



Electronic and vibrational absorption spectra in nickelblodite

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Received 19 May 1995, accepted 30 August 1995

Abstract : The electronic absorption bands of nickelblodite at 300 K in the region 200–1200 nm are reported here. A successful interpretation of all the bands could be made to Ni(II) ion with octahedral symmetry in the crystal. Three broad and intense bands observed at 9010, 14810 and 24995 cm^{-1} are attributed to the transitions, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(D)$ and the other two bands at 13695 and 21730 cm^{-1} are assigned to the transitions ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$ and ${}^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$ respectively. The crystal field and the Racah parameters are evaluated to be $D_q = 900$, $B = 850$ and $C = 3500 \text{ cm}^{-1}$. The vibrational spectrum of nickelblodite in IR region exhibited the characteristic bands of H_2O and SO_4^{2-} . The splitting of the degenerate modes ν_3 and ν_4 and the appearance of IR inactive mode ν_1 indicate the lowering of SO_4^{2-} from ideal T_d symmetry.

Keywords : Nickelblodite, absorption spectrum, octahedral symmetry

PACS Nos. : 33 20.Ea, 33 20.Kf

An attempt has been made to study electronic and vibrational absorption spectra of the nickel rich sulfate mineral, nickelblodite, collected from Carr Boyd Rocks in Western Australia and to compare with the Ni(II) bearing complexes.

Nickelblodite, $\text{Na}_2\text{Ni}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is the nickel analogue of blodite $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Blodite (also called Ashtrakanite) has monoclinic structure with space group $P2_1/a (C_{2h})^5$ and with the cell parameters $a = 11.03$, $b = 8.14$, $c = 5.49 \text{ \AA}$ and $\beta = 100^\circ 40' [1]$. In blodite Mg(II) is in nearly regular octahedral coordination surrounded by oxygen and water molecules. Na(I) is surrounded by four sulfate oxygen atoms and two water oxygen atoms [2]. The crystal structure and chemical analysis of the mineral have been reported [3]. The unit cell parameters of nickelblodite are appreciably smaller than those of blodite due to isomorphous substitution of Mg by Ni in sulfate, generally causes contraction of the unit cell.

On the basis of ionic radii and charge alone, it is expected that Ni(II) (0.77 Å) would readily substitute for six coordinate Mg(II) (0.80 Å) in hydrous nickel magnesium silicates [4]. The Ni(II)–Mg(II) diadochy is well established for this and other classes of silicate minerals [5].

A pale green coloured nickelblodite occurs as surface coating inter-grown with morenosite. As the material does not exhibit good crystal forms, its optical absorption spectrum has been recorded in nujol mull form on Cary 2390 spectrophotometer in the wavelength region 200 to 1200 nm. The IR spectrum of the sample is also recorded on Pye Unicam SP3-300 spectrophotometer in the frequency range 600–4000 cm^{-1} .

The ground term of Ni(II) (3d8) ion is 3F . The other excited terms are 3P , 1D , 1G and 1S . When the ion is considered in an octahedral crystal field, the 3F term splits into ${}^3A_{2g}$, ${}^3T_{2g}$ and ${}^3T_{1g}$ levels. Triplet term, 3P transforms into ${}^3T_{1g}$ while 1D , 1G and 1S gives rise to ${}^1E_g(D)$, ${}^1T_{2g}(D)$, ${}^1A_{1g}(G)$, ${}^1T_{1g}(G)$, ${}^1E_g(G)$, ${}^1T_{2g}(G)$ and ${}^1A_{1g}(S)$ levels respectively.

The terms ${}^3A_{2g}(F)$, ${}^1E_g(D)$ and ${}^1A_{1g}(G)$ corresponds to the strong field electronic configuration, $t_{2g}^6 e_g^2$. The terms ${}^3T_{1g}(F)$, ${}^3T_{2g}(F)$, ${}^1T_{1g}(G)$ and ${}^1T_{2g}(D)$ to first excited electron configuration, $t_{2g}^5 e_g^3$ and the terms ${}^3T_{1g}(P)$, ${}^1T_{2g}(G)$, ${}^1E_g(G)$ and ${}^1A_{1g}(S)$ to second excited electronic configuration, $t_{2g}^4 e_g^4$. In both the weak and strong crystal fields the ${}^3A_{2g}(F)$ is the ground state according to the Hund's rule.

