VIBRATIONAL SPECTRA OF TELLURIUM TRIOXIDE AND DITELLURYL SULFATE

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Dedicated to Prof. Dr. S. Škramovský on the occasion of his sevently-fifth birthday.

Infrared and Raman spectra of crystalline tellurium trioxide, β-TeO_3, and ditelluryl sulfate, $(Te_2O_3)SO_4$, were studied employing factor group analysis.

During the study of preparation of crystalline tellurium trioxide, β-TeO_3 (*I*), crystalline ditelluryl sulfate, $(Te_2O_3)SO_4$ (*II*), was prepared as well[1]. In the present work we study vibrational spectra of the two substances in order to complement their crystal structure investigation[2-4].

EXPERIMENTAL

The crystalline oxide *I* was prepared[1] by heating orthotelluric acid, $Te(OH)_6$, in a sealed ampoule at 350—400°C for 3 h. The sulfate *II* was obtained[3] from the reaction of orthotelluric acid with concentrated sulfuric acid in a sealed ampoule at 350°C.

Infrared spectra of *I* were scanned on a spectrophotometer Perkin-Elmer 621 applying the nujol mull and CsBr pressed disk techniques, and on a spectrophotometer Beckman IR 11 applying the nujol mull technique, in the range of 200—4000 cm^{-1}. The Raman spectrum of *I* was run on an instrument Raman-Spectrometer Physical Type, Coderg, in the region of 50 to 1150 cm^{-1} (He-Ne laser of OIP, Gent, line 632·8 nm, power 190 mW). The infrared spectrum of *II* in the region of 50—450 cm^{-1} was measured on a Fourier spectrometer RIIC FS-620 and in the region of 400—4000 cm^{-1} on an instrument UR 20, Zeiss, Jena, in nujol mulls and KBr pressed disks. The Raman spectrum of *II* was obtained from an apparatus JRS-S1, Jeol, from coarsely ground material in the region of 10—1750 cm^{-1} (Ar laser of Coherent Radiation CR 2, line 514·5 nm, power 200 mW). The differences between the spectra obtained by using the nujol mull and the pressed disk techniques were negligible. The wavenumbers of sharp bands could be read with the accuracy of 1—2 cm^{-1}, those of broad bands with the accuracy of 3—4 cm^{-1}. The wavenumbers given in Tables II and V are averages of at least four values. The relative band intensities in the infrared spectra were evaluated in the scale 1—4, in the Raman spectra in the scale 1—10.

RESULTS AND DISCUSSION

Tellurium trioxide, β-TeO_3. The oxide crystallizes in the trigonal crystal system, space group $R\bar{3}c$ (D_{3d}^6, No 167) with two formula units in the unit cell. The tellurium

atoms lie[2] in a special twofold position $2a$, the oxygen atoms in a special sixfold position $6e$. The structure is formed by an infinite threedimensional net of TeO_3 groupings, with each tellurium atom surrounded by six oxygen atoms in the shape of a deformed octahedron and each oxygen atom belonging to two tellurium atoms. The TeO_3 formations make up chains parallel to the threefold crystal axis.

The results of the factor group analysis carried out employing[5,6] are given in Table I. The significant parts of the spectra measured are shown in Figs 1 and 2. The band positions and intensities are summarized in Table II. All bands save those at 318, 397, and 666 cm^{-1} were attributed to fundamentals. The band at 666 cm^{-1} is attributed to the 2×336 cm^{-1} overtone. Under this assumption, five of the six expected infrared bands and all the four expected Raman bands could be found. The vibrational spectra are thus in accordance with the structure as determined by X-ray diffraction. The values of three bands of the infrared spectrum published[7] are in a good agreement with our spectra.

Ditelluryl sulfate, $(Te_2O_3)SO_4$. The sulfate crystallizes in the orthorhombic crystal system, space group $P2_1mn(C_{2v}^7$, No 31) with two formula units in the unit cell. Its structure is formed[3,4] by infinite layers $_\infty^2Te_2O_3$ parallel to the (001) plane, and by sulfate anions SO_4^{2-}. From this point of view, a unit cell contains one layer
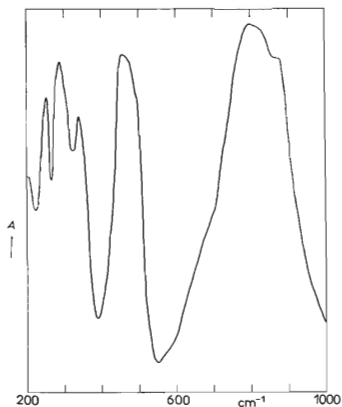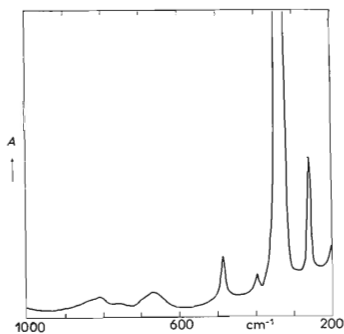

