

LIMITATIONS TO THE USE OF Pr^{3+} AS A SENSITIZER IN LUMINESCENT
 Gd^{3+} COMPOUNDS

A.J. de Vries and G. Blasse

Physical Laboratory, State University of Utrecht
P.O. Box 80.000, 3508 TA Utrecht
The Netherlands

and

R.J. Pet

Nederlandse Philipsbedrijven B.V., Lighting Division
P.O. Box 218, 5600 MD Eindhoven
The Netherlands

(Received April 24, 1987; Communicated by W.B. White)

ABSTRACT Transfer phenomena which influence the energy transfer processes in Pr^{3+} -sensitized Gd^{3+} compounds are discussed. Concentration quenching of the Pr^{3+} 4f5d emission at relatively low Pr^{3+} concentrations, and energy transfer from activator ions to Pr^{3+} limits strongly the use of Pr^{3+} as a sensitizer in the host lattice GdBO_3 .

MATERIALS INDEX: gadolinium, borates, calcium, phosphors

Introduction

The search for materials which can be used as efficient phosphors in fluorescent lamps deals with Gd^{3+} -based compounds after De Hair and Van Kemenade showed that $\text{GdMgB}_5\text{O}_{10}$ doped with Ce^{3+} and Tb^{3+} is a very efficient phosphor (1). The Gd^{3+} sublattice plays an intermediate role in the energy transfer from the sensitizer (Ce^{3+}) to the activator (Tb^{3+}). These and similar energy transfer phenomena have been observed

and discussed for several other compounds (2-6).

De Hair showed that Ce^{3+} , Bi^{3+} and Pr^{3+} (7,8) can be used as sensitizers in Gd^{3+} phosphors. Recently two of us formulated criteria which have to be fulfilled if Pr^{3+} is used as a sensitizer (9). Srivastava et al. used these criteria to point out that Pr^{3+} can be used as a sensitizer in GdBO_3 (10). They concluded that GdBO_3 doped with Pr^{3+} and an activator ion is a promising efficient photoluminescent material.

In this paper we report on the energy transfer processes in YBO_3 doped with Pr^{3+} and GdBO_3 doped with Pr^{3+} and Eu^{3+} . It will be shown that the use of Pr^{3+} as a sensitizer has certain limitations.

Experimental

The starting materials were Y_2O_3 , Gd_2O_3 , Eu_2O_3 , Pr_6O_{11} (Highways International, 99.999%) and H_3BO_3 (Merck). The starting materials, with an excess of H_3BO_3 , were dissolved in HNO_3 . This mixture was allowed to dry. The YBO_3 samples were fired at 900°C and the GdBO_3 samples were fired at 1100°C , both in a 1:3 H_2/N_2 atmosphere.

All samples were checked by X-ray powder diffraction. Diffuse reflection spectra were recorded on a Perkin-Elmer Lambda 7 spectrophotometer. The luminescence measurements were performed on a Perkin-Elmer MPF-44B spectrofluorometer. High resolution luminescence measurements and decay measurements were performed on a set-up described in ref. 11, equipped with an EG&G ORTEC 7100 multichannel analyser. The quantum efficiency and absorption measurements were performed with the apparatus described in ref. 12.

Results and discussion

Effect of the concentration on the Pr^{3+} 4f5d emission

One of the requirements for an efficient phosphor is a high absorption for the emission of the low-pressure Hg discharge. About 85% of this emission is located at 39.400 cm^{-1} . Table I gives the percentage of the Hg vapour discharge emission at 39.400 cm^{-1} which is absorbed by the Pr^{3+} ion for various Pr^{3+} concentrations in YBO_3 .

The Pr^{3+} emission in YBO_3 was monitored at different Pr^{3+} concentrations upon excitation in Pr^{3+} at 40.000 cm^{-1} . The results are given in figs 1 and 2. The total emission intensity (fig. 1) reaches a maximum value for approximately 2% Pr^{3+} . Not only the total emission intensity changes for increasing Pr^{3+} concentration, but also the intensity ratio between the different emission bands (fig. 2). These emission bands, with maxima at 38.000 cm^{-1} , 36.250 cm^{-1} , 33.500 cm^{-1} and 32.000 cm^{-1} , can be ascribed to transitions from the 4f5d to the 4f²

Table I

Absorption of Hg emission at 39.400 cm⁻¹ by Y_{1-x}Pr_xBO₃

x	% abs.
0.005	63
0.01	76
0.02	85
0.04	90

configuration of Pr³⁺ (10). An assignment is hampered by the presence of two crystallographic sites for this ion in the lattice. In contrast to the spectral data in ref. 10, the higher energy part of the emission spectra is more intense than the lower energy part. We have no explanation for this disagreement. Although the absorption increases, the total emission intensity decreases for Pr³⁺ concentrations larger than 2%. This is due to concentration quenching.

