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Vibrational Spectra of 1:2 Ordered Perovskites

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The infrared and Raman spectra of some perovskites with general formula $A_3BB_2'O_9$ are reported, viz. $Sr_3MgNb_2O_9$, $Sr_3CaNb_2O_9$, $Pb_3MgNb_2O_9$, and $Ba_3Gd_2WO_9$. The interpretation is by far not as simple as for 1:1 ordered perovskites. Only a rough assignment of the internal modes of the niobate and tungstate octahedra can be made. The spectra of the niobates are very sensitive to the degree of order between the divalent metal ions and the Nb^{5+} ions among the smaller cation sublattice. This is evaluated qualitatively.

Introduction

The vibrational spectra of 1:1 ordered perovskites $A_2BB'O_6$ have been described recently (*1*, *2*). It was found that the molecular groups in these compounds (e.g., WO_6 in Ba_2MgWO_6) show their internal vibrational modes very clearly in the Raman and infrared spectra. Their assignment was facilitated by the high symmetry of the B cation sites and of the space group of the crystal, viz. O_h.

It seemed interesting to investigate also the vibrational spectra of 1:2 ordered perovskites $A_3BB_2'O_9$. Examples of these compounds are $Sr_3MgNb_2O_9$ (*3*) and $Ba_3Gd_2WO_9$ (*4*). There are two reasons for such an investigation. (a) The site symmetry of the molecular group (niobate or tungstate) is lower than cubic, so that a splitting of the bands in the spectra of the 1:1 ordered perovskites must be expected. (b) The 1:2 order in the perovskite structure is difficult to achieve, perhaps due to a poor local charge balance (*5*). If the 1:2 order is achieved, the crystal structure becomes hexagonal (*3*). The smaller cation layers perpendicular to the body diagonal of the perovskite pseudocell are occupied in the sequence –B–B′–B′–B–B′–B′–.

Often, however, the X-ray pattern indicates a cubic unit cell the parameter of which is twice that of the perovskite pseudocell. This seems to indicate 1:1 order on the smaller cation sites. It has been suggested that the 1:1 order occurs between B′ and ($\frac{2}{3}B + \frac{1}{3}B'$) ions (*4*). Since vibrational spectroscopy may reveal further information on order–disorder problems (*6*), these compounds are challenging for such an investigation.

The 1:2 ordered perovskites offer the possibility to situate the center of the molecular group on B as well as on B′ in the general $A_3BB_2'O_9$. In $Sr_3MgNb_2O_9$, the center of the molecular group is on B′, in $Ba_3Gd_2WO_9$ it is on B. The crystallographic surroundings of B and B′ are different. It turned out that the vibrational spectra are very sensitive to the degree of order in the case that the center of the molecular group is at B′.

Experimental

Samples were prepared by usual techniques [see, e.g., (*4*)]. They were checked by X-ray analysis. Infrared spectra were measured in KBr and CsI pellets using a Hitachi EPI-G3 grating spectrometer and a Grubb Parsons DM4 spectrometer with a CsI prism. Raman spectra were measured on a Spectra Physics 700 Raman spectrometer using an argon ion laser (courtesy Dr. J. H. van der Maas). All measurements were performed at room temperature.

