Optical Study of Phase Transformations in Rare Earth Oxyhydroxides *

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The UV and dye laser excited luminescence spectra of the two crystalline forms of Eu(III) doped RE oxyhydroxides (RE=La, Gd, Lu and Y) were recorded at 300 and 77 K. Analysis of the spectra revealed small differences between monoclinic and tetragonal REOOH:Eu(III) luminescence. The differences could be correlated to changes in bonding characteristics between RE and oxygen atoms. The crystal field (c.f.) strength is significantly lower in the tetragonal form. On the other hand, greater distortions in RE coordination in the tetragonal form induce larger individual c.f. splittings. A similar effect caused by the general symmetry decrease from lutetium to lanthanum compound is observed in both REOOH series. Similarities in luminescence spectra between REOOH:Eu(III) and $(REO)_2S:Eu(III)$ support the presence of a trigonal $(REO)_n^{n+}$ complex cation as the basic structural unit of REOOH.

Rare earth oxysalts constitute a special group among RE compounds. Their structure consists of layers of $(REO)_n^{n+}$ complex cations alternating with layers of different anions.[1] Several mono- and polyvalent anions, *e.g.* fluoride, chloride, bromide, iodide, hydroxide, nitrate as well as oxide, sulfide, selenide, telluride, carbonate, sulfate, selenite, molybdate and tungstate ions, have been shown to yield the corresponding oxysalt.[2] These compounds are usually very stable and some of them have found important applications as efficient phosphors when doped with RE(III) ions. The stability of RE oxysalts is due to the $(REO)_n^{n+}$ unit which can be considered as a strongly bound structural entity.[3] Two structural types of these cations can be found according to the classification scheme of Caro.[4] Depending on the number of shared edges of ORE_4 tetrahedra a trigonal (C_3) or tetragonal (C_4) type unit is obtained. The C_4 group contains most of the known oxysalts, e.g. oxyhalides, oxysulfates and oxymolybdates,[2] whereas only the oxysulfides are known with certainty to belong to the trigonal group.

The REOOH system exhibits polymorphism according to the single crystal structure determinations.[5,6] A tetragonal form is obtained at high pressure and temperature[7] in addition to the monoclinic modification formed at ambient pressure. While the preparation, structure and magnetic properties of monoclinic RE oxyhydroxides are well character-

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ized [8-10] the corresponding properties of the tetragonal form are largely unknown. The study of the phase transformation occuring in oxyhydroxides, as well as the comparison of these two forms, have so far also been neglected. The aim of this paper is to present the luminescence properties of the two structural forms of Eu(III) doped RE oxyhydroxides. These properties are compared and used to characterize the phase transformation by means of the optical properties of REOOH:Eu(III).

CRYSTAL STRUCTURE OF RE OXYHYDROXIDES

Up to the present, the two forms of REOOH have been obtained for the whole rare earth series with the exception of the tetragonal lanthanum compound.[7,8] The low pressure and temperature modification crystallizes in a monoclinic system with $P2_1/m - C_{2h}^2$ ($Z=2$) as the space group. The RE atoms situate in a site of C_s symmetry and are coordinated to seven oxygens, three of which belong to the hydroxo groups. The coordination polyhedron is a slightly distorted monocapped trigonal prism with the capping atom on tetragonal face.

The structure of the high pressure and temperature form belongs to the tetragonal crystal system. The space group is $P\bar{4}2_1m - D_{2d}^3$ and $Z=4$. The tetragonal structure is more distorted than the monoclinic one, as it is often the case for high pressure forms. Since no detailed structure determination of both modifications has been carried out for the same RE element, the comparison of the RE–O distances between the tetragonal and monoclinic forms is difficult. The following comparison utilizes the Y–O bond lengths[5] as the monoclinic Yb–O lengths, after an appropriate correction for the difference in ionic radius between the seven coordinated yttrium and ytterbium ions.[11] There are practically no differences in the mean RE–O and RE–OH distances between the tetragonal (2.248 and 2.373 Å) and the monoclinic forms (2.245 and 2.385 Å, respectively).[5,6] The variation in bond lengths within the groups is much greater in the tetragonal form, however. The point symmetry of the RE site remains as C_s, and the coordination polyhedron can still be considered as a monocapped trigonal prism despite the greater distortions in the tetragonal form.

