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Vibrational Spectra of Compounds Ln_2MoO_6 and Ln_2WO_6

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The vibrational spectra of compounds Ln_2WO_6 and Ln_2MoO_6 (Ln = lanthanide, including Y and Bi) are reported. Neglecting details it is possible to assign the internal vibrations of the molybdate and tungstate group. The results are in agreement with the structural data known up till now and suggest further that tungsten in the unknown Y_2WO_6 structure is in six-coordination, that Bi_2MoO_6 shows still another modification than koechlinite and that vibrational spectroscopy may yield additional structural information for compounds like those under consideration.

1. Introduction

During recent years there have been a number of structural investigations of the compounds Ln_2MoO_6 and Ln_2WO_6 (Ln = lanthanide, including Y and Bi) (*1–10*). The structure of La_2MoO_6 is known with certainty and contains MoO_4 tetrahedra (*1*). This structure has also been found for the La–Sm molybdates (*2*, *3*), but for Sm_2MoO_6–Lu_2MoO_6, Y_2MoO_6 and Pr_2WO_6–Dy_2WO_6 a different structure has been proposed (*2–8*). This one can be derived from the scheelite structure and contains the hexavalent cations in a trigonal bipyramidal coordination (*7*). Four of the surrounding O^{2-} anions are at a shorter distance (1.71–1.84 Å) than the fifth anion (2.06 Å). The structure of the compounds Ho_2WO_6–Lu_2WO_6 and Y_2WO_6 is unknown up till now (*8*). Finally, Bi_2WO_6 and Bi_2MoO_6 have the koechlinite structure with the hexavalent cations in octahedral coordination (*9–11*).

A difficulty in the structure determination by X-ray diffraction is formed by the fact that oxygen contributes little to the X-ray pattern due to the relatively large scattering power of the cations concerned.

In the course of our studies on the vibrational spectra of tungstates and molybdates in solids it appeared interesting to investigate the vibrational spectra of the compounds Ln_2MoO_6 and Ln_2WO_6 with special stress on the internal modes of the molybdate and tungstate group in order to find out the coordination of the hexavalent cation. This is especially of interest for studies of the luminescence of these groups. The results of this study confirm the structures proposed and strongly suggest that in the unknown structure of, e.g., Y_2WO_6 the W^{6+} cations are in octahedral coordination.

2. Experimental

Samples were prepared as described previously (*2*, *10*). They were checked by X-ray powder analysis using Cu*Kα* radiation. Results were the same as reported in the literature with the exception of Bi_2MoO_6 for which we did not find the koechlinite phase. The X-ray pattern of Bi_2MoO_6 reminds strongly of that of La_2MoO_6, but there are a number of weak, additional lines.

The way in which the spectral measurements were performed has been described previously (*12*).

3. Results

It turns out that isomorphous compounds Ln_2MoO_6 and Ln_2WO_6 have very similar vibrational spectra. For that reason we will treat in this paper the spectra of only the following compounds: La_2MoO_6 [representative of the compounds with La_2MoO_6 structure (*1*)] and Nd_2MoO_6 (to illustrate the similarity of the spectra of two isomorphous compounds),

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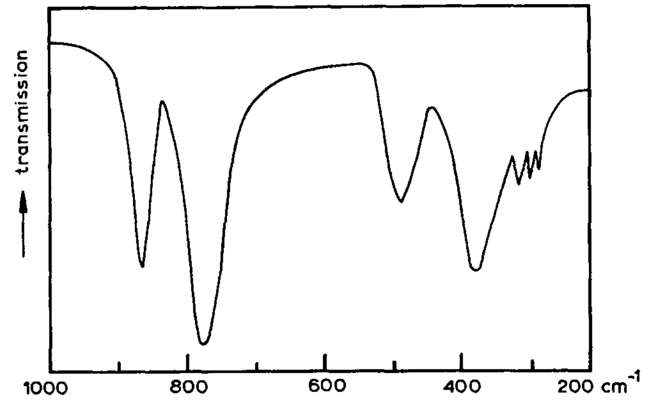

FIG. 1. Infrared spectrum of La_2MoO_6.

