

Reduction of Eu^{3+} and Doping the Same into Calcium Thiocyanate Dihydrate Using a Modified Jones Reductor

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Abstract: The reduction of Europium (Eu^{3+}) in aqueous solution and doping Eu^{2+} obtained into the host lattice $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ solution using a Modified Jones reductor is described here. The major goal is to dope Eu^{2+} into compounds that are difficult to dope through the melt method. $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ was obtained by the reaction of $\text{Ca}(\text{OH})_2$ and NH_4SCN with slow heating at 70°C . 0.05% M of EuCl_3 was used as the source of Eu ions. The host lattice was held in the receiver of the modified Jones Reductor, the solution of EuCl_3 is slowly passed through the reductor at the rate of $\approx 0.4 - 0.6\text{ml/min}$ under inert gas. The dried sample was prepared in a glove box for luminescence measurement.

$\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$ shows an intensive luminescence in the green spectral region. The emission spectra obtained in this work are all due to the f-d transitions of the Eu^{2+} ions, a small band due to Eu^{3+} was observed, The excitation spectra were measured at 80K at an emission of 19608cm^{-1} (510nm). A broad almost shapeless band was observed due to transitions to $4f^65d^1$ states of Eu^{2+} . The modified Jones Reductor was successfully used to reduce and dope europium into thermally unstable Host lattice.

Keywords: Calcium thiocyanate, Emission spectra, Europium, Excitation spectra, Host lattice, luminescence, Modified Jones Reductor, Reduction

I. Introduction

Increasing interest in the chemistry of lanthanides (Ln) has been noticed during the last two decades. Among the lanthanides, europium (Eu) seems to be the most popular due to the luminescent and catalytic properties of its complexes, and stability of the 2^+ oxidation state. Amongst the Lanthanides, it is only the element Europium (Eu), ytterbium (Yb) and samarium (Sm) that have significant chemistry (i.e. based on true Ln^{2+}) in this oxidation state.

A few methods are available for the reduction of lanthanides such as chemical reduction; example is the effect on the rate of reduction by Zn in HCl medium [2]. Selin et al [3] applied γ -irradiation to reduced Eu (III) to Eu (II) in aqueous solution of a mixture of rare earth elements. In another work Selin et al also used the method of radiolytic reduction [4] in dilute aqueous solution. They observed that the reduction of Eu (III) was enhanced by the presence of Sm^{3+} . Electrolytic reduction of Eu (III) in acidic chloride solutions with titanium cathode was used by Hirato et al [5] to examine the feasibility of the rare earth separation. They claimed to achieved complete reduction of 0.1mol of $\text{EuCl}_{3(\text{aq})}$ solution. But they observed that the final percent Eu(III) reduction of the solution from an industrial europium purification process which contained other rare earths, was lower than that of a synthetic EuCl_3 single electrolyte solution.

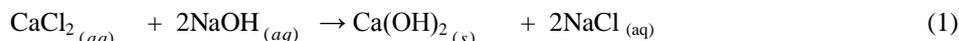
Polarographic reduction of europium ions on mercury-drop electrode in the presence of halide ions was used by Levitskaya et al [6] to determine the amounts of europium in Eu-base alloys. In 1987 Kaneko et al used a method similar to what is being used in this work i.e reduction of europium using zinc fixed beds [7] to separate europium from other rare earth metals. They passed their solution in the fixed bed for five hours at 2.4L/h rate and obtained 97% reduction. Electrochemical reduction as applied by Marina using nitrates, bromides and iodide media [8]. Among the elements of the lanthanides group, Eu^{3+} is characterised by its ability to be reduced to a bivalent state in aqueous solutions rather easily, even as compared to Sm^{3+} and Yb^{3+} . It is this property of europium, to be reduced in aqueous solution that is being exploited in this work, because Eu^{2+} plays an important role in luminescence sciences as it has emissions consisting of a $4f^7 - 4f^65d^1$ transition which is parity allowed and thus, very intensive.

