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Emission spectra and crystal field calculation of europium-doped C-type In_2O_3 oxide

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Abstract

The luminescent properties of the trivalent europium ion in the C-type indium oxide with two sites for the Eu^{3+} ion have been analysed. Because of the selection rules almost all emission arises from the C_2 point symmetry site, since the S_6 site does not allow electric dipole transitions. The energy level scheme of the 21 ^7F_J ($J = 0$–4) levels is well reproduced with an r.m.s. deviation of 3.9 cm^{-1} with 14 crystal field parameters allowed for the C_2 site symmetry. A comparison with the Y_2O_3:Eu^{3+} emission spectra was also carried out.

1. Introduction

The optical properties (absorption and luminescence spectra) of the rare earth sesquioxides possessing the b.c.c. structure have been studied by several researchers [1–5]. The complexity of the spectra is due to two non-equivalent rare earth atoms in the structure. Crystal field calculations have been performed for the C_2 and S_6 sites for Y_2O_3:Gd^{3+} [1]. The crystal field parameters (CFPs) appeared to be in agreement with those deduced for the europium ion in the same matrix for both the C_2 [3] and the S_6 [6] site.

In the present paper we report for the first time the luminescent properties of the europium ion in the indium sesquioxide, which crystallizes with the C-type Y_2O_3 structure. The CFPs deduced from the spectra reveal the evolution of the crystal field strength in an isostructural series. A comparison with the Eu^{3+}:C-Y_2O_3 energy level scheme was also carried out.

2. Experimental details

Polycrystalline samples of $In_{2-x}Eu_xO_3$, $x = 0.02$, were synthesized by firing an intimately ground mixture of corresponding oxides at 1100 °C for 24 h. The sample purity was checked by X-ray powder diffraction.

Non-polarized fluorescence spectra of the trivalent europium ion were recorded using UV excitation (Osram HBO 150 W mercury lamp centred at 300 nm) or the 457.9 nm blue line of a 5 W continuous wave argon ion laser. Dye laser excitation of the $^5D_0 \longrightarrow {}^7F_0$ (or $^5D_0 \longrightarrow {}^7F_1$) transition was also carried out. The spectra were recorded at 77 K by using standard techniques.

3. Crystal structure

Indium sesquioxide crystallizes in the C-type rare earth oxide structure, C-RE_2O_3 (RE ≡ Eu–Lu, Y) [7]. The crystal structure is b.c.c. ($a = 10.117$ Å; space group, $Ia3$, No. 206) with 16 molecules per unit cell. The 32 metal atoms are situated in the special positions 24(d) (C_2 point symmetry) and 8(b) (S_6 point symmetry). Both non-equivalent metal atoms are coordinated by six oxygen atoms as represented in Fig. 1.

4. Results and discussion

4.1. Fluorescence spectrum

The emission of the trivalent europium ion in In_2O_3 consists of fluorescence lines originating from both 24(d) and 8(b) sites occupied by rare earth ions. For

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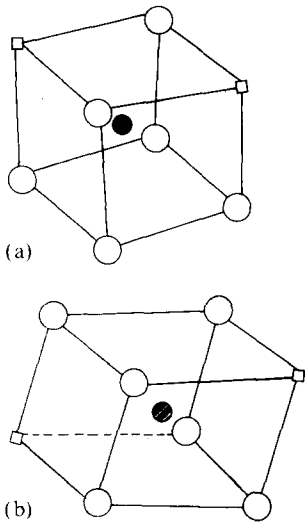

Fig. 1. Coordination polyhedra for two non-equivalent metal atoms in C-type rare earth oxides: (a) C_2 point symmetry site; (b) S_6 point symmetry site.

