SENSITIZATION OF Tb^{3+} LUMINESCENCE IN $NaGdSiO_4$

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ABSTRACT

The luminescence properties of the system $Na(Gd,S,Tb)SiO_4$ ($S = Ce^{3+}$ or Bi^{3+}) are reported, for the orthorhombic olivine modification as well as for the tetragonal NaF-stabilized modification. The Tb^{3+} luminescence can be sensitized by Ce^{3+}, Gd^{3+} or Bi^{3+}. The efficiencies of the several processes are discussed.

INTRODUCTION

There is a need for efficient green emitting luminescent materials. The Tb^{3+} ion is a suitable activator in this aspect. Since its price is high, it is imperative to combine low activator concentration to high light output. Sensitization is then necessary. A recent possibility is the use of a Gd^{3+} sublattice sensitized by ions like Ce^{3+} or Bi^{3+} [1-3].

In this paper we describe the results of a study on the sensitization of the Tb^{3+} luminescence in $NaGdSiO_4$. An interesting aspect of this compound is that it occurs in two modifications, viz. an orthorhombic olivine modification [4,5] and a NaF-stabilized tetragonal modification [6-8]. These will be called below O and T, respectively.
Their crystal structures are known. In the O modification the Gd^{3+} ions are in octahedral coordination, in the T modification they are in eightfold coordination. In this way we expected to obtain information on the transfer processes and the factors which determine their rates. It turns out that this silicate is not a suitable host lattice for our purpose. The reasons which are responsible for this failure are interesting in itself and have a wider validity.

EXPERIMENTAL

Samples with composition $Na(Gd, Ce, Bi, Tb)SiO_4$ were prepared from high-purity starting materials. The orthorhombic phase was obtained as described in [4]. The tetragonal phase was prepared by firing a starting composition $4NaGdSiO_4 \cdot 1NaF$ [6-8] with about 50% excess of NaF at final temperatures of about 1000° C. The firing atmosphere was nitrogen with a few percent of hydrogen. Samples were checked by X-ray diffraction and turned out to be pure 0 or T modification. When Bi^{3+} was used as a sensitizer, the T modification was obtained without the use of NaF.

The optical measurements were performed as described before [9].

RESULTS AND DISCUSSION

All samples showed high total quantum efficiencies for ultraviolet excitation at temperatures between 4.2 K and 300 K. Usually the emission consists of contributions from several luminescent ions. They are discussed now in several paragraphs.
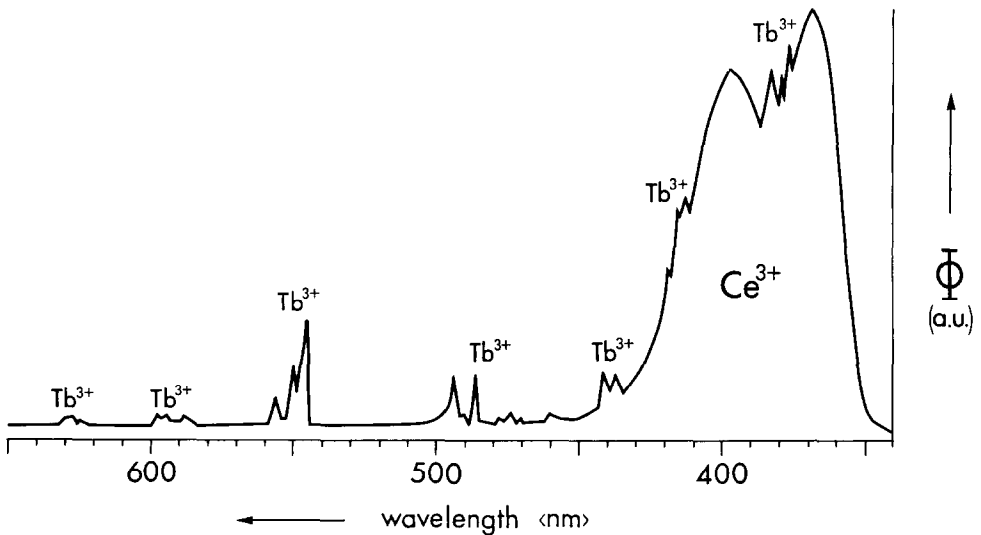

Fig. 1. Emission spectrum of $NaGdSiO_4 \cdot \frac{1}{4}NaF:Ce(1\%)$, $Tb(1\%)$ (tetragonal modification) at LHeT (4.2 K). Excitation is into the Ce^{3+} ion ($\lambda_{exc} = 320$ nm); Φ gives the spectral radiant power per constant wavelength interval in arbitrary units.

