

High-Resolution X-Ray-Excited Gd^{3+} Emission in the C-Type Y_2O_3 Structure

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Y_2O_3 , Lu_2O_3 , and Sc_2O_3 are isomorphous, crystallizing in the cubic space group $Ia\bar{3}$, and Gd^{3+} can readily be incorporated into each of these three compounds. The rare earths occupy two different sites with symmetry C_2 and S_6 . As a consequence, the $Gd^{3+} {}^6P_{7/2} \rightarrow {}^8S$ transition is split into eight crystal-field lines. Other electronic transitions as well as vibronic side bands are also observed and the differences between the spectra of the three compounds are discussed. © 1990 Academic Press, Inc.

Introduction

In a recent paper (1), we showed that a distinction of the Gd^{3+} emission arising from the C_2 and S_6 sites can be made for compositions such as $Y_{1.98}Gd_{0.02}O_3$. Because of the lack of resolution, such a distinction was not totally unambiguous and only four of the eight theoretical crystal-field split lines could be observed. It is of interest to see if trends as a function of the cation size and covalency can be detected for the Gd^{3+} emission. The present paper describes these spectroscopic differences for $Y_{1.98}Gd_{0.02}O_3$, $Lu_{1.98}Gd_{0.02}O_3$, and $Sc_{1.98}Gd_{0.02}O_3$.

Experimental

The materials were prepared by dissolving stoichiometric quantities of Y_2O_3 ,

Lu_2O_3 , Sc_2O_3 , and Gd_2O_3 (all of 99.9% purity from Rhône Poulenc) in dilute nitric acid and coprecipitating the oxalates with 10 M oxalic acid. After being filtered, washed, and dried, these precursors were converted into the oxides by firing them in Pt containers in air at 1250°C for 6 hr. The powders were then pressed into 1-in. diameter pellets and refired at 1600°C for 6 hr. These pellets were strong enough to be directly used for the spectroscopy. X-ray diffractometer patterns were obtained from the same samples with a Philips APD 3600-02 instrument, automated with a Data General Nova 4 X computer. Parameter refinements were carried out based on a local program. The spectroscopy was done in a setup described earlier (2). The major difference is that the $\frac{1}{4}$ m SPEX monochromator was replaced by a $\frac{1}{2}$ m instrument, permitting resolutions of 0.1

Å. It should also be pointed out that the intensity numbers are direct photon counts, unless arbitrary units are used for comparisons. The X-ray excitation conditions throughout the paper were 45 mA and 45 kVp, employing a SIEMENS Kristalloflex 710 generator.

Results and Discussion

The Y₂O₃ Structure

Y₂O₃ is representative of the cubic C-type rare earth oxides and its structure has been reported by several authors (3–5), with the neutron diffraction study of O'Connor (5) being the most accurate one at room temperature. In the space group *Ia3*, there are two crystallographically unique Y atoms with C₂ and S₆ site symmetries with both in distorted octahedral environments. There are three times as many Y atoms with C₂ than with S₆ symmetry and there are a total of 16 formula units per unit cell. The average Y–O distance for the S₆ position is 2.277 Å and that for the C₂ site is 2.285 Å (ave). These numbers are in excellent agreement with the sum of the ionic radii (6) of 2.28 Å. The Lu₂O₃ structure, on the other hand, appears to have been done only once by Zachariasen (7) in 1927, at which time he reported the acentric space group *I2*,3 and Lu in three different sites. He also reported unusually long Lu–O distances. This can only be explained if one assumes that the quality of Lu₂O₃ at that time was not very good and Lu₂O₃ was contaminated with substantial quantities of larger rare earths. Subsequently, several authors (8–10) checked Zachariasen's structure and came to the conclusion that it really should be *Ia3*. We support this centric space group, since we did not obtain any SHG (second harmonic generation) signal. Lacking detailed structural data for Lu₂O₃ we did an approximation of the structure by using the fractional coordinates given by O'Connor (5) for Y₂O₃. This yielded Lu–O distances of 2.230

