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Photoluminescence of Eu^{3+}-activated $GdTaO_4$ with both M type and M′ type structures

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A series of Eu^{3+} doped M and M′ type gadolinium orthotantalate $Gd_{1-x}Eu_xTaO_4$ ($x = 0$–0.20) have been synthesized by high temperature solid state reaction. The emission and excitation spectra for M and M′ type gadolinium orthotantalate are studied in detail. The structural difference between M and M′ type structure obviously influences their luminescence properties. The main excitation bands in M′ type $Gd_{1-x}Eu_xTaO_4$ shift to shorter wavelength because of a shorter distance of Ta-O in comparison with M type. The strong evidence from excitation spectra, emission spectra and diffusive reflection spectra of these two system show Gd^{3+} can play an intermediate role of energy transfer in the process of luminescence. There is energy transfer from TaO_4^{3-} to Gd^{3+} and finally to Eu^{3+} via the charge transfer states and spectral overlap. *© 2000 Kluwer Academic Publishers*

1. Introduction

Rare earth tantalate, especially $GdTaO_4$, proved to be an efficient luminescent host material. The previous studies on the structure of $GdTaO_4$ indicate that $GdTaO_4$ has two modifications, i.e. M type (fergusonite) and M′ type [1, 2]. The structural difference between M type and M′ type lies mainly in the coordination number of Ta atom. In the lattice of M type structure, the Ta atoms have a tetrahedral coordination, while in the M′ type, the Ta atoms exist in a distorted octahedron [3]. This structural difference may significantly influence luminescent properties of rare earth doped $GdTaO_4$. The luminescent properties of Eu^{3+} and Tb^{3+} doped M type $GdTaO_4$ have been studied by Blasse previously [4], and the energy transfer phenomena in the M type $GdTaO_4$ activated by Tb^{3+} have been reported by Lammers and Blasse [5]. Compared with other rare earth tantalate, such as $YTaO_4$, $GdTaO_4$ shows several advantages. $GdTaO_4$ has higher density, and does not show luminescence at room temperature due to the efficient energy transfer from TaO_4^{3-} to Gd^{3+} and a followed concentration quenching of Gd^{3+} [5]. Moreover, it was reported Gd^{3+} could play an intermediate role in luminescence, which enhances the efficiency of materials [6–9]. Tb^{3+} activated tantalate have attracted more attentions because it is a promising alternative phosphor for X-ray intensifying screen. While there is seldom study about precisely luminescence of Eu^{3+} doped tantalate. Actually Eu^{3+} has high luminescence efficiency and high quenching concentration. Eu^{3+}-activated orthotantalate is possibly an efficient red emission phosphor under high energy X-ray excitation.

We report here in more detail the preparation and luminescent properties of M and M′ type $GdTaO_4$ activated by europium. The difference of emission and excitation spectra for M and M′ type $GdTaO_4$: Eu is interpreted from the view of structure. Mainly we discuss the energy transfer phenomena between host lattice and activator ions in the process of luminescence. We find there is energy transfer from host lattice to the activator. Gd^{3+} can play an intermediate role in the process of energy transfer.

2. Experimental

Starting materials are Gd_2O_3 (99.99%), Ta_2O_5 (99.99%), Eu_2O_3 (99.99%), other reagents are all of analytical purity. Samples were prepared by a modified solid state reaction. Rare earth oxides and tantalum oxide were treated at 800–1000°C in advance to eliminate any contained moisture and the undecomposed oxalate. The rare earth oxides, Gd_2O_3 and Eu_2O_3, in desired ratio, were weighed and dissolved in HNO_3 solution. By adding oxalic acid solution, rare earth oxalates were precipitated. Then the oxalates were heated at 800 °C to obtain $(Gd, Eu)_2O_3$. Stoichiometric ratio of tantalum oxide and mixed rare earth oxide $(Gd, Eu)_2O_3$ were weighed and mixed extensively by grinding, and then heated at 1300 °C for 24 hours. The previous extensive grinding were necessary for obtaining

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single-phase product. The products thus obtained were M type $GdTaO_4:Eu$. The synthesis of M′ type $GdTaO_4:Eu$ has been described in previous paper [10]. After completely grinding and mixing Ta_2O_5 and $(Gd, Eu)_2O_3$ in a desired ratio, the blend were prefired at 1000°C for 12 h, then 20 wt% Li_2SO_4 as flux was added and mixed again. The blend materials were fired at 1000°C for another 12 h. At last, the fired products were washed with de-ionized water to free from flux and dried at 120°C.

