An Investigation of Energy Migration in Luminescent Diluted Gd³⁺ Systems

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Received December 13, 1985; in revised form March 3, 1986

The luminescence of yttrium-diluted Gd^{3+} compounds containing efficient trap centers is reported and discussed. By using a rough approach it is possible to derive the critical distance for energy transfer between Gd^{3+} ions. This approach implies a critical Gd^{3+} concentration above which the Gd^{3+} emission is quenched. This concentration can be related to the number of Gd^{3+} neighbors involved in the energy migration process among the Gd^{3+} ions. It is shown that the critical distance for energy transfer between Gd^{3+} depends on the ionic character of the compound. In fluorides this distance is approximately 5 Å, in oxides approximately 6.5 Å. For Gd^{3+} ions in oxides on a (nearly) centrosymmetric site, this distance is approximately 5 Å, as in the fluorides. These latter phenomena can be explained concerning the type of interaction between the Gd^{3+} ions. @ 1986 Academic Press, Inc.

Introduction

Recently several papers have been published on new efficient luminescent materials in which $Gd^{3+}-Gd^{3+}$ energy migration plays an important role (1-9). In most of these materials the Gd^{3+} ions are excited via a sensitizer (Bi^{3+} , Ce^{3+}), whereas the excitation energy is trapped by an activator (e.g., Tb^{3+} , Eu^{3+} , Dy^{3+}). The Gd^{3+} sublattice plays the role of a transport medium for the excitation energy. Both the ⁶I and ⁶P energy levels of the Gd^{3+} ion can contribute to this transport process. The energy transfer processes which can occur in these materials are presented in Fig. 1.

The probability for energy transfer between two Gd^{3+} ions depends strongly on

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the interionic distance. If this distance exceeds a critical value, R_c , energy transfer between Gd³⁺ ions becomes improbable. The average Gd³⁺-Gd³⁺ distance can be increased by replacing part of the Gd³⁺ ions by Y^{3+} , without disturbing the crystal structure drastically. If the average $Gd^{3+}-Gd^{3+}$ distance exceeds R_c , the long-range energy migration is hampered. As a consequence, Gd^{3+} emission is observed and the relevant composition loses its potential as a photoluminescent material with emission in the visible region. It is therefore of importance to determine the lowest Gd³⁺ concentration which allows efficient energy migration. This concentration must be related to the value of $R_{\rm c}$. On the one hand such a study will yield the lowest Gd³⁺ concentration necessary to obtain an efficient phosphor; on the other hand the values of R_c may

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FIG. 1. Schematic view of the possible energy transfer/migration processes in Gd^{3+} compounds. T, energy transfer; M, energy migration; E, excitation; \downarrow , emission (radiative decay); \checkmark , radiationless process (= nonradiative decay).

yield important information on the characteristics of energy transfer between Gd³⁺ ions.

Using new data as well as literature data, we will show that this aim is realized and that the results obtained depend strongly on chemical constitution and crystal structure.

Model

Let us consider a simple model system $Y_{1-x}Gd_xX_n$: S,A, where X is an anion or an anion group, S the sensitizer, and A the activator. The concentrations of S and A are chosen in such a way that direct transfer from S to A is of no importance. Let the energy migration process be given by

$$\xrightarrow{\text{excitation}} S \to \text{Gd} \xrightarrow{nx} \text{Gd} \to A \xrightarrow{\text{emission}}$$

as has been discussed before (2, 8). The term energy transfer indicates a one-step transfer process, the term energy migration indicates energy transport consisting of many one-step transfers. For x = 0 excitation into S yields mainly emission from S and only a small amount of emission from A (due to direct energy transfer). For x = 1excitation into S yields emission from A only. Let x_{cr} be the lowest Gd³⁺ concentration for which S excitation yields only A emission. For $x < x_{cr}$ we observe also Gd³⁺ emission indicating a hampering of the Gd³⁺ migration process.

