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EPR AND OPTICAL ABSORPTION SPECTRAL STUDIES ON VOGLITE MINERAL

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Abstract

A voglite mineral sample of Volrite Canyon #1 mine, Frey Point, White Canyon Mine District, San Juan County, Utah, USA is used in the present study. An EPR study on powdered sample confirms the presence of Mn(II) and Cu(II). Optical absorption spectral results are due to Cu(II) which is in distorted octahedron. NIR results are indicating the presence of water fundamentals.

1.1 Introduction

A significant number of compounds contain the uranyl ion.[1-4]. The study of the uranyl carbonates was undertaken since a long time due to its wide distribution [5,6]. Uranyl carbonates may be classified into tri-carbonates and a mono/single-carbonates. Uranyl carbonate mineral voglite is a rare mineral resulting from the oxidation of uraninite with a formula of some uncertainty is given as $\text{Ca}_2\text{Cu}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{CO}_3)6\text{H}_2\text{O}$ [3,7-11]. The mineral is monoclinic, with cell dimensions $a = 25.97$, $b = 24.5$, $c = 10.7 \text{ \AA}$ and with probable space group $P2_1$ or $P2_1/m$. The mineral is composed of tubular to scalar crystals in parallel stacked aggregates. Voglite is radioactive ($>70 \text{ Bq/gm}$) as defined in 49 CFR 173.403. Green granular voglite mineral from Volrite Canyon #1 mine, Frey Point, White Canyon Mine District, San Juan County, Utah, USA is used in the present work. Its chemical analysis is reported and is also compared with other origins [8]. The analysis is presented in Table 1.

Table 1
Chemical analysis of Voglite mineral from different origins

Element	Utah, USA Wt%	Czech Republic Wt%
CaO	14.72	14.09
UO ₂	35.44	37.0
UO ₃	---	37.54
CuO	10.44	8.40
H ₂ O	14.19	13.9
CO ₂	23.11	26.41
Total oxide	97.90	99.8

But from the Table-1 it is clear the chemical analysis varies from place to place. Also CuO and CO₂ have major changes composition.

Spectroscopic techniques like electron paramagnetic resonance (EPR) spectroscopy, optical absorption spectroscopy, infrared and Raman spectroscopies are widely employed for the study and analysis of uranyl containing minerals. Geochemically, Cu(II), Mn(II) and Fe(III) occur not only in many mineral groups but also in other natural environments like herbs, trees and fossils. These ions though present at low concentrations, affect the characteristics of compounds and thus their use in industry, medicine, etc.[12] Electron paramagnetic resonance (EPR) technique is quite useful to assess these impurities when present in lower concentrations. Electron paramagnetic resonance occurs between spin sub levels emerging in the external magnetic field following the splitting of the ground orbital state of the atom. In optical absorption spectroscopy, transitions proceed between orbital levels. Thus EPR spectroscopy is a natural sequel to optical spectroscopy. Thus optical absorption not only supplements but also complements the EPR results [13]. These techniques serve to find information about the molecular structure of minerals that is not obtained through X-ray diffraction (XRD) techniques using single crystal or powder. Further, no information on the orientation of hydroxyl groups will be obtained by XRD. No attempt, so far, has been made with respect to optical absorption and electron paramagnetic resonance (EPR) studies on voglite mineral. Therefore in this work the authors report the EPR, optical absorption, NIR spectral studies of voglite mineral at room temperature [12].

1.2 Experimental

The EPR spectrum of the powdered voglite mineral is recorded at room temperature (RT) on JEOL JES-TE100 ESR spectrometer operating at X-band frequencies ($\nu = 9.38253$ GHz, modulation 0.2 mT with 1mW power and amplitude 10),

having a 100 KHz field modulation to obtain a first derivative EPR spectrum. DPPH with a g value of 2.0036 is used for g factor calculations. Optical absorption spectrum of the compound is recorded at RT on Carey 5E UV Vis-NIR spectrophotometer in mull form in the range 200-1500 nm.

