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Spectroscopic Properties of Some Eu^{3+} Doped Scheelite-Related Rare Earth Sesquimolybdates and Sesquitungstates

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The optical properties of Eu^{3+} as a local structural probe are analyzed when incorporated in some rare earth and bismuth scheelite-related molybdates or tungstates: α-La_2 $(MoO_4)_3$, $Bi_2(MoO_4)_3$, α-Gd_2 $(MoO_4)_3$, and $Gd_2(WO_4)_3$. When the rare earth occupies more than one cristallographic position, the dye laser selective excitation technique is applied to determine the point symmetry of the site and to derive the energy level schemes. In α-$La_2(MoO_4)_3$, the occupation of vacant positions by Eu^{3+} is confirmed and the conditions for an enhancement of the occupation are discussed. The analogy of the α-$Gd_2(MoO_4)_3$ and $Gd_2(WO_4)_3$ spectra constitutes further evidence for their isostructural character.

Introduction

The rare earth–molybdenum(VI) oxides system constitutes a very rich family within which a great variety of compounds can be synthesized which differ in stoichiometry and structure. The general chemical formula of the compounds is $Ln_2Mo_nO_{3n+3}$, with n as integer or fractional. We previously published the spectroscopic properties of Eu^{3+} doped into some of these compounds, which were analyzed in terms of point site symmetry, energy level schemes, and, occasionally, in terms of crystal field parameters. We considered the oxymolybdates with $n = 1$ (*1*) and the tetramolybdate with $n = 4$ (*2*). Moreover, the parameterization of the transition intensities has also been performed by using Eu^{3+} as local probe (*3*).

The rare earth sesquimolybdates with $n = 3$ are probably the most interesting group of the family, since the compounds of this series are not isostructural and because they also exhibit some interesting physical properties (*4, 5*). They occur in at least eight structural types, depending on both the rare earth atom and on the conditions of synthesis. Some of the room temperature stable phases are related to the scheelite structure. They constitute a versatile host series, to which the spectroscopic analysis can be applied to confirm the structure.

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Since $Bi_2(MoO_4)_3$ and $Gd_2(WO_4)_3$ also have scheelite-related structures, we have undertaken the investigation of these compounds to investigate their structural relations with the α-$Ln_2(MoO_4)_3$ compounds. We report on the optical properties of the Eu^{3+} as a local structural probe, doped into α-$La_2(MoO_4)_3$, α-$Gd_2(MoO_4)_3$, $Bi_2(MoO_4)_3$, and $Gd_2(WO_4)_3$.

Crystallographic Background

Most of the rare earth sesquimolybdates or sesquitungstates $Ln_2(MO_4)_3$ (M = Mo, W), as well as $Bi_2(MoO_4)_3$, have a structure related to scheelite ($CaWO_4$). The structure is attained through a vacancy ordering of $\frac{1}{3}$ of the larger Ca cation sites, while the rare earth (or Bi) atoms occupy $\frac{2}{3}$ of these sites. Consequently, the chemical formula may be written as $Ln(Bi)_{\frac{2}{3}}\square_{\frac{1}{3}}MO_4$ where $\square$ indicates vacant sites (*5*). Contrary to the sesquitungstates series, the rare earth sesquimolybdates are not isomorphous; the number of scheelite subcells, as well as the arrangement of the vacancies, depend on the rare earth ion and on the conditions of synthesis.

The structures of $Eu_2(WO_4)_3$ (*6*) and $Bi_2(MoO_4)_3$ (*7*) are built up from three scheelite subcells, with similar cell parameters, but with differences in the arrangement of vacancies. The vacancies are located in the (001) plane for $Eu_2(WO_4)_3$ and in the (100) plane for $Bi_2(MoO_4)_3$. Thus, the structures are not equivalent: the space groups are $C2/c$ with $Z = 4$ for $Eu_2(WO_4)_3$ and $P2_1/c$ with $Z = 4$ for $Bi_2(MoO_4)_3$. For the former, the rare earth atoms occupy only one general crystallographic position $8f$, with C_1 site symmetry; the vacancies are at the $4e$ position (C_2). For the latter, the bismuth atoms are located at two nonequivalent general crystallographic positions $4e$ (C_1) and the vacancies at the $4e$ position (C_1).

The α-$La_2(MoO_4)_3$ structure is rather different, since 9 scheelite subcells constitute its network, with 12 molybdate molecules per unit cell (*8*). The space group is $C2/c$, and the rare earth atoms are located at three nonequivalent general crystallographic positions $8f$ (C_1), whereas the vacancies occupy the general position $8f$ (C_1) and the position $4e$ (C_2). For this type of compound an α–β phase transformation takes place at 848°C, which is reversible and associated with an order–disorder transition (*9*, *10*).

