

A Review of Lanthanides As Activators In Luminescence

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Abstract: In this study, an intensive review of lanthanides as activators is done. The literature was reviewed for works on lanthanides as activator. The general properties of the lanthanides are described here, followed by criteria for which an element or ion can be judged upon as a good activator, for which the lanthanides fulfilled these criteria. To understand how the lanthanides function as activators in luminescence, an indebt study of the theory of luminescence was done in this review. Green luminescence of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$ and that of $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ were used in this review to demonstrate the properties of the lanthanides as activators. The conclusion this review has reached is that the lanthanides using EU as an example are good activators in luminescence.

I. Introduction

The Lanthanides (Ln) are a family of electropositive metals in period 6, commonly referred to as rare earth, although they are not particularly rare. Unlike the transition metals, the chemical properties of the lanthanides are highly uniform. **Table 1.**[1] shows that the reduction potential is very similar with the exception of europium, and they have a 3+ oxidation state. However, some properties vary significantly such as the radii of the M^{3+} ions, hydration and enthalpy. Although the common oxidation state is M^{3+} , there are some typical oxidation states that are most prevalent when the ion can attain f^0, f^7 or f^{14} , sub-shell e.g. Ce^{3+} is f^1 and can easily go to f^0 to become Ce^{4+} and Eu^{3+} is f^6 and can easily go to f^7 to become Eu^{2+} .

Table 1: Some selected properties of the Lanthanides

At.Nr- Formular	Name	Config. of M^{3+}	$E^{\Phi/V}(\text{Ln}^{3+})$	$R(\text{M}^{3+})$ in Å	E^{Φ} $\text{Ln}^{3+}/\text{Ln}^{2+}$
57-La	Lanthanium	$[\text{xe}]6s^05d^0 4f^0$	-2.38	1.16	-3.1
58-Ce	Cesium	$[\text{xe}] " 4f^1$	-2.34	1.14	-3.2
59-Pr	Praseodymium	$[\text{xe}] " 4f^2$	-2.35	1.13	-2.7
60-Nd	Neodymium	$[\text{xe}] " 4f^3$	-2.32	1.11	-2.6
61-Pm	Promethium	$[\text{xe}] " 4f^4$	-2.29	1.09	-2.6
62-Sm	Samarium	$[\text{xe}] " 4f^5$	-2.30	1.08	-1.55
63-Eu	Europium	$[\text{xe}] " 4f^6$	-1.99	1.08	-0.35
64-Gd	Gadolinium	$[\text{xe}] " 4f^7$	-2.28	1.05	-3.9
65-Tb	Terbium	$[\text{xe}] " 4f^8$	-2.31	1.04	-3.3
66-Dy	Dysprosium	$[\text{xe}] " 4f^9$	-2.29	1.03	-2.6
67-Ho	Holmium	$[\text{xe}] " 4f^{10}$	-2.33	1.02	-2.9
68-Er	Erbium	$[\text{xe}] " 4f^{11}$	-2.32	1.00	-3.1
69-Tm	Thulium	$[\text{xe}] " 4f^{12}$	-2.32	0.99	-2.3
70-Yb	Ytterbium	$[\text{xe}] " 4f^{13}$	-2.22	0.99	-1.15
71-Lu	Lutetium	$[\text{xe}] " 4f^{14}$	-2.30	0.98	-

The rare earth ions have partially filled 4f shell of electrons. This means the partially filled shell is not on orbits on the outside of the ion, but on inner orbits, since the filled 5s,5p are outside the 4f shell. This property has great effects on the luminescence properties of these elements, therefore they are generally very good activators, and this is the focus of this review.

II. Methods

This review is carried out by intensive literature review, many workshave been done on Lanthanides and their properties have been studied elsewhere, but not particularly just focusing on their properties as activators, so here an intensive review is made to put together their properties that enhance their ability to be used as activators in luminescence. Green luminescence of $\text{Ca}(\text{SCN})_2 \cdot \text{H}_2\text{O}:\text{Eu}^{2+}$ and that of $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ were used in this review to demonstrate the properties of the lanthanides as activators.

III. Results And Discussion

III.I THE LANTHANIDES AS ACTIVATORS

To discuss the lanthanides as activators is important to mention some criteria for which an element or ion can be judged upon as a good activator, thus a good activator has the following properties;

- a) It must be optically active
- b) Posses a large band gap between emitting and ground state, in its crystalline environment.
- c) Have the proper valence state which is easily established in its crystalline environment
- d) Stabilize the valence state within the crystalline state.

