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Electron transfer between Eu and Tb in complex fluorides

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Abstract

Europium (II) and europium (III) have been observed in $MMgF_4$:*x*Eu, *y*Tb (M = Ca, Sr, Ba) phosphors using their typical photoluminescence spectra when are synthesized in Ar or an Ar/H_2 stream. The valence state of Eu is influenced by terbium. It is notable that the intensities of the electron spin resonance peaks corresponding to Eu^{2+} change in a regular way when terbium ions are incorporated which can be explained by an electron transfer mechanism.

Keywords: Electron transfer; Phosphors; Europium; Terbium

1. Introduction

Electron transfer is not a new concept, but only in recent years has it been used to describe the valency change process of the two conjugate electronic configurations of rare earth ions. It is well known that the most common valence state of rare earth ions is the trivalent one. Some ions are inclined to exist in abnormal valency, such as Sm^{2+}, Eu^{2+}, Yb^{2+} and Ce^{4+}, Pr^{4+}, Tb^{4+}. They all have a stable electronic configuration. After studying these ions in detail, we advanced a new electron transfer theory [1]: the two conjugate electronic configurations tend to exchange an electron in order to reach a more stable configuration. For example:

$Ce^{3+}(1) + Eu^{3+}(6) \rightarrow Ce^{4+}(0) + Eu^{2+}(7)$
$Eu^{3+}(6) + Tb^{3+}(8) \rightarrow Eu^{2+}(7) + Tb^{4+}(7)$
$Ce^{3+}(1) + Yb^{3+}(13) \rightarrow Ce^{4+}(0) + Yb^{2+}(14)$
(numerals in brackets are the 4f electron numbers).

Here, the two conjugate electronic configuration ions refer to those whose plus or subtraction of 4f electron number is seven or a multiple of seven. Besides the three electron transfer processes as mentioned above, other possible processes are given below:

$Tb^{3+}(8) + Yb^{3+}(13) \rightarrow Tb^{3+}(7) + Yb^{2+}(14)$
$Pr^{3+}(2) + Tm^{3+}(12) \rightarrow Pr^{4+}(1) + Tm^{2+}(13)$
$Pr^{3+}(2) + Sm^{3+}(5) \rightarrow Pr^{4+}(1) + Sm^{2+}(6)$
$Dy^{3+}(9) + Sm^{3+}(5) \rightarrow Dy^{4+}(8) + Sm^{2+}(6)$

However, there are few references prove these. So far, only a few cases, Ce–Eu in $LaPO_4$ [2] and Eu–Tb in Y_2O_2S [3], has electron transfer been reported. In this paper, an electron transfer reaction between Eu and Tb is reported in $MMgF_4$ matrices, which can proceed in two opposite directions.

2. Experimental

EuF_3 and TbF_3 were prepared with high-purity rare-earth oxides (99.99%). MF_2 (M = Ca, Sr, Ba) is of analysis purity. The starting materials are mixed in different mole ratios and grounded, then by a high-temperature solid state reaction $MMgF_4$:*x*Eu, *y*Tb phosphors are synthesized in a stream of Ar/H_2 (20:1) or Ar (0.6 l min^{-1}).

X-ray powder diffraction analysis was carried out with a Rigaku Denki 2028 D/max-IIB diffractometer using CuKα ($\gamma = 0.1542$ nm) radiation to check the samples for single phase [4,5]. The excitation and emission spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The electron spin resonance (ESR) spectra were obtained using an X-band spectrometer (JEOL model JES-FE-3AX), the resonant frequency of its cavity is 9.467 GHz.

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3. Results and discussion

3.1. Electron transfer phenomena

$MMgF_4$:1%Eu, y%Tb (y = 0, 0.1, 0.2, 0.4) and $MMgF_4$:x%Eu, 0.2%Tb (x = 0, 0.2, 0.5, 1.0) phosphors were synthesized. The photoluminescence spectra of the samples are as follows:

(1) In $MMgF_4$:1%Eu, a strong emission spectrum at 572.8 nm was observed when it is excited by 310.0 nm and 527.3 nm, which is proven to be due to Eu^{3+} (Fig. 1). The emission line is not influenced by matrix composition. A Eu^{2+} broad-band emission was also found with its maximum at about 430 nm. As can be seen in Fig. 2, the excitation and emission spectra of Eu^{2+} show a blue shift with the alteration from Ca to Sr and Ba which is caused by the rising of the 4f5d energy level bottom.