As far as we know, the structure of α-$Gd_2(MoO_4)_3$ has not been completely established. The X-ray powder pattern has been reported (*11*), but there is disagreement as to its interpretation. Nassau *et al.* (*12*) believe that the α-$Gd_2(MoO_4)_3$ type structure bears no relation to other sesquimolybdates (or sesquitungstates), whereas Brixner *et al.* (*11*) suggest that this compound should be isostructural with $Eu_2(WO_4)_3$. An α–β phase transformation also occurs at 857°C for the Gd compound, but it is not reversible, since, when the temperature is decreased to 159°C, a metastable β' phase appears.

Experimental

Preparation of the Compounds

All the compounds were prepared in powder form by solid state reactions. The starting materials were of high purity rare earth, molybdenum, and tungsten oxides. The rare earth oxides were prefired at 800°C for several hours for dehydration and decarbonization. The synthetic method consisted of first heating the intimately mixed oxides at 500°C for 12–16 hr, followed, after grinding, by new firing at 820°C for 24–30 hr for α-$La_2(MoO_4)_3 : Eu^{3+}$; at 900°C (30 hr) for $Gd_2(WO_4)_3 : Eu^{3+}$; at 700°C (24–30 hr) for α-$Gd_2(MoO_4)_3 : Eu^{3+}$ and at 600°C (70 hr) for $Bi_2(MoO_4)_3 : Eu^{3+}$. It is noteworthy that an alternative synthetic method, under high pressure, has been used for the preparation of α-$Gd_2(MoO_4)_3$ (30 Kb, 600°C, 1 hr) (*11*).

The synthesized compounds were routinely checked by X-ray powder diffraction analysis; they appeared to be single-phased. For the spectroscopic studies, Eu^{3+} (2–10 at%) doped samples were used.

Spectroscopic Measurements

The emission spectra of Eu^{3+} doped samples were analyzed at 300, 77, and 4 K with a 1-m Jarrell–Ash monochromator. The signal was recorded using standard techniques. The fluorescence was excited by a classical mercury lamp (OSRAM HBO 150 W) equipped with Wood filters, whereas the selective excitation of the $^5D_0$ level was achieved by means of a Rhodamin 6G tunable dye laser pumped by a continuous 4-W argon laser (Spectra Physics).

Results and Discussion

Some common features can be observed for the compounds studied here. Under classical fluorescence excitation, i.e., through the charge transfer state and/or the excited levels of the $4f^6$ configuration, the sesquimolybdates fluoresce with reasonable intensity. All the spectra are characterized by lines having mainly $^5D_0$ as the emitting level. Nevertheless, at low temperature, some weak lines can be attributed to $^5D_1 \rightarrow {}^7F_J$ transitions, whereas no transitions can be recorded from upper levels.

α-$La_2(MoO_4)_3$

Under uv excitation, the emission spectrum of α-$La_2(MoO_4)_3 : Eu^{3+}$ recorded in the wavelength range 5800–7000 Å is very rich. All the lines observed correspond to the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions. The spectrum is principally characterized by three lines for the $^5D_0 \rightarrow {}^7F_0$ transition (Fig. 1). By application of group theory and electronic transition selection rules, one deduces that at least three different point sites are present in the structure, whose symmetry is not higher than C_n, C_{nv}, or C_s. From the other $^5D_0 \rightarrow {}^7F_J$ transitions, one can also observe that these sites are not very different from each other since many lines appear to be triple. This is in agreement with the structure, where three sites of the rare earth ions have been recognized, whose symmetries are more or less distorted from S_4.

In spite of the relatively low $^5D_0 \rightarrow {}^7F_0$ transition intensities, it is possible to excite directly the $^5D_0$ level by means of a tunable dye laser adjusted to the chosen wavelength. Figure 1 shows the results of this selective excitation corresponding to the three sites: *A* (excitation wavelength 5800 Å), *B* (5802 Å), and *C* (5806 Å). When one site is excited, some lines from the other sites are detected but they are very weak, indicating a very low transfer rate from site to site, even lower than that for Ln_2MoO_6 (*1*). Thus, it is possible to attribute unambiguously one fluorescence line to "its" site, and to construct the energy level scheme ^7F_J (J = 0–4) for each site (Table I).