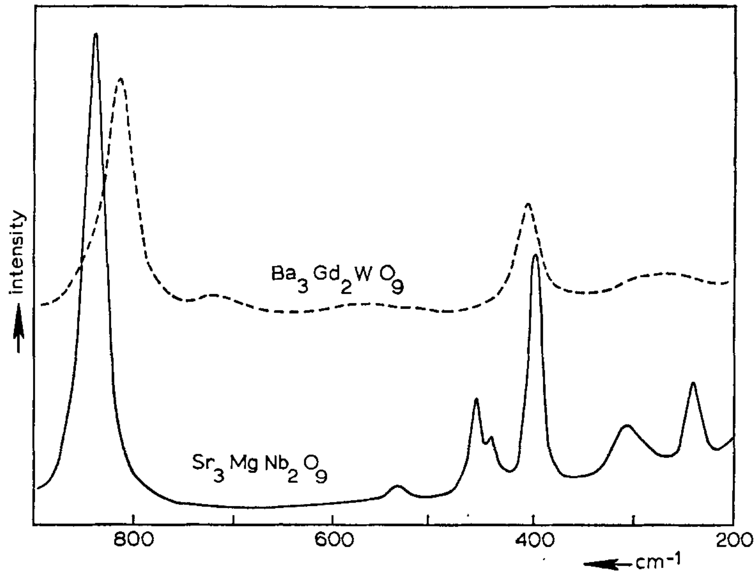

FIG. 1. Raman spectrum of $Sr_3MgNb_2O_9$ and $Ba_3Gd_2WO_9$.

Results

The Raman and infrared spectra of $Sr_3MgNb_2O_9$ and $Ba_3Gd_2WO_9$ are given in Figs. 1 and 2. Part of the Raman spectra of $Sr_3CaNb_2O_9$ is given in Fig. 3 together with a part of the X-ray diagram. Note that part of these samples have different Raman, but equal X-ray, spectra. Table I gives the spectra of the compounds studied together with a rough assignment of the internal vibrations to be discussed below.

Discussion

(a) $Sr_3MgNb_2O_9$

The X-ray pattern of $Sr_3MgNb_2O_9$ indicates clearly 1:2 order between the Mg^{2+} and Nb^{5+} ions among the smaller cation sites. An interpretation of the vibrational spectrum of such a compound is far more complicated than for the 1:1 ordered perovskites. The reason for this is that each unit cell contains two corner-sharing niobate octahedra. As a consequence, the crystal structure does not contain isolated niobate groups (as in the case of 1:1 ordered perovskites), but double layers of corner-sharing niobate octahedra. Only factor group analysis can lead to a more or less reliable assignment. Since we are working with powder samples only, such an approach cannot be very promising.

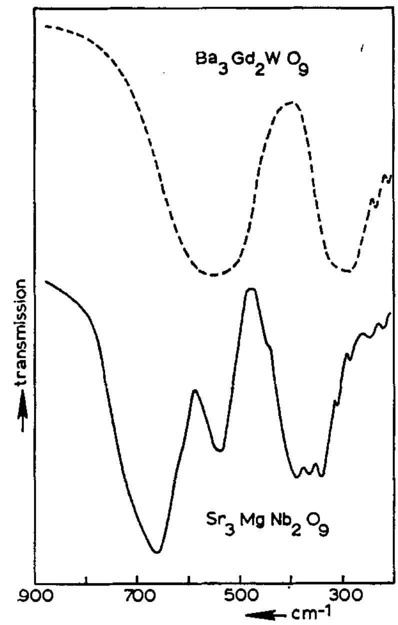

FIG. 2. Infrared spectrum of $Sr_3MgNb_2O_9$ and $Ba_3Gd_2WO_9$.

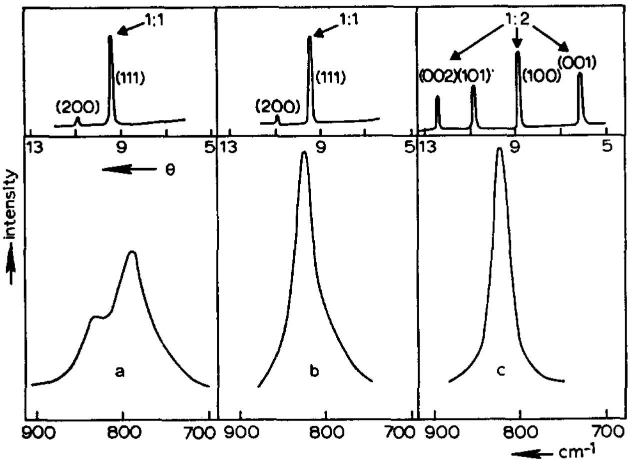

FIG. 3. The ν_1 band in the Raman spectrum and the X-ray powder patterns for low angles for $Sr_3CaNb_2O_9$. (a): firing temperature 1450°C, (b): 1450°C, (c): 1350°C. The superstructure reflections have been indexed on a cubic (1:1 order) or hexagonal (1:2 order) unit cell.

