

Normal Modes of the MoO_4^{2-} Ion in $\text{Tb}_{1.8}\text{Eu}_{0.2}(\text{MoO}_4)_3$ Single Crystal

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Polarized Raman spectra (single crystal) at 300 K and infrared spectra (powder) at 300 and 77 K in the region $250\text{--}1000\text{ cm}^{-1}$ of a binary molybdate of terbium and europium have been recorded. Based on C_{2v} symmetry, group theoretical analysis has been carried out and a vibrational assignment is proposed.

Introduction

Rare earth molybdates with chemical formula $R_2(\text{MoO}_4)_3$, where R is a rare earth element, crystallize in different structures (1, 2). Of these, the molybdates with $R = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb},$ and Dy are isotypic and crystallize in an orthorhombic $Pba2$ structure at room temperature and transform to tetragonal $P4_2m$ system above the Curie temperature (3, 4). They exhibit ferroelectric (5) and ferroelastic (6) properties below the Curie temperature ($T_c \sim 160\text{--}180^\circ\text{C}$). Binary molybdates of $\text{Sm}, \text{Eu}, \text{Gd}, \text{Tb},$ and Dy with varying proportions are found to crystallize in the same orthorhombic $Pba2$ structure (3, 4). $\text{Tb}_{1.8}\text{Eu}_{0.2}(\text{MoO}_4)_3$ (herein-after termed TEMO) is a binary molybdate in which 10 at.% of Eu^{3+} ion replaces the Tb^{3+} ion in the $\text{Tb}_2(\text{MoO}_4)_3$ structure (3).

Vibrational spectroscopic studies of gadolinium, terbium, and samarium molybdates have been reported (7-10). The soft mode (8) and temperature dependant Raman scattering studies on gadolinium molybdate have also been investigated in detail (7, 11). Koningstein and Predhomme (12) have studied the Raman spectrum of terbium molybdate single crystal in the region $750\text{--}1000\text{ cm}^{-1}$ in an attempt to identify its structural similarity with gadolinium molybdate and also to know the site symmetry of the MoO_4^{2-} ions. Polarized ir and Raman spectra of double molybdates of the type $\text{KLn}(\text{MoO}_4)_2$ where $\text{Ln} =$ lanthanide ion have been reported recently (13, 14). Very recently we have investigated the infrared and Raman spectra of gel grown lanthanum molybdate (15). A vibrational analysis of TEMO is expected to give information about the distribution of the vibrational energy levels of MoO_4^{2-} ions in an orthorhom-

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bic lattice. In the present investigation the Raman spectra (single crystal) at 300 K and the ir spectra (in powder form) at 300 and 77 K of TEMO have been reported. The observed spectra have been interpreted using factor group analysis.

Experimental

Melt-grown optically good quality single crystal of size $5 \times 6 \times 0.5$ mm was used for the investigation. X-ray and polarizing microscopes were used for the identification of the crystallographic axes. The crystals are cleavable perpendicular to the growth axis z . The ir spectrum was recorded on a Perkin Elmer 580 spectrophotometer at 300 and 77 K. A Specac low temperature cell with liquid nitrogen as the coolant was employed. A Spex Ramalog 1403 spectrometer equipped with a Spectra-Physics model 165 argon ion laser was used to obtain the Raman spectra. The spectra were obtained in the Stokes region of the green line at 5145 Å. The notation of Damen *et al.* (16) was used for describing the experimental configuration.

Factor Group Analysis

The binary molybdate TEMO is isotypic with terbium molybdate, crystallizes in an orthorhombic $Pba2(C_{2v}^8)$ structure at room

temperature (17) and has four molecular units in the primitive unit cell. A crystallographic projection of the elementary unit cell is shown in Fig. 1. The primitive cell contains 12 molybdenum atoms surrounded by oxygen tetrahedra. There are three crystallographically distinct MoO_4^{2-} groups. The Tb and Eu atoms have 7 oxygen atoms as nearest neighbors. All the Mo atoms are in general positions. This leads to a decrease in the overall symmetry of the MoO_4^{2-} ion from T_d to C_1 . The factor group analysis can be done either by correlating the site symmetry of MoO_4^{2-} 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 correlation table for the different normal modes of the MoO_4^{2-} ion between the free ion symmetry T_d , the site symmetry C_1 and the unit cell symmetry C_{2v} is shown in Table I. In this case all the species become ir and Raman active. Considering the whole unit cell, each vibration splits into 12 modes, $9(3A_1 + 3B_1 + 3B_2)$ of them being Raman and ir active and the other $3(3A_2)$ Raman active only. The analysis, based on the line splitting of the normal modes of free XY_4 ion is expected to provide a straightforward means for identifying the different normal modes.