For $x = x_{cr}$ each Gd^{3+} ion has roughly two Gd^{3+} neighbors to which it is connected by transfer; otherwise migration through the Gd^{3+} sublattice becomes impossible. Let the total number of crystallographic sites available for these two Gd^{3+} ions be N, then we have the approximate relation:

$$x_{\rm cr} \simeq 2/N. \tag{1}$$

Having determined x_{cr} by experiment, we find N from Eq. (1). This value of N can then be compared with the number of neighbors following from the crystal structure determination. In this way R_c is estimated. Consider for example a Gd³⁺ compound with a Gd³⁺ sublattice in which each

Gd³⁺ ion has 4 nearest Gd³⁺ neighbors at 4 Å, 2 next-nearest neighbors at 6 Å and 4 next-next-nearest neighbors at 8 Å and x_{cr} = 0.3. By using Eq. (1) we find N = 6. This means energy migration takes place not only over nearest neighbors, but also over next-nearest neighbors. The critical distance for energy migration must have a value in between 6 and 8 Å.

It is tempting to compare this situation with a very similar problem, viz., the energy migration in doped molecular crystals (10). Here a guest molecule is built into an array of host molecules (these are usually isotopic, e.g., $C_{10}H_8$ into $C_{10}D_8$). Migration over the guest molecules is monitored by the addition of a supertrap (e.g., β -methylnaphthalene). The role of the guest molecule is played by Gd³⁺, that of the (noninvolved) host molecule by Y^{3+} , whereas the Tb^{3+} ion acts as a supertrap. The migration in the molecular crystals has been described by percolation models. The percolation concentration (x_{perc}) is defined as the guest concentration for which the probability that excitation of the guest molecule will reach the supertrap via energy migration over many guest molecules, is finite. We note that $x_{perc} < x_{cr}$, since for x_{cr} this probability is 1. However, the difference between the values of x_{cr} and x_{perc} cannot be large. The larger the value of N, the smaller the difference between x_{cr} and x_{perc} will be.

For the time being we prefer the use of the rough model described by us above. First this is associated with data of practical importance. Second, x_{cr} is rather easy (although not accurately) to be determined. Also, the theoretical values of x_{perc} are only known for a restricted number of crystal structures.

Finally we note that our model has some limitations. The situation that the Gd^{3+} - Gd^{3+} transfer rate is not large relative to the Gd^{3+} radiative decay rate is such a limitation. In that case even for x = 1, S excitation yields still partly Gd^{3+} emission, in ad-

dition to the A emission. Also the trapping rate of A leads to a limitation of the model. If this rate is not large enough relative to the radiative decay rate of the Gd^{3+} ion, A emission as well as Gd^{3+} emission will be observed for x = 1 upon excitation in S.

We will now apply our model to experimental results on the Gd^{3+} concentration dependence of energy migration in $(Y,Gd)F_3$: Ce,Tb, Li $(Y,Gd)F_4$: Ce,Tb, Na $(Y,Gd)F_4$: Ce,Tb, $(Y,Gd)_3Li_3Te_2O_{12}$: Dy, and $(Y,Gd)_2O_3$: Dy and show the practical use of the approach. Results on $(Y,Gd)Al_3B_4O_{12}$ show the limitations of the approach.

Experimental

The materials used for the preparation of $(Y_{1-x},Gd_x)_2O_3$: Dy were Y_2O_3 , Gd_2O_3 and Dy_2O_3 (Highways Int. 99.999%). The samples were prepared by dissolving the oxides in hot concentrated HCl. The hydroxide was precipitated with ammonia. The precipitate was filtered off, washed thoroughly with distilled water, and allowed to dry. After 3 hr of heating at 900°C (11), only cubic $(Y,Gd)_2O_3$ was formed according to X-ray powder diffraction.

The preparation of $Li(Y_{1-x},Gd_x)F_4:Ce$, Tb, $Na(Y_{1-x},Gd_x)F_4:Ce$,Tb, and $(Y_{1-x},Gd_x)_3Li_3Te_2O_{12}:Dy$ has been described elsewhere (12–14). The luminescence spectra were recorded on a Perkin-Elmer MPF-3L spectrofluorometer equipped with a xenon lamp. The experimental results for the other two compounds were taken from the literature (1, 2). All data refer to room temperature.

