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Luminescence of the Eu^{3+} Ion in Zr^{4+} Compounds

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The luminescence of the Eu^{3+} ion in some Zr^{4+} compounds is reported in order to study the influence of the effectively negative charge of the Eu^{3+} ion on the quantum efficiency for charge-transfer excitation. This effectively negative charge of the Eu^{3+} ion does not in principle enhance radiationless relaxation rates in the excited charge-transfer state, but the presence of vacancies in the structure may lower the efficiency considerably. For the Eu^{3+} luminescence in ZrO_2 and ZrP_2O_7 the quantum efficiencies amount to about 30% and 60%, respectively. In these compounds the presence of vacancies may account for these values. In Li_2ZrO_3:Eu^{3+} with a relatively low Li^+ concentration it seems as though the partial incorporation of the Eu^{3+} ions on a Li^+ site accounts for the low efficiency (about 10% at room temperature). The incorporation of the Mg^{2+} ion as a charge compensator in the Li_2ZrO_3 lattice increases the quantum efficiency up to at least 60%.

Introduction

For years considerable efforts have been made in the search for lamp phosphors based on the luminescence of trivalent rare-earth (RE) ions. In these phosphors the RE ions are incorporated into compounds with a sublattice of trivalent cations, usually Gd^{3+}, La^{3+}, or Y^{3+}.[1] It appears that the use of ions with the same valency and a comparable size gives rise to efficient luminescent materials.

Recently we have started a study that deals with the influence of the effective charge of the RE ions on their luminescence, and especially on the quantum efficiency for charge-transfer (CT) excitation (q_{CT}). RE ions were incorporated into calcium compounds, since the Ca^{2+} ion and the RE ions have similar ionic radii.[2] In $CaSO_4$, for example, it was shown that the Eu^{3+} ion and the Ce^{3+} ion have interesting spectroscopic properties.[3] The Eu^{3+} ion exhibits a strong radiationless relaxation in the excited state, whereas for the Ce^{3+} ion the radiationless relaxation is almost absent. These observations were correlated to the effectively positive charge of the RE ions and the different nature of the excited states of both ions. Furthermore, it appeared that charge compensators like Na^+ or P^{5+} can influence the spectroscopic properties and may promote the incorporation of RE ions in the lattice. Other authors have also reported on the influence of charge compensating defects on the luminescence of RE ions.[4-9]

In this paper we report on the luminescence of the Eu^{3+} ion in compounds in which the Eu^{3+} ion has an effectively negative charge. This situation is realized by incorporating the Eu^{3+} ion in compounds with a sublattice of Zr^{4+} ions. The Eu^{3+} ion has about the same ionic radius as the Zr^{4+} ion, but its charge is lower. The Zr^{4+} compounds that have been investigated are ZrO_2, ZrP_2O_7, and Li_2ZrO_3. The spectral characteristics of the Eu^{3+} luminescence of the compounds ZrP_2O_7 and Li_2ZrO_3 will be discussed, whereas the luminescence of ZrO_2:Eu^{3+} has been discussed in the literature.[10,11] Furthermore q_{CT} of the Eu^{3+} luminescence is discussed.

Experimental Section

For the preparation of the powders the following starting materials were used: Eu_2O_3 (Highways Int., 99.999 %), $H_2C_2O_4\cdot 2H_2O$ (Baker Reagents), $MgCO_3\cdot Mg(OH)_2\cdot 3H_2O$, Li_2CO_3, $ZrOCl_2\cdot 8H_2O$ (50 ppm Ti), $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, and HCl, 37% (all Merck, p.a.). Firing procedures were carried out in air.

ZrO_2:Eu^{3+} (1 mol %) was prepared by first dissolving Eu_2O_3 in a small amount of hydrochloric acid. This solution was than diluted with distilled water. $ZrOCl_2\cdot 8H_2O$ was dissolved in this solution. An aqueous solution of $H_2C_2O_4\cdot 2H_2O$ was added under stirring to the solution containing Zr^{4+} and Eu^{3+} ions. The resulting precipitate was washed with distilled water and fired for 2 h at 1200 °C, followed by a refiring for 2 h at 1400 °C.

The powders of ZrP_2O_7:Eu^{3+} (0.1, 0.5, and 1.0%) were prepared by firing the starting materials with 5 mol % excess of $(NH_4)_2HPO_4$ for 2 h at 1000 °C, and refiring for 2 h at 1000 °C.