TABLE I
CORRELATION TABLE AND SELECTION RULES FOR THE MoO_4^{2-} ION IN TEMO CRYSTAL

Free ion T_d			Site C_1			Factor group C_{2v}	
Mode	Vibration	Activity ^a	Mode	Activity ^a	Mode	Raman Tensor	Activity ^a
$\nu_1 A_1$	$\nu_s(MoO_4)$	R			$27A_1$	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ α_{xy}	ir, R
$\nu_2 E$	$\nu_s(MoO_4)$	R			$27A_2$		R
			$9C_1$	ir, R			
$\nu_3 F_2$	$\nu_{as}(MoO_4)$	ir, R			$27B_1$	α_{zx}	ir, R
$\nu_4 F_2$	$\nu_{as}(MoO_4)$	ir, R			$27B_2$	α_{zy}	ir, R

^a R, Raman; ir, infrared.

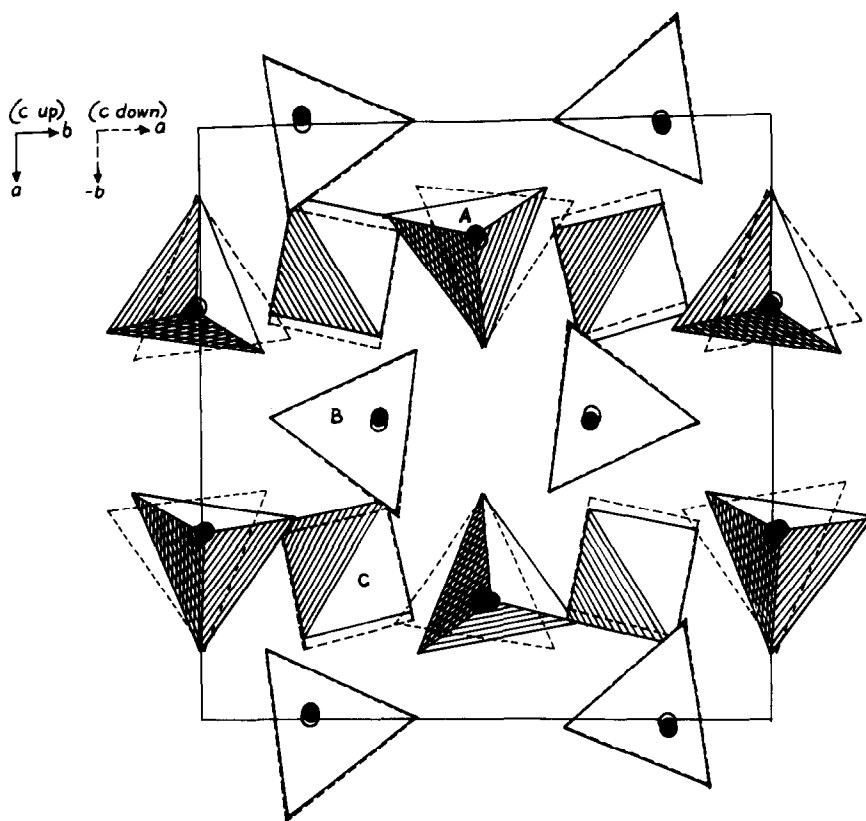


FIG. 1. Arrangement of RE³⁺ (circles) and MoO₄²⁻ ions in the TEMO unit cell. Solid lines represent atomic positions in a cell with orientation *a b c* and dashed lines are those in a cell with orientation *-b, a - c*. (after Ref. 17). A, B, C are the three crystallographically different MoO₄ tetrahedra.

