EPMA, EPR, electronic and vibrational spectral studies on natural aurichalcite

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Abstract. The electron probe micro analysis (EPMA), electron paramagnetic resonance (EPR), electronic and vibrational spectral studies on a natural mineral, aurichalcite were studied at room temperature. The EPMA analysis revealed the concentration of copper in the mineral to be 2.6 wt% and zinc as 24.5 wt%. The optical spectra revealed the presence of copper in D_{4h} symmetry with crystal field (Dq) and tetragonal field (Ds and Dt) parameters as 1250, 1600 and 520 cm^{-1} respectively. This further confirmed the presence of Cu(II) ion in an elongated tetragonal site. The EPR studies indicated the presence of Cu(II) ion, but hyperfine lines could not be resolved due to the high concentration of the paramagnetic impurity in the mineral. The IR spectrum confirmed the presence of water and carbonate ion.

Keywords. Aurichalcite; optical absorption spectra; EPR; Cu(II) ion.

1. Introduction

The Cu(II) is a transition metal ion that readily forms stable complexes. It has a very simple electronic configuration, namely one electron is missing from the complete d shell. The system is equivalent to a single positive charge in the 3d-shell. Hence, it is a very convenient system for checking some of the basic ideas of the crystal field theory in naturally occurring minerals. In this connection, a few copper bearing minerals have been investigated to explain the nature of the metal ion and its site symmetry by spectroscopic measurements (Reddy and Sarma 1981; Sarma *et al* 1982; Reddy *et al* 1987).

The chemical composition of copper bearing aurichalcite mineral is $\text{ZnCu}(\text{CO}_3)(\text{OH})_2$. In this mineral, copper and zinc are mutually replaceable and are surrounded by two O and four OH molecules in a less distorted octahedron. Crystal structure and chemical analysis of aurichalcite from different origins have been reported (Jambor and Pouliot 1965; Zirkel 1970; Leicht 1971; Palache *et al* 1976).

The present investigation is on the greenish blue mineral aurichalcite, collected from Banner district, dripping spring mountain, Gila Country, Arizona, USA supplied by WARDS Natural Science Estd., Inc., New York. Since, copper(II), being a d^9 system, is prone to Jahn–Teller distortion, an EPR study of this ion will give information about the type of distortion. Hence, IR and EPR techniques have been used in the present study to confirm the symmetry around the paramagnetic ion in the mineral at room temperature.

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2. Experimental

Microanalysis was carried out on thin polished section of aurichalcite using Camebax Micro EPMA at an operating voltage of 20 kV and a sample current of 2 n.amp. in a beam regulated mode. The measured data was corrected by ZAF correction on PDP 11/03 computer. Optical absorption spectrum of the sample in the form of powder was recorded on Cary 2390 spectrometer in the region 300 to 1200 nm. EPR spectrum of the sample in polycrystalline form was recorded using Varian E-112 EPR spectrometer operating at X-band frequencies ($\nu = 9.5$ GHz) having a 100 kHz field modulation and a phase sensitive detector to obtain a first derivative signal. DPPH with a g value of 2.0036 was used as the internal field marker. The infrared spectrum of the sample in KBr pellet form was recorded on Perkin-Elmer infrared spectrophotometer in the region 600 to 4000 cm^{-1} .

3. Results and discussion

3.1 Chemical composition

Elemental concentration of aurichalcite from EPMA is presented in table 1. Ideally pure aurichalcite has the structural formula $\text{ZnCu}(\text{CO}_3)(\text{OH})_2$. However, the analysis indicates the presence of Si varying from 13 to 18 wt%. This might be due to silica in the associated silicate of the rock detected by the probe. Table 1 shows that this mineral contains Zn to the extent of 24 to 28 wt% while the concentration of Cu varies from 2.4 to 2.8 wt%. X-ray scanning picture is taken for MnK_α line on the sample which revealed the presence of Mn in very low concentration and this could not be estimated.

3.2 Optical absorption spectrum

The optical absorption spectrum of the sample is shown in figure 1. Since the spectrum consists of three bands, the site symmetry of Cu(II) is presumed to be D_{4h} . Accordingly, the three bands observed at 9010 , 12500 and 14700 cm^{-1} are attributed to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ respectively. Therefore the energy expressions can be written as

$$4Ds + 5Dt = 9010\text{ cm}^{-1},$$

$$10Dq = 12500\text{ cm}^{-1},$$

$$10Dq + 3Ds - 5Dt = 14700\text{ cm}^{-1}.$$

Table 1. EPMA data of aurichalcite.

Element	Concentration in wt% (sets)					
	I	II	III	IV	V	VI
Cu	2.41	2.76	2.83	2.60	2.46	2.53
Zn	23.74	25.41	28.19	24.86	26.86	24.51
Si	18.39	17.79	17.71	18.19	12.87	16.84

Figure 1. Room temperature optical absorption spectrum of aurichalcite in powder form.

Table 2. Comparison of crystal field parameters of six-coordinated compounds.

Compound	Dq	Ds	Dt	Ref.
$\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$	1120	1600	560	[a]
$\text{Cu}^{2+}:\text{CaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	1000	1540	470	[b]
$\text{Cu}_8(\text{Si}_4\text{O}_{11})\text{OH}_4$	1070	1674	327	[c]
$\text{Cu}_5(\text{SiO}_3)_4 \cdot \text{OH}_2$	1333	1565	380	[c]
$\text{Cu}_{19}(\text{SO}_4)\text{Cl}_4(\text{OH})_{32} \cdot 3\text{H}_2\text{O}$	1205	1525	450	[d]
$\text{ZnCu}(\text{CO}_3)(\text{OH})_2$	1250	1600	520	Present case

[a] Billing and Hathway (1968); [b] Swamy *et al* (1980); [c] Sarma *et al* (1982); [d] Sreeramulu *et al* (1990).