For the synthesis of the Li_2ZrO_3 powders with 0.5 mol % of Eu^{3+} the compound $ZrOCl_2\cdot 8H_2O$ was decomposed into ZrO_2 by firing for 2 h at 800 °C. Then the starting materials were mixed with 5 (sample A) and 10 mol % (sample B) excess of Li_2CO_3, and fired for 2 h at 800 °C, followed by a refiring for 3 h at 1000 °C. The excesses of Li_2CO_3 were used to compensate for the losses of volatile Li_2CO_3 during the firing. The samples were prepared with different amounts of excess of Li_2CO_3 because of the changing spectral features. For the preparation of Li_2ZrO_3:Eu^{3+},Mg^{2+} (0.5 mol %) the excess of Li_2CO_3 amounted 5 mol %.

The structure of the powders was checked by X-ray powder diffraction using Cu Kα radiation.

The instrumentation for the optical measurements has been described in refs 3 and 12. The optical measurements were carried out at temperatures from 4.2 (liquid helium temperature, LHeT) to 300 K (room temperature).

Results and Discussion

In this section of luminescence of the Eu^{3+} ion in ZrP_2O_7 and Li_2ZrO_3 is discussed. The luminescence of ZrO_2:Eu^{3+} has been discussed in the literature.[10,11] It was shown that the luminescence of the Eu^{3+} ion in ZrO_2 is complex due to different charge-compensating mechanisms. The additional information on ZrO_2:Eu^{3+} was obtained from our spectra in the position of the maximum of the CT band

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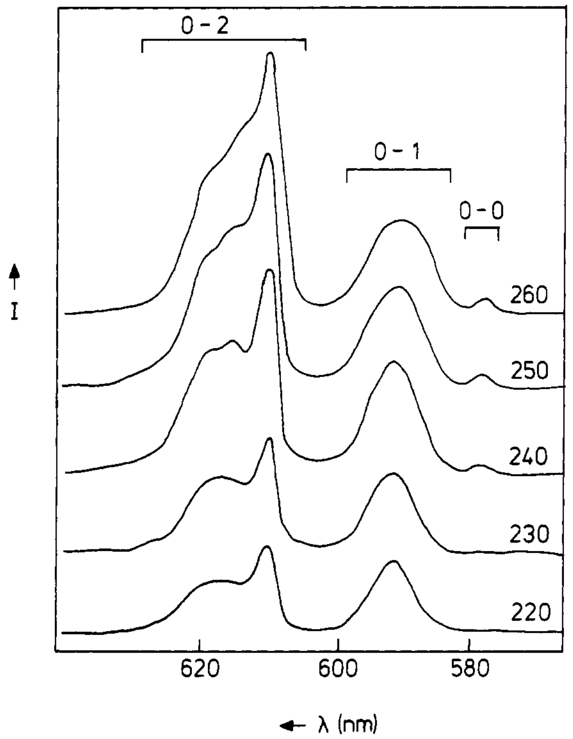

Figure 1. Emission spectrum of ZrP_2O_7:Eu^{3+} in the $^5D_0 \rightarrow {}^7F_{0,1,2}$ region under excitation at different wavelength in the CT band at room temperature. I gives the relative intensity. The figures denote the excitation wavelength.

of the Eu^{3+} ion (about 260 nm). This value was derived from the diffuse reflection spectrum and the excitation spectrum of the Eu^{3+} emission. The q_{CT} of the Eu^{3+} luminescence in ZrO_2 amounts to about 30%.

ZrP_2O_7:Eu^{3+}. The diffuse reflection spectrum of undoped ZrP_2O_7 shows an intense absorption band at about 200 nm with a shoulder toward longer wavelengths. The absorption at 200 nm is due to a CT transition in the zirconate group; the corresponding emission band has a maximum at 280 nm. These data are in agreement with literature data on this zirconate luminescence.[13,14] The absorption that is observed as a shoulder at longer wavelengths is ascribed to the presence of Ti^{4+} in the sample. This is due to the presence of Ti^{4+} in the starting material $ZrOCl_2 \cdot 8H_2O$. In ZrP_2O_7:Eu^{3+} an extra absorption band is observed with a maximum at about 220 nm. In the excitation spectrum of the Eu^{3+} luminescence the 220-nm absorption band is dominant and is ascribed to the Eu^{3+}–O^{2-} CT band reported before.[15] In the shorter wavelength region a shoulder is observed, probably due to zirconate excitation. After excitation in this region mainly zirconate emission is observed, pointing to an inefficient energy transfer from the zirconate to the Eu^{3+} ion.

