Chemical and electronic spectral studies of ullmannite \((\text{Ni}_4 \text{Sb}_4 \text{S}_4)\)

S N Reddy*, R V S S N Ravikumar*, B J Reddy* & Y P Reddy*  
* Spectroscopy Laboratories, Department of Physics, SV University College, Tirupati 517 502, India  
* Department of Physics, SV Degree College, Cuddapah 516 003, India  
Received 25 February 2000; accepted 18 September 2000

The streak grayish black coloured and almost opaque mineral ullmannite belonging to France received from Musée De Minéralogie, Ecole Natle, Supre Des Mines, Paris, France, has been investigated by atomic absorption spectroscopy (AAS) and optical absorption spectroscopy. The AAS analysis shows that the mineral contains the transition elements nickel (1.14%), iron (0.29%), cobalt (0.073%), copper (0.013%), and manganese (0.0031%). The bands observed at 25967, 24993, 21546, 14966, 12252 and 861 8 cm\(^{-1}\) in the optical absorption spectrum recorded at room temperature are assigned to different transitions of Ni(II) ion. The following crystal field parameters are evaluated: \(D_q = 860 \text{ cm}^{-1}\), \(B = 840 \text{ cm}^{-1}\), and \(C = 3350 \text{ cm}^{-1}\), respectively. These values confirm the octahedral symmetry for Ni(II) in the mineral ullmannite.

Ullmannite \(\text{Ni}_4 \text{Sb}_4 \text{S}_4\) has a pyrite type crystal structure\(^1\). It is essentially a sulfide-antimonide of nickel with cobalt and small amounts of iron substituting for nickel in addition to arsenic and bismuth substituting for antimony\(^2\). It is cubic with space group \(P2_13\). In ullmannite, the four metal atoms (Ni) occupy similar atomic positions\(^3\). Of the eight non metal atoms (4Sb + 4S), the four Sb atoms are oriented in one set of four atomic positions on the three fold axes and the four S atoms are ordered in the other set of four atomic positions on the three fold axes. The order and reduction in symmetry from the three fold axes. The lower symmetry of cubic space group \(P2_13\) is shown by the absence of the 010 reflection and the presence of the 011 reflection\(^4\). The cubic unit cell dimensions are equal and lie between 5.88 and 5.93 Å. The present studies are aimed at identifying the presence of transition metal ions and to confirm their coordination.

**Experimental Procedure**

The streak grayish black coloured and almost opaque mineral ullmannite is powdered nicely, mixed with nujol and its paste prepared. A thin layer of the paste is taken between two thin quartz plates and its optical absorption spectrum recorded in the region 350-1200 nm on Varian Cary-2390 spectrophotometer.

**Theory**

The Ni(II) ion with \(d^8\) configuration gives rise to \(^3F, ^3P, ^1D, ^1G\) and \(S\) terms of which \(^1F\) is the ground state. In a cubic crystal field, these terms transform as follows:

\[
\begin{align*}
^3F &\rightarrow ^3T_{1g} (F) + ^3T_{2g} (F) + ^3A_{2g} (F) \\
^3P &\rightarrow ^3T_{1g} (P) \\
^1D &\rightarrow ^1T_{2g} (D) + ^1E_g (D) \\
^1G &\rightarrow ^1T_{1g} (G) + ^1T_{2g} (G) + ^1E_g (G) + ^1A_{1g} (G) \\
^1S &\rightarrow ^1A_{1g} (S)
\end{align*}
\]

Of these crystal field terms, \(^3A_{2g}\) (F) is the ground state. In octahedral symmetry, three spin allowed transitions expected for Ni (II) ion are:

\[
\begin{align*}
^3A_{2g} (F) &\rightarrow ^3T_{1g} (P) \\
^3A_{2g} (F) &\rightarrow ^3T_{1g} (F) \\
^3A_{2g} (F) &\rightarrow ^3T_{2g} (F)
\end{align*}
\]

These transitions are governed by the approximate linear equations\(^5\), as given by:

\[
\begin{align*}
^3A_{2g} (F) &\rightarrow ^3T_{1g} (P) \Rightarrow 15 D_q + 13.5 B = v_1 \\
^3A_{2g} (F) &\rightarrow ^3T_{1g} (F) \Rightarrow 15 D_q + 1.5 B = v_2 \\
^3A_{2g} (F) &\rightarrow ^3T_{2g} (F) \Rightarrow 10 D_q = v_3
\end{align*}
\]

In addition to the above, some weak spin forbidden bands are also possible as a result of these transitions.

