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On the quenching of the luminescence of the trivalent cerium ion

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Abstract

The Ce(III) ion shows luminescence in many solids and in solution, but sometimes the luminescence is unexpectedly absent. Examples are La_2O_3:Ce(III), La_2O_2S:Ce(III), and the recently reported complexes of Ce(III) with carboxylate-containing ligands. This paper tries to find a general approach to the non-radiative transitions in a diverse series of Ce(III)-containing samples. It turns out that Ce(III) luminescence will appear if the optical absorption of its surroundings is at high energy, preferentially in the vacuum ultraviolet. If the absorption is at lower energy, photoionisation or electron transfer may quench the luminescence.

Introduction

The Ce(III) ion has, from a spectroscopical point of view, a very simple electron configuration in the ground and excited state: $4f^1$ and $5d^1$, respectively. The $4f^1$ state is split by spin–orbit coupling into a doublet ($^2F_{5/2}$, $^2F_{7/2}$) with an energy difference of 2000 cm^{-1}. The $5d^1$ state is split by the crystal field into several components with an averaged total splitting of some 10 000 cm^{-1} [1]. The 4f–5d transitions are fully allowed and turn up in the spectra as broad bands, sometimes with vibrational structure [2]. The emission consists of a transition from the lowest crystal-field component of the $5d^1$ state to the ground state. The life time is short (~30 ns, ref. 3). The emission band has two maxima due to the spin–orbit splitting of the ground state.

The Ce(III) ion is a model ion for the study of luminescence in solids [1, 4]. As far as the radiative emission is concerned, this is related to its simple electronic structure. How far is this also true for possible non-radiative transitions from the excited state to the ground state?

At first sight the Ce(III) ion seems to be an efficient luminescent ion [1, 4]. It shows efficient luminescence at room temperature in many solids, like borates, silicates, phosphates. Also in aqueous solution it emits efficiently [4, 5], as it does in polymers [6] and organometallic complexes [7]. However, sometimes the luminescence is quenched. An old example is Ce(III) in titanates, vanadates and tungstates [8]. Recently [5] it was reported that carboxylic-acid-containing ligands quench the Ce(III) emission completely, but no explanation was or could be offered. In our laboratory we observed that the, until now overlooked, simple composition La_2O_3:Ce(III) does not luminesce, not even at 4.2 K. Japanese workers came to the same conclusion for La_2O_2S:Ce(III) [9]. The latter observations are the more remarkable since many rare earth ions, also those with 4f–5d excitation transitions, luminesce efficiently in La_2O_3 and La_2O_2S.

In this paper we try to present an onset to an understanding of these phenomena. It is clear that our knowledge of non-radiative transitions is in a state which does not allow a quantitative approach of many diverse systems [10]. Therefore we use a qualitative one with the single-configurational-co-ordinate diagram as the basis physical model.

Two cases of Ce(III) luminescence quenching will be omitted. The first is trivial, namely the case that the Ce(III) absorption bands are overlapped by the host lattice itself. The second is the case of concentration quenching. This is due to energy migration over the Ce(III) ions to quenching centres [11], and depends on the interaction between Ce(III) ions.

Experimental and results

A sample of La_2O_3:Ce(III) with 0.5 at.% Ce was prepared by precipitating (La, Ce) oxalate. The

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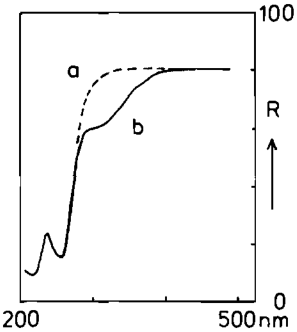

Fig. 1. Diffuse reflection spectra at 300 K of La oxalate (a) and (La, Ce) oxalate (b).

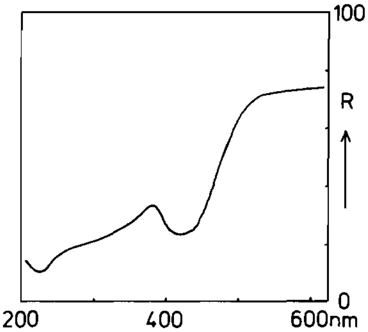

Fig. 2. Diffuse reflection spectrum at 300 K of La_2O_3:Ce(III).

precipitate was decomposed and finally fired at 1400 °C in a strongly reducing atmosphere (H_2). The product has the A-type rare earth oxide structure, is yellow, and does not luminescence, not even at 4.2 K. Figure 1 gives the diffuse reflection spectrum of La oxalate, (La, Ce) oxalate, and Fig. 2 that of La_2O_3:Ce. Luminescence studies were performed at 4.2 K using a Perkin-Elmer spectrofluorometer 44-B.

Discussion

First we want to discuss why the cerium ion in the La_2O_3 sample has to be considered trivalent. In the first place it is unlikely that in the strongly reducing atmosphere applied the cerium ion would be tetravalent. Also Ce_2O_3 can be prepared in this way; just as Ce_2O_3 is oxidized rapidly at the atmosphere [12], our yellow sample turns slowly colourless at the ambient.

