# The Vibrational Spectrum of Ni<sub>3</sub>TeO<sub>6</sub> and Mg<sub>3</sub>TeO<sub>6</sub>

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The infrared and Raman spectra of Ni<sub>3</sub>TeO<sub>6</sub> and Mg<sub>3</sub>TeO<sub>6</sub> are reported. The TeO<sub>6</sub> groups can be considered in good approximation as independently vibrating groups. Using crystallographic data a complete assignment is possible. The frequencies of the TeO<sub>6</sub> vibrations in Mg<sub>3</sub>TeO<sub>6</sub> are at higher wavenumbers than in Ni<sub>3</sub>TeO<sub>6</sub>.

### 1. Introduction

Recently the vibrational spectra of some ordered perovskites  $Ba_2CaM^{6+}O_6$  have been reported by Corsmit, Hoefdraad and Blasse (1). In this crystal structure the MO<sub>6</sub> group has cubic symmetry. The vibrational bands of the MoO<sub>6</sub>, WO<sub>6</sub>, and TeO<sub>6</sub> groups in this structure could in fact be assigned to the octahedral vibrational modes  $\nu_1$ ,  $\nu_2$ , and  $\nu_5$  (all Raman-active), and  $\nu_3$  and  $\nu_4$  (infrared-active). This paper describes the vibrational spectra of Ni<sub>3</sub>TeO<sub>6</sub> and Mg<sub>3</sub>TeO<sub>6</sub>. In these compounds the TeO<sub>6</sub> octahedra have lower symmetry than cubic symmetry. It was our aim to investigate the influence of this symmetry on the vibrational spectrum of the tellurate octahedron.

### 2. Experimental Methods

Samples were prepared by firing high-purity NiCO<sub>3</sub> (or MgCO<sub>3</sub>) and TeO<sub>2</sub> in the required proportion in O<sub>2</sub>. The final firing was carried out at 800°C. Samples were checked on a Philips X ray diffractometer using  $CuK\alpha$ -radiation.

Infrared spectra were recorded on a Hitachi EPI-G3 grating spectrometer (down to 400 cm<sup>-1</sup>, KBr pellets) and a Grubb-Parsons DM 4 spectrometer with a CsI prism (down to 200 cm<sup>-1</sup>, CsI pellets). Raman spectra were recorded on a Spectra Physics 700 Raman spectrometer using an argon ion laser (488 or 514.5 nm). All measurements were carried out at room temperature. The accuracy of the peak positions is typically 3-5 cm<sup>-1</sup>.

#### 3. Results

The spectra obtained contain a large number of absorption bands. Those situated above 300 cm<sup>-1</sup> are presented in column 3 and 4 of the Tables I and II for Ni<sub>3</sub>TeO<sub>6</sub> and Mg<sub>3</sub>TeO<sub>6</sub>, respectively. In addition the infrared spectrum of Ni<sub>3</sub>TeO<sub>6</sub> shows two other bands, one at about 300 cm<sup>-1</sup> and the other one at about 210 cm<sup>-1</sup>. Both are split. The infrared spectrum of Mg<sub>3</sub>TeO<sub>6</sub> shows similar bands at 280, 245, and 220 cm<sup>-1</sup>. The Raman spectra of both tellurates show strong peaks below 200 cm<sup>-1</sup>. The Raman spectrum of Ni<sub>3</sub>TeO<sub>6</sub> above 200 cm<sup>-1</sup> has a weak intensity, probably because the exciting radiation is partly absorbed by the green-colored sample.

# 4. Discussion

4.1.  $Ni_3TeO_6$ 

The crystal structure of  $Ni_3TeO_6$  has been determined by Newnham and Meagher (2). The space group is R3. The rhombohedral unit cell contains one formula unit, and the  $Te^{6+}$  ions occupy the I(a) position with site symmetry  $C_3$ . This symmetry implies a trigonal field at the site of the  $TeO_6$  octahedron. As a consequence the octahedral  $\nu_3$ ,  $\nu_4$ , and  $\nu_5$  vibrations with threefold degeneracy are expected to split into two. In addition the exclusion principle is no longer valid, since the inversion center is not present in symmetry  $C_3$ . As a consequence all vibrational modes may be found in the Raman, as well as in the infrared spectrum. Columns one and two of