Some extra lines are observed when sites *B* and *C* are selectively excited. These lines can not be attributed to a normal lattice site. To obtain further information, a systematic exploration of the $^5D_0 \rightarrow {}^7F_0$ wavelength range was performed, looking for the enhancement of the intensity of these extra lines. The fourth $^5D_0 \rightarrow {}^7F_0$ transition located at 5804 Å has not been observed in the classical fluorescence spectrum, probably because of its low intensity. Figure 2 shows the spectrum recorded under 5804-Å excitation. It is also possible to construct the energy level scheme corresponding to a fourth site called *D*, which is "abnormal" and has a low point symmetry. The origin of this site is interpreted by reference to the structure (Section II); there exist two types

TABLE I

TRANSITIONS AND ENERGY LEVEL SCHEME OF α-$La_2(MoO_4)_3:Eu^{3+}$

	Spectrum *A*			Spectrum *B*		
Transition	λ(Å)	*E*(cm^{-1})	Δ*E*(cm^{-1})	λ(Å)	*E*(cm^{-1})	Δ*E*(cm^{-1})
$^5D_0$–$^7F_0$	5800	17,240	0	5802	17,235	0
$^5D_0$–$^7F_1$	5898	16,955	285	5904	16,937	297
	5928	16,871	369	5924	16,880	355
	5957	16,787	453	5960	16,779	456
$^5D_0$–$^7F_2$	6085	16,434^a		6082	16,442^a	
	6128	16,319	921	6119	16,343^a	
	6150	16,259	981	6126	16,324	911
	6165	16,222	1018	6154	16,252	983
	6206	16,113	1127	6160	16,234	1001
				6205	16,116	1119
$^5D_0$–$^7F_3$	6490	15,408	1832	6498	15,388	1847
	6499	15,387	1853	6505	15,373	1862
	6507	15,368	1872	6514	15,353	1882
	6532	15,309	1931	6536	15,300	1935
	6544	15,282	1958	6547	15,274	1961
$^5D_0$–$^7F_4$	6930	14,430	2810	6920	14,451	2784
	6935	14,420	2820	6952	14,384	2851
	6959	14,370	2870	6967	14,352	2883
	6999	14,288	1952	6978	14,331	2904
	7004	14,279	2961	7006	14,272	2963
	7015	14,255	2985	7015	14,256	2979
	7026	14,233	3007	7025	14,235	3000
	7045	14,194	3046	7035	14,215	3020
				7053	14,178	3057

of vacancies for α-$La_2(MoO_4)_3$; moreover, α-$Eu_2(MoO_4)_3$ is not isostructural with α-$La_2(MoO_4)_3$. So, it is possible that the Eu^{3+} ions partially occupy the vacant sites, as reported elsewhere (*13, 14*). To confirm this possibility, we performed two types of experiments, looking for an enhancement of the fluorescence intensity of the *D* site, that is, for a preferential occupation of vacant sites by Eu^{3+}.

In the first experiment we increased the dopant percentage up to 10%. At this concentration, neither X-ray analysis nor spectroscopy exhibited supplementary lines corresponding to α-$Eu_2(MoO_4)_3$ or even β'-$Eu_2(MoO_4)_3$ "clusters" (*15, 16*). In the second experiment the synthesis was performed at a temperature higher than the α–β phase transformation temperature for a given concentration. For both experiments, an increase of the *D* site fluorescence intensity was observed. But in no case did we observe a fifth spectrum which might correspond to the occupation of the second type of vacancies available in the α-$La_2(MoO_4)_3$ structure.

Obviously, it is not possible to exclude the existence of a small amount of other phases such as La_2MoO_6, which could possibly be obtained by decomposition of the sesquimolybdate (*17*); but this can be rejected because of different energy positions for the spectrum *D*. Another possibility is the existence of microdomains such as $LaEu(MoO_4)_3$. To our knowledge, these types of compounds have been looked for

TABLE I—*Continued*

	Spectrum *C*			Spectrum *D*		
Transition	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})
$^5D_0$–$^7F_0$	5806	17,224	0	(5804)	(17,230)	0
$^5D_0$–$^7F_1$	5916	16,902	322	5900	16,949	281
	5923	16,883	341	5938.5	16,839	391
	5959	16,786	438	5953	16,798	432
$^5D_0$–$^7F_2$	6135	16,299	925	6085	16,434[a]	
	6157	16,243	981	6116	16,351[a]	
	6173	16,200	1024	6120	16,340[a]	
	6203	16,121	1103	6133	16,307	923
	6227	16,059	1165	6152	16,255	975
				6172	16,204	1026
				6205	16,116	1114
$^5D_0$–$^7F_3$	6507	15,368	1856			
	6525	15,326	1898	6500	15,385	1845
	6537	15,296	1928	6523	15,330	1900
	6550	15,267	1957	6538	15,296	1934
	6561	15,242	1982	6550	15,267	1963
$^5D_0$–$^7F_4$	6929	14,434	2790	6920	14,451	2779
	6958	14,372	2852	6950	14,388	2842
	6973	14,342	2882	6985	14,316	2914
	7003	14,280	2944	7002	14,282	2948
	7008	14,269	2955	7008	14,269	2961
	7028	14,230	2994	7017	14,250	2980
	7033	14,220	3004	7026	14,233	2997
	7040	14,205	3019	7038	14,208	3022
	7050	14,184	3040	7054	14,176	3054

[a] Indicates probable vibronic transitions.

only when the α-$Ln_2(MoO_4)_3$ structures are the same for the two rare earth ions (*5*). Our routine X-ray powder analysis is probably not sufficient to detect this occurrence even when the Eu^{3+} concentration is high. The last possibility is a local modification of the arrangement of vacancies, also creating microdomains.