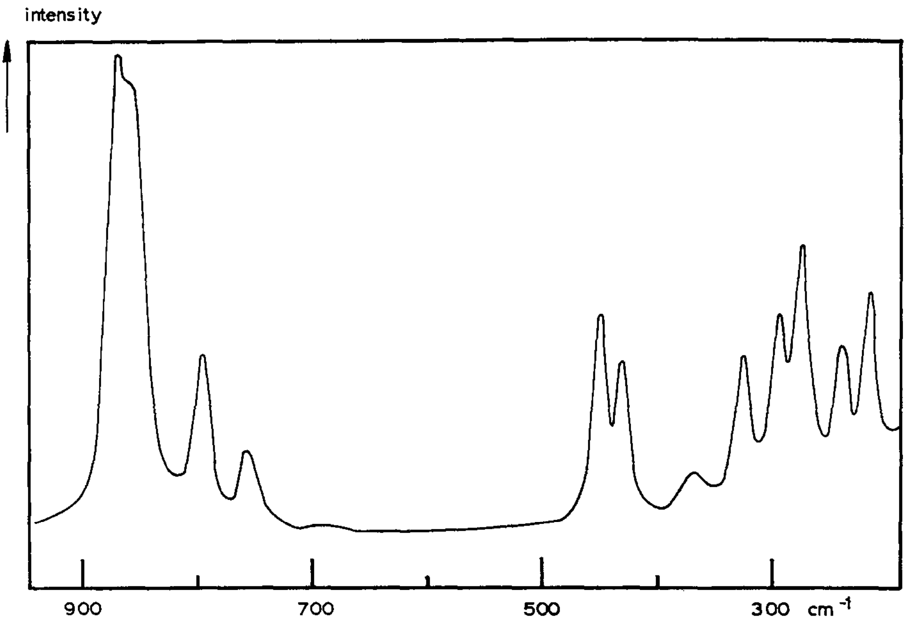

FIG. 2. Raman spectrum of La_2MoO_6.

Sm_2WO_6 [representative of the compounds with the Nd_2WO_6 structure (7)], Y_2WO_6 (representative of the compounds with the unknown Y_2WO_6 structure), Bi_2WO_6 and Bi_2MoO_6.

Figure 1 shows the infrared and Fig. 2 the Raman spectrum of La_2MoO_6. Figure 3 compares the infrared spectra in the region of the internal vibrations of the $Me^{6+}O_n$ group in several compounds.

Table I gives the vibrational spectra of La_2MoO_6 and Nd_2MoO_6 together with an assignment of the internal modes. The wavenumber difference between the two components of the infrared active ν_3 (865 and 775 cm^{-1} in the case of La_2MoO_6) is called Δ and plotted in Fig. 4 versus the c/a ratio of the tetragonal unit cell for the system $La_{2-x}Bi_xMoO_6$ which appeared to be single-phase up till $x \sim 0.8$ and for Nd_2MoO_6. Due to the fact that the body colour of Nd_2MoO_6 is blue the Raman spectrum was not of high quality, the laser beam being partly absorbed.

In Table II we have listed the vibrational spectra and an assignment of the internal WO_6 vibrations of Bi_2WO_6. Finally, Table III contains the spectra of Sm_2WO_6, Y_2WO_6 and Bi_2MoO_6.