Ce^{3+}- and Tb^{3+}-codoped $NaGdSiO_4 \cdot \frac{1}{4} NaF$ (T modification)

Upon excitation into the Ce^{3+} ion at 4.2 K up to 300 K, we observed a dominating broad-band emission from Ce^{3+} and additional narrow-line emission from Tb^{3+}. At 4.2 K (LHeT) the Ce^{3+} emission shows a doublet character with maxima at 372 and 402 nm (see Fig. 1). This corresponds to the ground level splitting ($^2F_{7/2}$, $^2F_{5/2}$). The intensity ratio of the Ce^{3+} and Tb^{3+} emissions does not depend markedly on the excitation wavelength. The excitation spectra of Tb^{3+} show Ce^{3+} bands and Gd^{3+} lines, indicating $Ce^{3+} \rightarrow Tb^{3+}$ and $Gd^{3+} \rightarrow Tb^{3+}$ transfer. The latter one occurs via Gd^{3+} migration as has been described before [1-3]. The $Ce^{3+} \rightarrow Gd^{3+}$ ($\rightarrow Tb^{3+}$) transfer does not occur, since the Ce^{3+} emission is at too low an energy to overlap the Gd^{3+} absorption lines.

By measuring the Ce^{3+}/Tb^{3+} emission intensity ratio as a function of the Tb^{3+} concentration, the $Ce^{3+} \rightarrow Tb^{3+}$ transfer can be characterized further. We observed 100%, 90% and 50% Ce^{3+} emission for Tb^{3+} concentrations of 0, 1 and 5 at.%, respectively. Here the Ce^{3+} concentration is constant and low, viz. 1 at. %. These data can be fitted to $I(x=0) = I(x) \cdot (1-x)^N$ [9]. Here I represents the Ce^{3+} emission intensity ratio, x the Tb^{3+} concentration and N the number of sites over which $Ce^{3+} \rightarrow Tb^{3+}$ transfer occurs. The value of N is about 15.

Since the structure of $NaGdSiO_4 \cdot \frac{1}{4} NaF$ contains about 90 $\mathring{A}^3$ per Gd^{3+} ion [6-8], the relation $4/3 \pi R_c^3 = 90$ N ($\mathring{A}^3$) yields the critical transfer distance R_c. Its value is 7 $\mathring{A}$. For the case of a broad band emitter and a narrow line acceptor with favourable spectral overlap in the near UV, the value of R_c is calculated to be 6.5 $\mathring{A}$ [3]. This gives an excellent agreement between theory and experiment. Actually the spectral overlap is favourable indeed, since the Ce^{3+} emission overlaps the $^5D_3$ level of Tb^{3+} in its maximum, and the Tb^{3+} emission shows $^5D_3$ as well as $^5D_4$ emission.

The Ce^{3+} ion sensitizes the Tb^{3+} ion as efficiently as possible. The function $(1-x)^N$ predicts that nevertheless a high Tb^{3+} concentration (x ⩾ 0.2) is required to quench the Ce^{3+} emission down to a few percent.

Since no Gd^{3+} emission is observed, the $Gd^{3+} \rightarrow Tb^{3+}$ transfer is very efficient as usual [1-3]. However the $Ce^{3+} \rightarrow Gd^{3+}$ transfer is clearly impossible. It is interesting to analyze the Ce^{3+} excitation spectrum with bands at 320 nm (31,000 cm^{-1}), 274 nm (36,500 cm^{-1}) and 250 nm (40,000 cm^{-1}). These are the crystal-field components of the 5d level of the Ce^{3+} ion. In the case of eight coordination these are in cubic coordination expected to be t_2 and e, in sequence of decreasing energy. Assigning the 31,000 cm^{-1} band to the e component, and ~ 38,000 cm^{-1} to the t_2 component, the approximate cubic-crystal-field splitting is 7,000 cm^{-1} and the centre-of-gravity of the 5d level about 35,000 cm^{-1}. These values agree reasonably with those reported for other oxides [10].

For efficient $Ce^{3+} \rightarrow Gd^{3+}$ transfer the lowest crystal field component should be situated at 34,000 cm^{-1} or higher, so that, after relaxation, the emission overlaps the Gd^{3+} levels. This is here not the case. It is also clear that it is not in the first place the value of the crystal-field splitting which is responsible for the low position of the Ce^{3+}

emitting state in $NaGdSiO_4 \cdot \frac{1}{4} NaF$ but the covalency at the rare-earth site, which places the centre-of-gravity of the 5d state rather low.

