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On the Luminescence of Rare-Earth Activated Bismuth Tungstates

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The luminescence properties of rare-earth activated bismuth tungstates with general formula $Bi_{2-x-y}La_xRE_yWO_6$ (RE = Pr, Sm, Eu, Tb, Dy, Er) are described. The quantum efficiency of the tungstate luminescence is low, even at 4.2 K. Energy transfer from the tungstate group to certain rare-earth ions can compete successfully with the nonradiative processes in the tungstate group, so that the total quantum efficiency is considerably increased. A lower limit for the value of the transfer probability is 10^8 sec^{-1}.

1. Introduction

Recently we reported on the luminescence properties of red-emitting bismuth tungstates, viz., Bi_2WO_6 and $Bi_{1.4}La_{0.6}WO_6$ (*1, 2*). The optical transitions involved were assigned to Bi^{3+}–W^{6+} charge-transfer transitions (see also Ref. (*3*)). We became interested in the luminescence of rare-earth ions in these compounds when we observed that the introduction of small amounts of Eu^{3+} in $Bi_{1.4}La_{0.6}WO_6$ results in a considerable amount of Eu^{3+} emission and, simultaneously, in an increase in the total quantum efficiency of the emission. In this paper we report on the luminescence properties of the bismuth tungstates $Bi_{2-x-y}La_xRE_yWO_6$ (RE = Pr, Sm, Eu, Tb, Dy, Er).

According to investigations by Watanabe *et al.* (*4–6*) the system $Bi_{2-x}La_xWO_6$ contains two solid-solution series on the bismuth-rich side, viz., one with Bi_2WO_6 structure in the region $0 \leqq x \leqq 0.2$ and one with strongly distorted La_2MoO_6 structure in the region $0.4 \leqq x \leqq 1.0$. The Bi_2WO_6 structure contains Bi_2O_2 layers and WO_4 layers consisting of corner-sharing tungstate octahedra (*7, 8*); the other structure, which has not been solved precisely, contains $(Bi,La)_2O_2$ layers and WO_4 layers consisting of WO_4 tetrahedra (*6*).

2. Experimental

Samples were prepared as described by Watanabe *et al.* (*4–6*). They were checked by X-ray diffraction analysis. The optical instrumentation is the same as in the previous paper (*1*). Quantum efficiencies were determined by comparison with a red-emitting standard phosphor, viz., NBS 1030, $(MgO)_x(As_2O_5)_y$–Mn (*9*).

3. Results and Discussion

3.1. General

As reported before (*1, 2*) the unactivated Bi_2WO_6 and $Bi_{1.4}La_{0.6}WO_6$ show a red luminescence below 100 K under long-wavelength ultraviolet excitation. The corresponding emission and excitation spectra consist of a broad band. The following activators have been introduced into $Bi_{1.4}$

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$La_{0.6}WO_6$: Pr, Sm, Eu, Tb, Dy, Er. Under certain circumstances, to be specified below, the characteristic emission of these ions is observed. It consists of sharp lines. The excitation spectra now also contain sharp lines due to direct excitation of the rare-earth ions. Taking Eu^{3+} as an example, we give now a general discussion of the spectra concerned.

Figures 1 and 2 present the emission and excitation spectra of the luminescence at 4.2 K of Bi_2WO_6–Eu and $Bi_{1.4}La_{0.6}WO_6$–Eu, respectively. The excitation spectra consist of a broad band and sharp lines. The former corresponds to host-lattice absorption, the latter to Eu^{3+} absorption in the well-known $4f^6$ energy levels. Excitation into the lines gives only line emission corresponding to the $^5D_0$–^7F_J transitions. The $^5D_1$ emission has been observed only for low Eu^{3+} concentrations (e.g., $Bi_{1.4}La_{0.59}Eu_{0.01}WO_6$) and under excitation into the Eu^{3+} excitation lines. Under excitation into the host lattice only $^5D_0$ emission is observed, together with broad-band host-lattice emission. The ratio between the two emissions depends on the Eu^{3+} concentration (see Table I). These values indicate a considerable amount of energy transfer from the host lattice to the activator. For simplicity the broad emission and excitation bands will be referred to as tungstate bands, although the Bi^{3+} ion plays an important role in the transitions involved. The