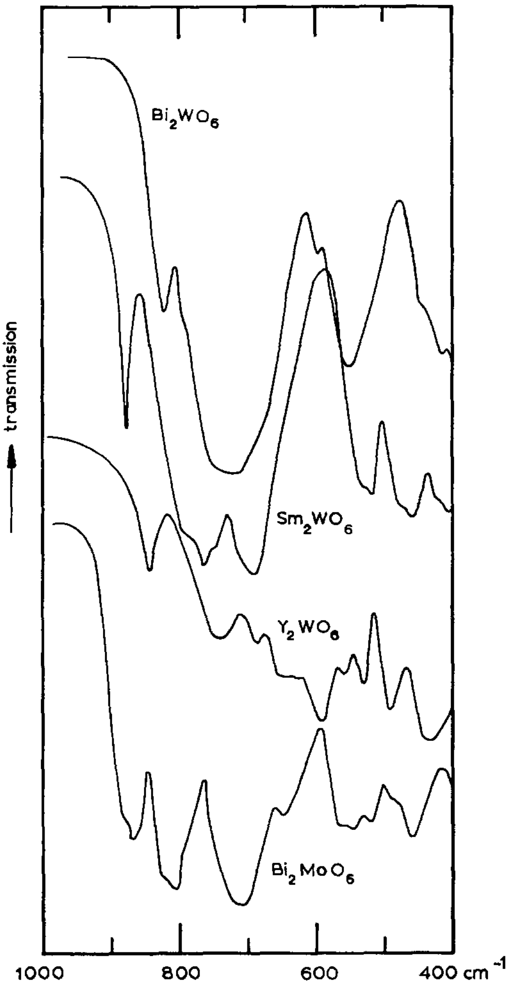

FIG. 3. Infrared spectrum of Bi_2WO_6, Sm_2WO_6, Y_2WO_6 and Bi_2MoO_6.

TABLE I

VIBRATIONAL SPECTRA OF La_2MoO_6 AND Nd_2MoO_6 (VALUES IN cm^{-1}) AND ASSIGNMENT OF THE INTERAL MODES[a]

			La_2MoO_6		Nd_2MoO_6	
	T_d	D_{2d}	Infrared	Raman	Infrared	Raman
ν_1	A_1	A_1	—	875 (s)	—	875 (s)
		B_2	865 (s)	860 (s)	870 (s)	850 (sh)
ν_3	T_2			800 (m)		790 (w)
		E	775 (s)	765 (m)	770 (s)	750 (w)
				695 (w)		—
ν_2	E	A_1	—	455 (m)	—	475 (m)
		B_1	—	435 (m)	—	435 (m)
ν_4	T_2	B_2	490 (s)	490 (w)	510 (s)	—
		E	380 (s)	375 (w)	385 (s)	375 (w)
			315 (w)	325 (m)	330 (w)	340 (m)
			298 (w)	295 (m)	295 (m)	—
			287 (w)	275 (m)		265 (m)
				240 (m)		—
				220 (m)		210 (m)

[a] Abbreviations: (s) strong, (m) medium, (w) weak, (sh) shoulder. Under D_{2d} symmetry the modes B_2 and E are infrared-active, and A_1, B_1, B_2 and E Raman-active.

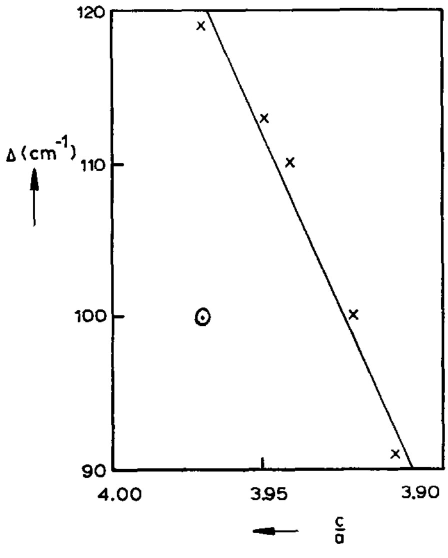

FIG. 4. The splitting of the ν_3 vibration (Δ) versus the crystallographic c/a ratio for the system $La_{2-x}Bi_xMoO_6$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ with c/a and Δ increasing with x) and the compound Nd_2MoO_6 (circle).

4. Discussion

a. La_2MoO_6

The structure of La_2MoO_6 consists of a succession of La_2O_2 and MoO_4 layers stacked along the c axis. The La_2O_2 layer has the same composition as in LaOCl, the MoO_4 layer consists of MoO_4 tetrahedra. The space group of La_2MoO_6 is D_{2d}^{11} ($I\bar{4}2m$). The site symmetry of the Mo^{6+} ion is D_{2d} and there is one Mo per primitive unit cell. Table I shows what happens with the internal tetrahedral vibrational modes of the MoO_4 group under this symmetry. It is well known that the separation of internal and external modes is quite successful in solids with molecular groups like molybdate and tungstate [see, e.g., Ref. (*12*)]. We were in fact able to assign these internal modes without difficulty taking account of the selection rules (see Table I) and the values for ν_1, ν_2, ν_3, ν_4 known from studies of MoO_4^{2-} in solution [Ref. (*13*): ν_1: 894 cm^{-1},