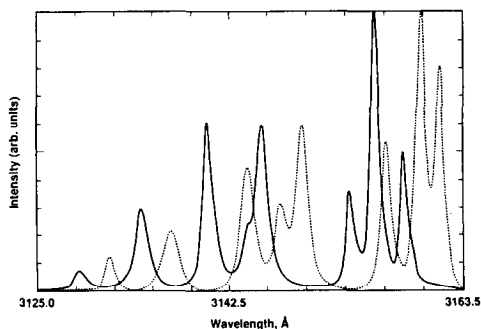


FIG. 1. Comparison of the crystal-field split Gd³⁺ emission in Y_{1.98}Gd_{0.02}O₃ and Lu_{1.98}Gd_{0.02}O₃ at 300 K. The solid line is for the Y and broken line for the Lu compound.

Å for Lu(1) (S₆) and 2.238 Å (ave) for Lu(2) (C₂), in good agreement with the sum of the ionic radii (6) of 2.24 Å. So there is no question that the Lu–O distances are indeed smaller than those for Y–O in their respective sesquioxides. Finally, we included Sc₂O₃ in the present study, because Sc³⁺ (*r* = 0.745 Å) is the smallest ion crystallizing in the *Ia3* structure. The Sc–O distances, based on a structure paper by Norrestam (11), are: 2.119 Å for Sc(1) (S₆) and 2.124 Å for Sc(2) (C₂) in good agreement with the sum of the radii of 2.125 Å.

The refined cell constants we obtained for the three compounds discussed in the present paper are:

$$\begin{array}{ll} \text{Y}_{1.98}\text{Gd}_{0.02}\text{O}_3 & a = 10.606 \pm 1 \text{ \AA} \\ \text{Lu}_{1.98}\text{Gd}_{0.02}\text{O}_3 & a = 10.392 \pm 1 \text{ \AA} \\ \text{Sc}_{1.98}\text{Gd}_{0.02}\text{O}_3 & a = 9.851 \pm 2 \text{ \AA}. \end{array}$$

Luminescence

The ${}^6P_{7/2} \rightarrow {}^8S$ transitions and their vibronic side bands. Figure 1 shows the electronic ${}^6P_{7/2} \rightarrow {}^8S$ emissions of Gd³⁺ in both Y_{1.98}Gd_{0.02}O₃ and Lu_{1.98}Gd_{0.02}O₃. Because of the intensity differences (Gd in Lu₂O₃ is a more efficient emitter), arbitrary units are used for this comparison. It is obvious that all eight theoretical crystal-field split lines

TABLE I
 LINE POSITIONS IN cm^{-1} AND ASSIGNMENTS OF THE ${}^6P_{7/2} \rightarrow {}^8S$ EMISSION OF Gd^{3+} IN Y_2O_3 , Lu_2O_3
 AND Sc_2O_3 .

nr.	$\text{Y}_2\text{O}_3 : \text{Gd}$ (cm^{-1})		$\text{Lu}_2\text{O}_3 : \text{Gd}$ (cm^{-1})	$\text{Sc}_2\text{O}_3 : \text{Gd}$
<i>e</i> 1	31,665	S_6	31,637	31,5540
<i>e</i> 2	31,691	C_2	31,653	31,555
<i>e</i> 3	31,713	S_6	31,686	31,616
<i>e</i> 4	31,792	C_2	31,759	31,675
<i>e</i> 5	31,803	S_6	31,778	31,712
<i>e</i> 6	31,840	C_2	31,809	31,734
<i>e</i> 7	31,903	C_2	31,879	31,828
<i>e</i> 8	31,961	S_6	31,937	31,875
ν 1	31,147	(<i>e</i> 1,2,3)—540		
ν 2	31,240	(<i>e</i> ,1,2,3)—450; (<i>e</i> 4,5)—540		
ν 3	31,346	(<i>e</i> ,4,5)—450; (<i>e</i> 7)—540		
ν 4	31,369	(<i>e</i> 1,2,3)—325		
ν 5	31,406	(<i>e</i> 8)—540; (<i>e</i> 6)—450		
ν 6	31,452	(<i>e</i> 7)—450		
ν 7	31,507	(<i>e</i> 8)—450; (<i>e</i> 6)—325		
ν 8	31,589	(<i>e</i> 7)—325		

