J. inorg. nucl. Chem., 1975, Vol. 37, pp. 1347–1351. Pergamon Press. Printed in Great Britain

VIBRATIONAL SPECTRA OF SOLID SOLUTION SERIES WITH ORDERED PEROVSKITE STRUCTURE

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(*Received* 2 *September* 1974)

Abstract—I.R. and Raman spectra are reported for the following three systems: $Ba_2CaMo_{1-x}Te_xO_6$, $Ba_{2-x}Sr_xMgWO_6$ and $Ba_2Ca_{1-x}Mg_xWO_6$. In the first series the internal vibrations of the $M^{6+}O_6$ octahedra do not influence each other. The intensity of ν_1 (MoO_6) is five times that of ν_1 (TeO_6). In the second system there is a gradual, but no linear variation with the composition parameter x. In the third system selection rules are lifted and new bands appear. Where possible these changes in the spectra are related to the structure of the compositions.

1. INTRODUCTION

RECENTLY there has grown interest in the vibrational spectra of 1:1 ordered perovskites[1–5]. These compounds with general formula $A_2BB'O_6$ offer a unique possibility to study the vibrational spectra of $B'O_6$ octahedra, if B' is a highly charged cation (I^{7+}, Mo^{6+}, Te^{6+}, W^{6+}, Nb^{5+}, Sb^{5+}). This is mainly due to the simple and highly symmetric crystal structure. It has been shown that the vibrational spectra give information on the symmetry of the $B'O_6$ octahedron[1, 2]. For these reasons it seemed interesting to study the vibrational spectra of mixed crystals with ordered perovskite structure. The spectra may show the influence of a mixed site occupation and, reversely, the dependence of the spectra on the composition of a mixed crystal series may give information on structural details of the series. In this work we have considered three series, in which the B', A and B ions are varied, respectively. These are $Ba_2CaMo_{1-x}Te_xO_6$, $Ba_{2-x}Sr_xMgWO_6$ and $Ba_2Ca_{1-x}Mg_xWO_6$. The deviations in the spectra of the mixed compositions from those of the end members of each series increase in this sequence.

2. EXPERIMENTAL

Samples were prepared as described previously[1–3]. They were checked by X-ray analysis. The vibrational spectra were measured in the same way as before[1–3]. All measurements were performed at room temperature. In the case of Ba_2CaMoO_6 extremely dry KBr has to be used for the pellets, since otherwise water reacts with the molybdate to give (Ba, Ca)MoO_4 and (Ba, Ca)$(OH)_2$.

3. RESULTS AND DISCUSSION

(a) *The system* $Ba_2CaMo_{1-x}Te_xO_6$

The series $Ba_2CaMo_{1-x}Te_xO_6$ shows complete miscibility. The vibrational spectra can be described by a superposition of the spectra of the end members ($x = 0$ and 1). The position of the internal vibrations of the MoO_6 and TeO_6 group does practically not depend on x. New bands are not induced. This is shown in Fig. 1 for the Raman spectrum of $Ba_2CaMo_{0\cdot1}Te_{0\cdot9}O_6$ as an illustrative example. This observation confirms the interpretation of the higher-frequency bands in the spectra of ordered perovskites as internal vibrations of the $B'O_6$ octahedron. Similar observations were made for the series $Ba_2CaW_{1-x}Te_xO_6$[6].

The study of solid solution series of this type makes it possible to arrive at a reasonably accurate estimate of the intensity ratio of the vibrational mode of two different $B'O_6$ octahedra. In the series $Ba_2CaMo_{1-x}Te_xO_6$ the most striking intensity difference is that for the ν_1 mode of the TeO_6 and MoO_6 group. Figure 1 shows that the composition with 10% molybdenum shows a Raman spectrum with comparable intensity of the ν_1 mode of the MoO_6 and TeO_6 octahedra. By taking integrated intensities we found that ν_1 (MoO_6) is five times more intense than the ν_1 (TeO_6). For the ratio between ν_1 (WO_6) and ν_1 (TeO_6) we found this ratio to be about two.

It seems not easy to account for this in a quantitative way. We can show, however, that the higher intensity for the d^0 complexes relative to the d^{10} complex is not unexpected. According to Kettle *et al.*[7] the intensity of ν_1 is proportional with $\nu^4(b+2a)^2$, where ν is the ν_1-frequency and b and a are the bond polarisation changes along and perpendicular the bond axis, respectively. The lower spectral position of ν_1 (TeO_6) is insufficient to explain the intensity ratio of five. In Ref.[1] we argued that the value of a is expected to be larger for the MoO_6 octahedron than for the TeO_6 octahedron. This explained the low intensity of the ν_2 mode in the Raman spectrum of the molybdates and tungstates. At the same time it can also be responsible for a higher ν_1 intensity. It is impossible, however, to predict in a simple way, how the factor b varies from molybdate, tungstate to tellurate.

