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Luminescence Properties of Europium(3+)-Doped Rare-Earth Oxyhydroxides

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Visible luminescence of Eu^{3+}-doped rare-earth (RE) oxyhydroxides, (RE)OOH (RE = La, Gd, Lu, Y), was detected at 300 and 77 K under both UV and dye laser excitation. The spectral characteristics were analyzed and correlated with crystal structure. The shifts and crystal field (cf) splittings of Eu^{3+} energy levels were connected with bonding characteristics in oxyhydroxides. Furthermore, the increases in some cf splittings were deduced to result from increasing distortions of the RE coordination from ideal C_{2v} symmetry. The transitions in excitation spectra were identified, and the enhancing effect of low charge-transfer-state energy on electric-dipole-induced transitions was evaluated. The classification of $[(RE)O]_n^{n+}$ complex cations on the basis of optical spectra was discussed. RE oxyhydroxide spectra were not found to resemble those of typical tetragonal RE oxy salts like oxyhalides and oxysulfates.

Introduction

The first attempts to prepare monoclinic rare-earth oxyhydroxides were made in 1938,[1] but not until the 1960s was the first structure, that of the yttrium compound, resolved.[2] The structure was refined later on by Nørlund Christensen,[3] who also reported the hydrothermal preparation and crystal structure of other RE oxyhydroxides.[4] Single-crystal studies were made by both X-ray[4] and neutron diffraction methods[5] to determine the orientation of hydrogen atoms.

The tetragonal form of (RE)OOH was prepared under high pressure and temperature,[6] and the crystal structure was subsequently determined by X-ray diffraction.[7] The magnetic properties[8-10] as well as the infrared spectra[11] of RE oxyhydroxides have been studied by several groups. So far, however, no study appears to have been made of the luminescence properties of these compounds.

Our interest in the luminescence properties of RE oxyhydroxides stems from the fact that they belong to the group of compounds called RE oxy salts.[12] Some compounds of this group, e.g. oxysulfides and oxyhalides, have found important applications as efficient host materials for RE-doped phosphors.[13,14] In this paper we report the luminescence properties of Eu^{3+}-doped RE oxyhydroxides, correlate the properties with crystal structure, and compare the properties with those of other RE oxy salts—oxyhalides, oxysulfates, and oxysulfides—which are already well-known.[15-18]

Experimental Section

Preparation of RE Oxyhydroxides. According to literature data, RE oxyhydroxides can be prepared by two different methods: (i) by thermal decomposition of the corresponding trihydroxides[19] or (ii) by hydrothermal means.[3] The former method is appropriate for the whole RE series—especially for the lighter members—whereas the latter gives only trihydroxides or mixed-phase products for the ceric group. In this work both methods were used since the hydrothermal method was found to yield products of better crystallinity.

Lanthanum and gadolinium compounds were obtained from the corresponding trihydroxides by heating under an N_2 atmosphere for 1 h at 700 and 600 K, respectively. In spite of a hydrothermal pretreatment of the starting materials, products of good crystallinity were not obtained. Yttrium and lutetium oxyhydroxides were easily prepared hydrothermally because of their greater stability against hydrolysis. Freshly precipitated trihydroxides were treated with concentrated sodium hydroxide solution at 480 K for 5 days.

All products were routinely checked by X-ray powder diffraction methods. (RE)OOH samples prepared hydrothermally were found to consist only of the desired phase, whereas the thermal decomposition products contained a small amount of trihydroxide or oxide depending on the heating temperature used.

For luminescence measurements the (RE)OOH powder samples were doped with trivalent europium replacing 1 mol % of the host cation. The uniform distribution of Eu^{3+} ions in cation sites was assumed on the basis of small differences in solubility between RE (oxy)hydroxides. All RE materials used were of minimum purity of 99.99% against other RE impurities.