Band component analysis was undertaken using the Jandel "PEAKFIT" software package which enabled the type of fitting function to be selected and specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Lorentz–Gauss cross product function with a maximum number of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.997

1.3 Theory

Several EPR parameters such as g , A , D and E are employed while interpreting EPR spectrum. The g parameter is a measure of the coupling between the unpaired electron's spin angular momentum (S) with its orbital angular momentum (L) [14]. The unpaired electron interacts (couples) with the nuclear spin (I) to form a $(2I + 1)$ line hyperfine structure centered on g and spaced with the distance quantified by the hyperfine coupling parameter A . The coupling between the nuclear and electron spins becomes stronger as the A parameter becomes larger. The combination of g and A parameters can be utilized to differentiate between electron environments of Fe^{3+} and Mn^{2+} ions. The EPR zero field splitting (ZFS) parameters, D and E , measure the deviation of the ion crystal field from ideal tetrahedral or octahedral symmetries and they apply to ions with more than one unpaired electron, e.g., low field Fe^{3+} and Mn^{2+} . However, the broad nature of EPR spectra of Fe^{3+} makes the determination of D and E difficult [15].

$Mn(II)$, being a d^5 ion, has total spin $S = 5/2$. This state splits into three Kramers' doublets, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$ separated by $4D$ and $2D$ respectively where D is the zero-field splitting parameter. The deviation from axial symmetry leads to a term known as E in the spin Hamiltonian. The value of E can be easily calculated from single crystal measurements. A non-zero value of E results in making the spectrum unsymmetrical about the central sextet.

$Cu(II)$ has an electronic configuration $[Ar] 3d^9$. In an octahedral crystal field, the corresponding ground state electronic configuration is $t_{2g}^6 e_g^3$ which yields 2E_g term. The excited electronic configuration, $t_{2g}^5 e_g^4$, corresponds to ${}^2T_{2g}$ term. Hence single electron transition ${}^2E_g \rightarrow {}^2T_{2g}$ is expected in an octahedral crystal field. Normally, the ground 2E_g state splits due to Jahn-Teller effect and hence lowering of symmetry is expected for $Cu(II)$ ion. This state splits into ${}^2B_{1g}(d_x^2 - y^2)$ and ${}^2A_{1g}(d_z^2)$ states in tetragonal symmetry and the excited term ${}^2T_{2g}$ also splits into ${}^2B_{2g}(d_{xy})$ and ${}^2E_g(d_{xz}, d_{yz})$ levels. In rhombic field, 2E_g ground state splits into ${}^2A_{1g}(d_x^2 - y^2)$ and ${}^2A_{2g}(d_z^2)$ whereas ${}^2T_{2g}$ splits into ${}^2B_{1g}(d_{xy})$, ${}^2B_{2g}(d_{xz})$ and ${}^2B_{3g}(d_{yz})$ states. Thus, three bands are expected for tetragonal (C_{4v}) symmetry and four bands are expected for rhombic (D_{2h}) symmetry. The wave numbers of the three transitions in the tetragonal field are given by the following equations [16]

$${}^2B_{1g} \rightarrow {}^2A_{1g} \quad : 4Ds + 5Dt$$

$${}^2B_{1g} \rightarrow {}^2B_{2g} \quad : 10Dq$$

$${}^2B_{1g} \rightarrow {}^2E_g \quad : 10Dq + 3D_s - 5Dt$$

In the above formulae, Dq is crystal field and Ds, Dt are tetragonal field parameters.

1.4 RESULTS AND DISCUSSION

1.4.1 EPR spectral analysis

Generally, whenever a mineral is formed under the earth's crust, the nearby impurities will enter the mineral in various locations such as interstitial, substitutional or both. EPR spectrum of the voglite mineral recorded at room temperature is given in Fig. 1. It is well known that the EPR studies of transition metal ion, Mn(II), is easily observed at room temperature, even if present in minute levels, compared to other ions. The spectra clearly indicate the presence of Mn(II) in the sample.

Fig. 1 contains a strong sextet at the centre of the spectrum corresponding to the electron spin transition $+1/2 \rightarrow -1/2$. Generally, in most of the cases, the powder spectrum is characterized by a sextet, corresponding to this transition. The other four transitions, corresponding to $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ are not seen due to their high anisotropy in D. If $E \neq 0$, the EPR spectrum will not be symmetrical about the central sextet. The observed EPR spectrum can be explained by the spin-Hamiltonian of the form [17].

$$\mathcal{H} = \beta B g S + D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} + S A I$$