The X-ray powder diffraction analyses were performed on a Rigaku D/MAX 2000 X-ray powder diffractometer with rotating anode working at 40 kV and 100 mA. Excitation and emission spectra were recorded with a Hitachi 850 fluorescence spectrophotometer. And diffusive reflection spectra were measured with a Shimadzu UV3100 UV-VIS-NIR recording spectrophotometer.

3. Result and discussion

The M′ modification of rare earth tantalate is known to be a low temperature phase, while M type phase can be obtained at relatively high temperature. X-ray powder diffraction analysis shows that the obtained samples as described above are of pure M or M′ type $GdTaO_4$ phase respectively. As far as ionic site and coordination preference is concerned, Eu^{3+} ions should occupy Gd^{3+} sites in lattice. X-ray diffraction analysis shows that all of the $Gd_{1-x}Eu_xTaO_4$ samples retain the M or M′ type $GdTaO_4$ structure respectively even for the samples with Eu^{3+} content up to $x = 0.20$.

Both M and M′ type $GdTaO_4:Eu$ shows red emissions under UV excitation. When Eu^{3+} concentration is less than 0.02, very weak Gd^{3+} emission around 313 nm can be detected. The main emission peaks for these two system are all at 612 nm, corresponding to Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition as shown in Fig. 1. That shows Eu^{3+} ions all situate on the non-central symmetric C_2 site of Gd^{3+} in $GdTaO_4$ with both M type and M′ type. It was known that the space group of M type structure is I2/a, while M′ type is P2/a [3]. Both structures have no symmetric center. In the low symmetric circumstance of lattice, Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission shows the strongest peak. The other groups of emission peaking around 592 nm, 658 nm, 690 nm and 706 nm originate from transitions of $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ respectively. Symmetry circumstance can efficiently split of $^5D_0 \rightarrow {}^7F_J$ emission. In M type, the splitting lines of transition of $^5D_0 \rightarrow {}^7F_1$ emission is three, that of $^5D_0 \rightarrow {}^7F_2$ transition emission is three, and of $^5D_0 \rightarrow {}^7F_4$ transition emission is three. In M′ type, the split of transition of $^5D_0 \rightarrow {}^7F_1$ emission is two, that of $^5D_0 \rightarrow {}^7F_2$ transition emission is four, and of $^5D_0 \rightarrow {}^7F_4$ transition emission is three.

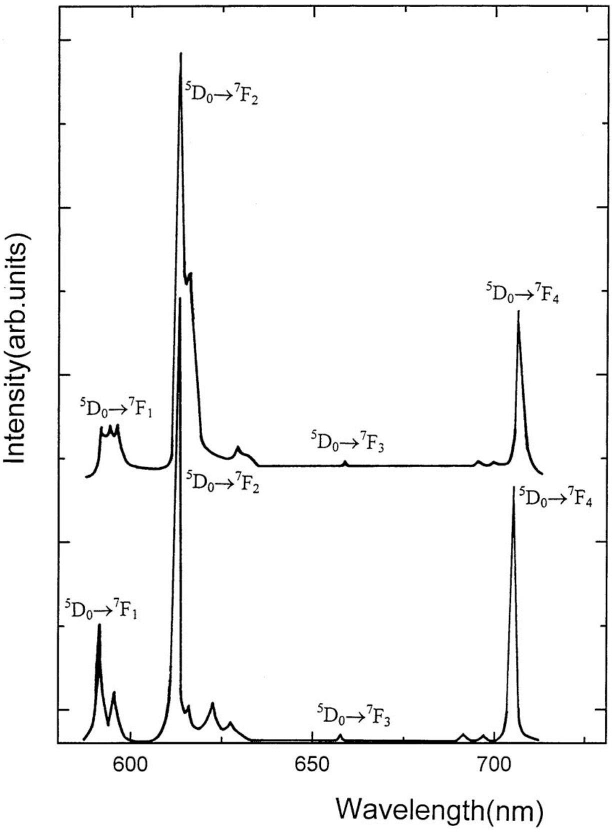

Figure 1 Emission spectra of $Gd_{0.99}Eu_{0.01}TaO_4$ under 220 nm UV light excitation Top: M type; Bottom: M′ type.