As pointed out by Nassau *et al.* (*18*), the rearrangement of vacancies for the different α-$Ln_2(MoO_4)_3$ types involves only a small difference of the network energy. From a spectroscopic point of view, the environment characterized by the spectrum *D* is different from that of α-$Gd_2(MoO_4)_3:Eu^{3+}$ (Section IV.3). It is noteworthy that the broadest lines indicate a less defined environment. Moreover, the high temperature synthesis—when the vacancies are disordered (β phase)—seems to favor the creation of *D* sites, preserved after cooling.

A few lines in the α-$La_2(MoO_4)_3:Eu^{3+}$ spectrum cannot be attributed to any site ([a] in Table I); they are probably vibronic. This is a common feature of a great number of rare earth molybdates and tungstates and will be discussed later.

$Bi_2(MoO_4)_3:Eu^{3+}$

The recorded spectrum of Bi_2(Mo

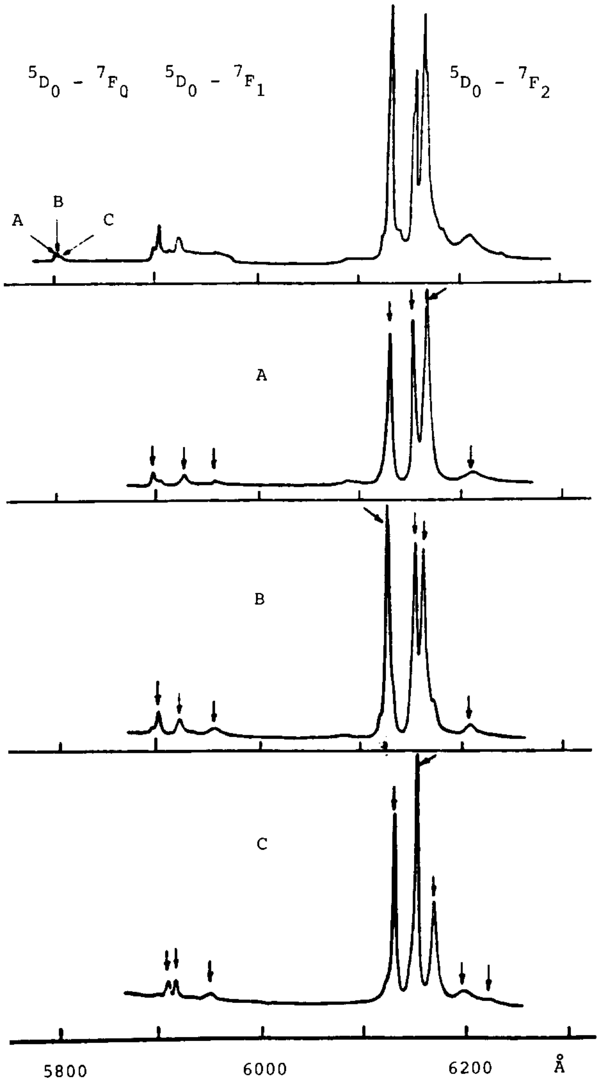

FIG. 1. Part of the fluorescence of α-$La_2(MoO_4)_3$: Eu^{3+} at 77K. Spectrum *A*: under laser excitation λ_e = 5800 Å; Spectrum *B*: under laser excitation λ_e = 5802 Å; Spectrum *C*: under laser excitation λ_e = 5806 Å. The top spectrum is recorded under uv excitation. Arrows indicate lines corresponding to the excited Eu^{3+} site.