Here the first term represents the electron-Zeeman interaction. The second term represents the zero field contribution and the third term represents the nuclear-Zeeman interaction. The extra set of resonances in between the main sextet is due to the forbidden transitions. From the forbidden doublet lines, the Zero field splitting parameter, D, has been calculated using the formula [18, 19].

$$\Delta H = \left(\frac{2D^2}{H_m} \right) \left[\frac{1 + 16(H_m - 8Am)^2}{9H_i H_m - 64Am} \right]$$

$$\text{Here } H_m = H_o - Am - \frac{[I(I+1) - m^2]A^2}{2H_o}$$

From the powder spectrum of the mineral, the following parameters have been calculated $g = 1.997$, $A = 9.6$ mT and $D = 31.6$ mT. The observed g, A and D values are comparable with other similar systems and agree well within the experimental error [20-23]. The large value of D indicates a considerable amount of distortion around the central metal ion. The hyperfine constant 'A' value provides a qualitative measure of the ionic nature of bonding with Mn(II) ion. The percentage of covalency of Mn-ligand bond has been calculated using 'A' (9.6 mT) value obtained from the EPR spectrum and

Matumura's plot [24]. It corresponds to an ionicity of 96%. Also the approximate value of hyperfine constant (A) is calculated by using covalency (C) equations [25,26]

$$A_{\text{iso}} = (2.04C - 104.5) 10^{-4} \text{ cm}^{-1}.$$

The value obtained is $91 \times 10^{-4} \text{ cm}^{-1}$. This calculated value agrees well with the observed hyperfine constant for the sample indicating ionic character for Mn-O bond in the mineral under study. The number of ligands around Mn(II) ion is estimated using the covalency [27] equation for C

$$C = \frac{1}{n} \left[1 - 0.16(X_p - X_q) - 0.035(X_p - X_q)^2 \right]$$

Here X_p and X_q represent electronegativities of metal and ligand. Assuming $X_p = X_{\text{Mn}} = 1.4$ and $X_q = X_{\text{O}} = 3.5$, the number of ligands (n) obtained are 30. This suggests that Mn(II) may be surrounded by six CO_3^{2-} . Further the g value for the hyperfine splitting is indicative of the nature of bonding. If the g value shows negative shift with respect to free electron g value of 2.0023, the bonding is ionic and conversely, if the shift is positive, the bonding is more covalent in nature [28]. In the present work, from the observed negative value of 5.3×10^{-3} , it is apparent that the Mn(II) is in an ionic environment. Depending on the charge considerations, the impurity might have entered the lattice in place of Ca(II).

EPR spectrum of mineral reveals that in between third and fourth manganese hyperfine resonance lines a very sharp peak at (33.5 mT) having a g value 2.001 and a peak at (32.6 mT) having a g value 2.063, are observed. These can be ascribed to a radical such as CO_3^{2-} , because the mineral contains CO_3 as a constituent. The absence of any super hyperfine structure in the radical suggests that the radical may be CO_3^{2-} [29].

To know the ions which are responsible for low field resonances in the spectrum, amplitude is changed from 10 to 100 without change in magnetic field scale and the same is recorded as above (Fig.1) on left side. The overall spectrum is normally symmetric with two components of g. From the EPR spectrum on low magnetic field side the g values obtained are $g_{11} = 2.27$ and $g_{\perp} = 2.19$. As the mineral contains a very high percentage of copper the hyperfine lines due to Cu(II) could not be resolved. Even though the g values are in agreement with previously reported data. [30,31]. When the sample cooled to 77 K, an EPR spectrum similar to RT has been obtained with a slight reduction in line width. If $g_{11} > g_{\perp}$, the ground state is ${}^2B_{1g}$, where as if $g_{\perp} > g_{11}$ or if $g_{11} = 2.00$, the ground state is ${}^2A_{1g}$. Further tetragonal cupric complexes with D_{4h} generally have g_{11} (corresponding to the magnetic field along the Z axis of the complexes) $> g_{\perp} > 2.04$ have the ground state $d_{x^2-y^2}$ [32-34]. In the present case $g_{11} > g_{\perp} > 2.00$ ($2.27 > 2.19 > 2.00$) and hence the ground state is ${}^2B_{1g}$ ($d_{x^2-y^2}$).

The EPR spectrum of the mineral exhibits a weak resonance centered at $g = 2.39$. It is attributed to the presence of isolated Fe(III) ion incorporated as an impurity in the mineral [35]. P..S. Rao, Spectrochim. Acta A 52 (1996) 1127-1134.