Many host lattices have been investigated such as oxides, chlorides and some pseudohalogenes. But thiocyanates are receiving attention as host lattice only of recent, among them Strontium Thiocyanate ($\text{Sr}(\text{SCN})_2$) and Barium Thiocyanate ($\text{Ba}(\text{SCN})_2$) have been doped with Eu^{2+} and measured [9]. It has been reported that the unusual surrounding of these thiocyanates causes quite a common and very intense green emission of the Eu^{2+} [10]. Calcium Thiocyanate ($\text{Ca}(\text{SCN})_2$) is considered to be an appropriate host lattice, but it decomposes at about 420°C and begins to melt at 408.8°C . This implies that decomposition begins immediately after melting. This makes it difficult to dope $\text{Ca}(\text{SCN})_2$ and other similar compounds with Eu^{2+} using solid-state reaction, since they are not thermally stable.

The aim of this study is to exploit how Eu³⁺ can be reduced in aqueous solution and to attempt to dope Eu²⁺ in Ca(SCN)₂ in solution using a Modified Jones Reductor.

II. Material and Methods

Calcium thiocyanate dihydrate was obtained by the reaction of Ca(OH)₂ and NH₄SCN with slow heating at 70°C according to reference [9]. To avoid the problem due to oxides in commercial compounds, the Ca(OH)₂ was prepared by the reaction of CaCl₂ with NaOH. The equations of the reactions are given in equations 1 and 2 below.



EuCl₃ was used in this work as the source of Eu ion. 0.05% M of EuCl₃ in respect to the host lattice was dissolved in water and used for the reduction. The water used was degassed by boiling it up to expel O₂ and then nitrogen gas bubbled into it before use. All the chemicals, substances and equipments used are given in Table 1 and 2 below. Two methods were tried as follows; doped Eu³⁺ into the host lattice then pass it through the Jones reductor, the second method was to hold the host lattice in the receiver and reduced only the Eu³⁺, then allow it flow into the receiver containing the host lattice. The second method was found to be better and it was carried out as follows: The host lattice was held in the receiver, which was dipped into a beaker containing water. The water was slowly heated to 60°C with stirring to allow for uniform temperature distribution on the receiver. One arm of the receiver was connected to inert gas (N₂) and one to vacuum. Before the solution of EuCl₃ was put into the reductor, the arm connected to inert gas was opened to float the system with N₂ so as to expel O₂. The flow of the inert gas was maintained during the reduction. The solution was then slowly passed through the reductor at the rate of ≈ 0.4 – 0.6ml/min. After the completion of the reduction, the arm to inert gas was closed and that to vacuum opened. The doped compound was slowly evaporated to dryness under vacuum; this takes one to two days. The dried sample was removed under inert gas, closed and taken into the glove box and prepared for luminescence measurement.

Table 1: Equipments Used

Equipment	Company
Argon glove box	Braun [Germany]
Fluorolog [®] -3 spectrofluorometer, FL3-22	Jobin Yvon [USA]
Liquid nitrogen cryostat, VNF-100	Janis research [Wilmington, MA]
Powder diffractometer D5000	Siemens [Germany]
Imaging Plate Diffraction System, IPDS	STOE [Darmstadt, Germany]
IFT-IR Spectrometer, IFS 113V	Bruker [Karlsruhe, Germany]
Vacuum Pump	ILMVAC GmbH [Germany]
Detector PSD- 50M	Braun München Germany

Table 2: Chemicals and Substances Used

Name	Formula	Purity (%)	Supplier
Calcium Chloride	CaCl ₂	p.a	Alfa
Sodium Hydroxide	NaOH	95	J.T Baker
Ammonium Thiocyanate	NH ₄ SCN	98.5	Merck
Europium (III) Chloride	EuCl ₃	99.9	Chempur
Nitrogen gas	N ₂		Uni-Siegen

The X-ray powder diffraction was measured using a D5000-diffractometer shown in fig 1. Fat and film were used in the sample holder preparations. CuK α₁ (λ = 154pm) Ge was used as irradiation source. The used detector was a PSD- 50M from company Braun (München). The sample was always grinded to fine powder. A small amount of the film was cut, put on one of the sample holder part and a very little amount of fat was applied before the sample was introduced to the film, after which the whole assembly were put into the big sample holder. The prepared sample holder was put into the diffractometer and the measurement run using a computer.



figure 1: X-Ray Powder Diffractometer (D5000)