**Results and Discussion**

**Chemical composition**

The chemical analysis of the mineral ullmannite is carried out by AAS employing Perkins Elmer Model 2380 spectrophotometer with monitorch. The analysis shows that the mineral contains the transition elements having concentration: nickel (1.14%), iron (0.29%), cobalt (0.073%), copper (0.013%) and manganese (0.0031%). Of these elements, nickel
appears to be in considerable quantity and the others in traces.

Optical absorption spectrum

The optical absorption spectrum of ullmannite mineral recorded at room temperature in UV–VIS-NIR region is shown in Fig. 1. Three broad bands at 24993 cm$^{-1}$ (400 nm), 14966 cm$^{-1}$ (668 nm) and 8618 cm$^{-1}$ (1160 nm) and three weak bands at 25967 cm$^{-1}$ (385 nm), 21546 cm$^{-1}$ (464 nm) and 12252 cm$^{-1}$ (816 nm) are observed in the spectrum. All these bands are the characteristic of Ni(II) ion in octahedral symmetry. The broad bands at 24993 cm$^{-1}$ ($v_1$), 14966 cm$^{-1}$ ($v_2$) and 8618 cm$^{-1}$ ($v_3$) are assigned to the spin allowed transitions from the ground state $^3A_{2g}$ (F) to $^3T_{1g}$ (P), $^3T_{1g}$ (F) and $^3T_{2g}$ (F) states, respectively. The other weak bands are assigned to the corresponding spin forbidden transitions with the help of Tanabe-Sugano diagram. The approximate values of $D_4$ and $B$ are calculated from the linear equations as $D_4=862$ cm$^{-1}$ and $B=836$ cm$^{-1}$. Based on these assignments, the energy matrices for $A_1$ configuration are solved for different values of $D_4$, $B$ and $C$ around the approximate values evaluated from the linear equations. The following values of $D_4=860$ cm$^{-1}$, $B=840$ cm$^{-1}$ and $C=3350$ cm$^{-1}$ give good fit of the experimental and calculated values of band heads. The observed and the calculated band energies and their assignments are depicted in Table I.

![Fig. 1—Room temperature optical absorption spectrum of the ullmannite mineral](image)

### Table I — Observed and calculated band energies with their assignments

<table>
<thead>
<tr>
<th>Transition from the ground state</th>
<th>Observed band positions</th>
<th>Calculated band positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3T_{1g}(G)$</td>
<td>385</td>
<td>25967</td>
</tr>
<tr>
<td>$^3T_{1g}(P)$</td>
<td>400</td>
<td>24993</td>
</tr>
<tr>
<td>$^3T_{2g}(D)$</td>
<td>464</td>
<td>21546</td>
</tr>
<tr>
<td>$^3T_{1g}(F)$</td>
<td>668</td>
<td>14966</td>
</tr>
<tr>
<td>$^3T_{2g}(F)$</td>
<td>816</td>
<td>12252</td>
</tr>
<tr>
<td>$^3T_{2g}(F)$</td>
<td>1160</td>
<td>8618</td>
</tr>
</tbody>
</table>

### Conclusions

The optical absorption spectrum indicates the presence of nickel in octahedral symmetry. Spectral features of no other transition metal ion are observed. This supports the relatively higher concentration of nickel in the AAS investigation.

### Acknowledgements

Sincere thanks to Prof. C Guillemi, Professor of Mineralogy, Musee De Mineralogie, Ecole Natle, Supre Des Mines, Paris, France, for supplying the mineral ullmannite. One of the authors, S N Reddy is grateful to Shri A G Reddy, Principal, SV Degree College, Cuddapah, for granting permission to continue the research programme at SV University, Tirupati.

### References

1. Randell L S, Am Mineral, 10 (1925) 281.