

Thermal quenching of Eu^{2+} 5d–4f luminescence in inorganic compounds

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Abstract

The thermal quenching of Eu^{2+} 5d–4f emission on Ba, Sr, or Ca sites in compounds is often attributed to a large displacement between the ground state and excited state in the configuration coordinate diagram. This work will demonstrate that the ionization of the 5d electron to conduction band states is the genuine quenching mechanism. A model is proposed to explain why in some types of compounds the quenching temperature decreases when going from the Ba variant via the Sr variant to the Ca variant and in other types of compounds the reverse behaviour occurs. The nature of the bottom of the conduction band plays an important role in this.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The interest in the thermal quenching of Eu^{2+} 5d–4f emission arose in the early days of research on lanthanide activated tube lighting and cathode ray tube phosphors [1]. In some compounds quenching already starts below room temperature which then degrades the room temperature quantum efficiency [2–4]. Soon a rule was observed for series of alkaline earth compounds; the quenching temperature $T_{0.5}$, i.e. the temperature at which the emission intensity has dropped to 50% of the low temperature value, tends to increase with increasing radius of the alkaline-earth ion. For example, in isomorphous compounds CaBPO_5 , SrBPO_5 , and BaBPO_5 the $T_{0.5}$ value increases from ≈ 300 K to ≈ 500 K and to ≈ 600 K, respectively [3, 5]. The quenching was explained by a large displacement between the ground and excited state in the configuration coordinate diagram [6, 7]. Other quenching models, for example thermal excitation of 5d electrons to conduction band states [4, 7, 8] or excitation of holes from Eu to valence band states [9], were also suggested.

In this work information on the absolute location of the Eu^{2+} 4f and 5d levels is used to study the relationship between the energy barrier for thermal quenching and the energy E_{dc} between the relaxed lowest 5d state at energy E_{d} and the bottom of the conduction band at

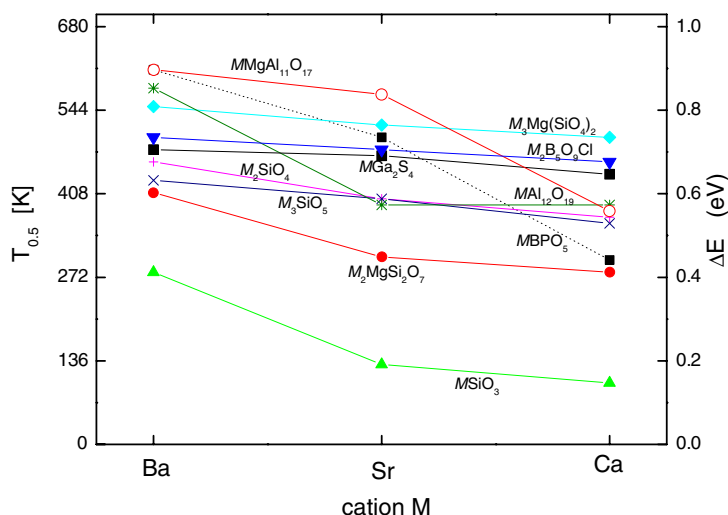


Figure 1. The quenching temperature $T_{0.5}$ of Eu^{2+} 5d–4f emission on M sites ($M = \text{Ba}, \text{Sr}, \text{or Ca}$) in type II compounds. The right hand scale shows a crude estimate of the activation energy for thermal quenching.

energy E_C . It will be concluded that quenching is not due to a large displacement between the ground and excited state in the configuration coordinate diagram and also not by excitation of a hole to the valence band. Instead it is caused by thermal excitation of the 5d electron to conduction-band-like states. After having established this, the relationship between E_{dC} and type of compound is further studied.

It is not the aim of this paper to provide a detailed account for the 5d–4f quenching of Eu^{2+} in one specific compound. The aim is to provide an overview that covers many different types of compounds. A phenomenological approach is chosen to identify the main trends. It is expected that knowledge on these trends will initiate more refined studies of the quenching behaviour and the relation with the absolute location of energy levels. The trends may also guide the search for more temperature stable Eu^{2+} activated phosphors.

2. Results

Table 1 compiles the quenching temperature $T_{0.5}$ of Eu^{2+} 5d–4f emission in compounds with Eu located on either a Ba, Sr, or Ca site. Occasionally different $T_{0.5}$ values were retrieved from different literature sources and then an average value is given. Some of the results from table 1 are shown in figure 1. $T_{0.5}$ clearly decreases with smaller size of the alkaline earth cation. That in the Ca compound is generally 50–200 K lower than in the corresponding Ba compound. This is a rule that was already observed a long time ago [5].

