JOURNAL OF SOLID STATE CHEMISTRY 42, 158–162 (1982)

Raman and Infrared Spectra of Lanthanum Molybdate

S. SHEIK SALEEM AND G. ARULDHAS*

Department of Physics, University of Kerala, Kariavattom 695581, India

Received August 17, 1981; in revised form November 4, 1981

The infrared and Raman spectra of gel-grown lanthanum molybdate were recorded. Group theoretical analysis was carried out and a vibrational assignment proposed based on C_{2h} symmetry. Factor group and site effects are discussed.

Introduction

Trivalent rare earth molybdates and tungstates with chemical formulas $L_2(MoO_4)_3$ and $L_2(WO_4)_3$, where L is a rare earth element, crystallize in at least seven different structures (*1*). The study of rare earth molybdates and tungstates is important because of their fluorescence (*2*), laser action (*3*), and ferroelectricity (*4*). The ferroelectric and ferroelastic properties of gadolinium molybdate, including the soft-mode study (*5*) and the temperature-dependent Raman scattering (*6, 7*), have been investigated extensively (*8–11*). A good deal of work on the mechanism of the ferroelectric phase transformation has been carried out on some of these rare earth molybdates (*12*). The NMR and ir of lanthanum molybdate and tungstate have been carried out to gain information about their crystal structures (*13*). However, not much work has been reported on the vibrational spectroscopy of these rare earth molybdates, except for gadolinium, terbium, and samarium molybdates. In the present investigation Raman and infrared spectra of gel-grown lanthanum molybdate were recorded and analyzed using factor group analysis.

Lanthanum molybdate belongs to an ordered defect scheelite type (*14*). The structure is related to the $CaWO_4$ scheelite structure (*15*), from which it can be derived through vacancy ordering of $\frac{1}{3}$ of the Ca sites so as to comprise nine scheelite subcells. The crystallographic formulas can be written as $La_{2/3}\,\square_{1/3}\,(MoO_4)_3$, where $\square$ indicates vacant sites.

Experimental

Gel-grown lanthanum molybdate was used for the investigation. The details of growth and morphology have been given by Kurien and Ittyachen (*16*). The infrared spectrum was recorded in a Perkin–Elmer 599 spectrophotometer. A Spex Ramalog 1401 spectrophotometer equipped with a Spectra-Physics Model 165 argon ion laser was used to obtain the Raman spectrum of the powdered sample, which was placed in a capillary tube. The spectra were obtained in the Stokes region of the blue line at 4880 Å. Plasma lines of the laser were used for calibration of the instrument. Spectral

---

* To whom correspondence should be addressed.

0022-4596/82/050158-05$02.00/0

slitwidths of 250 to 50 μm were employed for different regions of the spectrum.

Factor Group Analysis

$La_2(MoO_4)_3$ crystallizes in a monoclinic system with space group $C2/c$ (C_{2h}^6) and has 12 formula units per unit cell (*14*). The primitive cell contains 18 molybdenums surrounded by oxygen tetrahedra. Of the 18 molybdenums, 2 are in the $C_2(2e)$ site, and the remaining 16 are in a general site C_1 (4 × 4*f*). The factor group analysis can be done either by correlating the site symmetry of MoO_4^{2-} ions in C_1 and C_2 sites and the lanthanum ions in C_1 sites to the factor group or by correlating the site group of each atom in the primitive unit cell individually to the factor group. Both will give the same total number of modes for each symmetry species. The 18 MoO_4 units form 5 different sets (4 × 4*f* and 1 × 2*e*) in the primitive unit cell. Each set is formed by one or more pairs of MoO_4 units. Each member of a pair is related to the other member by a center of symmetry. Coupled vibrational motions of the pair(s) of MoO_4 units related by the center of symmetry cause factor group splitting of site group bands. Further splitting also occurs because of multisite effects due to different sets of pairs. Differences in the molybdate ions will further perturb the band-splitting pattern of the vibrational spectrum. Table I illustrates the correlation of the internal vibrational modes for the MoO_4 units of $La_2(MoO_4)_3$ from the free MoO_4^{2-} ion group to the factor group with the site effects. The total active normal modes for the six formula units of $La_2(MoO_4)_3$ in the Bravais cell, as given by the factor group analysis, are 76*Ag*, 77*Bg*, 75*Au*, and 75*Bu*. Of these, 162 are internal vibrations of MoO_4^{2-} ions. The remaining 141 external modes are subdivided into 35*Ag*, 37*Bg*, 34*Au*, and 35*Bu* modes.