Results

In Table I some data on the number of Gd^{3+} neighbors and their average distances toward a central Gd^{3+} ion are listed for the compounds studied. The data were calcu-

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NUMBER OF Gd ³⁺ NEIGHBORS AND DISTANCES
TOWARD A CENTRAL Gd ³⁺ ION IN GdF ₃ , NaGdF
LiGdF4, GdLi3Te2O12, Gd2O3 (CUBIC), AND
GdAl ₃ B ₄ O ₁₂

Compound	Number of Gd ³⁺ neighbors	Distances (Å)	
GdF3	$2^{2}_{2}_{6}_{12}_{6}_{2}$	$ \begin{array}{c} 3.7\\ 3.9\\ 4.3\\ 4.4 \end{array} $ $ \begin{array}{c} 4.2\\ 5.5 \end{array} $ $ \begin{array}{c} 5.5\\ 5.8 \end{array} $	
NaGdF₄	2) 1 2 1	6.0) 5.0 2.7 3.6 4.4	
LiGdF₄	2 4 4	5.6 3.8 5.2	
Gd ₃ Li ₃ Te ₂ O ₁₂	4 8	3.8 5.8	
Gd_2O_3	12 6	3.8 5,4	
	12 12	6.6 7.6	
GdAl ₃ B ₄ O ₁₂	6 6	5.9 7.3	

lated using the crystal structure of the compounds (15-20).

The values of x_{cr} were determined as follows. For (Y,Gd)F₃, Li(Y,Gd)F₄, Na(Y, Gd)F₄, (Y,Gd)₂O₃, and (Y,Gd)Al₃B₄O₁₂ the Gd³⁺ emission upon excitation in S or in the



FIG. 2. Gd^{3+} emission intensity versus Gd^{3+} concentration in $(Y_{1-x}, Gd_x)F_3$: Ce, Tb (after Ref. (2)).



FIG. 3. Gd^{3+} emission intensity versus Gd^{3+} concentration in $Li(Y_{1-x},Gd_x)F_4$: Cc, Tb.

Gd³⁺ levels was measured as a function of the Gd³⁺ concentration. The results are given in Figs. 2-6. In the case of $(Y,Gd)_3Li_3Te_2O_{12}$ the weakness of the signals forced us to use another method. For this compound the excitation spectrum of the Dy³⁺ emission around 580 nm was recorded as a function of the Gd³⁺ concentration. In Fig. 7 the intensity ratio between the Gd³⁺ line around 313 nm and the Dy³⁺ line around 320 nm in the excitation spectrum of the Dy³⁺ emission is plotted as function of the Gd³⁺ concentration. In Table II the results derived from these figures are listed. Also the values for N using Eq. (1) are given. The data in Table I are used to determine the neighbors involved in the en-



FIG. 4. Gd^{3+} emission intensity versus Gd^{3+} concentration in Na(Y_{1-x}, Gd_x)F₄: Ce, Tb.



FIG. 5. Gd^{3+} emission intensity versus Gd^{3+} concentration in $(Y_{1-x},Gd_x)_2O_3$: Dy.

ergy migration process. Also an estimation is given for the value of R_c .

For the value of x_{cr} the Gd³⁺ concentration was taken where the Gd³⁺ emission was quenched or the Gd³⁺ concentration where the Gd³⁺ emission reached a constant minimal value. For Gd₃Li₃Te₂O₁₂ the value of x_{cr} was determined in a different way (see below).

Discussion of Individual Systems

 $(Y,Gd)F_3$. In this system no Gd^{3+} emission was found for x > 0.3 (2). Because the literature data are limited, it was not possible to determine the exact concentration where the Gd^{3+} emission is totally quenched. However, its value must be in between x = 0.15 and x = 0.25. This yields, with Eq. (1), a value of N between 8



FIG. 6. Gd^{3+} emission intensity versus Gd^{3+} concentration in $(Y_{1-x},Gd_x)Al_3B_4O_{12}$ (after Ref. (1)).



FIG. 7. Relative intensity of the Gd³⁺ excitation lines in the Dy³⁺ excitation spectrum versus Gd³⁺ concentration in $(Y_{1-x},Gd_x)_3Li_3Te_2O_{12}$.

and 13. The number of nearest neighbors is 12 (Table I). Therefore the value of R_c is in between 4.4 and 5.5 Å.

 $Li(Y,Gd)F_4$. The Gd³⁺ emission in this system reaches a constant minimal value for x > 0.5. This indicates that $x_{cr} \simeq 0.5$, which gives N = 4. In LiGdF₄ there are 4 nearest neighbors at 3.8 Å so that energy transfer is restricted to nearest neighbors. The value of R_c is in between 3.8 and 5.2 Å. For LiGdF₄ the Gd³⁺-Gd³⁺ transfer probability was estimated considering exchange interaction to be the main interaction in the energy transfer process (12). This resulted in a probability for nearest neighbor transfer which is 10⁴ times larger than the probability for next-nearest neighbor transfer. This also indicates that energy migration is limited to transfer between nearest neighbors.