For Ni(II) ion, the ground state term is 3F . Another term with the same multiplicity is 3P . This leads to the three spin allowed transitions in the crystal field. They are ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ arising from the ground state term 3F and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ from the excited term 3P . Weak and narrow spin forbidden bands are also expected as a result of transitions

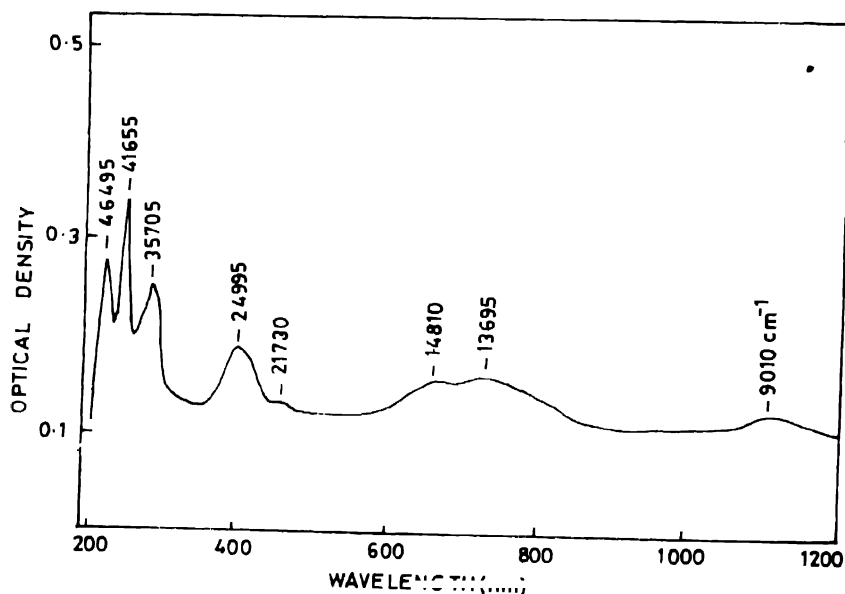


Figure 1. Optical absorption spectrum of nickelblodite in the region 200–1200 nm

from ${}^3A_{2g}$ to ${}^1E_g(D)$ and ${}^1A_{1g}(G)$ whereas the broad bands with weak intensity arise from the transitions into other singlet levels ${}^1T_{2g}(D)$ and ${}^1T_{1g}(G)$ occurring in the ultraviolet region.

Optical absorption spectrum is shown in Figure 1. The bands are expected to nickel ion due to higher concentration of nickel. The spectrum consists of three broad and intense bands at 9010, 14810 and 24995 cm^{-1} . The other two bands of less intensity are observed at 13695 and 21730 cm^{-1} . All these band features are characteristic of Ni(II) in octahedral symmetry.

The three broad and intense bands observed in the present case at 9010, 14810 and 24995 cm^{-1} are attributed to the transitions ${}^3A_{2g}(F)$ to ${}^3T_{2g}(F)$, ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ respectively. The energy expressions for Ni(II) in octahedral symmetry are given as follows [6].

$$\nu_1 : {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \Rightarrow 15Dq + 7.5B + 6B(1 + \Delta)^{1/2}$$

$$\nu_2 : {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \Rightarrow 15Dq + 7.5B - 6B(1 + \Delta)^{1/2}$$

$$\nu_3 : {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \Rightarrow 10Dq$$

where $\Delta = (10Dq - 9B)/12B$; is of the order of 0.01 since Dq and B are of similar magnitudes. If we neglect the value of Δ , the equation reduces as $\nu_1 - \nu_2 = 12B$.

Using these expressions, approximate values of Dq and B are calculated as $Dq = 900$ and $B = 850 \text{ cm}^{-1}$. With the help of Tanabe-Sugano diagram, the assignments of the other bands are made. The energy matrices for d^8 configuration [7] are solved for different values of Dq , B and C . The values which gave good fit to the observed band energies are $Dq = 900$, $B = 850$ and $C = 3500 \text{ cm}^{-1}$. The observed and calculated energies of the bands for

Table 1. Observed and calculated band positions and their assignments of Ni(II) in nickelblodite $B = 850$, $Dq = 900$ and $C = 3500 \text{ cm}^{-1}$.

Transitions	Observed band positions		Calculated wavenumber (cm^{-1})
	Wavelength (nm)	Wavenumber (cm^{-1})	
from ${}^3A_{2g}(F)$			
${}^3A_{2g}(F)$	1110	9010	9000
${}^1E_g(D)$	730	13695	13350
${}^3T_{1g}(F)$	670	14810	14730
${}^1T_{2g}(D)$	460	21730	21986
${}^3T_{1g}(P)$	400	24995	25019

Ni(II) in nickelblodite are compared and are presented in Table 1. The three higher energy bands observed at 35705, 41655 and 46495 cm^{-1} are characteristic of charge transfer bands. These bands might be due to electron transfer between the metal ion and the surrounding oxygen ligands [8,9].