This is probably a general situation for silicates, since Ce^{3+} emission in silicates is usually observed at such low energies [10,11]. Now we turn to the O modification with Ce^{3+}- and Tb^{3+}-dopants.

Ce^{3+}- and Tb^{3+}-codoped $NaGdSiO_4$ (O modification)

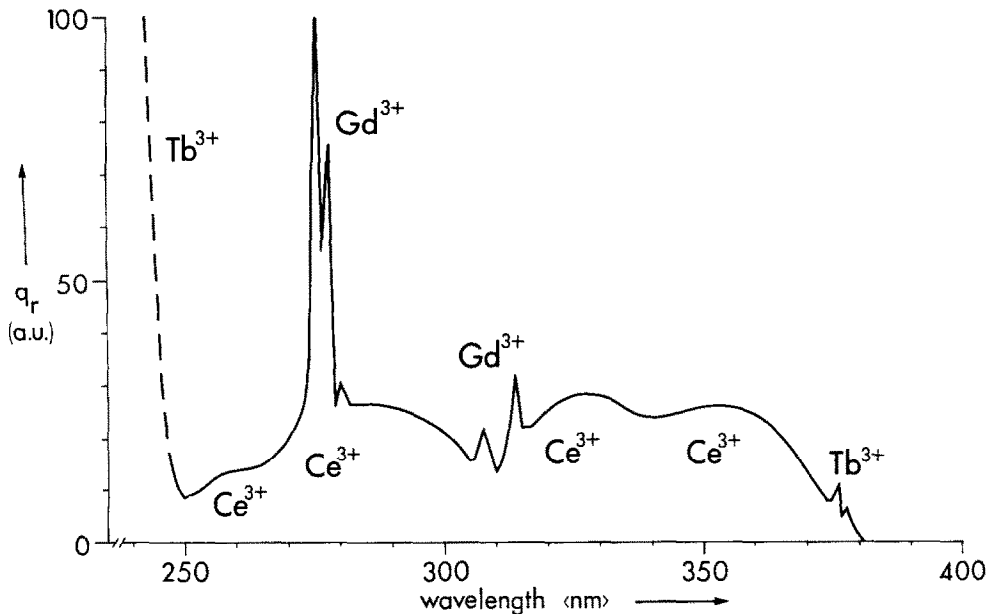The luminescence of the O modification shows differences in comparison with that of the T modification.

Fig. 2. Excitation spectrum of the Tb^{3+} $^5D_4$ emission ($\lambda_{em} \simeq 542$ nm) in $NaGdSiO_4$:Ce(1%), Tb(1%) (orthorombic modification) at LHeT; q_r gives the relative quantum output in arbitrary units.

In Fig. 2 we have drawn the excitation spectrum of the Tb^{3+} emission at LHeT. It is very complicated and consists of:
(i) transitions within the $4f^8$ configuration of Tb^{3+}, which will not be discussed further;
(ii) transitions on the Ce^{3+} ion (4f-5d) at about 350 nm (28,500 cm^{-1}), 325 nm (30,000 cm^{-1}), 290 nm (35,000 cm^{-1}) and 260 nm (39,000 cm^{-1}). These indicate $Ce^{3+} \rightarrow Tb^{3+}$ transfer. However, excitation into these bands yields mainly Ce^{3+} emission with maxima at 390 and 425 nm;
(iii) transitions within the $4f^7$ configuration of Gd^{3+}, indicating $Gd^{3+} \rightarrow Tb^{3+}$ transfer, as discussed above;

(iv) a strong band on the boundary of our instrument at about 240 nm (42,000 cm^{-1}). Excitation into this band yields only Tb^{3+} emission. It is ascribed to the lowest $4f^8 \rightarrow 4f^7 5d$ component on Tb^{3+}. It is situated about 12,500 cm^{-1} above the lowest $4f \rightarrow 5d$ transition of the Ce^{3+} ion, as is usually the case [12].