Figure 2 shows data on compounds from table 1 that seem to contradict this rule. In BaF_2 , SrF_2 , and CaF_2 the quenching temperature increases with smaller size of alkaline earth. Similar behaviour is found for SrS and CaS . Also $\text{MAl}_2(\text{SiO}_4)_2$ and MAl_2O_4 behave differently with a relatively low quenching temperature for the Ba compound.

The most simple equation to describe thermal quenching of luminescence intensity $I(T)$ with temperature T is given by

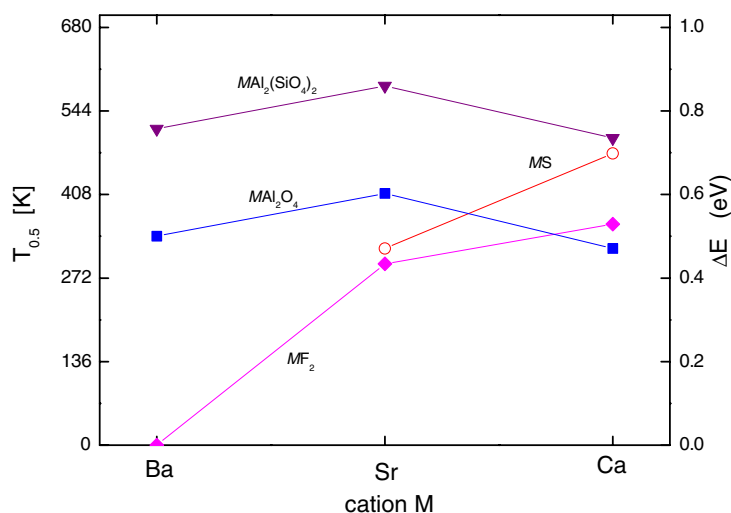


Figure 2. The quenching temperature $T_{0.5}$ of Eu^{2+} 5d–4f emission on M sites ($M = \text{Ba}, \text{Sr}, \text{or Ca}$) in type I and miscellaneous type compounds. The right hand scale shows a crude estimate of the activation energy for thermal quenching.

Table 1. Quenching temperature $T_{0.5}$ (K) of Eu^{2+} 5d–4f emission at an $M = \text{Ba}, \text{Sr}, \text{or Ca}$ site in inorganic compounds.

Compound	$T_{0.5}$ (Ba)	$T_{0.5}$ (Sr)	$T_{0.5}$ (Ca)	Reference
$\text{M}_2\text{B}_5\text{O}_9\text{Cl}$	500	480	460	[23]
MP_2O_7	—	470	407	[1]
MBPO_5	610 ± 40	500 ± 30	300 ± 20	[5, 3]
MSiO_3	280	130	100	[24]
$\text{M}_2\text{MgSi}_2\text{O}_7$	410 ± 40	305	280	[2, 5]
$\text{M}_3\text{Mg}(\text{SiO}_4)_2$	550	520	500	[5]
M_2SiO_4	460 ± 50	400	370	[25, 26, 2, 5]
MMgSiO_4	360	—	325	[5]
M_3SiO_5	455	400	360	[2]
$\text{MMgAl}_{11}\text{O}_{17}$	610	570	380	[27, 28]
$\text{MAI}_{12}\text{O}_{19}$	580 ± 50	390 ± 20	390 ± 20	[27, 28, 5, 29]
MGA_2S_4	480	470	440	[11, 12, 30]
$\text{MAI}_2(\text{SiO}_4)_2$	515	585	500	[31]
MAI_2O_4	340 ± 40	410 ± 30	320	[32–34]
MF_2	0	295	370	[35, 36]
MS	—	320	475	[8, 37]

$$I(T) = \frac{I(0)}{1 + \frac{\Gamma_0}{\Gamma_v} \exp\left(\frac{-\Delta E}{k_B T}\right)} \quad (1)$$

where Γ_v is the radiative decay rate of the 5d state of Eu^{2+} , Γ_0 is the attempt rate for thermal quenching, k_B is Boltzmann's constant, and ΔE is the energy barrier for thermal quenching. The related equation for the decay rate of the 5d state is given by

$$\Gamma(T) = \Gamma_v + \Gamma_0 \exp\left(\frac{-\Delta E}{k_B T}\right). \quad (2)$$