Table I. Transitions in the Excitation Spectrum of (Y,Eu)OOH[a]

final level	wavelength	energy	final level	wavelength	energy
$^5D_1$	530-535	18 700	^5G	380-385	26 000
$^5D_2$	465-470	21 300	$^5D_4$	365-370	27 200
$^5D_3$	410-415	24 200	^5H	325-335	30 300
$^5L_6$	390-395	25 300	^5F	300-305	33 000

[a] Wavelengths are in nm and energies in cm^{-1}. Assignments are made according to ref 15 and 16.

Structure of RE Oxyhydroxides. The two forms of lanthanoid and yttrium oxyhydroxides have been prepared for the whole RE series except lanthanum[6,19] and their crystal structures determined.[7,20,21] The low-pressure and low-temperature modification crystallizes in the monoclinic system with $P2_1/m$-C_{2h}^2 ($Z = 2$) as the space group.[3] The RE atom is coordinated to seven oxygens, four of which are free oxygens and the remaining three bonded to hydrogens. The RE–O distances of these two groups differ considerably—nearly 0.2 Å. The RE coordination polyhedron is a slightly irregular monocapped trigonal prism with the capping oxygen on the tetragonal face (Figure 1). A similar coordination of RE atoms is encountered in other compounds, as in monoclinic oxides and lithium double oxides.[6] In the (RE)OOH structure the RE atom occupies a site of C_s point symmetry not far from the ideal C_{2v} one.

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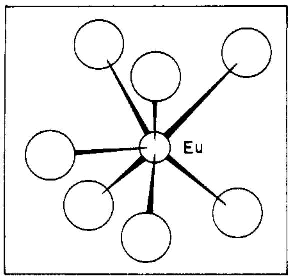

Figure 1. Structure of yttrium oxyhydroxide doped with Eu^{3+}.

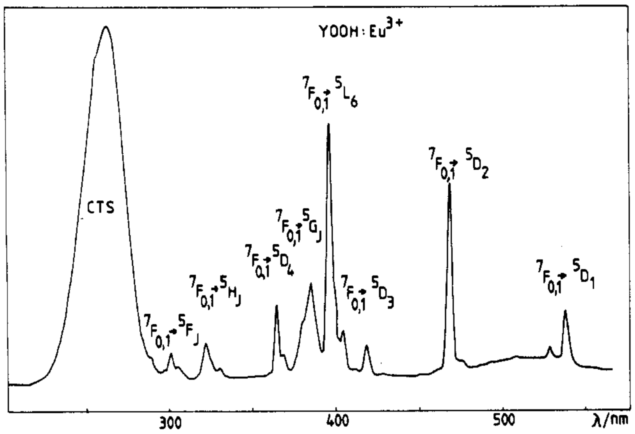

Figure 2. UV excitation spectrum of the $^5D_0 \rightarrow {}^7F_2$ lines in (Y,Eu)OOH at 300 K. No correction has been applied for the sensitivity of the apparatus and the spectrum of excitation source.

A comparison of RE–O distances across the RE series reveals increasing distortions from ideal C_{2v} symmetry from yttrium to lanthanum as the RE–O values for YOOH and HoOOH indicate: RE–O(av) = 2.27 and 2.27 Å and RE–OH(av) = 2.42 and 2.44 Å, respectively. This is in accordance with the general trend of increasing asymmetry, i.e. increased distortions within the RE coordination polyhedron, from lutetium to lanthanum in an isomorphic series of RE compounds.[22]

The tetragonal high-temperature form is a slightly expanded and distorted modification of the monoclinic (RE)OOH. The unit cell contains four (RE)OOH molecular units arranged according to space group $P42_1m$-D_{2d}^3.[7]

Optical Measurements. The luminescence emission spectra of (RE)OOH–Eu^{3+} powder samples were recorded at 300 and 77 K under both short-wave UV and dye laser excitation. The UV radiation from a 200-W mercury lamp was centered around 260 nm by wide-band filters to correspond approximately to the maximum of the charge-transfer-state (CTS) band of the materials excited. The dye laser excitation (rhodamine 6G pumped by a continuous-wave argon ion laser) was used to excite selectively the $^5D_0$ level of the europium ion (near 17 200 cm^{-1}) in order to avoid lines due to impurities or to transitions from higher excited levels. The luminescence was dispersed by a 1-m Jarrell-Ash monochromator and detected by a Hamamatsu R374 photomultiplier between 400 and 800 nm. The resolution of the monochromator was better than 2 cm^{-1}.