EXPERIMENTAL

Preparation of RE oxyhydroxides. The monoclinic RE oxyhydroxides were prepared by two different methods: the lighter REOOH (RE=La and Gd) were obtained as thermal decomposition products of the corresponding trihydroxides while the heavier REOOH were prepared hydrothermally. The freshly precipitated RE trihydroxides yield oxyhydroxide phase when heated in nitrogen atmosphere at 700 K (LaOOH) and 600 K (GdOOH) for 1 h. The phases were contaminated with small amounts of trihydroxides or oxides, depending on the heating temperature used. LuOOH and YOOH were obtained hydrothermally by treating RE trihydroxides with concentrated sodium hydroxide solution at 480 K for several days. The X-ray powder diffraction analysis of the products showed no other phases.

The tetragonal RE (RE=Gd, Y and Lu) oxyhydroxides were prepared hydrothermally from moist RE oxides in a "belt"-type apparatus according to Ref. 7. The pressure used varied from 4 to 8 GPa for lutetium and gadolinium, respectively. The temperature was kept constant at 1050 K. The tetragonal form of LaOOH has never been obtained but the preparation of this compound is planned for the near future. The routine X-ray diffraction analysis of the tetragonal REOOH revealed no contamination by other phases.

For optical measurements the REOOH samples were doped with trivalent europium replacing approximately one mole per cent of the total RE amount. The random, uniform distribution of the dopant was assumed as a result of the small mutual differences in solubilities of RE (oxy)hydroxides.

Optical measurements. The luminescence of the REOOH:Eu(III) powder samples was recorded at both ambient and liquid nitrogen temperatures. The luminescence was excited either by a conventional UV lamp or a rhodamine dye laser. A 200 W mercury lamp provided with a wide band filter to pass radiation around 250 nm was used as a global excitation source. The wavelength region at 250 nm corresponds to the strong charge transfer absorption band maxima of Eu(III) ion in REOOH:Eu(III).

A Spectra Physics 375/376 continuous wave dye laser (with rhodamine 6G) pumped by a Spectra Physics 164 argon ion laser was used to excite selectively the lowest excited ^5D level, $^5D_0$, near 580 nm. The emission was dispersed by a 1-m Jarrell-Ash monochromator and detected by a Hamamatsu R374 photomultiplier. The whole accessible wavelength range between 400 and 750 nm was scanned.

LUMINESCENCE OF TETRAGONAL REOOH:Eu(III)

The luminiscence properties of monoclinic REOOH:Eu(III) have been described elsewhere.[21] Strong red luminescence is obtained from Eu(III) doped tetragonal RE oxyhydroxides (RE=Gd, Y and Lu) under both UV and dye laser excitation. The luminescence in visible range between 580 and 750 nm consists of isolated groups of sharp lines. The lines which sharpen with decreasing temperature can be attributed to transitions between the $^5D_0$ level and the Stark components of the ground F septet. Only very weak emission could be observed from the higher $^5D_{1,2,3}$ levels which situate approximately 1700, 4200 and 7000 cm^{-1} above the $^5D_0$ level. The emission from these higher levels is quenched by efficient non-radiative processes. The most probable mechanism is the multi-phonon de-excitation since there are high frequency vibrations available in REOOH host lattice. The most energetic lattice vibrations extend to 3600 cm^{-1}, which together with less energetic vibrations provide efficient path to relax the excitation energy to the $^5D_0$ level. The energy gap between the $^5D_0$ level and the highest level of the ground term, $^7F_6$, is usually near 12 000 cm^{-1} and is thus much less affected by multi-phonon processes because of the high number of phonons required to fill the gap. In REOOH the four-phonon process involving the highest energy lattice vibration is evidently very weak owing to either electronic-vibronic selection rules or the inherent weakness of this coupling.