The attempt rate Γ_0 has similar magnitude as the maximum phonon frequency (typically 3×10^{13} Hz corresponding with phonon energies of 1000 cm^{-1}) in compounds. The radiative decay rate of the 5d–4f emission in Eu^{2+} is typically 1.1×10^6 Hz. Using these values in equation (1) one obtains

$$\Delta E = \frac{T_{0.5}}{680} \text{ eV} \quad (3)$$

as a crude relationship between the quenching temperature $T_{0.5}$ and the energy barrier ΔE . Equation (3) was used to transfer the left hand temperature scale in figure 1 into the right hand energy scale. It reveals that the thermal quenching energy barrier for the Ba compounds in figure 1 varies between 0.4 and 0.9 eV, and for the Ca compounds it is 0.2–0.3 eV smaller.

3. Discussion

The quenching of 5d–4f emission in Eu^{2+} was attributed in 1968 to a large displacement between the ground and excited states of Eu^{2+} in the configuration coordinate diagram [2, 7]. A model was presented by Blasse and Brill in 1970 to explain that the quenching temperature for Eu^{2+} on a Ba site is usually higher than that for Eu^{2+} on a Ca site in isomorphous compounds [5]. Alternative models on quenching of Eu^{2+} 5d–4f emission were also suggested. Davolos *et al* [10] proposed that the thermal activation from the 5d state to conduction band state causes the quenching in Ba thiogallates. A similar quenching model was demonstrated by Ando *et al* [8] for Eu^{2+} in CaS. On the other hand Najafov *et al* [9] attribute the thermal quenching in $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ to thermally excited release of a hole from Eu^{2+} to the valence band. The same model is followed by Chartier *et al* [11] for $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$. Jabbarov *et al* [12] studied the quenching behaviour of Eu^{2+} in BaGa_2S_4 . They conclude that the configuration diagram cannot explain the quenching behaviour and either thermal release of an electron to the conduction band or a hole to the valence band should be involved.

The Stokes shift between 4f–5d absorption and 5d–4f emission is directly related to the displacement in the configuration coordinate diagram. If the Blasse–Brill model holds then (1) the Stokes shift should scale with the size of the site occupied by Eu^{2+} and (2) a relationship between the Stokes shift and the quenching temperature should exist. The Stokes shift of Eu^{2+} 5d–4f emission is known and compiled for hundreds of different compounds, which allows testing of such relationship [17]. From that compilation and data gathered since, the average Stokes shift for Eu^{2+} on Ba, Sr, and Ca sites is found to be 0.27 ± 0.14 eV (56), 0.26 ± 0.14 eV (53), and 0.25 ± 0.13 eV (52), respectively (the number within brackets refers to the compounds over which the average is made). There appears no relationship between the size of the Stokes shift and the size of the site occupied. A relationship between the Stokes shift and the quenching temperature of 5d–4f emission could also not be established from the data available. Considering all this, the model by Blasse and Brill and more generally the idea that thermal quenching of 5d–4f emission is due to a large displacement between the ground and excited state in the configuration coordinate diagram must be reconsidered.

To understand quenching via either delocalization of the 5d electron or the hole from Eu^{2+} it is necessary to know the location of the energy levels of Eu^{2+} relative to the bands of the host compound [12]. Since recently a simple method can be used to estimate the absolute location of the Eu^{2+} 4f and 5d levels [13, 14]. The method was applied to explain the mechanism of persistent Eu^{2+} luminescence in $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+};\text{Dy}^{3+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+};\text{Dy}^{3+}$ [15, 16]. That work also revealed that thermal release of a hole from Eu^{2+} to the valence band requires a much too large amount of energy and cannot be part of the persistent luminescence mechanism. It is also not a possible route for thermal quenching. This holds quite generally for Eu^{2+} doped