Concentration quenching is observed in many systems upon increasing the concentration of the luminescent ion (13). It is caused by energy migration among the luminescent ions followed by energy transfer to quenching centers. The energy transfer between the luminescent ions can take place in a radiative or a nonradiative way (14). For energy transfer via the first way, a spectral overlap between the emission and excitation band(s) and a high absorption strength of the relevant transition are required. For Pr³⁺ in YBO₃ both criteria are fulfilled.

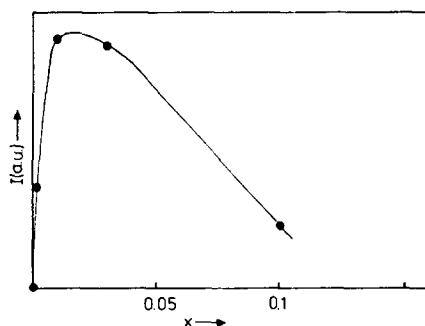


FIG. 1.

Total emission intensity of the Pr³⁺ 4f5d emission in Y_{1-x}Pr_xBO₃ as a function of the Pr³⁺ concentration for excitation at 40.000 cm⁻¹.

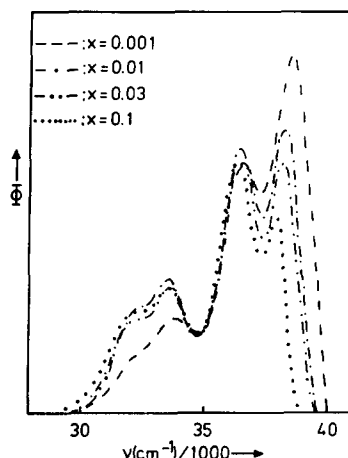


FIG. 2.

Emission spectrum of the Pr^{3+} 4f5d emission in $\text{Y}_{1-x}\text{Pr}_x\text{BO}_3$ for different Pr^{3+} concentrations. Φ gives the spectral radiant power per constant energy interval in arbitrary units. For clarity the spectra have been scaled differently.

The lowest-energy excitation band of Pr^{3+} ($4f^2$ -4f5d transition) overlaps the highest-energy emission band (ref. 10, fig. 2). The stronger quenching of the highest-energy emission band compared to the other emission bands is, therefore, ascribed to radiative transfer. This is a well-known phenomenon (15).

For non-radiative transfer, spectral overlap between the excitation and emission band(s) is a major requirement. Because the major criteria for radiative and nonradiative transfer are fulfilled for Pr^{3+} in YBO_3 , both transfer processes can occur and cause the concentration quenching of the 4f5d emission.

Energy transfer from the Pr^{3+} 4f5d state to Gd^{3+}

For an efficient energy transfer from the Pr^{3+} 4f5d state to Gd^{3+} , the Pr^{3+} 4f5d emission should overlap the ^6I and ^6P levels of Gd^{3+} (9). The spectral overlap between the Pr^{3+} 4f5d emission and the Gd^{3+} ^6I levels in GdBO_3 is approximately 2.5 eV^{-1} (assuming that the Pr^{3+} emission in GdBO_3 is the same as in isomorphous YBO_3). Using the same formulae and restrictions as in ref. 9 and crystal structure data (16), we find for the ratio $P_{\text{tr}}/P_{\text{r}} \approx 100$ (P_{tr} = transfer rate from Pr^{3+} to Gd^{3+} , P_{r} = radiative decay rate of Pr^{3+}) for GdBO_3 doped with Pr^{3+} . This value shows how strong the sensitizing action of Pr^{3+} is.

