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Vibrational Spectra and Structural Considerations of Compounds $NaLnTiO_4$

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The Raman and infrared spectra of compounds $NaLnTiO_4$ (Ln = lanthanide, including yttrium) are reported and discussed. Their most striking feature is a strong band in both spectra at about 900 cm^{-1}. This band is ascribed to a vibration localized in the Ti–O bond directed towards the Na–O layers. The relevant oxygen anion is very poorly charge compensated, and the Ti–O bond is, therefore, very strong. Pauling's electrostatic valence rule appears to be of great use in these considerations. These compounds do not show ferroelectricity.

Introduction

Some years ago one of us described the structure of a new series of compounds $NaLnTiO_4$ (Ln = lanthanide, including yttrium) (*1*). This structure can be derived from the K_2NiF_4 structure by ordering the Na^+ and Ln^{3+} ions among the larger cation sites. This superstructure is remarkable because there are double layers of Ln^{3+} ions and double layers of Na^+ ions perpendicular to the *c* axis (Fig. 1). As a consequence, a poor charge compensation between the titanate layers occurs. This structure was confirmed by a study of the luminescene of trivalent lanthanide ions in compounds $NaLnTiO_4$ (*2*).

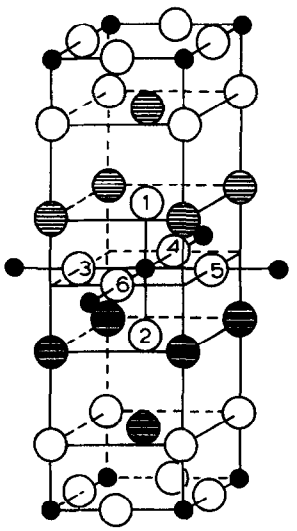

FIG. 1. Crystal structure of $NaLnTiO_4$. Black ions, Ti^{4+}; white ions, O^{2-}; ions hatched with thin lines, Na^+; ions hatched with thick lines, Ln^{3+}.

In the course of our studies on the vibrational spectra of solid tungstates, niobates, titanates, etc. (*3*), we became again interested in the compounds $NaLnTiO_4$. Last (*3*) has given a site group analysis of the infrared spectra of titanates with perovskite structure assigning two strong absorption bands to the ν_3 and ν_4 mode of the TiO_6 octahedron. The Raman spectrum of a.o. Sr_2TiO_4 has been given in Ref. (*4*) together with a factor group analysis. A complete site group analysis of the TiO_6 octahedron in solids was possible for La_2MgTiO_6 (*5*). This compound has ordered perovskite structure with one undistorted TiO_6 octahedron per primitive cell. The following assignment was made: ν_1, 725 cm^{-1}; ν_3, 600 cm^{-1}; ν_4, 460 and 412 cm^{-1}; ν_5, 487 and 499 cm^{-1}.

It is the aim of the present paper to investigate the vibrational spectra of the compounds

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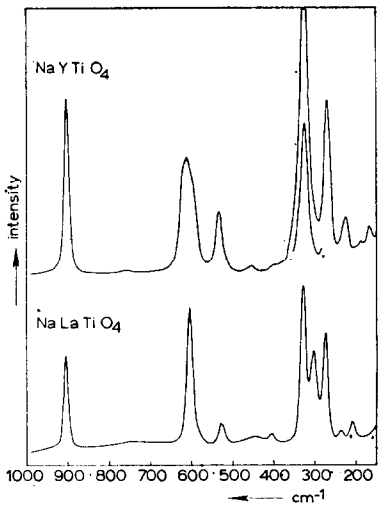

FIG. 2. Raman spectra of $NaLaTiO_4$ and $NaYTiO_4$.

$NaLnTiO_4$ and to compare the results with those for La_2MgTiO_6 with regular TiO_6 octahedra that do not have oxygen ions in common and with those for Sr_2TiO_4 to investigate the influence of the order of the Na^+ and Ln^{3+} ions on the Sr^{2+} sublattice of Sr_2TiO_4. This influence was found to be very profound.

Experimental

Samples were prepared as described earlier (*1*). They were checked by X-ray analysis using Cu$K\alpha$ radiation. The way in which the vibrational spectra were obtained has been described previously (*5*). All measurements were performed at room temperature.

Results

Figure 2 gives the Raman spectra of $NaLaTiO_4$ and $NaYTiO_4$. Figure 3 presents the infrared spectrum of $NaYTiO_4$. Table I tabulates other spectra.

Discussion

We start with a factor group analysis. For Sr_2TiO_4 (space group D_{4h}^{17}) the following vibrational modes are expected: $2\ A_{1g} + 2\ E_g + 3A_{2u} + B_{2u} + 4E_u$, yielding 4 Raman-active modes and 7 infrared-active modes. Experimentally 3 strong and 6 much weaker Raman lines have been observed (*4*) and 6 infrared bands (Table 1). This agrees reasonably with the expected numbers. For $NaLnTiO_4$ (space group C_{4v}^1) the situation is more complicated, since this space group is not body-centered as in the case of D_{4h}^{17}. The number of modes is therefore higher: $11\ A_1 + 2\ B_1 + 13\ E$. In view of this, we expect 26 Raman-active modes and 24 infrared-active modes.

