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Optical absorption and EPR studies on tenorite mineral

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Abstract

Optical absorption and EPR studies of the mineral tenorite, a cupric oxide, which originated from Mexico and contains 54.40 wt% of CuO. EPR spectral results indicate two Cu(II) closely interacting ions to give a d^2 type structure. The calculated spin Hamiltonian at Rt and LNT are g = 2.160 and D = 125 G . The intensity of resonance line is not the same in low and high field regions. The optical absorption spectrum is due to Cu(II) which three sets of energies indicating Cu(II) in two independent tetragonal C_{4v} symmetry, in addition to d^2 structure of octahedral coordination. The octahedral and tetragonal field parameters are compared with those reported for several other copper containing minerals.

Introduction

Among the most important metals, copper plays a vital role in various fields of science. Naturally this metal appears in various forms. Among them cupric oxide (CuO) is one. In nature, it occurs in the form of a mineral called tenorite. It is monoclinic with $C_{2h}^{6}(C2/C)$. point group. There are four CuO molecules in the unit cell and two CuO units in the primitive cell and thus the copper and oxygen occupy C_1 and C_2 symmetry positions respectively. Each Cu atom is situated at the center of the oxygen parallelogram. Each oxygen atom has a distorted tetrahedral copper atom [1-2]. Since CuO has been studied extensively towards super conducting material, a few references have been mentioned [3-5]. In the first paper [3], a series of monomer, dimer and tetramer copper complexes have been prepared. However, the results indicate a broad line and nothing about EPR zero field splitting parameter. It is also mentioned that the copper aggregates giving the EPR resonance are magnetically isolated from the main CuO cluster. The second paper [4] discusses the role of charge stripes in CuO to understand the super conducting nature. The third [5] paper deals the multi sub lattice structure of CuO. Tenorite is an interesting mineral. Moreover no electron paramagnetic resonance (EPR) and optical absorption studies so far were reported for the tenorite mineral. Divalent copper being a d^9 system is prone to Jahn-Teller distortion and EPR study of this ion will give valuable information about the type of distortion. The optical absorption spectral studies of transition metal complexes provide information on excited state energies, symmetrical and structural distortions. Therefore the authors propose to report the results of spectral studies by EPR and optical absorption techniques of tenorite mineral.

Experimental

Tenorite mineral originated from Mexico donated by Dr.Michel Deliens, is used in the present work. It is dark brownish black in colour. The copper content is determined by standard spectrophotometric method [6]. EPR spectra of the sample in powder form are recorded both at room temperature (RT) and liquid nitrogen temperature (LNT) on a Varian E-112 EPR spectrometer operating at X - band frequencies (υ = 9.07 GHz) having 100 kHz field modulation and phase sensitive detection to obtain first derivative spectra. The optical absorption spectra of the sample are recorded at room temperature on Carey 5E UV-Vis-NIR spectrophotometer in mull form in the range 200 - 2500 nm.

Theory

Cu(II) has the electronic configuration [Ar]3d^9, where [Ar] stands for the closed argon shell. To explain the observed EPR and optical absorption spectra the following options are kept in mind. (i) If the crystal contains two types of independent Cu(II) ions, this will lead to the arrangement of d^9 configuration. (ii)If two Cu(II) ions interact to form two unpaired electrons, this arrangement leads to d^2 or d^0 configuration. For d^2 configuration, ground state term is ^{3}F and excited state terms ^{3}P,^{1}G, ^{1}D and ^{1}S. The transitions from the ground state to the three states ^{1}G, ^{1}D and ^{1}S are spin forbidden and are very weak. The two remaining ^{3}F and ^{3}P can have spin-permitted transitions. In octahedral field, ^{3}P transformed to $^3T_{1g}$(P) state and ^{3}F split into $^3A_{2g}$(F), $^3T_{1g}$(F) and $^3T_{2g}$(F) states. Of these $^3T_{1g}$(F) state lies lowest according to Hund's rule and becomes ground state [7]. d^0 being diamagnetic, no EPR or optical spectra are expected. On the other hand, in an octahedral crystal field, d^9 ion has the corresponding ground state electronic configuration as $t_{2g}^6 e_g^3$ and yields ^2E_g term. The excited electronic configuration $t_{2g}^5 e_g^4$ corresponds to $^2T_{2g}$ term. Thus only one single electronic transition ^2E_g to $^2T_{2g}$ 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_{x^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}) where as $^2T_{2g}$ splits into $^2B_{1g}$ (d_{xy}) and $^2B_{2g}$(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 [8].