The Eu^{3+} emission under excitation in the UV region (see Figure 1) consists of relatively broad lines due to transitions from the $^5D_0$ level of the Eu^{3+} ion. The pyrophosphate group has vibrational frequencies up to 1100 cm^{-1}, inducing fast radiationless relaxation from the higher ^5D levels to $^5D_0$. The shape of the emission spectrum depends on the excitation wavelength. Going from shorter to longer excitation wavelength the $^5D_0 \rightarrow {}^7F_2$ emission gains intensity relative to the $^5D_0 \rightarrow {}^7F_1$ emission.

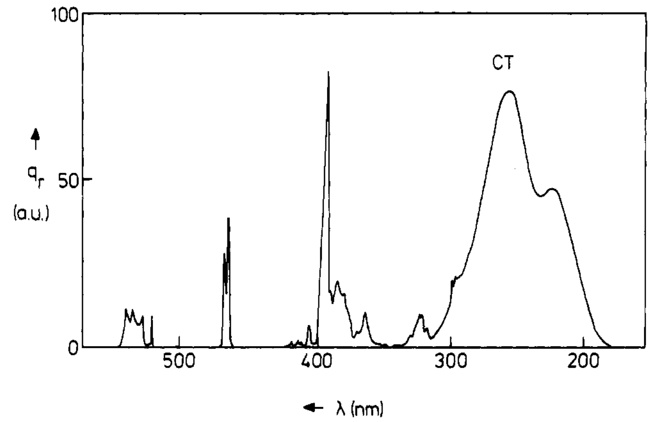

Figure 2. Excitation spectrum of the Eu^{3+} emission in Li_2ZrO_3, sample A, at room temperature. λ_{em} = 608 nm. q_r gives the relative quantum output in arbitrary units (au).

At LHeT an additional Eu^{3+} emission is observed under UV and 395-nm excitation ($^7F_0 \rightarrow {}^5L_6$). Since this emission is not observed at room temperature under $^7F_0 \rightarrow {}^5L_6$ excitation, this Eu^{3+} emission is probably quenched at that temperature. This suggests that this low-temperature emission is due to an Eu^{3+} ion in a concentrated Eu^{3+} compound. In fact, the observed emission spectrum resembles that of $LaPO_4$:Eu^{3+}.[16] Since $LaPO_4$ is isostructural to $EuPO_4$, the low-temperature emission is ascribed to Eu^{3+} in $EuPO_4$. Apparently the solubility of the Eu^{3+} ion in ZrP_2O_7 is limited. Even at 0.1 mol % of Eu^{3+} this second phase was observed.

Returning to the emission of Eu^{3+} in ZrP_2O_7 (see Figure 1), we note the presence of electric-dipole transitions ($^5D_0 \rightarrow {}^7F_{0,2}$). In the ZrP_2O_7 lattice, however, an octahedral site with S_6 site symmetry is available to the Zr^{4+} ion;[17] in the latter symmetry the electric-dipole transitions are forbidden. It seems, therefore, that in the ZrP_2O_7 lattice the incorporation of the Eu^{3+} ion on a Zr^{4+} site distorts the surroundings of the cation. In view of the need for charge compensation, it is likely that the distortion is due to an O^{2-} vacancy near the Eu^{3+} ion. An O^{2-} vacancy will lower the symmetry of the cation site from S_6 to a point symmetry without an inversion center, and electric-dipole transitions will become allowed. Since the Eu^{3+} emission changes under different excitation wavelengths in the UV region, we conclude that at least two types of Eu^{3+} ions are present in ZrP_2O_7. This might be due to different positions of the O^{2-} vacancy, relative to the Eu^{3+} ion. Each type shows considerable inhomogeneous broadening (see also discussion in ref 14).

Li_2ZrO_3:Eu^{3+} (Mg^{2+}). Undoped Li_2ZrO_3 is a colorless compound with an intense absorption band at about 200 nm. Under irradiation in this region at room temperature no emission is observed. A weaker absorption band that is observed as a shoulder at longer wavelengths is probably due to the presence of Ti^{4+} in the sample. The incorporation of the Eu^{3+} ion in Li_2ZrO_3 gives rise to spectral characteristics that are dependent of the amount of Li_2CO_3 in the mixture of the starting materials.