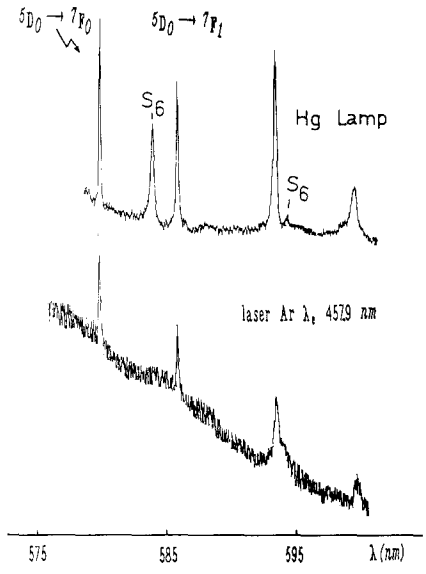

Fig. 2. Part of the emission spectra of Eu^{3+} ions in In_2O_3 under various excitations at 77 K.

the C_2 site, all $^5D_0 \longrightarrow {}^7F_J$ transitions are allowed by electric and magnetic dipole as well as by group theory selection rules. Only magnetic dipole transitions are allowed by these rules for the centrosymmetric S_6 site.

In In_2O_3:Eu^{3+} all emissions arise from the $^5D_0$ level, whereas both $^5D_1$ as well as the $^5D_2$ emission are completely quenched. Among 23 experimental lines, 21 can be attributed to the C_2 site while only 2 belong to the S_6 site. Table 1 reports the most intense emission lines.

The emission spectra depend on the excitation as follows.

(1) Under UV excitation the europium ions in both crystallographic sites are excited.

(2) The 457.9 nm laser excitation just above the $^5D_2$ levels excites selectively the C_2 site of the rare earth (Fig. 2).

TABLE 1. Positions of the most intense emission lines of Eu^{3+} in C-In_2O_3 at 77 K with their attributions

λ (nm)	E (cm^{-1})	Assignment	Site
580.2	17236	$^5D_0 \longrightarrow {}^7F_0$	C_2
584.3	17115	$^5D_0 \longrightarrow {}^7F_1$	S_6
586.2	17059	$^5D_0 \longrightarrow {}^7F_1$	C_2
593.6	16845	$^5D_0 \longrightarrow {}^7F_1$	C_2
594.7	16815	$^5D_0 \longrightarrow {}^7F_1$	S_6
599.8	16673	$^5D_0 \longrightarrow {}^7F_1$	C_2
610.9	16369	$^5D_0 \longrightarrow {}^7F_2$	C_2
612.0	16339	$^5D_0 \longrightarrow {}^7F_2$	C_2
632.4	15812	$^5D_0 \longrightarrow {}^7F_2$	C_2
648.2	15428	$^5D_0 \longrightarrow {}^7F_3$	C_2
650.3	15378	$^5D_0 \longrightarrow {}^7F_3$	C_2
664.4	15051	$^5D_0 \longrightarrow {}^7F_3$	C_2

(3) The selective dye laser excitation at 17 236 cm^{-1} (580.2 nm) of the $^5D_0 \longrightarrow {}^7F_0$ transition of the C_2 site yields emission only from the C_2 site.

(4) No emission is observed under dye laser excitation at 17 115 cm^{-1} (584.3 nm) of the $^5D_0 \longrightarrow {}^7F_1$ transition of the S_6 site.

This is different from the luminescence of Eu^{3+} in Y_2O_3, where the fluorescence lines from the S_6 site could be isolated by selective excitation in addition to those from the C_2 site [4, 5]. In the present study it has

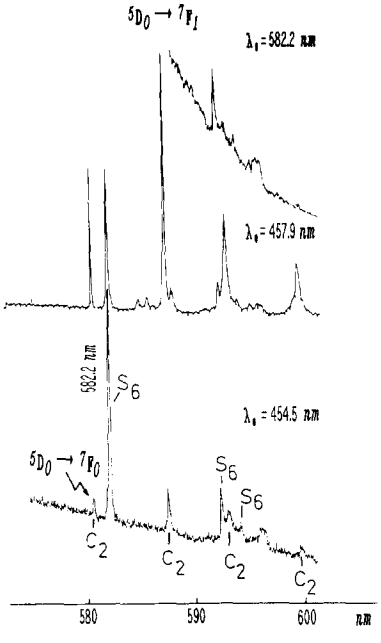

Fig. 3. Part of the emission spectra of Eu^{3+} ions in Y_2O_3 under various excitations at 77 K.

been found that the emission from the S_6 site in Y_2O_3:Eu^{3+} observed with the 457.9 nm excitation was more easily excited by the 454.5 nm line. The emission was also observed under dye laser excitation at 17 176 cm^{-1} (582.2 nm), corresponding to the lowest component of the $^5D_0 \longrightarrow {}^7F_1$ transition of the S_6 site (Fig. 3). The spectra observed here are similar to those mentioned by Su *et al.* [4]. With dye laser excitation of the $^5D_1 \rightarrow {}^7F_0$ transition (19 000 cm^{-1}, 526.3 nm) of Y_2O_3:Eu^{3+} all transitions with enhanced intensity are thus assigned to emission from the S_6 site.