The selection rules also influenced their properties as activators, therefore mention will be made here of these rules.

- Spin selection rule; This rule forbids electronic transitions between levels with different spin states ($\Delta s \neq 0$).
- Parity selection rule; This rule forbids electronic (electric-dipole) transitions between levels with same parity, example transition within the d, or within the f shell.

Transition metal ions and the rare earth ions constitute the most common optically active centres found in luminescent insulating materials, because they fulfil the above given conditions as will be reviewed [2]. Electromagnetic radiation can interact with the centre through the electric field of radiation i.e. an electric dipole process or through the magnetic field of the radiation i.e. magnetic dipole.

As mentioned, the rare-earth ions have partially filled 4f shell of electron i.e. inner orbits. The 4f electrons are shielded from the electric field of the neighbouring ions, and the effect of the crystal field on the 4f electrons is small. That is the weak field limit. The procedure for calculating the energy levels of the rare-earth ions in a solid begins by calculating the free ion ^{2s+1}L states and then to consider the effect of the crystal field J, using perturbation theory. One consequence of the weakness of the crystal field is that the energy levels of the rare-earth ions do not vary greatly from one host material to another. This is true in the Ln^{3+} ions but the Ln^{2+} are different e.g. Eu^{2+} has a $4f^65d^1$ excited state configuration and the d orbital is not shielded as the f orbital, therefore highly influenced by the environment [3]. For each trivalent rare earth ion, the states with energies up to around 6eV belong to the same $4f^n$ configuration and so have the same parity, hence parity forbidden transitions. For the divalent ions the low lying $4f^{n-1}5d$ states have opposite parity to the ground state, hence permit strong absorption transitions in the visible, since is parity allowed. Furthermore the 5d orbital is much more sensitive to the environment than the 4f orbital, as such is strongly affected by the crystal field increasing the inter-nuclear distance in the excited state. The result is increase in the value of ΔR and as such the $4f \rightarrow 5d$ transitions are broad. The presence of these broad strong absorption bands causes a deep colour in crystals doped with divalent rare earth ions.

III.II THEORY OF LUMINESCENCE.

To understand how the lanthanides function as activators in luminescence, there is a need to do an indebt study of the theory of luminescence. Luminescence is a term which describes a process in which energy is emitted from a material at a different wavelength from that at which it is absorbed. This implies that the luminescence centre can emit only when excitation energy is absorbed, to which many types of energy is known, e.g. photoluminescence by electromagnetic radiation, electroluminescence by an electric voltage, chemiluminescences by the energy of a chemical reaction, etc. The luminescence process consist of the excitation energy being absorbed and the activator is raised to an excited state followed by return to the ground state with emission of radiation, but this competes with non-radiative return. The absorption and excitation can be explained in details using the configurational coordinate diagram showed in **fig 1**. For luminescence to occur an activator and a host lattice is needed. Host lattice consist of cations combined with one of several different anions, hence have closed electron shells, and therefore are optically inactive. It is important that the host is optically transparent, for the absorption- excitation process to take place at the activator site. The studies of luminescence is concerned with the emission of visible light from red to blue, but other wavelength can be emitted, such as UV, or IR.