TABLE II

VIBRATIONAL SPECTRA OF Bi_2WO_6 (VALUES IN cm^{-1}) AND ASSIGNMENT OF THE INTERNAL MODES

	$O_h(D_{4h})$	C_2	Infrared	Raman
ν_1	$A_{1g}(A_{1g})$	A	820 (m)	830 (m)
				800 (s)
ν_3	$T_{1u}(A_{2u}+E_u)$	A + 2B	725 (s)	720 (m)
			~650 (sh)	
			595 (w)	605 (vw)
			550 (s)	
			~520 (sh)	525 (vw)
ν_2	$E_g(A_{1g}+B_{1g})$	2A	hidden under ν_3?	
ν_4	$T_{1u}(A_{2u}+E_u)$	A + 2B	450 (sh)	460 (vw)
			415 (w)	420 (w)
			345 (s)	335 (m)
			290 (m)	
ν_5	$T_{2g}(B_{2g}+E_g)$	A + 2B	hidden under ν_4	420 (w)
				310 (s)
				285 (s)
			265 (m)	265 (m)
			245 (m)	
			225 (m)	225 (m)
				210 (m)

ν_3: 833 cm^{-1}, ν_2: ~380 cm^{-1} and ν_4: 318 cm^{-1}] and solids [e.g., Ref. (*14*): averaged frequencies ν_1: 885 cm^{-1}, ν_3: 803 cm^{-1}, ν_2: 374 cm^{-1} and ν_4: 337 cm^{-1}]. Results are presented in Table I. It is assumed that the stronger component of the infrared active ν_3 and ν_4 components has the E representation and the weaker one the B_2 representation. For Nd_2MoO_6 the procedure is analogous (Table I).

In this way we arrive at the following averaged values for the MoO_4 tetrahedron in La_2MoO_6: ν_1: 875 cm^{-1}, ν_3: 805 cm^{-1}, ν_2: 445 cm^{-1}, and ν_4: 420 cm^{-1}. The stretching modes have about the same frequency as in the case of $CaMoO_4$, the deformation modes are situated at much higher wavenumbers than in $CaMoO_4$. The model of separable modes is, however, no longer correct in the case of the deformation modes of MoO_4 in La_2MoO_6, since the vibrational frequencies of the La_2O_2 layer are situated in the same spectral region. This can be derived from the vibrational spectra of LaOCl the structure of which consists of the same La_2O_2 layers separated by chlorine ion layers. According to Ref. (*15*) LaOCl shows strong absorption in the spectral region below 500 cm^{-1}.

The assignment of the vibrational frequencies in the region around 800 cm^{-1} in the Raman spectrum is incomplete. In the case of La_2MoO_6 there is a peak at 800 cm^{-1} with moderate intensity. A possible explanation may be a combination of the 375 cm^{-1} component of ν_4 and the 435 cm^{-1} component of ν_2 (yielding 810 cm^{-1}). This combination is not forbidden. There is another, but very weak peak at 695 cm^{-1} which we do not assign. Its counterpart in the spectrum of Nd_2MoO_6 is not observed. That of the 800 cm^{-1} peak, however, is present (at 790 cm^{-1}).

It is nevertheless obvious that the vibrational spectra agree with the tetrahedral coordination of molybdenum.

Finally we note that the splitting of $\nu_3(\Delta)$ increases, if La in La_2MoO_6 is replaced by Bi (see Fig. 4). This splitting is due to the tetragonal field

TABLE III

VIBRATIONAL SPECTRA OF Sm_2WO_6, Y_2WO_6 AND Bi_2MoO_6 (VALUES IN cm^{-1})[a]

Sm_2WO_6 Infrared	Sm_2WO_6 Raman	Y_2WO_6 Infrared	Y_2WO_6 Raman	Bi_2MoO_6 Infrared	Bi_2MoO_6 Raman
875 (ν_1)	875 (ν_1)	840 (ν_1)	935	880	905
				870	885
790	825	740	835 (ν_1)	825	870
765		690		810	830
745	760	660	710	790	795
690 + sh	740	630	695	710	730
	720	600	675	645	[b]
530	700	560	625	565	400
520		530	600	550	380
480	565	495	555	525	320
460	515	440	525	490	265
425	485	~390	505	460	230
410	440	350	450	380	210
380	400	335	430	~335	180
340	385	310	400	295	
295	345	290	370	~250	
270	315	270	345		
	285	255	315		
	245	240	290		
	220	230	275		
	170	215	260		
	150		240		
			225		
			200		
			185		
			145		

[a] Bands and peaks that are clearly separated in the spectra are also separated in the table.