 $Na(Y,Gd)F_4$. In this system the Gd³⁺ concentration dependence of the Gd³⁺ emission intensity is similar to the Gd³⁺ emission dependence in Li(Y,Gd)F₄. A constant minimal value for the Gd³⁺ emission intensity was found for x > 0.5. This indicates $x_{cr} = 0.5$ and N = 4. In NaGdF₄ the structure of the Gd³⁺ sublattice is somewhat more complex than in LiGdF₄. In NaGdF₄ there are two sites at 2.7 Å but the occupancy degree by Gd³⁺ is 50%. Also the two sites at 4.4 Å are only 50% occupied by Gd³⁺. The two sites at 3.6 Å are completely occupied by Gd^{3+} . This means that the distance variation for the nearest neighbors of the Gd^{3+} ion is quite large. The value of R_c is in between 4.4 and 5.6 Å.

 $(Y,Gd)_3Li_3Te_2O_{12}$. For this system it was not possible to measure the Gd³⁺ emission intensity as a function of the Gd3+ concentration due to the low intensities. This is related to the fact that the lattice absorption has its onset at wavelengths longer than the lowest Gd³⁺ excitation lines (14). Instead the excitation spectrum of the Dy³⁺ emission was monitored as a function of the Gd³⁺ concentration. If energy transfer from Gd³⁺ to Dy³⁺ takes place, the relative intensity of the Gd³⁺ lines in the excitation spectrum should increase with increasing Gd³⁺ concentration if $x < x_{cr}$. This is because the Gd³⁺ absorption will increase with increasing value of x. Above x_{cr} all the energy absorbed by the Gd³⁺ ions should be transferred to the Dy³⁺ ions if no other activator is present in the material and the curve should show an extra increase with x. However, in Ref. (14) it has been shown that an unknown defect in the tellurate garnet traps the excitation energy effectively. Our observations (Fig. 7) indicate that this is also the case here. The low concentration of defects traps the excitation energy (which migrates over the Gd³⁺ sublattice) so effectively that the Dy³⁺ ions cannot compete with them. Consequently we observe in Fig. 7 a curve bending downward instead of upward. What is of importance here is the fact that the value of x for which a straight line in the high Gd³⁺ region is reached corresponds to x_{cr} . The value of x_{cr} determined in this way is 0.5 so that only nearest neighbors (N = 4) are involved in the energy migration among the Gd^{3+} ions. R_c is in between 3.8 and 5.8 Å.

 $(Y,Gd)_2O_3$. Only at very low Gd^{3+} concentrations, Gd^{3+} emission was observed. The Gd^{3+} emission was totally quenched for x > 0.1. This indicates that N has a very high value, i.e., about 20, so that energy transfer takes place over more than the 12 nearest neighbors. For N = 18 (next-nearest neighbor transfer included), Eq. (1) gives $x_{cr} = 0.11$. We conclude that in the system (Y,Gd)₂O₃ energy transfer is not restricted to nearest neighbors, but also nextnearest neighbors are involved. R_c is in between 5.4 and 6.6 Å.

 $(Y,Gd)Al_3B_4O_{12}$. According to the literature (1) this system gives a different concentration dependence of the Gd³⁺ emission with regard to the other compounds. Main difference is the reasonable amount of Gd^{3+} emission in the concentrated Gd^{3+} compound (x = 1). There are two major differences with regard to the other systems. No trap (or sensor) was deliberately introduced into the material and the minimal $Gd^{3+}-Gd^{3+}$ distance in the lattice is very long, viz., 5.9 Å (versus approximately 4 Å in the other systems). This latter fact explains probably the difference with the other systems. The approach used for these systems assumes energy migration in the rapid transfer regime. For $GdAl_3B_4O_{12}$ the approach is probably not valid, because the Gd^{3+} - Gd^{3+} distance is too long, so that our model is not valid in this case. This implies that we are most probably dealing with diffusion-limited energy migration. For $(Y,Gd)Al_3B_4O_{12}$ a maximum in the Gd³⁺ emission intensity is observed around x = 0.3. The case with only nearest neighbor transfer (N = 6) gives $x_{cr} = 0.33$. This critical concentration is very near to the concentration with maximum Gd³⁺ emission. Therefore we conclude that in this compound only nearest neighbors are involved in the energy migration process. This means R_c is in between 5.9 and 7.3 Å.