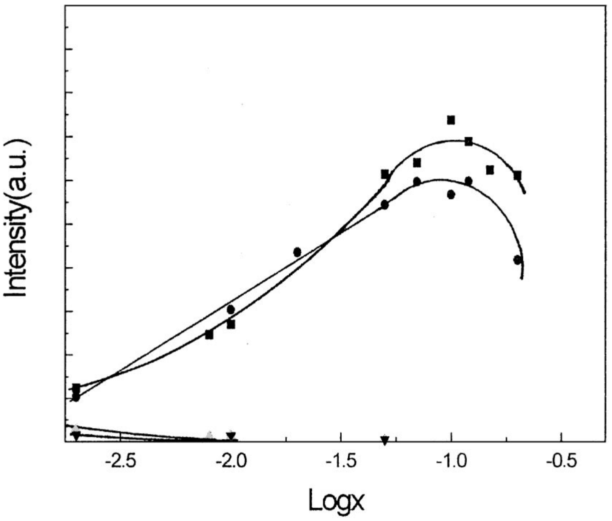

Figure 2 Eu^{3+} concentration dependence of emission intensities of M and M′ $Gd_{1-x}Eu_xTaO_4$(x = 0–0.20). ■ dot: Emission intensities of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition in M type; ▲ dot: Emission intensities of Gd^{3+} (λ = 313 nm) in M type; ● dot: Emission intensities of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition in M′ type; ▼ dot: Emission intensities of Gd^{3+}($\lambda = 313$ nm) in M′ type.

The influence of Eu^{3+} concentration on the emission intensities of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition ($\lambda = 612$ nm) and of Gd^{3+} are further studied and shown in Fig. 2. With increasing of Eu^{3+} concentration, the weak Gd^{3+} emission around 313 nm disappears, the emission intensity of Eu^{3+} increases and reaches to the maximum value when $x = 0.07$–0.12. After that, intensity of Eu^{3+} will decrease slowly as more Eu^{3+} are doped in $GdTaO_4$ due to the concentration quenching. We have observed a similar result in M′ $YTaO_4$: Eu as our previous paper reported [10].

The excitation spectra of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition in M′ and M type $GdTaO_4:Eu$ under UV excitation is shown in Fig. 3 and Fig. 4 respectively. There are three kinds of excitation in both the two spectra: (1) a group of excitation narrow lines in the range of 300–500 nm originates from Eu^{3+} f-f electron transitions; (2) narrow

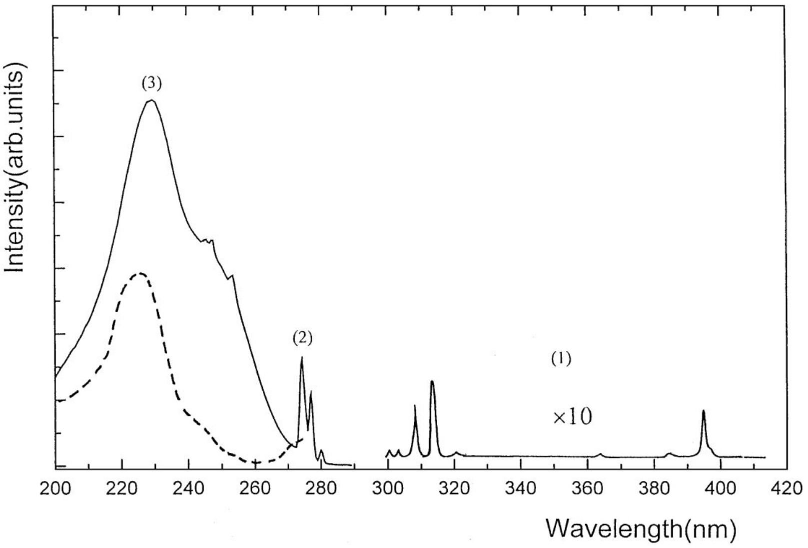

Figure 3 Excitation spectra of $Gd_{0.99}Eu_{0.01}TaO_4$ with M′ type. Solid line: Excitation spectrum of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission ($\lambda = 612$ nm); Dash line: Excitation spectrum of Gd^{3+} emission ($\lambda = 313$ nm).