The excitation spectrum shows that it is more or less possible to excite into Gd^{3+} without losing all this energy completely to Ce^{3+}. It is interesting to see that Gd^{3+} excitation of a sample with 1 at.% Ce^{3+} and 1 at.% Tb^{3+} yields 90% Ce^{3+} emission and 10% ($^5D_3$ and $^5D_4$) Tb^{3+} emission, whereas Ce^{3+} excitation yields 95% Ce^{3+} emission and 5% ($^5D_4$) Tb^{3+} emission (Fig. 3).
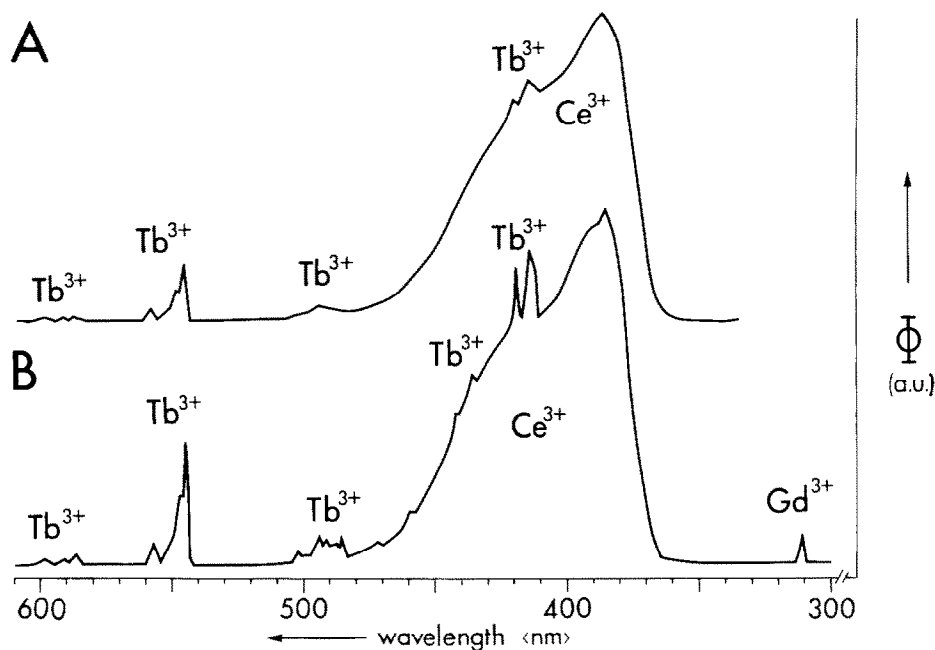

Fig. 3. Emission spectra of $NaGdSiO_4$:Ce(1%), Tb(1%) at LHeT upon excitation into A: the Ce^{3+} ion (λ_{exc} = 290 nm) and B: the Gd^{3+} ion (λ_{exc} = 275 nm).

This shows that Ce^{3+} transfers mainly to the Tb^{3+} $^5D_4$ level, whereas in the T modification the $^5D_3$ level was fed. This is a consequence of the lower-energy position of the Ce^{3+} emission band which now shows a larger overlap with the $^5D_4$ level. The Gd^{3+} excitation is mainly followed by a transfer to Ce^{3+}, but also seems to feed Tb^{3+} a little bit, via the $4f^8$ configuration, so that the $^5D_3$ emission is also observed. The data suggest that the $Gd^{3+} \rightarrow Ce^{3+}$ transfer rate is two orders of magnitude larger than the $Gd^{3+} \rightarrow Tb^{3+}$ transfer rate, in spite of the unfavourable spectral overlap in the former case (Fig. 2). However, the allowed character of the Ce^{3+} absorption transition can easily compensate for the poor spectral overlap [13].

The Ce^{3+} excitation bands can be analyzed as follows. The Ce^{3+} ion is now octahedrally coordinated, i.e. in the cubic approximation the level sequence will be t_2, e in sequence of increasing energy. The 28,500 and 30,000 cm^{-1} bands are probably the t_2 components as far as they can be observed. This yields for the t_2 level 29,500 cm^{-1}. For the e level we have then 37,000 cm^{-1}. The cubic-crystal-field splitting is then approximately 8,000 cm^{-1}, the centre-of-gravity of the 5d level 34,000 cm^{-1}.

In view of the accuracy of these data it is only possible to state that these values have approximately the same value in both modifications. In fact the octahedral and cubic crystal field splittings are of the same order of magnitude. Also the covalency is very similar. This places also the Ce^{3+} emission in the O modification at low energy. The fact that it is lower in the O than in the T modification is due to the reverse sign of the crystal field splitting which places t_2 lower in the octahedral coordination than e in the eight coordination.

