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Vibrational Spectra of Yttrium Niobate and Tantalate

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Infrared and Raman spectra of $YNbO_4$ and $YTaO_4$ are reported. These spectra show the internal vibrational modes of the NbO_4^{3-} and TaO_4^{3-} tetrahedra which occur seldom in solids. The ν_3 mode is situated at low wavenumbers relative to ν_1. This corresponds to low values of the force constants in the OVFF model.

Introduction

The vibrational spectra of scheelites like $CaWO_4$ have been studied intensively (*1*, *2*). Up till now the vibrational spectra of $YNbO_4$ and $YTaO_4$ have not been reported as far as the author is aware. These compounds have fergusonite structure which is a slight distortion of the scheelite structure (*3*). For this reason it seemed interesting to investigate their infrared and Raman spectra. Moreover these compounds are exceptional examples of Nb^{5+} and Ta^{5+} in tetrahedral coordination. Since we studied the vibrational spectra of the octahedral niobate group extensively (*4*), it was also of interest to investigate the spectra of the tetrahedral niobate group.

Experimental Methods

Samples were prepared by usual ceramic techniques and checked by X-ray powder diffraction using a Philips diffractometer (Cu*Kα* radiation). They appeared to be single phase. Vibrational spectra were measured as described before (*5*). The measurements were carried out at room temperature.

Results

The experimental results are collected in Table I and Fig. 1.

Discussion

The compounds $YNbO_4$ and $YTaO_4$ have fergusonite structure with I2-C_2^3 space group symmetry and site symmetry C_2 for the molecular NbO_4 and TaO_4 group. There are two of these groups per primitive cell. In our analysis we will only consider the internal vibrational modes of the molecular groups. Table I gives the correlation diagram for a single group. Since there are two groups per primitive cell both with C_2 site symmetry and the space group is C_2^3, we should expect twice as many bands as indicated in the second column of Table I in the Raman as well as in the infrared spectra.

Although this expectation is not completely substantiated, the combination of Raman and infrared data allows the assignment presented in

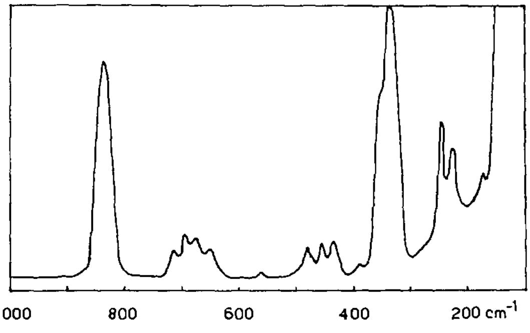

FIG. 1. Raman spectrum of $YNbO_4$.

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TABLE I

CORRELATION DIAGRAM AND RAMAN AND INFRARED SPECTRA OF THE MO$_4$ GROUP IN FERGUSONITE[a]

Free NbO$_4$ ion (T_d)	NbO$_4$ ion in YNbO$_4$ (C_2)	Experimental (values in cm^{-1})			
		YNbO$_4$		YTaO$_4$	
		Raman	Infrared	Raman	Infrared
ν_1: A_1(R)	A	832(s)	—	825(s)	—
		—	800(w)	—	810(m)
ν_3: T_2(R, ir)	$A + 2B$	715(w)	720(w)	720(w)	720(w)
		695(w)	—	705(m)	—
		675(w)	—	670(m)	—
		650(w)	655(s)	655(w)	660(s)
		—	590(w)	—	605(s)
		560(w)	540(w)	—	550(w)
ν_4: T_2(R, ir)	$A + 2B$	480(w)	470(m)	480(w)	470(m)
		455(w)	—	450(w)	—
		435(w)	—	—	415(m)
		—	400(m)	—	390(m)
		385(w)	385(m)	375(w)	380(m)
		—	360(w)	—	360(w)
ν_2: E(R)	2A	350(s)	—	345(s)	—
		340(s)	330(w)	320(s)	325(m)
External modes			280(w)		270(w)
		245(m)	245(s)		245(s)
		225(m)	220(m)	215(s)	220(s)
		170(w)		120(m)	

[a] (R) means Raman-active, (ir) infrared-active. For C_2 there are no selection rules; (s) means strong, (m) medium and (w) weak.