We, therefore, use a rather rough method. The site symmetry of the Nb^{5+} ion in $Sr_3MgNb_2O_9$ is C_{3v}: the niobate octahedron shares corners with three other niobate octahedra on one side and with three MgO_6 octahedra on the other side. In 1:1 ordered perovskites, this site symmetry is O_h: the niobate octahedron in, for example, $SrLaMgNbO_6$ shares corners with six MgO_6 octahedra.

Symmetry considerations inform us about the changes to be expected in the spectra, if the symmetry is lowered from O_h to C_{3v} (Table II). We further note that there is experimental evidence that the spectra of the

TABLE I

VIBRATIONAL SPECTRA AND APPROXIMATE INTERNAL MODE ASSIGNMENT OF SOME PEROVSKITES $A_3BB'_2O_9$[a]

$Sr_3MgNb_2O_9$		$Sr_3CaNb_2O_9$[b]		$Pb_3MgNb_2O_9$	
Infrared	Raman	Infrared	Raman	Infrared	Raman
	830 (s), ν_1	810 (w), ν_1	825 (s), ν_1		800 (m), ν_1
660 (s), ν_3		640 (s, br), ν_3	620 (w), ν_3	590 (s), ν_3	550 (w, br)
540 (m), ν_3	535 (w), ν_3(?)	510 (m), ν_3	515 (w), ν_3	425 (w)	
450 (w), ν_4	455 (m), ν_5		460 (w)	355 (s)	400 (w)
395 (s), ν_4	455 (w)		440 (m), ν_5	300 (s)	300 (s)
370 (s), ν_4	400 (m), ν_5		400 (w)	265 (m)	
340 (s)		370 (s, br), ν_4	390 (s), ν_5	230 (m)	
315 (m)	310 (w)		335 (w)	215 (w)	
285 (w)		290 (m)	295 (w)		
250 (w)	240 (w)	250 (m)			
225 (w)		230 (m)			

[a] All values in cm^{-1}. s = strong; m = medium; w = weak; br = broad.
[b] 1:2 ordered phase.

TABLE II

OCTAHEDRAL INTERNALS UNDER O_h AND C_{3v} SYMMETRY[a]

Mode	O_h	C_{3v}
ν_1	A_{1g} (R)	A_1 (R, ir)
ν_2	E_g (R)	E (R, ir)
ν_5	T_{2g} (R)	$A_1 + E$ (R, ir)
ν_3, ν_4	T_{1u} (ir)	$A_1 + E$ (R, ir)

[a] R = Raman-active; ir = infrared-active.

individual niobate octahedron is not drastically influenced by corner sharing (7). We therefore expect that the niobate vibrational spectra of $Sr_3MgNb_2O_9$ show in first approximation agreement with the spectrum expected for a niobate octahedron with C_{3v} symmetry. This is substantiated if one neglects details: the Raman-active ν_1 is found at 840 cm^{-1} (compare $SrLaMgNbO_6$ 790 cm^{-1}), the Raman-active ν_5 at 455 and 400 cm^{-1} ($SrLaMgNbO_6$ 440 cm^{-1}), the Raman-active ν_3 at 660 and 540 cm^{-1} (620 cm^{-1}), and the infrared-active ν_4 at 450, 395, and 370 cm^{-1} (435 and 385 cm^{-1}). The nondegenerate ν_1 remains single, the threefold-degenerate ν_3, ν_4, and ν_5 are split (especially ν_4 more than expected). Note that intensities are not influenced; the exclusion principle of the O_h symmetry is still observed experimentally. This assignment is rough, but in principle correct. It is useful to appreciate the large difference between the niobate vibrational spectra of $SrLaMgNbO_6$ and $Sr_3MgNb_2O_9$ and to indicate the main origin for this, viz. the difference in site symmetry.

