The Vibrational Spectrum of Ni_3TeO_6 and Mg_3TeO_6

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The infrared and Raman spectra of Ni_3TeO_6 and Mg_3TeO_6 are reported. The TeO_6 groups can be considered in good approximation as independently vibrating groups. Using crystallographic data a complete assignment is possible. The frequencies of the TeO_6 vibrations in Mg_3TeO_6 are at higher wavenumbers than in Ni_3TeO_6.

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_6 group has cubic symmetry. The vibrational bands of the MoO_6, WO_6, and TeO_6 groups in this structure could in fact be assigned to the octahedral vibrational modes v_1, v_2, and v_5 (all Raman-active), and v_3 and v_4 (infrared-active). This paper describes the vibrational spectra of Ni_3TeO_6 and Mg_3TeO_6. In these compounds the TeO_6 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 $NiCO_3$ (or $MgCO_3$) and TeO_2 in the required proportion in O_2. 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^{-1}, KBr pellets) and a Grubb-Parsons DM 4 spectrometer with a CsI prism (down to 200 cm^{-1}, 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^{-1}.

3. Results

The spectra obtained contain a large number of absorption bands. Those situated above 300 cm^{-1} are presented in column 3 and 4 of the Tables I and II for Ni_3TeO_6 and Mg_3TeO_6, respectively. In addition the infrared spectrum of Ni_3TeO_6 shows two other bands, one at about 300 cm^{-1} and the other one at about 210 cm^{-1}. Both are split. The infrared spectrum of Mg_3TeO_6 shows similar bands at 280, 245, and 220 cm^{-1}. The Raman spectra of both tellurates show strong peaks below 200 cm^{-1}. The Raman spectrum of Ni_3TeO_6 above 200 cm^{-1} 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 1(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 v_3, v_4, and v_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_h	Symmetry C_3	Experimental (cm^{-1})	
			Raman	Infrared
ν_1	A_{1g} (R)	A (R, IR)	680 (s)	~690 (m, sh)
ν_2	E_g (R)	E (R, IR)	590 (m)	590 (m)
ν_5	T_{2g} (R)	$A + E$ (R, IR)	430 (w)	~430 (w, sh)
			370 (w)	~375 (m, sh)
ν_3	T_{1u} (IR)	$A + E$ (R, IR)	~665 (w, sh)	665 (s)
				535 (s)
ν_4	T_{1u} (IR)	$A + E$ (R, IR)	~470 (w)	460 (s)
			~360 (w, sh)	365 (s)

[a] Abbreviations: R = Raman-active; IR = infrared-active; s = strong; m = medium; w = weak; sh = observed as a shoulder.

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_2CaTeO_6 where the TeO_6 octahedron occupies a site with cubic symmetry. From Ref. (1) we find:

Raman-active: ν_1 (752 cm^{-1}), ν_2 (618 cm^{-1}), and ν_5 (412 cm^{-1}).
Infrared-active: ν_3 (685 cm^{-1}), ν_4 (400 cm^{-1}).
The mode ν_6 is always inactive.

If we take into account that the infrared intensity of the ν_1, ν_2, and ν_5 vibration, and the

Raman intensity of the ν_3 and ν_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_6 group in Ni_3TeO_6 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 ν_3, ν_4, and ν_5 considerably. This is not surprising, since from structural considerations this field is expected to be strong. The crystal structure of Ni_3TeO_6 is a superstructure of α-Al_2O_3 (corundum). The cation octahedra form pairs by sharing octahedral faces. In Ni_3TeO_6 these pairs are Ni–Ni pairs and Ni–Te pairs (2).

	Symmetry O_h	Symmetry S_6	Experimental (cm^{-1})	
			Raman	Infrared
ν_1	A_{1g} (R)	A_g (R)	790 (s)	—
ν_2	E_g (R)	E_g (R)	695 (w)	
ν_5	T_{2g} (R)	$A_g + E_g$ (R)	500 (w)	
			475 (w)	
ν_3	T_{1u} (IR)	$A_u + E_u$ (IR)	—	750 (s), 725 (s)
				702 (s), 670 (m)
ν_4	T_{1u} (IR)	$A_u + E_u$ (IR)	—	520 (m), 465 (s)
				380 (m), 340 (s)

[a] For abbreviations see Table I.

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^{2+} site to be very small. They do not differentiate between the Ni^{2+} ions in the Ni–Ni pairs and those in the Ni–Te pairs. It seems to us that at least the Ni^{2+} ions in the Ni–Te pairs will endure a strong trigonal field.

Finally we assign the infrared bands at 300 and 210 cm^{-1} to Ni–O vibrations without further specification. The ν_6 vibration of the TeO$_6$ 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 ν_6 vibration is expected in the region around 280 cm^{-1}. This region is dominated by the 300 cm^{-1} band mentioned above, so that direct observation of ν_6 is not possible.

4.2. Mg$_3$TeO$_6$

The crystal structure of Mg$_3$TeO$_6$ has been refined by Schulz and Bayer (5). The space group is $R\bar{3}$. The rhombohedral unit cell contains two different Te^{6+} ions both with site symmetry S$_6$. This implies that also in Mg$_3$TeO$_6$ the TeO$_6$ 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^{6+} ions both with S$_6$ site symmetry and the space group is $R\bar{3}$.

Taking into consideration the results for Ba$_2$CaTeO$_6$ and Ni$_3$TeO$_6$ 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$_6$ octahedra is small: The interatomic distances differ 0.01 Å or less, the bond angles less than 1° (5). Further, the interaction between different TeO$_6$ 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 ν_3, as well as the ν_4 vibration show four bands in the spectra as expected. The trigonal field is considerably weaker than in the case of Ni$_3$TeO$_6$. 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^{-1} are ascribed to the Mg–O octahedra in the lattice. It can, however, not be excluded that the ν_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$_6$ group in Mg$_3$TeO$_6$ is situated at considerably higher wavenumbers than that of the TeO$_6$ group in Ni$_3$TeO$_6$. The values for Ba$_2$CaTeO$_6$ (see Sect. 4.1) are in between these extremes. In the literature we also found some data for the trirutiles Me$_2^{3+}$TeO$_6$ (6). These give information on ν_3 only. Since the site symmetry of the TeO$_6$ octahedron in trirutile is D_{2h}, the ν_3 vibration is expected to consist of three subbands as has been observed experimentally. The average value is about 650 cm^{-1}. We are, therefore, led to the conclusion that the stretching force constant of the TeO$_6$ group in Mg$_3$TeO$_6$ is relatively high and in Ni$_3$TeO$_6$ relatively low. An obvious explanation seems to be that in Mg$_3$TeO$_6$ the Mg–O bond is highly ionic so that the covalent character of the Te–O bond is high. In Ni$_3$TeO$_6$, however, the Ni–O bond will also have a certain covalent character due to the presence of d-orbitals. As a consequence the covalent character of the Te–O bond is lower than in Mg$_3$TeO$_6$. This problem is now investigated further.

References

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