CHAPTER VIII

CHEMICAL ANALYSIS, OPTICAL ABSORPTION, EPR AND IR SPECTRAL STUDIES OF FUCHSITE QUARTZ
1. Introduction

The optical absorption spectrophotometry is a facile means of providing information on the structures of transition metal bearing minerals, is now well established. Optical spectra have been used to determine the local symmetry of the anionic environment around the cation [1,2]. Other workers have studied minerals whose absorption spectra are complicated by the simultaneous presence of two or more transition metal ions, but in which site distortions from cubic symmetry are relatively unimportant in the spectral interpretations [3,4,5,6]. In the latter type of study, information has been obtained on the location and valence states of transition metals in a variety of minerals, the analytical implications of which are worthy of further study [7].

Chromium (atomic number z = 24) belongs to the first series of transition metal group. It occurs in the form of four stable isotopes $^{50,52,54}$Cr, I=0 with total natural abundance of 90.5% and $^{53}$Cr , I = 3/2 with natural abundance of 9.5% [8].

Cr(III) has the electronic configuration (Ar) 3d$^3$. Ions with 3d$^3$ electronic configuration, Cr(III) in particular, are widely used as paramagnetic probes to investigate the symmetry of intra crystalline electric fields [9]. The EPR study of transition metal ions doped in carboxylic salts have been carried out by several investigators [10].
Electronic spectra of Cr(III) complexes though restricted to six coordinated complexes, play a special role in the development of inorganic electron spectroscopy. This is ascribed primarily to the kinetic inertness of Cr(III), such that many varied complexes can be isolated and to the ready observation of all three spin allowed transitions and a number of clearly defined spin forbidden transitions. Since Cr(III) is neither a good reducing nor a good oxidising agent, charge transfer bands tend not to obscure d-d absorption. They are to be found in the ultraviolet region. The $^4T_{1g}$ transition is observable but tends to be weaker than the other d-d transitions. The study of the so called 'Ruby' lines have historic importance. These very narrow spin forbidden (quartet-doublet) transitions observed in most chromium complexes arise from a 'spin-flip' within the $t_{2g}$ set and to first order, have no dependence upon $D_q$ [11].

Fuchsite quartz is naturally occurring mineral containing chromium and silicates. Fuchsite belongs to muscovite group. The general formula of muscovite is $KAl_2(Si_3O_{10})(OH)_2$. Chromium containing muscovite is called fuchsite [12]. Since it consists of silicon group (SiO₂) it is named as fuchsite quartz. The crystal structure of muscovite is tetrahedral [13]. It is a 1M polytype with parameters $a=5.275(5)$, $b=9.045(5)$, $c=10.281(5)$Å and $\beta=101^\circ 80''$ [14]. Only optical absorption spectrum of fuchsite quartz has been reported and attributed to Cr(III) ion [15]. Therefore detailed investigations on optical absorption,
EPR and IR spectral studies of fuchsite quartz are made and presented here.

2. Experimental

A massive bluish green variety of the mineral, fuchsite quartz supplied by M/s Alminrock co., Bangalore, India is collected from Chitradurga, Karnataka, India. The chemical analysis of this sample has been made to know the presence of transition metal impurities in the mineral.

One gram of the fuchsite quartz is taken in a teflon crucible and is dissolved in hydrofluoric acid. Next the solution is evaporated by heating the crucible on a hot plate. Then the residue is dissolved in conc. HCl and made upto 100 ml in standard flask. This solution is used to estimate the amount of impurities present in the sample by AAS technique with 3410 ICP spectrophotometer with monitorch.

The optical absorption spectrum of the sample is recorded in nujol mull form on Cary 2390 Spectrophotometer at room temperature in the region 200-1200nm.

Electron paramagnetic resonance spectrum of the sample is recorded at room temperature on Varian E-112 EPR spectrometer operating at X-band frequencies with 100 kHz modulation. A phase sensitive detector is used to obtain a first derivative EPR signal.
Infrared spectrum of the sample is recorded on SP3 300 spectrophotometer in the region 600 to 4000 cm\(^{-1}\) at room temperature.