The excitation and emission spectra of $MMgF_4$:0.2%Tb are shown in Fig. 3. The typical line spectrum at 542.8 nm belongs to Tb^{3+}.

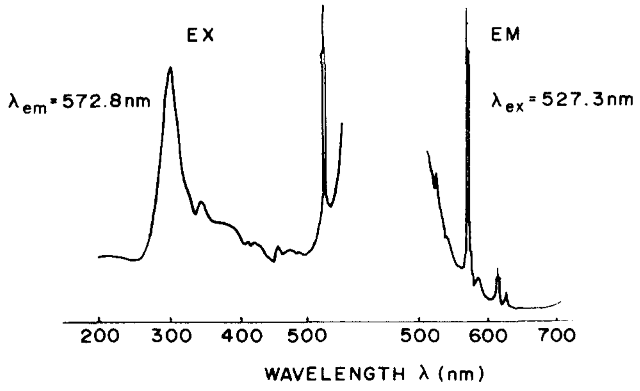

Fig. 1. Photoluminescence excitation (EX) and emission (EM) spectra of Eu^{3+} in $MMgF_4$:1%Eu (M = Ca, Sr, Ba).

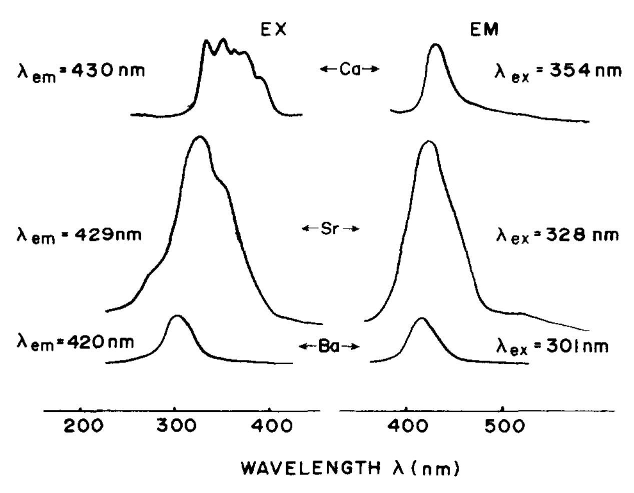

Fig. 2. Photoluminescence excitation (EX) and emission (EM) spectra of Eu^{2+} in $MMgF_4$:1%Eu (M = Ca, Sr, Ba).

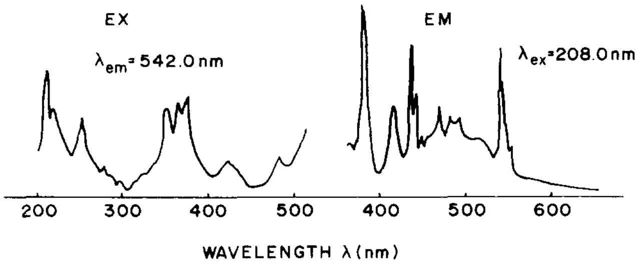

Fig. 3. Photoluminescence excitation (EX) and emission (EM) spectra of Tb^{3+} in $MMgF_4$:0.2%Tb (M = Ca, Sr, Ba).

In summary, europium exists in both the trivalent and divalent state in this system, while terbium is trivalent.

(2) When Eu and Tb are incorporated, their spectral structures are not altered, neither are their wavelengths. But, their intensities change in a systematic manner.

The intensity of the photoluminescence of Eu^{3+} in $MMgF_4$:1%Eu, y%Tb which were synthesized in a Ar/H_2 stream decreases as the concentration of terbium increases. On the contrary, that of Eu^{2+} increases. In $MMgF_4$:x%Eu, 0.2%Tb, the 542.8 nm emission peak of Tb^{3+} also decreases as the concentration of Eu^{3+} increases. These phenomena may be explained by the electron transfer mechanism. That is $Eu^{3+}(6) + Tb^{3+}(8) \rightarrow Eu^{2+}(7) + Tb^{4+}(7)$, so both Eu and Tb are driven towards their stable electronic configurations. If this is so, the ESR signals corresponding to Eu^{2+} will be increased.

