

Thermal Quenching of Characteristic Luminescence. II

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Received February 20, 1973

A model proposed earlier to explain the dependence of the quenching temperature (T_q) of a given luminescent center on the host lattice is extended to luminescent centers bearing a formally effective charge. Predictions from this model are compared with experimental data. The agreement is satisfactory. It turns out that effectively charged centers with charge-transfer excitation (e.g., Eu^{3+} , WO_4^{2-}) do not have a high value of T_q , whereas those with Rydberg excitation (e.g., Tl^+ , Tb^{3+}) can have a high value of T_q , especially if the host lattice is rigid.

1. Introduction

Recently we have described a simple model that accounts for the quenching temperature of characteristic luminescence of activators in solids (1, 2). An important role in this model is played by Δr , the difference between the equilibrium distances of the ground and luminescent state, and the radius and charge of the cations surrounding the relevant luminescent center. In our considerations we restricted ourselves to those luminescent compounds in which the luminescent center can be introduced without charge compensation (e.g., $\text{Y}_{2-2\delta}\text{Eu}_\delta^{3+}\text{O}_3$, $\text{Mg}_2\text{Sn}_{1-\delta}\text{Ti}_\delta\text{O}_4$ and $\text{Sr}_{1-\delta}\text{Eu}_\delta^{2+}\text{Al}_2\text{O}_4$).

In this paper we turn our attention to those phosphors in which the activator must be charge-compensated, e.g., trivalent rare-earth ions in Ca^{2+} compounds. There seem to be some general, suspicious rules on the quenching temperature (T_q) and efficiency of phosphors of this type. Activators which are excited in charge-transfer absorption bands, i.e., $\Delta r > 0$ (1, 2) (for example Eu^{3+} , W^{6+} in oxides) do not luminesce efficiently or with a high T_q in compounds where they need charge compensation (examples are given below). Activators which are excited in their own electronic levels [$\Delta r < 0$, Refs. (1, 2) the so-called Rydberg transitions], however, may show efficient luminescence with high T_q , even if charge compensation is necessary. Some of these have even found industrial application [e.g., $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{-Ce}^{3+}$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-Ce}^{3+}$, Ref. (3)].

We feel that our model should also be able to explain these phenomena, because the model appeared to be general and the above-mentioned rules also have a general validity. For this reason we tried to extend the model to phosphors with charge-compensated activators. Our results are positive and give again some idea of the factors that determine the quenching temperature of characteristic luminescence.

2. Experimental Results

Samples were prepared by usual ceramic techniques and checked by X-ray diffraction ($\text{CuK}\alpha$ radiation). For the following compositions we observed at 300 K as well as at 77 K only weak luminescence from the activator involved unless stated otherwise. The classification will become clear in the next section. Activator concentrations are 0.5–1.0 mole %.

- a. $\text{YPO}_4\text{-W}^{6+}$.
- c. $\text{ZrO}_2\text{-Eu}^{3+}$; $\text{ZrP}_2\text{O}_7\text{-Eu}^{3+}$.
 $\text{CaSO}_4\text{-Ti}^{4+}$; $\text{CaSO}_4\text{-V}^{5+}$

[yellow luminescence with moderate efficiency; the quenching temperature is much lower than for the emission of $\text{YP}_{1-x}\text{V}_x\text{O}_4$, 720 K (4)].

- $\text{YPO}_4\text{-Ti}^{4+}$.
 $\text{Mg}_3\text{TeO}_6\text{-Nb}^{5+}$.
- d. $\text{Y}_2\text{O}_3\text{-Pb}^{2+}$, $\text{Y}_2\text{SiO}_5\text{-Pb}^{2+}$,
 $\text{Ba}_2\text{SiO}_4\text{-Tl}^+$, $\text{BaSi}_2\text{O}_5\text{-Tl}^+$,
 $\text{ZrO}_2\text{-Bi}^{3+}$.