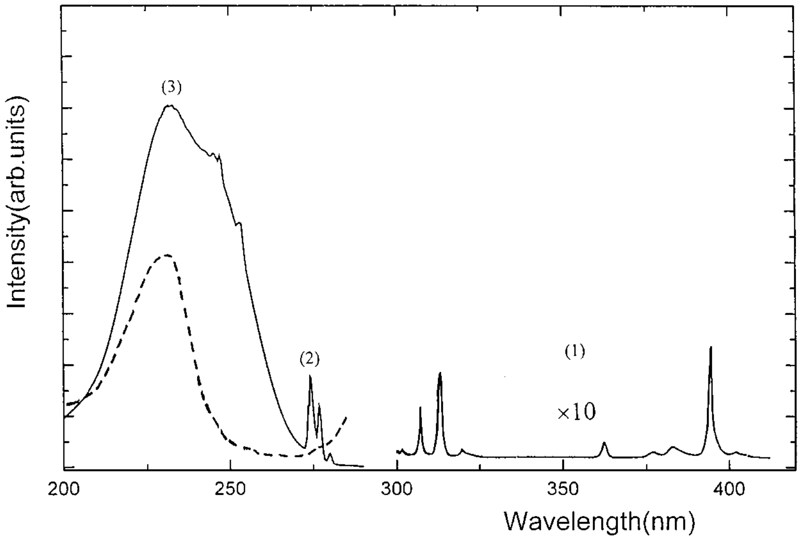

Figure 4 Excitation spectra of $Gd_{0.99}Eu_{0.01}TaO_4$ with M type. Solid line: Excitation spectrum of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission ($\lambda = 612$ nm); Dash line: Excitation spectrum of Gd^{3+} emission ($\lambda = 313$ nm).

lines peaking at 245, 248, 254, 274, 277, 280, 313 nm are transitions within 4f shell of Gd^{3+}; (3) a broad band at 200–260 nm; In fact, this wide band is formed with two parts, a broad peak and an attached shoulder. A further discussion about this will be made in next paragraph. Mayolet has observed two narrow lines appear at 310 and 270 nm on the excitation spectra of visible luminescence of Eu^{3+} or Tb^{3+} in gadolinium metaborate. He attributed them respectively to $^8S_{7/2} \rightarrow {}^6P_J$ and $^8S_{7/2} \rightarrow {}^6I_J$ transition in the ground configuration of Gd^{3+}, which implies an energy transfer from Gd^{3+} to activator [9]. The same result is obtained in GdB_3O_6-Eu^{3+} by Hao Zhiran and Blasse [8]. Therefore those narrow lines in (2) of Fig. 3 actually show there is energy transfer from Gd^{3+} to Eu^{3+} in tantalate system. Because the energy level of excitation band of charge transfer transition of TaO_4^{3-} (228 nm) [10] is higher than ^6D or ^6I level of Gd^{3+} ion, Gd^{3+} can be excited to higher levels. The emission of TaO_4^{3-} (260–400 nm) overlaps excitation band of Gd^{3+}, so TaO_4^{3-} group can possibly transfer energy to Gd^{3+} through a secondary absorption. In the excitation spectra (dash line in Fig. 3 and Fig. 4) of Gd^{3+} emission (313 nm), we also find a broad band that can be ascribed to the charge transfer excitation of TaO_4^{3-} group due to there is no Gd^{3+} energy level in this region. That means energy transfer from TaO_4^{3-} to Gd^{3+} can take place through charge transfer state. All these observation turns out that Gd^{3+} in this system can play an intermediate role in the process of energy transfer.

Because of resolution limit of our fluorescence spectrophotometer, we can not resolve the two excitation peaks completely in part (3) of Fig. 3 and Fig. 4. But using curving fitting described previously [10], we can draw a definite conclusion: the strong excitation band in the range of 220 to 260 nm of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission in M and M′ $GdTaO_4$: Eu in Fig. 3 and Fig. 4 is composed of two bands: one peaking at 228 nm with half-height width 24 nm is the band of TaO_4^{3-} charge transfer excitation; the other, peaking at

248 nm with half-height width 20 nm, can be attributed to the band of Eu^{3+} charge transfer excitation. This conclusion indicate energy transfer from host lattice to Eu^{3+} and is coincide with the results obtained by Blasse in $YTaO_4 : Eu$ of fergusonite structure and with those by ourselves in M′ $YTaO_4 : Eu$. The excitation spectra of Eu^{3+} emission in $Y_{0.97}Eu_{0.03}TaO_4$ with fergusonite structure and M′ type all consisted of the excitation of host lattice and the charge transfer excitation band of Eu^{3+}[4, 10]. Excitation energy can transfer from TaO_4^{3-} via Gd^{3+}, then to Eu^{3+}, or it can transfer directly from TaO_4^{3-} to Eu^{3+} for $GdTaO_4 : Eu$ in both M type and M′ type. The excitation transition within 4f shell of Eu^{3+} is poor, so the energy transfer from TaO_4^{3-} to Eu^{3+} directly is not efficient, and can not compete with that from TaO_4^{3-} to Gd^{3+}.