In the second place the position of the first absorption band (430 nm, Fig. 2) is in line with expectation. For La_2O_3:Pr(III) the lowest 4f–5d transition is at 290 nm [13]. It has been shown that the corresponding Ce(III) transition is to be expected at ~ 12 500 cm^{-1} lower energy [14]. This predicts the first absorption band for Ce(III) in La_2O_3 at about 450 nm, in good agreement with experiment (430 nm). Finally, for Ce(III) in the lanthanide oxysulfides with the same crystal structure this absorption band has been reported at a very similar spectral position, viz. 455 nm [9].

The absence of luminescence in the case of La_2O_3:Ce(III) and La_2O_2S:Ce(III) with the first absorption band at 430 and 455 nm, respectively, is in contradistinction with the efficient Ce(III) luminescence of $Y_3Al_5O_{12}$:Ce(III) where this band is at 460 nm [15].

Several explanations have been put forward to explain the quenching of Ce(III) luminescence, viz.

(i) quenching by photoionisation [16]

(ii) quenching by electron transfer [8]

(iii) large parabolae offset in the configurational coordinate diagram [9, 17].

In the first explanation the 5d electron of the excited Ce(III) ion is promoted into the conduction band because the relevant 5d level is situated in this band; in the second this electron is promoted to one of its nearest or next-nearest neighbours; in the third the 5d electron remains formally on the Ce(III) ion, but due to its diffuseness its radius is relatively large.

A first consequence of this would be that the Ce(III) ion luminesces efficiently and with relatively small Stokes shift in typically ionic coordination. This is in fact the case. Here we mention the following examples: LaF_3 [18], YF_3 [18], $LiYF_4$ [8], CaF_2 [19], many borates [20], $CaSO_4$ [2], YPO_4 and $LaPO_4$ [1], $[Ce \subset 2.2.1]^{3+}$ cryptate [4]. A remarkable exception is Rb_2NaYF_6:Ce with a 4f–5d transition at low energy and a large Stokes shift [21]. Strong arguments have been given why Ce(III) in this compound is more covalently bound than in other fluorides [8, 21].

As far as we are aware, the Stokes shift of the Ce(III) emission is never so large that it can explain quenching at low temperatures. This is illustrated by Ce(III) in a loose structure like glass where the Stokes shift is up to ~ 5000 cm^{-1} [22], or in an even looser medium like aqueous solutions where the Stokes shift reaches values up to 8000 cm^{-1} [4, 5]. However, these systems luminesce with reasonable efficiency.

Therefore the absence of Ce(III) luminescence at low temperatures must be ascribed to effects where the excited 5d electron more or less leaves the cerium ion. Examples of this are the couples Ce(III) + Eu(III) and Ce(III) + VO_4^{3-}. Quenching occurs via a so-called electron-transfer state [8, 17], which can be represented in these examples as Ce(IV) + Eu(II) and Ce(IV) + V(IV). In our opinion this can also explain the absence of Ce(III) luminescence in complexes with carboxylic-acid-containing ligands [5].

These ligands show characteristically optical absorption at about 250 nm due to n → π* transitions [23, 24]. Their lowest excited state is a π*-antibonding orbital belonging to carbon and oxygen. We propose that the electron-transfer process consists of the transition of the excited 5d electron to the π* orbital.

This is similar to what we have proposed for the Ce(III) nitrate couple [25]. In this case the nitrate absorption is at about 310 nm. The electron transfer can even be observed in the absorption spectrum at energies below the nitrate absorption. No luminescence is observed.

The ligand absorption transition can be correlated to the presence or absence of luminescence. For the pure ligand absorption the position of the lowest absorption band is 310 (nitrate), ~275 (vanadate) [26], ~250 (carboxylate), ~160 (borate, phosphate) nm [27]. Only for Ce(III) in borates and phosphates is luminescence observed, in solids [1] as well as in solutions [5], not for any of the other ligands. Obviously the lowest excited state of the ligand has to be at very high energy for luminescence to be observable.

In view of these results we investigated the precursor in the La_2O_3:Ce(III) synthesis, viz. (La, Ce) oxalate. Undoped La oxalate shows a luminescence which is very similar to that reported by Maria and McGlynn [28] for other metal oxalates. The band in the reflection spectrum at 260 nm (see Fig. 1) corresponds to the first absorption band of the oxalate group. La oxalate doped with 0.5 at.% Ce does not luminesce at room temperature in agreement with the results discussed above. At 4.2 K a weak luminescence appears. The intensity of the emission observed in undoped La oxalate is reduced to about 1/3. So the presence of Ce(III) quenches the oxalate emission. Excitation at 305 nm, in the additional band due to the presence of cerium (see Fig. 1), yields a weak blue emission with two weak features separated by some 1500 cm^{-1} (the oxalate stretching mode [28]). The Stokes shift is about 10 000 cm^{-1}. The large shift if the oxalate levels due to the presence of Ce(III), which ion is nearly as large as La(III), indicates an interaction between the excited states of the oxalate group and the Ce(III) ion. The spectral features observed may well be due to a Ce(III) oxalate charge-transfer transition. The luminescence efficiency involved is low. As far as absorption is concerned, there is a close analogy with the Ce(III) nitrate couple.