But samples of $CaMgF_4$ and $BaMgF_4$ which are synthesized in an Ar stream give the opposite result. When Tb^{3+} is incorporated, the emissions of Eu^{3+} are increased, but that of Eu^{2+} decreases as the concentration of Tb increases, while that of Tb^{3+} increases when europium is incorporated. The following may be another process which interprets it: $Eu^{2+}(7) + Tb^{4+}(7) \rightarrow Eu^{3+}(6) + Tb^{3+}(8)$.

In order to investigate further whether the electron transfer phenomenon exists, the ESR spectra of $MMgF_4$:1%Eu, y%Tb samples were obtained.

3.2. Evidence of electron transfer phenomena

Since there is no signal of Eu^{3+} at room temperature, the ESR peak intensities will reflect the concentration of Eu^{2+}.

The results given by the ESR spectra are in agreement with those from the fluorescence spectra. In $MMgF_4$:1%Eu, y%Tb which was synthesized in Ar/H_2 stream, the ESR peak intensities corresponding to Eu^{2+} increase as the concentration of terbium increases, as well as that in $SrMgF_4$:1%Eu, y%Tb which were synthesized in the Ar stream. Fig. 4 shows this example.

While the ESR peak intensities of Eu^{2+} in $BaMgF_4$ and $CaMgF_4$ which were synthesized in the Ar stream

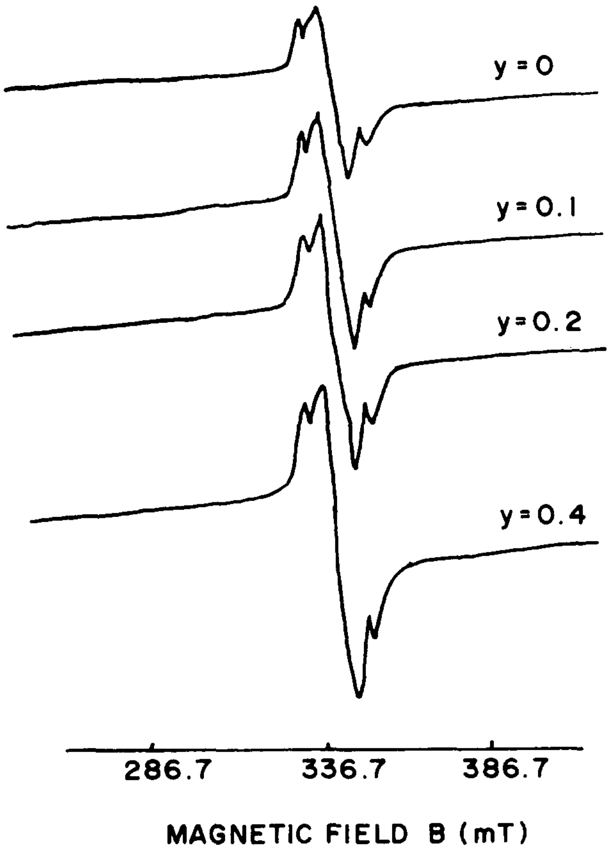

Fig. 4. ESR spectra of Eu^{2}+ in SrMgF$_4$:1%Eu, y%Tb synthesized in Ar stream.

decrease as the concentration of terbium increases. The ESR spectra of Eu^{2+} in BaMgF$_4$:1%Eu, y%Tb are given in Fig. 5.

Since the incorporation of terbium directly influences the concentration of Eu^{2+}, the electron transfer process in these matrices is demonstrated.

3.3. *Explanation of electron transfer phenomena*

The main result of these experiments is that two different electron transfer processes are obtained. The electron transfer process of $Eu^{3+} + Tb^{3+} \rightarrow Eu^{2+} + Tb^{4+}$ can be easily understood as both Eu^{2+}(4f^7) and Tb^{4+}(4f^7) are transformed into their stable configuration. But the process of $Eu^{2+} + Tb^{4+} \rightarrow Eu^{3+} + Tb^{3+}$ is not the same. There, the electron transfer process may exist as an equilibrium in a solid state reaction. The more important factors which decide the direction in which the equilibrium is shifted are the amount of O$_2$ on the surface of the phosphors and matrices, the stability of Eu^{2+}.

