Luminescence Properties of Octahedrally Coordinate Eu^{2+} ions

by

MURAT AYCIBIN

(Under the direction of Uwe Happek)

Abstract

In this dissertation, we investigated $\rm Eu^{2+}$ ion in $\rm CsCaF_3$ and $\rm Rb_2MP_2O_7$ with M=Ca, Sr.

The emission spectra of Eu^{2+} ion doped in CsCaF₃ shows a very unique behaviour. Depending on temperature, the peak of the emission shifts from 628 nm at 6 K to 520 nm at 300 K. This shift has been attributed to the presence of the two Eu^{2+} sites or alternatively to anomalous emission i.e, emission from an impurity bound exciton. From relevant optical data, the centroid shift, red shift, Stokes shift and the lowest excited-energy location are estimated. The luminescence parameters of Eu^{2+} in CsCaF₃ are discussed and arguments are presented to associate the luminescence with the anomalous emission transition.

We also report on the excitation and emission spectra of the octahedrally coordinated Eu^{2+} ions in Rb₂MP₂O₇ with M=Ca, Sr. Again, the centroid shift, red shift and Stokes shift and the energy of the lowest-excited state are estimated from optical data. The Eu²⁺ emission in these materials is characterized by a large Stokes shift, which, for phosphates, results in the lowest reported emission bands peak at 645 nm and 590 nm for Rb₂CaP₂O₇ and Rb₂SrP₂O₇, respectively. At this point, Eu²⁺ emission in these materials can be ascribed to a normal, although extreme case, of the intra-ion $4f^{6}5d^{1} \rightarrow 4f^{7}[^{8}S_{7/2}]$ transition.

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MURAT AYCIBIN

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Approved:

Major Professor: Uwe Happek

Committee:

William Dennis Kin-Keung Mon

Electronic Version Approved:

Maureen Grasso Dean of the Graduate School The University of Georgia December 2009

DEDICATION

I would like to dedicate this dissertation to those I love, to those who have helped me through the path of educational life. To my parents, I would like to thank for not giving up on me and supporting every single decision I made. Thanks to my sister and brother who always encouraged me to follow my education.

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Chapter 1

INTRODUCTION

1.1 BACKGROUND

Lighting includes indoor and outdoor lighting and is found in virtually every house in the United States. In 2001, lighting accounted for 101 billion kWh (8.8 percent) of U.S household electricity use.[1] Incandescent bulb (IB), which is commonly chosen as a light source by household owner, is a highly inefficient source of light because 90 percent of the energy used is lost in form of heat.[1] In addition to IB, there are other light sources such as the Fluorescent Light tube (FLT), Compact Fluorescent Light (CFL) and recently Light Emitting Diode (LED). In order to select the right light source, important performance variables should be considered such as: light output (Lumens), efficiency (Lumens/Watt), which is connected to the carbon dioxide emission (CDE), lamp life, and color rendering properties measured in terms of the Color Rendering Index (CRI), which is a 0-100 scale that measures a light source's ability to render colors that are close to true color.[2] Table (1.1) shows characteristics of common sources of light.

The FLT (including CFL) has two main parts: the gas-filled tube (also called bulb or burner) and the magnetic or electronic ballast. An electrical current from the ballast flows through the mixing gas combination (mercury vapor, argon, xenon, neon and krypton), causing the mercury vapor to emit ultraviolet light (mostly at 254 nm and 185 nm). The ultraviolet light then excites a phosphor coating on the inside of the tube. This coating then emits visible light.

LEDs can be manufactured to emit almost any color in the visible range. White light can be obtained in two different ways using LEDs. In the first method, a combination of two or

Light Source	Efficiency(lm/W)	Lamp life(h)	CDE(lb/year)	CRI
IB	5-20	750-1000	150	100
Standard FLB	60-100	10,000-20,000	37	80
CFL	20-55	15,000-20,000	37	80
LED	15-161[17]	50000	15	90
High-Pre sodium[19]	50-140	16,000-24,000	-	25(Poor)
Low-Pre sodium[19]	60-150	12,000-18,000	-	-44(very poor)

Table 1.1: Characteristics of Common Light Sources[3]

more monochromatic LEDs results white light. In the second method, a blue or UV LED is complemented with a phosphor to emit white light.

In addition to applications in lighting industry, phosphors can be used in a wide range of fields for example medical image devices, flat panel display and detector systems. Phosphors usually are rare earth elements or transition metals containing compounds and research into the understanding of these materials is a complex area that has many aspects. In this dissertation, we will expand the understanding of the optical properties of divalent europium ions occupying a six- coordinated octahedral site in a crystalline solid. Specifically, luminescence of Eu^{2+} doped in CsCaF₃ and Rb₂(Ca,Sr)P₂O₇ were investigated.

1.2 Europium Ions

Europium was discovered by Eugne-Antole Demaray, a French chemist, in 1896. He was able to produce relatively pure europium in 1901.[4] Europium is a member of the lanthanide series of elements, characterized by a partially filled 4f-electron shell. Eu ion has two stable oxidation states: Eu^{3+} and Eu^{2+} . In this dissertation, we will concentrate on the divalent ion of the Europium element.

 Eu^{2+} is the most stable lanthanide divalent ion due to its half-filled valence shell. Emission and absorption spectra of Eu^{2+} ion usually consist of broad bands due to transition



Figure 1.1: Schematic of the lowest Eu^{2+} energy levels in an octahedral site.[13]

between ${}^{8}S_{7/2}(4f)$ ground state and crystal field components of the $4f^{6}5d^{1}$ excited state configuration.[5] For most hosts, the emission spectra of Eu²⁺ are observed in the UV to visible range, specifically in the wavelength range from 390 nm to 640 nm.[7] The decay times of these transitions are usually in the range from 0.2 to 2 μ s, reflecting the dipole allowed nature of these transitions.[7] The host dependence of the emission spectra of Eu²⁺ can be explained as follows: In the divalent state, the europium ion has seven f electron which form a stable half-filled 4f valence shell. These seven 4f electron do not strongly interact with environment of the host material because they are effectively shielded by filled $5s^{2}$ and $5p^{6}$ shell and thus are affected weakly by changes in the environment. After one 4f electron is excited to the 5d level, this electron is strongly influenced by the crystal field, leading to broad, host dependent $5d \rightarrow 4f$ emission bands. The host lattice dependence of the emission is mainly connected with covalency (the nephelauxetic effect), the strength of the crystal field and the Stokes shift.[17]

For Eu²⁺ ions, two different emission types were distinguished: normal broad-band $4f^{6}5d^{1} \rightarrow 4f^{7}(^{8}S_{7/2})$ emission, and anomalous Eu²⁺ emission (the 4f \rightarrow 4f transitions are not observed for Eu²⁺, because the ⁶P f-levels are energetically above the 5d levels). In each case the emission can be excited via the lowest fd level of the Eu²⁺, the final state of the transition is the $4f^{7}(^{8}S_{7/2})$ ground state for each emission types.[13]

1.2.1 CURRENT RESEARCH

Optical properties of Eu^{2+} ions have been examined comprehensively.[10,11,12]. and over 300 Eu^{2+} ions containing compounds and their spectroscopic properties are complied and analyzed by Dorenbos.[13]

The energy scheme of Eu²⁺ ion in an octahedral coordination is shown in figure (1.1). The ground state electronic configuration of Eu²⁺ is 4f⁷, resulting in an ${}^{8}S_{7/2}$ ground state[14]. The five 4f⁶5d¹ orbitals are split by the octahedral crystal field into the t_{2g} (4f⁷(${}^{8}S_{7/2}$) \rightarrow 4f⁶5d¹ (t_{2g})) band with the triple degenerate xy, yz, and zx orbitals and the e_g (4f⁷(${}^{8}S_{7/2}$) \rightarrow 4f⁶5d¹

 (e_g)) band with the doubly degenerate $x^2 - y^2$ and z^2 orbitals. For octahedral symmetry, the t_{2g} band is lowest in energy, for a cubic site symmetry, the e_g band would be the lowest. The Crystal field splitting (10 Dq) is defined as the separation between the centroids of t_{2g} and e_g levels. The t_{2g} energy band of excitation spectrum of Eu²⁺ may include so-called staircase structure [12,14,16]. The origin of staircase structure is electronic interaction between six 4f electrons with 5d electron and from spin orbit interaction of 4f electron.