Using the formulae of the transitions, the crystal field (Dq) and tetragonal field (Ds and Dt) parameters are calculated as $Dq = 1250$, $Ds = 1600$ and $Dt = 520 \text{ cm}^{-1}$. In tetragonal field the values of Dt and Dq will have the same sign if there is an axial elongation and will have opposite sign if they have axial compression (Ferguson *et al* 1975). For the present case the values of Dt and Dq are found to have the same sign. This confirms the lowering of octahedral site to an elongated tetragonal site of $\text{Cu}(\text{II})$ ion in the crystal. A comparison of the parameters Dq , Ds and Dt of certain copper samples in tetragonal site (symmetries) is made (table 2). The present one agrees with those reported earlier.

3.3 EPR spectrum

The mineral was taken in a mortar and with a pestle was made into a fine powder. The powdered mineral was then transferred into an EPR quartz tube and the EPR spectrum was recorded at room temperature. The spectrum thus obtained is shown in

Figure 2. EPR spectrum of polycrystalline sample of aurichalcite at room temperature. Frequency = 9.501 GHz.

figure 2. It is clear from figure 2 that it contains a broad peak and a sextet pattern of sharp lines marked by arrows from the top. The line marked with * is due to the internal standard DPPH. The broad line has a g value of 2.28, which can be assigned to a Cu(II) ion in the mineral. Copper nucleus has two isotopes with mass numbers 63 and 65. Both these isotopes have nuclear spin of $3/2$ and also have almost identical magnetic moments (Weil *et al* 1994). As was mentioned in optical absorption spectrum analysis, copper ion undergoes elongated tetragonal distortion. Hence, one should expect more than one g value in the EPR spectrum. In the present case, one g value is 2.28 and the other g value, which will be around 2.06, was hidden under the broad line. In addition to this, since the concentration of copper is high (around 2.6 wt%), the hyperfine lines from the nuclear spin of copper nucleus could not be resolved due to dipolar–dipolar broadening.

The sharp six lines marked by arrows from the top, have a g value of 2.002 and a hyperfine coupling constant of 95(5) G. These values are typical for a Mn(II) ion impurity in the lattice (Rao 1993). Generally one would expect a sextet for Mn(II) in polycrystalline form, because the other four electron spin transitions (for a divalent manganese ion, total spin $S = 5/2$), that are $|\pm 5/2\rangle \leftrightarrow |\pm 3/2\rangle$ and $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ have very large anisotropy and hence often difficult to observe (Blanchard and Chasteen 1976). Also, the value of the zero-field splitting parameter indicates the number of lines (Sambasiva Rao 1993). The low intensity of these six lines indicate the low percentage of manganese in the mineral sample. The broad line under the sextet may be due to copper perpendicular g value, as mentioned above. Cooling the sample to 77 K does not change the general nature of the spectrum.

Figure 3. Infrared spectrum of aurichalcite in KBr pellet at room temperature.

3.4 Vibrational spectrum

Infrared spectrum of the sample recorded in the region 600 to 4000 cm^{-1} is shown in figure 3. The four groups of bands observed around 680 , 900 , 1090 and 1400 cm^{-1} are identified as the fundamental frequencies of CO_3^{2-} namely ν_4 , ν_2 , ν_1 and ν_3 . Among these, symmetry stretching mode ν_1 alone is infrared inactive. However, in the case of carbonate compounds, ν_1 can also be observed and hence the 1090 cm^{-1} band is identified as ν_1 . The bands at 870 and 935 cm^{-1} are due to out of plane bending mode ν_2 , whereas the bands at 1360 , 1420 and 1510 cm^{-1} are due to asymmetric stretching mode ν_3 . The in-plane bending mode ν_4 is assigned to the band at 680 cm^{-1} . The bands at 1640 , 3040 cm^{-1} are identified as due to water, the H–O–H bending ν_2 and OH symmetric stretching ν_1 respectively, whereas the other band at 3420 cm^{-1} is due to asymmetric OH stretching (Reddy *et al* 1986). The band observed at 2120 cm^{-1} might be due to low energy OH valence vibrations (Langer and Raith 1974).

4. Conclusion

Optical absorption spectrum of aurichalcite indicates that the replacement of Zn by Cu is in accordance with the crystal structure reported. The crystal field and tetragonal field parameters confirm further the lowering of octahedral site to an elongated tetragonal (D_{4h}) site of Cu(II) ion in the crystal.

The EPR spectrum indicates the presence of copper (II) in a lower symmetry. The dipolar–dipolar broadening made the hyperfine lines unresolved and the second g value for Cu(II) is hidden under the Mn(II) sextet (lower field side). The EPR analysis also indicates the presence of Mn(II) in traces, which was further confirmed by X-ray scanning picture for MnK_α line on the sample. This study indicates the significance of EPR technique to measure paramagnetic impurities present in traces in natural minerals, simultaneously with another paramagnetic impurity present in higher levels. The vibrational spectrum of the minerals exhibits the fundamental frequencies of water and carbonate ion.

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