3. Theory

The outer electronic configuration of Cr(III) ion is 3d\(^3\). Hence the Cr(III) ion has three unpaired d- electrons and gives rise to the free ion terms \(4_F, 4_P, 2_G\) and several other doublet states. When this ion is placed in an octahedral crystal field, \(4_F\) splits into \(4_{1g}, 4_{2g}\) and \(4_{g}\) states, and the \(4_{2g}\) level being the lowest. The next higher term \(4_P\) transforms as \(4_{1g}\). The \(2_G\) term gives rise to \(2_{1g}, 2_{1g}, 2_{2g}\) and \(2_{E}\) states.

In the case of strong field, the various electronic configurations are \(t_2 g^3, t_2 g^2 e_g, t_2 g e_g^2\) and \(e_g^3\). Now the states \(4_{A_2 g}(F), 2_{E_g}(G)\) and \(2_{T_2 g}(G)\) correspond to \((t_2 g^3)\). The states, \(4_{1g}(F)\) and \(4_{T_2 g}(F)\) correspond to \((t_2 g^2)(e_g)\) and \(4_{T_1 g}(P)\) corresponds to \((t_2 g)(e_g^2)\) [16]. Thus for Cr(III) ion in octahedral symmetry three spin allowed transions, \(4_{A_2 g}(F) \rightarrow 4_{T_2 g}(F), 4_{A_2 g}(F) \rightarrow 4_{T_1 g}(F), 4_{A_2 g}(F) \rightarrow 4_{T_1 g}(P)\) could be observed in addition to some spin forbidden transitions.

For Cu(II) with \(d^9\) configuration in octahedral symmetry, the ground state \(2_D\) splits into \(2_{E_g}\) and \(2_{T_2 g}\) states, giving rise to a single transition. Since the ground state is \(2_E\), it is often found to split under the Jahn - Teller effect. Thus Cu(II) does not experience perfect octahedral symmetry in any complex. In a
ABSORPTION (arbitrary units)

WAVELENGTH (nm)

- 24385
- 20400
- 16125
- 15620
- 14280
- 12190
- 8470 cm\(^{-1}\)
tetragonally distorted octahedral symmetry\((C_{4v})\), \(^2E_g\) splits into \(^2B_{1g}\) and \(^2\Lambda_{1g}\), while \(^2T_{2g}\) splits into \(^2B_{2g}\) and \(^2E\) levels [16].

4. Results and analysis

4.1 Chemical analysis

The chemical analysis of the fuchsite quartz sample is carried out on 3410 ICP spectrophotometer with monitor. The results are presented in the following Table.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.229</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0096</td>
</tr>
<tr>
<td>Cu</td>
<td>0.8492</td>
</tr>
</tbody>
</table>

From the data it is observed that the present sample contains predominantly copper, with a small quantity of Cr and traces of manganese as impurities.

4.2. Optical absorption spectrum

The optical absorption spectrum of the sample is recorded on Cary 2390 spectrophotometer is shown in Fig.1. It consists of a number of bands in UV-VIS and NIR regions. The three bands observed in NIR region at 8470, 12190 and 14280 cm\(^{-1}\) are broad and intense. The other bands in UV-VIS region at 15620, 16125, 20400 and 24385 cm\(^{-1}\) are comparatively weak.

The three broad bands in NIR region are characteristic of Cu(II) ion and is evident from the chemical analysis that the
sample contains predominantly copper impurity (0.8492%). The other bands in the UV-VIS region are attributed to Cr(III) ion since the sharp bands around 16000 cm$^{-1}$ and the two broad bands in the region 20000 - 25000 cm$^{-1}$ are normally expected for Cr(III) ion in any complex [17,18,19]. Thus the spectral features of Cr(III) are due to the presence of Cr as minor impurity.

For copper ion three d-d transitions are expected in C$_{4v}$ symmetry [20]. From the ionic theory of copper, in a tetragonally distorted octahedral symmetry (C$_{4v}$), $^2E_g$ splits into $^2B_{1g}$ and $^2A_{1g}$ while $^2T_{2g}$ splits into $^2B_{2g}$ and $^2E$ levels. Of these $^2B_{1g}$ is the ground state. Accordingly, the bands at 8470, 12190 and 14280 cm$^{-1}$ are attributed to the transitions $^2B_{1g}$ ----> $^2A_{1g}$, $^2B_{1g}$ ----> $^2B_{2g}$ and $^2B_{1g}$ ----> $^2E$ respectively.

