ENERGY TRANSFER FROM Gd^{3+} TO Tb^{3+} AND Eu^{3+}

G. BLASSE, G.P.M. VAN DEN HEUVEL
Physical Laboratory, State University Utrecht, 3508 TA Utrecht, The Netherlands

and

T. VAN DIJK
Twente University of Technology, Department of Inorganic Materials Science, 7500 AE Enschede, The Netherlands

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Energy transfer from Gd^{3+} to Tb^{3+} and Eu^{3+} in gadolinium zirconates occurs not only from the ^6P but also from t levels of Gd^{3+} to the $4f^75d$ levels of Tb^{3+} and the charge transfer levels of Eu^{3+}.

1. Introduction

Energy transfer in gadolinium compounds from the Gd^{3+} ions to Tb^{3+} and Eu^{3+} dopants is well known [1–3]. It is generally assumed that the excitation energy migrates through the gadolinium system until it is trapped at the dopant ion. During a study of the fluorite–pyrochlore transition by analysing the Eu^{3+} luminescence [4] we accidentally observed some additional features of the transfer process from Gd^{3+} to Tb^{3+} and Eu^{3+}. These are discussed in this letter.

2. Experimental

We investigated compositions $Gd_xZr_{1-x}O_{2-x/2}$ with $x = 0.427$ (fluorite), $x = 0.473$ (defect pyrochlore) and $x = 0.500$ (stoichiometric pyrochlore). The luminescence of the $x = 0.500$ sample was too weak to be measured. Samples were prepared wetchemically by means of the citrate synthesis [5]. They were heated at 1550°C for 70 h and were annealed after grinding at 1000°C for 100 h. From X-ray diffraction the samples proved to be homogeneous, whereas the samples with 47.3 and 50.0 at % Gd showed the characteristic pyrochlore superstructure reflections. Europium and terbium were not added intentionally. The Eu^{3+} concentration amounts to some 600 ppm, that of Tb^{3+} could nc found accurately but should be considerably lowe These analyses were performed by emission spectr graphical analysis. The sample composition was de mined by X-ray fluorescence. The optical measure were performed at room temperature on a MPF-2/ Perkin–Elmer spectrofluorimeter.

3. Results

Fig. 1 shows the excitation spectrum of the Eu· and the Tb^{3+} luminescence in the gadolinium zirc The spectra consist of a broad band on which are s imposed a number of strong and sharp lines. The b bands correspond to transitions to the charge-tran level of Eu^{3+} in the case of Eu^{3+} luminescence [6] to the $4f^75d$ levels of Tb^{3+} in the case of Tb^{3+} lur cence. The sharp lines correspond to transitions in Gd^{3+} ion. Those around 310 nm are the $^8S \rightarrow {}^6P$ t tions, those around 280 nm are the $^8S \rightarrow {}^6I$ transit The interesting feature is that the intensity ratio be these two groups of lines is strikingly different in t two excitation spectra: whereas the Eu^{3+} emission preferentially excited into the $^8S \rightarrow {}^6I$ transitions, Tb^{3+} emission does not show such a preference.

Diffuse reflection spectra of the samples learned

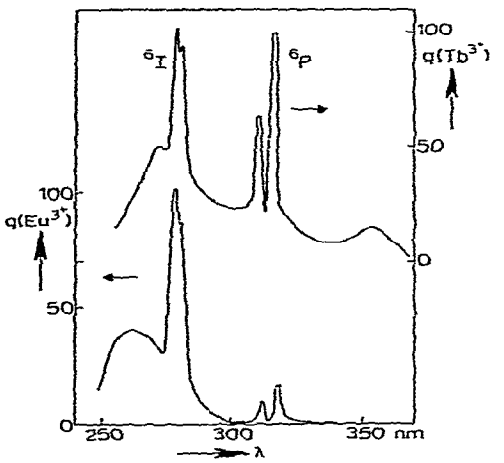

Fig. 1. Relative excitation spectrum of the 630 nm emission (mainly Eu^{3+}, lower part) and of the 490 nm emission (Tb^{3+}, upper part) of the sample $Gd_xZr_{1-x}O_{2-x/2}$ ($\lambda = 0.427$). The relative quantum output is plotted in arbitrary units (Eu^{3+}: left hand side; Tb^{3+}: right hand side). Upon excitation into the Gd^{3+} ^6P levels the quantum output of the total Eu^{3+} and total Tb^{3+} emission is about equal (after correction of simultaneous excitation into the Tb^{3+} 4f–5d absorption band).