When site symmetry of the Eu^{2+} is distorted, the degeneracy t_{2g} and e_g will be partly or fully removed.

This work focuses on the optical properties of Eu^{2+} doped pyrophosphate compounds $Rb_2(Ca, Sr)P_2O_7$ and an Eu^{2+} -activated fluoride, $CsCaF_3:Eu^{2+}$.

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Chapter 2

THEORETICAL BACKGROUND

The following section is based mostly on the books by Henderson and Imbusch and Gaft, Reisfeld and Panczer.[4,8]

2.1 LIGAND FIELD THEORY

Most of the electronic spectroscopy in ionic crystals can be interpreted by the well known Ligand Field theory (LFT). The term of LFT covers all aspects of the manner in which an ion or atom is influenced by the nearest neighbors. Many results of the LFT depend on the approximate symmetry of the ligand distribution around the central metal ion rather than on the particular ligands or details of their locations.

The splitting of the d orbital energies and its consequences are the main focus of the LFT. It is possible examine qualitatively the effect of the various arrangements of ligands atoms around the central ion upon its d orbitals. The d orbitals in an isolated ion are degenerate. If a spherically symmetric field of negative charges is placed around the metal, those orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbital. From a spherical to an octahedral symmetry, all orbitals are raised in energy, relative to free ion. However, the orbital which lie along these $axes(x^2 - y^2, z^2)$ will be destabilize more than the orbitals which lie in-between the axes (xy, yz, zx). The crystal field splitting, 10 Dq, is defined as the energy difference between these orbitals. Fig. (2.1) shows crystal field splitting of the d orbitals in an octahedral symmetry.



Figure 2.1: Schematic of the lowest Eu^{2+} energy levels in an octahedral site.[13]



Figure 2.2: Crystal structure of CsCaF₃.

2.2 Quantum Mechanics of Eu²⁺ in an Octahedral Ligand Field

The establish crystal structure of three materials is the following. In $Rb_2MP_2O_7$ contains calcium or strontium ions which are surrounded by six oxygen ions that exhibit an octahedral symmetry. For CsCaF₃ the calcium ion is surrounded by six fluoride ions. In both hosts, the Eu ion substitutes for a Ca or Sr ion. Figs. 2.2 and 2.3 present a perspective drawing of the Eu²⁺ site in the two investigated hosts.

2.3 LIGAND FIELD SPLITTING IN OCTAHEDRAL SYMMETRY

The excited state of the Eu²⁺ has only one d electron and a usual approach for its description is like a hydrogen-like ion in the octahedral symmetry.



Figure 2.3: Crystal structure of Rb₂MP₂O₇.

In the following discussion, we will start to calculate the Hamiltonian in more general. In this approach, the nucleus of the transition metal is placed at the origin of the coordinate system, surrounded by the ligands at their appropriate positions. If the ith electron of the transition metal is located at the position $\vec{r_i}$ from the origin and ligands can be described by a charge distribution $\rho(R)$, then the electrostatic potential at the position of the electron is given by

$$V(r_i) = \int \frac{\rho(R)}{|\vec{R} - \vec{r_i}|} d\tau_R$$
(2.1)

The term $\frac{1}{|\vec{R}-\vec{r}|}$ is expanded in spherical harmonics,

$$\frac{1}{|\vec{R} - \vec{r}|} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \frac{r_{\langle}^{l}}{r_{\rangle}^{l+1}} \sum_{m=-l}^{l} Y_{lm}(\theta_{i}, \phi_{i}) Y_{lm}^{*}(\theta, \phi)$$
(2.2)

where r_{\langle} and r_{\rangle} are the larger or smaller of r_i and R. R, θ , ϕ are the spherical polar coordinates of ligands. When the equation (2.2) is inserted in equation (2.1), we get

$$V(r_i) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_{lm}(\theta_i, \phi_i) \int \rho(\vec{R}) \frac{r_{\langle}^l}{r_{\rangle}^{l+1}} Y_{lm}^*(\theta, \phi) d\tau_R$$
(2.3)

with $r_{i}=R$ and $d\tau_r$ representing volume integration. If the ligand system is regarded as a collection of point charges, then

$$V(r_i) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{l,m} r_i^l Y_{l,m}(\theta_i, \phi_i), \qquad (2.4)$$

with

$$A_{l,m} = \frac{4\pi}{2l+1} \sum_{k} \frac{-q_k Y_{l,m}^*(\Theta_k, \Phi_k)}{R_k^{l+1}},$$
(2.5)

where \sum_{k} runs over the k nearest neighbor negatively charged ligands of charge q_k . The matrix elements of the ligand field Hamiltonian then become,

$$H_{LK} = -\sum_{i=1}^{N} eV(r_i).$$
 (2.6)

Inserting (2.4) and (2.5) into (2.6) we find

$$H_{LK} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{k} \frac{r^{l}}{R_{k}^{l+1}} q_{k} e \frac{4\pi}{2l+1} Y_{l,m}^{*}(\Theta_{k}, \Phi_{k}) Y_{l,m}(\theta_{i}, \phi_{i})$$
(2.7)

where the sum and the coordinates θ_i , ϕ_i of the ith d electron have been omitted for brevity. The matrix elements will involve integrals of the form

$$\langle Y_{l,m_i} | Y_{n,m} | Y_{l,m_j} \rangle. \tag{2.8}$$

If $n \leq 2l$ and if 2l+1 is even, above integrals are nonzero. For d electrons, only n=0,2,4 need to be considered. the n=0 term will not contribute to the splitting since Y_{00} is constant. Then the Hamiltonian for the d electrons becomes

$$H_{LK} = \sum_{k} \frac{eq_{k}r^{2}}{R_{k}^{3}} \sum_{m=-2}^{2} (-1)^{m} \frac{4\pi}{5} Y_{2,-m}(\Theta_{k}, \Phi_{k}) Y_{2,m}(\theta_{i}, \phi_{i}) + \sum_{k} \frac{eq_{k}r^{4}}{R_{k}^{5}} \sum_{m=-4}^{4} (-1)^{m} \frac{4\pi}{5} Y_{4,-m}(\Theta_{k}, \Phi_{k}) Y_{4,m}(\theta_{i}, \phi_{i})$$
(2.9)

$$H_{oct} = \frac{Ze^2}{4\pi} \left[\frac{6}{R} + \frac{7r^4}{2R^5} C_0^{(4)}(\theta, \phi) + \left(\frac{5}{14} \right)^{1/2} \left(C_4^{(4)}(\theta, \phi) + C_{-4}^{(4)}(\theta, \phi) \right] + r^6 + \cdots \right]$$
(2.10)

here

$$C_m^{(4)}(\theta,\phi) = (\frac{4\pi}{2m+1})Y_4^m(\theta,\phi)$$
(2.11)