Note. Electronic lines: *e*1–*e*8; vibronic lines; ν 1– ν 8 (Y_2O_3 only).

are observed. While the fourth and fifth lines are well separated for the Lu_2O_3 case, we only see them indicated as a shoulder for the Y_2O_3 case. When run in second order, the Gd lines in Y_2O_3 also appeared as two clearly separate lines as shown in Table I. While the spectral distribution as well as the total amount of splitting are very similar, the most significant difference in the two compounds is the downshift in energy for the Lu_2O_3 case. For $\text{Sc}_2\text{O}_3 : \text{Gd}$ the emission spectrum looks slightly different (see Table I). This is due to a shift of the individual lines relative to each other in addition to a further downshift in energy.

Let us start to consider $\text{Y}_2\text{O}_3 : \text{Gd}$ in more detail. In addition to the electronic lines, we observe eight vibronic lines as shown in Fig. 2 and tabulated in Table I. Using the arguments given in Ref. (1), it is possible to make a full, although tentative assignment of all the lines (see Table I). This assignment runs parallel with the one in Ref. (1). Since the

vibronic lines are broader than the electronic ones, the vibronic lines belonging to closely spaced electronic lines (like *e* 1, 2, 3 and *e* 4, 5) cannot be resolved. The vibrational frequencies are also the ones which have been observed for other dopant ions in Y_2O_3 (see Ref.(1)). An interesting aspect of the electronic line spectrum is the fact that the linewidth increases for the higher energy

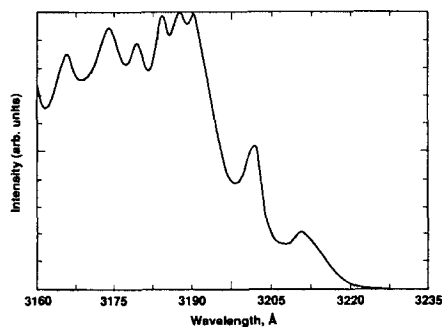


FIG. 2. The vibronic emission spectrum of the ${}^6P_{7/2} \rightarrow {}^8S$ transition of Gd^{3+} in $\text{Y}_{1.98}\text{Gd}_{0.02}\text{O}_3$ at 300 K.

TABLE II
DATA (IN CM⁻¹) ON THE Gd³⁺ ⁶P_{7/2} → ⁸S EMISSION
IN Y₂O₃, Lu₂O₃ AND Sc₂O₃

	C ₂ site		S ₆ site	
	bc ^(a)	Δ ^(b)	bc ^(a)	Δ ^(b)
Y ₂ O ₃	31,806	212	31,786	296
Lu ₂ O ₃	31,775	226	31,759	300
Sc ₂ O ₃	31,698	272	31,690	319
δ ^(c)	108	60	96	23

^a Center of gravity (barycenter) ⁶P_{7/2} → ⁸S.

^b Total crystal-field splitting ⁶P_{7/2} level.

^c Difference between the values for Y₂O₃ and Sc₂O₃.

components (Fig. 1). This is a clear illustration of a statement made, for example, by Caro *et al.* (12) that the upper crystal-field levels are broadened by phonon emission.

