

EPR, optical absorption, MIR and Raman spectral studies on libethenite mineral

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Libethenite, a copper phosphate mineral originated from Congo is used in the present studies. Optical absorption spectrum is due to Cu(II), which is in rhombic distortion. Whereas EPR results show that Fe(III) and Mn(II) are also present in the mineral. MIR and Raman spectral features are attributed to phosphate fundamentals and lattices vibrations of CuO respectively.

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1 Introduction

Copper never exist in native state and in general it occurs in +2 state many symmetrical environments which include square planar, distorted trigonal, tetragonal, rhombic, bipyramidal, square bipyramidal etc.,. In octahedral symmetry, there is a general distortion of four short and one or two longer bonds [1]. Copper is associated with carbonate, phosphate, arsenate, sulphates etc., in nature. The substitution of transitional metal ion results in lowering of symmetry in crystals and gives rise to more intense spectral features. Libethenite [Cu₂(PO₄)(OH)] is a secondary copper mineral found in the oxidized environment of copper ore deposits. It is orthorhombic with cell parameters a = 8.06, b = 8.39, c = 5.88 A.U. In libethenite, copper is surrounded by six oxygen atoms. Among these four oxygens are at less than 2.0 A.U. and the other at 2.394 A.U. from the central metal ion. Each phosphorous atom is bond to four crystallographically independent oxygen atoms. There is one crystallographically independent OH group in the unit cell [2-5]. Recently, copper phosphate minerals were studied by IR technique [2]. EPR and optical absorption data reveal that divalent copper in libethenite (originated from Zaire) is in tetragonally distorted octahedral environment. [6].

In the present investigation electron paramagnetic resonance (EPR), optical absorption and Raman spectra of libethenite originated from Mesa, Congo are presented.

2 Experimental methods

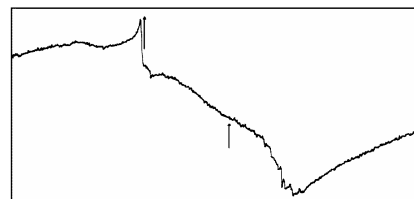
A green coloured libethenite containing about 66.55% of copper as CuO [7] is used in present investigations. The mineral is not a single crystal and hence is made into fine powder for spectroscopic studies.

Electron Paramagnetic Resonance EPR studies are carried out at room temperature (RT) on a JEOLJE TES 100 ESR spectrometer operating at X band frequencies ($\nu = 9.40656\text{GHz}$) having a 100 kHz field modulation and a phase sensitive detection to obtain a first derivative EPR signal. The EPR spectrum of

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powdered libethenite is shown in figure 1. It consists of a sharp line at low field and a broad line at high field with a sextant. These lines can be ascribed to Fe(III) resonances in the mineral sample [8].

Fig. 1 EPR spectrum of libethenite at room temperature ($\nu = 9.40646$ GHz).



Fe(III) containing five unpaired electrons and hence $S = 5/2$. The spin states in the absence of an external magnetic field are $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$. These three Kramer's doublets are separated by $2D$ and $4D$ respectively. Application of external magnetic field splits these Kramer's doublets into six levels labeled as $|-5/2\rangle$, $|-3/2\rangle$, $|-1/2\rangle$, $|1/2\rangle$, $|3/2\rangle$ and $|5/2\rangle$ respectively. EPR transitions between these levels will give rise to five resonances, known as fine structure lines. However, in case of Fe(III), the resonances range in the whole magnetic field of X-band EPR spectrometer, i.e., g values range very largely. This has been explained, by considering that the three Kramers doublets are populated at temperature of measurement. As mentioned in the literature [8] and references therein, the observed g values range from $30/7$ to $2/7$, 2 to 6 and $2/7$ to 6 depending upon the population of a particular Kramers doublet. However, in case of powder spectrum, the resonances at $30/7$ and 2 are generally attributed to large anisotropy in g values. In the present case, we have observed resonances at $g = 4.22$. In addition, the broad line at high field has $g \approx 2$ is due to Fe(III) impurity. The literature survey reveals that the observation of $g=30/7$ resonances confirms that the Fe(III) impurity is under the influence of a strong tetragonal distortion [8]. A close look at high field resonances indicates a sextet, in addition to the broad line, already discussed earlier. The g value is 2.007 and the hyperfine coupling constant is 90.4 G. These spin Hamiltonian parameters confirm that the impurity responsible for these resonances is Mn(II). The low intensity of the sextet indicates a very low concentration of impurity. The other resonances may be attributed to Mn(II) because of non-zero value of D . However, due to their low intensity the value of D cannot be estimated.