Results and Discussion

Müller *et al.* (18) reviewed the numerous studies regarding the distribution of vibrational levels of the MoO₄²⁻ ion in different normal molybdates. A discrepancy existed as to whether the symmetric bending $\nu_2 >$ the asymmetric bending ν_4 , or $\nu_4 > \nu_2$. The intensity studies on single crystal data and the comparative study of the various potential functions for the MoO₄ species conclusively proved that $\nu_4 > \nu_2$. The interpretation of the vibrational spectra is often difficult when the primitive unit cell becomes complex with fairly large number of

molybdate ions. The situation is further complicated when the molybdenum-oxygen coordination forms layered type compounds.

The normal modes of the molybdate ion are distinguishable from the external modes, since their intensities are an order of magnitude higher and bandwidths are narrower by at least a factor of three. (The spectra has been recorded in the region 250–50 cm⁻¹ which also gives the external modes.) The normal modes of the molybdate ion are expected to occur in the regions 750–975 cm⁻¹ (stretching) and 250–450 cm⁻¹ (bending) irrespective of its environment.

Raman Spectra

Raman spectra of TEMO single crystal in the region 250–1000 cm^{-1} are obtained for the five orientations $y(xx)z$, $x(yy)z$, $x(yx)z$, $y(zx)z$, and $y(zy)z$ (Fig. 1). Attempts to record the $y(zz)x$ spectra were unsuccessful. Observed lines are tabulated in Table II. The symmetries of the Raman active phonons that can participate in different orientations can be had from the matrix representations of the Raman tensors for the appropriate crystallographic point groups given by Loudon (19). For orthorhombic crystals the polarizability

tensor for the A_1 class is

$$\begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \quad a = \frac{\partial \alpha_{xx}}{\partial r_\mu},$$

$$b = \frac{\partial \alpha_{yy}}{\partial r_\mu}, \quad c = \frac{\partial \alpha_{zz}}{\partial r_\mu}.$$

This indicates that the particular lines in A_1 [(xx), (yy), and (zz)] should differ in intensity which is found to be true in the case of xx and yy spectra (Fig. 2).

The observed spectra is expected to be very complex with 108 modes (Table I) as the primitive unit cell contains 12 molyb-

TABLE II
FREQUENCIES, OCCURRING ORIENTATIONS, INTENSITIES^a AND ASSIGNMENTS IN RAMAN AND OBSERVED FREQUENCIES AT 300 K AND 77 K IN INFRARED SPECTRA OF TEMO CRYSTAL

$y(xx)z$ A_1	$x(yy)z$ A_1	$x(yx)z$ A_2	$y(zx)z$ B_1	$y(zy)z$ B_2	Infrared frequencies at	
					300 K	77 K
960 (750)	960 (560)	960 (560)	960 (120)	960 (275)		956, 950
942 (860)	942 (660)	942 (610) 920 Sh	942 (60) 919 Sh	942 (180) 917 Sh	943 915	943 915
905 (20)	905 (20) 851 (390)	902 Sh	850 (150)			
848 (330)		848 (870)	842 (150)	848 (360)	845	856, 850
838 (100) 825 (80)					824	846, 840 824, 810 807
	821 (140)			821 (1000)		
819 Sh		820 (205) 806 (90)	820 (800)			
801 (90)	803 (80)					
		762 (30)		761 Sh		
756 (20)	759 (25)				745	745
			742 (205)	743 (460)		
		738 (85)				
	735 (45)					

TABLE II—Continued

$y(xx)z$ A_1	$x(yy)z$ A_1	$x(yx)z$ A_2	$y(zx)z$ B_1	$y(zy)z$ B_2	Infrared frequencies at	
					300 K	77 K
734 (40)					720 Sh	720 Sh
			718 Sh	717 Sh		
449 (90)	712 Sh 449 (35)	713 Sh 449 (50)	449 (40)	449 (30) 415 (80)	415 w,Sh 410	410
			410 (25)		395 s,Sh	395 w,Sh
				389 (60)		
	388 (310)					
386 (590)			386 (65)			
		383 (1020)				
364 (540)	362 (340)					
		357 (420)				356
		347 Sh			352	
			345 Sh	348 (390)		
333 Sh				330 (980)	340 330	340 330 Sh
			329 (1240)			
	326 (500)					
324 (890)					325	
		323 (840)				
316 Sh				310 (170)		
					305	305
			306 (295)			
302 (70)	300 (70)					
		297 (130)		291 (180)		
288 (80)	288 (50)		288 (240)			286
		283 (140)				
					282	

Note. w = weak, s = strong, Sh = Shoulder.

