

Influence of metal components in Hopeite films on IR and laser Raman spectra

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Hopeite films on galvanized steel were formed in various zinc phosphate solutions. The metal component composition of various Hopeite films was determined by atomic absorption. By measuring the infrared (IR) spectra and the laser Raman spectra for these films, the influence of metal component composition on these spectra could be investigated. In IR spectra, peaks corresponding to ν_3 and ν_4 , the basic vibration mode of PO_4^{3-} , were seen, but the peak patterns of ν_4 were different for Hopeite containing manganese and that not containing it. In the Raman spectra, four clear peaks for various films were found in the region 1300 to 800 cm^{-1} . Although these spectra are due to PO_4^{3-} , ν_1 and ν_3 are found in this region. Essentially, ν_3 degenerates triply, but in the crystalline state of Hopeite films, the symmetry of the regular PO_4^{3-} tetrahedron will be distorted by the interaction. At that moment, the degenerations of ν_3 are untied and split into three peaks. Thus it was thought that spectra with four peaks of ν_1 were generated. However, the main peak corresponds to ν_1 and other three peaks correspond to ν_3 . The values of the Raman band for various Hopeite films were compared. The band shifted to the lower wavenumber region according to the increase of manganese or nickel in these films. The structure of Hopeite films modified by the action of manganese or nickel has been analysed to be $\text{Zn}_{3-x}\text{Me}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Me = Mn or Ni), but this structure is different from that of normal Hopeite films ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$).

1. Introduction

Two types of zinc phosphate film exist, one is Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$), and the other is Phosphophyllite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$). The bone structure of Hopeite is made up of the regular tetrahedron of $[\text{ZnO}_4]$, $[\text{PO}_4]$, and the octahedron of $[\text{ZnO}_2(\text{H}_2\text{O})_4]$ [1, 2].

When metal ions such as Mn^{2+} or Ni^{2+} are present in the zinc phosphating solution, they become incorporated in the zinc phosphate films. Expressing these metal components in the films as Me, the modified Hopeite may be shown as $\text{Zn}_{3-x}\text{Me}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The characterization of this modified Hopeite has been investigated using several analytical methods [3-12]. In the present work, the influence of these metal components in Hopeite films on the IR and laser Raman spectra with regard to $[\text{PO}_4]$ was investigated.

2. Materials and Methods

2.1. Steel sheet material

Galvanized steel sheets with δ_1 alloy phase of FeZn_7 were used. The coating mass was 60 g m^{-2} .

2.2. Degreasing and zinc phosphating

Alkaline degreasing of the steel sheets was carried out at 55°C for 120 sec; they were then subjected to zinc phosphating under the conditions given in Table I.

2.3. Sample preparation for measurements

After forming the Hopeite films on galvanized steel sheets, four types of Hopeite powder samples were

obtained by carefully scraping with cutter knife. Prior to analysis by IR and laser Raman spectroscopy, the metal component composition was determined by atomic absorption using a Hitachi 180-60 instrument.

2.4. Conditions of measurement for IR and laser Raman spectroscopy

A Bruker FT-IR IFS 113V as instrument was used for IR spectroscopy, with a DTGS detector, SiC as a source of light, a resolving power of 4 cm^{-1} , and with a Ge/KBr beam splitter. Measurement was performed under liquid nitrogen.

For laser Raman spectroscopy, a Jobin-Yvon Ramanor U-1000 as instrument was used with an RCA 31034/Photon counting system (Hamamatsu C1230) as detector, an Ar^+ Laser Innova 90-5, 514.5 nm excited wavelength, as a source of light, a resolving power of 0.15 cm^{-1} at 579.1 nm, and

TABLE I Specific values for zinc phosphating conditions

| | | Solution | | | |
|----------------------------------|--------------------|----------|-------|-------|-------|
| | | A | B | C | D |
| Chemical composition (p.p.m.): | Zn^{2+} | 1000 | 1000 | 1000 | 1000 |
| | Ni^{2+} | 0 | 800 | 0 | 800 |
| | Mn^{2+} | 0 | 0 | 800 | 800 |
| | PO_4^{3-} | 20000 | 20000 | 20000 | 20000 |
| | F^- | 0 | 0 | 500 | 500 |
| | ClO_3 | 500 | 500 | 0 | 0 |
| Temperature ($^\circ\text{C}$) | | 53 | 53 | 43 | 43 |
| Time (sec) | | 120 | 120 | 120 | 120 |