Results and analysis

EPR Studies

A poly crystalline sample of tenorite mineral is taken in a quartz EPR tube for room temperature measurements. EPR spectrum obtained at room temperature is given in Fig. 1 marked with RT. A look at the spectrum immediately points that we are dealing with a system, whose spin value is not equal to ½. Generally, a polycrystalline sample of copper ion gives a single broad line due to dipolar-dipolar broadening, around g ~ 2.3. However, the present spectrum is completely different.

Cu(II) being d^9 has one unpaired electron. If another Cu(II) is present near by having proper Cu-O-Cu angle with Cu-Cu bond, there exists a possibility of interaction between these two ions. If the two ions interact, it will result $S = 0$ (diamagnetic, paired, singlet) or $S = 1$ (paramagnetic, unpaired, triplet). As a well-resolved EPR spectrum is observed at room temperature, we can suggest unambiguously that we are having a triplet state EPR spectrum. For a system with $S = 1$, the electronic levels splits into $|\pm1>$ and $|0>$ in the absence of an applied magnetic field with separation equal to D (D being zero field splitting constant). When an external magnetic field is applied, these two levels split into three levels, $|+1>$, $|0>$ and $|-1>$ and one can observe two transitions, separated by 2D [9].

The room temperature EPR spectrum of tenorite mineral can be explained by considering interaction between two copper ions in the structure. The structure contains two types of O-Cu-O angles (84.5 and 95.5°): copper has four oxygen neighbours at 1.96 Å, the next nearest neighbours being two oxygens at 2.78 Å. The shortest Cu-Cu distance is 2.90 Å [2]. This close distance between the two copper ions is favorable for interaction between the ions. The calculated values are $g = 2.160$, $D = 125$ G. The resonance line on low field side is slightly more intense than the one on high field side. However, the half field line at g ~ 4.0 is not observed. This may be due to its low intensity (forbidden transition) or weak interaction with very low exchange coupling constant (J). The information about J needs extensive magnetic moment measurements at various temperatures down to 77 K [10].

The sample is cooled to 77 K and the EPR spectrum thus obtained is given in Fig. 1 marked with LNT. This is also very similar to RT spectrum. The calculated g and D values are 2.160 and 125 G. These values match fairly well with RT values. Here also, half field transitions could not be seen. However, the resonance line at low field is less intense than the one on high field side. This indicates that the ground state is |-1>. However, we did not notice any paramagnetic- antiferromagnetic phase transition, as observed in a few copper compounds [1]

Optical absorption studies

The optical absorption spectrum of tenorite mineral recorded in mull form at room temperature (RT) is shown in Fig. 2. The spectrum observed here has bands at 41670,35090,23250,18690,17850,16670,15530,12930,12170, 10310 and 8865 cm^{-1}. For easy analysis of the spectrum the bands are divided into three sets (a) 8865,10310, 12930 cm^{-1},(b) 12170,16670, 18690 cm^{-1} and (c) 15530, 17850, 23250, 35090 and 41670 cm^{-1}. Cu(II) being d^9 has one unpaired electron and generally gives optical absorption energies around 8000,10000 and 14000 cm^{-1} [11] and energies around 13000, 16000 and 18000 cm^{-1} [12] for octahedral geometry assuming C_{4v} site symmetry for Cu(II) ion in the sample. The bands observed at 8865, 10310 and 12930 cm^{-1} are assigned to $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_1$ and $^2B_1 \rightarrow {}^2E$ transitions respectively. The octahedral (Dq) and tetragonal (Ds, Dt) field parameters are evaluated from the following expressions:

$$4Ds + 5Dt \; : {}^2B_1 \rightarrow {}^2A_1$$

$$10Dq \; : {}^2B_1 \rightarrow {}^2B_1$$

$$10Dq + 3Ds - 5Dt \; : {}^2B_1 \rightarrow {}^2E$$

The parameters evaluated are found to be Dq = 1031 cm^{-1}, Ds = 1640 $cm^{-1}$and Dt = 461 cm^{-1}. The another set of bands at 12170 16670 18690 cm^{-1} are assigned to $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_1$ and $^2B_1 \rightarrow {}^2E$ transitions respectively. Using the above expressions the parameters evaluated are found to be Dq = 1667 cm^{-1}, Ds = 2027 cm^{-1} and Dt = 812 cm^{-1}. The band positions along with their assignments are given in Table – 1. The values of Dq and Dt are of the same sign in the present sample thus indicating tetragonally elongated octahedral site for Cu(II) ion [13]. The values of tetragonal parameters are higher in second sect when compared with the first set. It indicates tetragonal distortion is more in second set than in first set. For comparison the octahedral and tetragonal field parameters with those reported earlier in different copper bearing minerals are presented in Table –2. The observed parameters in the present sample match fairly with other samples.