The most intense transition in the luminescence spectra is the $^5D_0 \rightarrow {}^7F_2$ transition which is allowed as an electric dipole (e.d.) transition only in the absence of the inversion symmetry in the RE site. The free ion selection rule $\Delta J=2$, 4 or 6 allows two other e.d. transitions, *i.e.* $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_6$. The latter transition near 800 nm is very weak and was not observed with the present equipment. In addition to e.d. transitions a strong magnetic dipole (m.d.) transition, $^5D_0 \rightarrow {}^7F_1$, occurs near 590 nm as well.

In good agreement with their forbidden nature the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_5$ transitions have very low intensity. These transitions have mixed e.d. and m.d. character and arise because of the mixing of $^7F_{3,5}$ wavefunctions with $^7F_{1,2,4}$ ones.[12]

The luminescence spectra of tetragonal RE oxyhydroxides are characterized by an intense $^5D_0 \rightarrow {}^7F_0$ transition near 580 nm. This transition which is so typical for all RE oxysalts is forbidden by free ion selection rules whereas the group theory allows this transition for RE site symmetries C_{nv}, C_n and C_s.[13] The observation of the 0−0 transition is thus in accordance with the low point symmetry of the RE site in REOOH. The intensity of the 0−0 transition has been shown to depend on the mixing of the $^7F_{00}$ wavefunction mainly with the $^7F_{2M}$ ones.[14]

A closer examination of the c.f. fine structure of the $^5D_0 \rightarrow {}^7F_J$ transition yields (2J+1) closely spaced lines for each J value of the ground septet. These lines result from the low point symmetry of the RE site which lifts entirely the total angular momentum degeneracy
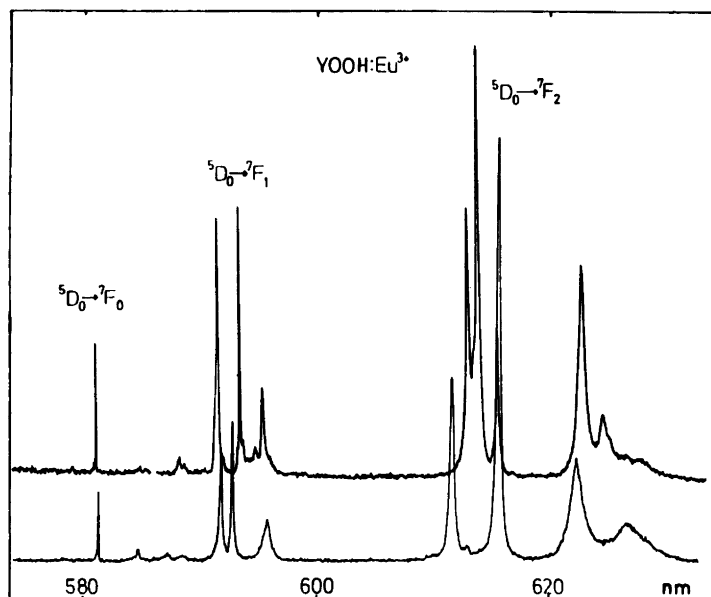
Fig. 1. Part of the UV excited emission spectra of tetragonal (upper curve) and monoclinic (lower curve) YOOH:Eu(III) at 77 K. The intensity on the vertical axis is expressed in arbitrary units.

of the ^7F_J levels. Furthermore, no selection rules restrict the number of lines to be observed.

The energy level schemes of the ground septet are characterized by the small total c.f. splitting of the $^7F_1$ level – approx. 100 cm^{-1} while the other ^7F_J level splittings are not particularly small. A non-negligible contribution to crystal field originates from covalency since the small $^7F_1$ splitting indicates weak electrostatic effect. The importance of covalency is supported by the low energy of the $^5D_0$ level which situates in the "covalent region" of the nephelauxetic scale [16] together with RE oxysulfides.

The small $^7F_1$ level splitting yields low second order c.f. parameter values which produce insufficient mixing of wave functions to explain the intense $^5D_0 \rightarrow {}^7F_0$ transition. The 0–0 transition may gain additional strength through the influence of the anisotropic coordination around the RE atom.

