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EPMA, OPTICAL, EPR and IR spectral studies of prehnite mineral

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Abstract Light apple – green mineral of Ireland donated by Musee De Mineralogie, Ecole Nationale Superier Des Mines, Paris, France, has been investigated by Electron Probe Micro Analysis (EPMA), Optical absorption, Electron Paramagnetic Resonance (EPR) and Infrared (IR) spectroscopy. The EPMA indicates the presence of iron as the major constitutent and titanium, manganese and nickel in traces. The optical absorption spectrum recorded at RT show eight bands at 9343, 10650, 19994, 22721, 15500, 23250, 24624 and 27710 cm^{-1}. The former four bands are attributed to Fe(III) and the rest to Fe(II). The crystal field parameters Dq, B and C evaluated for Fe (III) and Fe (II) are 694, 650, 2600 and 980, 885, 3800 cm^{-1} respectively. The EPR resonances at $g = 4.62$, 4.34, 3.85 and 3.66 indicate the presence of Fe(III) in octahedral symmetry in the mineral. The presence of manganese is confirmed by the sextet at $g = 2.00$ in the EPR spectrum. The vibrational spectrum in IR region exhibited the characteristic bands of water and silicates. The splitting of the triply degenerate mode of SiO_4 indicates the deviation of symmetry from the ideal T_d symmetry

Keywords EPR, Optical absorption, EPMA

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1. Introduction

Prehnite, a brittle and unique layered hydrosilicate [1] has the chemical formula $[Ca_2 (Al, Fe) (OH)_2] (Si_3AlO_{10})$. It is orthorhombic and belongs to the space group P_2 cm with two formula units in each unit cell. It consists of layers of Si and Al populated tetrahedra, a building block in the fundamental sheets parallel to (001), which consists of chains of tetrahedra along the *b*-axis, these being linked along the *a*-axis by single Si tetrahedra facing to both sides along the *c*-axis, the results being that each Al-Si-O layer has three levels [2]. The nets are linked *via* Al (2) octahedra having common edges with the outer Si tetrahedra. The Ca atoms with coordination number seven lie between the projecting Si tetrahedra and also serve to link the layers. The linking Al atom *i.e.* Al(2), lies in an octahedral environment of two hydroxyl $[2(OH)^-]$ and four oxygen $[4O^{2-}]$ ions. The two hydroxyl groups are at a distance of 1.92Å each from the Al(2) atom. Of the four oxygen atoms, two are at a distance of 1.93 Å and the rest are at 1.94 Å from the central Al(2) atom. The unit cell parameters are a = 4.646(2), b = 5.491(3) and c = 18.52(3) Å [3]. The survey of literature indicates that prehnite contains the transition metal ions Fe(II) and Fe(III) substituting Al [3]. The substitution is minor because of the difference between the ionic radii of Fe(III) (0.64 Å) and Al(III) (0.51 Å). The aim of the present investigation is to confirm the presence and the site symmetry of transition metal ions by electron probe micro analysis, optical and EPR spectral studies and the presence of silicates and sorosilicates by vibrational spectral studies.

2. Experimental

The light apple-green mineral collected from Ireland supplied by Musee De Mineralogie, Ecole Nationale Superier Des Mines, Paris, France, is used in the present work. As the mineral is brittle and translucent, powdered sample is used for all spectral recordings. The RT optical absorption spectrum of the sample is recorded on Varian Cary 2390 Spectrophotometer in the region 350-1150 nm. The room temperature operating at X-band frequencies ($\nu = 9.43$ GHz) having a 100 kHz field modulation and phase selective detector to obtain a first derivative signal. DPPH is used as an internal standard ($g = 2.0036$). The IR spectrum of the sample in the region 600-4000 cm^{-1} is recorded on Pye Unicam SP3-300 Spectrophotometer. The chemical composition of the sample is obtained by employing the EPMA technique.

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3. Theory

Trivalent iron :

A trivalent iron ion, Fe(III), has electronic configuration $3d^5$ corresponding to a half-filled d-shell and is particularly most stable. In crystalline fields, the usual high-spin state is common *i.e.*, $t^3_{2g}\, e^2_g$ configuration with one unpaired electron in each of the orbitals. The low spin state which is less common, has the t^5_{2g} configuration with two pairs of paired electrons and one unpaired electron. The behaviour of d^5 ion energy levels in the crystal field characterised by the following features :

1. The ground state of d^5 ions is ^6S which transforms into $^6A_{1g}$ state in the field of any symmetry and is the only sextet term. It does not split by the effect of crystal field and hence all the transitions are spin forbidden and of less intensity.
2. In excited states of d^5 ions are quartet (^4G, ^4F, ^4D, ^4P) and doublet (^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S) terms. The transitions from the ground to doublet states are more forbidden because the spin number changes by two and hence they are too weak to be seen from the spectrum. Thus practically sextet-quartet transitions are observed and are divided into :

