The process of scientific discovery is in a continuous flight from wonder.

..... Albert Einstein
INTRODUCTION

Most of the silicates contain first group transition metal ions as principal constituents, more frequently as minor ones or as impurities. In an attempt to gain information on these materials, a number of investigations have been devoted to an examination of the absorption spectra of various silicate minerals [1-4]. Such studies indicate the order of importance of the absorption species as Fe(III), Fe(II), Mn(II), Ti(III) and Cr(III). The role of Fe(III) and Fe(II) ions is important than the other ions because of their presence in many mineral complexes. Hence, spectroscopic studies on iron-rich zoisite are undertaken to investigate the ionic nature of iron and the approximate geometry of the site in which it is accommodated in the crystal lattice. As there is no information on iron-rich zoisite, a detailed study on this sample
was made employing Mössbauer, optical and EPR techniques. The electron probe micro analysis was also carried out to know the composition of the sample.

The epidote group minerals comprises a widespread and chemically complex family of rock forming silicates whose composition can be represented ideally as $A_2M_3Si_2O_7OH$. Here, 'A' is predominantly Ca and 'M' is principally Al(III) or Fe(III) or Mn(III). The ideal Al end member with monoclinic form is known as clino-zoisite and orthorhombic form is generally termed as zoisite [5]. The members of this group have the structure consisting of chains of AlO₆ and AlO₄(OH)₂ octahedra linked by independent SiO₄ and Si₂O₇ groups [6].

The substitution of transition metal ions causes a reduction of symmetry in crystals and gives rise to some interesting spectral features. The mineral, zoisite, whitish grey in colour was obtained from Thetford, Quebec, Canada. It is orthorhombic by nature and possesses the chemical formula Ca₂Al₂(SiO₄)-(Si₂O₇)O(OH) [7] with the cell parameters $a = 16.2$ Å, $b = 5.5$ Å and $c = 10.0$ Å [5]. Its composition is generally close to the formula. The only substitution being a small amount (upto about 10 atomic percent) of Fe(III) by Al [8].

**EXPERIMENTAL**

Electron probe micro analysis (EPMA) of the whitish grey zoisite mineral was carried out using CAMEBAX Micro EPMA at an operating voltage of 20 kV and a sample current of 22 nA in a beam regulator mode. The measured data were corrected on PDP 11/03 on line computer. A full ZAF correction procedure as described by Sweetman and Long [9] was used to calculate the final concentration. The Mössbauer spectrum of the sample was recorded on ECIL Mössbauer spectrometer with a multi channel analyser in time mode. A krypton filled proportional detector, 10 mCi $^{57}$Co in palladium matrix as source were used to record the spectrum.

The optical absorption spectrum of the sample was recorded on Hitachi U-3400 UV-VIS-NIR spectrophotometer in the wavelength region 300-1500 nm using the nujol mull form of the sample. The EPR spectra of the sample in polycrystalline form were recorded on Varian E-112 EPR spectrometer operating at X-band frequencies with 100 kHz field modulation. DPPH was used as an internal
field marker. The infrared spectrum of the sample was recorded on Pye Unicam
SP3-300 IR spectrophotometer in the wavelength region 4000-600 cm\(^{-1}\).

THEORY

Iron has the electronic structure \(\text{Ar}(3d)^{6} 4s^{2}\). In octahedrally co-ordinated
\(\text{Fe(II)}\) complex, the ground state configuration is written as \(t_{2g}^{6} e_{g}^{2}\). This
configuration gives rise to the free ion terms, \(5D, 2H, 1F\) etc. In moderate crystal fields,
the ground term \(5D\) splits into \(5T_{2g} \& 5E_{g}\) and \(3H\) term splits into \(3T_{2g}, 3T_{1g}, 3E_{g}\ & 3T_{1g}\)
states. Among these, \(5T_{2g}\) forms the ground state. The transition from \(5T_{2g}\) to \(5E_{g}\) is
only spin allowed and expected to be strong whereas all the other transitions are spin
forbidden and are very weak.