It is interesting to compare this ratio with the one for Pr³⁺ in Ca₃Gd₃(BO₃)₅ (CGB). In CGB-Pr³⁺ the lowest-energy 4f5d excitation band has its maximum around 40,000 cm⁻¹, as in GdBO₃, but the Stokes shift is larger (17). The spectrum of the Pr³⁺ 4f5d → 4f² emission in Ca₃La₃(BO₃)₅ (which is isostructural to Ca₃Gd₃(BO₃)₅ (18,19)) is presented in fig. 3. It consists of two broad bands with maxima at 34,500 cm⁻¹ and 30,000 cm⁻¹ due to Pr³⁺ 4f5d → 4f² transitions. The spectral overlap between the Pr³⁺ 4f5d emission and the Gd³⁺ 6I levels is approximately 0.7 eV⁻¹. For the ratio P_{tr}/P_r in CGB-Pr³⁺ we find P_{tr}/P_r ≈ 10. It should be realized that the data for Pr³⁺ → Gd³⁺ transfer in CGB are calculated using Pr³⁺ emission data for the La³⁺ compound. This throws some uncertainty on the value of the ratio P_{tr}/P_r, but it is certainly much lower than for GdBO₃-Pr³⁺. The difference is caused by two factors, viz. the smaller spectral overlap in CGB and the difference in the crystal structures of CGB and GdBO₃.

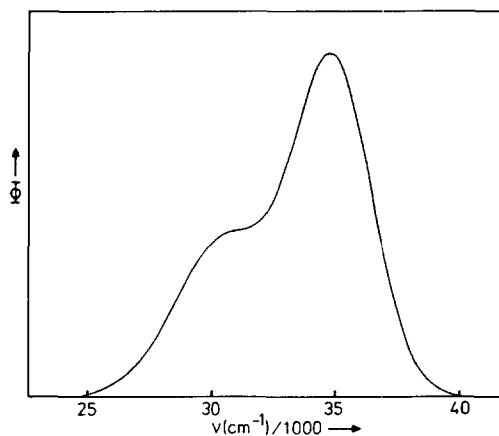


FIG. 3.

Emission spectrum of the Pr³⁺ 4f5d emission in Ca₃La_{2.91}Pr_{0.09}(BO₃)₅ after excitation at 40,000 cm⁻¹. Φ gives the spectral radiant power per constant energy interval in arbitrary units.

In CGB the Gd³⁺ 6I excitation lines do not have a maximal overlap with the Pr³⁺ emission, whereas in GdBO₃ this is the case. Further, the Pr³⁺ emission bands in CGB are broader than in GdBO₃. Both factors result in a 3½ times smaller spectral overlap between the Pr³⁺ 4f5d emission and the Gd³⁺ 6I levels in CGB compared with GdBO₃.

For the calculation of P_{tr}/P_r also the crystal structure dependent summation $\sum_i c_i / (R_i)^6$ is important. In case of Pr³⁺ → Gd³⁺ transfer, R_i presents the Pr³⁺ - Gd³⁺ distance for the ith type of neighbour and c_i

presents the number of Gd^{3+} ions at distance R_1 (9). In table II values for R_1 and c_1 are tabulated for CGB and $GdBO_3$. In $GdBO_3$, Gd^{3+} occupies two different crystallographic sites. This difference is neglected in table II and in the calculations in this paper. For $\sum c_1/(R_1)^6$ we find $9.42 \cdot 10^{-64} m^{-6}$ and $2.68 \cdot 10^{-63} m^{-6}$ for CGB and $GdBO_3$, respectively. From table II it is clear that this difference is caused by the more compact Gd^{3+} sublattice in $GdBO_3$.

Table II

Values for c_1 and R_1 in $Ca_3Gd_3(BO_3)_5$ and $GdBO_3$ (see also text)

i	$Ca_3Gd_3(BO_3)_5$		$GdBO_3$	
	c_1	$R_1(\text{\AA})$	c_1	$R_1(\text{\AA})$
1	4	4.36	6	3.83
2	2	5.02	4	4.84
3	2	5.50	4	5.55
4	2	6.51	6	6.63
5	2	6.65	8	6.74
6	4	7.02	4	7.26

The effect of the smaller value of P_{tr}/P_r in CGB compared to $GdBO_3$ is illustrated in fig. 4 where the emission spectra are presented for $Ca_3La_3(BO_3)_5$ and YBO_3 , both codoped with 4% Pr^{3+} and 15% Gd^{3+} , for excitation in the Pr^{3+} 4f5d band. In codoped $Ca_3La_3(BO_3)_5$, both Pr^{3+} and Gd^{3+} emission are present, whereas in codoped YBO_3 only Gd^{3+} emission is observed.