Evidence was presented in Ref. [5] that Eu^{3+}, Tb^{3+} and Eu^{2+} ions in the MMgF$_4$ lattices tend to substitute for M^{2+} ions due to charge compensation and ionic radii considerations. In the MMgF$_4$ lattice, the M^{2+} ions and Mg^{2+} ions are surrounded by eight and six

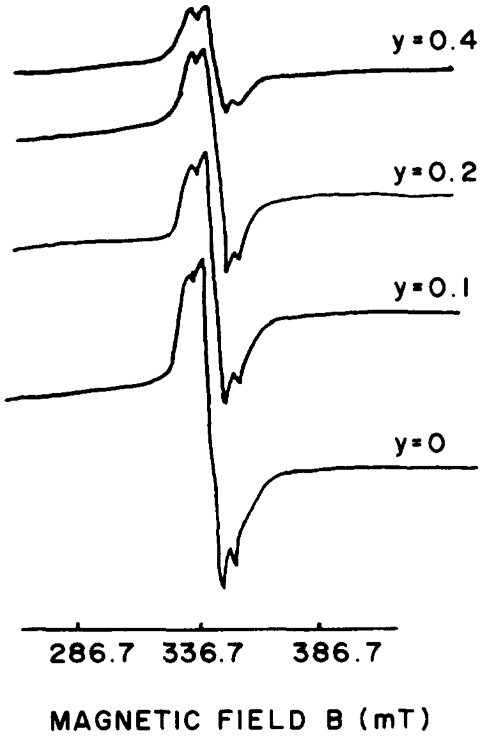

Fig. 5. ESR spectra of Eu^{2+} in BaMgF$_4$:1%Eu, y%Tb synthesized in Ar stream.

F$^-$ ions respectively. The ionic radii from Ref. [6] are: $R_{Ca}{}^{2+} = 112$ pm, $R_{Sr}{}^{2+} = 126$ pm, $R_{Ba}{}^{2+} = 142$ pm and $R_{Eu}{}^{2+} = 125$ pm (their coordination numbers are all eight). Therefore the order of stability for Eu^{2+} is more stable in SrMgF$_4$. So the electron transfer process can be $Eu^{3+} + Tb^{3+} \rightarrow Eu^{2+} + Tb^{4+}$ in SrMgF$_4$ phosphors either in the Ar or Ar/H$_2$ stream. There we consider Tb^{4+} substituting for the Mg^{2+} ion for $R_{Mg}{}^{2+} = 80$ pm, $R_{Tb}{}^{4+} = 76$ pm (CN = 6).

In CaMgF$_4$ and BaMgF$_4$, the stability of Eu^{2+} is smaller. So a small amount of O$_2$ in the Ar stream on the surface oxidizes the trivalent terbium to the tetravalent state. In other words, it causes the equilibrium to shift in the Eu^{3+} direction. However when the phosphors were synthesized in the Ar/H$_2$ stream, the oxidizing process of Tb^{3+} can be controlled, the process $Eu^{3+} + Tb^{3+} \rightarrow Eu^{2+} + Tb^{4+}$ predominates.

In summary, the electron transfer process exists as an equilibrium in the solid state reaction. If O$_2$ can be taken from the reaction system, and the matrices are reasonably chosen, the electron transfer process can exist in most matrices.

4. Conclusion

In order to prove the possibility of electron transfer between the two conjugate configurations, Eu^{3+} and Tb^{3+}, we chose the MMgF$_4$ matrices for their stability of Eu^{2+}, and then detected the concentration change of Eu^{2+} by their ESR spectra. In a different reaction stream, $MMgF_4$:xEu, yTb phosphors were synthesized, and two opposite electron transfer processes were obtained:

$$Eu^{3+}(6)+Tb^{3+}(8)\rightarrow Eu^{2+}(7)+Tb^{4+}(7)$$
$$Eu^{2+}(7)+Tb^{4+}(7)\rightarrow Eu^{3+}(6)+Tb^{3+}(8).$$

In the solid state reaction, this process exists as equilibrium.

Acknowledgement

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