First we discuss the luminescence of sample A. A comparison of the diffuse reflection spectrum of sample A with that of the undoped Li_2ZrO_3 shows that the incorporation of the Eu^{3+} ion in the lattice gives rise to an absorption band at about 250 nm, which is observed as a shoulder on

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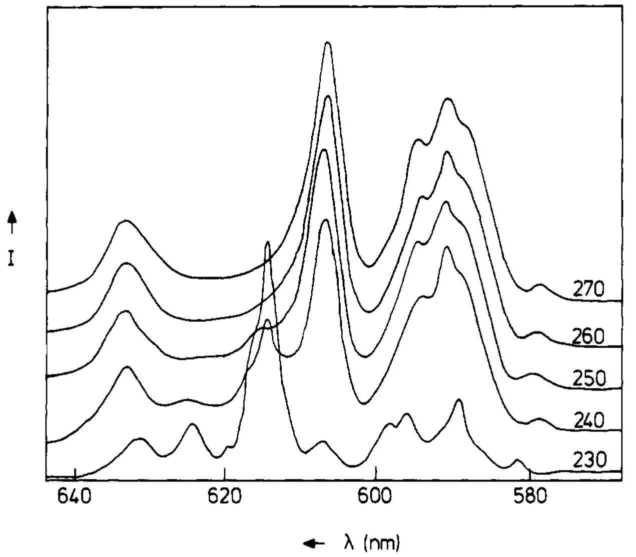

Figure 3. Emission spectrum of $Li_2ZrO_3:Eu^{3+}$, sample A, at room temperature in the $^5D_0 \rightarrow {}^7F_{0,1,2}$ region under excitation at different wavelengths in the CT band. In the figure the $^5D_0 \rightarrow {}^7F_J$ transitions are indicated. The figures denote the excitation wavelength.

Table I. Mechanisms for Charge Compensation in $Li_2ZrO_3:Eu^{3+}(Mg^{2+})$

sample	centers	symbol	CT band, nm/cm^{-1}	rel occurrence (est), %
$Li_2ZrO_3:Eu^{3+}$, Mg^{2+}	$Eu'_{Zr} + Mg_{Li}$	II	230/43 000	95
	$(Eu'_{Zr}{\cdot}Li_i)^x$	III	230/43 000	5
$Li_2ZrO_3:Eu^{3+}$ (sample B)	Eu'_{Zr}	II	230/43 000	50
	$Eu'_{Zr} + Li_i$	III	230/43 000	50
$Li_2ZrO_3:Eu^{3+}$ (sample A)	Eu_{Li}	I	250/40 000	60
	Eu'_{Zr}	II	230/43 000	40

the host-lattice absorption. It overlaps with the absorption band from the Ti^{4+} contamination.

In sample A we note the presence of a Eu^{3+} emission which is observed only at low temperatures both under CT and $^7F_0 \rightarrow {}^5L_6$ excitation. As in $ZrP_2O_7:Eu^{3+}$, this emission is ascribed to Eu^{3+} ions in a second phase which is probably a concentrated Eu^{3+} compound.

The excitation spectrum of the Eu^{3+} luminescence shows two overlapping CT bands with maxima at about 250 and 230 nm (see Figure 2). These bands are probably due to transitions on different Eu^{3+} ions. Under excitation with different UV wavelengths two different Eu^{3+} emissions are observed (see Figure 3). These spectral features point to the presence of at least two different Eu^{3+} centers in sample A. The emission that shows up under longer wavelength excitation (maximum absorption at about 250 nm) has $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of comparable strength and is ascribed to a Eu^{3+} center denoted below as center I (see Table I). The emission lines are relatively broad. At LHeT a 4-fold increase of the luminescence of center I is observed. This points to a strong, temperature dependent, nonradiative relaxation in the excited CT state of the Eu^{3+} ion on this particular site.

Under irradiation at about 230 nm a Eu^{3+} emission is observed with a dominant $^5D_0 \rightarrow {}^7F_2$ transition. This Eu^{3+} emission, denoted further as center II, consists of much narrower lines than for center I. Furthermore, the shape and the intensity of this Eu^{3+} emission under CT excitation is independent of temperature.

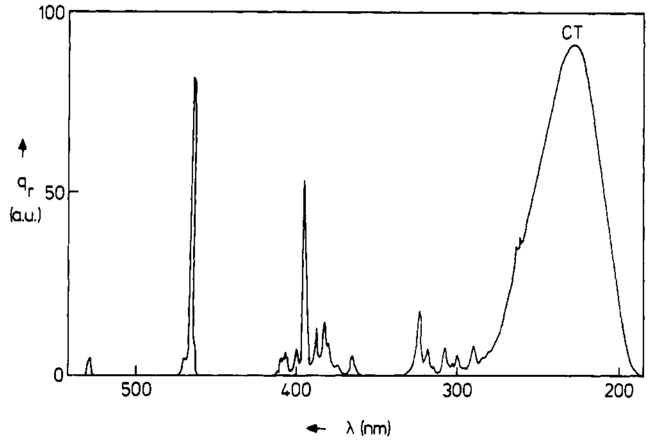

Figure 4. Excitation spectrum of the Eu^{3+} luminescence in Li_2ZrO_3, sample B, at LHeT. λ_{em} = 612 nm.