As mentioned in EPR spectral analysis where we assumed a two unpaired electrons to explain the observed one, here also we assumed two electrons present in the sample. The optical absorption spectrum also has two strong bands at 15530 and 23250 cm^{-1}, a weak band at 17850 cm $^{-1}$ along with charge transfer bands at 35090 and 41670 cm^{-1}. Some previously reported spectra for d^2 ion surrounded six oxygen ligands showed bands at 17400, 25200 cm^{-1} [14] and 16900, 23500 cm^{-1} [15]. The two stronger bands observed at 15530 and 23250 cm^{-1} are assigned to the transitions $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ respectively in an octahedral coordination. Using T-S diagram [16] for d^2 ion, 10Dq is calculated to be 16800 cm^{-1} and B = 600 cm^{-1} A third band could be expected to be charge transfer band [17]. Accordingly the band observed at 35090 cm^{-1} is attributed to $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$. The lower singlet energy transition $^3T_{1g}(F) \rightarrow {}^1E_g(D)$, $^1T_{2g}(D)$ is observed in the range 10200 – 12000 cm^{-1}[17] and this transition is spin-forbidden and is very weak. But in the observed spectrum the bands at 12 170 and 10310 cm^{-1} are intense and are not attributed d^2 ion. But the band observed at 17850 cm^{-1} is attributed to $^3T_{1g}(F) \rightarrow {}^1A_{1g}(G)$ transition of d^2 ion. The unassigned band at 41670 cm^{-1} may be due to charge transfer transition between metal and ligand.

Conclusions

Tenorite is copper mineral. Its analysis indicates that CuO is 54.40 wt%. The optical absorption spectrum is due to Cu(II) in two independent positions in tetragonal C_{4v} symmetry. Further it might be noticed that Cu(II) + Cu(II) are in a weaker interaction to form a d^2 configuration. The energies are attributed to octahedral coordination of Cu(II) + Cu(II) with d^2 configuration. EPR spectrum reveals the presence of only d^2 ion but not d^9 ion. The calculated values are g = 2.160 and D = 125 G. Even at low temperature no changes are observed in the EPR spectrum ruling out any phase transition. The intensity of resonance line is not uniform in low and high field regions and shows that the ground state is $|-1>$. Thus the results of the optical and EPR investigations reported in the present communication conclusively prove that the site symmetry of Cu(II) + Cu(II) (d^2) ion in tenorite mineral is octahedral coordination with $^3T_{1g}(F)$ as ground state.

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Table – 1

Assignments of Cu(II) bands in tenorite mineral

Transitions	Band positions	
	Observed Wave number	Calculated Wave number
Site 1		
$^2B_1 \rightarrow {}^2A_1$	8865	8865
$^2B_1 \rightarrow {}^2B_1$	10310	10310
$^2B_1 \rightarrow {}^2E$	12930	12925
Site 2		
$^2B_1 \rightarrow {}^2A_1$	12170	12168
$^2B_1 \rightarrow {}^2B_1$	16670	16670
$^2B_1 \rightarrow {}^2E$	18690	18691
Site 3		
$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$	15530	
$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$	23250	
$^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$	35090	
$^3T_{1g}(F) \rightarrow {}^1A_{1g}(G)$	17850	
Charge transfer	41670	

Table - 2

Comparison of octahedral and tetragonal field parameters for Cu(II) in different Minerals

Sl.No.	Name of the mineral	Dq (cm^{-1})	Ds (cm^{-1})	Dt(cm^{1})	Reference
1	Melanterite	1053	1510	414	[18]
2	Pseudo-malachite	1149	1617	491	[19]
3	Connellite	1205	1525	450	[20]
4	Cornetite	1257	1434	380	[21]
5	Tenorite	1031	1640	461	Present work
6	Chrysocolla	1400	3000	800	[12]
7	Chalcanthite	1250	3240	710	[22]
8	Malachite	1250	3245	700	[22]
9	Tenorite	1667	2027	812	Present work

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List of Figures

Fig. 1 EPR spectrum of tenorite mineral at room and liquid nitrogen temperature.

Fig.2.Optical absorption spectrum of tenorite mineral at room temperature.

