

Investigación

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

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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-O₆ and Fe/Mn-O₆ 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-O₆ y Fe/Mn-O₆ 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 (Nb₂O₅ and Ta₂O₅) which find important applications in electronic and optical industries [1-3]. Columbite-tantalite has the general formula AB₂O₆ 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 (FeNb₂O₆), manganocolumbite (MnNb₂O₆), manganotantalite (MnTa₂O₆) and magnocolumbite (MgNb₂O₆), with their crystal structure related to that of brookite (TiO₂) or α -PbO₂. 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 Ercit [7] observed that in columbite-tantalite with variable composition the degree of order increases with higher Mn-content. Ercit [8] derived an empirical equation to estimate the degree of cation order in columbite: % order ($\pm 5\%$) = 1727 - 941.6(c - 0.2329a).

Mössbauer spectroscopy of ⁵⁷Fe 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 v₃ 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_{2h}^{14} , N° 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_1) and 41% (sample M_4). The high degree of order observed in sample M_1 (manganocolumbite) is in good agreement with the high percentage of Mn present in the mineral, as proposed by Cerny *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 $LiNbO_3$ and $H-Nb_2O_5$ crystals which form NbO_6 octahedra. The essential difference between both compounds is that in $LiNbO_3$ the NbO_6 octahedra share only corners while in $H-Nb_2O_5$ the NbO_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 $H-Nb_2O_5$.

Based on these structural evidences the bands at around 700 and 630 cm^{-1} have been assigned to the (3 mode in the corner-shared NbO_6 octahedron and the additional two bands at around 830 and 500 cm^{-1} are attributed to the edge-shared NbO_6 octahedron. The sharper band (sample M_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.

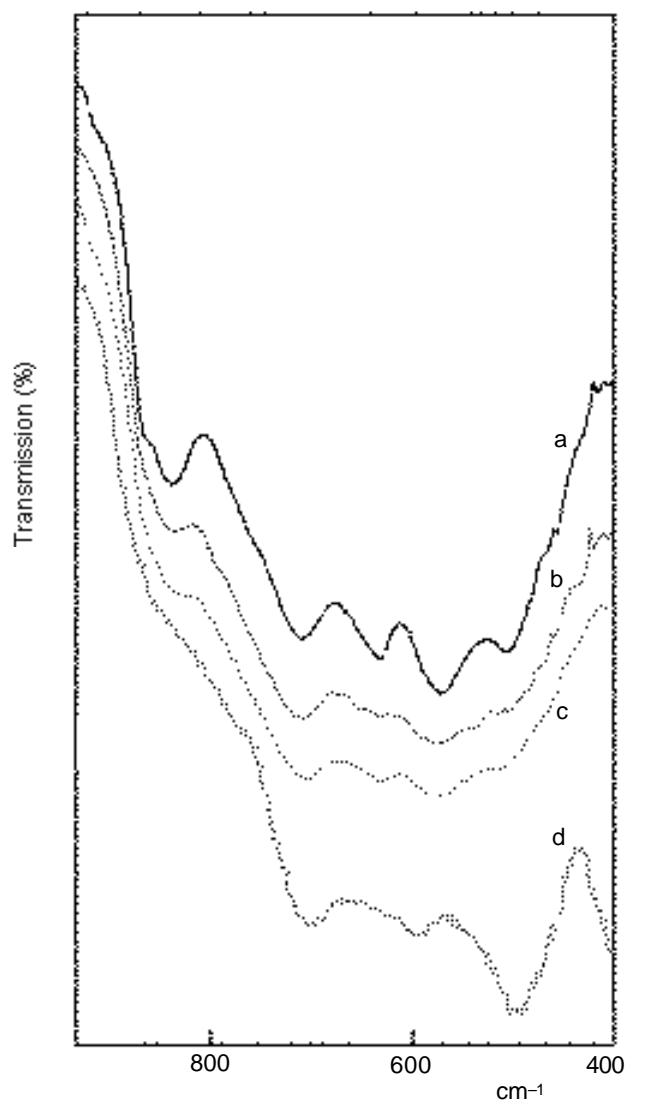


Fig. 1. Columbite-tantalite FTIR spectra: a) sample M_1 , b) sample M_2 , c) sample M_3 , d) sample M_4 .