The luminescence measurement was done using a Fluorolig-3 (FL3-22) spectrofluorometer fig 2. This spectrofluorometer is equipped with a 450w xenon lamp, two double grated monochromators for emission and excitation. It also contains a photomultiplier with a photon counting system. The measurement procedure is as follows: The cryostat was evacuated for about 15minutes and then floated with N₂ gas, then cooled down to 80K using liquid nitrogen cryostat. After cooling the heater was started and the sample intensity adjusted to obtain maximum intensity possible. Two spectra were measured from the Jones Reductor results, they were then analysed using DATAMAX computer program and the obtained spectra drawn using another computer program called Origin. During measurement emission spectra was corrected for the photomultiplier sensitivity and excitation spectra corrected for the intensity of the excitation source.



figure 2: Fluorolig-3 (FL3-22) Spectrofluorometer

III. Results and Discussion

3.1) Preparation of Calcium Thiocyanate Dihydrate (Ca(SCN)₂ · 2H₂O)

The structure of Ca(SCN)₂ has already been solved [2]. The prepared compound was tested for the phase purity by measuring the X-ray powder diffraction pattern which fit into the dihydrate pattern as presented in fig 3. This confirmed that the host lattice used was pure phase of Ca(SCN)₂ · 2H₂O. This host lattice is very hygroscopic; therefore the preparations were always done in a glove box.

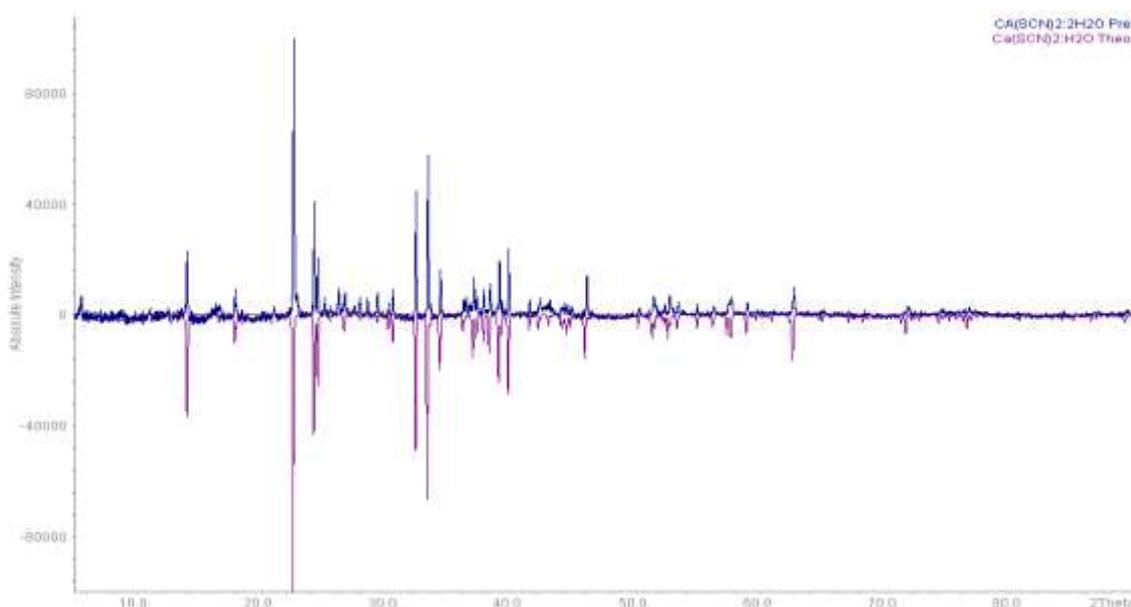


figure 3: X-Ray powder diffraction of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$

3.2) Degree of Conversion of Eu^{3+} TO Eu^{2+}

Two spectra were measured from the Jones Reductor results; **Fig 4** below shows the first one. The emission was obtained at 80K by exciting at 24390cm^{-1} (400nm). The emission shows a broad band with the maximum at 19685cm^{-1} (508nm), which is due to transition from $4f^65d^1$ to $4f^7$ of Eu^{2+} . The peak has full width at half maximum $\Gamma = 1362\text{cm}^{-1}$. A second peak can be seen at 14317cm^{-1} which can be assigned to the f-f transition of Eu^{3+} . The Eu^{2+} had relative intensities of 2731292cps and that of Eu^{3+} was 175403cps.