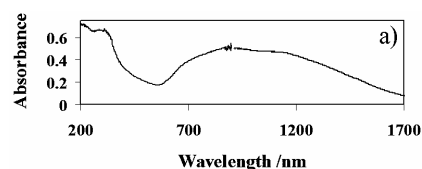
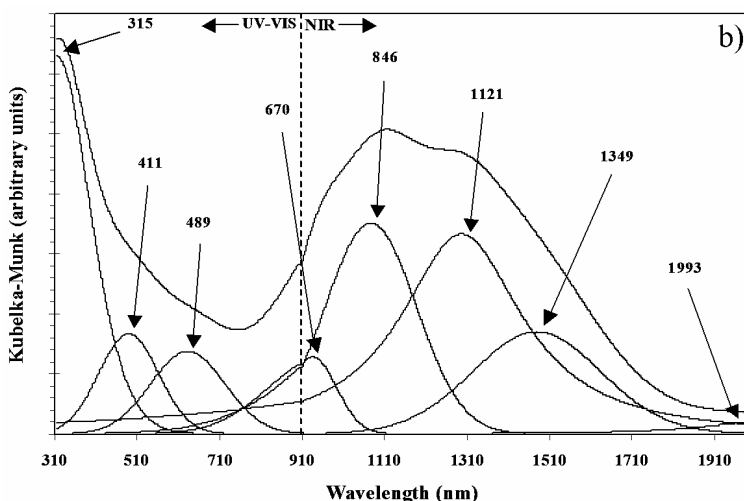


Fig. 2 a) Optical absorption spectrum of libethenite at room temperature. b) Optical absorption spectrum of libethenite at room temperature.



Optical absorption spectrum Optical absorption spectrum of the sample was recorded at room temperature in the region 200- 2000 nm on a Varian Cary 5E UV-Vis- NIR spectrophotometer. The spectra were transformed according to the Kubelka-Munk algorithm. NIR spectrum of the sample was recorded on a Nicolet Nexus FT-IR spectrometer with a Nicolet near IR fibreport accessory. A white light source was employed with a quartz beam splitter and TECNIR.

The powdered mineral sample was placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system. Raman spectra

were excited by He-Ne laser (633nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Other details of the experimental technique have already been reported [9-10].

Spectroscopic manipulations such as baseline adjustment, smoothing and normalization were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA) 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 Gauss-Lorentz cross product function with a minimum number of component bands used for the fitting process. The Gauss-Lorentz 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 0.995.

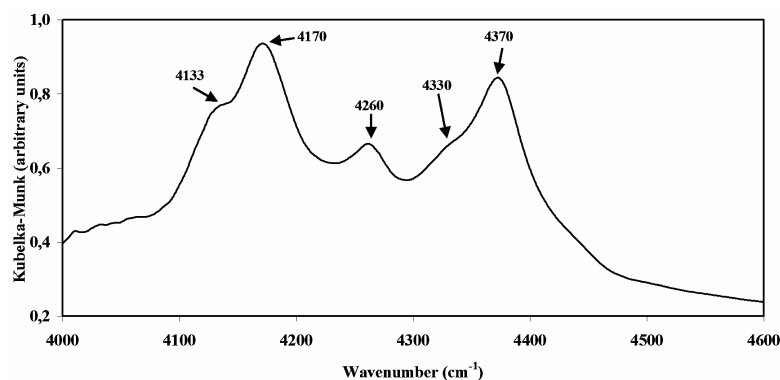


Fig. 3 IR spectrum of libethenite at room temperature.

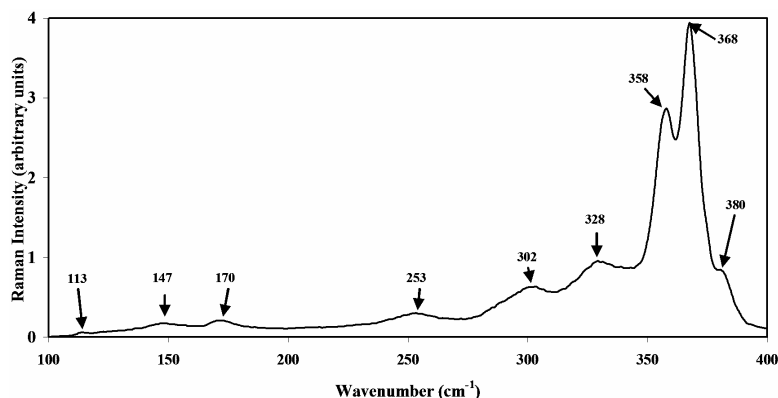


Fig. 4 Raman spectrum of libethenite for lattice vibrations.

3 Results and analysis

Cu(II) has an electronic configuration $[\text{Ar}] 3d^9$. 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 [11].