The energy values of different terms for Cu(II) ion in tetragonal field are given as [21].

\[
\begin{align*}
^2B_{1g} & \rightarrow -6Dq - 2Ds + Dt \\
^2A_{1g} & \rightarrow -6Dq + 2Ds +6Dt \\
^2B_{2g} & \rightarrow 4DQ - 2Ds + Dt \\
^2E_g & \rightarrow 4DQ + Ds -4Dt 
\end{align*}
\]

Therefore three bands are observed which correspond to the following transitions.
\[ 2B_{1g} \rightarrow ^2A_{1g} \quad 4D_s + 5D_t = 8470 \]
\[ 2B_{1g} \rightarrow ^2B_{2g} \quad 10D_q = 12190 \]
\[ 2B_{1g} \rightarrow ^2B_{1g} \quad 10D_q + 3D_s - 5D_t = 14280 \text{ cm}^{-1} \]

From the equations, the crystal field (Dq) and tetragonal field parameters (Ds & Dt) are calculated as Dq = 1219, Ds = 1509 and Dt = 487 cm\(^{-1}\).

For Cu(II) ion the location of the band near 12000 cm\(^{-1}\) is an indication of approximate octahedral symmetry in the mineral [22]. It corresponds to 10 Dq band.

The assignment of the bands are made for tetragonal symmetry, with \( ^2B_{1g} \) as the ground state. The same assignments have been made by several authors for similar band positions in different copper complexes [23,24,25,26,27,28].

In tetragonal field, the value of Dt and Dq have the same sign if there is an axial elongation and have opposite sign if there is an axial compression [29]. Therefore in fuchsite quartz the values of Dt and Dq have the same sign indicating the elongated octahedral site symmetry for Cu(II) ion and confirms the ground state. [30].

In the optical absorption spectrum the other weak bands observed at 15620, 16125, 20400 and 24385 cm\(^{-1}\) are attributed to Cr(III) ion which is also confirmed by the chemical analysis (Cr = 0.229%).
Three types of electron configurations are associated with octahedrally coordinated and tetrahedrally coordinated trivalent Cr. Octahedral coordination has only one type since there is no distinction between the high spin state and the low spin state. Whereas tetrahedral coordination may have the spin state or the low spin state. The tetrahedrally coordinated high spin state is less stable because of smaller crystal field stabilization energy. The tetrahedrally coordinated low spin state is stable at low temperatures and becomes unstable at high temperatures as a result of site expansion [31]. The higher the temperature the more likely the Cr(III) will be found in the high spin state. However, this state is unstable and the Cr(III) eventually becomes highly stabilized in octahedral sites and high temperatures. Consequently, the Cr(III) spectra may be analysed assuming octahedral coordination [32].

The absorption spectrum of fuchsite quartz shown in Fig. 1 consists of two sharp line-like bands R and R' and two broad bands. The R and R' lines are located at 15620 and 16125 cm\(^{-1}\) and the two broad bands are observed at 20400 and 24385 cm\(^{-1}\).

The line or band is sharp if the number of \(t_2\) electrons is same both in the excited and ground states [16]. Therefore the two sharp lines are called R and R' lines at 15620 and 16125 cm\(^{-1}\) are assigned to the transitions \(^4A_2g(F) \rightarrow ^2E_g\) and \(^4A_2g(F) \rightarrow ^2T_{1g}\) respectively. The octahedrally coordinated trivalent Cr(III) exhibits three spin allowed transitions. Of
these the \( ^4A_{2g} \rightarrow ^4T_{1g} \) involves a double electron jump and results in a weak band. Hence only two spin allowed transitions will be observed [32].

The spin allowed transitions should be broad [33]. Accordingly the two broad bands at 20400 and 24385 cm\(^{-1}\) are assigned to spin allowed transitions \(^4A_{2g}(F) \rightarrow ^4T_{2g} \) and \(^4A_{2g}(F) \rightarrow ^4T_{1g}(F) \) respectively.