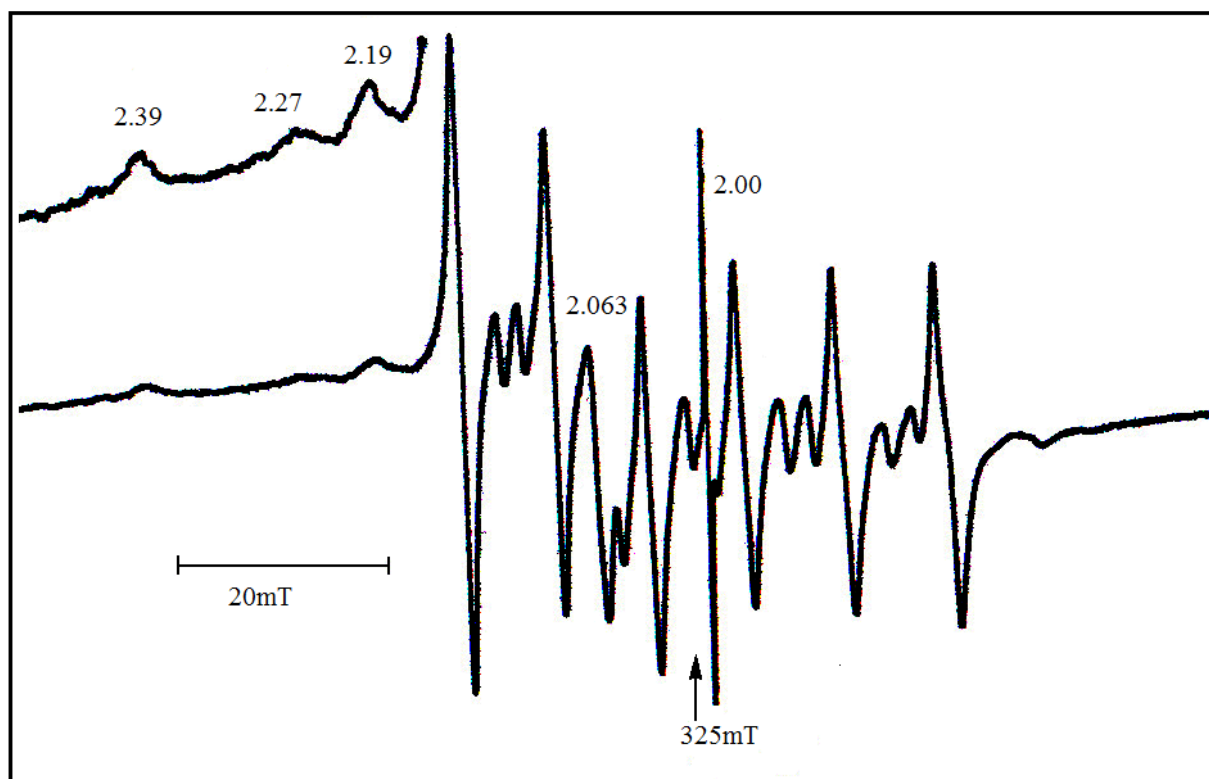


Fig. 1. EPR spectrum of voglite mineral recorded at (RT) temperature ($\nu = 9.38253$ GHz)

1.4.2 Optical absorption spectral analysis

UV-Vis spectroscopy

The optical absorption spectrum of voglite mineral recorded at room temperature in the range from 400 – 1200 nm is shown in Fig. 2(a) and NIR spectrum (1200 to 1500 nm) is shown in Fig. 2(b) and charge transfer spectrum(200 to 400 nm) in Fig. 2(c). The optical absorption spectrum shows energies at 8300 8570, 9500, 10560, 12995, and 14785 cm^{-1} . The optical absorption spectrum is analysed based on chemical analysis and EPR spectra of the mineral. The bands are divided into two sets for easy analysis of the spectrum. The bands at 8300, 10560 and 12995 cm^{-1} are considered as first set 8570, 10560 and 14785 cm^{-1} are treated as second set

The bands observed at 8300, 10560 and 12995 cm^{-1} in the first set and 8570, 10560 and 14785 cm^{-1} in the second set are attributed to the same transitions from ${}^2B_{1g}$ to 2E_g , ${}^2B_{2g}$ and ${}^2A_{1g}$ respectively for Cu(II) ion. Based on these assignments, the octahedral field (Dq) and tetragonal field (Dt and Ds) parameters, evaluated using the formulae given in the literature, are given in Table 1.

