

Spectroscopic Properties of Eu^{3+} in Lanthanum Chlorotungstates

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The spectroscopic properties of Eu^{3+} doped into two lanthanum chlorotungstates matrices, namely LaWO_4Cl (1-1) and $\text{La}_3\text{WO}_6\text{Cl}_3$ (3-1), are investigated. The fluorescence spectra of these compounds, recorded at room and liquid nitrogen temperatures, show that the lanthanide ion occupies only one site with the low symmetry, C_2 , in both cases. From the energy level schemes of the 7F_J levels ($J = 0, 1, 2, 3, 4, 5$), two sets of crystal field parameters (cfp) are deduced, in a C_2 approximated point symmetry (i.e., 9 cfp), simulating the experimental data, correctly. Furthermore, for the 3-1 compound, the data is complete enough to extend the calculations to the real point group, C_3 (14 cfp). © 1990 Academic Press, Inc.

Introduction

In their studies of the rare earth oxychloride-tungsten oxide chemical systems, Brixner *et al.* (1-3) identified two series of compositions: the 1-1 REWO_4Cl (RE = Y, La-Tm) and the 3-1 $\text{RE}_3\text{WO}_6\text{Cl}_3$ (RE = La-Gd) compounds. The 3-1 phase represents one structural type, with $P6_3/m$ as crystallographic space group (176). Two structural types are found for the 1-1 phase, depending on the rare earth ion size: an orthorhombic $Pbcm$ structure (57) from lanthanum to samarium and a monoclinic symmetry $C2/m$ (12) from europium to thulium, and also including yttrium.

The same authors also reported some physicochemical properties such as IR, diffuse reflectance, Raman, and luminescence spectra of the pure REWO_4Cl and $\text{RE}_3\text{WO}_6\text{Cl}_3$ compounds as well as some rare

earth-doped lanthanum hosts. This paper, the first of a series of spectroscopic studies on these chemical systems, reports the detailed measurements of the energy levels of Eu^{3+} in these matrices, in order to derive sets of crystal field parameters.

Experimental

Synthesis

The samples, in powder form, are synthesized as indicated in Ref. (1), by a solid state reaction between stoichiometric ratios of rare earth oxychloride and tungsten oxide. The finely ground mixture is fired at 900°C for 12 and 24 hr for REWO_4Cl and $\text{RE}_3\text{WO}_6\text{Cl}_3$, respectively. Single phased samples are obtained. We differ slightly from Ref. (1) for the rare earth oxychloride synthesis. It is prepared by melting the rare earth hydrated chloride (with a 1 and 5 mol% amount of Eu^{3+} doping) and a large excess of CaCl_2 , at 700°C. After reaction, CaCl_2 is

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removed by washing the mixture with diluted acetic acid (4).

Crystal Structures

The structure of the 1-1 compound REWO_4Cl for $\text{RE} = \text{La}$ to Sm is orthorhombic (1, 5-7). The coordination of the tungsten atom is a trigonal bipyramid of 5 oxygens. The coordination polyhedron of the lanthanum atoms is a monocapped square antiprism with 5 oxygens and 4 chlorine atoms. In that $Pbcm$ crystallographic group, the rare earth occupies two atomic positions of the same type, each with C_s symmetry for the point site. The structure can be described with a subcell along the b axis, with an approximated $Pm\bar{c}n$ (62) space group. The optical results will confirm that the rare earth occupies one point site in that structure.

The structure of the 3-1 compound $\text{RE}_3\text{WO}_6\text{Cl}_3$ is the same from lanthanum to gadolinium (3, 8-10). The tungsten atoms have an unusual trigonal prismatic 6-fold coordination. The lanthanum atoms are in the 10-fold coordination with 6 oxygens and 4 chlorine atoms.

Optical Measurements

The fluorescence spectra of $\text{REWO}_4\text{Cl}:\text{Eu}^{3+}$ and $\text{RE}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$ were obtained by UV lamp or argon laser line excitations. A tunable continuous dye laser was used to selectively excite the $^5\text{D}_0$ level. The fluorescence was detected by using standard techniques at room and liquid nitrogen temperatures in the 400-700 nm wavelength range.

