

VIBRATIONAL SPECTRA OF ORDERED PEROVSKITES

A. F. CORSMIT, H. E. HOEFDRAAD and G. BLASSE
Solid State Chemistry Department, University of Utrecht, Utrecht, The Netherlands

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Abstract—The vibrational spectra of the molecular $M^{6+}O_6$ ($M = Mo, Te, W$) group in ordered perovskites of the type $Ba_2M^{2+}M^{6+}O_6$ are reported. These groups have symmetry O_h , whereas their site symmetry is also O_h . An assignment of the internal vibrations is presented.

INTRODUCTION

THE VIBRATIONAL spectra of octahedral anionic groups in solids are usually considered to be more complex than those of the analogous tetrahedral groups (see e.g. Refs. [1, 2]). Remembering the successful efforts to interpret the vibrational spectra of molecules like SF_6 in the gaseous or liquid phase [3] it seems tempting to start investigations on regular octahedral anionic groups in solids with high symmetry. A very suitable crystal structure for this purpose is the ordered perovskite structure [4]. This structure has been found for e.g. Ba_2CaWO_6 . In this compound the WO_6 octahedra are regular, i.e. O_h symmetry, the field at the octahedral group has also O_h symmetry, and in addition, the WO_6 octahedra do not have oxygen ions in common. Each primitive unit cell contains one tungstate group only. In this paper the vibrational spectra of Ba_2CaMoO_6 , Ba_2CaTeO_6 , Ba_2CaWO_6 and Ba_2MgWO_6 are presented. To our knowledge only Hauck [5] has published i.r. data on compounds of this type. These, however, are incomplete.

EXPERIMENTAL

Samples were prepared by usual techniques (see e.g. Refs [4, 6]). Starting materials were high-purity $BaCO_3$, $CaCO_3$, $MgCO_3$, MoO_3 , TeO_2 and WO_3 . Final firing was carried out in air or O_2 at $1200^\circ C$ or higher. Samples were checked on a Philips X-ray diffractometer using $CuK\alpha$ radiation.

I.R. 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. All measurements were carried out at room temperature.

RESULTS

In Fig. 1 the Raman spectra of Ba_2CaWO_6 and Ba_2CaTeO_6 are presented. The intensity of the Raman band at about 650 cm^{-1} was extremely low in the case of the molybdate and the tungstates.

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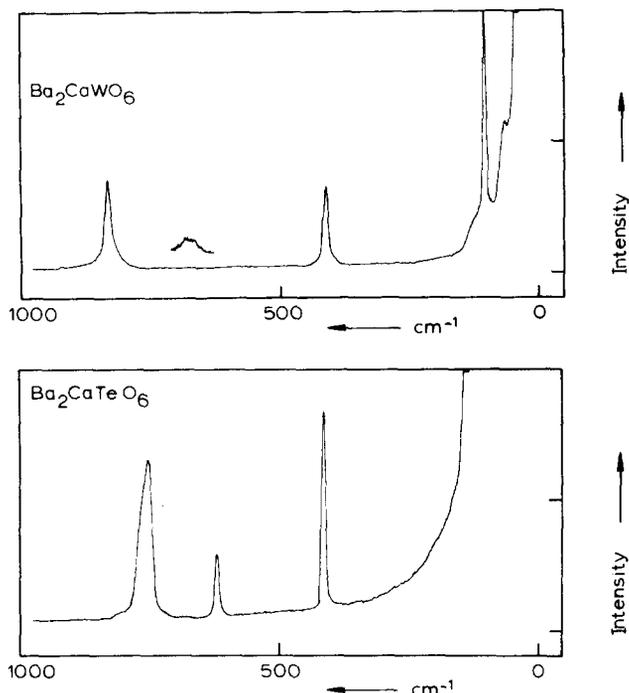


Fig. 1. Raman spectra of Ba_2CaWO_6 and $\text{Ba}_2\text{CaTeO}_6$. The inset around 675 cm^{-1} in the case of Ba_2CaWO_6 has been enlarged by a factor of 20.

The i.r. spectra show three bands. The strong band in the region $600\text{--}700\text{ cm}^{-1}$ shows clearly a shoulder. In the far i.r. region ($200\text{--}400\text{ cm}^{-1}$) two distinct bands are observed.

In Table 1 the frequencies corresponding to the maxima of the vibrational bands are given.

We further noted that part of the compounds under investigation, viz. $\text{Ba}_2\text{CaMoO}_6$ and Ba_2CaWO_6 react violently with water under the formation of $(\text{Ba}, \text{Ca})\text{MoO}_4$ or $(\text{Ba}, \text{Ca})\text{WO}_4$ and $(\text{Ba}, \text{Ca})(\text{OH})_2$. The compound $\text{Ba}_2\text{CaTeO}_6$ reacts much slower, whereas Ba_2MgWO_6 does not react at all. This decomposition is of importance if the KBr and CsI used for the pellet-technique is not completely dry.