(b) $Sr_3CaNb_2O_9$

The compound $Sr_3CaNb_2O_9$ has the same structure as $Sr_3MgNb_2O_9$, viz. 1:2 ordered perovskite (3). Its vibrational spectra, however, show a number of interesting phenomena. The most striking of these is the relation between the Raman-active ν_1 and the ordering lines in the X-ray pattern. This is shown in Fig. 3.

Depending on the firing temperature, the X-ray powder patterns show the reflections characteristic of 1:1 or 1:2 ordering. This indicates that we have samples with varying degree of order. The infrared spectra of these different samples are essentially equal, the Raman spectra, however, different. The most striking difference occurs in the region around 800 cm^{-1}, where the ν_1 mode is expected. There are also differences in the region where ν_5 is expected, but these are less pronounced and therefore not discussed further.

In the ν_1 region we find two bands, one at about 790 cm^{-1} and the other at about 830 cm^{-1}. The latter one becomes more intense if the 1:2 order reflections in the X-ray pattern become more pronounced. Its position is very near to the ν_1 band in $Sr_3MgNb_2O_9$ (840 cm^{-1}), where only 1:2 order was observed in the X-ray diagrams.

The samples of $Sr_3CaNb_2O_9$ with 1:1 order reflections in their X-ray pattern show also a 790 cm^{-1} band in the Raman spectrum which in one of the samples is relatively strong. This indicates that in the samples with 1:1 order X-ray reflections there is a niobate octahedron present with surroundings different from the niobate octahedron in the 1:2 superstructure and that the Raman-active ν_1 is a very sensitive measure for its concentration.

It seems impossible to derive from these data information on the surroundings of these niobate octahedra. Nevertheless it is tempting to relate the 830 cm^{-1} band to the ν_1 of $Sr_3MgNb_2O_9$ (840 cm^{-1}) and the 790 cm^{-1} band to the ν_1 of $SrLaMgNbO_6$ (790 cm^{-1}). If this would be correct, the 830 cm^{-1} band is due to a niobate octahedron with an asymmetric surroundings (NbO_6 octahedra on one side and MgO_6 octahedra on the other side), and the 790 cm^{-1} band to a niobate octahedron with symmetric surroundings (i.e., symmetry O_h).

This model is at least not contrary to the idea that the 1:1 order reflections stem from order between Nb_A and ($\frac{2}{3}Mg + \frac{1}{3}Nb_B$). This can be shown as follows: the Nb_BO_6 octahedra share corners with six Nb_AO_6 octahedra, so that their direct surroundings are comparable with that of the NbO_6

octahedron in $SrLaMgNbO_6$. The symmetry is O_h. The surrounding ions, however, are different: Mg in the case of $SrLaMgNbO_6$, Nb in the case of Nb_BO_6. The Nb_AO_6 octahedron has surroundings that differ strongly from that of the Nb_BO_6 octahedron: the Nb_AO_6 octahedron shares corners with on the average 4 MgO_6 and 2 NbO_6 octahedra. So there are two different types of octahedra in $Sr_3CaNb_2O_9$, if it has this 1:1 order. Tentatively we assign the 830 cm^{-1} band to the Nb_AO_6 octahedron and the 790 cm^{-1} band to the Nb_BO_6 octahedron. We realize again the roughness of this model and stress that no correlation effects have been taken into account.