Results

The fluorescence of neither compound is very intense. The spectra essentially consist of the emission from the $^5\text{D}_0$ level, which is convenient for the determination of the Eu^{3+} energy level scheme. At 77 K more

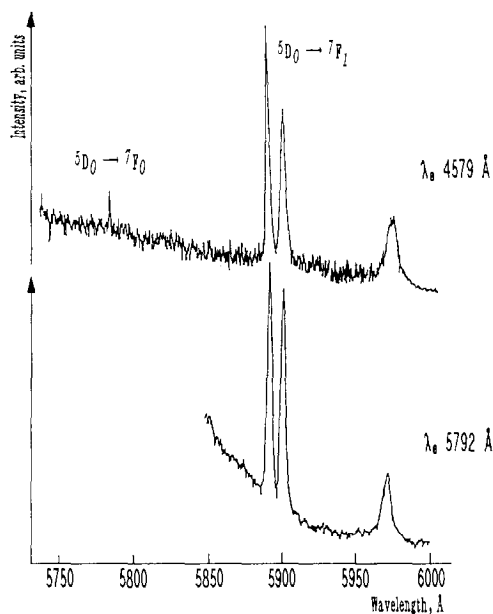


FIG. 1. Part of the fluorescence spectra of $\text{LaWO}_4\text{Cl}:\text{Eu}^{3+}$ at 77 K. The bottom part is from the dye laser excitation.

fluorescence lines are observed for $\text{RE}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$, occurring from $^5\text{D}_1$ and $^5\text{D}_2$ excited levels. Thus, some transitions from these levels are overlapping others from $^5\text{D}_0$, which justifies the dye laser selective excitation.

$\text{LaWO}_4\text{Cl}:\text{Eu}^{3+}$

Figure 1 shows a part of the fluorescence spectrum at 77 K. Only lines from $^5\text{D}_0$ are recorded. This very simple spectrum clearly underlines that the rare earth occupies a single point site, with the low symmetry, C_s . It is surprising to note that the lack of the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transition. Usually, the intensity of that transition is low, but always detected. That transition, forbidden in first order by the electric/magnetic dipole selection rules, is observed only as a consequence of the J -mixing, which mixes the $^7\text{F}_3$ wavefunctions with other $^7\text{F}_j$ ones, through the second- and fourth-order crystal field param-

ters. This feature is consistent with the relatively small values of the fourth-order cfp (see below). From the spectrum we can derive part of the 7F_J energy level scheme (Table I), i.e., 14 levels.

$La_3WO_6Cl_3 : Eu^{3+}$

At 77 K the $RE_3WO_6Cl_3 : Eu^{3+}$ spectrum exhibits about 40 well-resolved fluorescence lines. Only one ${}^5D_0 \rightarrow {}^7F_0$ transition is recorded at $17,265\text{ cm}^{-1}$, which confirms that the rare earth occupies only one point site. The unambiguous assignment of the transitions is deduced from the dye laser selective excitation (Fig. 2). An energy level scheme is derived from the spectrum (28 levels), more complete for a simulation in the real crystal field potential, involving 14 cfp.

Crystal Field Calculations

The $4f^6$ configuration of trivalent europium is a convenient case for crystal field calculations. This is due to a lowest term of the configuration 7F_J ($J = 0-6$), well isolated from the rest of the term series (about $12,000\text{ cm}^{-1}$ between 7F_6 and 5D_0). Furthermore, this term is alone of this multiplicity and, consequently, not mixed by the crystal field.

Thus, instead of considering the complete $4f^6$ configuration, involving a very large secular determinant (3003×3003), the crystal field calculation can be performed on the strongly reduced $[{}^7F_J]$ basis with only a 49×49 matrix size. Naturally, other interactions, i.e., free ion and second-order spin-orbit effects, are neglected. These computations can be performed on a simple AT-type PC.