Bi^{3+}- and Tb^{3+}- codoped $NaGdSiO_4$ (T modification)

It turns out that the lowest absorption band of the Bi^{3+} ion in $NaGdSiO_4$ is at high energy, viz. about 250 nm (40,000 cm^{-1}). Upon excitation into the Bi^{3+} ion at LHeT, we obtain an emission spectrum which consists mainly of a broad Bi^{3+} emission band with a maximum at about 405 nm on which we observe the characteristic $^5D_3$ and $^5D_4$ emission lines of Tb^{3+}. The Bi^{3+} to Tb^{3+} intensity ratio is about 10 : 1. The Stokes shift of the Bi^{3+} emission is large, viz. 18,000 cm^{-1}. The transfer from Bi^{3+} to Tb^{3+} is not efficient. The transfer efficiency equals that for Ce^{3+} to Tb^{3+} transfer.

At room temperature the Bi^{3+} emission is practically quenched. The excitation spectrum of the Tb^{3+} emission yields the following features:
(i) the characteristic Tb^{3+} lines within the $4f^8$ configuration;
(ii) the characteristic Gd^{3+} lines within the $4f^7$ configuration, indicating effective $Gd^{3+} \rightarrow Tb^{3+}$ transfer (see above);
(iii) the Bi^{3+} excitation band, which is weak due to the low transfer efficiency.

The excitation spectrum of the Bi^{3+} emission at LHeT shows only the Bi^{3+} excitation band. There is no $Bi^{3+} \rightarrow Gd^{3+}$ nor $Gd^{3+} \rightarrow Bi^{3+}$ transfer. Actually the Bi^{3+} and Gd^{3+} ions are completely disconnected (Fig. 4). This is due to the fact that the emitting Gd^{3+} level shows no relaxation after excitation, whereas the emitting Bi^{3+} level relaxes considerably. As a consequence the Gd^{3+} emission line does not overlap the Bi^{3+} absorption band, nor does the Bi^{3+} emission band overlap the Gd^{3+} absorption lines.

The larger Bi^{3+} relaxation, responsible for the absence of $Bi^{3+} \rightarrow Gd^{3+}$ transfer, is related to the amount of space available in the lattice [3,14]. In eight coordination such a large Stokes shift is not unexpected. It has, for example, also been observed for Bi^{3+} in $LaPO_4$ [15].
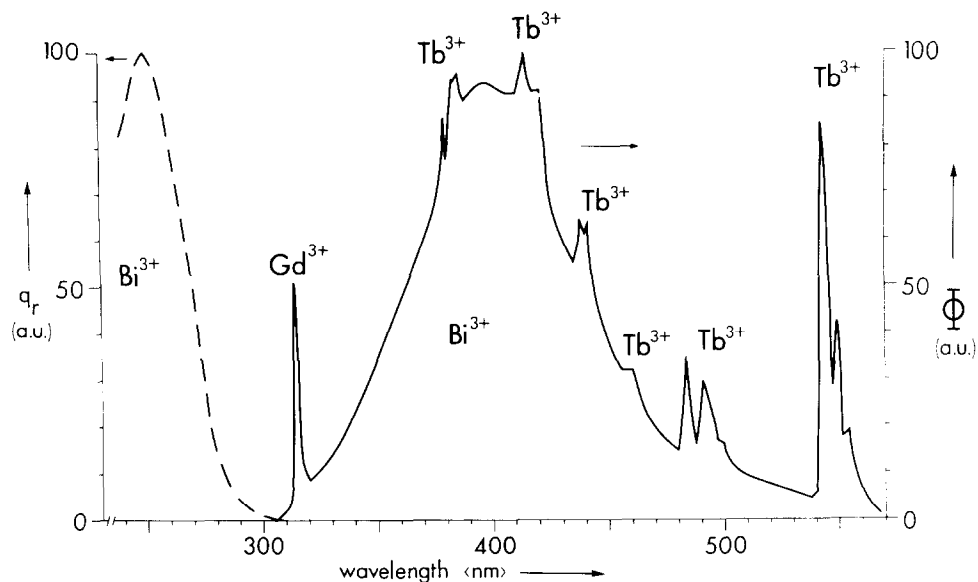
Fig. 4 Excitation spectrum (broken curve) of the Bi^{3+} $^1S_0 - {}^3P_{0,1}$ emission ($\lambda_{em} \simeq 350$ nm) and emission spectrum (solid curve) upon excitation into the Bi^{3+} ion ($\lambda_{exc} \simeq 250$ nm) at LHeT for $NaGdSiO_4$:Bi(1%), Tb(1%) (tetragonal modification).

CONCLUSIONS

We have unravelled the factors which influence the efficiency of sensitization of the Tb^{3+} luminescence in $NaGdSiO_4$.

ACKNOWLEDGEMENTS

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