The excitation spectra of (RE)OOH–Eu^{3+} were measured at 300 K between 200 and 550 nm by a Perkin-Elmer MPF-44A fluorescence spectrophotometer. A 150-W xenon lamp was used to excite the emission beyond 580 nm.

Results and Discussion

Excitation Spectra. The excitation spectra of all the europium-doped RE oxyhydroxides showed sharp lines between 300 and 550 nm and a strong wide band between 200 and 300 (Figure 2). The sharp lines can be attributed to intraconfigurational 4f–4f transitions from the ground $^7F_0$ level (at 300 K also from $^7F_1$ levels), whereas the wide band originates from transitions to charge-transfer states (CTS) due to europium–oxygen interactions. The analysis of the YOOH–Eu^{3+} excitation spectrum presented in Table I follows the assignments made in ref 15 and 16. The crystal field fine structure is obscured by the high temperature and the large number of transitions involved.

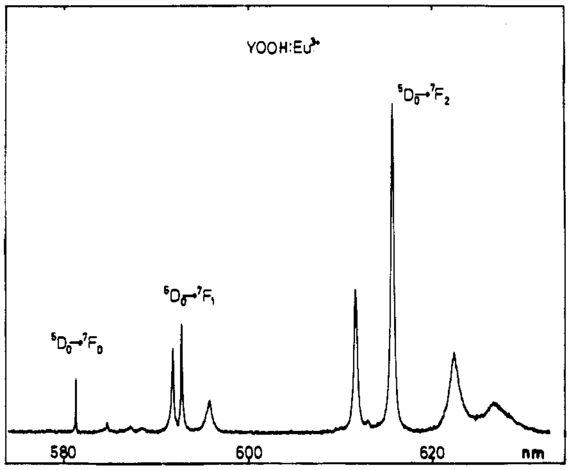

Figure 3. Part of the emission spectrum of (Y,Eu)OOH at 77 K under UV excitation.

The position of the sharp lines varied only weakly across the RE series. In addition to the lines due to the direct excitation of europium ions some supplementary groups of lines were observed in the GdOOH–Eu^{3+} excitation spectrum. Since these occur between 300 and 310, 275 and 280, and 245 and 255 nm they can be attributed to transitions from the ground $^8S_{7/2}$ level of gadolinium ion to the excited ^6P, ^6I, and ^6D levels, respectively.[23] The presence of these lines indicates energy transfer from gadolinium to europium ions.

The energy of the wide CTS band varied strongly across the RE series, as would be expected from its origin. The energy increases with decreasing ionic size of the host cation from 36 400 (lanthanum) to 38 500 cm^{-1} (gadolinium) and from 38 900 (yttrium) to 39 700 cm^{-1} (lutetium). A similar evolution has been observed for other RE oxy salt series, for example oxyhalides[15] and oxysulfates.[17] The increase in CTS energy is due to the fact that the smaller the radius of the host cation, the more stable is the O^{2-} ion and thus the more energy is required to remove an electron from the oxygen.

Emission Spectra. The (RE)OOH–Eu^{3+} samples studied showed strong red luminescence under both short-wave UV and dye laser excitation. The groups of sharp lines were easily assigned to transitions from the lowest excited ^5D level, $^5D_0$, to $^7F_{0-5}$ levels. Only very weak emission from higher ^5D levels was observed, indicating efficient multiphonon deexcitation by high-energy lattice vibration modes. Closer examination of the emission spectra revealed the total lifting of the ^7F level degeneracy resulting usually in $2J + 1$ lines for each $^5D_0 \rightarrow {}^7F_J$ transition (Figure 3). The number of lines is in accordance with the low point symmetry of the RE site, C_S, obtained from the structural data. For C_s symmetry no selection rules apply and all transitions between cf Stark levels are allowed. The weakness or even the total absence of certain lines was tentatively attributed to the closeness of the RE site symmetry to C_{2v}. In this symmetry the selection rules allow no transitions from the $^5D_0(A_1)$ level to $^7F(A_2)$ levels, thus reducing the number of lines to be observed. The breakdown of the free-ion selection rule $\Delta J = 2$, 4, or 6 for electric dipole transitions caused weak transitions to $^7F_{3,5}$ levels. The presence of these transitions has been shown to result from J mixing of $^7F_{3,5}$ wave functions with $^7F_{2,4,6}$ ones by crystal field effects.[24]