The band observed at 20400 cm\(^{-1}\) which corresponds to the transition \(^4A_{2g} \rightarrow ^4T_{2g}(F) \) represents the 10 Dq value. Therefore the Dq value is taken to be 2040 cm\(^{-1}\). The other band 24385 cm\(^{-1}\) corresponding to the transition \(^4A_{2g}(F) \rightarrow ^4T_{1g}(F) \) is \(\tilde{\tau}_2\). Therefore the value of the interelectronic repulsion parameter \(B\) is calculated by substituting the values of \(\tilde{\tau}_1\) and \(\tilde{\tau}_2\) in the following expression [34]

\[
B = \frac{(2\tilde{\tau}_1 + \tilde{\tau}_2 - 3\tilde{\tau}_1\tilde{\tau}_2)}{(15\tilde{\tau}_2 - 27\tilde{\tau}_1)}
\]

The value of \(B\) obtained in the present case is 675 cm\(^{-1}\). Using the values Dq = 2040 and B = 675 cm\(^{-1}\) cubic energy matrices [35] are solved for different values of \(C\). The value of \(C\) which gives good fit is \(C = 2900\) cm\(^{-1}\).

The wavelengths, wavenumbers and the assignments of the observed bands are presented in Table 2.
Table - 1

The observed band positions and assignments of Cu(II) in fuchsite quartz

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment with respect to ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1180</td>
<td>8470</td>
<td>²A₁</td>
</tr>
<tr>
<td>820</td>
<td>12190</td>
<td>²B₂</td>
</tr>
<tr>
<td>700</td>
<td>14280</td>
<td>²E</td>
</tr>
</tbody>
</table>

Table 2

Observed and calculated band positions for Cr(III) in fuchsite quartz

<table>
<thead>
<tr>
<th>Transition from ⁴A₂g</th>
<th>Observed band positions</th>
<th>calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavelength (nm)</td>
<td>Wavenumber (cm⁻¹)</td>
</tr>
<tr>
<td>²E₉(G)</td>
<td>640</td>
<td>15620</td>
</tr>
<tr>
<td>²T₁₉(G)</td>
<td>620</td>
<td>16120</td>
</tr>
<tr>
<td>⁴T₂₀(G)</td>
<td>490</td>
<td>20400</td>
</tr>
<tr>
<td>⁴T₁₀(F)</td>
<td>410</td>
<td>24385</td>
</tr>
</tbody>
</table>
4.3. EPR spectrum

A small piece of fuchsite quartz mineral is made into a fine powder and EPR spectrum is recorded [Fig.2]. The presence of Cr(III) in EPR spectrum is not detected. Where as Cu(II) signals are identified at 2.390 and 2.06. The EPR signal of Cr(III) also normally appear around 2.00 [36]. Since the concentration of Cu is more than Cr, the EPR signal might have been suppressed by Cu(II). The EPR spectrum of fuchsite quartz consists of two sets of lines, one centered at 2.390 and other a set of six lines and broad line beneath the six lines. In a previous EPR study of fuchsite quartz collected from Jawanahalli, Karnataka, reported the presence of Fe(III), Mn(II) and Cr(III) as paramagnetic impurities [36]. Where as the present sample of different origin (Chitradurga, Karnataka) exhibits EPR signals due to Mn(II) and Cu(II) ions and these impurities are evident from the chemical analysis of the sample. In the present case, the six hyperfine lines with \( g = 2.002 \) and hyperfine coupling constant of 90(3)G are due to Mn(II) impurity [36]. The line centered at 2.390(\( g_\| \)) and the broad line with \( g = 2.06(3) \) (\( g_\perp \)) could be attributed to Cu(II) impurity in the mineral. Larger \( g_\| \) value is typical of an ionic Cu-ligand bonding. Since \( g_\| > g_\perp \), \( ^2E_\perp \) level corresponding to \( d_{x^2-y^2} \) orbital forms ground state. However, due to the higher concentration of copper impurity, the hyperfine lines due to copper ion were not resolved. The presence of Cu in high concentration results dipolar-
dipolar interactions. The spin-orbit reduction parameters $K_\parallel$ and $K_\perp$ can be calculated using the equations [37]

\[
\begin{align*}
g_\parallel &= g_e - \frac{8 K_\parallel^2}{(\Delta E_1)} \\
g_\perp &= g_e - \frac{2 K_\perp^2}{(\Delta E_2)}
\end{align*}
\]

\[E_1 = 2B_{1g} \rightarrow 2B_{2g}\]
\[E_2 = 2B_{1g} \rightarrow 2E_g\]