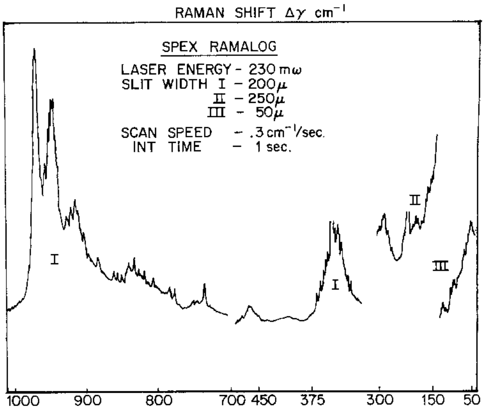
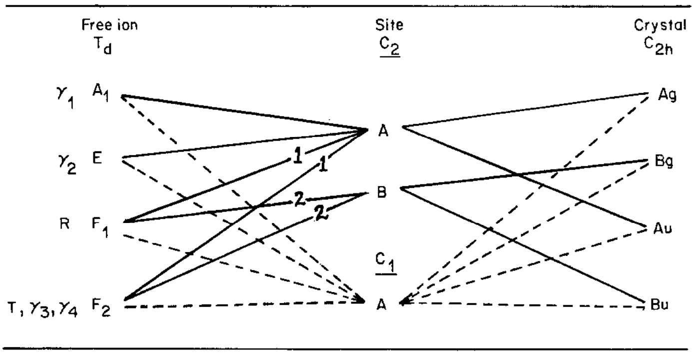


FIG. 1. Raman spectrum of $La_2(MoO_4)_3$.

Assignments and Discussion

The internal modes of the molybdate ion are expected to occur in the stretching

TABLE I



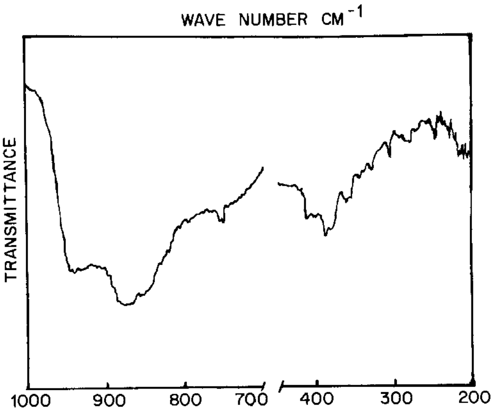


FIG. 2. Infrared spectrum of $La_2(MoO_4)_3$.

(750–950 cm^{-1}) and bending (250–400 cm^{-1}) regions, irrespective of its environment. For the external modes, the frequency strongly depends on the type of motion (translation or rotation) and on the nature of the cation. It is possible to make symmetry assignments by comparison with the normal modes of free molecules.

The observed spectra are expected to be very complex due to the presence of six formula units in the primitive unit cell. Also, group theory predicts 72 stretchings, (18*Ag*, 18*Bg*, 18*Au*, 18*Bu*) and 90 bendings (23*Ag*, 22*Bg*, 23*Au*, 22*Bu*). The Raman spectrum shows this complexity both in the stretching and bending regions. The infrared spectrum shows a very broad absorption in the stretching region (800–960 cm^{-1}) with four distinct peaks. The bending region is complex with 11 lines.

The rotational and translational modes of the molybdate ion and the lattice modes will fall in the low-frequency region, 0–250 cm^{-1}. The normal modes (stretching and bending) of the molybdate ion fall in the high-frequency region, 250–1000 cm^{-1}. The Raman and infrared spectra are shown in Figs. 1 and 2, respectively, and the vibrational frequencies are tabulated in Table II.

1000- to 250-cm^{-1} Region

Twenty-three lines observed in the Raman spectrum between 969 and 737 cm^{-1} are due to the γ_1 and γ_3 of the molybdate ion. All the 36 stretchings predicted by group theory could not be observed. The oxygen environment of the five different molybdenum atoms in $La_2(MoO_4)_3$ is almost perfectly tetrahedral with Mo–O distances between 1.73 and 1.82 Å; the averages for each molybdenum atom vary between 1.771 and 1.781 Å (*14*). A calculation of the phonon energies for the Mo–O stretchings, making use of the different Mo–O distances given by Jeitschko (*14*), is expected to give closely spaced energies,