Now we can calculate the matrix element for $|5dm_1\;\rangle\;states.$

$$\langle 5d0|H_{oct}|5d0\rangle = \frac{1}{4\pi\epsilon_0} \frac{7Ze^2}{2R^5} \langle r^4 \rangle_{5d} \frac{6}{21} = 6Dq$$
(2.12)

and

$$\langle 5d1|H_{oct}|5d1\rangle = \langle 5d(-1)|H_{oct}|5d(-1)\rangle = \frac{1}{4\pi\epsilon_0} \frac{7Ze^2}{2R^5} \langle r^4 \rangle_{5d} \frac{-4}{21} = -4Dq \qquad (2.13)$$

where

$$D = \frac{1}{4\pi\epsilon_0} \frac{35Ze^2}{4R^5} \quad \text{and} \quad q = \frac{2}{105} \langle r^4 \rangle_{5d}$$
(2.14)

The strength of the octahedral ligand field can be characterized by Dq parameter which is called *the field strength parameter*. The matrix element for all of the other non-vanishing terms can be calculated and obtain the general ligand field matrix $\langle 5dm_l | H_{oct} | 5dm_s \rangle$. It should be noted that the state function are to be taken as those with quantum number m_l and m_s rather than those of the individual d electrons. Then the matrix elements

If we diagonalize above matrix, eigenstates could be obtained t_{2g} which are triply degenerate with eigenstates of -4 Dq and the states e_g which are doubly degenerate with eigenstates of 6 Dq. We listed wave function below and the 10 Dq splitting can be see in fig. (2.1).

$$d_{z^{2}} = |5d0\rangle$$

$$d_{x^{2}-y^{2}} = \frac{1}{\sqrt{2}}(|5d2\rangle + |5d-2\rangle)$$

$$d_{xy} = \frac{-i}{\sqrt{2}}(|5d2\rangle - |5d-2\rangle) \qquad (2.16)$$

$$d_{yz} = \frac{i}{\sqrt{2}}(|5d1\rangle - |5d-1\rangle)$$

$$d_{zx} = \frac{-1}{\sqrt{2}}(|5d1\rangle - |5d-1\rangle)$$

In Fig. (2.4), the graphical representation of the five atomic orbitals for a 5d electron is shown. Every single 5d orbital has 12 lobes. The t_{2g} band includes d_{xy} , d_{yz} and d_{zx} which have lobes which point in 'between' ligands. The e_g band has two orbitals, namely d_z^2 and $d_{x^2-y^2}$. These two orbitals have lobes directed at ligands , thus becoming the higher-energy doublet.

2.4 JAHN-TELLER EFFECT

For an orbital degenerate state, all non-linear nuclear configurations are unstable. This principle has profound consequence for electronic states in highly symmetric crystal lattices. Jahn-Teller theory states, any molecule or complex ion in an electronically degenerate state will be unstable relative to a configuration of lower symmetry in which the degeneracy is absent.

As an example, consider a complex with a full t_{2g} level and one electron in the e_g level. The ground state for the system is ²E, which is degenerate and maybe regarded as involving either occupation of the d_{z^2} or $d_{x^2-y^2}$ orbital. There will be vibrations which involve the simultaneous closer approach of the two ligands along the z axis and the moving outwards



Figure 2.4: Schematic representation of the d electron orbitals. When located at an octahedrally coordinated site, the three lower orbitals in picture are associated with the t_{2g} and the two higher orbital are associated with the $e_g[11]$

of the four ligand along the x - y axes. This will increase the overlap of the z axis ligands and decrease that of the x and y axis ligands. The d_{z^2} orbital rises in energy while the $d_{x^2-y^2}$ levels are lowered. This results in the lifting of the degeneracy of the ²E ground state.[12]

Thus, if a single electron is in the $d_{x^2-y^2}$ orbital, the energy of the complex will be lowered and the distortion favored in accordance with the Jahn-Teller theorem. The Jahn-Teller theorem is a general theorem that does not predict the magnitude of the distortion.

2.5 NEPHELAUXETIC EFFECT

Nephelauxetic Effect is described as "expansion of electron cloud and increasing electron delocalization in ligand -metal bonding". In other words, the cationic valency is reduced if some electron of ligand move into the orbital of the central ion. Due to this reduction, the d-electron wave function expand toward the ligands and the distance between electrons can increase and interaction of electron reduces. This effect is called *Nephelauxetic effect*.

2.6 References

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Chapter 3

EXPERIMENTAL DETAILS

3.1 SAMPLE PREPARATION

3.1.1 CsCaF₃:Eu²⁺

Polycrystalline sample of $CsCaF_3:Eu^{2+}$ were synthesized by a standard solid-state reaction technique. An XDR pattern confirmed the phase purity of the obtained material. Since the final product were to be found hygroscopic all measurement carried out with the sample sealed in quartz tubes.

$3.1.2 \quad RB_2(CA, SR)P_2O_7$

Polycrystalline samples of Eu^{2+} activated $(Rb_2M^{2+}P_2O_7)$ where $(M^{2+}=Ca,Sr)$ were synthesized by classic solid-state reaction techniques. Starting materials used were analytical grade Rb_2CO_3 (10 mole percent excess) $CaCO_3$, $SrCO_3$ and $(NH_4)_2HPO_4$ (10 mole percent excess) and Eu_2O_3 . The samples were heated at 300 C for one hour in air and then heated twice at 800 C for 5 hrs in a slightly reducing atmosphere with intermediate grindings. In both materials, the XRD pattern confirmed the formation of phase pure material. Since the final products were found also to be hygroscopic, all optical measurements were carried out in sealed quartz tubes.

3.2 Emission

Emission or photoemission spectroscopy is a technique which examines the wavelengths of the photon emitted by an atom or a molecules during the transition from the excited energy state to a lower energy state.

Once the sample is excited, it may have several relaxation channels to return lower energy level. It is possible to define two decay times: the radiative decay time and the actual observed decay time, which may be temperature dependent, as will usually occur when there are internal non-radiative channels.

3.2.1 RADIATIVE DECAY TIME

Radiative transition is a transition between two states of a molecule, the energy differences of two state is being emitted or absorbed as a photon. For an allowed emission transition, the decay time is short, approximatively 10^{-7} or 10^{-8} s, for strongly forbidden emission transition, the life time is longer, up to 10^{-3} s. If there are no non-radiative transition involved, the observed life time will equal the radiative lifetime.

3.2.2 Non-Radiative decay time

Radiative transition from excited state to ground state is not the only transition possible. The alternative is non-radiative transition, where the energy which is absorbed by the material and not emitted as radiation is dissipated to lattice .

3.2.3 EXPERIMENT

For the emission spectra of three material, we used similar techniques. The emission spectra were measured for several excitation energies using multiple collection methods and varying temperatures regimes.