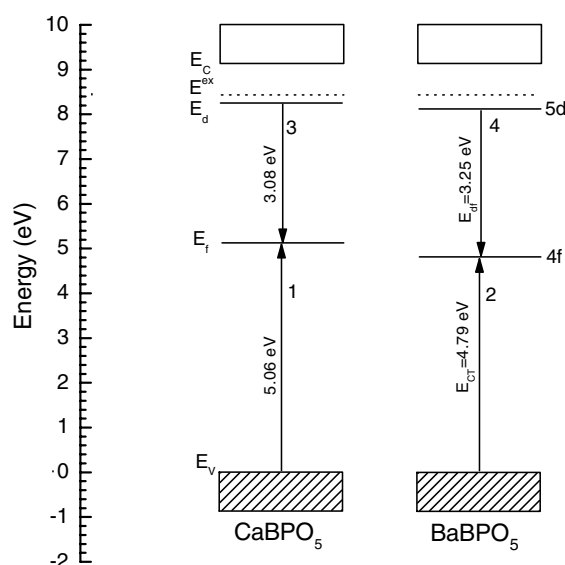


Figure 3. The energies of the lowest 4f and lowest 5d state of Eu^{2+} in CaBPO_5 and BaBPO_5 as found from the energy of charge transfer E^{CT} (arrows 1 and 2) and the energy for the 5d–4f emission (arrows 3 and 4).

compounds and what remains as the mechanism for thermal quenching is the thermal excitation of the 5d electron to the conduction band.

To relate the energy barrier for thermal quenching to the energy difference E_{dC} between the relaxed lowest 5d state of Eu^{2+} and the bottom of the conduction band, the absolute location of energy levels needs to be determined. In the case of Eu^{2+} this information can be retrieved from the energy of the Eu^{3+} charge transfer band and the energy of Eu^{2+} 5d–4f emission [13, 14]. Figure 3 illustrates the method for Eu in the two isomorphous compounds CaBPO_5 and BaBPO_5 . The energy needed to excite an electron from the valence band to Eu^{3+} is 5.06 and 4.79 eV [13], and the energy of the 5d–4f emission is 3.08 and 3.25 eV [17] in these two compounds respectively.

The final state in the charge transfer to Eu^{3+} is the 4f ground state of Eu^{2+} together with a hole on the neighbouring anion. In [14] it was shown that the energy of charge transfer is about the same as the energy difference E_{Vf} between the top of the valence band at E_{V} and the 4f Eu^{2+} ground state at E_{f} . Arrows 1 and 2 show the transitions in both compounds. Adding the energy of the 5d–4f emission (arrows 3 and 4), the energy of the relaxed lowest 5d states at E_{d} is obtained.

The first excitation maximum at energy E^{ex} of the host lattice is at practically the same energy for Ca-, Sr-, and BaBPO_5 . In figure 3 the room temperature value of 8.4 eV was used from [20]. To reach the bottom of the conduction band at energy E_{C} the electron–hole binding energy of this exciton-like state should be added. As motivated in [13] we assume that $E_{\text{C}} \approx 1.08 \times E^{\text{ex}} = 9.1$ eV. With these data we find for CaBPO_5 and BaBPO_5 values for E_{dC} of 0.9 and 1.0 eV, respectively.

The energy barrier for thermal quenching is not necessarily the same as E_{dC} . After delocalization of the 5d electron to conduction band states the electron can still be bonded by the effective positive charge on Eu^{3+} left behind. This can be interpreted as an electron orbiting around Eu^{3+} in an impurity-trapped exciton configuration: a similar state as postulated

to explain the so-called anomalous emission of Eu^{2+} and Yb^{2+} in compounds [18, 19]. The only difference is that with anomalous emission the return to the Eu^{2+} ground state is radiative whereas with thermal quenching it is non-radiative. Despite the fact that ΔE is probably smaller than E_{dC} , a more or less proportional relationship between both energies is expected.

Using the data tabulated in [13, 17] on E^{CT} , E^{ex} , and E_{df} for Eu on Ba, Sr, or Ca sites one generally finds that the relaxed 5d state is always located within about 1.0 eV below the bottom of the conduction band. This finding is consistent with the magnitude of ΔE and it provides strong support for a quenching mechanism that involves excitation to conduction band states.

In figure 3 the 5d state in BaBPO_5 is 0.1 eV deeper below the bottom of the conduction band than in CaBPO_5 whereas figure 1 suggests that the 5d state in BaBPO_5 is almost 0.5 eV deeper below. The values for both ΔE and E_{dC} are subject to a considerable error. Errors as large as 0.5 eV can be present in the values for E_{dC} . This means that the method to position energy levels relative to the conduction band is not accurate enough to explain the trends seen in figure 1.