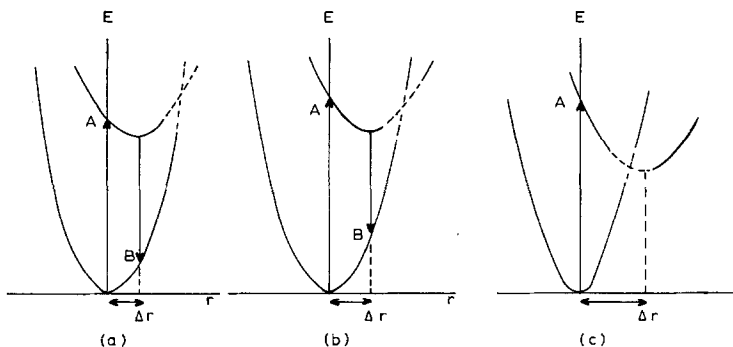


FIG. 1. Schematic configuration coordinate diagrams. (a) Mott-Seitz model with the intersection of the two curves above A. (b) Dexter-Klick-Russell model with the intersection below A. (c) Seitz model with the minimum of the excited state outside the curve of the ground state. Arrow upwards: absorption (excitation); arrow downwards: emission.

Tb in ZrO_2 appeared to be tetravalent (5). Further experimental data were taken from the literature.

3. Theoretical Model

The model presented before (1, 2) is based on the well-known configuration coordinate diagram. Examples of those diagrams are given in Fig. 1. Absorption of radiation (excitation of luminescence) is indicated by the arrow upwards, emission by the arrow downwards. Thermal quenching of the luminescence occurs if the system can be excited thermally from the bottom of the "excited curve" to the intersection of the two curves. This is the Mott-Seitz model (Fig. 1a). If the intersection level lies below the level reached after absorption (A in Fig. 1b), radiationless transition to the ground state is possible even at low temperatures (Dexter-Klick-Russell model). The situation of Fig. 1c (the Seitz model which explains the absence of luminescence) clearly does not permit a radiative return to the ground state.

The difference between the equilibrium distance of the ground and excited state is called Δr (see Fig. 1). The larger the value of Δr the lower the quenching temperature of the luminescence will be.

We assumed that the quenching temperature (T_q) of the luminescence of a given type will be high, if the center is built into a rigid lattice so that Δr is expected to be as small as possible. The centers were divided into two groups: those with $\Delta r > 0$ (charge-transfer transitions) and those with $\Delta r < 0$ (Rydberg transitions). If a high T_q is desired, centers with $\Delta r > 0$ should be

substituted for smaller ions (e.g., Eu^{3+} for Lu^{3+}) and centers with $\Delta r < 0$ for larger ions (e.g., Eu^{2+} for Ba^{2+}). This is compatible with the requirement to have Δr as small as possible (1, 2). This is summarized in Table I.

Up till here it has been assumed that charge compensation is not required. We will now turn to systems where the luminescent cations have a charge different from the charge of the host lattice cation whose site they occupy. The luminescent centers may bear an effective positive charge (e.g., Tb^{3+} on Ca^{2+} sites) or an effective negative charge (e.g., Eu^{3+} on Zr^{4+} sites). We distinguish four different cases, viz,

- Effective charge positive and $\Delta r > 0$. Examples are Eu^{3+} in alkaline-earth compounds and tungstate groups in phosphates.
- Effective charge positive and $\Delta r < 0$. Examples are Ce^{3+} or Tb^{3+} in alkaline-earth compounds.
- Effective charge negative and $\Delta r > 0$.

TABLE I

SUMMARY OF MODEL WITHOUT EFFECTIVE CHARGE ON THE LUMINESCENT CENTER

	$\Delta r < 0$ (e.g., Tl^+ , Tb^{3+})	$\Delta r > 0$ (e.g., Eu^{3+} , WO_4)
Activator > host lattice ion	T_q low	T_q high
Activator < host lattice ion	T_q high	T_q low
Lattice with small ions with high charge	T_q high	T_q high

Examples are Eu^{3+} in Zr^{4+} -compounds and Ti^{4+} or V^{5+} in sulfates.

d. Effective charge negative and $\Delta r < 0$. Examples are Tl^+ in alkaline-earth compounds and Pb^{2+} in Y_2O_3 .