A trivalent iron \{Fe(III)\} ion with the electronic configuration \(\text{Ar}(3d)^{5}\) gives
rise to \(2(S,P,D,F,G,H), 4(P,D,F,G)\) and \(6S\) terms. In an octahedral field, these terms
give rise to \(6A_{1g}, 4A_{1g}, 4A_{2g}, 4E_{g}, 4T_{1g}, 4T_{2g}\) and some other states of which \(6A_{1g}\) lies
lowest as per the Hund’s rule. All these transitions are spin forbidden and hence are
expected to be weak.

RESULTS AND DISCUSSION

Chemical Analysis

The electron microprobe analysis was carried out at different points on thin
section of the zoisite mineral and the data is presented in Table 4.1 along with the
average values. In the table, \(\text{FeO}\) represents the total iron present in the sample
\((\text{Fe}_{2}\text{O}_{3} \& \text{FeO})\). From the table 4.1, it is observed that iron is a dominant transition
metal impurity present in the sample (0.36%) when compared to Mn which is found
in traces (0.03%). Hence, the optical absorption spectrum of whitish grey zoisite can
be attributed to iron only.

Mössbauer Spectrum

Mössbauer spectrum of zoisite recorded at room temperature is shown in
Fig 4.1. Although a long counting time was employed, the spectrum of the sample is
weak due to its low iron content. It consists of two main lines; a more intense lower
velocity peak and a less intense higher velocity peak with a still less intense peak in
between the two peaks. So the spectrum is fitted with two doublets. A statistically
**TABLE 4.1:** Electron probe micro analysis (EPMA) of zoisite mineral

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Set 1</th>
<th>Set 2</th>
<th>Set 3</th>
<th>Set 4</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.40</td>
<td>45.41</td>
<td>46.04</td>
<td>45.27</td>
<td>45.53</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>28.05</td>
<td>25.93</td>
<td>25.95</td>
<td>25.56</td>
<td>25.87</td>
</tr>
<tr>
<td>FeO</td>
<td>0.36</td>
<td>0.33</td>
<td>0.34</td>
<td>0.38</td>
<td>0.36</td>
</tr>
<tr>
<td>MnO</td>
<td>--</td>
<td>0.01</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>27.18</td>
<td>27.19</td>
<td>27.13</td>
<td>27.73</td>
<td>27.31</td>
</tr>
<tr>
<td>Na₂O</td>
<td>--</td>
<td>0.08</td>
<td>0.02</td>
<td>--</td>
<td>0.05</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.03</td>
<td>0.06</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>BaO</td>
<td>0.08</td>
<td>--</td>
<td>--</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>Total</td>
<td>99.17</td>
<td>99.08</td>
<td>99.62</td>
<td>99.28</td>
<td>99.38</td>
</tr>
</tbody>
</table>
Fig 4.1. Mössbauer spectrum of zoisite mineral.
satisfactory fit is obtained (rms Chi Value 1.589) when the doublet is constrained to have equal area lines but independent line widths matched to this spectrum. The intense doublet gives an isomer shift (IS) of 1.2750 mm s\(^{-1}\) and quadrupole splitting (QS) of 1.8741 mm s\(^{-1}\). This intense doublet has the characteristic centre shift for Fe(II) ion. The other doublet fitted with the less intensity has an isomer shift of 0.7751 mm s\(^{-1}\) and quadrupole splitting of 1.2986 mm s\(^{-1}\). These values correspond to the Fe(III) ion which is octahedrally coordinated [10,11]. The intense peak (I = 67\%) with an higher isomer shift of 1.2750 mm s\(^{-1}\) shows more abundance of Fe(II) ion when compared to the less intense peak (I = 33\%) with isomer shift of 0.7751 mm s\(^{-1}\) which corresponds to Fe(III) ion. From Mössbauer studies, it is confirmed that the presence of iron impurity is in two states, i.e., in Fe(II) and Fe(III) and it is also observed that the presence of Fe(II) is almost twice to that of Fe(III).