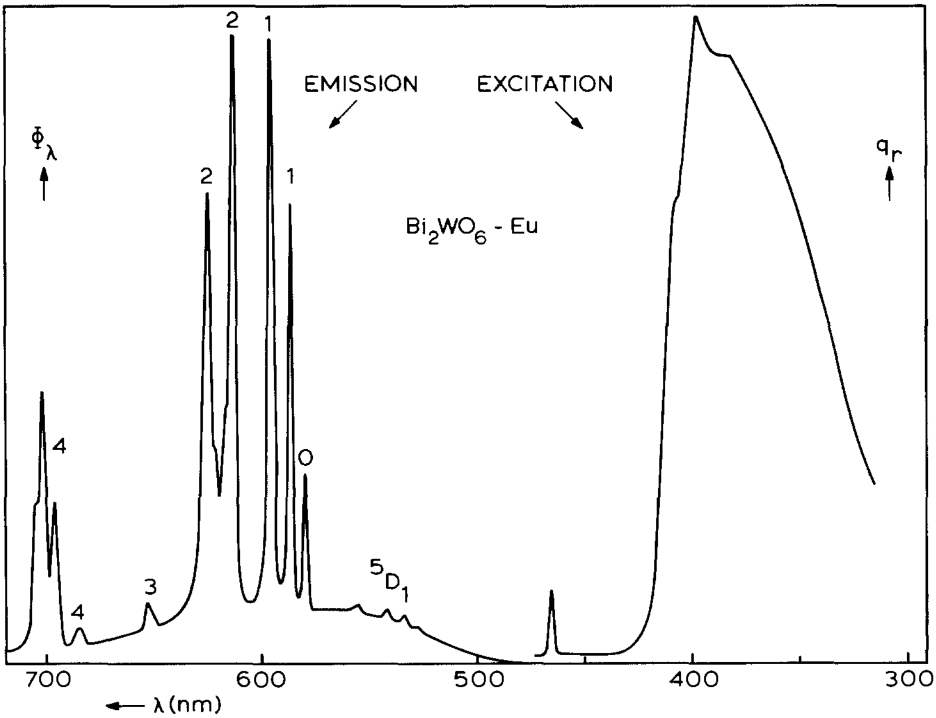

FIG. 1. Emission and excitation spectra of the luminescence of $Bi_{1.97}Eu_{0.03}WO_6$ at 4.2 K. The emission spectrum is for 366 nm (host lattice) excitation. The excitation spectrum is monitored for ~615 nm emission. Φ_λ gives the spectral radiant power per constant wavelength interval and q_r is the quantum output, both in arbitrary units. The lines in the excitation spectrum correspond to Eu^{3+} absorption, the broad band to host-lattice absorption. The emission spectrum shows a broad band (tungstate emission), weak Eu^{3+} lines from the $^5D_1$ level (marked $^5D_1$), and Eu^{3+} lines from the $^5D_0$ level. The latter are marked by the J value of the terminating level ^7F_J.