In Wybourne's formalism (11) the crystal field Hamiltonian is expressed as a sum of products of spherical harmonics and cfp:

$$H_{cf} = \sum_{kq} [B_{kq}(C_{kq} + (-1)^q C_{kq}) + iS_{kq}(C_{kq} - (-1)^q C_{kq})].$$

TABLE I
EXPERIMENTAL AND CALCULATED ENERGY LEVELS
OF $LaWO_4Cl : Eu^{3+}$ (1-1) AND $La_3WO_6Cl_3 : Eu^{3+}$ (3-1)

State $2s+1L_J$	1-1		3-1		
	Experi- mental	Calculated C_{2v}	Experi- mental	Calculated C_{2v}	Calculated C_s
7F_0	0	0	0	0	0
7F_1	298	295	287	288	288
	321	314	354	347	347
	530	529	446	453	455
7F_2	937	943	871	875	881
	994	990	919	921	920
	1,033	1034	961	962	966
	1,137	1128	1,178	1180	1171
	1,191	1185	1,213	1204	1203
7F_3	—	1858	1,815	1828	1829
	—	1860	1,846	1851	1853
	—	1861	1,874	1861	1857
	—	1945	1,900	1901	1889
	—	1947	1,909	1908	1907
	—	1955	1,937	1932	1935
	—	2016	—	2047	2043
7F_4	2,669	2678	2,512	2499	2506
	—	2692	2,761	2758	2787
	—	2782	2,813	2828	2833
	—	2782	—	2889	2837
	—	2794	—	2915	2922
	2,865	2863	2,970	2980	2942
	2,915	2921	3,007	3004	3017
	2,945	2935	—	3020	3046
	3,014	3021	3,102	3097	3089
	—	—	3,774	3779	3772
7F_5	—	—	3,814	3806	3808
	—	—	3,860	3863	3858
	—	—	3,948	3955	3966
	—	—	3,957	3967	3977
	—	—	4,053	4043	4033
	—	—	4,113	4114	4106
	—	—	4,127	4123	4129
	—	—	4,139	4140	4148
	—	—	—	4193	4187
	—	—	—	4215	4192
5D_0	17,271	—	17,265	—	—
5D_1	—	—	18,981	—	—
	—	—	19,001	—	—
5D_2	—	—	19,021	—	—
	—	—	21,267	—	—
	—	—	21,405	—	—
—	—	21,539	—	—	

Note. All values are in cm^{-1} units.

In the C_{2v} point symmetry, all S_{kq} values vanish, which gives 9 cfp. On the contrary, the cfp involved in the C_s symmetry have a nonzero imaginary part, S_{kq} , which gives

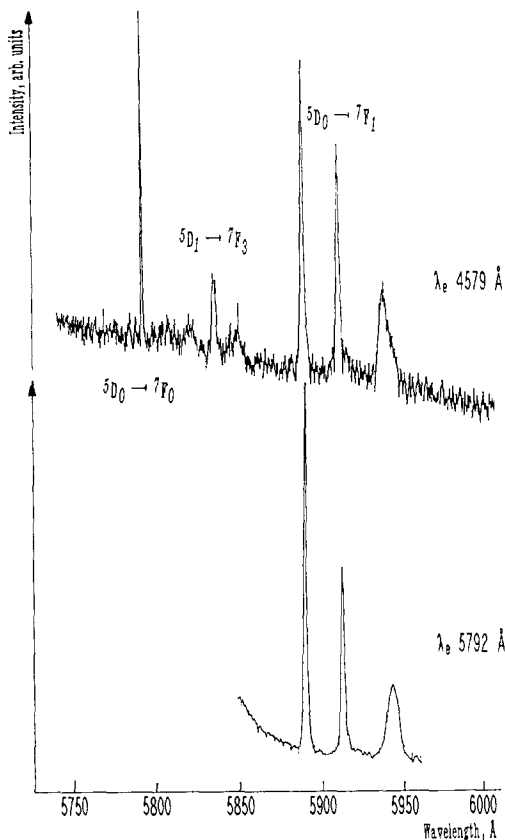


FIG. 2. Part of the fluorescence spectra of $\text{La}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$ at 77 K. The bottom part is from the dye laser excitation.

