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ENERGY TRANSFER PHENOMENA IN LANTHANIDE METABORATES (LnB_3O_6)

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It is shown that GdB_3O_6 is an excellent host lattice to obtain efficient photoluminescent materials. For this purpose we need a sensitizer (S) of the Gd^{3+} sublattice and an activator (A). Energy transport from S to A occurs via the Gd^{3+} sublattice. We studied S = Sb^{3+}, Bi^{3+}, Ce^{3+} and A = Eu^{3+}, Tb^{3+}. Results confirm the transport process $S \rightarrow Gd(\rightarrow Gd)_n \rightarrow A$.

1. INTRODUCTION

In recent years there is a growing interest in gadolinium compounds as host lattices for sensitizers and activators to obtain in this way new and efficient photoluminescent materials. In fact one of us proposed that a luminescent centre in a Gd^{3+} compound can transfer its excitation energy to the Gd^{3+} sublattice and that an activator can trap this energy when it migrates among the Gd^{3+} ions[1,2]. De Hair *et al.* applied this principle to prepare efficient phosphors[3-5]. In this laboratory the work was continued with GdF_3 (ref.6) and $GdMgB_5O_{10}$ (ref.7).

Here we report results on GdB_3O_6 as a host lattice. We used Sb^{3+}, Bi^{3+} and Ce^{3+} as possible sensitizers of the Gd^{3+} sublattice and Tb^{3+} and Eu^{3+} as activators. The crystal structure of the compounds LnB_3O_6 (Ln = La - Tb) has been described by Abdullaev *et al.*[8]. In this paper we report on double-doped borates; the single-doped were reported elsewhere[9].

2. EXPERIMENTAL

The experimental techniques were described in ref.9.

3. RESULTS AND DISCUSSION

3.1. GdB_3O_6-Sb^{3+},Tb^{3+}

Results at room temperature are simple, since the Sb^{3+} emission is quenched at 300 K. The excitation spectrum of the Tb^{3+} emission shows only Tb^{3+} and Gd^{3+} lines. At 4.2 K a weak band at 260 nm appears. This is the Sb^{3+} excitation band.

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Excitation into this band irradiates also the Gd^{3+} lines around 250 nm ($^8S \rightarrow {}^6D$). The resulting emission shows mainly Sb^{3+} emission with a small amount of Gd^{3+} and Tb^{3+} emission lines. The transfer from Sb^{3+} to Tb^{3+} will be inefficient, because of the low concentrations (both 1 at. %). Therefore, the transfer characteristics of GdB_3O_6-Sb^{3+},Tb^{3+} are as follows: (a) excitation into Sb^{3+} yields mainly Sb^{3+} emission; (b) excitation into Gd^{3+} yields mainly Tb^{3+} emission due to energy migration in the Gd^{3+} sublattice.

3.2. GdB_3O_6-Bi^{3+},Ln^{3+} (Ln = Eu, Tb, Dy)

Extremely efficient luminescent materials can be obtained from GdB_3O_6 by using Bi^{3+} as a sensitizer and several of the lanthanide ions as an activator. It has been shown that the Bi^{3+} ion transfers all of its excitation energy to the Gd^{3+} sublattice[9]. The lanthanide ions are able to trap the energy migrating in the Gd^{3+} sublattice. As an example we present in fig.1 the excitation spectrum of the Eu^{3+} emission of GdB_3O_6-Bi^{3+},Eu^{3+}. Excitation into Bi^{3+} or Gd^{3+} results mainly in Eu^{3+} emission with only a few percent of Gd^{3+} emission. These results are obtained at 300 K as well as at 4.2 K. If we use LaB_3O_6 as the host lattice instead of GdB_3O_6, excitation into the Bi^{3+} ion results mainly in Bi^{3+} emission. This shows that the Gd^{3+} ions play an intermediate role in the $Bi^{3+} \rightarrow Eu^{3+}$ energy transfer in GdB_3O_6.

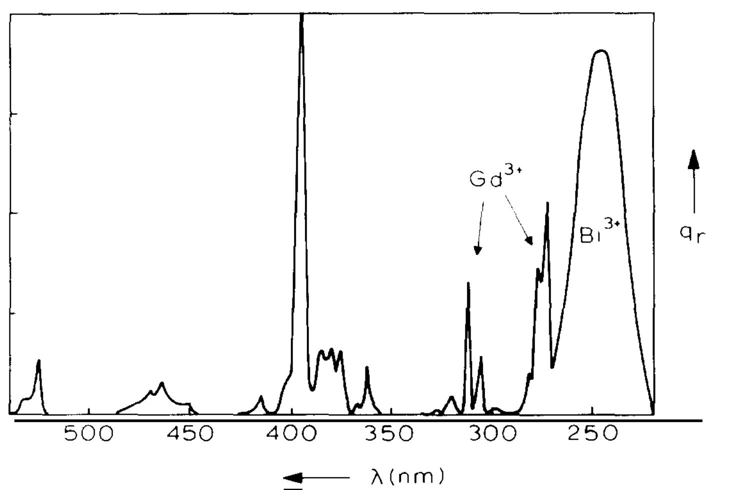

FIGURE 1
Excitation spectrum of the Eu^{3+} emission of GdB_3O_6-Bi,Eu at 300 K.

3.3. GdB_3O_6-Ce^{3+},Ln^{3+} (Ln = Eu, Tb)

There is no essential difference between the results for samples GdB_3O_6-Bi^{3+}, Ln^{3+} and GdB_3O_6-Ce^{3+},Ln^{3+} with one exception of minor importance, viz. the Ce^{3+} ion does not transfer all of its excitation energy to the Gd^{3+} sublattice[9]. For the composition $Gd_{0.98}Ce_{0.01}Tb_{0.01}B_3O_6$, for example, the total light output under Ce^{3+} excitation consists for 15 % of Ce^{3+} emission and for 85 % of Gd^{3+} and Tb^{3+} emission.

Results for the mixed host lattice $(La,Gd)B_3O_6$ confirm our results and will be presented elsewhere[9].

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