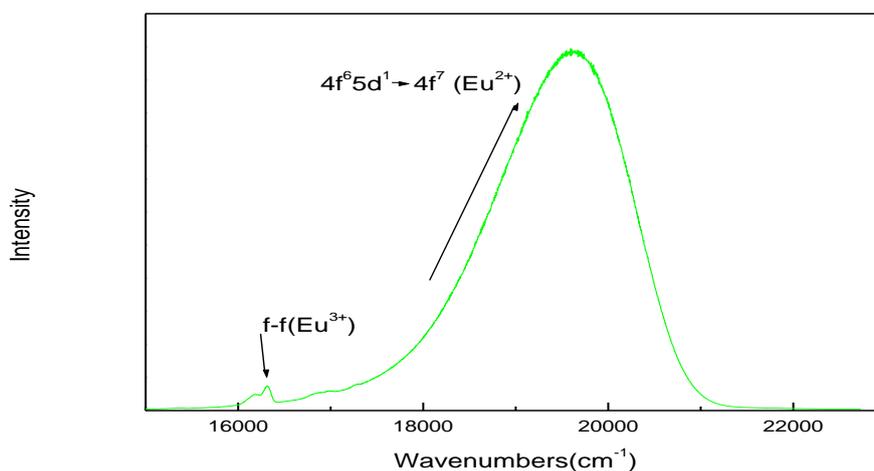


figure 4: Emission Spectra of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$ (First Result from Jones Reductor) $\nu_{\text{ex}} = 23923\text{cm}^{-1}$, $T = 80\text{K}$

Figs 5 below are spectra from the second result of the Jones reductor. The broad band due to f-d transition of Eu^{2+} with maximum at 19685cm^{-1} (508nm) was still observed in the emission spectra. 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 peak due to Eu^{3+} is smaller compared to the first, suggesting only very small Eu^{3+} still remain.

The result of the reduction of Eu^{3+} using the Jones reductor is in good agreement with previous literature findings. Shpigun et al [10] used a flow- in system to reduce and measure Eu^{3+} . Their system made it possible to avoid the problem of handling europium (II) after reduction, because reduction and determination were performed in closed flow-injection system. The implication is that detecting this unstable oxidation state should be done within less than 30seconds after its formation in solution. Their results showed a conversion degree of europium (III) to europium (II) at a flow rate of 0.4 to 0.6ml/min to be optimum.

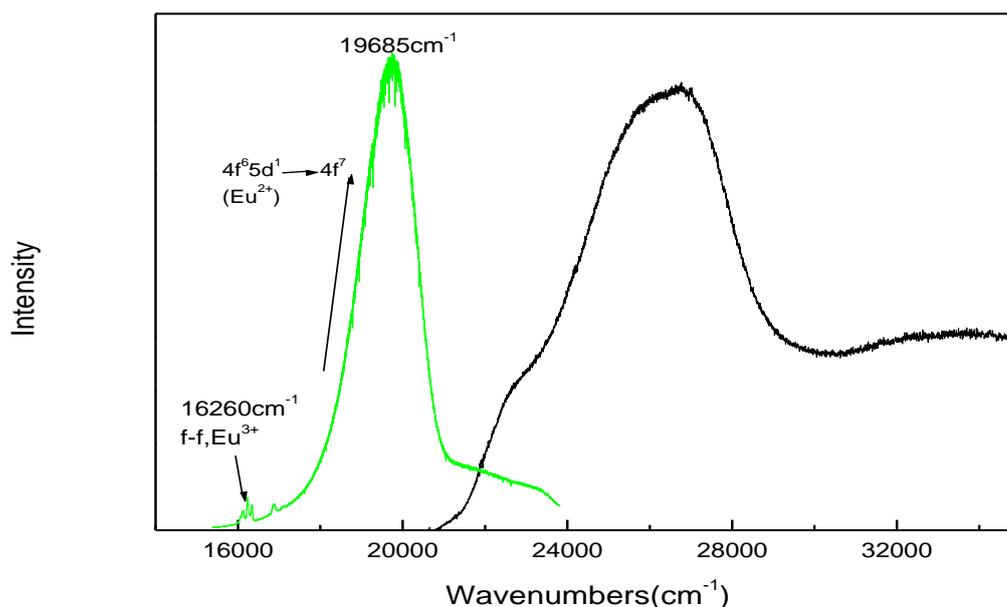


figure 5: Emission and excitation Spectra of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$. (Second reduction from Jones reductor) $v_{\text{ex}} = 24390\text{cm}^{-1}$, $v_{\text{em}} = 19608\text{cm}^{-1}$, $T = 80\text{K}$