   (a) transitions to level dependent on crystal field strength Dq that gives rise to broad bands usually denoted as

   $^6A_{1g} \rightarrow {}^4T_{1g}$ and

   $^6A_{1g} \rightarrow {}^4T_{2g}$,

   (b) the transitions which are independent of Dq resulting in sharp bands :

   $^6A_{1g} \rightarrow {}^4E_g + {}^4E_{1g}$

   $^6A_{1g} \rightarrow {}^4E\,(^4D)$ etc.
3. The unsplit ground state term behaves alike in both octahedral and tetrahedral symmetries and gives rise to same energy level diagrams for octahedral, tetrahedral and cubic coordination with the usual difference in the magnitudes *i.e.*,

$$Dq_{octa} : Dq_{tetra} : Dq_{cubic} :: 1 : 4/9 : 8/9 \text{ or } 9 : 4 : 8.$$

Divalent iron :

In a divalent iron, the free ion ground term is ^5D and the excited terms are triplet (^3H, ^3P, ^3F, ^3G, ^3D) and singlet (^1I, ^1D). In an octahedral field the ^5D term splits into an upper ^5E_g level and a lower $^5T_{2g}$ level of which the latter forms the ground state. The only allowed transition $^5T_{2g} \rightarrow {}^5E_g$ gives an intense broad absorption band. This band splits into two bands due to Jahn-Teller effect. The average of these two bands is to be taken as $10Dq$ band. The transitions, other than the spin allowed, arising from the excited triplet states are spin forbidden and are weaker than the $10D_q$ band.

4. Results and discussion

(i) Chemical composition :

Electron probe microanalysis has been carried out on three grains collected from different parts of the sample and the results of which appear in Table 1. As seen from the table, the sample possesses the transition elements iron, titanium, manganese and nickel. Of these elements iron is in considerable quantity and the other three are in traces.

Table 1. Electron probe micro analysis data of prehnite

Oxide of the element	Concentration in wt%			
	Set I	Set II	Set III	Average
SiO_2	43.21	42.34	43.81	43.12
TiO_2	0.03	0.04	0.02	0.03
Al_2O_3	24.51	23.62	24.45	24.19
FeO*	0.53	0.50	0.41	0.48
MnO	0.03	0.04	0.02	0.03
CaO	28.31	27.54	25.52	27.12
Na_2O	0.02	0.01	0.00	0.01
K_2O	0.04	0.05	0.04	0.04
NiO	0.00	0.00	0.04	0.01
Total	96.68	94.14	94.31	95.03

*All Fe present in the sample has been analysed as FeO only

(ii) Optical absorption spectrum :

The optical absorption spectrum of prehnite recorded at room temperature in the region 350 – 1150 nm is shown in Figure 1. The spectrum is characteristics of Fe(II) and Fe(III) in octahedral (O_h) symmetry. It consists of eight bands at 9343, 10650, 15500, 19994, 22721, 23250, 24624 and 27710 cm^{-1}. Of them, four bands at 15500, 23250, 24624 and 27710 cm^{-1} are attributed to Fe(III) and the other four to Fe (II). No characteristic bands of Mn(II), Ni(II) and Ti(III) are observed in the spectrum due to their extremely lower concentration.

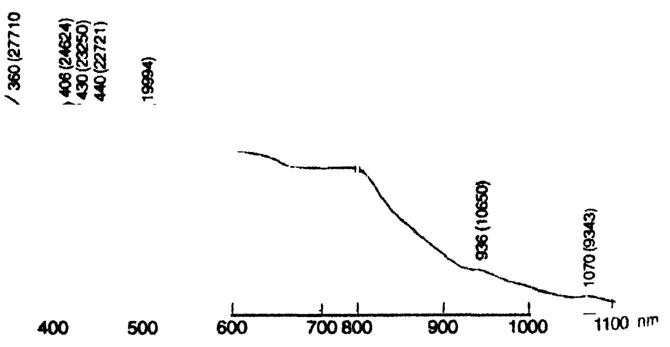

Figure 1. Optical absorption spectrum of Fe(III) and Fe(II) in prehnite mineral.

(iii) Trivalent iron :

The two broad bands observed at 15500 and 23250 cm^{-1} are assigned to the transitions ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and other two bands at 24624 and 27710 cm^{-1} are assigned to the transitions ${}^6A_{1g}(S) \rightarrow {}^4E_g(D)$ and ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(P)$ respectively. The observed band positions, their assignments with the calculated band positions are presented in Table 2. Based on these assignments the cubic field matrices of d^5 configuration with Tree's correction term $\alpha = 90$ cm^{-1} [4] are solved for different values of Dq, B and C. The parameters, which give good fit to the experimental data, are 694, 650 and 2600 cm^{-1} respectively.