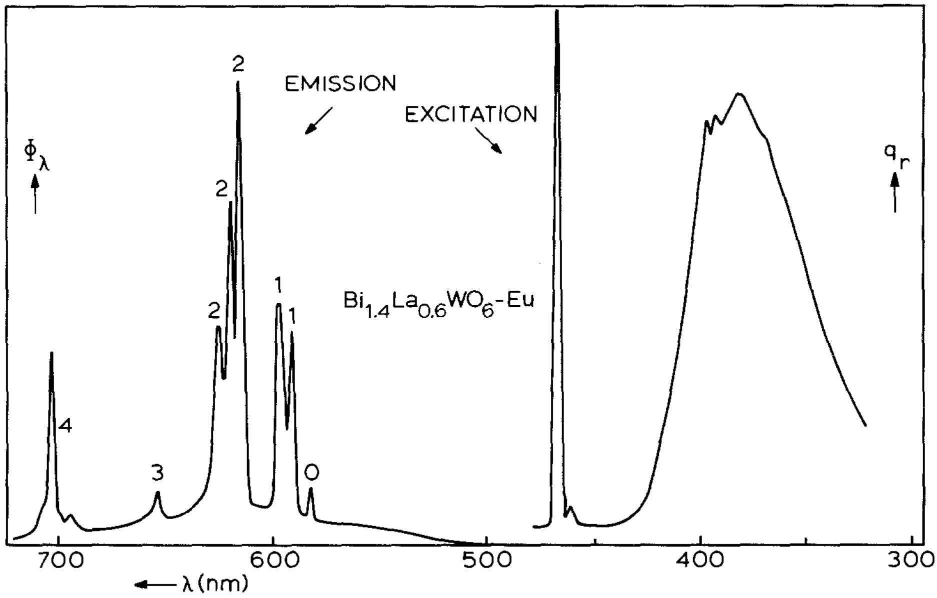

FIG. 2. Emission and excitation spectra of the luminescence of $Bi_{1.4}La_{0.57}Eu_{0.03}WO_6$ at 4.2 K. For further details, see Fig. 1. Note the absence of $^5D_1$ emission.

narrow rare-earth lines will only be assigned here as far as appropriate for the systems under discussion. This assignment is standard and does not offer any difficulties.

Let us now compare in more detail the Eu^{3+} emission of Bi_2WO_6–Eu and $Bi_{1.4}La_{0.6}WO_6$–Eu in order to determine the influence of the crystal structure change on the Eu^{3+} emission. Since the structure of $Bi_{1.4}La_{0.6}WO_6$ is not known in detail, we start from the undistorted crystal structures. In the undistorted Bi_2WO_6 structure the Bi^{3+} ion has C_{4v} symmetry, and in the undistorted La_2MoO_6 structure of $Bi_{1.4}La_{0.6}WO_6$, C_{2v} symmetry. In Table II the number of lines has been summarized. The theoretical values are compared with the experimental values, obtained by using high resolving power on the apparatus (i.e., ≃ 1 nm).

A study of Table II together with Figs. 1 and 2 leads to the following conclusions:

—The difference between the crystal

TABLE I

QUANTUM EFFICIENCIES (%) AT 4.2 K FOR 366 nm EXCITATION FOR SAMPLES $Bi_{2-x-y}La_xRE_yWO_6$

	WO_4		WO_4	Eu		WO_4	*RE*
Bi_2WO_6	25	$Bi_{1.4}La_{0.59}Eu_{0.01}WO_6$	8.5	3.5	$Bi_{1.4}La_{0.57}Pr_{0.03}WO_6$	4	7
$Bi_{1.4}La_{0.6}WO_6$	10	$Bi_{1.4}La_{0.57}Eu_{0.03}WO_6$	8	9	$Bi_{1.4}La_{0.57}Sm_{0.03}WO_6$	8	9
$BiLaWO_6$	10	$Bi_{1.4}La_{0.5}Eu_{0.1}WO_6$	5	30	$Bi_{1.4}La_{0.57}Tb_{0.03}WO_6$	10	0
$BiYWO_6$	~0	$Bi_{1.4}La_{0.3}Eu_{0.3}WO_6$	0	60	$Bi_{1.4}La_{0.57}Dy_{0.03}WO_6$	10	0
		$Bi_{1.4}Eu_{0.6}WO_6$	0	50	$Bi_{1.4}La_{0.57}Er_{0.03}WO_6$	6	2.5
		$BiEuWO_6$	0	20			
		$Bi_{1.97}Eu_{0.03}WO_6$	18	15			

TABLE II
NUMBER OF LINES IN THE Eu^{3+} $^5D_0$–^7F_J EMISSION TRANSITIONS

	Bi_2WO_6		$Bi_{1.4}La_{0.6}WO_6$	
	Theory (C_{4v})	Experimental	Theory (C_{2v})	Experimental
$^5D_0$–$^7F_0$	1	1	1	1
$^5D_0$–$^7F_1$	2	2	3	3
$^5D_0$–$^7F_2$	2	4	4	4

See also text.

structures of Bi_2WO_6 and $Bi_{1.4}La_{0.6}WO_6$ is also apparent from the Eu^{3+} emissions.

—The Bi_2WO_6 structure seems to be more distorted from the ideal structure than that of $Bi_{1.4}La_{0.6}WO_6$. This may be due to the presence of the La^{3+} ions which tend to a more symmetrical coordination than the Bi^{3+} ions. Watanabe *et al.* (*6*) have used a similar argument.