The bands at 600-500 cm^{-1} correspond to the v_3 and v_4 vibrational modes of the Fe/MnO_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 1. Unit cell parameters (a, b, c), volume (V) and degree of cation order (% order) (XRPD data) of columbite-tantalite samples.

Sample	a(Å)	b(Å)	c(Å)	V (Å) ³	Cationic % order ± 5%
M_1	14.348 ± 0.006	5.759 ± 0.002	5.086 ± 0.002	420.30	84
M_2	14.329 ± 0.004	5.746 ± 0.001	5.115 ± 0.001	421.15	53
M_3	14.338 ± 0.005	5.750 ± 0.001	5.118 ± 0.004	420.30	52
M_4	14.324 ± 0.004	5.755 ± 0.001	5.127 ± 0.001	422.62	41

densed layers A and B such as in other species with large cations [16].

In the low frequency region (500-400 cm⁻¹), the vibrational behavior strongly depends on the nature of the divalent cation and is mainly influenced by Fe (II) and Mn (II) in this case. The absorption bands in this part of the spectrum are of complex origin and correspond to contributions of bending and lattice modes.

A better definition of the spectra was not attained at lower temperature. Spectra were recorded for sample M₃ (Fig. 2) at room temperature and at 80 K, using a liquid nitrogen cooled cell (RIIC-Beckman). The expected spectral splitting at low temperature normally caused by the symmetry lowering effects in the crystal lattice, i.e. in relation to the point group of the octahedra, has not been observed.

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 CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) 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.

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

Mode	M ₁	M ₂	M ₃	M ₄
Frequencies in cm ⁻¹				
v (Nb/Ta-O) (edge)	838(m)	827(m)	832(m)	
709(s)	700(w)	707(w)	709(w)	
v ₃ (Nb/Ta-O) (corner)				
632(s)	628(sh)	650(sh)	605(w)	
v ₃ (Fe/Mn-O)	571(w)	571(w)	574(w)	?
v ₄ (Fe/Mn-O) + v (Nb/Ta-O) (edge)	505(s)	503(w)	500(sh)	500(w)
bending and lattice modes	455(sh)	?	?	460(sh)

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

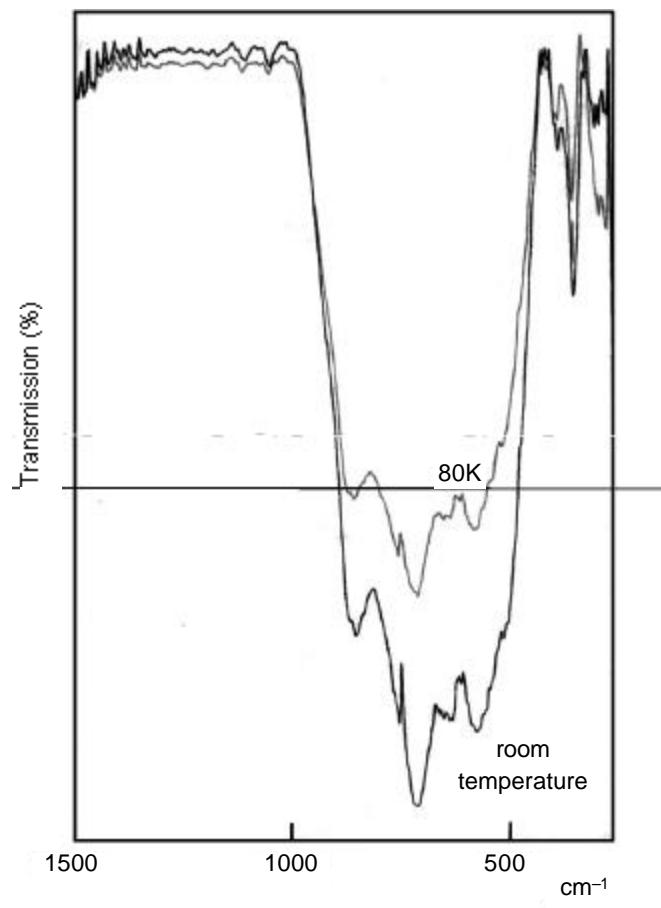


Fig. 2. Columbite-tantalite FTIR spectra at room temperature and 80 K: sample M₃.

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