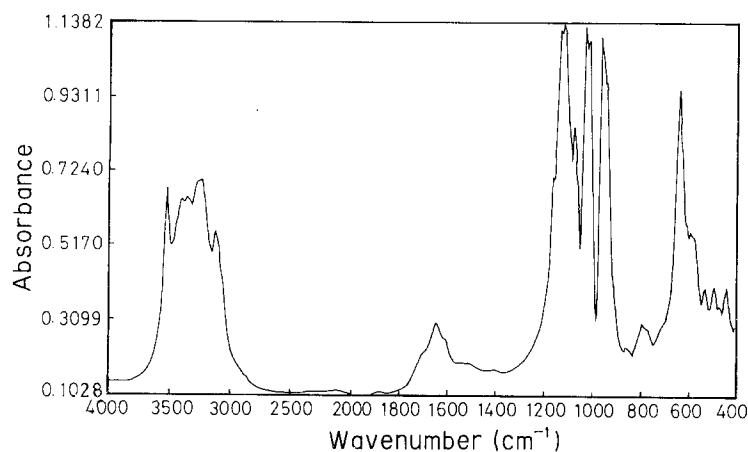


Figure 1 Intermediate infrared transmission spectrum for Hopeite films formed in solution A.

a plane holographic grating (110 mm × 110 mm). Measurement was carried out at room temperature.

3. Results and discussion

The metal components of the four kinds of Hopeite films are shown in Table II. IR spectra were measured for these films. The intermediate infrared transmission spectrum for Hopeite films formed in solution A is shown in Fig. 1. The far infrared transmission spectrum for the same samples is shown in Fig. 2. In the intermediate range, peaks appeared at 3500 to 3000, 1640, 1200 to 900 and 640 cm⁻¹. It was thought that the peak at 3500 to 3000 cm⁻¹ corresponded to the stretching vibration of O-H in H₂O, that at 1640 cm⁻¹ to the deformation of H-O-H in H₂O, and the three peaks at 1200 to 900 and that at 640 cm⁻¹ to PO₄³⁻ in the Hopeite films.

PO₄³⁻ is formed of five atoms producing a tetrahedron structure with phosphorus as the centre atom. In general, for a non-linear molecule which is constituted by *N* atoms, the degrees of freedom of the vibration is expressed as 3*N* - 6 [12]. Accordingly, in the case of five atoms, as in PO₄³⁻, the degree becomes nine, and nine vibration modes are expected. However, in the case of a gas or liquid phase, it is possible for PO₄³⁻ to exist as a free molecule, the regular tetrahedron structure being formed and four basic vibration modes of *v*₁, *v*₂, *v*₃ and *v*₄ are generated. Here, *v*₁ is the symmetrical stretching vibration A₁, *v*₂ is the double degeneracy vibration E with deformation, *v*₃ is the triple degeneracy vibration F₂ of stretching type, and *v*₄ is the triple degeneracy vibration F₂ of deformation type. However, *v*₁ and *v*₂ are inactive in IR absorption whereas *v*₃ and *v*₄ are active. For this reason, it was thought that the three peaks at 1200 to 900 cm⁻¹ correspond to the *v*₃ mode and that at 640 cm⁻¹ to the *v*₄ mode. In the far infrared region of Fig. 2, a clear peak of *v*₄ was observed and, although the small peaks were continually confirmed below

550 cm⁻¹, they were considered to belong to the vibration between the metal component and the ligand.

The intermediate and far infrared transmission spectra are compared in the same way for Hopeite films formed in solution C in Figs 3 and 4. The differences between the *v*₃ and *v*₄ peaks for Hopeite films with and without manganese could then be evaluated. The three *v*₃ peaks for Hopeite films containing manganese were sharply split, and the left-hand peak (higher region of wavenumber) of the three shifted to a lower wavenumber by 10 cm⁻¹ compared to those for Hopeite films without manganese. The wavenumber of peak location was determined by acquiring the centre of the absorption band. The *v*₄ peak for the same samples generated a new peak at 580 cm⁻¹.