**Optical Absorption Spectrum**

Optical absorption spectrum of the zoisite is shown in Fig.4.2. The spectrum consists of a broad band with splitting around 10,000 cm\(^{-1}\) and a number of bands with small intensities.

It is well known that the spectrum of Fe(II) ion exhibits an intense and broad band at 10,000 cm\(^{-1}\) which corresponds to the transition \(5\text{I}_{2g} \rightarrow 5\text{E}_g\) [12-14]. It has been reported that in an octahedral oxygen environment this will split into two bands. Accordingly, the observed two bands at 10870 & 12420 cm\(^{-1}\) are assigned to \(5\text{I}_{2g} \rightarrow 5\text{E}_g\) transition. The splitting of this band may be explained in terms of one or more of the complicating factors namely (1) spin-orbit coupling, (2) static distortion of the octahedron and (3) dynamic Jahn-Teller effect [13]. For Fe(II) the spin-orbit coupling constant is only 100 cm\(^{-1}\). But the observed splitting (12420-10870) is 1550 cm\(^{-1}\). Therefore the splitting of the \(5\text{I}_{2g} \rightarrow 5\text{E}_g\) band may not be due to the spin-orbit interaction.

For cubic symmetry the splitting due to Jahn-Teller effect is of the order of 2,000 cm\(^{-1}\). As reported by previous investigators [13-15], this splitting may not be due to static distortion of the octahedron and hence this splitting is considered to be due to dynamic Jahn-Teller effect in the excited \(5\text{E}_g\) state [4,16]. In the dynamic Jahn-Teller effect alone the energy level will split symmetrically to the centre of gravity. So the average value of the two bands (11645 cm\(^{-1}\)) is taken as 10 Dq band.
Fig 4.2. Optical absorption spectrum of Fe(II) and Fe(III) ions in zolite mineral.

Absorbance (arbitrary units)

-27020
-24665 cm⁻¹
-22470
-19225
-16390
-14280
-13240
-12420
-10870
-7870 cm⁻¹
The transition $^{5}T_{2g} \rightarrow ^{5}T_{1g}$ is spin allowed and is expected to be broad and intense. So the other transitions arising from excited triplet states are considerably weaker than the 10 Dq band since they are spin forbidden [17, 18]. As seen from figure, a number of less intense bands are observed in the region 300 to 800 nm. Among these bands, two bands at 13240 and 16390 cm$^{-1}$ are broad and intense. These two bands and the 10 Dq band are identified as due to Fe(II) ion, which are differentiated from the other weak bands observed in the spectrum. Using Tanabe-Sugano diagram drawn between Dq/B and C/B for d$^6$ configuration, the transitions for the bands at 13240 and 16390 cm$^{-1}$ are assigned. The energy matrices for d$^6$ configuration given by Tanabe-Sugano [19] were solved for different Dq, B and C values. The parameters which gave good fit to the experimental data are Dq = 1165 cm$^{-1}$, B = 740 cm$^{-1}$ and C = 4750 cm$^{-1}$. The observed and calculated energy values are compared and are presented in Table 4.2.

The other less intense bands observed in the region 300-800 nm are attributed due to Fe(III) ion. In order to identify the weak bands clearly, the spectrum was also scanned separately in 350-650 nm range and is shown in Fig.4.3. The bands at 14280 and 19225 cm$^{-1}$ are attributed to $^{6}A_{1g}$ (S) $\rightarrow$ $^{4}T_{1g}$ (G) and $^{6}A_{1g}$ (S) $\rightarrow$ $^{4}T_{2g}$ (G) transitions respectively. With the help of Tanabe-Sugano diagram for d$^5$ configuration [19], the assignments of the other bands are made and are presented in Table 4.2. Cubic field matrices for d$^5$ configuration with Tree's correction term α = 90 [20] were solved for various values of Dq, B and C. The parameters which gave good fit to the observed data are Dq = 940 cm$^{-1}$, B = 829 cm$^{-1}$ and C = 2500 cm$^{-1}$.