Table 1. Vibrational spectra of ordered perovskites (cm^{-1})

Compound	Raman				Infrared	
$\text{Ba}_2\text{CaMoO}_6$	812 (s)	650 (vw)	416 (m)	598 (s,sh)	357 (s)	292 (s)
$\text{Ba}_2\text{CaTeO}_6$	752 (s)	618 (m)	412 (s)	685 (s,sh)	400 (s)	284 (s)
Ba_2CaWO_6	832 (s)	675 (vw)	410 (s)	628 (s,sh)	327 (s,sh)	289 (m)
Ba_2MgWO_6	817 (s)	680 (vw)	444 (s)	622 (s)	388 (s)	319 (m)
Assignments	ν_1	ν_2	ν_5	ν_3	ν_4	

(s): strong, (m): medium, (vw): very weak, (sh): shoulder.

DISCUSSION

We assume that the binding forces in the $M^{6+}O_6$ octahedron are large compared with the crystal-binding forces. In that case the frequencies of the internal vibrations of this group in the solid ought to be close to the frequencies of the free-ion modes. Furthermore, the external modes ought to lie at lower frequencies than the internal modes. Group theoretical considerations represent the normal vibrations of an octahedral molecule as

$$A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}.$$

The modes A_{1g} , E_g and T_{2g} are Raman-active, the two modes T_{1u} i.r.-active, whereas T_{2u} is inactive. Since there is only one $M^{6+}O_6$ group per primitive unit cell we expect three bands in the Raman and two in the i.r. spectra.

Our Raman spectra show in fact three bands if we neglect a number of bands at very low wavenumbers (external modes). The strong Raman line with the highest frequency is assigned to $\nu_1(A_{1g})$, the line with the lowest frequency to $\nu_5(T_{2g})$. In between these two we find $\nu_2(E_g)$ with very low intensity in the case of WO_6 and MoO_6 . Woodward *et al.*[7, 8] have drawn attention to strong variations of the intensity of the $\nu_2(E_g)$ vibration. They related these variations to differences in bonding type.

The ratio of the intensity I_1 of ν_1 to I_2 of ν_2 can be given by

$$\frac{I_1}{I_2} = \frac{5A_1[1 + (2\alpha'_p/\alpha'_i)]^2}{13A_2[1 - (\alpha'_p/\alpha'_i)]^2}$$

where $A_1 = (\nu_0 - \nu_1)^4/\nu_1[1 - \exp(-h\nu_1/kT)]$, ν_0 being the exciting frequency[7].

Further α'_i and α'_p are the derived bond polarizabilities with respect to bond stretching along and perpendicular to the bond direction respectively.

A high value of I_1/I_2 as observed for the WO_6 and MoO_6 group indicates a value of α'_p/α'_i approaching one. This can be realized only if the amount of π -bonding is considerable. We can expect that in the case of W^{6+} and Mo^{6+} with p^6 configuration, i.e. with low-lying empty $t_{2g} - d$ orbitals, π -bonding is of more importance than in the case of Te^{6+} with d^{10} configuration. This has been applied by one of us in structural considerations on oxides with cations of these types[9]. We, therefore, assume that the low intensity of the ν_2 vibration is another indication of the importance of π -bonding in the case of highly-charged cations with noble-gas configuration in octahedral coordination. In accordance with this a very low intensity of ν_2 has been observed for the $Nb^{5+}Cl_6$ and $Ta^{5+}Cl_6$ octahedra[10]. In K_2NiF_6 , however, ν_2 has an intensity roughly equal to that of ν_1 [11]. In the $Ni^{4+}F_6$ group π -bonding cannot be important because the t_{2g} orbitals are completely filled (Ni^{3+} has d^6 low-spin configuration).

We now turn to the i.r. spectra. Two bands are expected, viz. $\nu_3(T_{1u})$ and $\nu_4(T_{1u})$. In fact we find three bands. The two bands at higher frequency are assigned to ν_3 and ν_4 (see Table 1). The band around 300 cm^{-1} is ascribed to an

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external vibration. It is not impossible that this vibration belongs to the $M^{2+}O_6$ octahedron. Evidence for these assignments comes from the following facts

(a) If $M^{2+} = Ca^{2+}$ the latter frequency is nearly independent of the choice of M^{6+} (in contradistinction to the other frequencies).

(b) Tarte [12] gives the region $300-450\text{ cm}^{-1}$ for the i.r. absorption of the MgO_6 octahedron in oxides. Our value of 319 cm^{-1} is within this range.

(c) In K_2NiF_6 with the same structure (Ni^{4+} on the M^{6+} sites, but a vacancy on the M^{2+} sites) only two i.r. bands have been observed [11].

The fact that at least part of the i.r. bands of the $M^{6+}O_6$ group show a shoulder seems to indicate deviations from pure cubic symmetry. Our X-ray diagrams do not show evidence for this. It is a well-known fact, however, that pseudo-cubic perovskites can show serious deviations from cubic symmetry at the octahedral cation-sites (see e.g. Ref.[13]). In order to study this problem further the present work is now extended to ordered perovskites with serious deviations from cubic symmetry.

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