There are some difference in the excitation spectra for M and M′ type (Fig. 3 and Fig. 4), which may be due to different structure of M and M′ type. For the samples with same Eu^{3+} concentration, the peak of the broad band situating at 200–260 nm shifts to shorter wavelength in M′ type than that in M type. In Fig. 3, it is at 229 nm, while in Fig. 4, it is at 233 nm. As we know above, the broad band is a mixing result of charge transfer excitation of TaO_4^{3-} and charge transfer excitation of Eu^{3+}. The Gd sites in both M and M′ structures are the same. Obviously the wavelength shift is due to the difference of TaO_4^{3-} charge transfer excitation. In TaO_4^{3-} group, the excitation band is originated from one of the 2p electron of the coordinating oxygen ions goes to the empty 5d orbit of Ta ion [10]. The difference between M and M′ structure is the coordination number of Ta atom. It is 6 for M′ type, and 4 for M type. In M′ $GdTaO_4$, Ta atom situates in a distorted octahedral coordination, with four shorter Ta-O bonds at around 1.93 Å and two Ta-O longer bonds at 2.20 Å [11]. While in M type the average Ta-O distance is longer than that of M′ type. The shorter the Ta-O distance, the greater the energy difference between the Ta 5d and O 2p electrons. The average Ta-O distance in M′ structure is shorter than that in M structure. So the charge transfer excitation band of TaO_4^{3-} in M′ type should be at higher energy than that in M type. Therefore, the mixing results of charge transfer excitation of TaO_4^{3-} and charge transfer excitation of Eu^{3+} is different. The broad band in M′ type $GdTaO_4 : Eu$ excitation spectra should have a little blue shift in comparison with the same band of M type $GdTaO_4 : Eu$.

Lammers and Blasse have studied the excitation spectra of M type $GdTaO_4$ activated by Tb^{3+} at liquid helium temperature (LHeT) [5]. At LHeT there appears weak Gd^{3+} emission, TaO_4^{3-} intrinsic emission and a defect tantalate emission around 420 nm. And the broad band of excitation is somewhat narrower.

We have studied the luminescent properties of M type $GdTaO_4 : Eu$ at liquid nitrogen temperature (LNT). The emission spectrum of Eu^{3+} is similar to the emission spectrum at room temperature. Lammers and Blasse believe that only at low enough temperature ($T < 30$ K) there is Gd^{3+} emission in $GdTaO_4$ [5]. At LNT we can not detect the Gd^{3+} emission and the intrinsic tantalate emission. We find a very weak and broad emission around 400 nm, which can be ascribed to the defect tantalate emission. While in other tantalate, the defect tantalate emission is supposed at 440 nm [4, 5, 12]. The excitation spectrum of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition at LNT is shown Fig. 5. The relative intensity of the broad band and sharp lines are very weak. And the main excitation band at LNT is narrower than that at room temperature due to the disappearance of tantalate charge transfer excitation, which implies the energy transfer from TaO_4^{3-} to Eu^{3+} can be possibly neglected at LNT. The excitation intensity of sharp lines of Gd^{3+} 4f-f transition is stronger than the broad band. A new sharp line peaking at 262 nm is detected, which can not be seen at room temperature due to the strong intensity of the mixing broad band. So the energy transfer from Gd^{3+} to Eu^{3+} may be very efficient. At LNT energy transfer from Gd^{3+} to Eu^{3+} ion is also a dominating process. In the excitation of the defect tantalate emission, we find a band peaking around 250 nm, an attached band around 260–270 nm and several narrow lines peaking at 245 nm, 248 nm and 276 nm. These three parts in the excitation spectrum can be possibly ascribed to charge transfer excitation of Eu^{3+}, the excitation of defect tantalate and Gd^{3+} excitation within 4f shell respectively. The excitation spectra of the defect tantalate emission contain excitation of Eu^{3+} and Gd^{3+}. So it may be conclude that at LNT activator and sensitizer possibly transfer energy back to host lattice. The excitation spectra of the defect tantalate emission ($\lambda = 420$ nm) of M type $Gd_{0.998}Tb_{0.002}TaO_4$ contains also the Gd^{3+}