Data on E^{CT} , E^{ex} , and E_{df} for Eu on trivalent rare earth ($\text{RE} = \text{La}, \text{Gd}, \text{Y}, \text{Lu}, \text{Sc}$) sites in compounds is more abundant than on divalent alkaline earth sites. We can use the data on RE compounds to study phenomenologically the trends in level positions with type of compound and then apply those trends to the alkaline earth compounds.

In order to understand the 0.2–0.3 eV decrease of ΔE in figure 1 with smaller size of the alkaline earth we have to understand the factors that influence E_{dC} . For that we need to uncover three relationships: the change of (1) the energy E^{CT} of charge transfer to Eu^{3+} that provides us the location of the 4f ground state, (2) the energy E_{df} that provides us the position of the relaxed 5d state, and (3) the change in the bandgap energy E_{VC} with alkaline earth site size.

The trends in E^{CT} were studied in [13]. There it was found that the energy of charge transfer to Eu^{3+} on a La^{3+} site in a RE compound is usually 1 eV smaller than that for Eu^{3+} on the 18 pm smaller Lu^{3+} site in the same type of RE compound. This was attributed to a smaller Madelung potential because of the larger distance between Eu and the negative nearest neighbour anions. A similar situation exists when comparing the energy of charge transfer to Eu^{3+} on Ba, Sr, or Ca sites. Data on fluoride and oxide compounds compiled in [13] reveal that, in general, the energy of the 4f ground state of Eu^{2+} rises by ≈ 0.5 eV when changing from the Ba, via the Sr, to the Ca variant of the compound. In the example of figure 3 the difference is 0.27 eV.

The change in E_{df} with decrease of site size is also well studied. Due to a larger crystal field splitting of the 5d configuration with smaller site size, E_{df} tends to decrease. However, the effect is not very large. From the data compiled in [17] it is found that the energy of 5d–4f emission on average decreases by only a few tenths of an eV when changing from the Ba variant, via the Sr variant, to the Ca variant of a compound. The decrease in E_{df} is smaller than the increase in E^{CT} , which implies that the lowest 5d state of Eu^{2+} on Ba sites is in general several tenths of an eV closer to the valence band than on Ca sites.

The next parameter is the location of the bottom of the conduction band. To explain the experimentally observed trends in $T_{0.5}$ two types of compounds are distinguished: (I) compounds where the bottom of the conduction band is formed by the same cations as the ones replaced by Eu^{3+} ; (II) compounds where the bottom of the conduction band is dominated by cations other than the one replaced by Eu^{3+} .

The binary compounds MF_2 , MO , and MS belong to type I. The bandgap in these compounds increases strongly (1–2 eV) with smaller size of the alkaline earth. Also compounds like REAlO_3 and RE_2O_3 where $\text{RE} = \text{La}^{3+}, \text{Gd}^{3+}, \text{Y}^{3+},$ or Lu^{3+} belong to type I; the bottom of the conduction band is formed by the 5d orbitals of the lanthanide ions. The increase of

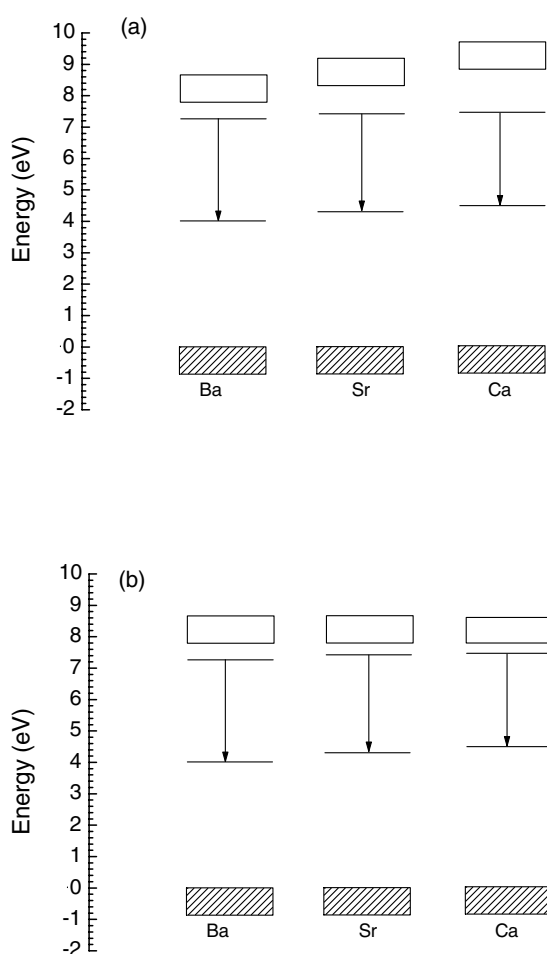


Figure 4. (a) The characteristic scheme of level energies in type I compounds. (b) The characteristic scheme of level energies in type II compounds.