Finally we draw attention to the spectra of the end member Ba_2CaMoO_6. Although this compound has been reported as a cubic perovskite with $a = 8\cdot355$ Å[8], our spectra reveal that the symmetry of the MoO_6 octahedron must be considerably lower than cubic. In Fig. 2 the ν_3 mode in the i.r. spectrum is shown. For purely cubic symmetry this should be a single mode (symmetry species

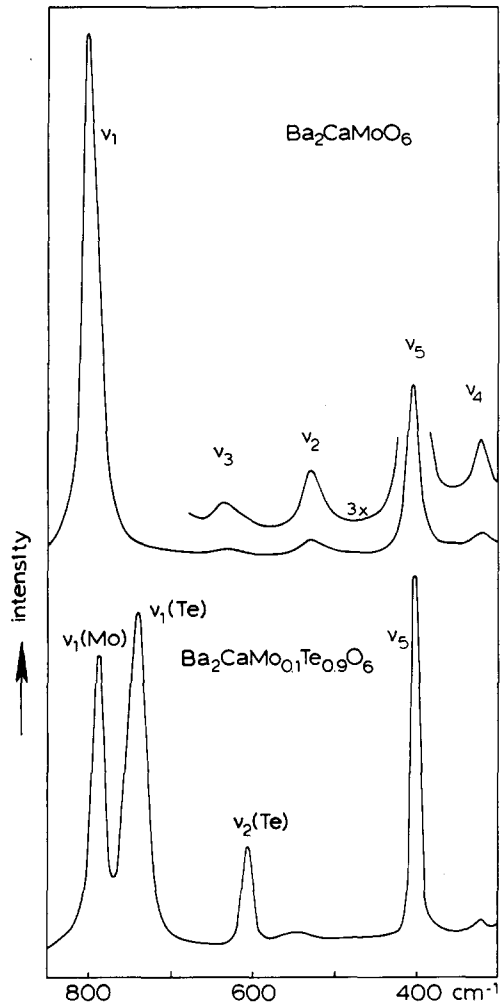

Fig. 1. Raman spectra of Ba_2CaMoO_6 and $Ba_2CaMo_{0.1}Te_{0.9}O_6$.

T_{1u}). The spectrum shows, however, that the threefold degeneracy has been removed completely. Its Raman spectrum (Fig. 1) shows also that the deviation from O_h symmetry must be considerable, since components of the ν_3 and ν_4 modes (both T_{1u} and, therefore, forbidden in the Raman spectrum) are observed in the Raman spectrum. This is not the case for the corresponding tungstate and tellurate [1]. Note that this assignment differs slightly from Ref. [1] and agrees with Ref. [4].

The marked distortion of the MoO_6 octahedron in Ba_2CaMoO_6 may be due to the fact that the Mo^{6+} ion is somewhat too small to fit an octahedral oxygen ion coordination. This in turn may be related to the non-existence of a number of molybdates with ordered perovskite structure, whereas the corresponding tungstates and tellurates are known [8, 9].

(b) *The system* $Ba_{2-x}Sr_xMgWO_6$

This series also forms a solid solution series for all values of x. There is a slight deviation from Vegard's rule

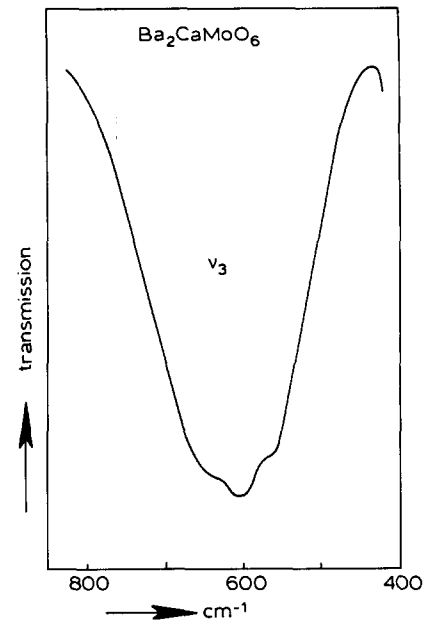

Fig. 2. I.R. spectrum of Ba_2CaMoO_6 in the Mo–O stretching frequency region.

