in HCl at a concentration of 0.16 mol l^{-1}, differed from that for the solid hopeite. The spectrum showed three peaks; however, the spectral pattern and peak bands were quite different from that of solid hopeite.

4. It was confirmed that $[H_2PO_4^-]$ due to the dissociation of $[H_3PO_4]$ has an influence on hopeite films dissolved in HCl but not on diluted H_3PO_4 aqueous solution.

5. The relative intensity of the PO_2 symmetrical stretching vibration for $[H_2PO_4^-]$ seen at 1075 cm^{-1} indicates the dissociation level.

6. The analysis method by laser Raman spectroscopy was very useful for clarifying basic chemical structure of hopeite films.

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