Table 1**Observed and calculated energies of the bands with their assignments in voglite**

For Cu(II): Site I $D_s = 1534$, $D_t = 433$ and $Dq = 1056 \text{ cm}^{-1}$
Site II $D_s = 1828$, $D_t = 252$ and $Dq = 1056 \text{ cm}^{-1}$

Site I			Site II			Transition from ${}^2B_{1g}$
Wave length (nm)	Wave number (cm^{-1})		Wave length (nm)	Wave number (cm^{-1})		
	Observed	Calculated		Observed	Calculated	
1204	8300	8301	1167	8570	8572	${}^2A_{1g}$
946.7	10560	10560	946.7	10560	10560	${}^2B_{2g}$
769.4	12995	12997	676.3	14785	14784	2E_g

The same sign obtained for Dq and Dt indicates an axial elongation in the tetragonal field and also confirms the ground state [36,37]. Since, two copper ions are present, one will form one set and the other form another set. This may be the reason for obtaining two types of copper(II) ions in the optical spectrum.

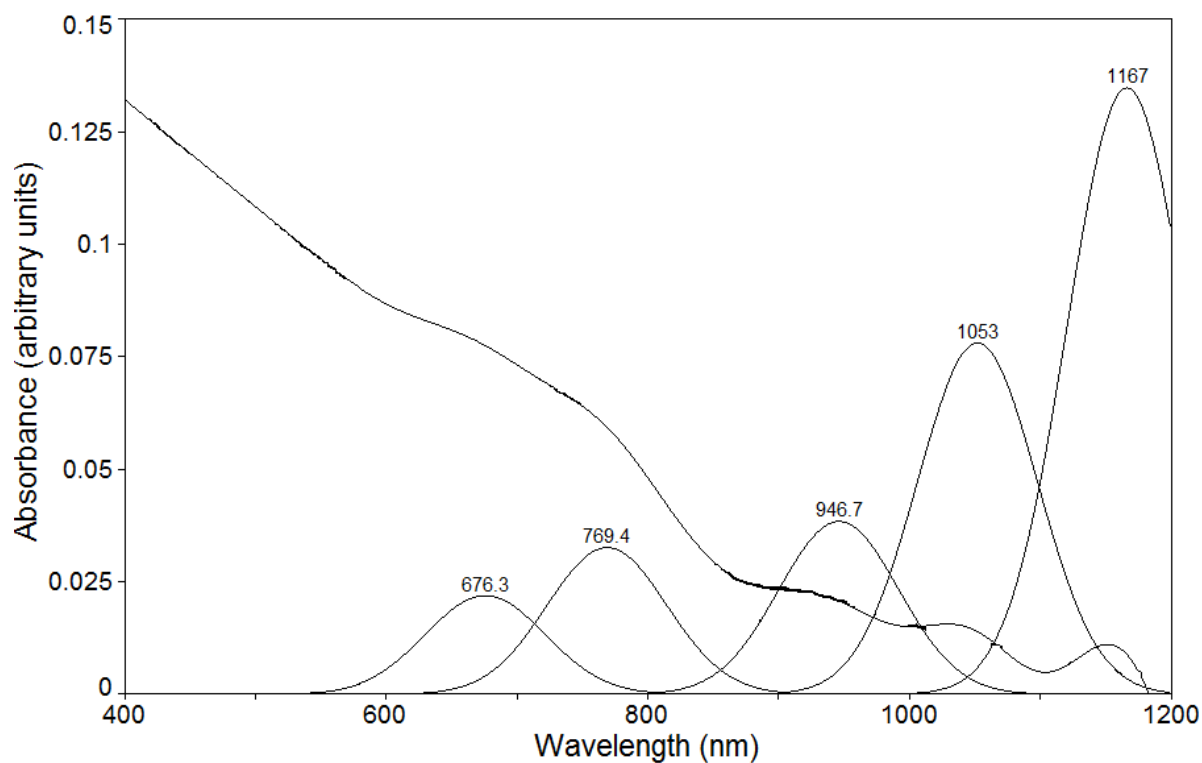


Fig. 2 (a) Optical absorption spectrum of voglite mineral at room temperature