the bandgap is caused by a more negative Madelung potential with smaller M or RE site size. The same Madelung potential increases the energy of charge transfer to Eu^{3+} . However, the bandgap increases faster than the energy of charge transfer. Apparently the Madelung effect works more strongly for the bandgap increase than for E^{CT} [13]. This can be attributed to lattice relaxation around Eu^{3+} that counteracts the effect of the changing site size and accompanying changing Madelung potential.

For type I compounds we arrive at a situation illustrated in figure 4(a). Going from Ba via Sr to Ca the energy of charge transfer tends to increase. In figure 4(a) a realistic value of 0.5 eV is used. The bandgap increases faster than the energy of charge transfer and in figure 4(a) we have used an increase by 1 eV. The energy of the 5d–4f emission decreases with smaller site size by a few tenths of an eV. In figure 4(a) a decrease by 0.3 eV was used. The end result is that the energy difference between the relaxed lowest 5d state and the bottom of the conduction band increases from the Ba compound to the Ca compound. ΔE and the quenching temperature of Eu^{2+} 5d–4f emission increases in that same order. This is what is observed for the MF_2 compounds and for CaS and SrS in figure 2. Exactly the same line of reasoning applies

for Ce^{3+} 5d–4f emission in type I RE compounds. The quenching temperature of Ce^{3+} 5d–4f emission on La sites should be lower than when on a smaller Y site. Indeed Ce^{3+} does not emit in LaAlO_3 ($T_{0.5} = 0$ K), $T_{0.5} = 380$ K in GdAlO_3 [21], and $T_{0.5} = 650$ K in YAlO_3 [22].

Let us now turn to type II compounds. In these compounds the bottom of the conduction band is formed by a cation other than Ca, Sr, or Ba. In this case the bandgap does not depend much on the type of alkaline earth cation. Approximately one obtains the situation shown in figure 4(b). It is similar to figure 4(a) but the location of the conduction band is now kept constant with alkaline earth cation. One observes that ΔE is largest for the Ba compound and smallest for the Ca compound. The end result is now that the quenching temperature decreases with smaller size of the alkaline earth cation. This is what is observed in figure 1.

Of course there are compounds where the conduction band states from the alkaline earth are at about the same energy as those from other cations in the compound. This may create the situation that for the Ba compound the bottom is composed of mainly Ba states whereas for the Sr and Ca compound it is mainly from other cation states. This may be the case for $\text{MAI}_2(\text{SiO}_4)_2$ and MAI_2O_4 , where figure 2 shows a relatively small $T_{0.5}$, although for these compounds one may also not exclude that differences in crystal structure play a role.

4. Summary and conclusions

Different quenching models on the Eu^{2+} 5d–4f emission in alkaline-earth compounds have been reported in the literature. In this work it is concluded that the quenching is not due to a large displacement between the ground and excited states of Eu^{2+} in the configuration coordinate diagram, and it is also not explained by thermal release of a hole from Eu^{2+} to the valence band. Instead, thermal excitation of the 5d electron to conduction band states appears the genuine mechanism. Probably the 5d electron remains bonded in an Eu^{3+} trapped exciton state from which it returns non-radiatively to the Eu^{2+} ground state.

The energy barrier for thermal quenching agrees qualitatively with the energy difference between the lowest 5d state and the bottom of the conduction band. To understand the quenching behaviour with type of alkaline-earth cation site occupied by Eu^{2+} two types of compounds were distinguished: (I) compounds where the bottom of the conduction band is formed by the same cations as the ones replaced by Eu^{3+} and (II) compounds where the bottom of the conduction band is dominated by cations other than the one replaced by Eu^{3+} . In type I compounds the activation energy for thermal quenching increases with smaller size of the alkaline earth cation. In type II compounds the situation is reversed and the activation energy for thermal quenching decreases with smaller site of the alkaline earth cation. The ideas and models on thermal quenching of 5d–4f emission of Eu^{2+} on divalent alkaline earth sites can equally well be applied to the 5d–4f emission of Ce^{3+} on a trivalent rare earth site.

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