Starting from the assignment in Table I, we arrive at the center of gravity and the total crystal-field splitting of the ⁶P_{7/2} level for the two sites as follows: for C₂ 31,806 cm⁻¹ and 212 cm⁻¹, and for S₆ 31,786 cm⁻¹ and 296 cm⁻¹, respectively. These values agree with those reported by Antic-Fidancev *et al.* (13) from absorption measurements: for C₂ 31,808 cm⁻¹ and 216 cm⁻¹, and for S₆ 31,788 and 304 cm⁻¹, respectively. Unfortunately, however, these authors do not give any details about the way in which they derived and analyzed their data.

Another interesting comparison is that with results for A-type La₂O₃:Gd³⁺ (13). Here we have only one site for the La ion and the four lines for the Gd³⁺ ion with C_{3v} symmetry are at: 31,839, 31,851, 31,874, and 31,964 cm⁻¹. This yields a center of gravity of 31,882 cm⁻¹ and a total crystal-field splitting of 125 cm⁻¹.

In Table II the centers of gravity and total crystal-field splittings are compared for the three hosts. The combination of all these data illustrates the nephelauxetic effect (i.e., the displacement of energy levels as a function of the ligands), which is usually assumed to be related to covalency (15). The

present data show that this effect becomes stronger in the sequence La₂O₃ < Y₂O₃ (C₂) < Y₂O₃ (S₆) < Lu₂O₃ (C₂) < Lu₂O₃ (S₆) < Sc₂O₃(C₂) < Sc₂O₃ (S₆), which suggests a correlation with the metal-oxygen distance.

The total crystal-field splitting runs parallel with the nephelauxetic effect, but these parameters are not proportional (see Table II). The crystal-field splitting of the S₆ site is clearly less dependent in the host than that of the C₂ site. This may be due to the less symmetrical coordination of the C₂ site, which makes a larger variation of the crystal-field parameters possible if large ions are on that site. The problem of connecting nephelauxetic effects with crystal-field parameters is a complicated one which has been discussed in Ref. (13); it appears that a solution to this problem is still far away and requires further and detailed calculations.

Finally, we compare the present results with a calculated set of ⁶P_{7/2} levels for Gd³⁺ on the C₂ sites of Y₂O₃ (16). The total crystal-field splitting was predicted to be 215 cm⁻¹, which can be compared with our experimental value of 212 cm⁻¹. In Ref. (16), the ⁶P_{7/2} center of gravity was taken arbitrarily to coincide with that in aqueous solution. If we correct the calculated values using our experimental center of gravity for the C₂ sites, we arrive at (calculated) 31,694, 31,789, 31,832, 31,912 cm⁻¹ to be compared with (experimental, see Table I) 31,691, 31,792, 31,840, 31,903 cm⁻¹. This can be considered as very good agreement.

The ⁶P_{5/2} → ⁸S transition. Theory predicts three lines for a single site in a noncubic environment. Given the two different sites in the present case, we should see six lines for this transition. Figure 3 shows the example of Lu_{1.98}Gd_{0.02}O₃ where we can see all six lines despite the fact that the emission intensity is only about 10% of that of the ⁶P_{7/2} transition.

The ⁶I_j → ⁸S transitions. If all of the ⁶I_j → ⁸S transitions were split into the C₂ and C₆

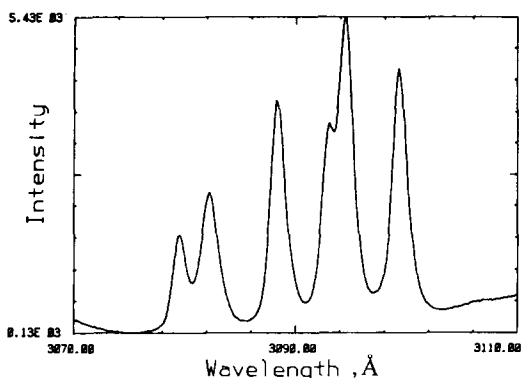


FIG. 3. The ${}^6P_{3/2} \rightarrow {}^8S$ transitions of Gd^{3+} in $Lu_{1.98}Gd_{0.02}O_3$ at 300 K.