Energy transfer in $GdBO_3$ codoped with Pr^{3+} and Eu^{3+}

As suggested in ref. 10 codoped samples $GdBO_3-Pr^{3+}$, A may show high A efficiencies upon Pr^{3+} (4f5d) excitation. The $Pr^{3+} \rightarrow A$ transfer occurs via the Gd^{3+} ions. However, for a sample $Y_{0.77}Pr_{0.02}Eu_{0.01}Gd_{0.20}BO_3$ we observed a quantum efficiency for Pr^{3+} (4f5d) excitation of only 15%. Using Bi^{3+} as a sensitizer (20) in the same composition yields 85%. Without the activator Eu^{3+} , the quantum efficiencies (for the Gd^{3+} emission) are equal (50%). This suggests an interaction between Pr^{3+} and Eu^{3+} which is quite conceivable in view of the 4fⁿ energy level schemes of these ions (21).

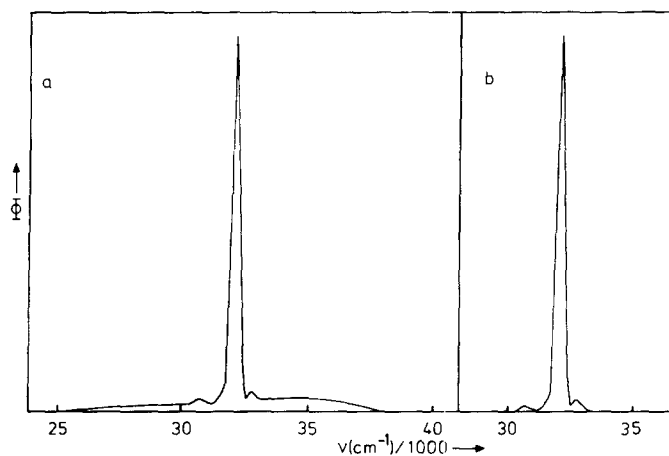


FIG. 4.

a Emission spectrum of $\text{Ca}_3\text{La}_{2.43}\text{Pr}_{0.12}\text{Gd}_{0.45}(\text{BO}_3)_5$ after excitation at 40.000 cm^{-1} .

b Emission spectrum of $\text{Y}_{0.81}\text{Pr}_{0.04}\text{Gd}_{0.15}\text{BO}_3$ after excitation at 40.000 cm^{-1} .

Φ gives the spectral radiant power per constant energy interval in arbitrary units.

To elucidate this observation, we investigated the luminescent properties of $\text{Y}_{0.99}\text{Eu}_{0.01}\text{BO}_3$, $\text{Y}_{0.98}\text{Pr}_{0.01}\text{Eu}_{0.01}\text{BO}_3$ and $\text{Y}_{0.99}\text{Pr}_{0.01}\text{BO}_3$ ($4f^2$ emission) in more detail. The results are as follows.

The Eu^{3+} ion was excited at 21.360 cm^{-1} ($^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition) and showed an intense luminescence. The emission spectrum of Eu^{3+} in YBO_3 was the same as the emission spectrum of Eu^{3+} in GdBO_3 (22). The decay curves of the $\text{Eu}^{3+} ^5\text{D}_0 - ^7\text{F}_J$ emission at room temperature were exponential with a decay time of $4150\text{ }\mu\text{s}$. This decay time is the radiative lifetime of the Eu^{3+} ion in this host lattice.

In $\text{YBO}_3\text{-Pr}^{3+}$, the Pr^{3+} ion was excited in the $^3\text{H}_4 - ^1\text{I}_6$ transition at 22.000 cm^{-1} . Between 15.500 and 16.500 cm^{-1} three groups of very weak Pr^{3+} emission peaks were found. These groups consist of peaks at: 15.950 and 15.970 cm^{-1} ; 16.360 , 16.390 and 16.440 cm^{-1} ; 16.530 and 16.570 cm^{-1} . The last emission group coincides with the lowest absorption peaks of the $^1\text{D}_2$ level, as observed in the diffuse reflection spectrum. Therefore, we ascribe the last emission group to the $^1\text{D}_2 - ^3\text{H}_4$ transition. The low emission intensity is ascribed to nonradiative losses due to the high-frequency vibrations of the borate groups. We were not able to determine unambiguously the origin of the other two emission groups. Within the accuracy of our instrumental set-up, the decay of the $^1\text{D}_2 - ^3\text{H}_4$ emission was exponential and the decay time of this emission in $\text{Y}_{0.99}\text{Pr}_{0.01}\text{BO}_3$ was $40\text{ }\mu\text{s}$.