Table 2. Band head data of Fe(III) and Fe(II) in prehnite

Transition	Band position		
	Observed		Calculated
	Wavelength Nm	Wave number cm^{-1}	Wave number cm^{-1}
For Fe(III) Ion			
${}^6A_{1g}$ (S) $\rightarrow$ ${}^4T_{1g}$ (G)	645	15500	15546
${}^6A_{1g}$ (S) $\rightarrow$ ${}^4T_{2g}$ (D)	430	23250	23267
${}^6A_{1g}$ (S) $\rightarrow$ ${}^4E_g$ (D)	406	24624	24625
${}^6A_{1g}$ (S) $\rightarrow$ ${}^4T_{1g}$(P)	360	27710	27713
For Fe(II) Ion			
${}^5T_{2g} \rightarrow {}^5E_g$	1070	9343	9800
${}^5T_{2g} \rightarrow {}^5E_g$	936	10650	
${}^5T_{2g} \rightarrow {}^3T_{1g}$	500	19994	19942
${}^5T_{2g} \rightarrow {}^3E_g$	440	22721	22728

(iv) Divalent iron :

The broad and intense band observed at 10650 cm^{-1} is assigned to the transition ${}^5T_{2g} \rightarrow {}^5E_g$ and the intense band at 9343 cm^{-1} is assumed to be the split component of the main band under Jahn-Teller effect [5]. The average of these two-band energies 9996 cm^{-1} is a measure of 10Dq for Fe(II) [6]. The difference in the energies of these bands (1307 cm^{-1}) indicates that Fe(II) is in distorted octahedral site [7]. The other two bands at 19994 and 22721 cm^{-1} are assigned to the transitions ${}^5T_{2g}$ T_{1g} and ${}^5T_{2g} \rightarrow {}^3E_g$ respectively. The observed band positions, their assignments and calculated band positions are given in Table 2. With these assignments, the energy matrices for d^6 configuration are solved for various values of Dq, B and C. The values that give good fit to the observed band energies, are Dq = 980, B = 885 and C = 3800 cm^1 respectively.

5. EPR spectrum

The room temperature EPR spectrum of the polycrystalline prehnite sample is shown in Figure 2. The spectrum consists of a number of lines below 2000 G, and a weak sextet centered on DPPH (internal standard with g value of 2.0036). The low field lines with g-values 4.62, 4.34, 3.85 and 3.66 can be attributed to the Fe(III) impurity in the mineral. As was mentioned earlier [8], g values around 30/7 are generally observable, if Fe(III) impurity is in an octahedral environment superposed by a strong tetrahedral crystal field environment. In the present study, Fe(III) substitutes Al (III), which is in an octahedral environment This has been further confirmed by the optical absorption spectral data. The other part of the spectrum consists of weak sextet around g = 2.00 and a hyperfine coupling constant of 95 G. This is due to the substitution of Mn (II) probably in place of Ca(II). The broad line at g = 2.00, (enlarged portion in Figure 2), underneath the main Mn(II) sextet with g = 2.00 can also be obtained for a Fe(III) impurity [8]. However, the amount of Mn(II) impurity may be very little in comparison to Fe(III) in mineral. Divalent iron ion, has six electrons in the outer shell with S = 2, does not resolve to any resonance lines in normal conditions So the observed EPR signal can be attributed to Fe(III) centers only.

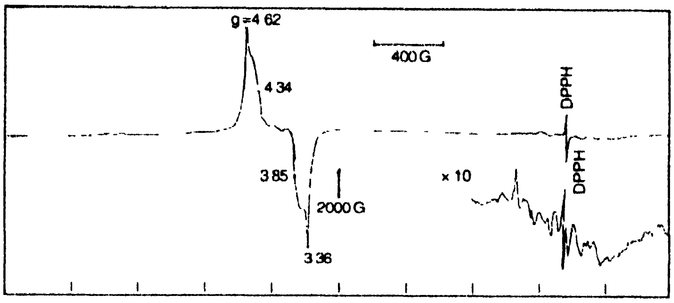

Figure 2. X-Band EPR spectrum of prehnite at 2000G (ν = 9.43GHz).

6. Infrared spectrum

Figure 3 shows the room temperature vibrational absorption spectrum of prehnite recorded in the region 600-4000 cm^{-1}. The spectrum consists of characteristic bands of silicates and water.