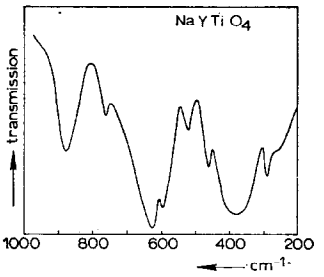

FIG. 3. Infrared spectrum of $NaYTiO_4$.

TABLE I

VIBRATIONAL SPECTRA OF SOME OF THE COMPOUNDS STUDIED (ALL VALUES IN cm^{-1})[a]

	$NaLaTiO_4$	$NaGdTiO_4$		Sr_2TiO_4
	IR	IR	R	IR
ν_1	890	880	905	
		760	770	
ν_3	610	625		585
			620	
		600 (*sh*)		525 (*sh*)
ν_5(?)	535	520	535	
				480
		430 (*sh*)	455	
ν_4	375	385		370
			345	
			320	
	280	290	270	~300 (*sh*)
	220	230	240	235
			220	

[a] R, Raman spectrum IR, infrared spectrum

Such large numbers are not observed, however. Counting even weak lines and bands, the total number of modes observed experimentally is about half the number predicted from a factor group analysis.

This seems to indicate that the influence of the superstructure at the larger cation sublattice is not profound. A superficial comparison between the vibrational spectra of $NaLnTiO_4$ and Sr_2TiO_4 reveals that this cannot be true. The spectra of the compounds $NaLnTiO_4$ contain a strong band at about 900 cm^{-1}. This band is absent in Sr_2TiO_4. In view of its spectral position this band can only be due to a Ti–O vibrational mode. The fact that this mode is observed at relatively high wavenumbers must be connected with the superstructure on the larger cation lattice.

Since factor group analysis is not very promising to investigate this phenomenon further, we tried the internal mode approach. Let us consider the TiO_6 octahedron in $NaLnTiO_4$ as a molecular group with internal modes in which the other lattice constituants do not participate in first approximation. The site symmetry of the TiO_6 octahedron is C_{4v} (see Fig. 1). Table II gives the vibrational modes to be expected in comparison with those for a regular octahedron. We will now discuss where the internal modes of the TiO_6 octahedron can be expected:

ν_1. This symmetrical stretching mode has been observed in the Raman spectrum of La_2MgTiO_6 at 725 cm^{-1} (*5*). The strong band in the Raman and infrared spectra at about 900 cm^{-1} in the case of $NaLnTiO_4$ must be due to ν_1. It is situated at very high wavenumbers. Its strong intensity in the infrared spectrum where it is completely forbidden for a regular octahedron indicates a strong deviation from cubic symmetry. We will try to explain the peculiar behavior of the ν_1 mode in $NaLnTiO_4$ below.

ν_3 *and* ν_4. These modes (asymmetrical stretching and bending, respectively) are always observed as strong absorption bands in the infrared in the case of titanate perovskites or related compounds: in La_2MgTiO_6 at 600 and about 435 cm^{-1} (*5*), in $SrTiO_3$ at 610 and 395 cm^{-1} (*3*), and in Sr_2TiO_4 at 585 and 370 cm^{-1}, respectively. We, therefore, assume that the strong bands at about 610 and 375 cm^{-1} in the infrared spectra of $NaLnTiO_4$ (values for Ln = La) are essentially the ν_3 and ν_4 modes, respectively. In view of the C_{4v} symmetry (see Table II), a splitting is to be expected. This is observed experimentally (Table I and Fig. 3). The splitting increases in the sequence La→Lu. It is quite plausible that the tetragonal field strength increases also in this sequence (compare Fig. 1). As a consequence, the strong Raman line at about 610 cm^{-1} is also assigned to the ν_3 mode. Its high intensity indicates again the strong deviation from inversion symmetry.

ν_2. This mode has usually extremely weak intensity (*6*), so that it is not discussed here.

The weak band at 760 cm^{-1} observed in the greater part of the spectra is at very high wavenumbers if it should correspond to ν_2. Perhaps this band is an overtone of the strong infrared absorption band at 375 cm^{-1} (ν_3).

ν_5. In La_2MgTiO_6 this mode is observed around 495 cm^{-1}. It is therefore tempting to ascribe the bands around 500 cm^{-1} to this mode.

This gives a rough and incomplete assignment of the vibrational spectra of compounds $NaLnTiO_4$. We are left with some strong bands around 300 cm^{-1}. These must be due to external lattice modes. In view of the ionic charges in the present compounds, these are probably located in the Ln–O layer. In this connection, it may be remarked that the compounds

TABLE II

SELECTION RULES FOR VIBRATIONAL MODES OF AN OCTAHEDRAL GROUP UNDER O_h AND C_{4v} SYMMETRY[a]

Mode	Representation	
	O_h	C_{4v}
ν_1	A_{1g} (R)	A_1 (R, IR)
ν_2	E_g (R)	A_1 (R, IR) + B_1 (R)
ν_3, ν_4	T_{1u} (IR)	$A_1 + E$ (both R, IR)
ν_5	T_{2g} (R)	B_2(R) + E (R, IR)

[a] R, Raman active; IR, infrared active.