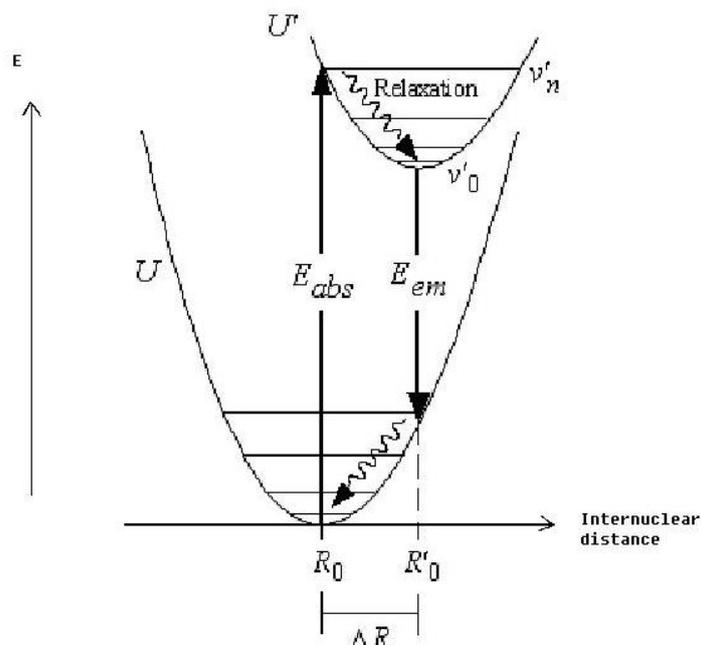


Fig 1; Configurational coordinate diagram for divalent lanthanides

Fig 1 shows a configurational coordinate diagram where energy is plotted against internuclear distance. In the first curve (ground state), the minimum, R_0 corresponds to the equilibrium distance in the ground state with levels 0, 1, 2, etc. In the excited state the equilibrium position is at R'_0 because the parabola is shifted relative to each other over a value of ΔR . The configurational coordinate diagram helps to consider the interaction between the electrons and the vibrations of the activator. ΔR is therefore very informative, if $\Delta R \neq 0$, the $v = 0$ level will have the maximal vibrational overlap with several levels $v' > 0$, and a broad absorption band will be observed. In **fig 1** both the ground state and the excited state have vibrational levels. When absorption occurs the centre moves to high vibrational level of the excited state, which then returns first to the lower vibrational level of the excited state i.e. relaxation. From the lowest level of the excited state the centre now returns to the ground state spontaneously with emission of radiation i.e. radiative return. However the return is first to the highest vibrational level of the ground state from where another relaxation occurs to the lowest vibrational level of the ground state. Therefore, conclusively, the broader the absorption band, the larger the value of ΔR . This implies that there is large difference in chemical bonding between the excited state and the ground state.

II.III THE THEORY OF ENERGY LEVELS OF DIVALENT LANTHANIDES

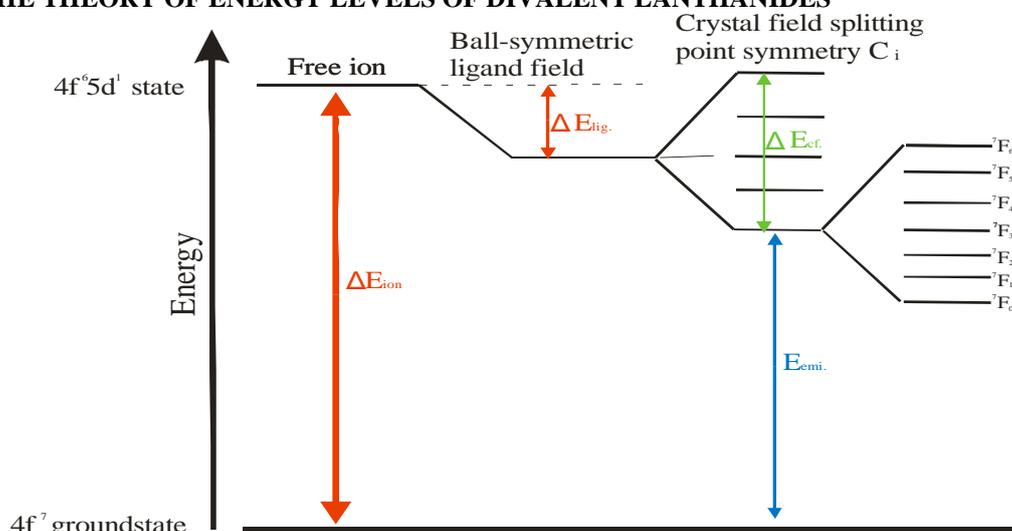


Fig 2 Energy level diagram for Eu^{2+} .

In the previous research already reported elsewhere (Danja) the divalent lanthanide was used to dope into the host lattice to obtain luminescence, that is why in this review the energy levels of the divalent is focused upon. The energy levels of the trivalent rare earth (Ln^{3+}) ions arise from the $4f^n$ configuration. The energy state relative to the ground state is not dependent on the host lattice, since this $4f^n$ electrons are shielded by the $5s5p$ orbital from the environment. If this energy levels are showed in a configuration coordinate diagram, they will appear as parallel parabolas i.e. $\Delta R \approx 0$. Ln^{3+} emission consist therefore of sharp lines

In Eu^{3+} these sharp lines corresponds to transitions from excited f-states (5D_0) to the ground state (7F_J). The excited state will not be split by the crystal field since $J = 0$. If the site occupied has inversion symmetry, f-f transitions will be strictly forbidden as electric-dipole transitions, but can occur as magnetic- dipole transitions (i.e. weak transitions). But if in the site occupied there is no inversion symmetry, the uneven crystal field components can mix opposite-parity states into the $4f^n$ -configurational levels, therefore the electric- dipole transitions are no longer strictly forbidden, i.e. forced-dipole transitions. It is possible to excite electrons into the $4f^n5d^1$ excited state of the trivalent lanthanides, but this state has normally very high energy i.e. in the vacuum-UV region.

