Infrared Spectroscopy and X-Ray Diffractometry Assessment of Order-Disorder in Oxide Minerals (Mn/Fe)(Nb/Ta)$_2$O$_6$

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Dedicated in memoriam to Professor Jacobo Gómez-Lara

Abstract. The degree of cation order of four columbite-tantalite from San Luis Range (Argentina) was evaluated from X-ray diffractometry and FTIR spectroscopy. Data were compared with those obtained by Mössbauer spectrometry. Based on structural evidences, a general assignment for the Nb/Ta-O$_6$ and Fe/Mn-O$_6$ octahedra internal vibrations is proposed.

Key Words: columbite-tantalite, FTIR spectroscopy, X-ray diffractometry, Mössbauer.

Resumen. Se evaluó el grado de orden catiónico de cuatro columbita-tantalitas de las Sierras de San Luis (Argentina) a partir de difractometría de Rayos X y espectroscopía FTIR. Los resultados fueron comparados con los obtenidos por espectroscopía Mössbauer. Se propone una asignación general para los modos internos de vibración de los octaedros Nb/Ta-O$_6$ y Fe/Mn-O$_6$ en base a evidencias estructurales.

Palabras clave: columbita-tantalitas, difractometría de Rayos X, espectroscopía FTIR, Mössbauer.

Introduction

Columbite-tantalite group minerals are the main source of niobium and tantalum oxides (Nb$_2$O$_5$ and Ta$_2$O$_5$) which find important applications in electronic and optical industries [1-3]. Columbite-tantalite has the general formula AB$_2$O$_6$ and shows a wide compositional range with the A position mostly occupied by Fe(II), Mn(II) and to a lesser extent by Mg(II), and the B position mainly occupied by Nb(V), Ta(V) and subordinately by Ti(IV), W(VI) and Sn(IV) [4]. The end members of these orthorhombic minerals are ferrocolumbite (FeNb$_2$O$_6$), manganocolumbite (MnNb$_2$O$_6$), manganotantalite (MnTa$_2$O$_6$) and magnocolumbite (MgNb$_2$O$_6$), with their crystal structure related to that of brookite (TiO$_2$) or α-PbO$_2$. The atoms at the A and B sites in the crystal structure of columbite are coordinated to six oxygens which form distorted octahedra. These octahedra are stacked along the crystallographic a-axis in a sequence of ABBABB layers, in which A-type octahedra share corners while B-type octahedra share edges. Although the 3d transition metals occupy mainly the A site, there exists a considerable degree of cation occupation disorder between sites A and B; i.e. Fe, Mn, Nb or Ta are found to occupy both sites A and B in different proportions. Different cationic occupancy of the sites from one end-member to another leads to changes of the unit cell dimensions and to distortions in the oxygen octahedra.

Disorder evaluation of these oxide minerals is important because it has considerable effects on the magnetic properties [5]. In general, the columbite-tantalite cation order-disorder has been estimated from X-ray powder diffraction data (XRPD) or, recently by Mössbauer spectroscopy (MS). Other criteria have been established to estimate the degree of cation order by FTIR.

Evaluating X-ray powder diffraction data (XRPD), Komkov [6] found that the a/c ratio of these minerals significantly varies with changing Mn/Fe ratio, where a and c are the lattice parameters. Cerný and Erçit [7] observed that in columbite-tantalite with variable composition the degree of order increases with higher Mn-content. Erçit [8] derived an empirical equation to estimate the degree of cation order in columbite: % order (± 5%) = 1727 – 941.6(c – 0.2329a).

Mössbauer spectroscopy of $^{57}$Fe has been successfully applied in mineral studies to find the oxidation state and iron occupation sites [9].

Other criteria have been established to estimate the degree of cation order by FTIR. A sharp band for $\nu_3$ vibrational mode
(Nb/Ta-O) on FTIR spectra indicate a high degree of order in the lattice [10].

Four columbite-tantalite samples from different pegmatite bodies from the San Luis Range (Argentina) have been analyzed by X-ray powder diffractometry (XRPD) and infrared spectroscopy (FTIR). The X-ray powder diagrams were attained to characterize the structural state and the degree of cation order. The columbite-tantalite FTIR spectra are reported here for the first time. The infrared absorption bands could be assigned to the internal vibrations of the Nb/Ta-O and Fe/Mn-O bonds. Furthermore, it was possible to estimate a comparative degree of order. The results are consistent with those obtained from Mössbauer spectra.

Results and Discussion

The XRPD patterns were indexed to the Pbcn (D\textsubscript{14}h, Nº 60), space group, with Z = 4. A modified version of the program PIRUM [11] was used for determining the unit-cell parameters and the cation order was calculated following Ercit’s formula [8] (see Table 1). Our samples have a degree of order between 84% (sample M\textsubscript{1}) and 41% (sample M\textsubscript{4}). The high degree of order observed in sample M\textsubscript{1} (manganocolumbite) is in good agreement with the high percentage of Mn present in the mineral, as proposed by Cerny \textit{et al.} [6].