Whenever OH$^-$ exists as a part of the structure or the presence of water in the mineral, OH$^-$ stretching mode appears in NIR region as overtone (2 νOH) [21]. Accordingly, the broad band observed at 7870 cm$^{-1}$ (Fig.4.2) is assigned due to the overtone of the OH$^-$ stretching mode.

The optical absorption spectra of the sample subjected to different heat treatments (1273 and 1473 K) were also recorded. But no change was observed in the spectral features of the sample even after heat treatment.

EPR Spectrum

A typical EPR spectra obtained from the zoisite powder is shown in Fig.4.4. A number of lines centered from 800 to 3500 G can be seen very clearly. This kind of observation, i.e., a number of resonances having 'g' values ranging from 8 to 1.9 can
<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed band position</th>
<th>Calculated Wave number (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavelength (nm)</td>
<td></td>
</tr>
<tr>
<td><strong>Fe(II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5T₂g (D) → 5E₉ (D)</td>
<td>920</td>
<td>10370</td>
</tr>
<tr>
<td></td>
<td>805</td>
<td>12420</td>
</tr>
<tr>
<td>5T₂g (D) → 3T₁₉ (H)</td>
<td>755</td>
<td>13240</td>
</tr>
<tr>
<td>5T₂g (D) → 3T₂₉ (H)</td>
<td>610</td>
<td>16390</td>
</tr>
<tr>
<td><strong>Fe(III)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6A₁₉ (S) → 4T₁₉ (G)</td>
<td>700</td>
<td>14260</td>
</tr>
<tr>
<td>6A₁₉ (S) → 4T₂₉ (G)</td>
<td>520</td>
<td>19225</td>
</tr>
<tr>
<td>6A₁₉ (S) → 4E₉ (G)</td>
<td>445</td>
<td>22470</td>
</tr>
<tr>
<td>6A₁₉ (S) → 4T₂₉ (D)</td>
<td>405</td>
<td>24645</td>
</tr>
<tr>
<td>6A₁₉ (S) → 4E₉ (D)</td>
<td>370</td>
<td>27020</td>
</tr>
</tbody>
</table>
Fig 4.3. Optical absorption spectrum of zoisite in the region 350 to 650 nm.
Fig 4.4. X-band EPR spectra of zoisite before and after heat treatment.
be observed in Fe(III) systems, when the paramagnetic impurity is under the influence of a strong tetragonal distortion [22]. As mentioned in the introduction, the most probable site for Fe(III) is Al(III). In our previous study [23] where the results on Mn-rich zoisite were reported, the samples contained high Mn(II) relative to Fe, whereas in the present investigation, the zoisite is rich in iron than Mn. This kind of observation has been further verified by microprobe analysis. The observation of 'g' values in the whole region of X-band indicates that the three Kramer's doublets of $d^5$ \{Fe(III)\} formally labelled as $|\pm 5/2>, |\pm 3/2>\text{ and } |\pm 1/2>$ are populated at room temperature [22].

In the case of alunite and talc minerals [24,25], the EPR spectrum of Fe(III) was simplified after heat treatment at a temperature below the melting point of the mineral. Hence, zoisite was subjected to heat treatment at two different temperatures 1273 and 1473 K for a period of 12 hours. The EPR spectra of these samples (after heat treatment) are also included in the figure. As expected, the spectra are simplified. The EPR spectrum at 1273 K contains resonances around 1000, 1250 & 1500 G and a strong feature at $\approx 3300$ G. The rest of the lines from the original spectrum (before heat treatment) have disappeared. The EPR spectrum at 1473 K contains resonances centred around $\sim 1500$ G and a strong feature at 3300 G. The resonance around 3300 G ($g$ is around 2) became more intense at 1473 K and indicates that the iron centres, which are at different locations in the mineral, gets stabilized at the lowest energy configuration [26]. In all the three spectra, one can observe a set of six lines around $g \approx 2$. These can be attributed to Mn(II) impurity.

Divalent iron ion has six electrons in the outer shell with $S = 2$. This will not resolve to any resonance lines in normal conditions. So the observed EPR signals can be attributed due to Fe(III) centres only.