These facts imply that the incorporation of manganese into Hopeite films will affect to the coordination state of PO₄³⁻ and cause the splitting or shifting of peaks.

Laser Raman spectra were then measured for these Hopeite films. The spectrum for Hopeite films formed in solution A is shown in Fig. 5. A spectrum with four peaks in the region between 1150 and 930 cm⁻¹ was observed, the main peak appearing at 996 cm⁻¹. The spectra for Hopeite films formed in solutions B, C and D are shown in Figs 6, 7 and 8, respectively. Although the patterns of the spectra were almost the same, the wavenumbers of each peak were slightly different. In

TABLE II Metal contents in various Hopeite films

| Metal content (wt %) | | | |
|----------------------|------------|------------|------------|
| Solution A | Solution B | Solution C | Solution D |
| Zn: 42.6 | Zn: 41.6 | Zn: 38.5 | Zn: 37.3 |
| | Ni: 1.7 | Mn: 4.7 | Ni: 1.3 |
| | | | Mn: 4.5 |

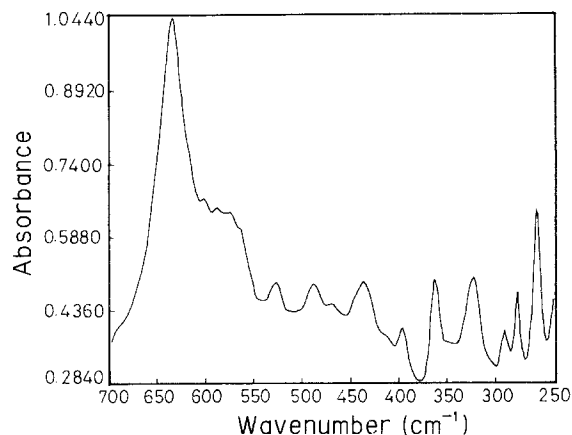


Figure 2 Far infrared transmission spectrum for Hopeite films formed in solution A.

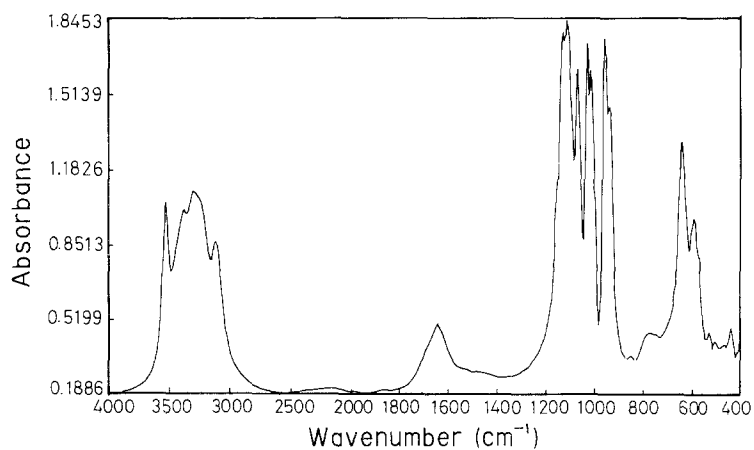


Figure 3 Intermediate infrared transmission spectrum for Hopeite films formed in solution C.

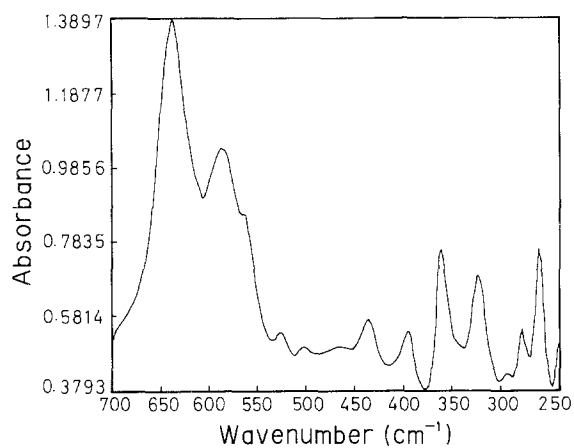


Figure 4 Far infrared transmission spectrum for Hopeite films formed in solution C.