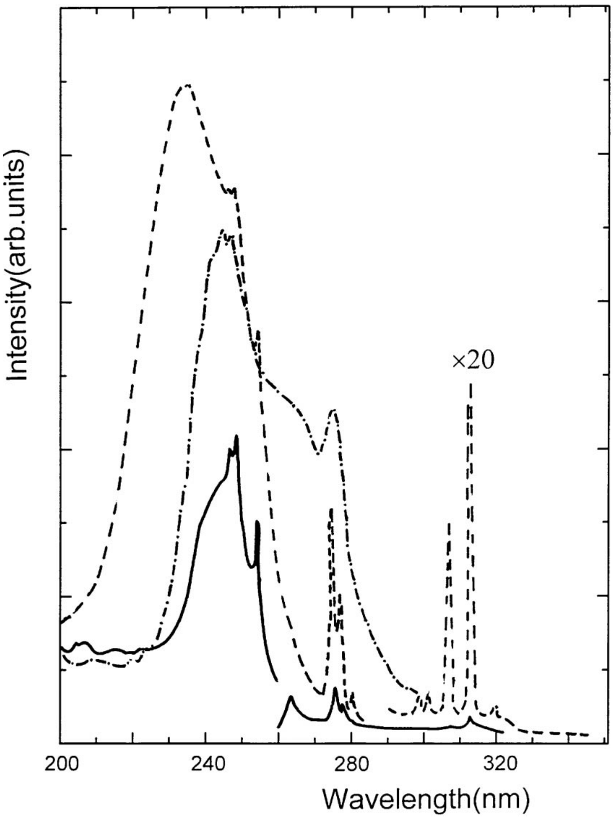

Figure 5 Excitation spectra of $Gd_{0.998}Eu_{0.002}TaO_4$ with M type. Solid line: Excitation spectrum of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission ($\lambda = 612$ nm) at liquid nitrogen temperature; Dash line: Excitation spectrum of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission ($\lambda = 612$ nm) at room temperature; Chain line: Excitation spectrum of defect TaO_4^{3-} emission ($\lambda = 400$ nm).

lines around 277 nm, and this points to energy transfer from Gd^{3+} to the defect tantalate group [5]. In Fig. 5 we also found the reduction of the intensities of Gd^{3+} $^8S \rightarrow {}^6P$ excitation peak at LNT as observed in the excitation spectra of M type $Gd_{0.998}Tb_{0.002}TaO_4$ at LHeT [5], which means that the energy transfer from Gd^{3+} to Eu^{3+} at LNT is less efficient for excitation into ^6P than into the ^6I level of the Gd^{3+}. We can draw the same conclusion as Lammers and Blasse did [5].

4. Conclusion

Eu^{3+}-activated $GdTaO_4$ with both M type and M′ type are efficient red phosphors. There is energy transfer between host and activator in the process of luminescence. In the excitation spectra of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition emission in M and M′ type $GdTaO_4$: Eu, there appear excitation of Gd^{3+} and TaO_4^{3-} group, which indicate energy transfer from Gd^{3+} and TaO_4^{3-} group to Eu^{3+} in the process of luminescence. The excitation spectra of Gd^{3+} emission including strong excitation of charge transfer of TaO_4^{3-} group show energy transfer from host lattice to Gd^{3+}. So there are two ways of energy transfer in $GdTaO_4$: Eu system. Gd^{3+} acts as a media in the energy transfer process. The structural difference between M and M′ type $GdTaO_4$: Eu can efficiently influence their luminescent properties. The main excitation band of Eu^{3+} is a little blue shift for M′ type $GdTaO_4$: Eu compared to M type $GdTaO_4$: Eu because of shorter Ta-O bonds in M′ type structure than that in M type. At liquid nitrogen temperature, energy transfer from Gd^{3+} to Eu^{3+} appears clear in the process of luminescence. Moreover, Gd^{3+} and Eu^{3+} possibly transfer energy back to a kind of defect tantalate group at LNT.

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