$O_4)_3$: Eu^{3+} is not as well resolved as for other molybdates or tungstates. Even modifications in the synthetic conditions did not significantly reduce the broadness of transition lines. The spectrum is also complicated by the existence of several point sites occupied by the substituting ion. Figure 3 shows part of the classical fluorescence spectrum under uv excitation. Two lines for $^5D_0 \rightarrow {}^7F_0$ transition are recorded at 5804 Å (site *A*) and 5807 Å (site *B*), indicating that the Eu^{3+} ions occupy at least the two nonequivalent point sites of the Bi^{3+} ion. However, the number of lines observed for $^5D_0$

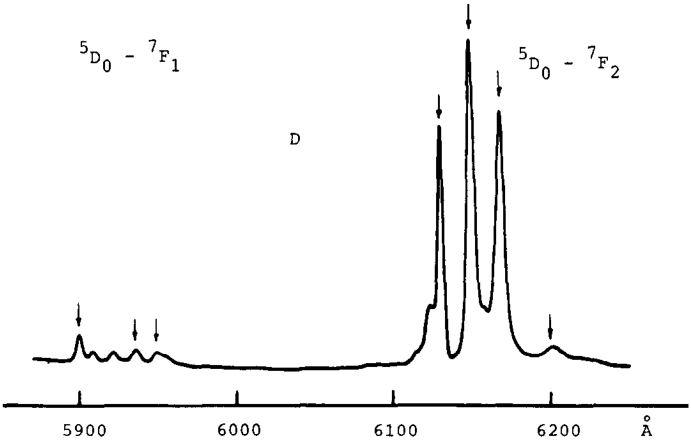

FIG. 2. Part of the emission spectrum of Eu^{3+} at vacant sites under laser excitation λ_e = 5804 Å at 77 K.

$\rightarrow$ $^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, 8 and 12, respectively, probably implies occupation of more than two sites.

The selective excitation of site A, corresponding to the $^5D_0$ level having the highest energy, yields a simple spectrum without any ambiguity. The energy transfer to site B is very small, characterized only by some weak lines. For each transition the number of lines observed corresponds to a maximum lifting of the degeneracy, indicating a point site symmetry not higher than C_2, which agrees with the crystallographic results. Moreover, some extra lines are attributed to vibronic transitions. Thus, it is possible to derive from experiment the energy level sequence for the ^7F_J multiplet (J = 0–4) (Table II).

The spectrum recorded under selective excitation of the lower $^5D_0$ level, does not present any line corresponding to site A. However, the number of lines observed for the $^5D_0 \rightarrow {}^7F_{1,2,3}$ transitions is too great to correspond to only one point site. A slight

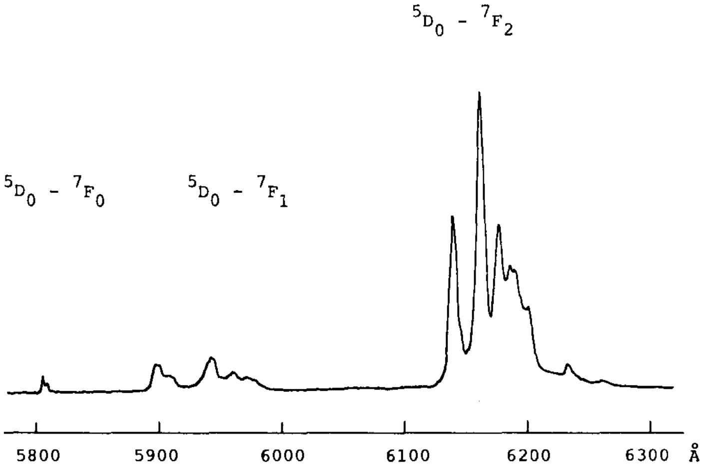

FIG. 3. Characteristic fluorescence spectrum of $Bi_2(MoO_4)_3 : Eu^{3+}$ under uv excitation at 77 K.

TABLE II

TRANSITIONS AND ENERGY LEVEL SCHEME OF $Bi_2(MoO_4)_3 : Eu^{3+}$

	Spectrum A			Spectrum $B + C$		
Transition	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})
$^5D_0$–$^7F_0$	5803.5	17,231	0	5806.5	17,222	
$^5D_0$–$^7F_1$	5896.5	16,959	272	5895	16,964	
	5938	16,841	390	5902.5	16,942	
	5957.5	16,786	445	5941	16,832	
				5955	16,793	
				5969	16,753	
$^5D_0$–$^7F_2$	6068	16,480[a]		6071	16,472[a]	
	6123	16,332[a]		6126	16,324[a]	
	6132	16,308[a]		6136.5	16,296	
	6135	16,300	931	6142	16,281	
	6157	16,242	989	6158.5	16,238	
	6171	16,205	1026	6173	16,200	
	6180.5	16,180	1051	6182	16,176	
	6186.5	16,164	1067	6197	16,137	
				6228	16,057	
$^5D_0$–$^7F_3$	6417.5	15,582[a]		6421	15,574[a]	
	6435.5	15,539[a]		6436	15,538[a]	
	6462.5	15,474[a]		6465	15,468[a]	
	6474.5	15,445[a]		6477.5	15,438[a]	
	6502.5	15,379	1852	6496	15,394	
	6513	15,354	1877	6501.5	15,381	
	6530	15,314	1917	6504	15,375	
	6550	15,267	1964	6522.5	15,332	
	6557.5	15,250	1981	6532.5	15,308	
	6564	15,235	1996	6543	15,284	
				6551.5	15,264	
				6558.5	15,247	
$^5D_0$–$^7F_4$	6908	14,476	2755	6887	14,520	
	6932	14,426	2805	6903.5	14,485	
	6941	14,407	2824	6950.5	14,387	
	6950	14,388	2843	6969	14,349	
	6976	14,335	2896	6977.5	14,332	
	7009	14,267	2964	6998	14,290	
	7028	14,229	3002	7009	14,267	
	7053	14,178	3053	7017.5	14,250	
	7057.5	14,169	3062	7030	14,225	
				7056	14,172	
				7062	14,160	
				7073	14,138	