[b] Some very weak bands in the region 450–750 cm^{-1}.

at the MoO_4 tetrahedron as a consequence of the layer character of the structure. It is therefore not surprising to find a relation between Δ and c/a. It is noteworthy however, that the Bi^{3+} ion brings about a much higher value of c/a than the La^{3+} and Nd^{3+} ion (see Fig. 4). This has been ascribed previously to the outer electron configuration (s^2) of Bi^{3+} (*10*).

b. Bi_2WO_6

Another structure type for which the crystal structure (and especially the oxygen coordinates) has been determined definitely is that of Bi_2WO_6. This has been done by neutron diffraction (*11*). The structure can be described as an orthorhombic distortion of the Bi_2NbO_5F structure with the tungsten ions in octahedral coordination. The space group of Bi_2WO_6 is C_{2v}^{17} (*B2 cb*) and the site symmetry of tungsten is C_2. There are two different tungsten ions per primitive unit cell. Note, however, that the symmetries of the undistorted structure should give a reasonable approximation (Bi_2NbO_5F, space group D_{4h}^{17} or *I* 4/*mmm*, relevant site symmetry D_{4h}, one Nb per primitive unit cell). The WO_6 octahedra share edges and have, therefore, oxygen ions in common. It has been shown previously, that such a situation does not shift the position of the absorption bands drastically in comparison with those of the isolated group (*16*). The representations of the vibrations that should be expected for the site symmetries mentioned above are given in Table II starting with the regular octahedral internal modes. It is possible to make a rough assignment (see Table II), because the vibrational modes of the isolated and purely octahedral WO_6 group in solids is known from studies of ordered perovskites (*12*, *17*). For Ba_2CaWO_6, for example, ν_1: 832 cm^{-1}, ν_2: 675 cm^{-1}, ν_3: 628 cm^{-1}, ν_4: 327 cm^{-1} and ν_5: 410 cm^{-1}. Our approximate assignment in terms of the vibrational modes of an isolated WO_6 octahedron follows from Table II. Figure 3 shows that the spectral region where the asymmetrical stretching vibration (ν_3) is expected contains mainly two strong bands (at 725 and 550 cm^{-1}). In our opinion these are the bands that are expected for D_{4h} symmetry (Bi_2NbO_5F approximation), viz. A_{2u} and E_u. Assigning the more intense one (725 cm^{-1}) to E_u gives an approximate averaged value of 670 cm^{-1}. This is to be compared with the region 610–670 cm^{-1} where ν_3 is situated for the WO_6 group in ordered perovskites (*17*). The agreement is good and shows again that the ν_3 mode is not sensitive to corner sharing of WO_6 octahedra.

For the lower absorption bands the assignment is more difficult, but the proposal made in Table II is not unreasonable. The experimental data agree with the octahedral coordination of tungsten. The most marked difference between the spectra of the tetrahedral and isolated octahedral tungstate group in solids is the fact that for octahedral coordination the wavenumber difference between the internal symmetric (ν_1) and asymmetric (ν_3) stretching mode is at least twice the value observed for the tetrahedral case. Compare, for example, La_2MoO_6 with averaged values of 875 and 805 cm^{-1}, respectively, with Ba_2CaWO_6 with 832 and 628 cm^{-1} and Bi_2WO_6 with ~815 and ~670 cm^{-1}. We were interested to see how this would come out for five-coordination and whether this could be used for coordination predictions.

c. Sm_2WO_6

The compound Sm_2WO_6 belongs to the tungstates and molybdates with Nd_2WO_6 structure. This structure has been solved by Belov and co-workers (*7*) and contains tungsten in five-coordination. Its space group is C_{2h}^6 (*C*2/*c*) and there are four tungsten ions per primitive unit cell with no local symmetry elements. As a consequence the vibrational spectrum (Table III) is very complicated. We tried to make a rough assignment of the internals in the following way. The tungstate group in Sm_2WO_6 can be considered as a distorted tetrahedron, since there are four O^{2-} ions at considerably shorter distances than the fifth (*7*). In this approximation we expect that the tetrahedral ν_1 mode will give two infrared active and two Raman active components in the spectrum of the tungstate group in Sm_2WO_6. Both spectra show in fact a clear ν_1 vibrational mode at 875 cm^{-1} (see Fig. 3 and Table III). A splitting of this band is not observed.