3.2.4 Excitation source

- For *low* temperature measurement (6 K 300 K): Third harmonic output of a Spectra Physics Quanta-Ray DCR-11 Nd: YAG laser(λ) = 355 nm (all three samples)
- For *high* temperature measurement(T > 300 K): UV multi line output of a Spectra Physics Stabilite 2017-AR Argon laser plus 350 nm band filter full width half maximum (FWHM) 10 nm (just CsCaF₃:Eu²⁺)

3.2.5 Collection Method

An VIS/NIR thermoelectrically cooled CCD (Charge coupled device Model ST-6 Opto head) to -20° attached to a Acton Research Cor. Spectra $pro^{\textcircled{R}}$ O-275 meter Triple Grating Monochromator/Spectrograph with 50 grooves/nm grating blazed at 600 nm. The monochromator was driven by a Spectra Drive Stepping Motor scan controller. Data were collected during 10 s integration times over a spectral range of 600 nm with resolution of 0.5 nm/pixel. The spectra were collected using manufacturer supplied software. The input to the slits were coupled to a UV grade fiber optic cable and various appropriate lenses and filters were used to obtain one to one images of the sample luminescence onto the fiber entrance. (for all three samples)

3.2.6 SAMPLE PREPARATION AND TEMPERATURE HANDLING

- Emission spectra, at various temperatures (6 K 300 K for CsCaF₃ and 80 K 300 K for Rb₂(Ca,Sr)P₂O₇) were obtained by placing the samples into the optical chamber of a flow through cryostat, Oxford Instruments flow-through cryostat.
- Room Temperature emission spectra were obtained in open air with custom built sample holder for quartz tube sample holder. (all three materials).
- Emission spectra (T) 300 K) were obtained by placing sample in a custom built sample holder for a high temperature furnace. The temperature was controlled with

an Omega temperature controller custom modified to meet the requirements of the furnace. $(CsCaF_3:Eu^{2+})$.

3.3 Absorption and Excitation

The following section is based mostly on the books by Henderson and Imbusch, Vij, Gaft, Reisfeld and Panczer.[1,2,3]

3.3.1 Absorption

Absorption is a measure of the interaction of electromagnetic radiation with matter. Absorption spectroscopy provides information on the wavelengths of electromagnetic radiation that can be absorbed by samples under study. This is determined by varying wavelength and recording the intensity of the transmitted beam. The reasons have been stated in the sections on splitting and Hamiltonians.

A rule due to Beer and Lambert is that the light absorbed per unit length in a sample depends at any wavelength is proportional to the light intensity:

$$\frac{dI(\lambda)}{dx} = -\alpha(\lambda)I(\lambda) \tag{3.1}$$

where $\alpha(\lambda)$ is a proportionality constant called the absorption coefficient. Integrating above equation, the attenuation of a light beam traveling a light absorption medium is :

$$I_T(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)d}.$$
(3.2)

where $I_T(\lambda)$ is the transmitted light intensity, $I_0(\lambda)$ is the incident light intensity, $-\alpha(\lambda)$ is the absorption coefficient and d is the length of the light path in the sample. In these terms, the transmittance spectrum is given following:

$$T(\lambda) = \frac{I_T(\lambda)}{I_0(\lambda)}$$
(3.3)

and absorption coefficient can be determined using

$$\alpha(\lambda) = \frac{1}{d} \ln \left(\frac{I_0(\lambda)}{I_T(\lambda)} \right)$$
(3.4)

Absorption spectra are most useful when attempting to measure the transitions that do not lead to photoemission.

3.3.2 EXCITATION

In an excitation spectrum, the wavelength of the exciting light is varied and the intensity of the emitted light at a fixed emission wavelength is measured as a function of the excitation wavelength. The excitation spectrum gives information on the position of the excited states and crystal field splitting.

The sample luminescence, $S(\lambda)$, as it relates to the Beer-Lambert law is

$$S(\lambda) = CI_0(\lambda)(1 - e^{-\alpha(\lambda)d})$$
(3.5)

where C is a constant depending on the experimental details. If $\alpha(\lambda)$ is less than 1, we may Taylor expand second term of the right site of the equation. This enables us to relate the absorption coefficient to the emission intensity.

$$S(\lambda) = CI_0(\lambda)\alpha(\lambda)d \tag{3.6}$$

3.3.3 EXPERIMENT

Excitation spectra were recorded in a modified Cary 14 spectrophotometer. The three samples were excited by chopped radiation of tungsten lamp in the near ultraviolet and visible regions (350-700 nm) and a deuterium lamp in the ultraviolet region (200-350 nm). All three materials were placed into an Oxford Instruments flow-through cryostat, located in the sample chamber of the spectrophotometer. Luminescence was observed at right angles with either a Hamamatsu R212 photomultiplier tube (PMT) for CsCaF₃ or a red sensitive Hamamatsu R1477 (PMT) for Rb₂(Ca, Sr)P₂O₇, the detection wavelength was determined

by narrow band interference filters at multiple regions of interest that will be indicated on the presented figures. To increase the signal to noise ratio and to suppress the dark current of the PMT, the signals from the three materials were processed with a Stanford Model SR 830 DSP Lock-In Amplifier. By using the lock-in-amplifier, we are further able to deduce the relative phase of emission from different active centers in the host crystal. The excitation spectra were corrected for excitation photon flux using a calibrated Hamamatsu photodiode as reference detector.

3.4 LIFETIME: TIME RESOLVED SPECTROSCOPY MEASUREMENTS

Time resolved measurements were obtained with an UV LED excitation source filtered through a narrow band interference filter ($\lambda = 380$ nm, 10 nm FWHM for CsCaF₃ and $\lambda = 400$ nm, 10 nm FWHM for Rb₂(Ca, Sr)P₂O₇). The LED was driven by the amplified (Avantec) pulses of an Avtech AVP-C pulse generator. The emission was filtered by a 570 nm for CsCaF₃ and , 620 nm and 640 nm narrow band filters for Rb₂CaP₂O₇ and Rb₂SrP₂O₇, respectively, and detected with the Hamamatsu R212 PMT detector for CsCaF₃ and the Hamamatsu R1477 PMT detector for Rb₂(Ca, Sr)P₂O₇. The time resolved fluorescence was recorded through a photon counting system, consisting of an Ortec 567 time-to-amplitude converter in conjunction with an EGG pulse height analyzer. The temporal response for this experimental setup was measured to be 2 ns. Again the sample was mounted in a temperature variable Oxford Cryostat for measurements between 6 K and 300 K for CsCaF₃ and 80 K and 300 K for Rb₂(Ca, Sr)P₂O₇. For high temperature measurement (up to 550 K), a high temperature furnace was used.

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Chapter 4

Experimental results of $CsCaF_3:Eu^{2+}$

In this chapter, we will present system where the Eu^{2+} ion occupies an octahedral site: CsCaF₃:Eu²⁺ sample.

4.1 EXCITATION

The excitation spectra of $CsCaF_3:Eu^{2+}$ at 80 K and 300 K are shown in figure (4.1) and (4.2) respectively. The 5d band splits into the triple t_{2g} and doublet e_g bands as expected from the site symmetry. The high-energy band e_g is located between 42,500 cm⁻¹ and 50,000 cm⁻¹. The low-energy band t_{2g} is located between 23,000 cm⁻¹ and 32,500 cm⁻¹ and shows characteristic lines that are referred to as *staircase structure*. The high-energy band e_g is structureless.

The crystal field splitting(10 Dq) is given by the centroid separation of the t_{2g} and e_g bands. The centroid (C's) for these two bands were calculated by the method of moments as described in [1]. The first zeroth order moment, M_0 is defined as the area under the emission or excitation band.

$$M_0 = \int I(\nu) d\nu, \qquad (4.1)$$

where $I(\nu)$ is the intensity of the band as a function of wavenumber (ν) . The integral is calculated over the domain of each band of interest. Next, we define the first moment, M₁ by

$$M_1 = \frac{1}{M_0} \int I(\nu)\nu \, d\nu \tag{4.2}$$


Figure 4.1: Excitation Spectra of $\rm Eu^{2+}$ in CsCaF_3 T=80 K



Figure 4.2: Excitation Spectra of $\rm Eu^{2+}$ in CsCaF_3 T=300 K

By definition, the *centroid* of the band is equal to its first moment: $C \equiv M_1$. After determining the centroid of the t_{2g} and e_g bands, 10 Dq is to be found 17,400 cm⁻¹ at 80 K.