In closing this section, we note that the vibrational spectra of 1:2 ordered $Sr_3CaNb_2O_9$ differ from those of $Sr_3MgNb_2O_9$ by the fact that the exclusion principle is no longer valid for the calcium compound. The ν_1 is also visible in the infrared and ν_3 in the Raman spectrum. This indicates that the trigonal field at the niobate octahedron is larger in the calcium than in the magnesium compound. This is not unexpected, since the size difference between Ca^{2+} and Nb^{5+} is large in comparison with that between Mg^{2+} and Nb^{5+}. Next to the charge difference, this size difference will also contribute to the trigonal field component.

(c) $Pb_3MgNb_2O_9$

This lead compound has been reported to have perovskite structure without any long-range ordering at all (*8*). It was suggested, however, that ordering occurs over small regions of the crystal (~100 Å) in order to explain the electron-diffraction patterns. The vibrational spectra reveal that the degree of order is considerably less than in the case of the strontium compounds. The infrared spectrum shows one broad band at about 590 cm^{-1}, where ν_3 is to be expected. The ν_1 mode in the Raman spectrum is situated at 800 cm^{-1}. It is certainly not the most intense line in the spectrum as is the case for the strontium compounds. Note that for a completely disordered structure, the intensity of ν_1 would vanish. The vibrational spectra support, therefore, the information on order obtained from the X-ray pattern.

(d) $Ba_3Gd_2WO_9$

From the discussion above, it is obvious that the vibrational spectra depend strongly on the degree of order of perovskites $A_3BNb_2O_9$. It is not self-evident that this is also true for perovskites $A_3WB_2'O_9$, like $Ba_3Gd_2WO_9$. Table III shows that there is a close agreement between the vibrational spectra of the tungstate internal modes of $Ba_3Gd_2WO_9$ and Ba_2CaWO_6 (Ref. *1*; 1:1 ordered perovskite). The main difference is that the exclusion principle holds for Ba_2CaWO_6 (site symmetry O_h), whereas the infrared-active ν_3 and ν_4 appear also weakly in the Raman spectrum of Ba_3GdWO_9 and that the gadolinium compound shows broader bands than the calcium compound.

The perovskite $Ba_3Gd_2WO_9$ has been described as a perovskite without crystallographic order (*4*). The X-ray pattern of the present sample reveals very weak reflections characteristic of 1:1 order. Since the scattering powers for X-rays of these ions differ only slightly, this indicates a certain degree of order, although the order is certainly not complete, i.e., 1:2. This can also be concluded from the spectral energy distribution of Eu^{3+} in $Ba_3Gd_2WO_9$ (*9*).

The vibrational spectra do not give further information. The reason for this is, that in 1:2 ordered $Ba_3Gd_2WO_9$, the WO_6 octahedron

TABLE III

INTERNAL MODES OF THE TUNGSTATE OCTAHEDRON IN Ba_2CaWO_6 AND $Ba_3Gd_2WO_9$[a]

Mode	Ba_2CaWO_6	$Ba_3Gd_2WO_9$
ν_1	832 (R)	815 (R)
ν_2	675 (R)	720? (R)
ν_3	628 (ir)	~570 (ir); ~570 (R)
ν_4	327 (ir)	~300 (ir); ~275 (R)
ν_5	410 (R)	405 (R)

[a] All values in cm^{-1}. R = observed in Raman spectrum; ir = observed in infrared spectrum. Compare Figs. 1 and 2. Data for Ba_2CaWO_6 from Ref. (*1*).

would share corners with six GdO_6 octahedra. The site symmetry O_h would be a very good approximation. The exact site symmetry is D_{3d}, but the trigonal field component will be weak. Since there is only one W per primitive unit cell, we find that our vibrational spectra correspond rather well to this situation except for the broadness of the bands and the occurrence of ν_3 and ν_4 in the Raman spectrum. This points to a deviation from complete 1:2 order.