CHARACTERIZATION OF THE MONOCLINIC → TETRAGONAL PHASE TRANSITION

A comparison of the general appearence of the luminescence spectra of the two Eu(III) doped REOOH forms reveals no major differences (Fig. 1). Owing to the well shielded position of the 4f electrons below the outer shells, the energies of the "free ion" $^5D_0 \rightarrow {}^7F_J$ transitions remain relatively constant. Anyway, there are some differences between the two structural forms in transition intensities as well as in the c.f. effect on the energy level scheme of the ground septet.

Although a detailed analysis of the transition intensities is out of the scope of this work, a few remarks can be made on the evolution of transition intensities between the monoclinic and tetragonal forms. When the intensity of the magnetic dipole transition, $^5D_0 \rightarrow {}^7F_1$, is
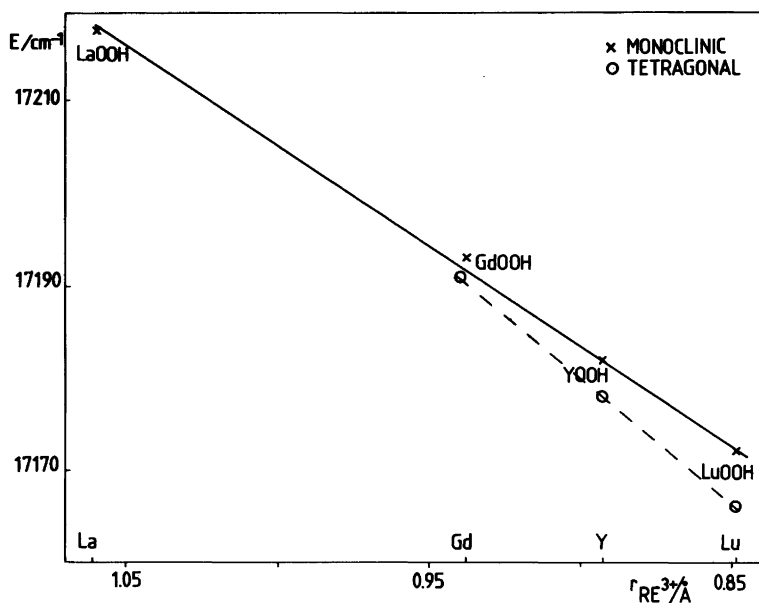
Fig. 2. Evolution of the $^5D_0$ level energy as a function of the host cation in REOOH:Eu(III).

taken as a reference – owing to its independency on c.f. effects – the intensities of the $^5D_0 \rightarrow {}^7F_{0,2}$ transitions are slightly stronger in the tetragonal form. This phenomenon can be connected with the energy position of the *CTS* absorption band. The band maxima deduced from the excitation spectra lie at 39000 and 39700 cm^{-1} for the monoclinic YOOH and LuOOH, and at 38300 and 38800 cm^{-1} for the tetragonal oxyhydroxides, respectively. The transition intensities shown in Fig. 1. follow the general trend increasing with decreasing *CTS* energy.[17] This kind of correlation holds not only for compounds of the same crystal structure but also for compounds with quite different structures. In the case of the REOOH system this trend can be observed both within and between the two structural series.

The differences in c.f. effect between the two REOOH forms can be found by a careful inspection of the energy level schemes of the Eu(III) ion. In both oxyhydroxide series the $^5D_0$ level energy shows evolution similar to the nephelauxetic effect, *i.e.* increases with increasing size of the host cation (Fig. 2). This correlation seems to hold for any isostructural series even if a reverse behaviour is theoretically possible.[16] The $^5D_0$ energies are slightly – a few cm^{-1} – lower in the tetragonal form than in the monoclinic one. This small difference may be due to the differences in RE-oxygen distances. However, the situation becomes even more complex since not only the electrostatic repulsion is responsible for the energy position of the $^5D_0$ level position but the spin-orbit and crystal field effects must be considered as well.