In the divalent, these states i.e. $4f^n5d^1$ are shifted to lower energy and lie in the UV-Vis region. This energetically low lying $4f^n5d^1$ state makes the phosphors of the divalent lanthanides to give intensive colours, example of this intensive colour is the one shown by $\text{Ca}(\text{SCN})_2:\text{Eu}^{2+}$ in fig.3 below already reported elsewhere (Danja). Transitions between the excited $4f^n5d^1$ state and the $4f^{n+1}$ ground state are electronic- dipole allowed, hence is to a factor of 10^6 more intensive than the f-f transitions. One characteristic of the $4f^n5d^1$ to the $4f^{n+1}$ transition is the strong interaction of the d-orbital with the ligands. Important is the condition of the excited state $4f^n5d^1$ in the free ion, as showed in fig 2 this state is fivefold split. The difference in the free ion from the ground state to the excited state in terms of energy is ΔE_{ion} , this is constant for a given ion and correlate with the reduction potential $\text{Ln}^{2+}/\text{Ln}^{3+}$. The splitting of the energy state by the crystal field is dependent on the point symmetry, the d-state coordination sphere with high symmetry have only a partial splitting e.g. O_h is split into t_{2g} and e_g , while by the lower symmetry e.g. C_1 , C_2 , and C_5 , 5 single 5d- state are found. The crystal field lower the energy condition of the 5d-states with an amount ΔE_{lig} . The stronger the energy is lowered, the more covalent the environment is (nephelauxetic effect). ΔE_{lig} depends on the position of the ligand in the coordination sphere, this is shown in **fig2**, i.e. the energy states of the divalent lanthanides. The cation- ligand distance also plays an important role, a small distance will cause a big crystal field splitting and so shift the lower excited state of the d state to lower energy. Luminescence as described above occurs due to excitation to highest state and return to ground state with emission of radiation.

The ground state of Eu^{2+} is $4f^7$ ($^8F_{7/2}$) with two possible excitation 6P_j (f-f), and $4f^65d^1$ (f-d). Whether the transition will be intra-configurational (f-f) or inter-configuration (f-d) depends mainly on the effect of the crystal field on the Eu^{2+} energy level. The polarity and the second coordination sphere also have influence on the emission, as they also influenced the energy of the f-d states. Because of the many influence on the emission, the prediction of the exact wavelength of emission is not easy.

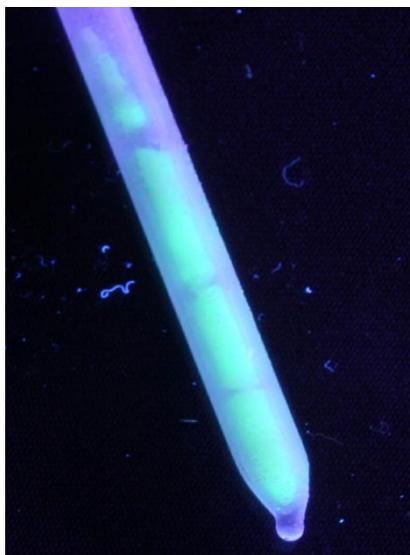


Fig. 3 Green luminescence of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$. [4]

The emission and absorption of this luminescence is shown in fig 4 and 5 below as reported in literature [4, 5]. From the curves obtained it can be seen that these are intensive emission and it is due to the lanthanide which is Eu^{2+} being used in the study reported. $\text{Ca}(\text{SCN})_2 \cdot \text{H}_2\text{O}:\text{Eu}^{2+}$ shows an intensive luminescence in the green spectral region at low temperature because of the energetically low lying $4f^65d^1$ state as already discussed above. This intensive green luminescence is shown in fig 3. The emission spectra are all due to the f-d transitions of the Eu^{2+} ions, as already mentioned above. Apart from the band due to Eu^{3+} as reported (Danja), only one band is observed for the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} . This shows that all Eu^{2+} ions occupy identical sites; this is expected since there is only one crystallographically distinct Ca^{2+} ion.