Vibrational Spectrum

The vibrational spectrum of the sample, zoisite, is shown in Fig.4.5. The spectrum reveals the existence of vibrational frequencies due to SiO$_4$ & H$_2$O.

There are three fundamental modes of vibration for H$_2$O molecule. They are the symmetric OH stretch ($v_1$), the asymmetric stretching mode ($v_2$) and the H- O-H bend ($v_3$). Generally these modes would appear at 3652, 3756 and 1595 cm$^{-1}$ in vapour phase and at 3220, 3400 and 1620 cm$^{-1}$ in solid state. The observed shifts of $v_1$ and $v_3$ towards lower frequency side and $v_2$ towards higher frequency side are the
Fig 4.5. Infrared spectrum of zoisite mineral in the region 4000-600 cm$^{-1}$. 
characteristic of hydrogen bonding. In the present spectrum, the bands observed at 3340, 3500 and 1620 cm\(^{-1}\) are ascribed accordingly as \(\nu_1\), \(\nu_2\) and \(\nu_2\) modes of \(\text{H}_2\text{O}\) which is present in the lattice structure since water commonly associates with rocks and minerals [21].

\(\text{SiO}_4\) molecule has four fundamental vibrational modes (\(\nu_1\), \(\nu_2\), \(\nu_3\) and \(\nu_4\)). Of these, \(\nu_3\) & \(\nu_4\) are infrared active and are triply degenerate. \(\nu_2\) is a doubly degenerate mode and \(\nu_1\) is non-degenerate. Both these \(\nu_1\) & \(\nu_2\) modes are infrared inactive. Generally the symmetry of \(\text{SiO}_4\) ion is distorted from the ideal \(T_d\) symmetry. This distortion removes the degeneracy of infrared active modes \(\nu_3\) and \(\nu_4\) and also allows the inactive modes to appear. In the present investigation the three bands observed at 745, 780, 820 cm\(^{-1}\) are attributed to the triply degenerate \(\nu_4\) mode. The three components which are well defined at 950, 990 and 1080 cm\(^{-1}\), correspond to the \(\nu_2\) mode which is also triply degenerate. The two bands observed at 630 & 670 cm\(^{-1}\) are ascribed to \(\nu_2\) and the band at 865 cm\(^{-1}\) is identified as \(\nu_1\) mode. The splitting of the degenerate modes and the appearance of the two infrared inactive modes in the spectrum indicate the distortion of \(\text{SiO}_4\) tetrahedron from its ideal \(T_d\) symmetry [27].

CONCLUSIONS

Electron microprobe analysis of the whitish grey zoisite revealed the presence of two transition metal impurities, iron and manganese as 0.36 and 0.03 wt.% respectively. The Mössbauer spectrum of the sample, fitted with two doublets revealed that iron is in two oxidation states and the concentration of Fe(II) is twice to that of Fe(III).

The optical absorption spectrum of zoisite is attributed to both Fe(II) and Fe(III) ions substituted in the place of Al surrounded by \(-\text{O}_2(\text{OH})_2\) ligands. The broad and intense band with a splitting around 10,000 cm\(^{-1}\) is attributed to \(5T_2(D)\rightarrow 3E_g(D)\) spin allowed transition of Fe(II) ion. It is confirmed that the splitting of this band is due to dynamic Jahn-Teller effect of Fe(II) ion. The other weak bands in UV-VIS region are assigned to the spin forbidden transitions of Fe(III) ion.

From EPR studies it is observed that Fe(III) ion is in strong tetragonal distortion. The presence of Mn(II) impurity in traces is further confirmed by EPR
spectra. In the EPR spectrum, heating the sample has resulted in stabilising the impurity which is at many random positions before heating, to more stable configuration. The assignments of the vibrational frequencies in the IR spectrum of the sample indicate the association of H₂O and SiO₄ within the mineral and also suggest the distortion in SiO₄ tetrahedron from its ideal T₄ symmetry.
REFERENCES