that the absorption strength of the group of $^8S \rightarrow {}^6I$ transitions is about twice as high as that of the $^8S \rightarrow {}^6P$ group. Because the quantum output of the Eu^{3+} and Tb^{3+} emission under excitation into the $^8S \rightarrow {}^6P$ transitions of Gd^{3+} is about equal and the Eu^{3+} concentration much higher than the Tb^{3+} concentration, our results point to a considerably higher probability of transfer from Gd^{3+} concentration, our results point to a considerably higher probability of transfer from Gd^{3+} to Tb^{3+} than to Eu^{3+} under $^8S \rightarrow {}^6P$ excitation.

4. Discussion

4.1. Excitation into the ^6P levels of Gd^{3+}

Under ^6P excitation the total amount of energy transferred from Gd^{3+} to Tb^{3+} is about equal to that transferred from Gd^{3+} to Eu^{3+}. Since the Eu^{3+} concentration is much higher than the Tb^{3+} concentration, this means that the transfer probability for the $Gd^{3+} \rightarrow Tb^{3+}$ couple must be much higher than for the $Gd^{3+} \rightarrow Eu^{3+}$ couple. There is an obvious explanation for this. The Gd^{3+} ^6P levels coincide approximately with energy levels of the $4f^8$ Tb^{3+} and the $4f^6$ Eu^{3+} configuration. The optical transitions involved are strongly forbidden. The ^6P levels overlap also with the 4f → 5d absorption band of the Tb^{3+} ion (see fig. 1; the low intensity of this band is due to the low Tb^{3+} concentration), but not with the Eu^{3+} charge transfer band. The 4f–5d transition is an allowed optical transition. As a consequence the Gd → Tb transfer has a much higher probability than the Gd → Eu transfer, if the energy transfer originates at the Gd^{3+} ^6P levels These levels overlap with an allowed transition in the Tb^{3+} ion, but only with forbidden transitions in the Eu^{3+} ion.

4.2. Excitation into the ^6I levels of Gd^{3+}

If the Gd^{3+} ion after excitation into the ^6I levels would relax to the ^6P levels before transferring its energy, it is hard to understand why the ratio of the ^6I and ^6P excitation peaks is so different for the Eu^{3+} and the Tb^{3+} luminescence. The only way to explain the present results is to assume that transfer from Gd^{3+} to Eu^{3+} can also occur from the ^6I levels with a probability which is considerably higher than for transfer from the ^6P levels. The reason for such a higher probability immediately becomes clear from fig. 1. The ^6I levels overlap with the allowed charge-transfer band of Eu^{3+}, whereas the ^6P levels overlap only with the forbidden transitions within the $4f^6$ configuration of Eu^{3+}. For transfer from the ^6I levels of Gd^{3+} to either Eu^{3+} or Tb^{3+} there should not be a very different transfer probability, because in both cases there is overlap with an allowed transition. In fact excitation into the ^6I levels yields about 8 times more Eu^{3+} than Tb^{3+} luminescence which is well in line with their concentration difference.

The reason for the slow $^6I \rightarrow {}^6P$ relaxation in the Gd^{3+} ion in the gadolinium zirconates is probably due to the fact that the energy difference between these levels (at least 2500 cm^{-1} [7]) must be taken up by a 4 to 5 phonon process, the highest infrared band being observed between 400 and 600 cm^{-1} [8].

In conclusion we have shown that energy transfer from Gd^{3+} to Tb^{3+} and Eu^{3+} may occur also from the ^6I levels and that the transfer probability depends strongly on the fact whether the Gd^{3+} levels overlap an allowed or forbidden transition of the acceptor ion.

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