Apart from electric dipole (ed) transitions a strong magnetic dipole (md) transition, $^5D_0 \rightarrow {}^7F_1$, was observed as well. The intensity ratio between the ed transition $^5D_0 \rightarrow {}^7F_2$ and the md transition $^5D_0 \rightarrow {}^7F_1$ increases from lutetium to lanthanum host while the energy of the CTS band simultaneously decreases. A

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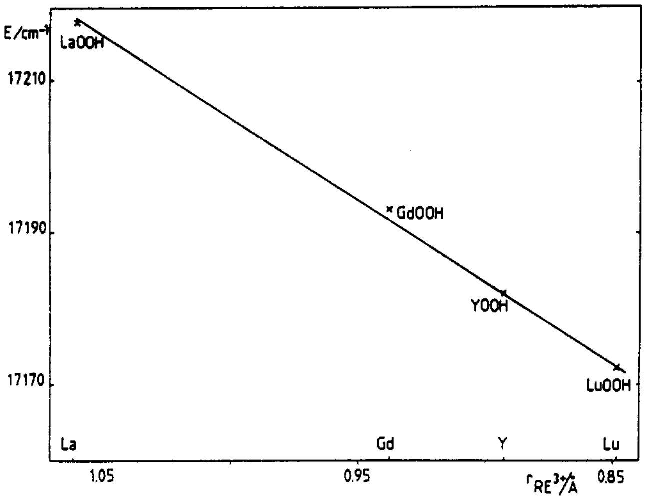

Figure 4. Energy shift of the $^5D_0$ level as a function of the RE host cation.

connection between these two phenomena has been shown,[25] and in light of the classical Judd–Ofelt theory of ed transition intensities it may be argued that the charge-transfer states can induce ed transitions by acting as an intervening configuration of opposite parity into the 4f one.

Another spectral feature of interest, the $^5D_0 \rightarrow {}^7F_0$ transition, had a fair intensity though formally forbidden as a free-ion transition. However, the group theoretical selection rules allow the 0–0 transition in compounds of C_{nv} or lower symmetry for the RE site. In spite of controversial reports on its presence—let alone on its origin—in different luminescent materials, it seems to be a familiar feature in RE oxy salt spectra.

All lines observed in the (RE)OOH–Eu^{3+} emission spectra are of pure electronic origin; no vibronically induced transitions could be found. This is in strong contrast to the case for Eu(OH)$_3$,[26] where abundant vibronic structure has been detected. The line widths in (RE)OOH–Eu^{3+} spectra are about 2 Å with the exception of two broad $^5D_0 \rightarrow {}^7F_2$ lines. The temperature dependency of their intensity gave no support to vibronic origin, however, and thus the broadening may be due to local distortions or crystal imperfections. The latter inference is confirmed by the observation of the corresponding lines in emission from the $^5D_1$ level.

The energies of excited ^5D levels of the europium ion increase with increasing ionic radius of the host cation (Figure 4). A similar evolution has been observed for nearly every isomorphic series of RE compounds.[27] This phenomenon is usually attributed to the well-known nephelauxetic effect due to change in interelectronic repulsion. The nephelauxetic effect has been subsequently used to evaluate the importance of covalent character in RE bonding. However, it is known that cf effects—owing to the *J* mixing of the $^5D_0$ wave function—can produce similar shifts in $^5D_0$ level energy. The latter interpretation is supported by the absence of significant changes in Racah parameters, i.e. in interelectronic repulsion, for different RE oxyhalide hosts.[15,16] The correlation between the cf strength and the ^5D level shifts holds for the (RE)OOH series, too, since the cf strength increases slightly from lutetium to lanthanum (when measured as the splitting of the $^7F_1$ level). The answer to this problem, however, must await the exact calculation of free-ion and cf parameters.