Silicates, in ideal tetrahedral symmetry, generally show four fundamental modes of vibration. Of these, ν_1 and ν_2 are non-degenerate and doubly degenerate respectively and are infrared inactive. The other two modes ν_3 and ν_4 are triply degenerate and are infrared active. But, in general, the symmetry of SiO$_4$ ion is distorted from the ideal T$_d$ symmetry and removes the degeneracy of infrared active modes ν_3 and ν_4 and also allows the non-active vibrations to appear. In the present investigation, the three component bands observed at 700, 750 and 790 cm^{-1} are assigned to the triply degenerate ν_4 mode. The other three components present at 1045, 1100 and 1200 cm^{-1} are ascribed to the triply degenerate ν_3 mode of SiO. The splitting of the bands and the appearance of infrared inactive modes in the spectrum indicates the removal of degeneracy partially and suggests deviation from ideal T$_d$ symmetry [9]. The band at 970 cm^{-1} is assigned to ν_1 mode and the other two bands at 2040 and 2200 cm^{-1} are attributed to the overtones of SiO$_4$ vibration modes 2ν_1 and 2ν_3 respectively. The bands at 610 and 650 cm^{-1} are characteristic of sorosilicates [9] (groups of two or more SiO$_4$,

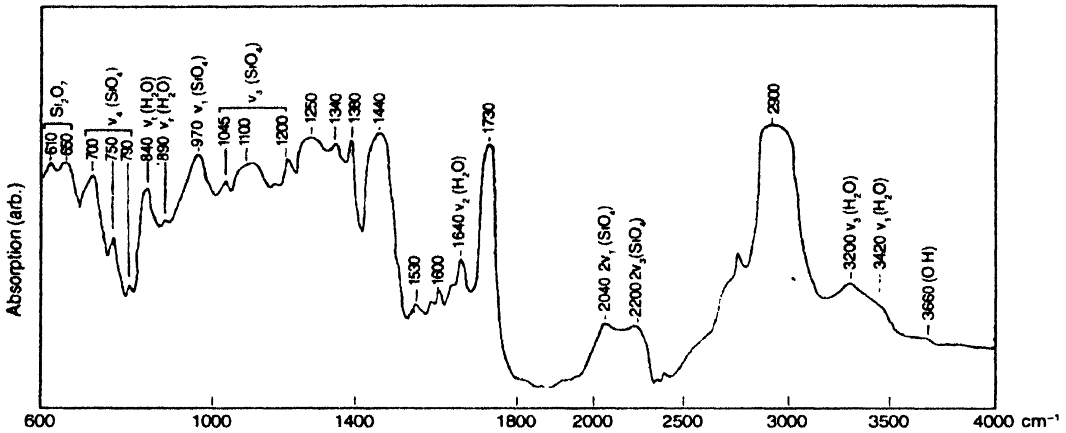

Figure 3. Infrared spectrum of prehnite mineral.

tetrahedra, generally Si_2O_7). Normally, water molecule possesses three fundamental modes of vibration : symmetric O-H stretch (ν_1), the H-O-H bend (ν_2) and the asymmetric O-H stretch (ν_3). In vapour phase these bands occur at 3652, 1595 and 3765 cm^{-1} [10] and in solid phase they are shifted to 3400, 1640 and 3200 cm^{-1} respectively due to hydrogen bonds [11].

In the present study the three bands observed at 1640, 3200 and 3420 cm^{-1} are attributed to the modes ν_2, ν_1 and ν_3 respectively. The bands observed at 840 and 890 cm^{-1} are assigned to twisting and rocking modes of water respectively. The band observed at 3660 cm^{-1} is assigned to OH group in the crystal lattice. The unassigned bands below 1640 cm^{-1} might be due to the overtones of the vibrational modes of silicates and above this might be due to water and hydroxyl groups. The band positions and their assignments are presented in Table 3.

Table 3. Observed vibrational frequencies and their assignments in Prehnite.

Observed band positions cm^{-1}	Assignment
0610	Si_2O_7
0650	
0700	$\nu_4(SiO_4)$
0750	
0790	
0840	ν_t (twisting)
0890	ν_r (rocking)
0970	$\nu_1(SiO_4)$
1045	$\nu_3(SiO_4)$
1100	
1200	
1640	ν_2 (H_2O)
2040	$2\nu_1$ (SiO_4)
2200	$2\nu_3$ (SiO_4)
3200	ν_3 (H_2O)
3420	ν_1 (H_2O)

7. Conclusions

The optical absorption spectrum indicates the replacement of aluminium by iron. The presence of iron in the sample is confirmed by chemical analysis and EPR spectrum. The observation of a number of resonances in the EPR spectrum at around $g = 4.00$ is an indication of octahedral symmetry for Fe(III) in the mineral. The presence of manganese is confirmed by the sextet in the EPR spectrum. The vibrational spectrum in IR region exhibited the characteristic bands of water and silicates. The splitting of the triply degenerate mode of SiO_4 indicates the deviation of symmetry from the ideal symmetry.

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