(see Fig. 3). The influence of the chemical composition upon the internal vibrations of the tungstate group is small. There is a gradual shift in the position of the maxima as a function of x and the observed bands are broader for the solid solutions than for the end members

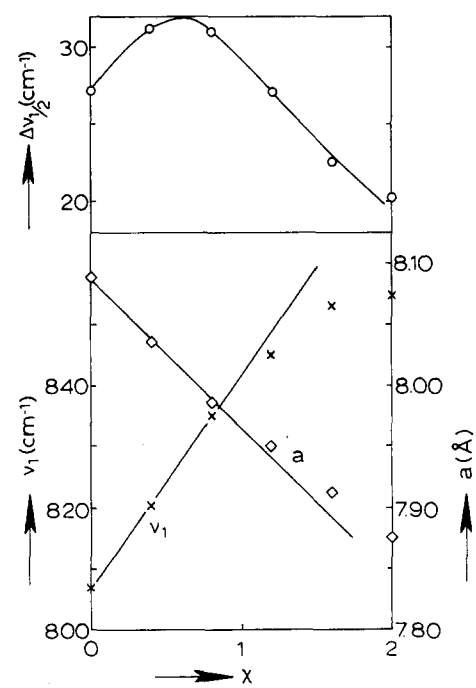

Fig. 3. Lattice parameter a, position of ν_1 frequency and half width of ν_1, $\Delta\nu_{1/2}$, in the system $Ba_{2-x}Sr_xMgWO_6$.

(especially in the Raman spectra). The data for ν_1 in the Raman spectra are given in Fig. 3 as an illustrative example. We note that the curve of $\Delta\nu_{1/2}$ vs x is strongly asymmetric due to the large difference in width of the ν_1 peak in the Raman spectra of Ba_2MgWO_6 and Sr_2MgWO_6. This may indicate a larger deviation from complete crystallographic order in Ba_2MgWO_6 than in Sr_2MgWO_6[10]. The increase of $\Delta\nu_{1/2}$ for mixed occupation of the A sites substantiates the arguments used in Ref.[10] to propose a deviation from complete order in these compounds.

It is further noteworthy that the position of the internal WO_6 vibrational bands is stronger influenced by replacing Ba in Ba_2MgWO_6 by Sr than by replacing Sr in Sr_2MgWO_6 by Ba (see Fig. 3). The experimental results suggest that the non-linearity of the ν_1 position vs x is connected with the non-linearity of the lattice parameter vs x (Fig. 3). A possible explanation may be the following. The Ba compound shows a smaller deviation from cubic symmetry than the Sr compound (see also below). This suggests that in the Sr compound there is a larger amount of cooperative buckling of the corner-shared octahedra which enlarges the unit cell[8, 11]. The deviation from Vegard's rule in the Sr-rich region of the system can then be ascribed to the occurrence of buckling. Introduction of Sr in the Ba compound will cause in first approximation a shortening of bond lengths, resulting in an increasing value of a.o. the ν_1 frequency. At higher Sr concentrations there will also occur buckling of the octahedra as certainly is present in the Sr compound. This may influence the internal WO_6 frequencies less than bond length shortening, resulting in a curve of the type observed experimentally.

Finally we compare the spectra of the Sr and the Ba end members of this series. In Fig. 4 the i.r.-active ν_3 has been drawn for both compounds. The ν_3 band for Sr_2MgWO_6 shows a more extensive splitting than the corresponding band for Ba_2MgWO_6 indicating a larger deviation from cubic site symmetry for the W^{6+} ion in $SrMgWO_6$. We further observed that ν_2 appears weakly in the Raman spectrum of Sr_2MgWO_6 (at 590 cm^{-1}), whereas it is absent in the Ba compound. This value agrees with those observed by Lentz[4] for other tungstates and may indicate that the previous assignment of the extremely weak 680 cm^{-1} band in the Raman spectrum of Ba_2MgWO_6[1] is incorrect. The different intensity of ν_2 indicates that the bonding in the WO_6 octahedra of the Sr and the Ba compound is slightly different.