FIG. 1

Infrared Spectrum of β-TeO$_3$

FIG. 2

Raman Spectrum of β-TeO$_3$

$^2_\infty$Te$_2$O$_3$ and two sulfate anions. The layers are mutually bonded by those anions, one of them being bonded more strongly to the layer of its unit cell and the other to that of the neighbouring cell. The layers are formed by —Te—O(2)—Te—O(2)— screws, which are parallel to the [100] direction. The screws are linked by the 0(1) oxygen. This bridge oxygen, sulfur, and two oxygens of the sulfate anion, 0(4) and 0(5), lie in the symmetry plane m_{XZ} and occupy a special twofold position 2a. The other atoms have a general fourfold position 4b. The Te$_2$O$_3$ grouping as well as the sulfate anions possesses the symmetry $m(C_s)$.

TABLE I

Factor Group Analysis of β-TeO$_3$ — $R\bar{3}c$

Atom	Position	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
Te	2b	0	0	0	1	1	2
O	6e	1	2	3	1	2	3
N_{tot}		1	2	3	2	3	5
T_A						1	1
N_{opt}		1	2	3	2	2	4
Activity		Ra	—	Ra	—	IR	IR

TABLE II

Infrared and Raman Spectrum of β-TeO$_3$

Infrared		Raman		Infrared		Raman	
position cm^{-1}	relative intensity[a]	position cm^{-1}	relative intensity[b]	position cm^{-1}	relative intensity[a]	position cm^{-1}	relative intensity[b]
249	1			455	2		
		258	2	483	sh	485	1
281	2					666	1
318	sh			796	4		
334	1	336	10			804	0·5
		397	0·2	857	sh		

[a] In the scale 1—4, sh — shoulder; [b] in the scale 1—10.

TABLE III

Factor Group Analysis of $(^2_\infty Te_2O_3)SO_4 - Pmn2_1$

Atom	Position	A_1	A_2	B_1	B_2
Te	4b	3	3	3	3
O(1)	4b	3	3	3	3
O(2)	2a	2	1	1	2
S	2a	2	1	1	2
O(3)	4b	3	3	3	3
O(4)	2a	2	1	1	2
O(5)	2a	2	1	1	2
N_{tot}		17	13	13	17
T_A		1	0	1	1
R_{SO_4}		1	2	2	1
$N_{int(SO_4)}$		6	3	3	6
$T_{SO_4} + T_{Te_2O_3}$		3	2	1	3
$(R + N_{int})_{Te_2O_3}$		6	6	6	6
Activity		IR, Ra	Ra	IR, Ra	IR, Ra

TABLE IV

Correlation Table for SO_4 in $(Te_2O_3)SO_4$

Free ion T_d	Site symmetry $C_s(\sigma_{YZ})$	Factor group C_{2v}
$\nu_1(\ 981\ cm^{-1})$ [a],	$A_1 \longrightarrow A' \Big\langle$	A_1 / B_2
$\nu_2(\ 451\ cm^{-1})$,	$E \Big\langle \begin{matrix} A' \\ A'' \end{matrix}$	A_1 / B_2 / A_2 / B_1
$\nu_3(1\ 104\ cm^{-1})$, $\nu_4(\ 613\ cm^{-1})$,	$2F_2 \Big\langle \begin{matrix} 4A' \\ 2A'' \end{matrix}$	$4A_1$ / $4B_2$ / $2A_2$ / $2B_1$

[a] According to ref.[9].

The space group $P2_1mn$ describing the structure of the substance does not possess the standard orientation of axes[8]. For the interpretation of the vibrational spectra the transformation to the standard space group $Pmn2_1$, with the m_{YZ} mirror plane, was therefore performed. All the data given in this paper are related to that orientation.

The factor group analysis was carried out according to [5,6] and the results are given in Table III. The site group of the Te_2O_3 grouping is the same as the so-called polymeric site group[5] of the $^2_\infty Te_2O_3$ layer, i.e. the mirror plane $m(\sigma)$.

For the sulfate anion, correlations exist between the vibrations in the point group T_d, site group C_s, and factor group C_{2v} as shown in Table IV.