Where $g_e = 2.0023$ using $\Delta E_1$ and $\Delta E_2$ obtained from optical spectrum of Cu(II), the values obtained for $K_\parallel$ and $K_\perp$ are 0.7888 and 0.4946 respectively. These values are consistent with the values reported for Cu(II) in diopside [38]

4.4. IR spectrum

In figure 3, the infrared spectrum of the fuchsite quartz recorded in the region 4000-600 cm\(^{-1}\) at room temperature, is presented. The spectrum consists of characteristic bands of silicates and water.

Quartz(SiO\(_4\)) and its polymorphs, although oxides by composition are placed in testosite subclass of the silicate minerals. Silicates generally shows four fundamental modes of vibration. Of these $\nu_1, \nu_4$ are infrared active. In the present investigation one band with two components at 770 and 790 cm\(^{-1}\) is observed. It is assigned to $\nu_4$ mode. The splitting of the band indicates removal of degeneracy partially and suggests deviation from ideal $T_d$ symmetry [39]. A broad band is observed around 1100 cm\(^{-1}\). This is attributed to the triply degenerate,
mode ($\nu_2$). The band at 690 cm$^{-1}$ is the characteristic of sorosilicates ($Si_2O_7$) [39].

Normally $H_2O$ exhibits three fundamental modes of vibration. Of these, $\nu_1$ and $\nu_2$ are symmetric and asymmetric stretching frequencies respectively. The $\nu_3$ vibration is the H-O-H bend. In the present investigation two bands are observed at 1610 and 3160 cm$^{-1}$. The band at 1610 cm$^{-1}$ is attributed to $\nu_3$ mode. The 3160 cm$^{-1}$ band is assigned to the $\gamma_1$ mode.

The shifts of these bands from their vapour phase values ($\nu_3 = 3765, \nu_1 = 3652$ and $\nu_2 = 1595$ cm$^{-1}$) to solid phase indicate hydrozoen bonding [40].

The observed vibrational frequencies and their assignments are listed in Table 3.

5. Conclusions

The chemical analysis of the mineral confirms the presence of three transition metal impurities namely Cu, Cr and Mn. Of these copper is predominant (0.8492%) and the other two are relatively small (Cr = 0.22%, Mn = 0.009%). The presence of Cr(III) and Cu(II) ions in the sample is revealed by optical absorption spectrum. The bands observed due to Cu(II) in the NIR region are distinguished from those observed in UV-VIS region due to Cr(III). The optical absorption spectrum is characteristic of Cr(III) in octahedral and Cu(II) in tetragonal environments.
<table>
<thead>
<tr>
<th>Observed band position (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>sorosilicate ($\text{Si}_2\text{O}_7$)</td>
</tr>
<tr>
<td>770, 790</td>
<td>$\delta_4$ ($\text{Si}_4\text{O}_4$)</td>
</tr>
<tr>
<td>1100</td>
<td>$\delta_3$ ($\text{Si}_4\text{O}_4$)</td>
</tr>
<tr>
<td>1610</td>
<td>$\nu_2$ ($\text{H}_2\text{O}$)</td>
</tr>
<tr>
<td>3160</td>
<td>$\nu_3$ ($\text{H}_2\text{O}$)</td>
</tr>
</tbody>
</table>
A characteristic six line pattern of Mn(II) observed in the EPR spectrum of the sample suggests the presence of manganese in traces. The spin orbit coupling parameters $K_{||}$ and $K_{\perp}$ are calculated for Cu(II) by the correlation of EPR and optical spectra. The concentration of copper is more than that of Chromium in the sample. So the EPR signal of Cr(III) has been suppressed by Cu(II). Hence the EPR signal of Cr(III) could not be observed.

The IR spectrum is characteristic of water and silicates.
REFERENCES


31. Ikeda, K. and Yagi, K. Contributions to Mineralogy and petrology, 61, 91 (1977)