The infrared spectrum of nickelblodite is shown in Figure 2. It exhibits the bands due to vibrations of H_2O and (SO_4^{2-}) . The assignments of bands are given in Table 2. In the present investigation the broad band observed at 1670 cm^{-1} is attributed to the asymmetric OH stretch (ν_2) vibrational mode and the other two broad bands at 3160 and 3400 cm^{-1} are attributed to symmetric O-H stretch (ν_1) and H-O-H bend (ν_3) vibrational modes of water

molecule respectively. The other two bands at 730 and 860 cm^{-1} might be due to twisting (ν_t) and rocking (ν_r) vibrational modes of water molecule [10]. Two bands observed at 1100

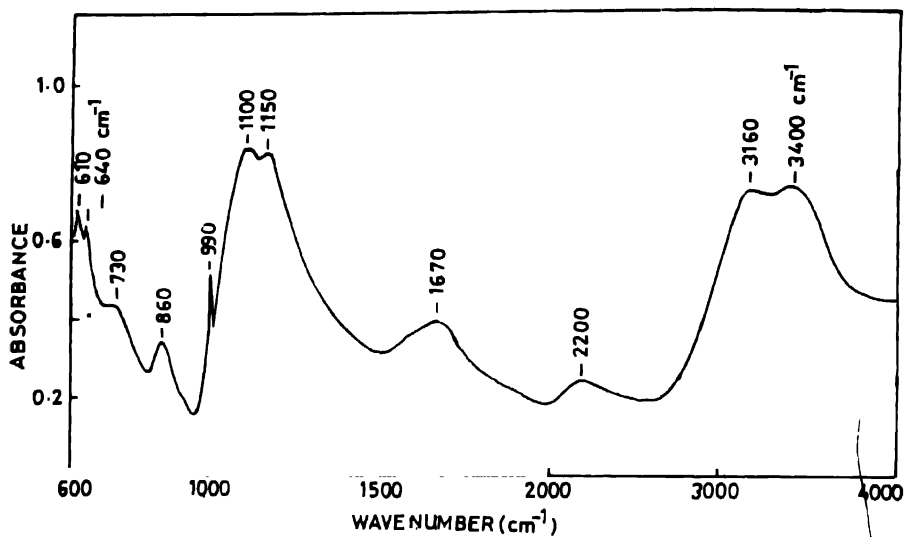


Figure 2. Infrared spectrum of nickelblodite in the region 600–4000 cm^{-1}

and 1150 cm^{-1} are attributed to triply degenerate ν_3 mode, the sharp band at 990 cm^{-1} is attributed to nondegenerate ν_1 vibrational mode of SO_4^{2-} ion. The other two bands at 610 and 640 cm^{-1} are attributed to triply degenerate ν_4 vibrational mode. The weak and broad band at 2200 cm^{-1} might be due to the overtone ($2\nu_3$) of the ν_3 fundamental mode of SO_4^{2-} .

Table 2. Observed vibrational frequencies with their assignments in nickelblodite.

Observed band positions (cm^{-1})	Assignments
610	ν_4 (SO_4^{2-})
640	
730	ν_t (twisting)
800	ν_r (rocking)
990	ν_1 (SO_4^{2-})
1100	
1150	ν_3 (SO_4^{2-})
1670	ν_2 (H_2O)
2200	$2\nu_3$ (SO_4^{2-})
3160	ν_1 (H_2O)
3400	ν_3 (H_2O)

The optical absorption spectrum of Ni(II) ion in nickelblodite exhibits features similar to those observed for O_h symmetry with oxygen and 'OH' ligands [11,12]. The crystal field and inter-electronic repulsion parameters (Dq and B) calculated for

nickelblodite are compared with the other nickel bearing minerals and doped complexes in octahedral symmetry and are presented in Table 3, shows that Dq and B values are close to those reported earlier. It confirms the octahedral symmetry for Ni(II) ion in nickelblodite. The lowering of B value (850 cm^{-1}) from that of free ion (1080 cm^{-1}) in nickelblodite indicates the decrease of (20%) in the degree of ionic nature of the metal oxygen bond.

Table 3. Crystal field parameters, B and Dq of Ni(II) in octahedral field in different nickel bearing samples.

Sample	B (cm^{-1})	Dq (cm^{-1})	References
MgO	890	815	Pappalardo <i>et al</i> [13]
Olivine	900	870	Wood [6]
	882	768	Wood [6]
Diopside	881	840	White [11]
Clinoenstatite	1030	690	White [11]
Garnierite	947	910	Faye [14]
Zaratite	899	820	Sarma <i>et al</i> [15]
Takovite	940	910	Sarma <i>et al</i> [15]
Annabergite	833	850	Sarma <i>et al</i> [15]
$\text{Rh}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	890	920	Sivaprasad <i>et al</i> [16]
$\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	944	941	Sviridov and Sviridov [17]
$\text{KMgClSO}_4 \cdot 3\text{H}_2\text{O}$	905	940	Rao <i>et al</i> [18]
Nickelblodite	850	900	Present work

The vibrational spectrum of nickelblodite in IR region exhibited the characteristic bands of H_2O and SO_4^{2-} . The splitting of the degenerate modes, ν_3 and ν_4 and the appearance of IR inactive mode ν_1 indicate the lowering of SO_4^{2-} from ideal T_d symmetry.

Acknowledgments

The authors wish to express their thanks to Dr. E H Nickel, Division of Mineralogy, CSIRO, Wembley, Australia for generously donated nickelblodite mineral and the University Grants Commission, New Delhi for financial assistance during the course of investigation.

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