[a] Indicates probable vibronic transitions.

variation of the excitation wavelength near 5807 Å does not modify the relative fluorescence intensities. The attempted excitation of the $^5D_0$ level through the $^7F_1 \rightarrow {}^5D_0$ transition did not succeed, contrary to the $Y_2MoO_6 : Eu^{3+}$ case (*1*), because of the broadness of the lines.

It is difficult to determine completely the

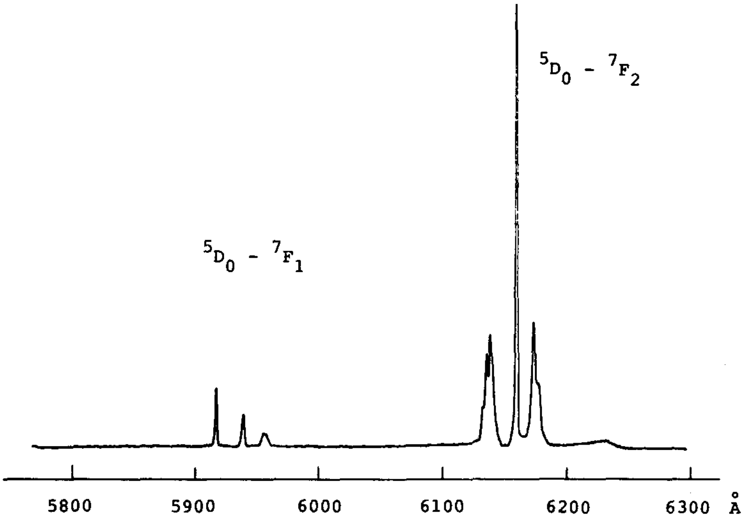

FIG. 4. Characteristic fluorescence spectrum of α-$Gd_2(MoO_4)_3$: Eu^{3+} under uv excitation at 77 K.

origin of the extra lines. Some of them can be correlated with those of spectrum *A*, and have a vibronic nature. However, it seems impossible to attribute all of the observed lines to vibronic transitions, especially those located in the $^5D_0 \rightarrow {}^7F_4$ wavelength range. Perhaps a third site exists whose $^5D_0$ level coincides exactly with the $^5D_0$ of site *B*. We already noted this situation for Y_2MoO_6:Eu^{3+} (*1*). In fact, the structure of $Bi_2(MoO_4)_3$ has two available positions for Eu^{3+}: substituting bismuth and the vacant positions. Similar to α-$La_2(MoO_4)_3$, it appears that α-$Eu_2(MoO_4)_3$ is not isomorphous to $Bi_2(MoO_4)_3$, and the Eu^{3+} ion can partially occupy the vacant positions existing in the structure. However, in this case it was not possible to confirm this possibility by spectroscopic methods. Moreover, this compound has both oxygen and molybdenum defects which induce a slight variation of the local crystal field. This fact might explain the broadness of the observed fluorescence lines.

$Gd_2(WO_4)_3$: Eu^{3+} and α-$Gd_2(MoO_4)_3$: Eu^{3+}

The fluorescence spectra of Eu^{3+} doped in these matrices are much simpler than those of the preceding compounds (Figs. 4 and 5). This is in agreement with the structure of $Gd_2(WO_4)_3$ (*6*), where the rare earth occupies only one point site. Moreover, the spectra are very similar, and this constitutes further proof that the two compounds are isostructural, as suggested by Brixner *et al.* (*11*). We observe one line for the $^5D_0 \rightarrow {}^7F_0$ transition, although with a relatively weak intensity for the tungstate, and detected only at liquid helium temperature for the molybdate. From other transitions, it appears that the degeneracy of the levels is nearly lifted, which indicates a point site symmetry not higher than C_2. An energy level scheme is derived from the experiment by comparing the data with lines having $^5D_1$ as the emitting level (Table III). The spectra of Eu^{3+} in $Gd_2(WO_4)_3$ and α-$Gd_2(MoO_4)_3$ are similar in position and relative intensities, particularly for the $^5D_0 \rightarrow {}^7F_{3,4}$ transitions. This can be related to the values of the sixth-order crystal field parameters, contributing largely to the splitting of these transitions, that are not very sensitive to slight variations in the atomic positions and/or the cell parameters. On the other hand, the spectra observed here are analo-