1.4.2(b) NIR spectrum

The Near-IR spectral regions are divided into two regions (a) high wave number region $>8000\text{ cm}^{-1}$ where bands appear due to electronic transitions of copper (b) low wave number region $7950\text{-}5000\text{ cm}^{-1}$ bands which are of vibrational origin. The bands in the Near-IR spectrum are shown in the Fig. 2 (b). The bands in low wave number region between 7950 and 6300 cm^{-1} are attributed to the first overtone of the fundamental hydroxyl-stretching mode. Water in fluid inclusions in the voglite probably causes these bands [38].

Charge spectra of the voglite mineral recorded from 200 to 400 nm is shown in Fig. 2©. The spectrum clearly indicates energies at 35690 , 36640 , 42140 , 45145 and 48970 cm^{-1} . These energies are attributed to charge transfer transitions between ligand and metal ion.

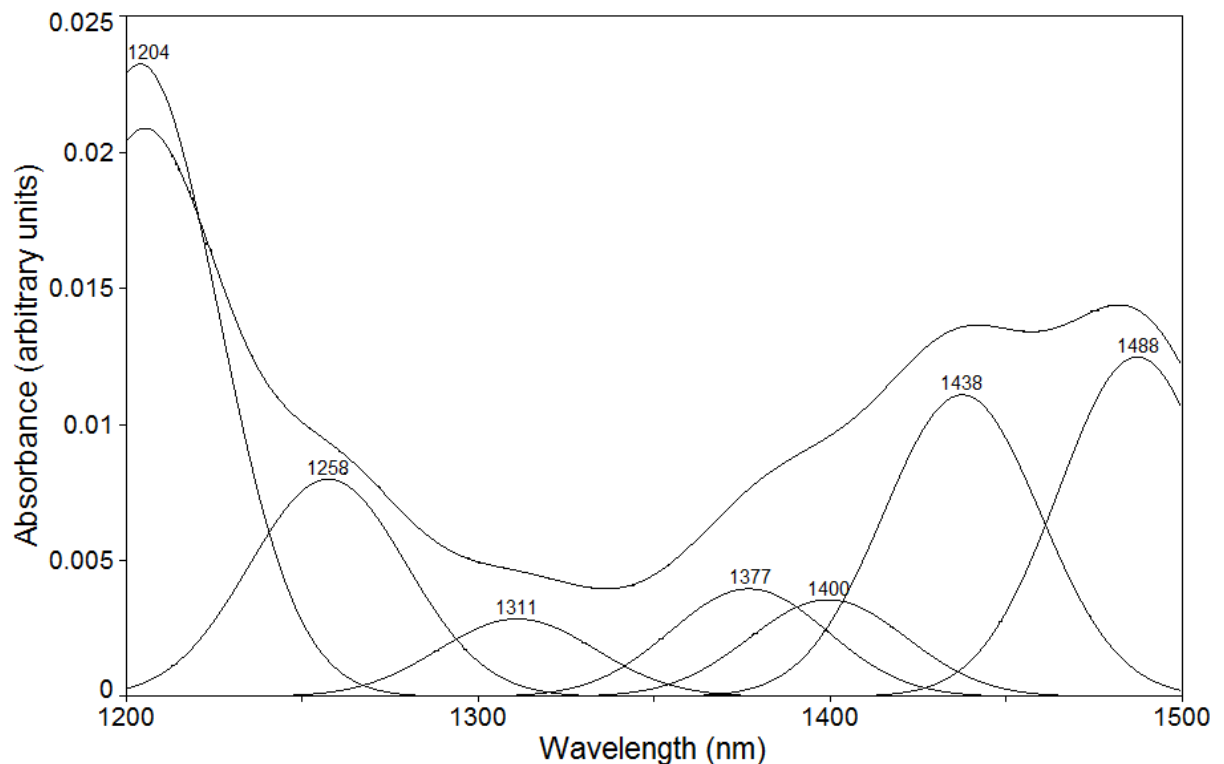


Fig. 2(b) NIR spectrum of voglite mineral at room temperature.