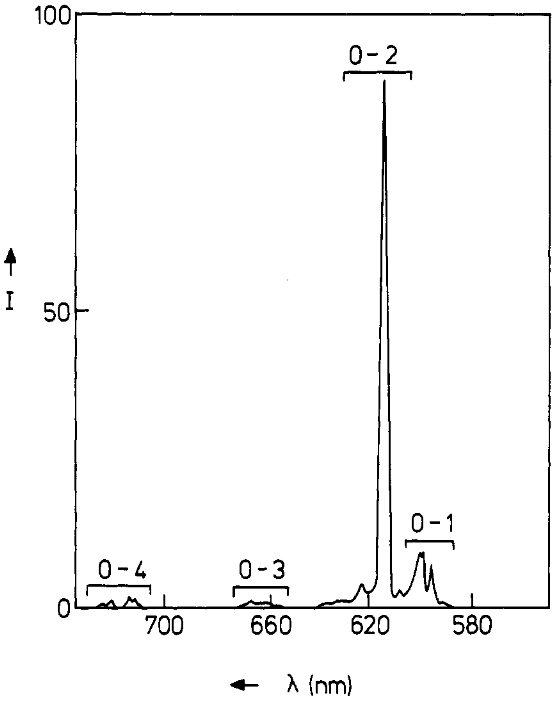

Figure 5. Emission spectrum of $Li_2ZrO_3:Eu^{3+}$, sample B, at room temperature with the indication of the $^5D_0 \rightarrow {}^7F_J$ transitions. λ_{exc} = 230 nm.

The spectral features of the Eu^{3+} luminescence in sample B are different from those of sample A. The excitation spectrum of the Eu^{3+} emission consists of a single CT band at about 230 nm and of the well-known sharp f–f transitions of the Eu^{3+} ion (see Figure 4). The emission spectrum under CT excitation is shown in Figure 5 and resembles the emission of center II in sample A. Under excitation at different wavelengths in the region of the CT band no change of the emission spectrum is observed. Furthermore the Eu^{3+} emission is independent of temperature. Under selective dye-laser excitation in the $^7F_0 \rightarrow {}^5D_1$ transition of the Eu^{3+} ion in sample B, two different Eu^{3+} emissions are observed under high resolution (see Figure 6). The Eu^{3+} emission under 530.2-nm excitation is the same as center II in sample A. The Eu^{3+} emission under 527.9-nm excitation is ascribed to another center, denoted further as center III.

From the high-resolution spectra an estimate can be made of the quantity of Eu^{3+} ions on the two sites, since all Eu^{3+} ions have the same absorption strength for the $^7F_0 \rightarrow {}^5D_1$ magnetic-dipole transition. It follows that both sites have a comparable population of Eu^{3+} ions.

In Li_2ZrO_3 it is obvious to use the Mg^{2+} ion as a charge compensator, since a Eu^{3+} ion on a Zr^{4+} site with an effectively negative charge can be compensated by a Mg^{2+}

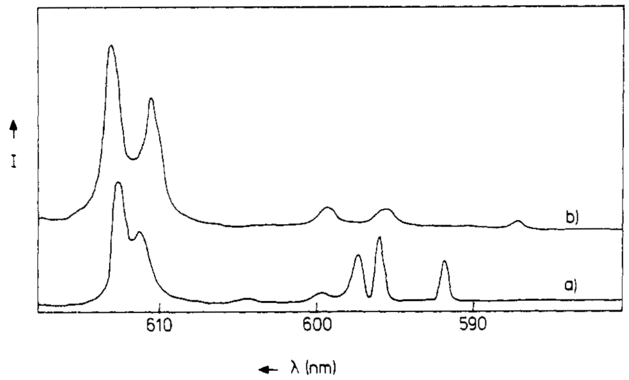

Figure 6. High-resolution emission spectra of $Li_2ZrO_3:Eu^{3+}$, sample B, at LHeT in the $^5D_0 \rightarrow {}^7F_{0,1,2}$ region: (1) λ_{exc} = 530.2 nm; (b) λ_{em} = 527.9 nm (dye-laser excitation).

ion on a Li^+ site with an effectively positive charge, and the ionic radii of Li^+ and Mg^{2+} are about equal. The spectral features of $Li_2ZrO_3:Eu^{3+},Mg^{2+}$ resemble those of sample B. The difference concerns the number of ions on the two centers. We estimate that about 5% of the Eu^{3+} ions are in center III, whereas 95% of the Eu^{3+} ions are in center II.