The bands in the region 700–800 cm^{-1} represent the asymmetrical stretching vibration (ν_3). For both spectra we expect six bands. The infrared spectrum gives at least four bands, the Raman spectrum four bands. It is not possible to decide whether the 825 cm^{-1} band in the Raman spectrum stems from ν_1 or ν_3.

Below about 550 cm^{-1} there is a large number of bands (see Table III) which we do not assign further. These are the vibrations stemming from the internals ν_2 and ν_4, the Sm–O skeleton and other externals.

Although this assignment is incomplete and unsatisfactory it gives a rough idea of what the averaged values of ν_1 and ν_3 are, viz. about 875 cm^{-1} and about 725 cm^{-1}, respectively. The value for ν_1 is similar to that observed for La_2MoO_6, $CaWO_4$ and $CaMoO_4$ (14). Here it should be borne in mind that the vibrational spectra of the molybdate and tungstate group are usually very similar (*13*, *14*, *17*). The value of ν_3, how inaccurate it may be, is definitely lower than the usual values found for the tetrahedral MoO_4 group (La_2MoO_6, 805 cm^{-1}; $CaWO_4$, 799 cm^{-1}; and $CaMoO_4$, 803 cm^{-1}). We assume that this decrease is caused by the fact that the tungsten is in fact five-coordinated and conclude that the position of the symmetrical stretching vibration is not as sensitive to the coordination number as that of the asymmetrical stretching vibration. This will now be applied to Y_2WO_6 and Bi_2MoO_6.

d. Y_2WO_6

The structure of Y_2WO_6 is unknown at the moment. Reliable lattice parameters seem to be $a = 11.010$, $b = 15.962$, $c = 10.081$ Å and $\beta = 91°46$ (*8*). This implies that the unit cell of Y_2WO_6 is twice as large as that of Sm_2WO_6, so that the number of tungstate groups per unit cell is probably also larger. A complicated infrared and Raman spectrum was observed by us (see Table III and Fig. 3). It is nevertheless possible to deduce from these data a probable averaged value for ν_1 and ν_3. The ν_1 mode will be situated somewhere at 835 cm^{-1} (infrared band at 840 cm^{-1}, strong Raman line at 835 cm^{-1}). The weaker Raman line at 935 cm^{-1} is probably a combination tone. The infrared spectrum indicates (Fig. 3) that the averaged value of ν_3 is 625 cm^{-1} (accuracy some 50 cm^{-1}). In spite of their inaccuracy these values are strong evidence that the tungsten ion in compounds with Y_2WO_6 structure is six-coordinated. This is in contradiction to an earlier prediction by one of us (*2*) but that one was based upon X-ray diffraction. Vibrational spectroscopy is a more sensitive tool to predict the tungsten coordination in this case.

e. Bi_2MoO_6

Bi_2MoO_6 has found to be isomorphous with Bi_2WO_6 (with WO_6 octahedra). There are indications, however, that Bi_2MoO_6 is polymorphic (*10*). This follows also from the vibrational spectrum we obtained (Fig. 3 and Table III). Although the spectra of our Bi_2MoO_6 are complicated, they differ definitely from those of Bi_2WO_6. We assume that the molybdenum in our Bi_2MoO_6 modification is not in six-coordination for two reasons:

a. The spectra indicate a value of about 875 cm^{-1} for the ν_1 mode. This is the value for tetrahedral coordination (see above).

b. For ν_3 we find a value in between 700 and 800 cm^{-1}. This excludes octahedral coordination [unless the octahedra share faces or edges (*16*)], points to tetrahedral coordination, but does not exclude five-coordination. Our Bi_2MoO_6 is certainly not isomorphous with one of the structure types mentioned in this paper.

In conclusion, we see that vibrational spectroscopy in the region 500–1000 cm^{-1} can give additional information on the crystal structure and especially the hexavalent cation coordination. This may be useful if the coordinates of the oxygen ions are difficult to determine and may therefore be of use for the many compounds in the systems Ln_2O_3–WO_3 and Ln_2O_3–MoO_3 (*8*).

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