1.4.2 © Charge transfer spectrum

Charge transfer spectra of the voglite mineral recorded from 200 to 400 nm is shown in Fig. 2©. The spectrum clearly indicates energies at 35690 , 36640 , 42140 , 45145 and 48970 cm^{-1} . The occurrence of ligand to metal charge transfer transition (LMCT) bands can be expressed in terms of optical electro negativities of X ligand and X

metal. We propose the wave number of the transition is expressed as $\bar{\nu} = C[X_L - X_M]$ [39]. Here $C = 30000 \text{ cm}^{-1}$, X_L (3.5 for oxygen or water or carbonate or hydroxyl electro negativity) ligand and X_M metal electro negativities. Optical electro negativities have values comparable to Pauling electro negativities if we take $C = 30000 \text{ cm}^{-1}$. The observed energies at 35690, 36640, 42140, 45145 and 48970 cm^{-1} gave ($X_M = 2.3, 2.28, 2.10, 2.1, 2.00$ and 1.87 and its average is 2.11) 2.11. This value is nearly agreeing with Cu (1.95) Pauling electro negativity than Mn(1.40) and U(1.7). The ratio of any two successive charge transfer bands energy is almost same (1.08) and is constant. It is further supporting that the optical absorption spectrum is due to Cu(II) only.

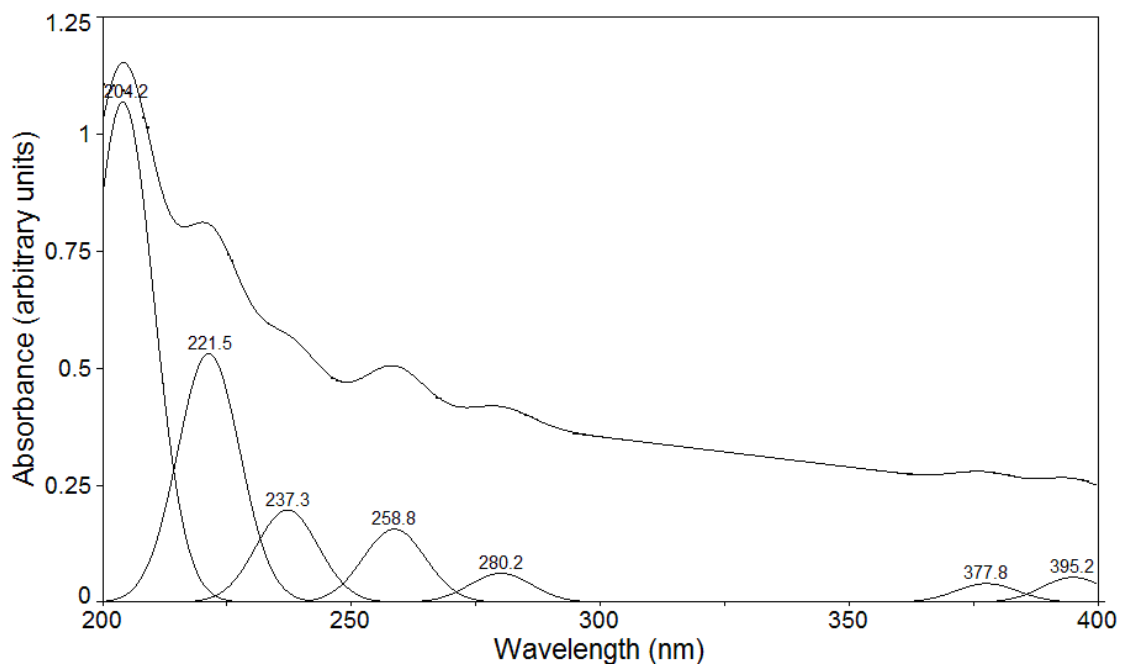


Fig. 2© Charge transfer spectrum of voglite mineral at room temperature

1.5 Conclusion

- The optical absorption spectrum of mineral voglite is due to copper only which is in a distorted octahedron environment.
- The EPR results confirm the presence of copper as its constituent and manganese and iron impurities in the mineral. Further it is evident from the chemical analysis that copper is present in higher concentration. EPR results are suggesting Mn(II) impurity might have entered the lattice in place of Ca(II).
- The optical absorption spectrum is due to only Cu(II) and charge transfer bands are explained basing on electro negativities and are supporting that spectrum is due to Cu(II) only but not either manganese or iron impurity

- NIR results confirm the presence of water fundamentals, which also supports the formula of the mineral.

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