This different way of determining x_{cr} was also successfully used for Eu³⁺ compounds (21). In these compounds energy migration is usually diffusion limited. This also indi-

Compound	x _{cr}	$N = \frac{2}{x_{\rm cr}}$	Neighbors involved in the transfer process	$R_{\rm c}$ (Å)	Reference
GdF3	0.2 ± 0.05	10 ± 2.5	Nearest neighbors	$4.4 < R_{\rm c} < 5.5$	This work
LiGdF₄	0.5	4	Nearest neighbors	$3.8 < R_{\rm c} < 5.2$	This work
NaGdF₄	0.5	4	Nearest neighbors	$4.4 < R_{\rm c} < 5.6$	This work
Gd ₃ Li ₃ Te ₂ O ₁₂	0.5	4	Nearest neighbors	$3.8 < R_{\rm c} < 5.8$	This work
Gd ₂ O ₃	~0.1	~ 20	Next-nearest neighbors	$5.4 < R_{\rm c} < 6.6$	This work
GdAl ₃ B ₄ O ₁₂			Nearest neighbors	$5.9 < R_{\rm c} < 7.3$	(1)
GdMgB ₅ O ₁₀		_	Next-nearest neighbors	$R_{\rm c}\sim 6.5$	(4)

TABLE II DATA ON x_{cr} , THE NEIGHBORS INVOLVED IN THE TRANSFER PROCESS, AND R_c FOR VARIOUS Gd³⁺ COMPOUNDS

cates that energy migration in $GdAl_3B_4O_{12}$ is probably diffusion limited.

General Discussion

In Table II the results for the different compounds are summarized. In Fig. 8 a schematic view is given for the distance dependence of the energy migration among the Gd^{3+} ions in the different compounds. In the table the results for $GdMgB_5O_{10}$ are included. They were obtained in a different way, viz., by using some quantitative data on the energy migration in the Gd^{3+} sublattice.

There is a striking difference between the R_c values of the fluorides and the oxides: for GdF₃, LiGdF₄, and NaGdF₄, R_c is approximately 5 Å; for Gd₂O₃, GdAl₃B₄O₁₂, and GdMgB₅O₁₀, R_c is approximately 6.5 Å. Gd₃Li₃Te₂O₁₂ has a R_c value of 5 Å, although it is an oxide. These results can be explained in the following way.

Fluorides are more ionic than oxides. Therefore, the 5d level of the Gd^{3+} ion in the fluorides lies at higher energy than in oxides (22). Since the admixture of 5d wavefunctions into the 4f wavefunctions by odd terms in the crystal field expansion is responsible for the forced electric-dipole transitions within the $4f^n$ configuration, transitions in the oxides have a stronger electric-dipole character than in the fluorides. In the fluorides the energy transfer between two Gd^{3+} ions is mainly due to exchange interaction (12), so that it is restricted to short distances. In the oxides the electric-dipole interaction will increase the transfer probability for longer distances, so that in these compounds the critical dis-



FIG. 8. Schematic view of the $Gd^{3+}-Gd^{3+}$ distance dependence of energy migration in various compounds. \mathbb{Z} , area with energy migration between Gd^{3+} ions; \mathbb{S} , area with no energy migration between Gd^{3+} ions; \mathbb{m} , intermediate region with critical distance for energy migration.

tance for energy migration will be larger than in the fluorides. Even if the interaction in fluorides would not be mainly exchange, this argument still holds.

In Gd₃Li₃Te₂O₁₂ the Gd³⁺ ion is on a site with approximate inversion symmetry. If there is a centre of symmetry, the odd crystal field terms vanish so that the electricdipole interaction contribution vanishes too. This means that in Gd₃Li₃Te₂O₁₂ the interaction between Gd³⁺ ions is exchange regulated, so that the value of R_c should be equal to that found for the fluorides.