TABLE II

VIBRATIONAL FREQUENCIES AND ASSIGNMENTS OF $La_2(MoO_4)_3$

Frequencies of free MoO_4^{2-} ion (cm^{-1})	Raman frequency (cm^{-1})	Infrared frequency (cm^{-1})	Assignment
$\gamma_1 = 891\ (A_1)^a$	969, 959 952, 950 948, 946 943	940 s, br	Symmetric stretching
$\gamma_2 = 381\ (E)$	374, 366 338, 330 323, 315	407, 397 m 352, 320 m	Symmetric bending
$\gamma_3 = 833\ (F_2)$	926, 916 913, 902 899, 885 859, 852 839, 834 824, 818 805, 780 744, 737	880 vs, br 855 s, br 750 s, sh	Asymmetric stretching
$\gamma_4 = 318\ (F_2)$	358, 342 333, 327 302, 291 284, 274 264	382 ms 377 sh 336, 300 w 287 vw 272 w, br 265 w	Asymmetric bending
	232, 209 201, 193 183	240, 255 w 210, 205 w	Rotational modes
	165, 161 134, 122 112		Translational modes
	100, 74 53		

[a] Symmetry: vs, very strong; s, strong; ms, medium strong; m, medium; vw, very weak; w, weak; br, broad; sh, shoulder.

which is actually the case observed for gadolinium molybdate (*17*). Even with single-crystal work on gadolinium molybdate, only 68 modes in total could be observed out of a possible 201 Raman active modes (*5b*).

The frequencies of the different normal modes of a free MoO_4^{2-} ion and their symmetries (*18*) are shown in Table II. The totally symmetric line at 969 cm^{-1} has been assigned to γ_1 of the molybdate ion at a C_2 site. The primitive unit cell contains two molybdate ions at a C_2 site. Hence, there should be two stretchings. The broadness of the line at 969 cm^{-1} may be due to these two γ_1 modes, vibrating with very close energy. Exact overlapping of these modes is equally possible since these two MoO_4^{2-} ions are in crystallographically equivalent sites. The strong broad band centered at 948 cm^{-1} with factor group splittings at 943, 946, 950, 952, and 959 cm^{-1} may be assigned to the γ_1 of the molybdate ions in general sites C_1. An assignment of this band to γ_3, the asymmetric stretching of the molybdate ion at the C_2 site, also seems reasonable since the band has the exact predicted factor group splittings. If this is the case, the broad band centered at 916 cm^{-1} with splittings at 926, 922, 913, and 899 cm^{-1} has to be assigned to γ_1 of the molybdate ions in the general site C_1. However, the intensity of this line (916 cm^{-1}) is very low when compared to the lines at 948 and 969 cm^{-1}. Further, this assignment tends to increase the difference in frequency between γ_1 of the molybdate ions at the C_2 and C_1 sites, which is not expected as all these ions are almost tetrahedral and their average Mo–O distances are very close. Therefore, the assignment of the line at 948 cm^{-1} to γ_1 of the molybdate ions in general site C_1 seems more probable. This assignment gives a factor group splitting of 16 cm^{-1} to the γ_1 mode and 27 cm^{-1} to the γ_3 mode, which is in conformity with the general observation that the factor group splitting of the γ_3 mode is larger than that of γ_1 (*19, 20*).

Discrepancies exist (*21–24*) in the assignments of γ_2 and γ_4 of the MoO_4^{2-} ion. From single-crystal data and valence force field analysis, an assignment of $\gamma_4 > \gamma_2$ is preferred (*25*). However, Busy and Keller (*18*) and Ullman *et al.* (*7*) prefer the assignment $\gamma_2 > \gamma_4$. Ullman *et al.* (*7*), in their work on $Gd_2(MoO_4)_3$, assign the lines between 385 and 300 to γ_2 and between 404 and 279 cm^{-1} to γ_4. In the present work there are 15 lines between 374 and 264 cm^{-1}. The exact number of lines could not be estimated because of the overlapping of the plasma line at 351 cm^{-1}. The labeling of γ_2 and γ_4 as internal modes is only approximate as mixing is expected with the lattice modes. Identification of the γ_4 and γ_2 components is difficult without single-crystal data. However, a tentative assignment is given in Table II.

In the infrared, a strong broad absorption between 740 and 960 cm^{-1} with distinct peaks at 750, 855, 880, and 940 cm^{-1} was observed in the Mo–O stretching region. The strong broad absorption is also indicative of closely spaced phonon energies. The assignment of the 11 lines between 407 and 265 cm^{-1}, which are due to the γ_4 and γ_2 modes of the molybdate ion, is given in Table II.