This classification was also used in the section on Experimental Results. No mechanism for the way in which the charge compensation is realized is discussed at the moment. We will now discuss our expectations for the thermal quenching of the luminescence within each of these groups.

a. There are two reasons why we do not expect high T_q (i.e., efficient luminescence at higher temperatures) within this group. Let us consider a specific example, viz, Eu^{3+} in a Ca^{2+} compound. In the first place the surroundings of the Eu^{3+} center contain relatively low-charged ions (Ca^{2+}) resulting in a large value of Δr , especially if their concentration in the lattice is high. In the second place we note that the equilibrium distance in the ground state will be relatively small due to the effective positive charge of the central ion [compare calculations like those in Ref. (6)]. This does not hold for the excited state (charge-transfer), where now the surrounding anions become effectively positive. As a consequence Δr will be larger than in the case without effective charges.

Conclusion: In group a we do not expect a high T_q .

b. The first argument used above for group a is still valid. The second, however, is not. The optical transition is not a charge-transfer but a Rydberg transition. In the ground state the equilibrium distance is relatively short (effective positive charge). Since $\Delta r < 0$, the absolute value of Δr will be relatively small: the lattice has already contracted in the ground state.

Conclusion: In group b we expect a high T_q , if the number of cations for which the activator is substituted (i.e., Ca^{2+} , if we consider Tb^{3+} in a Ca^{2+} compound) in the formula unit is not too high; i.e., if cations of another type are also present.

c. If the effective charge of the central ion of the luminescent center is negative (e.g., Eu^{3+} in a Zr^{4+} -compound) the surroundings of the center are relatively rigid and promote a small value of Δr . There are other reasons, however, why we do not expect high values for T_q in this group and the next group. If the effective charge of the cation is negative, the potential field at the surrounding anions is low. As a consequence the

charge-transfer transition is situated at relatively low energy (7). If the charge-transfer level is situated at low energy, the thermal deactivation energy decreases and T_q will be low. This has been substantiated for a number of systems (2, 7).

Conclusion: In group c we do not expect a high T_q .

d. If Δr is negative, its absolute value will be rather large in group d for the same reason why it is small in group b. The ground state has a large equilibrium distance (effective negative charge) so that a considerable contraction is possible after excitation. This is counteracted by the relatively rigid surroundings (compare discussion for group c). Our conclusion is, therefore, not very definite: In group d a necessary, but perhaps not sufficient condition for a high T_q is the requirement that the lattice is very rigid. This section is summarized in Table II.

4. Comparison with Experimental Data

Group a. We are not aware of luminescent materials within this class with high T_q . This agrees with our prediction. The case of Eu^{3+} in alkaline-earth compounds is a good example. Their luminescence does not show a high T_q for excitation into the charge-transfer band of Eu^{3+} (i.e., $\Delta r > 0$). The phosphor $\text{Ca}_3(\text{VO}_4)_2\text{-Eu}^{3+}$ seems to be an exception to this rule (8). This is not the case upon closer inspection. In this compound the vanadate group is excited by ultraviolet excitation. This process is followed by energy transfer from the vanadate group to the Eu^{3+} ion, so that the Eu^{3+} ion is not excited in its charge-transfer state (where radiationless losses may occur), but in one of the levels of the

TABLE II
SUMMARY OF PREDICTIONS FOR T_q IN THE CASE OF LUMINESCENCE FROM CENTERS BEARING AN EFFECTIVE CHARGE

	Effective charge	
	Positive	Negative
$\Delta r > 0$	Group a T_q low	Group c T_q low
$\Delta r < 0$	Group b T_q high (in rigid lattices)	Group d T_q high (in rigid lattices)

$4f^6$ configuration (where radiationless decay is rather improbable) (1).