The Eu^{3+} ion can be used as a probe for the strength of the electric-dipole interaction between the Gd³⁺ ions. The Eu³⁺ ${}^{5}D_{0}$ - ${}^{7}F_{1}$ transition is a magnetic-dipole transition, the ${}^{5}D_{0}-{}^{7}F_{4}$ is a forced electric-dipole transition (23). In GdF_3 : Eu, for example, mainly ${}^{5}D_{0}-{}^{7}F_{1}$ emission was observed (24), whereas in GdAl₃B₄O₁₂: Eu strong ${}^{5}D_{0}-{}^{7}F_{4}$ emission was observed (25), although in both crystal lattices the Eu³⁺ ion occupies a site without inversion symmetry. In the compound with a large value for $R_{\rm c}$ $(GdAl_3B_4O_{12})$, strong $Eu^{3+} {}^5D_0 - {}^7F_4$ emission is observed, in a compound with a small value for R_c (GdF₃), mainly ${}^{5}D_{0}-{}^{7}F_{1}$ emission is observed. This is due to the fact that the ${}^{5}D_{0}-{}^{7}F_{4}$ transition can only gain a reasonable amount of intensity if the opposite-parity levels are not too far away, which is the same requirement as proposed above for the occurrence of high R_c values for Gd³⁺-Gd³⁺ transfer.

The model we derived for the Gd^{3+} emission intensity in Gd^{3+} systems has, as mentioned above, at least two limitations.

(i) If the energy migration is not fast, the model cannot be applied any longer. This is the case for $GdAl_3B_4O_{12}$. In this compound a reasonable amount of Gd^{3+} emission is present, even for x = 1 (see above).

(ii) The other limitation is that the trapping rate should be much faster than the radiative rate of the Gd^{3+} ion. An example, where this condition is not fulfilled, can be found in the literature. For $(La_{1-x}, Gd_x)B_3$ O_6 : Bi, Tb the Gd³⁺ emission was measured upon excitation into the Bi^{3+} ion. In the x = 1 composition Gd^{3+} emission is still present. Upon decreasing the amount of Gd³⁺, the Gd³⁺ emission intensity increases down to x = 0.15. No constant minimal value of the Gd³⁺ emission intensity was found (8). Recent investigations on the energy migration in GdB_3O_6 showed that the energy migration among the Gd³⁺ ions is of the fast-diffusion type (26). The trapping rate of Tb³⁺ is 6×10^{5} sec⁻¹, and the radiative rate of Gd³⁺ is 200 sec⁻¹ in GdB₃ O_6 : Bi, Tb. In the case of fast-diffusion energy migration a simple equation can be used for the ratio between the amount of Tb^{3+} emission and Gd^{3+} emission (26), viz.,

$$\frac{I_{\rm Tb}}{I_{\rm Gd}} = \frac{x_{\rm Tb} \cdot W_{\rm Gd \to Tb}}{x_{\rm Gd} \cdot W_{\rm Gd}}$$

where $I_{\text{Tb}(\text{Gd})}$ is the emission intensity of $\text{Tb}^{3+}(\text{Gd}^{3+})$ upon excitation in Bi^{3+} ; $x_{\text{Tb}(\text{Gd})}$ is the fraction of $\text{Tb}^{3+}(\text{Gd}^{3+})$; $W_{\text{Gd}\to\text{Tb}}$ is the trapping rate of Tb^{3+} ; and W_{Gd} is the radiative rate of Gd^{3+} . For the Tb^{3+} concentration used in Ref. (8) (1%), the Tb^{3+} emission intensity is 30 times higher than the Gd^{3+} emission intensity, so that Gd^{3+} emission is still observed. If we define efficient trapping by the condition that the Gd^{3+} emission is approximately 200 times weaker than the A emission, then the trapping rate of A should be 2×10^4 times larger than the radiative rate of Gd^{3+} (for 1% A), i.e., $W_{\text{Gd}\to A} \approx 4 \times 10^6 \text{ sec}^{-1}$.

Conclusion

In the new generation of fluorescent lamp phosphors, energy migration among Gd^{3+} ions plays an important role. Because Gd_2O_3 is more expensive then Y_2O_3 , part of the Gd^{3+} ions in these materials can be replaced by Y^{3+} . In this way materials could be produced at lower costs, but with the same quantum efficiency. Most suitable will be Gd^{3+} compounds with Gd^{3+} ions on a noncentrosymmetric crystallographic site. The derived values of R_c , viz., 5 Å for fluorides and 6.5 Å for oxides if inversion symmetry is absent, together with crystal structure data, make it possible to predict the values of x_{cr} , the minimal amount of Gd^{3+} necessary for efficient excitation energy transport.

Acknowledgments

The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Foundation for Technical Research (STW).

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