We now try to elucidate the nature of the Eu^{3+} centers in $Li_2ZrO_3:Eu^{3+}(Mg^{2+})$. For this it is necessary to consider the crystal structure of Li_2ZrO_3. This structure can be considered as a superstructure of the rocksalt lattice.[18-20] The structure contains alternating cation layers. One of the layers consists of Li^+ ions, the other of $^2/_3Zr^{4+}$ and $^1/_3Li^+$. The Li^+ and Zr^{4+} ions are octahedrally coordinated. Their site symmetry is C_1, so that all transitions of Eu^{3+} are allowed and the number of lines contains no further information on the site symmetry.

In $Li_2ZrO_3:Eu^{3+},Mg^{2+}$ one dominating center is observed (center II). It is obvious that in this system the Eu^{3+} ion replaces a Zr^{4+} ion and the Mg^{2+} ion replaces a Li^+ ion to account for the charge compensation. Also in $Li_2ZrO_3:Eu^{3+}$ (sample B) such a Eu'_{Zr} site is observed. This implies that the spectral features under consideration are hardly influenced by whether or not one of the nearest Li^+ neighbors of the Eu'_{Zr} center is replaced by Mg^{2+}, because it is hard to imagine that Eu^{3+} and Mg^{2+} would not partly associate. The other center in sample B is obviously charge-compensated in a different way. It is well-known that lithium-rich compounds with ordered rocksalt structure may contain the Li^+ ion in tetrahedral sites.[21-23] Therefore, we propose that center III consists of Eu'_{Zr} associated with an interstitial Li^+ ion: $(Eu'_{Zr}{\cdot}Li_i)^x$. Since sample B was synthesized with the larger excess of lithium, this proposal is not unreasonable. In $Li_2ZrO_3:Eu^{3+},Mg^{2+}$ the latter site is hardly observed, since the Mg^{2+} ions account for the charge compensation.

In sample A, the $Li_2ZrO_3:Eu^{3+}$ sample with the lower excess of lithium, center III with the Li_i ions is lacking. Therefore, another charge-compensating mechanism is proposed, viz., the incorporation of two Eu^{3+} ions on two Zr^{4+} sites (center II), giving two effectively negative charges, and one Eu^{3+} ion on a Li^+ site (center I), giving two effectively positive charges: $2Eu'_{Zr} + Eu^{\cdot\cdot}_{Li}$. This implies the formation of a solid solution in the system Li_2ZrO_3–$LiEuO_2$. The $Eu^{\cdot\cdot}_{Li}$ center (center I) is assumed to reside in the mixed cation layers. The proposal is able to explain the difference between the positions of the CT bands of the Eu^{3+} ions on centers I and II. On center I the Eu^{3+} ion has a double effectively positive charge. This facilitates ligand-to-metal CT, so that the CT band is positioned at lower energies (40 000 cm^{-1}). Since Eu^{3+} on a Zr^{4+} site (centers II and III) has an effectively negative charge, the CT band is positioned at higher energies (43 000 cm^{-1}; see Table I). In the next section we will show that the proposed nature of the Eu^{3+} centers in Li_2ZrO_3 is able to explain the values of q_{CT}.

Quantum Efficiency. 1. Results. The q_{CT} of the Eu^{3+} luminescence in the Zr^{4+} compounds was estimated with a method described earlier.[12,24] This method is based on the fact that the transition probabilities of the $^7F_0 \rightarrow {}^5D_1$ magnetic-dipole transition and the CT transition of the Eu^{3+} ion are not strongly influenced by the surroundings of the Eu^{3+} ion.

Two facts complicate the estimation of the quantum efficiency of the Eu^{3+} luminescence. At first, the presence of titanium in the samples originating from the starting material $ZrOCl_2{\cdot}8H_2O$ gives rise to a competitive absorption in the region of the CT band. To quantify this effect, we compared the absorption strengths of the Eu^{3+} ion and the Ti^{4+} ion in aqueous solution. It appeared that the absorption strength of Ti^{4+} is about 10 times larger than that of Eu^{3+}. The values of q_{CT} were corrected for this effect. A second problem in estimating the quantum efficiencies is the high energetic position of the CT bands, since the lamp sources used are not very intense in that region. Both factors result in an estimated absolute error in the values of q_{CT} of at least 10%.