15 parameters. But, it is always possible to choose a particular reference axis system in order to fix S_{22} to zero, and to consider only 14 nonzero cfp. Thus, when the experimental data is not enough large, or when the computing time has to be saved, it is convenient to remove the imaginary part of the crystal field potential (12). In the present case, the C_{2v} symmetry is a good approximation.

For an energy level scheme deduced from the fluorescence of microcrystalline powders, the lack of polarized light measurements increases the difficulty of a simulation because the Stark levels are not attributed

to their irreducible representations. At first order, for example, the ${}^7\text{F}_1$ splittings are reproduced only through the B_{02} and B_{22} effects. There are three sets of these parameters simulating the splittings. The same occurs for other parameters, acting on other levels. Finally, there are many possible B_{kq} parameter sets.

The refining procedure consists of making a three-step calculation. The first finds the B_{2q} sets simulating the ${}^7\text{F}_1$ splitting. The second keeps B_{2q} fixed and includes the fourth-order cfp B_{4q} , and experimental ${}^7\text{F}_2$ levels in order to test the possible values, to choose the best B_{4q} set from the smallest rms deviation. The last step includes other B_{kq} parameters and other experimental levels, before freely varying all cfp. Naturally, we have to keep in mind that these cfp also have to simulate the crystal field effect for other rare earth ions in the same matrix.

This procedure is relatively involved. It could be simplified if the starting values of cfp could be estimated by an ab initio calculation from atomic positions in the structure. We made some attempts by using the "three parameter method" (13), considering an effective charge for oxygen and tungsten ions. The set of cfp obtained does not constitute a good starting value set. We suppose that this is a consequence of the unusual coordination of the tungsten. We prefer to consider the "pure" phenomenological simulation.

$\text{LaWO}_4\text{Cl}:\text{Eu}^{3+}$

The energy level scheme is poor. We cannot perform the simulation in the real point symmetry, but in the C_{2v} approximation. Calculated levels are compared to the experimental data in Table I. The crystal field parameters are listed in Table II. As mentioned before the fourth-order parameters are small, especially B_{40} , and the J -mixing is also small, which explains the nonobserved ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ transition. The rms deviation is

TABLE II
CRYSTAL FIELD PARAMETERS OF $\text{LaWO}_6\text{Cl}_3:\text{Eu}^{3+}$
(1-1) AND $\text{La}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$ (3-1)

Parameters B_{kq}	3-1		
	1-1 C_{2v}	C_{2v}	C_s
B_{20}	749 (25)	-84 (23)	-82 (23)
B_{22}	86 (24)	-327 (16)	-318 (16)
B_{40}	-115 (48)	-1186 (28)	-1110 (36)
B_{42}	-363 (36)	141 (39)	55 (49)
S_{42}	—	—	-197 (82)
B_{44}	-218 (40)	726 (22)	705 (25)
S_{44}	—	—	157 (63)
B_{60}	-593 (63)	223 (37)	367 (49)
B_{62}	-662 (53)	-310 (32)	-73 (47)
S_{62}	—	—	244 (59)
B_{64}	698 (43)	1169 (21)	1114 (27)
S_{64}	—	—	36 (61)
B_{66}	36 (40)	-338 (30)	-462 (41)
S_{66}	—	—	-44 (55)
Nb. Lev.	14	29	29
Residue	633	1461	1324
σ	10.3	8.3	8.6

Note. All values are in cm^{-1} units.

not very good; not as a consequence of a bad simulation, but because of the bad ratio number of levels/number of parameters. The small value of the residue shows that the simulation is satisfying.

$\text{La}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$

The energy level scheme is quite complete (Table I). Anyway, a first satisfying attempt is made in the approximated C_{2v} symmetry. A more complete simulation with the C_s point symmetry gives quite the same rms (with 5 added cfp) and a better residue. It is noteworthy that all imaginary parts of the cfp are relatively small, which justifies the previous approximation (Table II).

Conclusion

The optical properties of the Eu^{3+} doped into two rare earth chlorotungstates have been examined. The energy level schemes have been simulated, with good rms within the crystal field theory frame. These cfp will be used as starting values for a more complete simulation on the $4f^2$ and $4f^3$ configurations of Pr^{3+} and Nd^{3+} ions in these matrices.

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