The FTIR spectra and band assignments are displayed in Fig. 1 and Table II, respectively. In spite of the broad absorption bands and low definition it was possible to sort out the bands corresponding to Ta/Nb-O and Mn/Fe-O modes.

By comparison with the IR-absorption bands of synthetic similar species [10, 12-15] most important vibrational modes could be identified. Some of these synthetic species correspond to LiNbO\textsubscript{3} and H-Nb\textsubscript{2}O\textsubscript{5} crystals which form NbO\textsubscript{6} octahedra. The essential difference between both compounds is that in LiNbO\textsubscript{3} the NbO\textsubscript{6} octahedra share only corners while in H-NbO\textsubscript{3} the NbO\textsubscript{6} octahedra share both edges and corners, as in columbite-tantalite with disorder between sites A and B [14,15]. Our assignment is in good agreement with H-Nb\textsubscript{2}O\textsubscript{5}.

Based on these structural evidences the bands at around 700 and 630 cm\textsuperscript{-1} have been assigned to the (3 mode in the corner-shared NbO\textsubscript{6} octahedron and the additional two bands at around 830 and 500 cm\textsuperscript{-1} are attributed to the edge-shared NbO\textsubscript{6} octahedron. The sharper band (sample M\textsubscript{1}, Fig. 1) indicates a higher degree of order of the crystal lattice and is consistent with the high structural order (84%) calculated from XRPD data.

The bands at 600-500 cm\textsuperscript{-1} correspond to the ν\textsubscript{3} and ν\textsubscript{4} vibrational modes of the Fe/MnO\textsubscript{6} octahedra. The expected splitting by the symmetry lowering effects in the lattice in relation to the point group of the octahedral species, is not observed in our spectrum. Besides, there are no significant couplings between the octahedra vibrational modes in con-

<table>
<thead>
<tr>
<th>Sample</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>V (Å\textsuperscript{3})</th>
<th>Cationic % order ± 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>M\textsubscript{1}</td>
<td>14.348 ± 0.006</td>
<td>5.759 ± 0.002</td>
<td>5.086 ± 0.002</td>
<td>420.30</td>
<td>84</td>
</tr>
<tr>
<td>M\textsubscript{2}</td>
<td>14.329 ± 0.004</td>
<td>5.746 ± 0.001</td>
<td>5.115 ± 0.001</td>
<td>421.15</td>
<td>53</td>
</tr>
<tr>
<td>M\textsubscript{3}</td>
<td>14.338 ± 0.005</td>
<td>5.750 ± 0.001</td>
<td>5.118 ± 0.004</td>
<td>420.30</td>
<td>52</td>
</tr>
<tr>
<td>M\textsubscript{4}</td>
<td>14.324 ± 0.004</td>
<td>5.755 ± 0.001</td>
<td>5.127 ± 0.001</td>
<td>422.62</td>
<td>41</td>
</tr>
</tbody>
</table>
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Conclusions

X-ray and infrared spectroscopy are powerful methods to identify and characterize the structural state of columbite-tantalite in a simple and rapid way. The results of both methods are coherent and indicative for the degree of order of the crystal structure (cationic distribution and distortion). Our results also concur with the degree of order obtained by the interpretation of Mössbauer spectra.

Experimental

The XRPD patterns were obtained in a Rigaku D-MAX III diffractometer using Ni-filtered CuKα radiation (λ = 1.5418 Å) and a scan speed of 2° 2θ/min. NaCl was used as an internal calibration standard. FTIR spectra in the 4000-400 cm⁻¹ range were recorded with a Bruker IFS25 spectrophotometer, using the KBr pellet technique. The spectral resolution is better than 2 cm⁻¹ between 4000 and 2000 cm⁻¹ and better than 1 cm⁻¹ in the spectral range under 2000 cm⁻¹.

Acknowledgements

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Table 2. Band assignments for the FTIR spectra of columbite-tantalites.

<table>
<thead>
<tr>
<th>Mode</th>
<th>M₁</th>
<th>M₂</th>
<th>M₃</th>
<th>M₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequencies in cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν (Nb/Ta-O) (edge)</td>
<td>838</td>
<td>827</td>
<td>832</td>
<td></td>
</tr>
<tr>
<td>709 (s)</td>
<td>700</td>
<td>707</td>
<td>709</td>
<td></td>
</tr>
<tr>
<td>v₁ (Nb/Ta-O) (corner)</td>
<td>628</td>
<td>650</td>
<td>605</td>
<td></td>
</tr>
<tr>
<td>632(s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ν₂ (Fe/Mn-O)</td>
<td>571</td>
<td>571</td>
<td>574</td>
<td></td>
</tr>
<tr>
<td>ν₁ (Fe/Mn-O) + ν (Nb/Ta-O) (edge)</td>
<td>505</td>
<td>503</td>
<td>500</td>
<td>500</td>
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<tr>
<td>bending and lattice modes</td>
<td>455</td>
<td>?</td>
<td>?</td>
<td>460</td>
</tr>
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</table>

s: strong  m: medium  sh: shoulder  w: wide.
References