TABLE III

TRANSITIONS AND ENERGY LEVEL SCHEMES OF α-$Gd_2(MoO_4)_3:Eu^{3+}$ AND $Gd_2(WO_4)_3:Eu^{3+}$

	α-$Gd_2(MoO_4)_3:Eu^{3+}$			$Gd_2(WO_4)_3:Eu^{3+}$		
Transition	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})
$^5D_1$–$^7F_0$	5271	18,972				
	5276	18,954				
$^5D_1$–$^7F_1$	5355	18,673		5360.5	18,655	
	5357.5	18,665		5366	18,636	
	5362.5	18,648		5371.5	18,617	
	5374	18,608		5386.5	18,565	
	5376	18,601		5392.5	18,544	
	5381	18,584				
	5388.5	18,558				
	5391.5	18,548				
	5396.5	18,531				
$^5D_1$–$^7F_2$	5536	18,064		5534.5	18,068	
	5543.5	18,039		5541	18,047	
	5554.5	18,003		5554.5	18,003	
	5557.5	17,994		5561.5	17,981	
	5562	17,979		5563.5	17,974	
	5567	17,963		5570	17,953	
	5572.5	17,945		5607.5	17,833	
	5611.5	17,821				
	5618.5	17,798				
$^5D_1$–$^7F_3$	5849.5	17,095		5847.5	17,101	
	5859.5	17,066		5865	17,050	
	5875	17,021		5871	17,033	
	5902.5	16,942		5897.5	16,956	
$^5D_0$–$^7F_0$	5810	17,212[a]	0	5809.5	17,213	0
$^5D_0$–$^7F_1$	5915	16,906	306	5923	16,883	330
	5938	16,841	371	5930.5	16,862	351
	5953	16,798(sh)[b]		5955	16,793	420
	5956.5	16,791	421	5956	16,790(sh)[b]	

gous to spectra of $Na_5Ln(MO_4)_4:Eu^{3+}$, double molybdates (tungstates) (*19*) whose structure is also derived from the scheelite, and where the rare earth occupies a 4*b* crystallographic position, having S_4 site symmetry (*20, 21*). This analogy can also explain the relatively low intensity of the $^5D_0 \rightarrow {}^7F_0$ transition.

For these two compounds, some problems remain concerning the interpretation of the $^5D_0 \rightarrow {}^7F_{1,2,3}$ transitions, since the most intense lines are accompanied by various extra lines or shoulders ([c] and sh in Table III). All of these lines are always present under selective excitation. Fortunately, by comparing transitions having $^5D_0$ as emitting level with those of $^5D_1$, it is possible to assign the various lines corresponding to electronic transitions.

Vibronic Transitions

In connection with the matrices studied here, we noted that some of the spectral lines can be attributed to vibronic transitions. It is a common feature for the Eu^{3+}

TABLE III—*Continued*

	α-$Gd_2(MoO_4)_3 : Eu^{3+}$			$Gd_2(WO_4)_3 : Eu^{3+}$		
Transition	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})	λ(Å)	E(cm^{-1})	ΔE(cm^{-1})
$^5D_0$–$^7F_2$	6102	16,387[c]		6103	16,385[c]	
	6111	16,365[c]		6126	16,324[c]	
	6123	16,333[c]		6136.5	16,296	917
	6131	16,311(sh)[b,c]		6139.5	16,288(sh)[b,c]	
	6133	16,305	907	6146	16,271[c]	
	6138	16,292[c]		6161	16,231	982
	6159.5	16,235	977	6171.5	16,204	1009
	6174	16,197	1015	6220	16,077	1136
	6177	16,189(sh)[b]		6229.5	16,053	1160
	6220	16,077	1135			
	6229.5	16,052	1160			
$^5D_0$–$^7F_3$	6453	15,485[c]		6457	15,486[c]	
	6495	15,396[c]		6482.5	15,426[c]	
	6511	15,359	1853	6493.5	15,400[c]	
	6515	15,349	1863	6509.5	15,362	1851
	6526	15,323	1889	6515.5	15,349	1864
	6545	15,279	1933	6526.5	15,322	1891
	6577.5	15,203	2009	6543.5	15,282	1931
				6576.5	15,206	2007
$^5D_0$–$^7F_4$	6935	14,420	2792	6931	14,428	2785
	6947	14,394	2818	6952.5	14,383	2830
	6966	14,355	2857	6963	14,362	2851
	6980	14,327	2885	6982.5	14,322[a]	2891
	7013	14,258	2954	7014.5	14,256	2957
	7026	14,233	2979	7024	14,237	2976
	7037	14,211	3001	7036.5	14,212	3001
	7065	14,154	3058	7064.5	14,155	3058