LnOCl (*7*) and Ln_2MoO_6 (*8*), which also contain Ln–O layers with a slightly different structure, show also strong absorption in the region around 300 cm^{-1}.

We will now try to account for the strong deviation from cubic symmetry of the TiO_6 octahedron using structural arguments. For this purpose, we have numbered the oxygen ions around the Ti^{4+} ion as indicated in Fig. 1. None of these oxygen ions obeys Pauling's electrostatic valence rule (*9*). According to this rule, the valence of each anion (in our case, 2) is exactly or nearly exactly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations. This strength s is defined as $s = z/v$, where ze is the electric charge of the cation and v its coordination number. For oxides, Pauling's rule reads

$$\sum_i z_i/v_i = 2.$$

For O_1 in $NaLnTiO_4$, however, the left-hand side of this equation yields only $1\frac{2}{9}$. For O_2, on the other hand, this value is much higher than 2, viz. $2\frac{1}{3}$. For the other O anions (inside the titanate layer) it is $2\frac{2}{9}$. In the case of Sr_2TiO_4 Pauling's rule is also not satisfied (O_1 and O_2, $1\frac{7}{9}$; the other O's $2\frac{2}{9}$). It is the order of the Na^+ and Ln^{3+} ions which yields values that are unacceptable: $1\frac{2}{9}$ for O_1! There is one obvious possibility to compensate the shortage of electrostatic bond strength of this anion, viz. a displacement of the Ti^{4+} ion from the octahedral center towards the O_1 ion. As a consequence we expect that the Ti–O_1 bond strength is exceptionally high. The consequence of this model is that the ν_1 mode situated at relatively high wavenumbers is thought of as a stretching vibration located mainly in the Ti–O_1 bond. This explains also the high intensity of ν_1 in the infrared spectrum.

It is interesting to compare our value for ν_1 (about 900 cm^{-1}) with values observed for the Ti–O stretching vibration in some molecular compounds. Siebert (*10*) states that the Ti–O bond has considerable double-bond character, if the stretching vibration lies above 800 cm^{-1}. Dehnicke (*11*) gives 836 cm^{-1} for Ti–O stretching in $TiOCl_2$ and 1078 cm^{-1} for Ti–O in $TiOCl_2 \cdot 2POCl_3$. He assumes that this value corresponds to a real double bond and quotes also the value for the V=O stretching of $VOCl_3$: 1035 cm^{-1} (*12*). In $VOCl_3$ the presence of a vanadyl group is generally accepted.

From these values we learn that our value of 900 cm^{-1} indicates that the Ti–O_1 bond is very strong. Qualitatively, it is somewhere between a single and a double bond. This occurs because of the superstructure of the Na^+ and Ln^{3+} ions which results in a poor charge compensation. It may be even anticipated that the Ti^{4+} ion is so strongly displaced that it must be considered as five-coordinated. In view of this, a crystal structure refinement of the compounds $NaLnTiO_4$ is challenging, but, we ourselves are not able to perform it.

Considerations like those presented above have a more general applicability. Consider, for example, the crystal structure of Gd_2SiO_5 (*13*). This structure contains two types of oxygen anions: 80% belong to the SiO_4 tetrahedral complex, 20% are not silicon bonded. The latter type of oxygen anions are surrounded tetrahedrally by four Gd^{3+} ions, three of which have seven-coordination, the fourth nine-coordination. Pauling's valence rule gives for this oxygen ion 1.62, a value much too low. This is compensated by a short distance between the Gd^{3+} ions and these anions. This is comparable to the shift of the Ti^{4+} ion described above.

Further Felsche (*14*) has given a striking correlation between the individual Si–O bond lengths in a large number of silicates and the charge balance on the oxygen ions. He, however, used a correction on Pauling's electrostatic valence rule for the cation–anion distance which seems to be quite reasonable.

Finally, we note that in none of the infrared spectra of titanates compiled in a recent publication (*15*) has a strong absorption around 900 cm^{-1} been observed, except in the case of what the authors call $Bi_2(TiO_3)_2$. In view of phase diagram studies (*16*), this material probably consists of mainly $Bi_4Ti_3O_{12}$. The latter compound has a layer structure consisting of perovskite-like and Bi–O layers (*17*). This compound has very short Ti–O distances in the perovskite layer (1.75 Å). These bonds might be responsible for the infrared absorption around 900 cm^{-1}. We prepared $Bi_4Ti_3O_{12}$ and found that its infra-

red spectrum resembles very much the spectrum of "$Bi_2(TiO_3)_2$", but that the band at about 940 cm^{-1} is absent. The one at 810 cm^{-1}, however, is present. The Raman spectrum shows a strong line at 855 cm^{-1}. In addition, both spectra contain bands in the region 550–600 cm^{-1} (asymmetric Ti–O stretching, ν_3), so that those present in the region 800–850 cm^{-1} may be due to the Ti–O bonds with short distances.

In conclusion, we note that we did not observe ferroelectricity for these compounds, either at 300°K or at 77°K.

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