When they used metal solutions prepared in 0.1M HCl, the degree of reduction was 75%, but in 0.25M HCl the degree of reduction was up to 95%. In this work this much of HCl cannot be used as the Cl^- ion will interfere with the luminescence property of the phosphor. Although here the detection of Eu^{2+} was not done within 30 seconds after reduction, it may be suggested that 96% reduction was obtained as calculated from reduction done in the construction of the Jones Reductor. 0.1M HCl was used to dissolved EuCl_3 , which was further diluted with 50ml of water, therefore in comparison with Shpigun et al results only a very dilute acid was used here. Equally only a small amount (0.05%) of the EuCl_3 salt was used, as such the reduction done here was for a dilute solution of the europium salt. This could account for the high percentage of reduction in comparison with their result. One can account for the presence of some Eu^{3+} in two ways. One possibility is re-oxidation considering the long time gap between reduction and measurement. The second possibility is that the reduction was not complete, only some percentage was reduced and a small percentage remains in solution.

3.3) Luminescence of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$.

The reduction and doping of 0.05% Eu^{2+} into the above mentioned host lattice were done several times to obtain maximum results. Among the two methods mentioned in the experimental section, reducing Europium in solution and doping it after reduction produced better result. The first method of doping the EuCl_3 into the Host Lattice in solution before passing it into the Jones reductor was not successful. This was because after the reduction, no Eu^{2+} could be detected in the thiocyanate. This could be explained by the fact that only very small amount of Eu^{3+} (0.05%) was used and this could be shielded from the reducing metal by the thiocyanate. $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$ shows an intensive luminescence in the green spectral region at low temperature because of the energetically low lying $4f^65d^1$ state. The green luminescence is shown in fig 6. The emission spectra obtained in this work 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+} , 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.

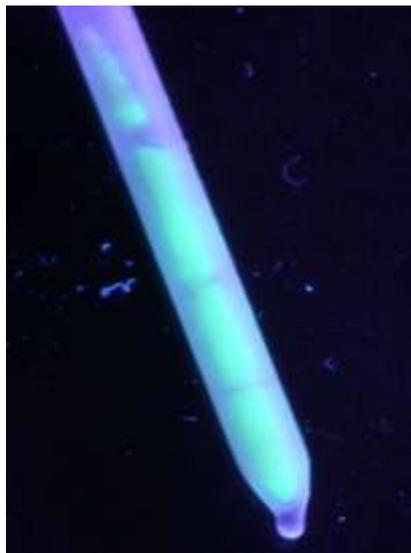


figure 6: Green luminescence of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$.

$\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ melt at a very low temperature (60°C), as such attempt was made to dope Eu^{2+} into it by the melt. The spectra from the melt are very comparable to that obtained from the Jones reductor, only without traces of Eu^{3+} . **Fig 7** shows the spectra obtained by the melt at 100°C . The emission was obtained by exciting at 25000cm^{-1} (400nm). The emission spectrum shows a broad band with a maximum at 19685cm^{-1} (508nm) and full width at half maximum $\Gamma = 1535\text{cm}^{-1}$, which is quite similar to that obtained from the Jones Reductor. Since $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ decomposed at a very low temperature, complete doping could not be achieved, only a small quantity was used for the doping, as such the green luminescence as obtained from the Jones Reductor doping could not be obtained for the one through the melt.