Owing to the low point site symmetry of RE atoms in (RE)OOH the actual parametrization of cf effects is somewhat difficult. Some inferences can be made on the basis of energy level schemes alone. The small splitting of the $^7F_1$ level—around 100 cm^{-1}—indicates a weak cf effect. RE oxyhydroxides—obtained as intermediate decomposition products from trihydroxides—have approximately the same $^7F_1$ splitting as RE(OH)$_3$[26] though no close structural relationships can be established. No similar resemblance exists to the energy level scheme of the final decomposition product, (Y,Eu)$_2$O$_3$.[28]

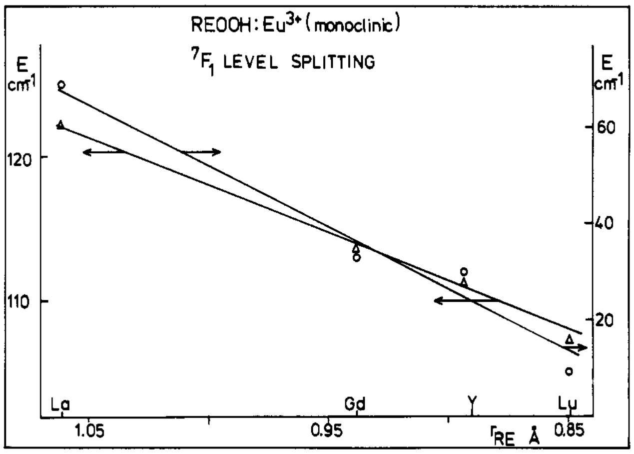

Figure 5. Splitting of the $^7F_1$ level as a function of the RE host cation. The left-hand scale refers to the total splitting.

Table II. Second-Order Cf Parameter Values for Selected Europium(3+)-Doped RE Oxy Salts[a]

[(RE)O]X	B_0^2	B_2^2	S[b]	ref
YOCl	−813		813	15
YOBr	−964		964	16
$(YO)_2SO_4$	−1007	204	1027	17
$(YO)_2S$	124		124	18
$(YO)_2O$	−276	−740	790	32
$(LaO)_2MoO_4$	−981	117	988	33
YOOH	326	58	331	*c*

[a] All values in cm^{-1}. [b] $S = (B_0^{22} + B_2^{22})^{1/2}$. [c] This work (calculations are based only on the $^7F_1$ level splittings).

The total splitting of the $^7F_1$ level increases slightly from 105 to 125 cm^{-1} from lutetium to lanthanum compounds. This increase is entirely due to the increase between the two lower Stark sublevels (Figure 5). An evolution of this kind can be connected to the greater structural distortions in the (RE)O$_7$ coordination polyhedra of lighter oxyhydroxides (cf. Experimental Section) in accordance with the general trend.[22] In contrast to the $^7F_1$ level the total cf splittings of other ^7F_J levels decrease from lutetium to lanthanum host. This might indicate increasing tendency toward covalent bonding in heavier (RE)OOH compounds, especially since the $^7F_1$ splitting is known to arise mainly from the electrostatic contribution to the cf effect. A similar conclusion can be drawn from the shift of ^5D level energy as a function of the host cation.

Classification of the $[(RE)O]_n^{n+}$ Complex Cation in RE(OOH). After introducing the concept of the $[(RE)O]_n^{n+}$ complex cation as a basic structural unit in RE oxy salts,[12] Caro then proposed a classification scheme for the different complex cation species.[29] Depending on the linkage of O(RE)$_4$ tetrahedra—linked by either three or four edges—a C_3 or C_4 type complex cation is obtained, respectively. More recently, several C_4 type RE oxy salts doped with europium have been shown to possess common optical properties.[30] The cationic part has also been deduced to determine the optical properties of the corresponding oxy salt to a much greater extent than the anionic part.