If the temperature is increased, the following changes occur. Upon excitation into the host lattice, the total emission is quenched in a temperature region around 100 K. Note that also the line emission is quenched. Upon excitation into the lines, the characteristic line emission is observed up to room temperature. In the case of Eu^{3+} practically no temperature quenching is observed under line excitation. In the case of the other activators some quenching occurs, but not as drastic and complete as under host-lattice excitation.

For $Bi_{1.4}La_{0.5}Eu_{0.1}WO_6$ we measured the decay time of the Eu^{3+} emission under host-lattice excitation. At 4.2 K and in the quenching region (120 K) its value is 600 μsec. This excludes nonradiative decay in the Eu^{3+} center itself. We will discuss the processes responsible for the luminescence properties of the present materials in more detail in the next section, using the system $Bi_{1.4}La_{0.6-y}Eu_yWO_6$ as an example.

3.2. The System $Bi_{1.4}La_{0.6-y}Eu_yWO_6$

As described above, the luminescence property which depends strongly on the Eu^{3+} concentration y is the quantum efficiency (q) of the emission (see Table I). For $y = 0$, q is rather low (10%). Note that for increasing values of y, the total value of q increases strongly (up to 60% for $y = 0.3$). The subsequent decrease is due to concentration quenching of the Eu^{3+} emission and as such is trivial. The strong increase, however, is remarkable.

In view of the large Stokes shift of the host-lattice emission, the tungstate excited state cannot be mobile at 4.2 K (*10*). The only possibility of explaining the increase in q is to assume that the probability for energy transfer from the tungstate group to the Eu^{3+} activator exceeds the probability for radiative and, especially, nonradiative decay in the tungstate group. We will now show that a calculation on the basis of this assumption explains our results satisfactorily.

Consider a composition $(Bi,La,Eu)_2WO_6$ and assume that the Eu^{3+} ions are distributed at random among the sublattice of the Bi^{3+} and La^{3+} ions. Let the probability of finding a Eu^{3+} ion on such a site be z (i.e., $z = \frac{1}{2}y$), so that the probability of finding either Bi^{3+} or La^{3+} on that site is $(1 - z)$. Consider an excited tungstate group in this composition. The probability for tungstate emission K_W is $(1 - z)^n \cdot q_W$ and the probability for europium emission K_{Eu} is $\{1 - (1 - z)^n\}$. Here, n is the number of (Bi,La) sites around the tungstate group which lie within the critical distance for energy transfer from the tungstate group to the Eu^{3+} ion. If none of these sites is occupied by Eu^{3+}, either radiative or nonradiative decay within the tungstate group will occur (q_W is the quantum efficiency of the luminescence of such a tungstate group). If one or more of these sites is occupied by Eu^{3+} ions, energy transfer to Eu^{3+} occurs, followed by Eu^{3+} emission. For $z = 0$, $K_{Eu} = 0$ and $K_W = q_W = 0.1$ (see Table I). For increasing values of z, the value of K_W decreases and that of K_{Eu} increases.

A typical value for the radiative decay of an excited tungstate group surrounded by $6s^2$ ions is about 10^6 sec^{-1} (*3*). In view of $q_W = 0.1$, the nonradiative decay rate at 4.2 K should be about 10^7 sec^{-1}. For our model to work, the transfer rate should be 10^8 sec^{-1} or higher. Only very few transfer rates of this type are known, but 10^8 sec^{-1} does not seem to be unreasonably high (*10*).

We could fit our data to this model reasonably well using $n = 8$. This means that the critical transfer distance exceeds the shortest (Bi,La)–W distance somewhat and is about 5 Å. Figure 3 shows a comparison between experiment and model. In view of the error in the quantum efficiencies the agreement is good.

The model did not take into account concentration quenching of the Eu^{3+} luminescence. This occurs above about $y = 0.4$ (see Table I and Fig. 3). For this purpose we also considered $BiEuWO_6$ as the only possibility of increasing the Eu^{3+} concentration above $y = 0.6$.

If the temperature increases, the only rate which will also increase considerably is the tungstate nonradiative decay rate. This follows from the low-temperature quenching of unactivated $Bi_{1.4}La_{0.6}WO_6$. This also explains the temperature behavior of the Eu^{3+}-activated samples. As soon as the nonradiative decay rate can compete with the transfer rate, the Eu^{3+} emission intensity will drop with temperature under host-lattice excitation. Excitation energy which has reached the Eu^{3+} ions will not be back-transferred, so that the decay time of the Eu^{3+} emission is temperature independent. Excitation into the Eu^{3+} ions does not lead to temperature-dependent processes under room temperature.