^a Intensity values given in brackets not normalized.

date ions. All the predicted modes could not be observed. The oxygen environment of the 3 crystallographically different molybdenum atoms is almost tetrahedral with average Mo–O distances 1.762, 1.761, and 1.753 Å (17). A calculation of the phonon energies for the Mo–O stretching and bending vibrations, making use of the different

Mo–O distances is expected to give closely spaced phonon energies, which has been the case for gadolinium molybdate (20). Even with the LO–TO recordings of gadolinium molybdate single crystal at 77 K all the predicted modes could not be observed (11b).

The two strong lines at 960 and 942 cm⁻¹

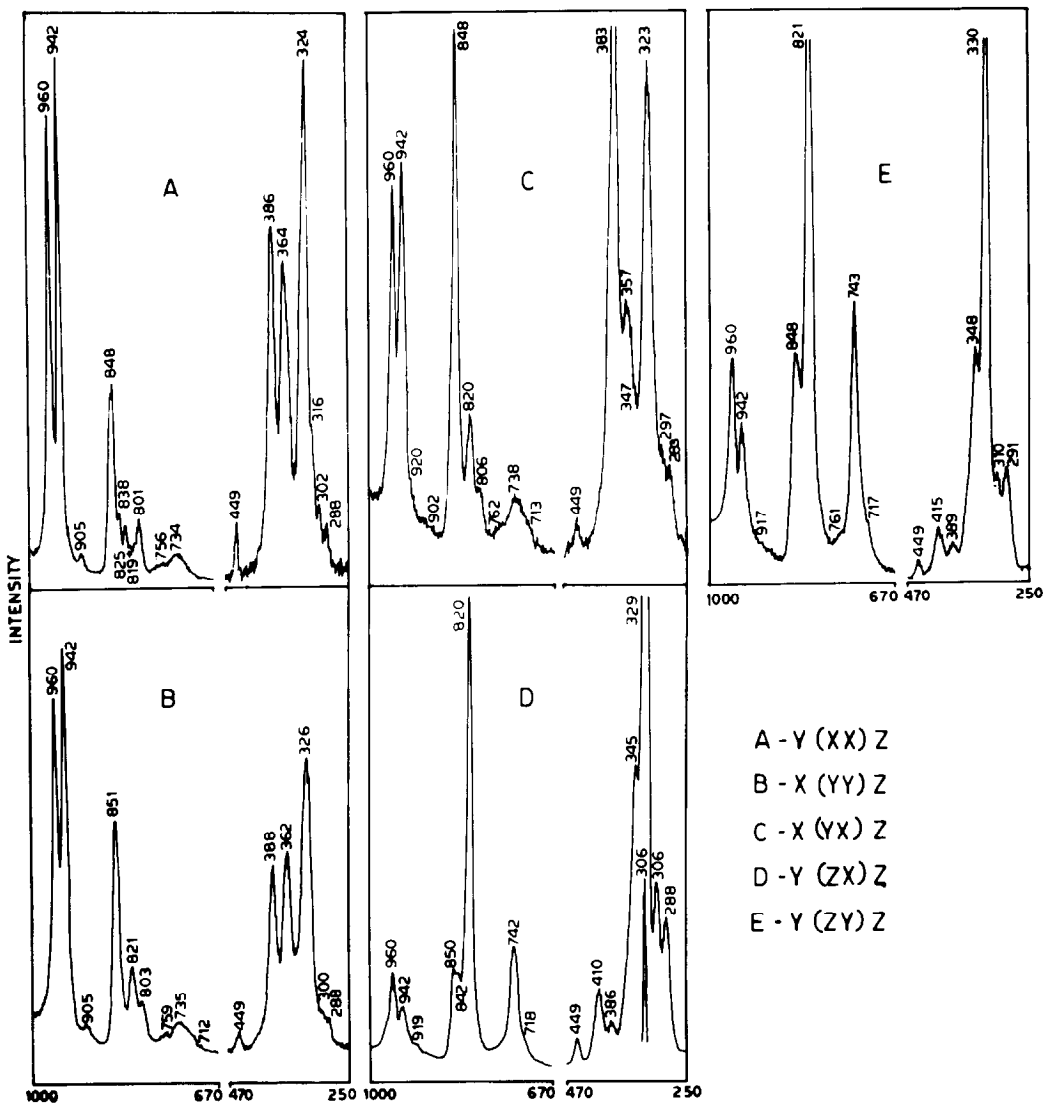


FIG. 2. Raman spectra of TEMO single crystal.

(*xx* and *yy* spectra) are assigned to the totally symmetric vibrations of MoO_4 groups. Factor group splittings are not observed for these lines. Theoretically there should be 12 symmetric stretchings since there are 12 MoO_4 units present in the primitive unit cell. These 12 MoO_4 units form 3 sets of 4 crystallographically different MoO_4 units with average Mo–O distances of 1.762, 1.761, and 1.753 Å. Even if the 3 sets are

vibrating with the same energy, there should be 3 lines for the symmetric stretching in the observed spectra. The presence of 2 lines can only be justified by assuming that there is an accidental degeneracy between 2 sets of 4 MoO_4 units with average Mo–O distances 1.762 and 1.761 Å. Hence the line at 942 cm^{-1} is assigned to these 2 sets of 4 MoO_4 units and the 960 cm^{-1} to the third set with the average Mo–O distance