Upon excitation of the Eu^{3+} ions in $\text{YBO}_3\text{-Pr,Eu}$ we observed the same Eu^{3+} emission, and a very weak extra emission. This emission consists of the Pr^{3+} lines at 16.530 cm^{-1} and 16.570 cm^{-1} . The decay curve of the Eu^{3+} emission was non-exponential (see fig. 5). The decay of the two additional weak emissions was equal to the decay of the Eu^{3+} emission.

The non-exponential decay of the $\text{Eu}^{3+} {}^5\text{D}_0$ emission in $\text{YBO}_3\text{-Pr,Eu}$ indicates energy transfer from Eu^{3+} to Pr^{3+} . Energy transfer from Eu^{3+} to Pr^{3+} has been reported before (23). The $\text{Eu}^{3+} {}^5\text{D}_0$ level in $\text{YBO}_3\text{-Pr,Eu}$ is only some 10 cm^{-1} below the highest energy component of the $\text{Pr}^{3+} {}^1\text{D}_2$ level.

We tried to fit the decay curve of the Eu^{3+} emission to the model for direct transfer developed by Inokuti and Hirayama (24) assuming electric dipole interaction or exchange interaction, but this was not succesful. Probably the energy transfer is governed by both mechanisms (exchange interaction effective at short distances, and electric-dipole interaction effective at larger distance (25)). Also the different crystallographic sites should be considered in this evaluation.

The fact that the decay of the $\text{Pr}^{3+} {}^1\text{D}_2$ emission in $\text{YBO}_3\text{-Pr,Eu}$ upon Eu^{3+} excitation is equal to the Eu^{3+} decay itself shows that the rate of transfer from the Eu^{3+} ion to the $\text{Pr}^{3+} {}^1\text{D}_2$ level is much slower than the decay rate of the ${}^1\text{D}_2$ level.

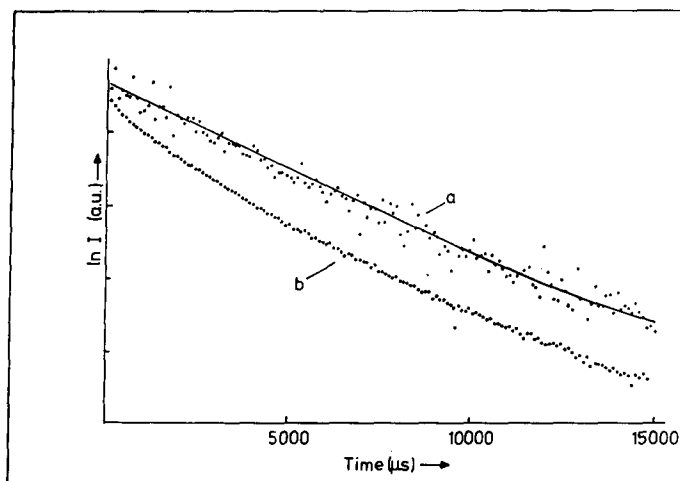


FIG. 5.

- a Decay of the $\text{Eu}^{3+} {}^5\text{D}_0\text{-}^7\text{F}_2$ emission in $\text{Y}_{0.99}\text{Eu}_{0.01}\text{BO}_3$ after excitation at 21.360 cm^{-1} . The drawn line is a fit to a one-exponential function.
- b Decay of the $\text{Eu}^{3+} {}^5\text{D}_0\text{-}^7\text{F}_2$ emission in $\text{Y}_{0.98}\text{Pr}_{0.01}\text{Eu}_{0.01}\text{BO}_3$ after excitation at 21.360 cm^{-1} .