The ligands (SCN) in this host lattice are covalent. It is known that for increasing covalence the interaction between the electrons is reduced since they spread out over wider orbital. Consequently, electronic transitions between energy levels with an energy difference which is determined by electron interaction shift to lower energy for increasing covalence (Nephelauxetic effect). This effect shifts the centre of gravity to lower energy, hence shifting the lowest excited $5d(^7F_0)$ state to lower energy. Since the excited d state depends very strongly on the host lattice, this emission is therefore influenced by the Ca^{2+} surrounding. Another factor that could lead to broadening of emission band is the nature of the substance used. This happens when powder is handled, because external and internal surface are different. In this case the Eu^{2+} near the surface experience a covalence and a crystal field which differs from the bulk and can lead to spectra broadening. In this work the host lattice is crystal, hence the amount of covalence is the main factor of influence.

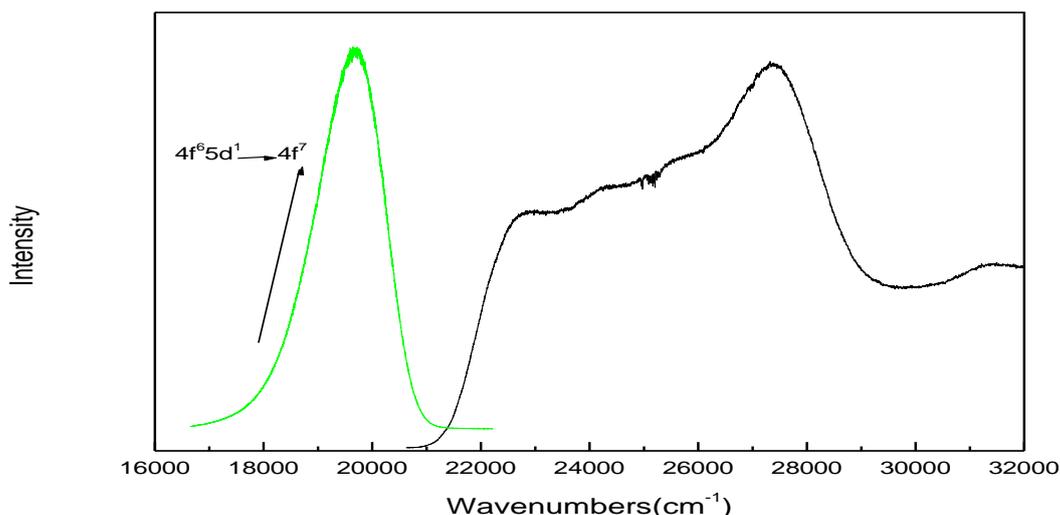


figure 7: Emission and Excitation Spectra of $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}:\text{Eu}^{2+}$ (doped from the melt), $T = 80\text{K}$, Emission Max = 19685cm^{-1} , $V_{\text{ex}} = 25000\text{cm}^{-1}$, $V_{\text{em}} = 19230\text{cm}^{-1}$

The excitation spectra in figure 5 and 7 were measured at 80K at an emission of 19608cm⁻¹ (510nm). A broad almost shapeless band is observed due to transitions to 4f⁶5d¹ states of Eu²⁺. The lowest excited state is split to five levels due to the C₂ point symmetry. The first excitation maximum, taken from fig 7 is at 22862cm⁻¹. All the three emission bands shown above are not completely Gaussian shaped, but rather nearly symmetrical with a sharp drop on the high energy side. This suggest the stoke shift should not be extremely large, implying that the change in the metal-ligand distance in the ground and excited state is not very large. The stoke shift calculated from fig 7 using the maximum of the emission and the first maximum of the excitation band is 3084cm⁻¹. Transitions to the individual ⁷F_J states of the 4f⁶5d¹ levels are not well resolved. But the excitation band from the melt shows a bit of resolving of these states. The fact that these states are not well resolved only proves that the exchange interaction between the six 4f⁶ electrons and the 5d¹ electron is large. This is expected for thiocyanates host lattice.

IV. Conclusion

The following conclusions can be made from the results obtained in this work.

The modified Jones Reductor was successfully used to reduce Eu³⁺ in solution to Eu²⁺ and doping the same into thermally unstable Host lattice, namely Ca(SCN)·2H₂O, but from the Luminescence of Ca(SCN)₂·2H₂O:Eu²⁺ measured the problem of re-oxidation due to the long time needed must be addressed. The Modified Jones Reductor provides a good solution for doping Eu²⁺ into thermally unstable host lattice.

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