1.753 Å. Further, the intensity distribution of these 2 lines (intensity of 942 cm⁻¹ > intensity of 960 cm⁻¹) supports our reasoning. A low temperature measurement of LO-TO splittings is expected to resolve these lines.

Out of the 36 asymmetric stretchings predicted, only 25 could be observed (Table II). These lines fall in the range 712–917 cm⁻¹. The observed splitting of 205 cm⁻¹ for the ν_3 stretchings is fairly large. There are lines with a difference of 1 or 2 cm⁻¹ if the different orientations are taken together. For example, the 848 cm⁻¹ in (yx) spectra and 850 cm⁻¹ in (zx) spectra cannot be considered as "leakage" (from misalignment and the effect of collecting angle of the focusing lens) in view of the fact that the phonon energies are very closely spaced. This point is further confirmed by

the lines at 848 cm⁻¹ (xx spectra) and 850 cm⁻¹ (yy spectra). The intensity distribution of these lines with respect to the 960 or 942 cm⁻¹ lines is also very much different.

From intensity considerations, Müller *et al.* (18, 21) have shown that ν_2 has a higher intensity than ν_4 in Raman and the reverse in infrared. This condition along with the earlier stated one that $\nu_4 > \nu_2$ have been used in the assignment of ν_2 and ν_4 . The lines at 386, 364 cm⁻¹ (xx); 388, 362 cm⁻¹ (yy) are assigned to ν_2 of the different molybdate ions. The strong line at 324 cm⁻¹ (xx) with factor group splittings at 316 and 302 cm⁻¹ is also assigned to ν_2 . The following lines: 383, 357, 297, and 283 cm⁻¹ (yx) spectra; 410, 345, 329, 306, and 288 cm⁻¹ (zx) spectra; 415, 348, 330, 310, and 291 cm⁻¹ (zy) spectra are assigned to ν_4 . The present assignment differs from the one due