The excitation spectrum of CsCaF₃:Eu²⁺ is suffering from saturation. The reason is that CsCaF₃:Eu²⁺ material is hygroscopic and all measurement carried out with the sample sealed in quartz tube, and in this configuration, $\alpha(\lambda)d$ is no longer much smaller than 1. To deal with saturation, thin samples need to be used and we prepared such a sample by placing a small amount of material onto a piece of scotch tape. Fig. (4.3) shows the excitation spectrum of Cs₂CaP₂O₇ for the thin sample and optically thick sample. The saturation in the excitation spectrum taken with the think sample is evident.

We would like to point out that the excitation spectra at low and room temperature are very similar. We might note at this point already that Sommerdjik and Brill [2] have previously stated that the reason for a dramatic shift in the emission spectra (to be discussed) as a function of temperature can be attributed to two distinct Eu^{2+} sites that dominate the emission at different temperatures. The observed similarity of the exitation spectra at 80 K and at 300 K, rules out this explanation and we conclude that the observed emission in CsCaF₃ is due to a single Eu^{2+} center.

4.2 LOCATION OF ${}^{7}\mathrm{F}_{i}$

The low-energy band t_{2g} of excitation spectrum of Eu^{2+} in CsCaF₃ shows characteristic *staircase* structure. The staircase structure is due to transition to ${}^{7}F_{j}$ (j=0,6) levels of the Eu^{3+} core superimposed on top of the t_{2g} state additional the 5 d electron. ${}^{7}F_{0}$ pertains to the first steps of the characteristic staircase structure in f \rightarrow d absorption and excitation spectra of Eu^{2+} . In our sample the *steps* are not well resolved and the sharp features that are observed may in fact stem from absorption features of residual Eu^{3+} ions and thus the staircase approach cannot be applied effectively.

The position of lowest excited energy level of ${}^{7}F_{0}$ can be estimated using the so-called mirror-image relation.[6] This relationship is characteristic of a phonon-broadened emission



Figure 4.3: Excitation spectra of Eu^{2+} doped in $Cs_2CaP_2O_7$ sample at 80 K with thin and thick sample

with the same phonon energy for both ground and excited states.[8] For this purpose, the relation between the centroid of emission peak and Zero Phonon Line (ZPL) equals to the difference between ZPL and lowest excited energy state level.

$$C^{^{7}F_{0}} - ZPL = ZPL - C^{em}$$

$$\tag{4.3}$$

$$C^{7}F_{0} = 2ZPL - C^{em} (4.4)$$

In our case, ZPL has not been measured yet. We cannot use this methods to determine the position of lowest excited energy level of ${}^{7}F_{0}$.

The t_{2g} energy band can be fitted by seven Gaussian functions to estimate location of ${}^{7}F_{0}$. The important part for this method is that signal should not be saturated and the crystal symmetry should not be distorted. If the symmetry is distorted, we may need to use more than seven Gaussian function to fit excitation spectrum. With this approach we find the lowest excited state is to be at 24,980 cm⁻¹ (T = 300 K).

4.3 Emission

The temperature dependence of the emission spectra of Eu^{2+} in CsCaF₃ is shown in figure (4.4) and figure(4.5) (the figures have been normalized to equal heights in order to emphasize the shift and the shape of the emission spectra at various temperatures). A Gaussian shaped emission band is centered at 16,000 cm⁻¹(625nm) between at 6 K and at 50 K. As it is seen figure(4.4), starting at 50 K, the emission spectrum begins to shift towards higher frequencies with increasing temperature till room temperature. Simultaneously, the emission band starts to broaden and assuming an asymmetric shape. The peak of the emission moves 3,500 cm⁻¹ between at 50 K and 300 K. Above at 450 K, the quality of emission spectra deteriorates due to thermal quenching. Our result agree with those of Sommerdijk and Brill (at 80 K and 300 K).[1,3,4]



Figure 4.4: Lowest excited state location

Figure (4.5) shows the high temperature dependence of the emission. Between 300 K and 475 K the emission peak shifts by about 8 nm to the shorter wavelength, which can be attributed to the expansion of the lattice, reducing 10 Dq.



Figure 4.5: Temperature Dependence(T \leq 300 K) of the emission of Eu²⁺ in CsCaF₃

4.4 The Stoke Shift ΔS

When a system absorbs a photon, it gains energy and an electron is promoted to a transient excited state. While in the exited state, the ligand configuration relaxes to a new equilibrium position, hereby transferring energy to the vibrational modes of the host. Thus an emitted photon has on average a lower energy than an absorbed photon, and the difference between



Figure 4.6: Temperature Dependence (T ${\geq}300$ K) of the emission of Eu^{2+} in ${\rm CsCa}F_3$

these energies is usually called the Stokes Shift.[17] It is implied that the absorption and emission occurs between the same electronic levels.

$$\Delta S = |E^{em} - E^{ex}| \tag{4.5}$$

The value of E^{em} and ΔS are shown table(3.1) depending on temperature. The Stokes shift is 1.11 eV at 6 K, 0.89 eV at 80 K and 0.68 eV at 300 K. Evidently, this shift cannot be explained by thermal expansion of the lattice, and phase transitions of the host, as well as different emission centers can be ruled out due to the similarity of the excitation spectra at low and high temperatures. We do observe a dramatic broadening of the emission spectrum with increasing temperature (see Table 4.1), and thus we propose that the complex emission characteristics can be explained by a Eu ions occupying a single site, but exhibit two emission processes: the ordinary dipole allowed d-f transition and emission from an impurity bound excitonic state (usually referred to in the literature as 'anomalous emission').

Temperature (K)	$\Delta \mathrm{S}(\mathrm{cm}^{-1})$	$\mathrm{E}^{em} (\mathrm{cm}^{-1})$	$\Gamma^{em}(cm^{-1})$
6	8,980	15,980	3,310
80	7,200	17,440	3,900
300	5,480	19,500	5,000

Table 4.1: Depending on Temperature Stokes shift

Dorenbos compiled more than 300 Eu²⁺ doped samples.[7] The most common the Stokes shift is around 1,350 cm⁻¹ and the emission band width (FHMW) is around 1600 cm⁻¹. The anomalous emission is characterized by one or more following observation: a much larger Stokes shift (ΔS) 4000cm⁻¹), and much larger bandwidth (Γ_{em} > 3000 cm⁻¹), shift of the emission wavelength, lifetime. The Stokes shift and emission band width for CsCaF₃:Eu²⁺ as a function of temperature are given Table (3.1). The values for the Stokes shift are on the order of one electron volt, thus much larger than the average value for the normal Eu emission.

4.5 LIFE TIME: TEMPERATURE DEPENDENCE AND QUENCHING

Electron relaxation rates are measured by the Time Resolved Spectroscopy(TRS). The rated of the relaxation of the excited state electrons to the ground state is a function of the total number of the excited electrons and their transition probability. Thus, the relaxation rate decreases exponentially over time as the number of the electrons if ion has *one* emission center.

Relaxation curves were collected for every 010 K for $(T \leq 100)$ and every 25K $(T\rangle100)$. The luminescence decay curves for CsCaF₃:Eu²⁺ sample at 010 K, 150 K and 425 K are shown in figure (4.6)(detection wavelength $\lambda = 570$ nm). The signal rises rapidly within the pulse width of the excitation source and relaxes exponentially. A single exponential function resulted in excellent fits (solid lines, Fig. 4.6). The single exponential profile and the rapid signal rise allow us to conclude (in addition to the excitation data) that the two-center model proposed by Sommerdijk and Brill [1] is not supported by our experimental data and we find that the emission is due to single optical center.