components, we would indeed have a very complicated spectrum, since Carnall (17) observed (in absorption as well as by calculation) as many as 39 transitions for a single site (C_2 in LaF_3) case. In fact, as Fig. 4 shows, we were unable to observe any reliable signal for the ${}^6I_{11/2}$ level and the spectrum for the ${}^6I_{7/2, 9/2, 17/2}$ looked remarkably similar to another another single site (C_{4v}) case, $LaOBr:Gd$. We therefore conclude that the ${}^6P_{7/2} \rightarrow {}^8S$ emission consists of four lines only instead of the expected eight.

In view of the results for the ${}^6P_{7/2} \rightarrow {}^8S$ emission, it is hard to imagine that this is

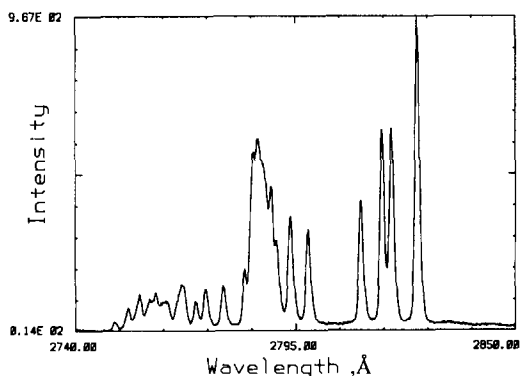


FIG. 4. The ${}^6I_{7/2} \rightarrow {}^8S$ transitions of Gd^{3+} in $Lu_{1.98}Gd_{0.02}O_3$ at 300 K.

TABLE III
ENERGIES, BARYCENTERS, AND TOTAL CRYSTAL-FIELD SPLITTING FOR THE LOWEST ENERGY ${}^6I_7 \rightarrow {}^8S$ TRANSITIONS OF Gd^{3+} IN Y_2O_3 , Lu_2O_3 , AND Sc_2O_3

Line number	$Y_{1.98}Gd_{0.02}O_3$ (cm^{-1})	$Lu_{1.98}Gd_{0.02}O_3$ (cm^{-1})	$Sc_{1.98}Gd_{0.02}O_3$ (cm^{-1})
1	35,435	35,393	35,289
2	35,513	35,473	35,373
3	35,542	35,505	35,411
4	35,605	35,571	35,480
Barycenter	35,523	35,486	35,388
Total splitting	170	178	191

due to insufficient resolution. Therefore, we propose a different explanation. The ${}^6I_{7/2} \rightarrow {}^8S$ transition is, according to Detrio's calculations (18), barely allowed as a magnetic-dipole transition. This means that Gd^{3+} ions, which are on a site with inversion symmetry (such as S_6) and in the ${}^6I_{7/2}$ level, have practically no possibility to decay radiatively to the 8S ground level and the nonradiative decay to the 6P_3 levels is more probable. Therefore, the four ${}^6I_{7/2} \rightarrow {}^8S$ lines are ascribed to Gd^{3+} ions on the C_s sites. The barycenters and energies for all three cases are summarized in Table III.

Conclusions

In summary, we can state that the improved experimental setup permitted us to observe all theoretically predicted lines of the Gd^{3+} emission for the ${}^6P_{7/2}$ and the ${}^6P_{5/2} \rightarrow {}^8S$ transitions, when it was incorporated into C-type Y_2O_3 , Lu_2O_3 , and Sc_2O_3 . For all observed transitions the barycenters shift toward lower energies as the size of the host ion decreases, while the total amount of splitting increases. The present data only support the fact that the problem of connecting the nephelauxetic effects with crystal-field parameters is indeed a complicated one with several properties of the host structure involved. If the crystal data and the spectra of this paper can be used to perform crystal-

field calculations, it will have served its purpose.

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