Let us now turn to the absence of luminescence in La_2O_3:Ce(III). The optical absorption edge of the host is situated at 230 nm [29]. For the isostructural La_2O_2S it is at 280 nm [9]. Yokono *et al.* have ascribed the absence of luminescence in La_2O_2S:Ce(III) to a large offset in the parabolae configurational coordinate diagram [9]. However, in view of the arguments given above this seems less probable.

A better explanation may originate from a consideration of the experiments by Pedrini *et al.* [30] and Hamilton *et al.* [31] on $Y_3Al_5O_{12}$:Ce(III). It is well known that excitation into the lowest Ce(III) level yields efficient Ce(III) luminescence; however, for excitation into the higher levels of Ce(III) the efficiency drops down [1]. In refs. 30 and 31 it is shown that the one-but-lowest level is already close to the conduction band. Figure 3 gives a simplified energy level diagram. This implies that excitation in the higher levels results in photoionisation which reduces the luminescence yield considerably. In view of this we ascribe the absence of luminescence in La_2O_3:Ce(III) and La_2O_2S:Ce(III) to photoionisation, i.e. we assume that the lowest excited Ce(III) level is already in the conduction band.

That Ce(III) is not very stable in La_2O_3 follows also from the fact that La_2O_3:Ce(III) is oxidised at the ambient and from the existence of many compositions in the CeO_x phase diagram [32]. For Y_2O_3:Ce(III), with a different crystal structure, we also did not observe any luminescence at 4.2 K.

The series Ln_2O_2S (Ln = La–Lu) is isostructural. For Y_2O_2S:Ce(III) and Lu_2O_2S:Ce(III) Yokono *et al.* [9] observed a strongly Stokes-shifted emission in the red below 170 K. The Stokes shift is about 7000 cm^{-1}. Their excitation spectra show that excitation of this emission is only possible in the lowest absorption band of Ce(III). It may be that in Y_2O_2S and Lu_2O_2S the bottom of the conduction band is higher than in La_2O_2S. It may also be that this red emission is due to impurity-trapped exciton recombination [33].

In principle there is no difference between quenching by electron transfer and quenching by photoionisation. The former originates from molecular science, the latter from the solid state field. This implies that in our model there is no difference between quenching of the Ce(III) emission by carboxylate ligands and by photoionisation. Therefore, the red emission in Y_2O_2S and Lu_2O_2S can be compared

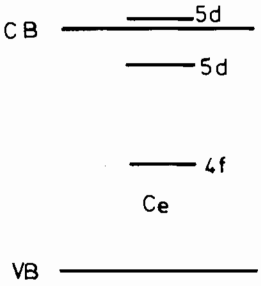

Fig. 3. Energy level scheme of $Y_3Al_5O_{12}$:Ce(III). VB: valence band; CB: conduction band.

with that induced by cerium in La oxalate. In both cases the weakly emitting level cannot be simply the lowest crystal-field level of the excited $5d^1$ configuration of the Ce(III) ion. The emitting level consists of a state in which the 5d orbital is strongly mixed with orbitals of the surroundings.

In conclusion, the Ce(III) ion may be expected to luminesce in surroundings which have optical absorption far in the ultraviolet. However, if this optical absorption shifts to lower energies, quenching by electron transfer or photoionisation becomes a competing process which rapidly eliminates the luminescence.

There is, of course, an important exception to this rule, viz. the situation in which the 5d electron of Ce(III) is strongly localized, or, in other words, if the trivalency of cerium is stabilised. The most obvious example of this occurs in solids where the Ce(III) ion may have an effective positive charge. This is the case if Ce(III) substitutes for a divalent ion, like, for example, Ca^{2+}. In such a situation photoionisation or electron transfer may not occur. The literature gives some interesting examples.

First we mention the case of $CaSO_4$:Ce(III), V(V) [34]. In this composition the luminescent species do not quench each others luminescence, like in YVO_4:Ce(III) [8]. This has been ascribed to the presence of the effective charges on Ce(III) and V(V), which make the electron transfer energetically less favourable.

In the second place we cite the efficient Ce(III) emission in some covalent hosts. Examples are MgS, CaS and CaSe [35]. The small Stokes shift of the emission $(-1000\ \text{cm}^{-1})$ and the occurrence of vibrational structure in the spectral bands point indeed to localisation. Photoionisation does not occur, which can be ascribed to the effective positive charge of Ce(III) in these compounds.

It is obvious that electron-donating ligands or ions will also not quench the Ce(III) luminescence, because the electron-transfer state will be at high energy.

The present considerations seem to be able to explain qualitatively the absence or presence of Ce(III) emission in cerium-containing compositions.

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