The crystal structure has the most pronounced effect on the crystal field splittings of the "free ion" ^7F_J levels. The total splittings are 20 to 30 % larger in the monoclinic form than in the tetragonal one (Fig. 3). This indicates weaker c.f. effect on the tetragonal RE site which seems to be justified when the structural differences are taken into account. In tetragonal form two hydroxo oxygens situate considerably farther away from the RE ion than in the monoclinic form. Although this effect is partly compensated by changes in other RE-oxygen
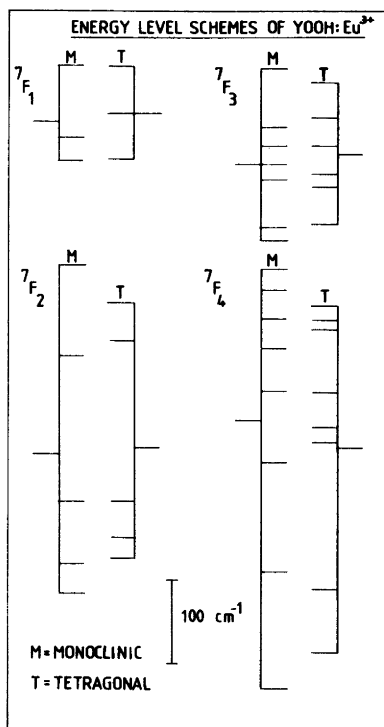
Fig. 3. Comparison of the $^7F_{0-4}$ energy level schemes of tetragonal and monoclinic YOOH:Eu(III).

distances the diminution of c.f. strength is significant.

The effect of the more distorted coordination around the RE atoms in tetragonal REOOH can be seen in an increase in a few individual c.f. splittings. The clearest example is the splitting between the two lower Stark components of the $^7F_1$ level which increases in both REOOH series from lutetium to lanthanum host (Fig. 4). A similar, but stronger increase can be observed from monoclinic to tetragonal form. This increasing splitting as a function of the RE host cation can be attributed to the general increase in distortions of RE
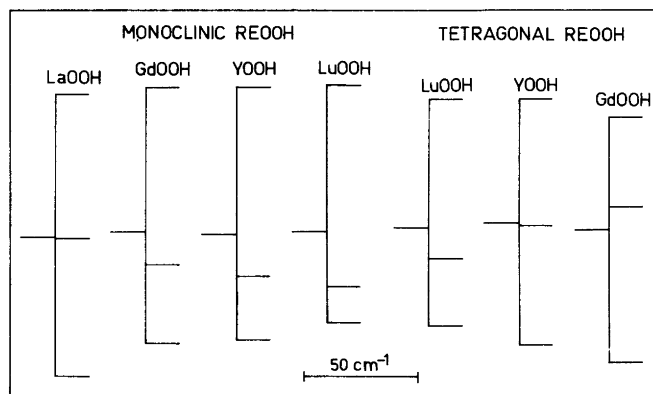

Fig. 4. Splitting of the $^7F_1$ level as a function of the RE host cation.

compounds with increasing size of the RE host cation.[18] According to the structural data an increase in distortions occurs from monoclinic to tetragonal form and this increase has to be responsible for the increased c.f. splittings. The magnitude of the variation in c.f. splittings supports the preceeding interpretation since the changes in structure are far more important between the two REOOH forms than within the individual REOOH series.

Both the weakness of the $^7F_1$ level splitting and the position of the $^5D_0$ level energy in the nephelauxetic scale underline the similarities between the REOOH:Eu(III) and $(REO)_2S$:Eu(III) luminescence spectra.[19] This can be used as conclusive information of the type of the $(REO)_n^{n+}$ complex cation encountered in RE oxyhydroxides. In disagreement with the structural data [20] the luminescence properties of REOOH:Eu(III) place oxyhydroxides in the group with the trigonal type of the $(REO)_n^{n+}$ complex cation.

CONCLUSIONS

The object of this paper is to show how the visible luminescence of Eu(III) doped rare earth materials can be used as a probe of RE-ligand interactions and, especially, of the changes therein. Valuable information can be obtained on the coordination number and geometry of RE ions in solid state. The study of the Eu(III) luminescence in RE oxyhydroxides established the spectra-structure relationships through a detailed analysis of the energy level schemes of Eu(III) ion. The changes in spectra as the evolution of level energies and c.f. splittings were correlated to structural changes as bond lengths and the extent of distortions in RE-oxygen coordination. Finally, the characteristic features common to all RE oxysalts were utilized to classify RE oxyhydroxides.

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