The energy transfer from Eu³⁺ to Pr³⁺, mainly resulting in a non-radiative loss of excitation energy, explains the difference in the quantum efficiencies of (Y,Gd)BO₃-Pr,Eu and (Y,Gd)BO₃-Bi,Eu. The Pr³⁺ ion plays the role of a sensitizer (via the 4f5d state) as well as the role of a quenching site (via the 4f² states). From the viewpoint of application, the latter is an undesirable effect. This type of energy transfer occurs probably also for other activator ions. The ⁵D₄ level of Tb³⁺, for example, is nearly resonant with the ³P_J levels of Pr³⁺. In fact we find for the quantum efficiency of the Tb³⁺ emission of Y_{0.43}Pr_{0.02}Gd_{0.50}Tb_{0.05}BO₃ only 25%.

Another mechanism which may lead to a decrease of the quantum efficiency of (Y,Gd)BO₃-Pr,Eu, is electron transfer from Pr³⁺ to Eu³⁺. Electron transfer from Ce³⁺ to Eu³⁺ has been reported before. For this couple an excited charge-transfer state (Ce⁴⁺-Eu²⁺) is responsible for the quenching of the Ce³⁺ and the Eu³⁺ emission in several host lattices (26).

We conclude that the use of Pr³⁺ as a sensitizer in GdBO₃ is limited.

Acknowledgement

The authors are indebted to mr. E.D. Schutten and mrs. C. Staats who performed part of the measurements.

References

- 1) J.Th.W. de Hair and J.T.C. van Kemenade, paper no. 54 presented at the Third International Symposium on the Science and Technology of Light Sources, Toulouse, 18-21 April 1983
- 2) G. Blasse, Phys. stat. sol. (a) 73, 205 (1982)
- 3) G. Blasse, Recl. Trav. Chim. Pays-Bas 105, 143 (1986)
- 4) H.S. Kiliaan, A. Meyerink and G. Blasse, J. Lum. 35, 155 (1986)
- 5) H.S. Kiliaan, J.F.A.K. Kotte and G. Blasse, J. Electrochem. Soc. to be published.
- 6) M. Leskelä, M. Saakes and G. Blasse, Mat. Res. Bull. 19, 151 (1984)
- 7) J.Th.W. de Hair, J. Lum. 18/19, 797 (1979)
- 8) J.Th.W. de Hair, J. Solid State Chem. 33, 33 (1980)
- 9) A.J. de Vries and G. Blasse, Mat. Res. Bull. 21, 683 (1986)

- 10) A.M. Srivastava, M.T. Sobieraj, S.K. Ruan and E. Banks, *Mat. Res. Bull.*, 21, 1455 (1986)
- 11) P.A.M. Berdowski, M.J.J. Lammers and G. Blasse, *Chem. Phys. Lett.* 133, 387 (1985)
- 12) A. Bril and W. Hoekstra, *Philips Res. Repts.* 16, 356 (1961)
- 13) D.L. Dexter and J.H. Schulman, *J. Chem. Phys.* 44, 1067 (1968)
- 14) See e.g. *Energy transfer processes in condensed matter* (ed. B. diBartolo), Plenum Press, New York (1984)
- 15) Ref. 14, p. 497
- 16) W.F. Bradley, D.L. Graf and A.S. Roth, *Acta Cryst.* 20, 283 (1966)
- 17) R.J. Pet and J.G. Verlijsdonk, unpublished results.
- 18) A.A. Voronkov and N.G. Šumjackaja, *Kristallografija SSSR* 13, 246 (1968)
- 19) B. Kindermann, *Z. Krist.* 146, 67 (1977)
- 20) A. Wolfert, E.W.J.L. Oomen and G. Blasse, *J. Solid State Chem.* 59, 280 (1985)
- 21) G.H. Dieke, *Spectra and Energy levels of Rare Earth Ions in Crystals*, John Wiley and Sons Inc., New York (1968)
- 22) A. Bril and W.L. Wanmaker, *J. Electrochem. Soc.* 111, 1363 (1964)
- 23) H.C. Kandpal and H.B. Tripathi, *Solid State Comm.* 40, 673 (1981)
- 24) M. Inokuti and F. Hirayama, *J. Chem. Phys.* 43, 1978 (1965)
- 25) J.C. Vial and R. Buisson, *J. Physique Lettres* 43, L-745 (1982)
- 26) G. Blasse and A. Bril, *J. Chem. Phys.* 47, 1920 (1967); G. Blasse and N. Sabbatini, *Mat. Chem. Phys.* 16, 237 (1987).