50- to 250-cm^{-1} Region

Ten lines observed between 232 and 53 cm^{-1} may be due to rotational and translational modes. The possibility that some of the lines are lattice modes cannot be excluded. Further, to distinguish between rotational and translational modes also is very difficult. But in general rotational modes are expected to have higher wavenumber and intensity than the translational modes. A tentative assignment is shown in Table II.

The observed broad structure of the

spectra may be due to the perturbation caused by the disorder, introduced into the crystal structure by vacancy ordering.

To conclude, the site approximation without the inclusion of factor group effect is insufficient to interpret the large number of bands and the mutual exclusion of frequencies observed in the spectra. The Mo–O stretching and bending frequencies occupy a wide range of the spectrum indicative of a large number of molybdate ions in the primitive unit cell.

Acknowledgments

The authors are thankful to Professor P. S. Narayanan for making available the Spex Ramalog for recording the spectrum and for the cordiality shown to one of us (S.S.S.) during his stay in I.I.Sc., Bangalore. Thanks are also due to Mr. K. V. Kurien, teacher fellow, Department of Physics, for providing the crystal. One of the authors (S.S.S.) is grateful to the CSIR for the award of a fellowship.

References

1. K. NASSAU, H. J. LEVINSTEIN, AND G. M. LOIACONO, *J. Phys. Chem. Solids* **28**, 1805 (1965).
2. R. E. McDONALD, J. J. VOGEL, AND J. W. BROOKMAN, *IBM J. Res. Dev.* **6**, 363 (1962).
3. G. E. PETERSON AND P. M. BRIDENBAUGH, *Appl. Phys. Lett.* **4**, 173 (1964).
4. L. E. CROSS, A. FOUSKOVA, AND S. E. CUMMINS, *Phys. Rev. Lett.* **21**, 812 (1968).
5. B. N. GANGULY, F. G. ULLMAN, R. D. KIRBY, AND J. R. HARDY, (*a*) *Solid State Commun.* **17**, 533 (1975); (*b*) *Phys. Rev. B* **13**, 1344 (1976).
6. P. A. FLEURY, *Solid State Commun.* **8**, 601 (1970).
7. F. G. ULLMAN, B. J. HOLDEN, B. N. GANGULY, AND J. R. HARDY, *Phys. Rev. B* **8**, 2991 (1973).
8. A. FOUSKOVA, *J. Phys. Soc. Japan* **27**, 1699 (1969).
9. A. W. SMITH AND G. BURNS, *Phys. Lett. A* **28**, 501 (1969).
10. A. KUMADA, *J. Appl. Phys. Japan* **39**, 258 (1970).
11. K. AIZU, A. KUMADA, H. YOMOTO, AND S. ASHIDA, *J. Phys. Soc. Japan* **27**, 511 (1969).
12. H. J. BORCHARDT AND P. E. BIERSTEDT, *Appl. Phys. Lett.* **8**, 50 (1966).
13. A. M. GOLUB, K. S. AGANIYASOV, V. V. MANK, AND YA. YA. SHCHERDAK, *Theor. Exp. Chem.* **3**, 286 (1970).
14. W. JEITSCHKO, *Acta Crystallogr. Sect. B* **29**, 2074 (1973).
15. A. ZALKIN AND D. H. TEMPLETON, *J. Chem. Phys.* **40**, 501 (1964).
16. K. V. KURIEN AND M. A. ITTYACHEN, submitted for publication.
17. L. L. BOYER AND J. R. HARDY, *Phys. Rev. B* **8**, 2205 (1973).
18. R. H. BUSY AND O. L. KELLER, JR., *J. Chem. Phys.* **41**, 215 (1964).
19. S. SHEIK SALEEM AND G. ARULDHAS, *Polyhedron,* in press.
20. P. J. MILLER, *Spectrochim. Acta Part A* **27**, 957 (1971).
21. R. G. BROWN, J. DENNING, A. HALLET, AND S. D. ROSS, *Spectrochim. Acta Part A* **26**, 963 (1970).
22. J. F. SCOTT, *J. Chem. Phys.* **48**, 874 (1968).
23. P. J. MILLER, R. K. KHANNA, AND E. R. LIPPINCOTT, *J. Phys. Chem. Solids* **34**, 535 (1973).
24. R. A. JHONSON, M. T. ROBERS, AND G. E. LEROI, *J. Chem. Phys.* **56**, 789 (1972).
25. L. J. BASILE, J. R. FERRARO, P. LABONVILLE, AND M. C. WALL, *Coord. Chem. Rev.* **11**, 21 (1973).