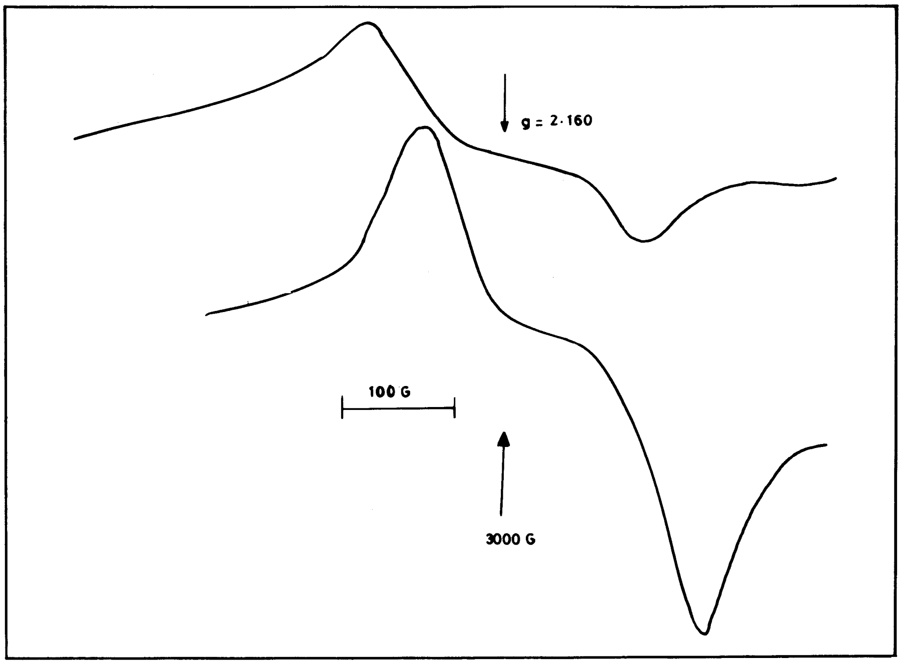

Figure 1

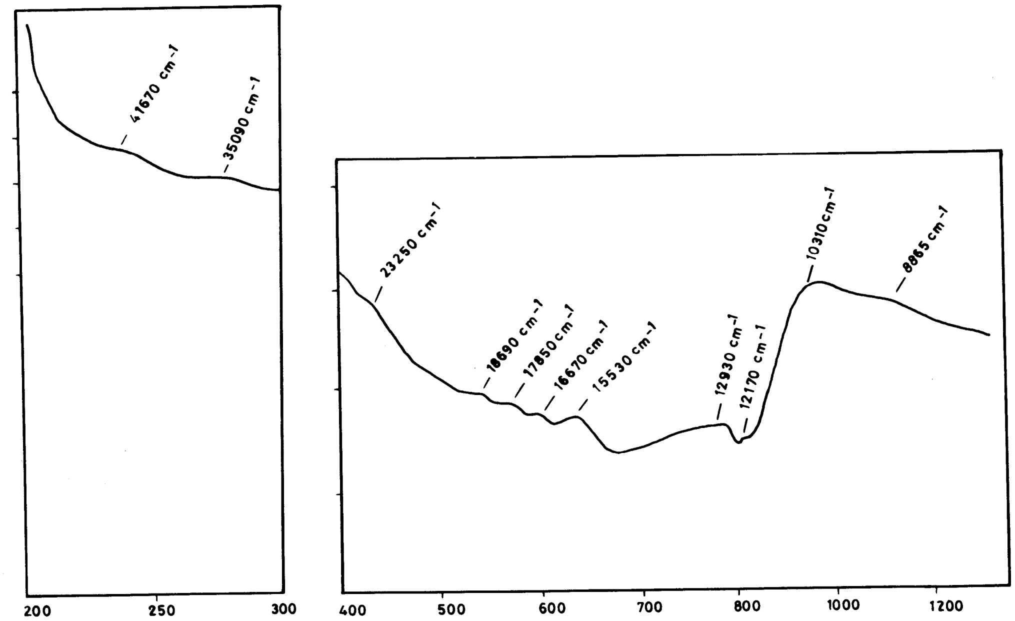
41670 cm-1
35090 cm-1
23250 cm-1
18690 cm-1
17850 cm-1
16670 cm-1
15530 cm-1
12930 cm-1
12170 cm-1
10310 cm-1
8865 cm-1
200
250
300
400
500
600
700
800
1000
1200

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Figure 2