Other groups with charge-transfer excitation do not luminesce either in hosts where they are effectively positive. Some examples are: Ti^{4+} in ZrO_2 is a very efficient luminescent center (9), the isoelectronic Nb^{5+} in ZrO_2 , however, is not (10). V^{5+} in YPO_4 is efficient (4), the isoelectronic W^{6+} in YPO_4 is not.

Group b. Our model predicts the possibility of luminescence with high T_q in this group. Many examples have been found indeed. Among these are the phosphors $Sr_3(PO_4)_2-Ce^{3+}$, $Ca_2MgSi_2O_7-Ce^{3+}$ and $Ca_2Al_2SiO_7-Ce^{3+}$ (3), $Sr_3(PO_4)_2-Tb^{3+}$ (11), Tb^{3+} in alkaline-earth borates (12), Tb^{3+} in Mg_2SiO_4 (13), Sb^{3+} in calcium halophosphate (14), Bi^{3+} in several calcium compounds (15, 16) and Eu^{2+} in the system $SiO_2-Al_2O_3$ [where it bears an effective positive charge being an interstitial ion (17, 18)]. In agreement with the prediction the concentration of ions for which the activator is substituted is not high in the host lattices mentioned, because all of them contain other ions too (phosphorus, silicon, etc.).

Group c. Up to our knowledge no high T_q has been reported for systems where activator ions with charge-transfer excitation bear an effective negative charge. Kotera, for example, observed in sulfates only efficient luminescence for W^{6+} and Mo^{6+} , and not for ions with lower charge (19). The quenching temperature of the luminescence of $CaSO_4-V^{5+}$ was found by us to be low. Further we found that Ti^{4+} in YPO_4 practically does not luminesce, whereas the isoelectronic V^{5+} is very efficient (4) and that Nb^{5+} in Mg_3TeO_6 luminesces only weakly, whereas the isoelectronic W^{6+} is very efficient in this lattice (20). Eu^{3+} in Zr^{4+} -compounds does not yield efficient phosphors. All this agrees with the prediction.

Group d. For this group the occurrence of high T_q is not excluded, if the lattice is rigid. A few examples of efficient luminescence with high T_q are known within this group, viz, Tl^+ in $Ca_3(PO_4)_2$ (21) and Cu^+ in alkaline-earth phosphates (22). It is interesting to note that Tl^+ in the less rigid $Ba_3(PO_4)_2$ has a much lower efficiency (21) and that T_q of the Tl^+ emission of $Ca_3(PO_4)_2-Tl^+$ depends on the lattice parameters of "modified" $Ca_3(PO_4)_2$ (23). Introduction of Sr^{2+} gives larger lattice parameters (and lower T_q), introduction of Zn^{2+} gives smaller lattice parameters (and higher T_q). This follows also from our model.

These examples, however, are exceptional.

In general T_q is low within this group (see also our experimental results).

5. Discussion

In general the agreement between the predictions of our model and the experimental data is good, especially if the roughness of the model is taken into account. We can explain in this way the fact that ions with $\Delta r > 0$ do not luminesce efficiently, if they bear an effective charge, whereas those with $\Delta r < 0$ luminesce under certain conditions. The results may be handled as guiding rules, if one tries to find new efficient phosphors with characteristic emission.

It is at first sight surprising that the compensating defect does not play a role in our model. It seems impossible to ascribe this fact merely to dissociation of the luminescent center and its compensation [see also Ref. (24)]. It is difficult to account for the role of the compensating defects in this general model, because many types of them are possible even within one of the four groups. In general, however, the defect influences only one specific side of the luminescent center, whereas our considerations involve its complete surroundings. Due to the roughness of our model we feel that at this moment it is impossible to account for the role of the compensating defects in a more elaborate way.

Acknowledgment

The author is indebted to Mr. W. Hordijk for the preparation of the samples mentioned in Sect. 2.

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