The form of fitting function is

$$N = c + N(t_0)e^{-\frac{(t-t_0)}{\tau}}$$
(4.6)

where N is the number of the photon counts observed at t time, c is a constant background factor, t_0 is the initial start of decay, N_0 is the number of the counts at t_0 (amplitude) and τ is the lifetime of emission. the luminescent of any optical center depends on the temperature. As the temperature increases, at some critical point the lifetime of the emission will decrease and at some point that center will no longer radiate. The temperature dependence of the emission of CsCaF₃ is shown in figure (4.7). In general, the lifetime at any temperature, $\tau(T)$, is given by the equation

$$\frac{1}{\tau(T)} = \frac{1}{\tau_0} + \frac{1}{\tau_{NR}(T)}$$
(4.7)



Figure 4.7: Transient luminescence of $\rm Eu^{2+}$ in $\rm CsCaF_3$

where τ_0 is zero temperature radiative life time, $\tau_{NR}(T)$ is the non-radiative life time. Assuming $\tau_{NR}(T)$ varies according to an Arrhenius law, we can use above equation to fit data.

$$\frac{1}{\tau_{NR}} = Ae^{\frac{-\Delta E_2}{kT}} \tag{4.8}$$

Here ΔE_2 is the activation energy of the thermal quenching level, k is the Boltzmann constant and A is the constant.

In CsCaF₃, the radiative life time is defined as follows:

$$\frac{1}{\tau_0} = \frac{1/\tau_{exc} + 3e^{(-\Delta E_1/kT)}(1/\tau_d)}{1 + 3e^{(-\Delta E_1/kT)}}$$
(4.9)

 τ_{exc} and , τ_d are the excitonic level life time and the d level life time respectively, and ΔE_1 is the energy difference between excitonic level and d level. The radiative lifetime equation is derived in Chapter (4.8).

If we insert Eqs. (4.9) and (4.10) in equation (4.8), we find

$$\frac{1}{\tau(T)} = \frac{1/\tau_{exc} + 3e^{(-\Delta E_1/kT)}(1/\tau_d)}{1 + 3e^{(-\Delta E_1/kT)}} + Ae^{\frac{-\Delta E_2}{kT}}$$
(4.10)

From the modified Arrhenius fit fig. (4.8), we obtain an activation energy to the quenching level $\Delta E_2 = 3300 \text{ cm}^{-1}$, the energy differences between *excitationlevel* and d level $\Delta E_1 = 235 \text{ cm}^{-1}$, the excitation lifetime $\tau_{exc} = 1.56 \ \mu\text{s}$ and the d level emission lifetime $\tau_d = 1.19 \ \mu s$. The parameters will be discussed in detail in Chapter (4.7), here it is sufficient to note that our model gives and excellent fit to the data.

4.6 CENTROID SHIFT AND RED SHIFT

The centroid shift ϵ_c is defined as the energy shift of the 5d configuration of Eu²⁺ in the lattice relative to the free ion value. For Eu²⁺ in octahedral configuration, ϵ_c can be estimated from following equation:



Figure 4.8: Relaxation time for $CsCaF_3:Eu^{2+}$ as a function of temperature. The red curve is the Modified Arrhenius plot fit Eq. (4.8)

$$\epsilon_c = E_c(free) - \left[E^{ex} + 0.37 + \frac{10Dq}{r(A)}\right]eV$$
(4.11)

 E_c (free)(4.93 eV) is the barycenter energy of the high spin $4f^65d$ levels in free Eu²⁺, r(A) determines the fraction of 10Dq that contributes the red shift and it is 5/2 for octahedral sites. E^{ex} is the peak energy of the $4f^7 \rightarrow 4f^6$ excitation transition (centroid) and the factor 0.37 eV accounts for the 7F_j levels that result in the 0.74 eV wide first $4f^65d$ band. From the excitation spectra at 300 K, 10Dq is to be found 16,700 cm⁻¹ (2.07 eV) and E^{ex} is 24,980 cm⁻¹ (3.07eV). The ϵ_c is to be found ≈ 0.64 eV.

Dorenbos compiled centroid shift values for some compounds.[12] The ϵ_c value of CsCaF₃ is 0.63 eV which is in agreement with our result at room temperature.

The red shift D(2+,A) for divalent lanthanides in a given host material A, which is a combination of the centroid shift and the crystal field splitting of the Eu²⁺ electronic configuration, can be calculated from following relation.[8,10]

$$D(2+,A) = E^{free} - E^{ex} (4.12)$$

where E^{free} is the energy differences between the ground state and the Eu²⁺ 4f⁶5d¹ excited state in the free ion 34,036 cm⁻¹ (4.22 eV). The red shift for this metarial is found to be 9,056 cm⁻¹ (1,12 eV).

4.6.1 DISCUSSION

The emission spectra of Eu^{2+} doped in CsCaF₃ shows very interesting result. The centroid of emission spectra is 625 nm at 50 K and it start to shift to higher energy values which coincides with a temperature at which the relaxation time start to drop. Moreover, the shift ceases at room temperature, when the initial drop of the relaxation time ceases as well. After reaching room temperature, the shift of emission spectra is only about 300 cm⁻¹ between at 300 K and at 475 K. From all observation, we can suggest two models to explain emission spectra shifting: Excitonic emission and Jahn-Teller effect. The model of two emission center suggested by Sommerdjik and Brill [4] was ruled out according to our data results.

In the Jahn-Teller model, strong relation of ligands would result in a lowering of the local symmetry, thus splitting the t_{2g} lower energy band into doublet and singlet. Here, the emission would shift due to population of the upper component of the split triplet with the increase of the observed relaxation rate being due to the known cubic frequency dependence of the optical transition.

In the excitonic emission, the emission would occur from excitonic level at low temperature. Thermal population of the Eu^{2+} 5d level of deviated temperature would result in a shift of the emission spectra to higher energies values. In this interpretation, the excitonic relaxation rate would be only slightly lower than that of the Eu^{2+} dipole allowed d-f transition.

4.7 EXCITONIC EMISSION

Dorenbos collected information on anomalous emission of divalent lanthanide ions and he studied the systematic variation with the type of host and type of lanthanide compound[10]. Figure(3.8) shows the wavelength of emission on Eu^{2+} doped in a variety of host materials. The CsCaF₃ sample was listed as system with suspected anomalous emission.[10] The identification number was used in fig. (3.8) to demonstrate relationships between the crystal field depression and specific properties of the host lattice.

The broadband emission spectra of Eu^{2+} is classified into two type emission by Dorenbos [10]: Normal and anomalous d-f emission. In the first case, the emission is due to the electric dipole and spin-allowed transition between $4f^65d^1 \rightarrow 4f^7$ (ground state). The second one is due to characterized by one or more of following observation:

• Large Stokes shift $\Delta S \rangle 4000 \text{ cm}^{-1}$



Figure 4.9: The wavelength of Eu^{2+} emission in fluoride compounds. The normal d-f emission is represented by \blacktriangle and the anomalous emission is represented by \blacktriangle . [10]

- The width of emission spectra (FHWM) Γ_{em} > 3000 cm⁻¹
- The emission intensity is usually quenched around 450 K
- The lifetime of emission is generally larger than 100 μ s
- The emission spectra may show anomalous temperature dependence behavior

Under these 5 aspects which are important keys to ascribe emission as a anomalous emission, we can investigate our results.