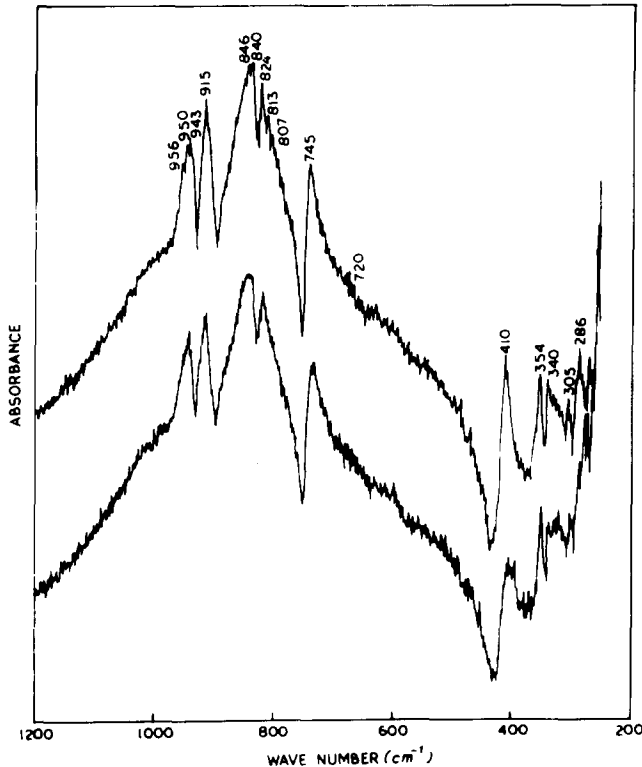


FIG. 3. Infrared spectra of TEMO (KBr pellet).

to Ullman *et al.* (7) which is based on the assumption $\nu_2 > \nu_4$. It may be noted that the labeling of ν_2 and ν_4 as internal modes is only approximate since mixing is expected with lattice modes.

Infrared Spectra

The room temperature and the liquid nitrogen temperature spectra are shown in Fig. 3. The spectra at 77 K shows some splittings and an enhancement in intensity which is pronounced in the ν_2 and ν_4 regions of the molybdate ions. All the ν_1 and ν_3 modes fall in the broad contour from 600 to 1000 cm^{-1} . The 943 cm^{-1} band at 300 K shows splittings at 950 and 956 cm^{-1} when the temperature is lowered. These are assigned to the symmetric stretching vibration of molybdate ions. The symmetric nature of the band at 915 cm^{-1} warrants an assignment of ν_1 for this. However, there is no corresponding Raman line in the *xx* or *yy* spectra. An assignment of ν_1 for 915 cm^{-1} tends to increase the difference in frequency between the crystallographically different molybdate ions, which is not expected since all these ions are almost tetrahedral and their average Mo–O distances are very close. Further, the shoulder at 917 cm^{-1} in the *zx* geometry in Raman has been assigned to ν_3 . Hence, the band at 915 cm^{-1} has to be taken as a ν_3 component. The broadbands centered at 845 cm^{-1} and 824 cm^{-1} at 300 K with splittings at 850, 846, 840, 824, 810, and 807 cm^{-1} at 77 K also belong to ν_3 . The highly asymmetric band at 745 cm^{-1} with a shoulder at 720 cm^{-1} has to be associated with an asymmetric stretching. The intensity rule (18, 21) dictates that ν_3 has a higher intensity than ν_1 in infrared and the reverse in Raman holds good in our study.

The bending region (ν_2 and ν_4) shows frequencies corresponding to that observed in Raman. There are three band contours. The first one centered at 410 cm^{-1} has a weak shoulder at 415 cm^{-1} and a strong one at 395

cm^{-1} . Nearing 77 K this band gains in intensity and in the process the weak shoulder at 415 cm^{-1} disappears and the strong one is observed as a weak but prominent one at 395 cm^{-1} . In conformity with the intensity rule and Raman assignment, the lines at 415 and 410 cm^{-1} have been assigned to ν_4 and the line at 395 cm^{-1} to ν_2 . The second band contour extends from 300 to 370 cm^{-1} with peaks at 352, 340, 330, and 325 cm^{-1} at room temperature. At 77 K the 352 cm^{-1} shifts to 356 cm^{-1} without gaining intensity and the asymmetric nature is more pronounced on the higher wavenumber side. This band is assigned to a ν_4 mode. The line at 340 cm^{-1} gains some intensity and during the process the lines at 325 and 330 cm^{-1} coalesce, forming a shoulder at 330 cm^{-1} . The 340 and 325 cm^{-1} are assigned to ν_2 and the 330 cm^{-1} to ν_4 . The line at 305 at both the temperatures belongs to a ν_2 component. The third band contour centered at 282 cm^{-1} at 300 K shifts to 286 cm^{-1} at 77 K. This has been assigned to a ν_4 component.

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

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