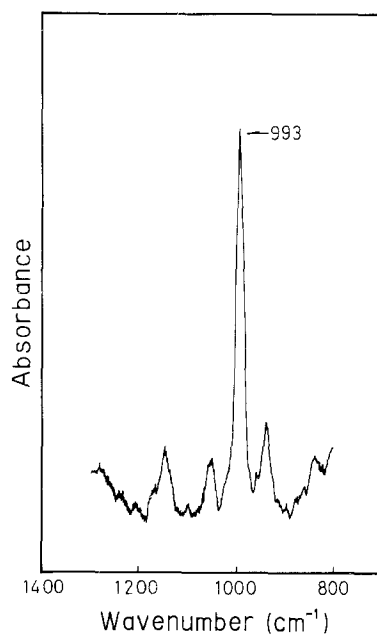


Figure 6 Raman spectrum for Hopeite films formed in solution B.

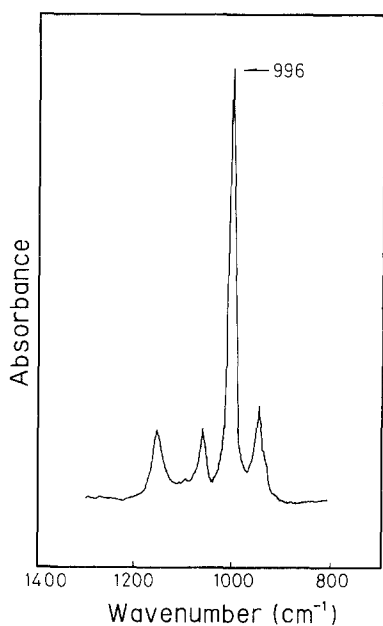


Figure 5 Raman spectrum for Hopeite films formed in solution A.

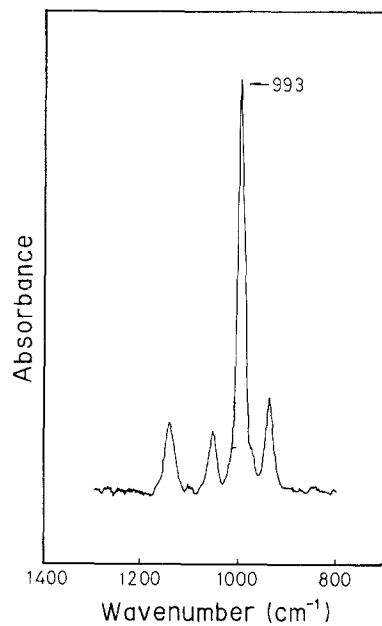


Figure 7 Raman spectrum for Hopeite films formed in solution C.

TABLE III Raman spectra for various Hopeite films

| Raman band (cm ⁻¹) | | | |
|--------------------------------|------------|------------|------------|
| Solution A | Solution B | Solution C | Solution D |
| 1149 | 1149 | 1145 | 1141 |
| 1056 | 1054 | 1055 | 1052 |
| 996 | 993 | 993 | 992 |
| 940 | 940 | 937 | 938 |

particular, the main peak for Hopeite films formed in solution D appeared at 992 cm⁻¹.

To investigate the movement of the Raman band within this wavenumber region, the peak location of the Raman band was determined and is shown in Table III. The data of this table correspond to the various Hopeite films having the different metal compositions shown in Table II. The four peaks were due to the PO₄³⁻ which constitutes Hopeite films. PO₄³⁻ has four basic vibration modes, ν_1 , ν_2 , ν_3 and ν_4 , all modes being Raman active. At 1300 to 800 cm⁻¹, shown in Figs 5 to 8, ν_1 and ν_3 are observed. When this ion exists in Hopeite films as a perfect regular tetrahedron, only peaks of ν_1 and ν_3 should appear in this region. But in practice, there were four peaks. The reason for this is thought to be as given below.

PO₄³⁻ in Hopeite films affects the symmetry of the regular tetrahedron structure by interaction with the surrounding crystalline structure, so that the symmetry will become distorted. As a result, it is thought that the degeneracy of the vibration modes shown in Fig. 9 will be untied and split. The number of degenerations is different in ν_1 and ν_3 , the former is single and the latter is triple. Accordingly, if the degeneracy is untied, ($\nu_1 + \nu_3$) = (1 + 3) is brought into being, so the degrees of freedom of vibration becomes four. It is thought that this is the reason why four peaks appear in the Raman spectrum.