(c) *The system* $Ba_2Ca_{1-x}Mg_xWO_6$

This series shows a broad miscibility gap from x is about 0·3 to about 0·8. This is probably due to the difference between the ionic radii of Mg^{2+} and Ca^{2+}. We note, however, that this broad miscibility gap forms an exception to the rule of thumb that the (linear) lattice parameters of isomorphous compounds must differ less than 5 per cent to have complete miscibility[12]. In the present case this difference is only 3·5 per cent. Note that $Ba_{2-x}Sr_xMgWO_6$ where this value is 3 per cent does not show a miscibility gap. Of all systems described in this paper the single-phase compositions $Ba_2Ca_{1-x}Mg_xWO_6$ show the strongest influence of a mixed occupation of one of the crystallographic sites on their spectra.

Figure 5 shows Raman spectra of Mg-rich compositions and Fig. 6 those of Ca-rich compositions. In Fig. 7 the i.r. ν_3 band of the end members Ba_2MgWO_6 and Ba_2CaWO_6 is compared

First we consider the magnesium-rich single-phase region. Inspection of Fig. 5 learns that the replacement of

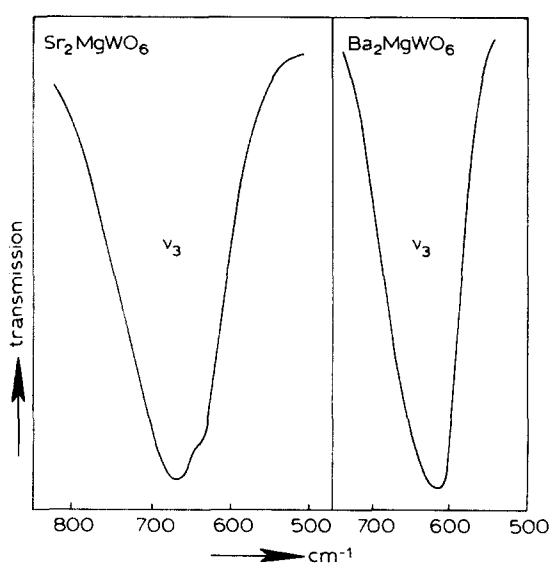

Fig. 4. I.R. spectra of Sr_2MgWO_6 and Ba_2MgWO_6 in the W–O stretching frequency region.

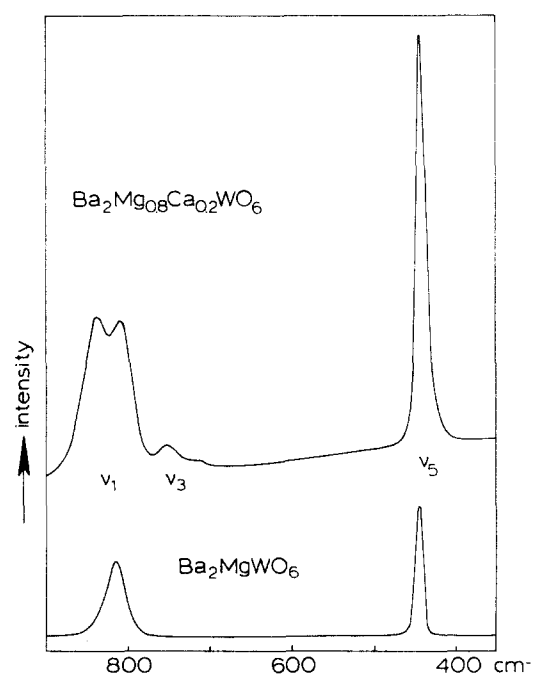

Fig. 5. Raman spectra of Ba_2MgWO_6 and $Ba_2Mg_{0\cdot8}Ca_{0\cdot2}WO_6$.

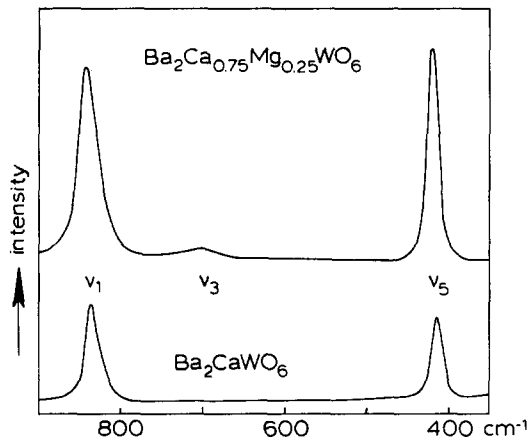

Fig. 6. Raman spectra of Ba_2CaWO_6 and $Ba_2Ca_{0.75}Mg_{0.25}WO_6$.