A comparison of the B_q^2 cf parameters of several RE oxy salts—both C_3 and C_4 type—reveals some fundamental differences in these two groups: the B_0^2 values for C_4 group are *large and negative* whereas those for the C_3 group are *small and positive* (Table II). The (Y,Eu)OOH values (calculated on the basis of the $^7F_1$ splittings alone with the method presented in ref 15) clearly

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resemble those for the C_3 group, i.e. (Y,EuO)$_2$S, and consequently YOOH should be counted with this group. However, it has earlier been shown on grounds of crystal structure that (RE)OOH compounds belong to the C_4 group.[31]

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Registry No. LaOOH, 12195-45-8; GdOOH, 12160-84-8; LuOOH, 12141-10-5; YOOH, 12026-07-2; Eu^{3+}, 22541-18-0.

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Theoretical Studies of Bridging-Ligand Effects in Quadruply Bonded Dichromium(II) Compounds

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Generalized molecular orbital (GMO) and configuration interaction (CI) calculations are reported for Cr$_2$(O$_2$CH)$_4$ and Cr$_2$((NH)$_2$CH)$_4$ at various Cr–Cr bond lengths. The results show a bond shortening of 0.48 Å when the formato ligands are replaced by amino iminato ligands. Analysis of the CI wave function shows that the stronger donating ligand, (NH)$_2$CH, causes the Cr atomic orbitals to expand and thereby increases the Cr–Cr overlaps. Thus, the inductive effect of the bridging ligand may be an important factor in determining the Cr–Cr bond length.

Introduction

Quadruply bonded dichromium(II) compounds exhibit an unusually wide range of Cr–Cr bond lengths from 1.828 to 2.541 Å.[1] With only a few exceptions these compounds can be divided into two groups.[2] The first group of compounds have Cr–Cr bond lengths that range from 2.283 to 2.541 Å. This group of compounds is characterized by four carboxylato ligands and some kind of interaction in the axial position, either in the form of solvent molecules or of a molecular structure in which the carboxylato units are arranged in infinite chains with intermolelar O···Cr interactions. The second group of compounds have Cr–Cr bond lengths of less than 1.90 Å. This second group is characterized by ligands derived from weaker acids and usually has no axial interactions.

The cause of this wide range in Cr–Cr bond lengths has been the subject of many experimental[2–15] and theoretical[16–24] investigations in recent years. In general, the wide variability of bond lengths has been attributed to two possible causes.[5] The first of these is the effect of axial ligand interaction, which has been investigated experimentally. Cotton, Ilsley, and Kaim reported[2] a series of compounds containing zero, one, and two tetrahydrofuran ligands in the axial position and very similar bridging ligands. As expected, the Cr–Cr bond length increased from 1.873 to 2.023 to 2.221 Å in this series. More recent work by Cotton and Wang,[15] on a series of 14 compounds in which the axial and bridging ligands were varied systematically, led them to conclude that the presence or absence of axial ligands was the determining factor in the Cr–Cr bond length.

The second possible cause, the inductive effect of the bridging ligand, has not been as thoroughly investigated experimentally. Berry and co-workers[25] did report a study of the correlation of chromium–chromium bond lengths with chromium orbital ionization energies. In the compounds they studied, the chromium–chromium separation followed the electron-withdrawing or -releasing properties of the bridging ligands. Also, Cotton and Wang[15] have reported structures of five tetrakis(carboxylato)dichromium compounds, all with axial pyridine groups, in which the bridging ligand was varied. This series does show a change of 0.2 Å in the Cr–Cr bond length over the series of compounds. However, no *systematic* experimental approach has resolved whether or not the chromium–chromium bond length in unsolvated dichromium tetracarboxylates would be in the supershort range. This is due in large part to difficulties in synthesizing these compounds. Thus, the question of the bond length in such complexes remains open.

We felt that a theoretical approach to this question might provide some insight into the competing effects on the Cr–Cr bond length. We have recently reported preliminary results on tetra-

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