The tungstate emission peaks at about 15,600 cm^{-1}, which is below the $^5D_0$ level of Eu^{3+} (17,300 cm^{-1}). Transfer is only possible to the $^5D_0$ level and not to the $^5D_1$ level (19,000 cm^{-1}) in view of the spectral overlap. This agrees with the experimental observations. Back-transfer from $^5D_0$ to the host-lattice excited states (ultraviolet) is clearly impossible.

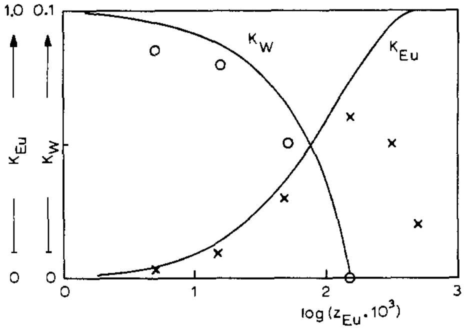

FIG. 3. Drawn lines give K_W and K_{Eu} as a function of the europium concentration according to the formulas in the text. $q_W = 0.1$ and $n = 8$. Circles give the experimental quantum efficiencies of the tungstate emission, crosses those of the europium emission. The discrepancy between K_{Eu} and the crosses for high z values is due to concentration quenching of the Eu^{3+} emission. Temperature is 4.2 K.

If P_{tr} is the transfer probability, and P_{nr} and P_r are the probabilities for nonradiative and radiative decay of the tungstate group, respectively, the situation at 4.2 K is characterized by $P_{tr} > P_{nr} > P_r$, and that at 300 K by $P_{nr} > P_{tr} > P_r$. This makes it possible for the Eu^{3+} activator to compete successfully with the nonradiative decay in the tungstate group at 4.2 K. Such a case has not been described before for rare-earth activated tungstates and related compounds as far as we are aware.

3.3. Other Rare-Earth Ion Activators

To compare the results for the Eu^{3+} activated system with those for other rare-earth ion activators, we investigated compositions $Bi_{1.4}La_{0.57}RE_{0.03}WO_6$ (RE = Pr, Sm, Eu, Tb, Dy, Er). Quantum efficiencies are given in Table I.

The Tb^{3+} and Dy^{3+} activators do not interact with the host lattice; i.e., excitation into the host lattice gives tungstate emission with the quantum efficiency of the unactivated host lattice and no rare-earth emission. Excitation into the narrow rare-earth absorption lines gives the characteristic rare-earth emission. An explanation for the absence of energy transfer from the tungstate group to Tb^{3+} or Dy^{3+} is straightforward: in the spectral area of the tungstate emission these ions have no energy levels available, so that energy transfer is impossible.

For Sm^{3+} the results of the quantum efficiency measurements are similar to those of Eu^{3+}. In fact the ${}^4G_{5/2}$ emitting level is situated at about the same height as the ${}^5D_0$ level of the Eu^{3+} ion. For Pr^{3+} the transfer probability seems to be somewhat larger than that for Eu^{3+} (see Table I). The ${}^1D_2$ level of Pr^{3+} lies a little closer to the tungstate emission maximum than the ${}^5D_0$ level. This results in a higher transfer probability, although it need not be the only reason. When the Pr^{3+} ion was excited directly, we observed a considerable amount (about 10%) of green Pr^{3+} emission from the ${}^3P_0$ level. This is not the case for host-lattice excitation. This shows that the transfer occurs solely via the ${}^1D_2$ level as is to be expected from the resonance condition for transfer.

The higher transfer probability in the case of Pr^{3+} in comparison with that of Eu^{3+} also becomes clear from the fact that even at room temperature it is possible to excite the Pr^{3+} emission (weakly) in the host-lattice excitation band, which is impossible in the case of Eu^{3+}. This higher transfer probability is not reflected in the sum of the quantum efficiencies of tungstate and rare-earth emission at 4.2 K. For Eu^{3+} and Sm^{3+} this amounts to 17%, for Pr^{3+} only 11%, whereas a value higher than 17% is expected. This may be due to nonradiative processes in the Pr^{3+} ion itself.