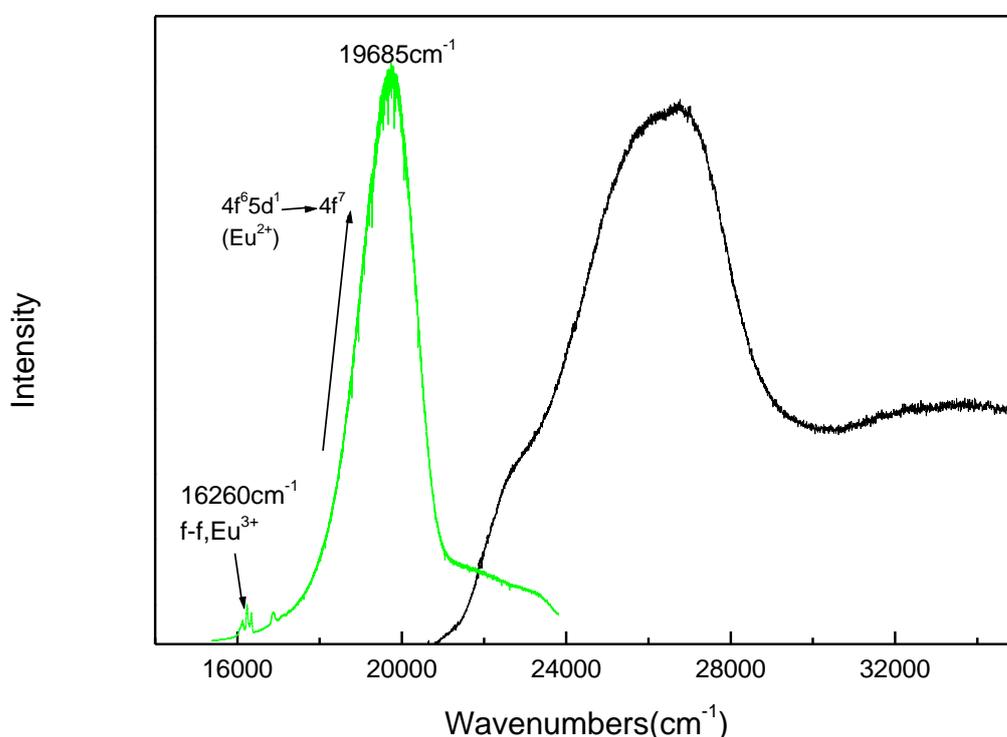


Fig 4: **Emission and excitation Spectra of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$.**
 $\nu_{\text{ex}} = 24390\text{cm}^{-1}$, $\nu_{\text{em}} = 19608\text{cm}^{-1}$, $T = 80\text{K}$ [4]

Fig 4 above are spectra of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$. The broad band due to f-d transition of Eu^{2+} with maximum at 19685cm^{-1} (508nm) was still observed. A second peak is observed at 16260cm^{-1} (615nm) due to the f-f transition of Eu^{3+} . It may be seen here that the emission is very intensive from the sharp curve.

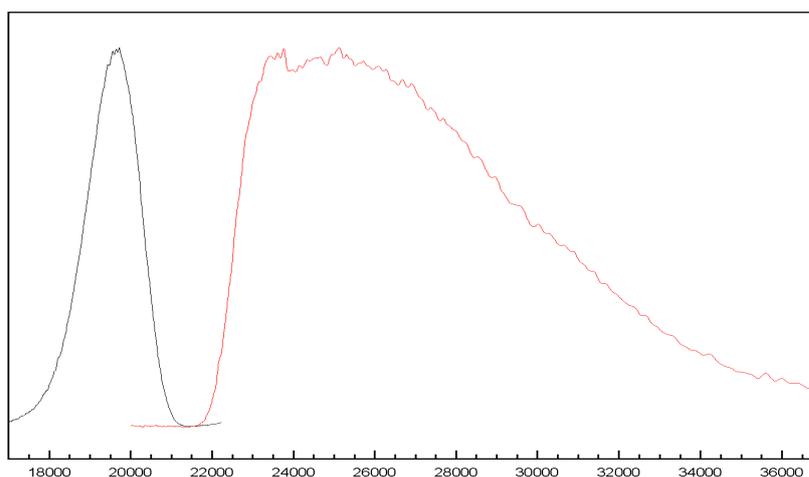


Fig. 5 Luminescence spectra of $\text{Sr}(\text{SCN})_2:\text{Eu}^{2+}$ left emission, right excitation [5].

The emission maximum of $\text{Sr}(\text{SCN})_2$ is at 19685cm^{-1} (508nm) as can be seen in fig 5 above. The same as in the emission in $\text{Ca}(\text{SCN})_2 \cdot \nu\text{H}_2\text{O}:\text{Eu}^{2+}$, the emission is very intensive, the curves are indications of the intensity of the emissions.

IV. Conclusion

The lanthanides especially EU have been intensively discussed here, and their properties make them to be very good activators. It is the position of this paper that they can be of great used in the lamb industries as activators.

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