For $ZrO_2:Eu^{3+}$ we arrive at a q_{CT} of about 30%, independent of temperature from 4.2 to 300 K. This value is an overall efficiency, i.e., a total efficiency for all Eu^{3+} centers in the sample.

The q_{CT} of the Eu^{3+} luminescence in ZrP_2O_7 amounts to about 60%, a value independent of temperature. As in $ZrO_2:Eu^{3+}$, q_{CT} is a total value for both Eu^{3+} centers in ZrP_2O_7.

For the system $Li_2ZrO_3:Eu^{3+}(Mg^{2+})$ q_{CT} is different for the several samples. In $Li_2ZrO_3:Eu^{3+}$ (sample A) q_{CT} amounts to about 40% at 4.2 K and 10% at 300 K. In $Li_2ZrO_3:Eu^{3+}$ (sample B) and $Li_2ZrO_3:Eu^{3+}(Mg^{2+})$ q_{CT} is independent of temperature and amounts to about 60%.

2. Discussion. In this section we try to relate the values of q_{CT} in the zirconium compounds to the effective charge of the Eu^{3+} ions. To do so, a model is presented that includes the influence of an effectively charged ion on the radiationless rates in the CT state. This model is based on the configurational coordinate model.[25,26] As a reference point for the discussion, the situation for a Eu^{3+} ion without an effective charge (Eu^{3+} on a Y^{3+} site, for example) is depicted in Figure 7. The ground state and the excited state of the latter situation are depicted in an arbitrary way to allow a good comparison with the situation of effectively charged Eu^{3+} ions.

Starting with the effectively positive charged Eu^{3+} ion, a relatively small Eu^{3+}–O^{2-} distance is expected in the ground state. This is due to the fact that the trivalent europium ion will attract the O^{2-} ion more strongly than the divalent cation that it replaces. In the excited state charge transfer from the O^{2-} ion to the Eu^{3+} ion takes place, resulting in an expansion of the Eu^{3+}–O^{2-} complex.

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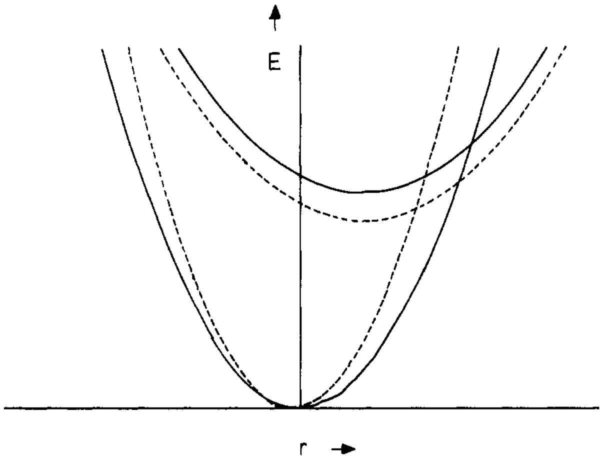

Figure 7. Configurational coordinate model for the explanation of the radiationless losses in the excited CT state of the Eu^{3+} ion: parabolas of the excited CT states and ground states of a Eu^{3+} ion with an effectively positive charge (dashed lines), and without an effective charge (solid lines). For clarity all parabolae of the excited $4f^6$ levels have been omitted. What is of importance is that in the dashed system the nonradiative return from CT to ground state is much easier than in the solid line system.

The reason for the contraction in the ground state is now at least partly lifted, so that the expansion in the CT state is relatively large. This favors radiationless processes from the CT state to the ground state (see Figure 7). Other effects that may influence the radiationless loss of excitation energy are the energetic position of the CT state and the force constant. The positive charge of the Eu^{3+} ion lowers the CT position to a certain extent, which increases the radiationless rate.[27] The shorter Eu–O distance in the ground state implies a higher force constant, i.e., a steeper parabola, which effect disappears in the excited state. This also increases the radiationless rate.

For an effectively negative charged Eu^{3+} ion the situation is the reverse. In the ground state the Eu^{3+}–O^{2-} distance will be fairly large, since the Eu^{3+} ion on a Zr^{4+} site will cause a weaker attraction on the O^{2-} ion than the Zr^{4+} ion which it replaces. In the excited CT state the Eu^{3+}–O^{2-} complex will expand. A restricted expansion is expected, since the Eu^{3+}–O^{2-} distance was already fairly large in the ground state, and the reasons for this effect are not lifted by charge transfer. Furthermore the position of the CT state in Zr^{4+} compounds in expected to be at high energy. This can be understood from the effectively negative charge of the Eu^{3+} ion. Also, the change in force constant will be less than for a positive charge on Eu^{3+}. Zr^{4+} compounds are, therefore, expected to show a high q_{CT} for Eu^{3+}.