The optical absorption spectrum of the sample recorded at room temperature is shown in figure 2a and its peak fit analysis is shown in figure 2b. It shows energy of bands at 5017 (1993 nm), 7413 (1349 nm), 8920 (1121 nm), 11820 (846 nm), 14925 (670 nm) 20450 (489 nm), 24330 (411 nm) and 31745 (315 nm) cm^{-1} . The bands at 8920 , 11820 , 14925 and 20450 cm^{-1} in the UV-Vis region are assigned to Cu(II) in rhombic symmetry. The general ordering of the energy levels for rhombic symmetry is as follows [11] $A_{1g}(d_x^2 - y^2) < {}^2A_{2g}(d_z^2) < {}^2B_{1g}(d_{xy}) < {}^2B_{2g}(d_{xz}) < {}^2B_{3g}(d_{yz})$. Accordingly, the optical absorption bands observed of libethenite are 8920 , 11820 , 14925 and 20450 cm^{-1} [given in table 1]. These energies are comparable with the other data

reported for copper containing samples [14-17]. The bands observed at 24330 cm^{-1} and 31745 cm^{-1} might be a charge transfer band. The energies observed at 5017 and 7413 cm^{-1} are not d-d transitions. The OH⁻ stretching mode gives rise to the most common features in near infrared region. Hydroxyl exists as part of the structure and the stretching mode appears whenever water is present in any form [the range 3645 to 3677 cm^{-1}]. The ν_{OH} overtone ($2\nu_{\text{OH}}$) gives rise to a band in the MIR spectrum [12]. Accordingly the band observed at 7413 cm^{-1} ($3706 \times 2 = 2\nu_{\text{OH}}$) is assigned to the first overtone of OH. The band at 5017 cm^{-1} is the combination of the frequency lattice modes [13].

Table 1 Comparison of energies of the bands with their assignments for Cu(II) in rhombic octahedral coordination with ground state ${}^2A_{1g}(d_x^2-y^2)$.

Sample	${}^2A_{1g}(d_z^2)$		${}^2B_{1g}(d_{xy})$		${}^2B_{2g}(d_{xz})$		${}^2B_{3g}(d_{yz})$		Reference
	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}	nm	
Antlerite $\text{Cu}_3\text{SO}_4(\text{OH})_4$	8475	1180	9435	1060	10990	910	16390	610	[14]
Turquoise $\text{CuAl}_6(\text{PO}_4)(\text{OH})_8\cdot 4\text{H}_2\text{O}$			14970	668			18354	545	[15]
ZPPH $(\text{ZnKPO}_4)6\text{H}_2\text{O}$	7750	1290	9613	1040	12117	825	13330	750	[16]
Atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$	8049	1242	10296	971	11083	902	15380	650	[17]
Libethenite $\text{Cu}_2\text{PO}_4\text{OH}$	8920	1121	11820	846	14925	670	20450	489	present work

Table 2 Band head assignments for phosphate ion in libethenite mineral.

Observed cm^{-1}	Assignments	Calculated cm^{-1}
4133	$2\nu_1 + 2\nu_3$	4126
4170	$\nu_1 + 2\nu_3 + 2\nu_4$	4176
4260	$3\nu_3 + 2\nu_4$	4279
4330	$3\nu_1 + \nu_2 + 3\nu_4$	4333
4370	$3\nu_1 + \nu_2 + \nu_3$	4386

MIR Spectral analysis The MIR spectrum of libethenite is shown in figure 3. It shows a sharp band at 4170 cm^{-1} with shoulders on either side at 4133 and 4260 cm^{-1} . Another sharp band at 4370 cm^{-1} with component at 4330 cm^{-1} do not belong to the metal ion. Therefore these bands are assigned to vibrational frequencies of phosphate radical. The fundamental modes of vibration of phosphate are $\nu_1 = 980$, $\nu_2 = 363$, $\nu_3 = 1083$ and $\nu_4 = 515$ cm^{-1} [18]. The overtone and combination frequencies are expected in the near infrared region [19]. These values presented in Table 2 are in good agreement with those of the observed values.

Lattice Vibrations Raman and IR spectra were studied [2] in the range of 400 - 4000 cm^{-1} . Raman spectrum of libethenite (Fig 4) reveals more intense bands at 302, 328, 358, 368 and 380 cm^{-1} . The bands in this region are often ascribed to lattice vibrations [20] of CuO (such bands are not observed in the normal, mid IR spectrum). Weak bands are also observed at 113, 147, 170 and 253 cm^{-1} . The intensity of these bands suggests that symmetric vibration is involved involving the OH group.

Conclusions

Libethenite, a copper phosphate mineral obtained from Mesa, Congo contains about 66.55% of copper as CuO [7]. The optical absorption spectrum is analysed using peak fit analysis reveals that copper is in rhombic distortion. EPR results are due to iron and manganese. Lattice vibrations are attributed to CuO. The MIR spectrum is clearly due to phosphate overtones and combinations. These results conclusively prove that copper in the sample is in rhombic distortion surrounded by oxygen ligands.

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