Table I. Frequencies below 300 cm^{-1} are assigned to external vibrations. The assignment of ν_2 is based on intensity considerations (under T_d symmetry ν_2 is only allowed in the Raman spectrum). Only for ν_2 we have not enough experimental frequencies (two in stead of four). The fact that we observed in general a too low number of Raman as well as infrared bands is probably due to the fact that the space group symmetry deviates only slightly from a much higher space group symmetry, viz, C_{4h}. This is due to the fact that fergusonite ($C_2{}^3$) is a slightly distorted form of scheelite (C_{4h}^6). As a consequence the splitting of certain bands, degenerate under C_{4h} symmetry, will be small and the intensity of bands, forbidden under C_{4h} symmetry, will be low.

From the experimental values it is now possible to deduce a value for the frequencies of the NbO$_4$ tetrahedral modes, if there would be no interaction or lowering of T_d symmetry. These values are ν_1: 816 cm^{-1}, ν_3: 650 cm^{-1}, ν_4: 420 cm^{-1}, ν_2: 340 cm^{-1}. A comparison with the analogous values for electronically similar groups reveals that the value of ν_3 (asymmetrical stretching) is extremely low for the NbO$_4^{3-}$ and TaO$_4^{3-}$ group in fergusonite in comparison with the values of ν_1 (see Table II). This is typical for the oxide tetrahedron, because ν_3 lies at even higher wave numbers than ν_1 in the case of NbS$_4^{3-}$ and NbSe$_4^{3-}$ tetrahedra (*7*).

For the octahedral niobate group such a deviation from a general pattern does not occur since the frequencies of the vibrational modes are about equal for niobate and tungstate. As an example we give the following data for two

TABLE II

INTERNAL MODES OF SOME MO_4 TETRAHEDRA IN THE T_d APPROXIMATION[a]

	NbO_4 in $YNbO_4$[b]	MoO_4 in $CaMoO_4$[c]	VO_4 solution[d]
ν_1	816	885	824
ν_3	650	803	790
ν_4	420	337	340
ν_2	~340	374	340

[a] All values in cm^{-1}.

[b] Present work.

[c] Ref. (*2*).

[d] Ref. (*6*).

ordered perovskites: Ba_2MgWO_6 ν_1: 818 and ν_3: 620 cm^{-1}, $SrLaMgNbO_6$ ν_1: 790 and ν_3: 619 cm^{-1} (*8*).

A simple force field calculation also yields that the niobate tetrahedron is exceptional. The OVFF constants are k_1 (bond stretching), k_α (angle bending) and A and B/R (interaction between nonbonded atoms). Such a calculation has been carried out by Krebs and Müller (*6*) for a number of tetrahedral anions that are isoelectronic with the niobate tetrahedron. Their values for A and B/R do not differ strongly from the values we find for NbO_4^{3-} (viz, $A = 0.45$ and $B/R = 0.0$). The values of k_1 and k_α, however, are much lower for NbO_4^{3-} (2.6 and 0.2 mdyn/Å, respectively) than for VO_4^{3-} (3.55 and 0.43 mdyn/Å, respectively), MoO_4^{2-} (4.41 and 0.72 mdyn/Å) and WO_4^{2-} (4.77 and 0.52 mdyn/Å). Although our values are certainly not very reliable, it is clear that they are relatively low.

This seems to be connected with the relatively long Nb–O distance. The average Nb–O distance in $YNbO_4$ amounts to 1.90 Å (*3*). The V–O distance in several lanthanide vanadates is 1.72 Å (*9*), the W–O distance in $CaWO_4$ 1.79 Å (*10*). In fact the Nb^{5+} ion is a little too large to fit into an oxygen-anion tetrahedron which is probably the reason that the niobate tetrahedron occurs very seldom.

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