	Symmetry O <sub>h</sub>	Symmetry C <sub>3</sub>	Experimental (cm <sup>-1</sup> )	
			Raman	Infrared
$\nu_1$	$A_{1g}(\mathbf{R})$	A (R, IR)	680 (s)	~690 (m, sh)
$\nu_2$	$E_{a}(\mathbf{R})$	$E(\mathbf{R}, \mathbf{IR})$	590 (m)	590 (m)
ν <sub>5</sub>	$T_{2q}(\mathbf{R})$	$A + E(\mathbf{R}, \mathbf{IR})$	430 (w)	~430 (w, sh)
			370 (w)	$\sim$ 375 (m, sh)
$\nu_3$	$T_{1u}$ (IR)	$A+E(\mathbf{R},\mathbf{IR})$	$\sim$ 665 (w, sh)	665 (s)
				535 (s)
$\nu_4$	$T_{1u}(IR)$	A + E(R, IR)	~470 (w)	460 (s)
	*** *		~360 (w, sh)	365 (s)

TABLE I

VIBRATIONAL SPECTRUM OF TeO<sub>6</sub> OCTAHEDRON IN Ni<sub>3</sub>TeO<sub>6</sub> <sup>a</sup>

Table I show the correlation between  $O_h$  and  $C_3$  symmetry, and the selection rules.

An assignment of the vibrational absorption bands observed experimentally to the vibrational modes expected was made possible starting from the results for Ba<sub>2</sub>CaTeO<sub>6</sub> where the TeO<sub>6</sub> octahedron occupies a site with cubic symmetry. From Ref. (I) we find:

Raman-active:  $\nu_1$  (752 cm<sup>-1</sup>),  $\nu_2$  (618 cm<sup>-1</sup>), and  $\nu_5$  (412 cm<sup>-1</sup>). Infrared-active:  $\nu_3$  (685 cm<sup>-1</sup>),  $\nu_4$  (400 cm<sup>-1</sup>).

The mode  $v_6$  is always inactive.

If we take into account that the infrared intensity of the  $\nu_1$ ,  $\nu_2$ , and  $\nu_5$  vibration, and the

Raman intensity of the  $\nu_3$  and  $\nu_4$  vibration will be relatively low in the case of  $C_3$  symmetry, the assignment is straightforward. Results are given in Table I.

It seems justified to consider the TeO<sub>6</sub> group in Ni<sub>3</sub>TeO<sub>6</sub> as a more or less isolated group in the lattice. The exclusion principle is in fact violated as required by  $C_3$  symmetry. It is also seen that the trigonal field splits the threefold-degenerate vibrations  $\nu_3$ ,  $\nu_4$ , and  $\nu_5$  considerably. This is not surprising, since from structural considerations this field is expected to be strong. The crystal structure of Ni<sub>3</sub>TeO<sub>6</sub> is a superstructure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum). The cation octahedra form pairs by sharing octahedral faces. In Ni<sub>3</sub>TeO<sub>6</sub> these pairs are Ni-Ni pairs and Ni-Te pairs (2).

TABLE II

VIBRATIONAL SPECTRUM OF TeO<sub>6</sub> OCTAHEDRON IN  $Mg_3TeO_6$ <sup>4</sup>

	Symmetry O <sub>h</sub>	Symmetry $S_6$	Experimental (cm <sup>-1</sup> )	
			Raman	Infrared
$\nu_1$	$A_{1g}(\mathbf{R})$	$A_{q}(\mathbf{R})$	790 (s)	_
$\nu_2$	$E_q(\mathbf{R})$	$E_{q}(\mathbf{R})$	695 (w)	
$\nu_5$	$T_{2g}(\mathbb{R})$	$A_a + E_a(\mathbf{R})$	500 (w)	
•	-3 . ,		475 (w)	
$\nu_3$	$T_{1u}(IR)$	$A_u + E_u$ (IR)	_	750 (s), 725 (s)
•	,	,		702 (s), 670 (m)
$\nu_4$	$T_{1\mu}(IR)$	$A_u + E_u$ (IR)		520 (m), 465 (s)
•	1- \ /	,		380 (m), 340 (s)

<sup>&</sup>lt;sup>a</sup> For abbreviations see Table I.

<sup>\*</sup>Abbreviations: R = Raman-active; IR = infrared-active; s = strong; m = medium; w = weak; sh = observed as a shoulder.

It is obvious that in such a Ni-Te pair the field at the Te-site is strongly trigonal.

In this connection the recent results of Zupan, Kolar and Urbanc (3) become doubtful. They estimated the trigonal-field component at the Ni<sup>2+</sup> site to be very small. They do not differentiate between the Ni<sup>2+</sup> ions in the Ni-Ni pairs and those in the Ni-Te pairs. It seems to us that at least the Ni<sup>2+</sup> ions in the Ni-Te pairs will endure a strong trigonal field.