The 1:1 X-ray reflections indicate an order of the type $Ba_3\{Gd_{1.5}\}\{Gd_{0.5}W\}O_9$. In this model, the WO_6 octahedron shares corners also with six GdO_6 octahedra and O_h should also be a good site symmetry approximation. The vibrational spectra do not contradict this type of order. The only thing which is pertinent is the fact that the high intensity of ν_1 in the Raman spectrum excludes a statistical distribution of Gd^{3+} and W^{6+} ions.

We conclude that the information on the order in $Ba_3Gd_2WO_9$ to be obtained from vibrational spectra is only poor. This is in striking contradistinction with $Ba_3Fe_2WO_9$ with the hexagonal perovskite structure, where vibrational spectroscopy solved the type of superstructure (*10*).

(*e*) *Further comments on 1:1 Ordering in Perovskites*

The sensitivity of the Raman ν_1 line to ordering phenomena has lead us to reinspect the Raman spectra of some 1:1 ordered perovskites. Figure 4 shows the ν_1 mode in the Raman spectra of $SrLaMgM^{5+}O_6$ (M = Sb, Nb, Ta). In the case of Nb and Ta, this band is highly asymmetrical. In the case of Sb, however, it is fairly symmetric around 790 cm^{-1}. These data can now be interpreted as follows. Since ν_1 is a single mode (this is strictly true for 1:1 ordered perovskites), the strong asymmetry indicates the presence of several types of NbO_6 octahedra. This is only possible if the degree of order of the 1:1 ordered perovskite is less than 100%. We, therefore, conclude that the degree of order in $SrLaMgSbO_6$ is fairly high, but that in the analogous Nb and Ta compounds the order is incomplete. This is corroborated by the fact that the ordering reflections in the X-ray patterns are much stronger in the Sb than in the Nb compound and about as strong in the Sb and Ta compound. This cannot only be explained from the different scattering powers for X rays for these ions.

It is also interesting to note that the asymmetry in the ν_1 band is on the high-energy side. This suggests a band reminiscent of ν_1 in the case of 1:2 ordered $Sr_3MNb_2O_9$ (M = Mg and Ca) which was ascribed to asymmetrically surrounded NbO_6 octahedra. As a matter of fact, the "disordered" Nb^{5+} ions in $SrLaMgNbO_6$ and their neighbor Nb^{5+} ions are also asymmetrically surrounded. This result agrees with the observation that order in perovskites is achieved more easily for cations with d^{10} configuration than for ions with d^0 configuration (*4*). Sb^{5+} belongs to the former, Nb^{5+} and Ta^{5+} to the latter class.

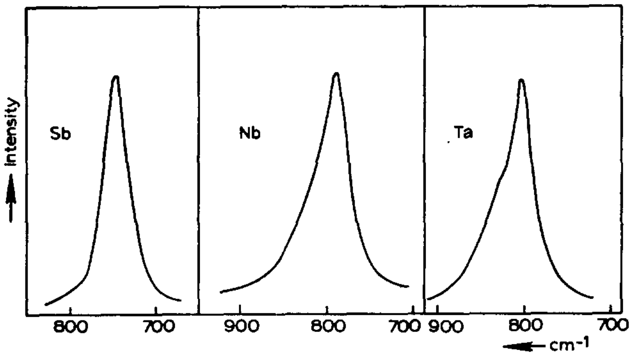

FIG. 4. The ν_1 band in the Raman spectrum of $SrLaMgM^{5+}O_6$ (M = Sb, Nb, Ta).

Such a complicated behavior of ν_1 in 1:1 ordered perovskites has also been observed (2) for Ba_2YNbO_6 which has been described as a disordered perovskite (*11*). Here ν_1 consists of three sub-bands at 855, 830, and 765 cm^{-1}. This shows that this compound is indeed strongly disordered.

In conclusion, we have found that the vibrational spectroscopy of ordered perovskites may yield information on the degree of order in these compounds, although this is of a qualitative nature at the present time.

Acknowledgments

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