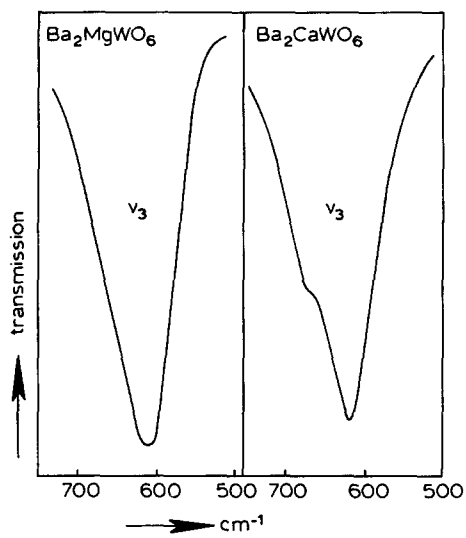

Fig. 7. I.R. spectra of Ba_2MgWO_6 and Ba_2CaWO_6 in the W–O stretching frequency region.

Mg in Ba_2MgWO_6 by Ca changes the Raman spectrum drastically: there occur clearly two ν_1 bands in the region 800–850 cm^{-1} and additional new, but weak bands in the region 700–750 cm^{-1}. The stretching region of the infrared changes too: the ν_3 band with a maximum at 610 cm^{-1} (see Fig. 7) in the case of Ba_2MgWO_6 obtains a marked shoulder at about 700 cm^{-1}, if Mg is replaced by Ca and a new, weak band appears at about 810 cm^{-1}. These results are interpreted as follows.

The two Raman ν_1 lines peak at 815 and 840 cm^{-1}. The former coincides with the ν_1 peak of Ba_2MgWO_6 and shows a decreasing intensity with increasing Ca contents. It is therefore assigned to the ν_1 mode of a WO_6 octahedron surrounded by six Mg^{2+} ions. The 840 cm^{-1} peak shows an increasing intensity with increasing Ca contents. It is ascribed to the ν_1 mode of a WO_6 octahedron with five Mg^{2+} ions and one Ca^{2+} ion (configurations with more Ca^{2+} ions have a considerably lower concentration in this single-phase region and have their ν_1 peak probably in the region at somewhat higher wavenumbers). The 700 cm^{-1} shoulder in the infrared spectrum is ascribed to the same complex. Note that the Ca^{2+}-surrounded WO_6 groups have their stretching frequencies at higher wavenumbers than those without Ca^{2+}. This may be due to the fact that the large Ca^{2+} ion on a Mg^{2+} lattice site forces the surrounding oxygen ions to expand so that the W–O distances will shorten resulting in higher stretching frequencies.

A WO_6 group with a mixed surroundings does not posses inversion symmetry as the regular WO_6 group in Ba_2MgWO_6. Consequently the exclusion principle is not strictly valid. We therefore assign the weak Raman peaks in the region 700–750 cm^{-1} to components of the ν_3 mode of WO_6 groups with mixed surroundings and the weak i.r. peak around 810 cm^{-1} to the ν_1 mode of these groups.

The changes in the Ca-rich single-phase region are less pronounced. This is shown in Fig. 6 for the Raman spectra. The ν_1 peak shifts only slightly to higher wavenumbers upon introduction of Mg in Ba_2CaWO_6. At the same time a new band appears at about 700 cm^{-1} (see Fig. 6). In the i.r. spectrum the ν_3 band shows a slight broadening. No new bands occur. The Raman band at 700 cm^{-1} is assigned to ν_3 due to the absence of inversion symmetry for WO_6 octahedra with mixed surroundings.

In Fig. 7 the ν_3 bands of Ba_2MgWO_6 and Ba_2CaWO_6 are compared. It is clear that the splitting in the case of the calcium compound is more pronounced than for the magnesium compound. The former compound will therefore show a larger deviation from cubic site symmetry for tungsten. The result of the replacement of Ca in Ba_2CaWO_6 by Mg may then be a decrease of the amount of buckling of the octahedra. This can explain the small influence of Mg upon the vibrational spectra of Ba_2CaWO_6 in contrast with the influence of Ca upon the spectra of Ba_2MgWO_6 where bond distances, not bond angles are influenced. This argument runs parallel with considerations used above for the system $Ba_{2-x}Sr_xMgWO_6$.

Acknowledgements—The author is greatly indebted to Mr. G. P. M. van den Heuvel for the preparation of the samples and the i.r. measurements and to Dr. J. H. van der Maas for the measurement of the Raman spectra.

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