This model for effectively charged Eu^{3+} ions has been proved to be useful in explaining the low q_{CT} of the Eu^{3+} luminescence in $CaSO_4$:Eu^{3+},Na^+. In this system q_{CT} amounts to about 30%. In Li_2ZrO_3:Eu^{3+} (sample B) and Li_2ZrO_3:Eu^{3+},Mg^{2+}, where the Eu^{3+} ions have an effectively negative charge, q_{CT} is 60%. This higher efficiency is in agreement with the model. In Li_2ZrO_3:Eu^{3+}, sample A, most of the Eu^{3+} ions replace Li^+ ions in the structure. q_{CT} for this Eu^{3+} ion is low (about 10% at room temperature) and supports, therefore, the suggestion for strong radiationless losses of excitation energy for effectively positive charged Eu^{3+} ions (as for Eu^{3+} in $CaSO_4$:Eu^{3+},Na^+).

In ZrO_2 and ZrP_2O_7 an additional effect influences the rate of radiationless return to the ground state. This is the presence of vacancies in the vicinity of the Eu^{3+} ion. These vacancies make a large offset in the excited state possible, which lowers q_{CT}.

By comparison with systems in which the Eu^{3+} ion replaces the Y^{3+} ion, q_{CT} in the Zr^{4+} compounds investigated is lower, although the model predicts high values for q_{CT}. We suggest that this disagreement is due to the second coordination sphere of the Eu^{3+} ion. Since the Eu–O complex expands in the excited state, the second coordination sphere accounts for the possibility of an expansion of the Eu–O complex in the CT state. If the alignment of the Eu–O bond with the ions (say X) in the second coordination sphere is axial, implying a Eu–O–X angle of 180°, the second coordination sphere will counteract the expansion in the excited state to a great extent. Recently we have studied the system CaO:Eu^{3+}.[28] In the rocksalt structure of CaO the Eu–O–Ca angle is 180°, and q_{CT} amounts to about 50%, which is higher than for Eu^{3+} in $CaSO_4$ (q_{CT} = 30%) where this Eu–O–Ca angle is about 135°.

Returning to the q_{CT} values in the Zr^{4+} compounds, we note a Eu–O–X angle in Li_2ZrO_3 (rocksalt-like structure) of 180°. The fact that q_{CT} is not higher that 60% is probably due to the inability of the small and low-charged Li^+ ion to counteract the expansion considerably. In view of this discussion we suggest that high values of q_{CT} may be obtained if the Eu^{3+} ion is incorporated into Zr^{4+} compounds with perovskite or rocksalt-like structures and highly charged cations in the second coordination sphere. A proposal for such a compound is $SrZrO_3$. By adding La^{3+} as a charge compensator, the Eu^{3+} ion is incorporated on the Zr^{4+} site giving a Eu–O–Zr alignment of 180°. Unfortunately it turned out that the Eu^{3+} luminescence in this system is obscured by the zirconate absorption in the region of the CT band of Eu^{3+}.[29]

Conclusions

The luminescence of the Eu^{3+} ion in Zr^{4+} compounds is determined to a great extent by the effective charge of the Eu^{3+} ion on the Zr^{4+} site. In Li_2ZrO_3 the influence of the sign of the effective charge of the Eu^{3+} ions on q_{CT} is apparent. For a Eu^{3+} ion on a Zr^{4+} site, with an effectively negative charge, q_{CT} amounts to about 60% at room temperature, whereas for a Eu^{3+} ion on a Li^+ site this value amounts to about 10% at room temperature.

The value of q_{CT} for the Eu^{3+} luminescence in ZrO_2 amounts to about 30%, and in ZrP_2O_7 q_{CT} is about 60%. In these systems the presence of vacancies is instrumental in decreasing q_{CT}. To obtain high values of q_{CT}, it is mandatory to incorporate the Eu^{3+} ion in very stiff surroundings.

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Registry No. Eu^{3+}, 22541-18-0; ZrO_2, 1314-23-4; ZrP_2O_7, 13565-97-4; Li_2ZrO_3, 12031-83-3; $H_2C_2O_4$, 144-62-7; $MgCO_3$·$Mg(OH)_2$, 23303-17-5; Eu_2O_3, 1308-96-9; Li_2CO_3, 554-13-2; $ZrOCl_2$, 7699-43-6; $(NH_4)_2HPO_4$, 7783-28-0; Mg, 7439-95-4.

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