Three peaks, except for main peak, will correspond to the stretching vibration mode of ν_3 split into three peaks; the main peak around 990 cm⁻¹ will correspond to the symmetrical stretching vibration of ν_1 . The level

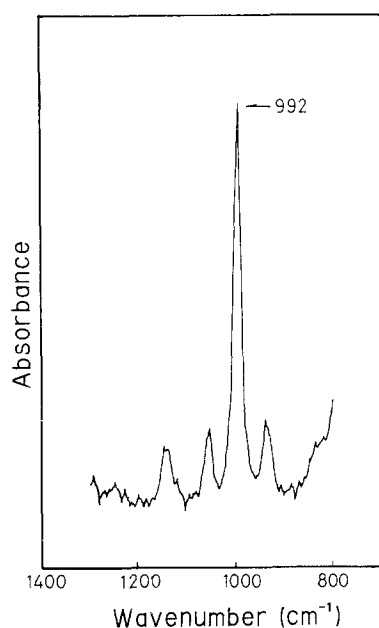
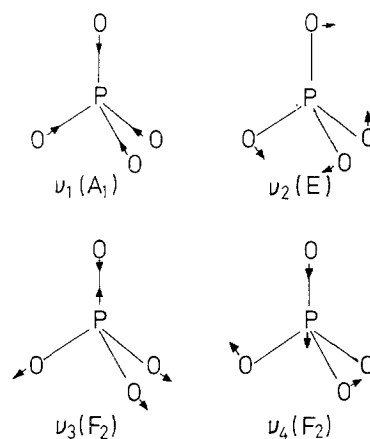


Figure 8 Raman spectrum for Hopeite films formed in solution D.

Figure 9 Structural model of basic vibration modes for PO₄³⁻.

of interaction of PO₄³⁻ with its surroundings or the degree of collapse of the symmetry will affect the number of basic vibrations, the Raman band or the intensity of the Raman spectrum.

The relationship between metal component composition in Hopeite films and the Raman band was investigated by comparing the data of Tables II and III. As shown in Figs 5 to 8, the Raman band of the main peak shifted to a lower wavelength, but in addition the three peaks of ν_3 shifted to a lower region with increasing manganese or nickel content in the Hopeite films. Thus increasing the metal content in Hopeite films has an increasing effect on the data of Raman band. Also, the tendency to shift ν_3 to a lower wavelength with increasing manganese or nickel content could be correlated with the data of the IR spectra. But basically, Raman spectra showed a sensitivity to the degree of modification of Hopeite films by metal components to a greater extent than did the IR spectra.

4. Conclusions

1. IR spectra for Hopeite films showed ν_3 and ν_4 to be the basic vibration modes of PO₄³⁻; the peaks of ν_3 were observed at 1200 to 900 cm⁻¹ and that of ν_4 at 640 cm⁻¹.

2. The three ν_3 peaks for Hopeite films containing manganese split sharply and shifted to a lower wavenumber region than did those for Hopeite films without manganese.

3. The ν_4 peak for Hopeite films containing manganese generated a new peak at 580 cm⁻¹.

4. The Raman spectra for Hopeite films showed four peaks at 1300 to 800 cm⁻¹. These peaks were due to PO₄³⁻.

5. Of these four peaks, the main peak at 990 cm⁻¹ corresponded to ν_1 , the symmetrical stretching vibration of PO₄³⁻ as the tetrahedron structure. The other three peaks corresponded to ν_3 , the triple degeneracy stretching vibration.

6. The reason for ν_3 showing three peaks is because the symmetry of the regular tetrahedron structure of PO₄³⁻ became distorted, the degeneracy was untied and split into three peaks.

7. The Raman bands of ν_1 and ν_3 for Hopeite films with manganese or nickel shifted to a lower wave-

number region than that for Hopeite films without the metals.

8. The influence of metal components in Hopeite films could be seen in ν_3 and ν_4 of the IR spectrum, and ν_1 and ν_3 of the Raman spectrum.

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