Finally we assign the infrared bands at 300 and 210 cm<sup>-1</sup> to Ni-O vibrations without further specification. The  $\nu_6$  vibration of the TeO<sub>6</sub> octahedron is Raman- as well as infrared-active in  $C_3$  symmetry. Using Wilson's rule [ $\nu_5 = \sqrt{2} \cdot \nu_6$ , see Ref. (4)] the  $\nu_6$  vibration is expected in the region around 280 cm<sup>-1</sup>. This region is dominated by the 300 cm<sup>-1</sup> band mentioned above, so that direct observation of  $\nu_6$  is not possible.

# $4.2. Mg_3TeO_6$

The crystal structure of Mg<sub>3</sub>TeO<sub>6</sub> has been refined by Schulz and Bayer (5). The space group is  $R\overline{3}$ . The rhombohedral unit cell contains two different  $Te^{6+}$  ions both with site symmetry  $S_6$ . This implies that also in Mg<sub>3</sub>TeO<sub>6</sub> the TeO<sub>6</sub> octahedron endures a trigonal field. In this lattice, however, the inversion center remains present so that the exclusion principle is expected to be valid. The first and second column of Table II show the correlation between  $O_h$  and  $S_6$ symmetry and the selection rules. It must be kept in mind that we should expect twice as many absorption bands in the spectra as follows from this table, since the unit cell contains two different Te<sup>6+</sup> ions both with S<sub>6</sub> site symmetry and the space group is  $R\bar{3}$ .

Taking into consideration the results for Ba<sub>2</sub>CaTeO<sub>6</sub> and Ni<sub>3</sub>TeO<sub>6</sub> the assignment of the vibrational bands observed experimentally is straightforward (Table II). In the Raman spectrum we do not observe a doubling of the number of bands. In fact the difference between the two types of TeO<sub>6</sub> octahedra is small: The interatomic distances differ 0.01 Å or less, the bond angles less than  $1^{\circ}$  (5). Further, the interaction between different TeO<sub>6</sub> octahedra is expected to be weak, since they do not have oxygen ions in common. In the infrared spectrum, however, a doubling is observed. The  $\nu_3$ , as well as the  $\nu_4$  vibration show four bands in the spectra as expected. The trigonal field is considerably weaker than in the case of Ni<sub>3</sub>TeO<sub>6</sub>. We do not find any indication that the exclusion principle is violated.

The hypothesis of an isolated  $TeO_6$  octahedron is also in this case very helpful for the assignment of the vibrational spectrum at not too low energies. The infrared bands at 280, 245, and 220 cm<sup>-1</sup> are ascribed to the Mg-O octahedra in the lattice. It can, however, not be excluded that the  $\nu_4$  vibration mode is not a pure tellurate vibration. It seems even rather probable that it corresponds to complex vibrations involving the simultaneous participation of the  $TeO_6$  and the  $MgO_6$  octahedra.

## 4.3. Comparison with Other Tellurates

If one compares the last columns of Tables I and II, it is clear that the vibrational spectrum of the TeO<sub>6</sub> group in Mg<sub>3</sub>TeO<sub>6</sub> is situated at considerably higher wavenumbers than that of the TeO<sub>6</sub> group in Ni<sub>3</sub>TeO<sub>6</sub>. The values for Ba<sub>2</sub>CaTeO<sub>6</sub> (see Sect. 4.1) are in between these extremes. In the literature we also found some data for the trirutiles Me<sub>2</sub><sup>3+</sup>TeO<sub>6</sub> (6). These give information on  $\nu_3$  only. Since the site symmetry of the TeO<sub>6</sub> octahedron in trirutile is  $D_{2h}$ , the  $v_3$ vibration is expected to consist of three subbands as has been observed experimentally. The average value is about 650 cm<sup>-1</sup>. We are, therefore, led to the conclusion that the stretching force constant of the TeO<sub>6</sub> group in Mg<sub>3</sub>TeO<sub>6</sub> is relatively high and in Ni<sub>3</sub>TeO<sub>6</sub> relatively low. An obvious explanation seems to be that in Mg<sub>3</sub>TeO<sub>6</sub> the Mg-O bond is highly ionic so that the covalent character of the Te-O bond is high. In Ni<sub>3</sub>TeO<sub>6</sub>, however, the Ni-O bond will also have a certain covalent character due to the presence of dorbitals. As a consequence the covalent character of the Te-O bond is lower than in Mg<sub>3</sub>TeO<sub>6</sub>. This problem is now investigated further.

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