[a] Recorded at 4 K.
[b] sh = shoulder.
[c] Indicates probable vibronic transitions.

spectra to associate this type of transition with the emission of the $^5D_0$ level. Judd (*22*) correlated this fact with the hypersensitivity of the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition; effectively, almost all rare earth hypersensitive transitions are accompanied by such vibronics. For the molybdates and tungstates, the Raman spectra are very rich (*23–25*), and present intense transitions, especially between 300 and 1000 cm^{-1}, corresponding to the vibrations of the distorted $MoO_4^{=}$ tetrahedron. By considering these frequencies, only the vibronic transitions observed here in the energy range 15,400–15,500 cm^{-1}—near $^5D_0 \rightarrow {}^7F_3$—can be correlated with $^5D_0 \rightarrow {}^7F_2$. The other, located near 16,400 cm^{-1}, should correspond to vibronics associated with $^5D_0 \rightarrow {}^7F_0$, since $^5D_0 \rightarrow {}^7F_1$ represents a dipolar magnetic transition, usually not associated with significantly intense vibronic transitions. In fact, the $^5D_0 \rightarrow {}^7F_0$ transition can be also considered as a hypersensitive transition (*26*). When allowed by the selection rules (*27*), the extreme variation of the intensity of $^5D_0 \rightarrow {}^7F_0$ transition is due to two factors. The

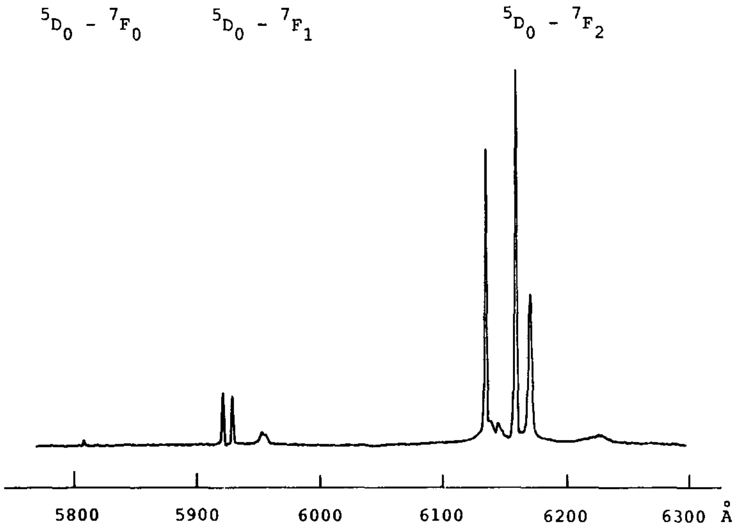

FIG. 5. Characteristic fluorescence spectrum of $Gd_2(WO_4)_3 : Eu^{3+}$ under uv excitation at 77 K.

first is the value of the phenomenological intensity parameters, including the effect of the polarizability of the ligand, say, the B_{210} and B_{230} parameters. Since a $J = 0 \rightarrow J' = 0$ transition is always forbidden, the second factor in the intensity arises from the admixture of the $|^7F_{20}\rangle$ ket in the $^7F_{00}$ wavefunction (*28*). Finally, the $^5D_0 \rightarrow {}^7F_0$ transition exists through its "$^5D_0 \rightarrow {}^7F_2$" admixture, which confers to it a hypersensitive character.

Conclusion

In this work, it was possible to construct unambiguously the energy level sequences for the Eu^{3+} ion occupying the different crystallographic positions encountered in the series of compounds, by using the dye laser selective excitation technique. Some vibronic transitions associated with $^5D_0 \rightarrow {}^7F_0$ as well as with $^5D_0 \rightarrow {}^7F_2$ transitions have also been assigned. The spectroscopic results resolve the ambiguity about the structure of α-$Gd_2(MoO_4)_3$, which appears to be isostructural with $Gd_2(WO_4)_3$. The point symmetries of all sites occupied by the rare earth ion are lower than or equal to C_2. It is not realistic to perform direct crystal field calculations, due to the relatively low number of levels and to the high number of parameters involved. However, most of these compounds have scheelite-related structures, and the procedure of descending symmetry might be applied to them, if we are able to find a compound having a higher site symmetry for the rare earth. This will be attempted when a complete analysis of the optical properties of some double molybdates or tungstates is performed; the site symmetry occupied by the rare earth in these scheelite-related compounds is S_4, and we noted that their optical spectra are quite similar to those of phases studied here.

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