Three lines can be assigned unambiguously to the S_6 site emission at 582.2 nm (17 176 cm^{-1}), 592.4 nm (16 880 cm^{-1}) and 594.2 nm (16 829 cm^{-1}) (Fig. 3). The two last lines correspond to a splitting of the E irreducible representation and are probably induced by electron–phonon coupling [6]. The 596.1 nm (16 776 cm^{-1}) line is possibly of a vibronic origin [5].

4.2. Simulation of the energy level scheme

The europium ion is very convenient for crystal field calculations. This is due to the position of the ^7F term, isolated from the rest of the configuration. The crystal field calculation can be performed accurately on a very reduced basis.

The crystal field potential is written as follows:

$$H_c = \sum_{kq} B_q^k [C_q^k + (-1)^q C_q^k] + iS_q^k [C_q^k - (-1)^q C_{-q}^k]$$

The number of non-zero parameters depends on the symmetry. They are 4 for the S_6 and 15 for the C_2 site. For the S_6 site only B_0^2 can be roughly estimated to -1700 cm^{-1} [1]. A crystal field calculation was out for the europium ion in the C_2 site. The starting set of CFPs was taken from ref. 3. The 14 phenomenological parameters out of 15, since S_2^2 cancelled by the proper choice of reference axis system, reproduce well the experimental energy level scheme (Table 2). The CFP values for Eu^{3+} in In_2O_3 are somewhat greater than for Eu^{3+} in Y_2O_3 (Table 3). This characterizes larger ^7F_J level splittings: 388 cm^{-1} instead of 349 cm^{-1} for the $^7F_1$ level and 562 cm^{-1} instead of 518 cm^{-1} for the $^7F_2$ level in In_2O_3 and Y_2O_3 respectively. Finally, we note a smooth variation in the CFPs along the rare earth series, which is consistent with the slight decrease in the Ln–O distances in the network.

TABLE 2. Experimental and calculated crystal field energy levels of the Eu^{3+} ion in the C_2 site of C-In_2O_3

$^{2S+1}L_J$ level		E(exp.) (cm^{-1})	E(cal.) (cm^{-1})
$^7F_0$	A	0	0
$^7F_1$	B	176	170
	A	393	396
	B	564	565
$^7F_2$	A	866	862
	B	899	899
	B	921[a]	925
	A	—	1248
	A	1428	1430
$^7F_3$	A	1804	1812
	B	1856	1852
	B	1888[a]	1884
	A	—	1996
	B	2041	2040
	B	2190	2187
	A	2219[a]	2217
$^7F_4$	A	2671	2671
	B	—	2771
	A	2846	2847
	B	3044	3045
	A	3089	3090
	B	3133	3133
	A	3225	3224
	B	—	3242
	A	3270	3270
$^5D_0$	A	17236	—

[a]Weak lines.

TABLE 3. Crystal field parameters for Eu^{3+} ion in the C_2 site of C-In_2O_3 (the corresponding values for Y_2O_3 have been taken from refs. 2 and 3)

Parameter	E (cm^{-1})		
	C-In_2O_3: experimental	C-Y_2O_3	
		Experimental [3]	PCEM [2]
B_0^2	−54	−196	−1220
B_2^2	−743	−695	−470
S_2^2	0	0	0
B_0^4	−1400	−1264	−760
B_2^4	−1803	−1519	−725
S_2^4	−370	−321	−130
B_4^4	1273	1092	616
S_4^4	552	255	406
B_0^6	398	267	133
B_2^6	382	228	29
S_2^6	271	276	8
B_4^6	959	894	232
S_4^6	442	281	111
B_6^6	−3	157	10
S_6^6	254	95	20

Number of experimental levels, 21; residue, 178 cm^{-1}; r.m.s. deviation, 3.9 cm^{-1}; PCEM, point charge electrostatic model.

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