4.7.1 The Stokes shift

The Stokes shift of the Eu²⁺ in CsCaF₃ is abnormally large and it depends on temperature. It is estimated at 9,000 cm^{-1} at 6 K, 7,480 cm⁻¹ at 80 K and 5,480 cm⁻¹ at 300 K. All three

Compound	$\Gamma_{em}(ns)$	$\Delta S \ \mathrm{cm}^{-1}$	$ au(\mu s)$	ref
BaS	3980	7790	Afterglow	10
$Ba_2LiB_5O_{10}$	2419	10807	2.9	7,12,13
Ba_2SiO_5	3791	7743	12.6	7,12,13
BaF_2	4110(77K)	9195	1.8	7,12,13
Sr_2LiSiO_4F	3950	6210	1.2	7,13
$Sr_3(BO_3)_2$	4030	3305	2.5	14

Table 4.2: The optical properties of the Eu²⁺ ion in materials suspected of exhibiting anomalous emission. τ is reported for 4.2 K.

values of the Stokes shift are larger than what is expected normal emission indication. This observation supports the observation of anomalous emission in $CsCaF_3$.

4.7.2 Emission Band Peak

The full width half maximum (FWHM) for emission spectra, Γ^{em} , is very broad in divalent europium compounds exhibiting anomalous emission. Γ^{em} in CsCaF₃ sample is variying from 3,250 cm⁻¹ at 6 K to 5,100 cm⁻¹ at 300 K. It is to be found that at both temperature, Γ^{em} is larger than 3,000 cm⁻¹, again supporting the model of anomalous emission.

4.7.3 LIFETIME

Normal Eu²⁺ emission transition, $4f^{6}5d^{1} \rightarrow 4f^{7}$, the typical value of decay time is around 1,1 μ s. While this value is much shorter than the 100 μ s that Dorenbos presents, Table (3.3) shows compounds which have anomalous emission but lifetime values that are comparable to the one that we find.

The decay time of the Eu^{2+} in $CsCaF_3$ is to be found 1, 56 μ s at 6 K and 1,31 μ at room temperature. Both values are higher than normal emission decay time value. This is also indication of anomalous emission transition.

4.7.4 Thermal Quenching of the Eu^{2+} emission

Another indication of anomalous emission is a low quenching temperature. Normal Eu^{2+} emission may quench at relatively low temperature if the excited $4f^{6}5d^{1}$ level located close to the conduction band. There is also connection between location of the 5d levels relative to conduction band states and the presence of anomalous emission.[10] The thermal quenching temperature is to be found around 375 K for our sample. This is in the range where the thermal quenching temperature can be ascribed as an indication for the anomalous emission.

4.7.5 Emission Peak depending on Temperature

For the anomalous emission, there is shift of the emission peak (on the order of 100's of nanometers) toward shorter wavelengths as the temperature is increased. The emission peak of Eu^{2+} was measured at 625 nm at 6 K and 510 nm at 300 K. The shift is 115 nm between these two temperature values supports the anomalous emission model.

4.8 Model

According to above five aspects, we may conclude that Eu doped $CsCaF_3$ exhibits anomalous emission.

In this model, three assumptions were made: First, the exited state levels are in thermal equilibrium. Second, we assume that the energy of the individual levels are not changing substantially with temperature. Third, we include only the lowest energy level of the excitonic state. The rate equation for the model is the following:

$$\Gamma_R = n_{ex}\Gamma_{ex} + 3n_d\Gamma_d \tag{4.13}$$

where n_d and n_{ex} are the population number of the three degenerate t_{2g} and excitonic levels, respectively, and Γ_d and Γ_{ex} are the corresponding transition rate coefficients, with

$$n_{ex} + 3n_d = 1. (4.14)$$



Figure 4.10: Position of d level (t_{2g}) and Excitonic level

The relative population of the two levels in thermal equilibrium are related by Boltzmann's law

$$\frac{n_d}{n_{ex}} = e^{\Delta E_1/kT} \tag{4.15}$$

From the three equation given above , we can calculate \mathbf{n}_{ex} and $n_d.$

$$n_d = e^{\Delta E_1/kT} n_{ex} \tag{4.16}$$

Inserting this in equation (4.14)

$$n_{ex} + 3e^{\Delta E_1/kT} n_{ex} = 1$$

$$n_{ex} = \frac{1}{1 + 3e^{\Delta E_1/kT}}$$
(4.17)

Then we can get \mathbf{n}_d

$$\frac{1}{1+3e^{\Delta E_{1}/kT}} + 3n_{d} = 1$$

$$3n_{d} = 1 - \frac{1}{1+3e^{\Delta E_{1}/kT}}$$

$$3n_{d} = \frac{3e^{\Delta E_{1}/kT}}{1+3e^{\Delta E_{1}/kT}}$$

$$n_{d} = \frac{e^{\Delta E_{1}/kT}}{1+3e^{\Delta E_{1}/kT}}$$
(4.18)

inserting Eq. 4-15 and 4-16 into the rate Eq. 4-14 we find:

$$\Gamma_R = \frac{1}{1 + 3e^{-\Delta E_1/kT}} \Gamma_{ex} + \frac{3e^{-\Delta E_1/kT}}{1 + 3e^{-\Delta E_1/kT}} \Gamma_d$$
(4.19)

and

$$\Gamma_R = \frac{\Gamma_{ex} + 3e^{-\Delta E_1/kT}\Gamma_d}{1 + 3e^{-\Delta E_1/kT}}$$
(4.20)

The relation between transiton rate and life time is

$$\Gamma = \frac{1}{\tau} \tag{4.21}$$

Using this relationship, the radiative life time for the model is the following:

$$\tau_R = \frac{1}{\Gamma_R}$$

$$\tau_R = \frac{1 + 3e^{-\Delta E_1/kT}}{\Gamma_{ex} + 3e^{-\Delta E_1/kT}\Gamma_d}$$
(4.22)

The Arrhenius Function is defined by Eq. (4.8). If we insert the radiative lifetime Eq. (4.20) and non-radiative lifetime Eq. (4.9) we can find a Modified Arrhenius function for this system

$$\frac{1}{\tau(T)} = \frac{1/\tau_{exc} + 3e^{(-\Delta E_1/kT)}(1/\tau_d)}{1 + 3e^{(-\Delta E_1/kT)}} + Ae^{\frac{-\Delta E_2}{kT}}$$
(4.23)

or

$$\tau(T) = \frac{1}{\frac{\Gamma_{ex} + 3e^{(-\Delta E_1/kT)}(\Gamma_d)}{1 + 3e^{(-\Delta E_1/kT)}} + Ae^{\frac{-\Delta E_2}{kT}}}$$
(4.24)

Here ΔE_1 is energy differences between the excitonic level and the d levels (t_{2g}) , ΔE_2 is the activation energy to a quenching level, k is Boltzmann constant and T is temperature. The fig(4.10) shows location of the d levels (t_{2g}) and the excitonic level. Fig. (4.11) shows our model for Eu²⁺ in CsCaF₃. Note that the activation energy is 14 times larger than the energy difference between the excitonic and the d-levels (t_{2g}) . This justifies the use of a single quenching energy for both the excitonic and the d-levels (t_{2g}) .