For this reason we also tried Er^{3+} as an activator. This ion has several energy levels near the tungstate emission maximum, so that energy transfer is possible. However, nonradiative processes in Er^{3+} itself are rather probable, since the energy levels of this ion are rather close and the host lattice involved has large phonons available (*6*). The experiment shows that transfer from tungstate to Er^{3+} occurs, but that considerable nonradiative losses occur in the Er^{3+} ion: the quantum efficiency of the tungstate emission decreases from 10 to 6%, but that of the Er^{3+} emission is only 2.5%, whereas it should be some 10% in view of the value observed for Eu^{3+} and Sm^{3+} (see Table I).

We conclude that only the Eu^{3+} and Sm^{3+} ions are able to compete successfully with the nonradiative losses in the host lattice. The Pr^{3+} and Er^{3+} ions do so in principle, but they show internal nonradiative losses.

3.4. Bi_2WO_6–Eu

Since Bi_2WO_6–Eu is only able to accept low concentrations of rare-earth ions, it was not investigated in detail and we restricted ourselves to a study of $Bi_{1.97}Eu_{0.03}WO_6$. From the resulting quantum efficiencies we can only conclude that the situation is not strikingly different from that in the case of $Bi_{1.4}La_{0.57}Eu_{0.03}WO_6$ (see Table I). However, q_W is considerably higher in the case of Bi_2WO_6, viz., 25%. This has been ascribed to the smaller Stokes shift (*1*). The total quantum efficiency increases upon the introduction of Eu^{3+}, but less outspoken than in the case of $Bi_{1.4}La_{0.57}Eu_{0.03}WO_6$. Using $q_W = 0.25$ and $n = 10$, our formulas give $K_W = 0.21$ and $K_{Eu} = 0.15$ to be compared with the experimental values of 0.18 and 0.15, respectively. Although the reliability of these values is low due to the lack of data, the agreement is satisfactory.

The emission maximum of Bi_2WO_6 is situated at energies higher than that of $Bi_{1.4}La_{0.6}WO_6$ (*1*), viz., 16,700 cm^{-1} vs

15,600 cm^{-1}, respectively. This improves the spectral overlap with the Eu^{3+} absorption lines. The larger transfer probability becomes apparent from the higher value of n (larger critical distance for energy transfer) and the observation of $^5D_1$ emission under host-lattice excitation (see Fig. 1). The latter observation indicates that the energy transfer occurs also via the $^5D_1$ level.

3.5. Experiments with $BiLaWO_6$ and $BiYWO_6$

Experiments with $BiLaWO_6$ gave results comparable with those obtained for materials based on $Bi_{1.4}La_{0.6}WO_6$. The total quantum efficiencies are somewhat lower in compositions based on $BiLaWO_6$, making the results less reliable. Both host compositions have the same crystal structure (*6*). The results with $BiYWO_6$ are different insofar that this composition did not luminesce at all, so that here we have the situation $P_{nr} \gg P_r$. Obviously the presence of the yttrium ions increases the probability of nonradiative decay in the tungstate group. Even then the Eu^{3+} ions can trap some of the excitation energy; for the composition $BiY_{0.97}Eu_{0.03}WO_6$ we found the quantum efficiency of the Eu^{3+} luminescence at 4.2 K to be about 3%. This is considerably less than for the corresponding lanthanum composition, but also shows that P_{tr} cannot be very much smaller than P_{nr}.

4. Conclusion

The most important result of this study is the fact that it appeared possible to convert the radiationless losses of the tungstate group into radiative emission by the introduction of suitable rare-earth ions. This possibility is restricted to low temperatures due to the strong temperature dependence of radiationless processes. Until now rare-earth activated tungstates (and vanadates, niobates, etc.) have only been investigated if radiationless processes in the tungstate group could be neglected. Examples are YVO_4, $YNbO_4$, and Y_2WO_6 (*3, 10, 11*). Especially in the case of $Bi_{1.4}La_{0.6}WO_6$ the radiationless processes dominate over the radiative ones. The probability for energy transfer to the rare-earth ions has a lower limit of 10^8 sec^{-1}.

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