TABLE V

Infrared and Raman Band Positions, $\tilde{\nu}$ (cm^{-1}), and Intensities, I, of $(Te_2O_3)SO_4$

IR		Ra		Assignment	IR		Ra		Assignment[c]
$\tilde{\nu}$	I^a	$\tilde{\nu}$	I^b		$\tilde{\nu}$	I^a	$\tilde{\nu}$	I^b	
		50	1		360	sh			
85	2	80	5		375	sh	400	3	
		91	10		410	sh			$\nu_2 SO_4$
		107	sh		433	2	429	1·5	+
120	3						455	8	δTe
		133	3		462	1			+
145	3	149	5	lattice			499	1	νTe
		179	1	vibrations	512	2			
200	3	194	2·5		584	sh	573	0·5	
		229	sh				611	1	$\nu_4 SO_4$
235	3				625	4	630	1	+
		247	1		654	4			νTe
		272	0·5				724	sh	
290	3								
315	3	305	0·5		774	2	778	0·5	$B_1 Te$
							802	sh	$A_2 Te$
					969	3	964	1	$\nu_1 SO_4$
					1 011	3	992	sh	
							1 038	1	
					1 055	3	1 057	sh	
							1 140	1	$\nu_3 SO_4$
							1 174	sh	
					1 195	2	1 200	sh	

[a] In the scale 1—4; [b] in the scale 1—10; [c] Te stands for $^2_\infty Te_2O_3$ layer.

Significant parts of the spectra measured are shown in Figs 3, 4, and 5, the band positions and intensities are given in Table V. Three distinguished ranges are seen in the spectra, *viz.* 350—550, 550—850, and 850—1250 cm^{-1}. In the Raman spec-
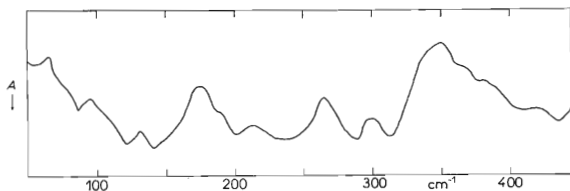

FIG. 3
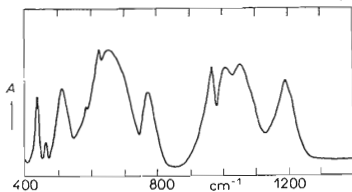Infrared Spectrum of $(Te_2O_3)SO_4$ in the Region of 50—445 cm^{-1}

FIG. 4

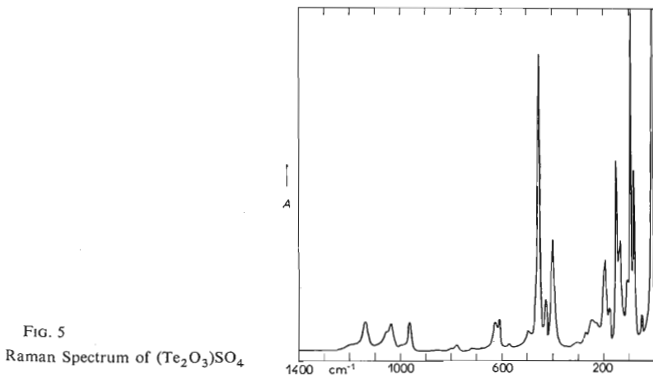Infrared Spectrum of $(Te_2O_3)SO_4$ in the Region of 400—1400 cm^{-1}

FIG. 5

Raman Spectrum of $(Te_2O_3)SO_4$

trum there are two such ranges, at $10-350$ and $350-550$ cm^{-1}. The infrared spectrum of II is very similar to that of TeO$_2$ (α-modification, $P4_12_12 - D_4^4$) in the range of $550-850$ cm^{-1} (ref.[10]). The vibrational types were attributed to the bands based on published data for the sulfate anion[9,11] and for the Te$_2$O$_3$ layer[12,13]; the assignment is given in Table V. Comparing the infrared and Raman spectral data we attribute the band at 774 cm^{-1} (778 cm^{-1}) formally to the stretching vibration of the Te$_2$O$_3$ layer of the B_1 type and the shoulder at 802 cm^{-1} to the A_2 type. The bands in the range of $550-750$ cm^{-1} comprise stretching vibrations of both the SO$_4$ groups and the Te$_2$O$_3$ layer. In the Raman spectrum a marked intense band appears at 455 cm^{-1}. As so intense a band does not occur in Raman spectra of sulfates, we attribute it to a vibration of the Te$_2$O$_3$ grouping. A more detailed elucidation of the spectra does not seem to be possible, as the bands of the sulfate group and of the telluryl layer overlap considerably. The separation to internal and external vibrations and distinguishing between the stretching and bending types is to be regarded as approximate.

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