After determined energy differences d level (t_{2g}) and excitonic level, we can calculated the population in thermal equilibrium for each band.

$$\frac{n_d}{n_{ex}} = e^{-\Delta E_1/kT} \tag{4.25}$$

 ΔE_1 is obtained 235 cm⁻¹, corresponding to 325 K, from the modified Arrhenius function. Inserting ΔE_1 in eq. 426 and taking T=300 K

$$\frac{n_d}{n_{ex}} = e^{-325/T} \tag{4.26}$$

$$\frac{n_d}{n_{ex}} = 0.32\tag{4.27}$$

so n_d equals to 1/6 and n_{ex} equals to 1/2. Now we can calculate intensity ratio of d level versus excitonic level.

$$\frac{I_d}{I_{ex}} = \frac{3n_d\Gamma_d}{n_{ex}\Gamma ex} = \frac{8}{11} \tag{4.28}$$



Figure 4.11: Excitonic level and d level of $\rm Eu^{2+}$ in $\rm CsCaF_3$

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Chapter 5

EXPERIMENTAL RESULTS OF RB₂(CA, SR)P₂O₇ SAMPLES

In this chapter, we will present another system where the Eu^{2+} ion occupies an octahedral site, i.e., $Rb_2(Ca, Sr)P_2O_7:Eu^{2+}$.

5.1 EXCITATION SPECTRA

Figs. (5.1) and (5.2) show the excitation spectra of $\text{Rb}_2\text{CaP}_2\text{O}_7:\text{Eu}^{2+}$ and $\text{Rb}_2\text{SrP}_2\text{O}_7:\text{Eu}^{2+}$ at 80 K, respectively. Clearly evident is the splitting of the $4f^65d^1$ electronic configuration into the lower-energy t_{2g} and high-energy e_g components. The low and high-energy bands in the excitation spectra of both sample are associated with the $4f^7[^8S_7] \rightarrow 4f^65d^1$ [t_{2g}] and $4f^7 [^8S_7] \rightarrow 4f^65d^1[e_g]$ transition. The high-energy bands, e_g , are located between 40,000 cm⁻¹ and 50,000 cm⁻¹. The low-energy bands, t_{2g} , are located roughly between 23,000 cm⁻¹ and 33,000 cm⁻¹ and both materials show evidence of the *staircase structure* while the highenergy bands, e_g , are essentially devoid of any structure.

The crystal field splitting, 10 Dq, determination method is given in the previous chapter. Using this method, the crystal field splitting is to be found at 17,570 cm⁻¹ or 2.18 eV for Rb₂CaP₂O₇ and 16,260 cm⁻¹ or 2.08 eV for Rb₂SrP₂O₇ at 80 K. This result is consistent with the expected reduction of the crystal field strength due to an increase of the lattice constant that occurs the calcium ion is replaced by strontium ion. Table (5.1) shows the centroids of both the low-energy and high-energy bands, the 10 Dq values and the full width half maximum for both materials.



Figure 5.1: The excitation spectrum of $Rb_2CaP_2O_7:Eu^{2+}$ sample at 80 K.

Table 5.1: The centroid of the $4f^{6}5d^{1}(t_{2g})[C^{t_{2g}}]$ and $4f^{6}5d^{1}(e_{g})[C^{e_{g}}]$ electronic configuration, crystal field splitting(10 Dq) and spectra width of $t_{2g}[\Gamma_{t_{2g}}]$ and $e_{g}[\Gamma_{e_{g}}]$ excitation bands at 80 K; all values in cm⁻¹.

Host	$C^{t_{2g}}$	C^{e_g}	10 Dq	Γ_{t_2g}	Γ_{e_g}
$Rb_2SrP_2O_7$	28,500	44,765	16,260	5,990	6565
$Rb_2CaP_2O_7$	27,810	45,390	17,570	5461	6210



Figure 5.2: The excitation spectrum of $Rb_2SrP_2O_7:Eu^{2+}$ sample at 80 K.

5.2 Emission Spectra

The emission spectra of $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$ at 80 K are shown in figure (4.3) and (4.4). The emission peak of $Rb_2CaP_2O_7$ activated with Eu^{2+} is to be found around 645 nm (15,474 cm⁻¹ (1.92 eV)) and the peak for $Rb_2SrP_2O_7$ is around 590 nm (16,940 cm⁻¹ (2.10 eV)), both values are for T = 80 K.

The emission spectra of Eu^{2+} doped in $Rb_2(Ca,Sr)P_2O_7$ show much less dynamics than the CsCaF₃ system with temperature: while the $Rb_2SrP_2O_7$ sample exhibits merely a broadening with rising temperature, the $Rb_2CaP_2O_7$ sample shows a distinctive, but weak shift towards higher frequencies with increasing temperatures. We attribute this behavior tentatively to a splitting of the t_{2g} component due to a distortion of the octahedral symmetry, either because of the non-ideal octahedral site symmetry (the Ca/Sr octahedral site is slightly distorted [1]) or to spontaneous symmetry reduction due to a Jahn-Teller distortion, in addition to the expected shift due to thermal expansion.

5.3 CENTROID SHIFT, RED SHIFT AND STOKES SHIFT

For Eu^{2+} in octahedral coordination, the centroid shift can be estimated from the following formula[2]:

$$\epsilon_c = E_c^{free} - \left(E^{ex} + 0.37 + \frac{10Dq}{r}\right) \tag{5.1}$$

In this equation(5.1) $E_c^{free}=4.93 \text{ eV}$ which is the barycenter energy of the high spin $4f^65d^1$ levels in free Eu²⁺, r(A)=5/2 and 10 Dq values depend on the material. The E^{ex} value is the lowest excited state of $4F_j$ (j=0-6) multiples. The location of E^{ex} value on low-energy band t_{2g} was discussed in the previous chapter. The relation between ZPL and centroid of the emission spectrum can be used to locate E^{ex}. Unfortunately, we have not measured location of ZPL yet. The other method, based on fitting the t_{2g} band with seven Gaussian functions yielded results. The lowest excited state is to be found 25,300 cm⁻¹ for Rb₂SrP₂O₇ and



Figure 5.3: Emission spectra of $Rb_2SrP_2O_7:Eu^{2+}$



Figure 5.4: Emission spectra of $Rb_2CaP_2O_7:Eu^{2+}$.

24,950 cm⁻¹ for Rb₂CaP₂O₇. The 10 Dq values at 300 K are 17035 cm⁻¹ for Rb₂CaP₂O₇ and 15190 cm⁻¹ for Rb₂SrP₂O₇.

From these values, the centroid shift can be estimated at 300 K:

$$\epsilon_{cSr} = 4.93 - \left(3.136 + 0.37 + \frac{1.97 * 2}{5}\right) eV \tag{5.2}$$

$$\epsilon_{c_{Sr}} = 0.64 eV. \tag{5.3}$$

and

$$\epsilon_{c_{Ca}} = 4.93 - \left(3.1 + 0.37 + \frac{2.11 * 2}{5}\right) eV \tag{5.4}$$

$$\epsilon_{c_{Ca}} = 0.61 eV. \tag{5.5}$$

The Stokes shift at 80 K can be obtained following formulation:

$$\Delta S = E^{ex} - C^{em} \tag{5.6}$$

For $Rb_2(Sr, Ca)P_2O_7$ samples,

$$\Delta S_{Sr} = 25300 cm^{-1} - 16934 cm^{-1} = 8366 cm^{-1}.$$
(5.7)

and

$$\Delta S_{Ca} = 24950 cm^{-1} - 15474 cm^{-1} = 9475 cm^{-1}.$$
(5.8)

Table 5.2 summarizes all values.

The red shift is calculated from the following relation[3]:

$$D(2+,A) = E^{free} - E^{ex}$$
(5.9)

Table 5.2: Peak energy of the $4f^7 \rightarrow 4f^6[4^7 F_0]5d^1$ excitation transition $[E^{ex}]$, peak energy of emission band (C^{em}) , spectral width of the emission band (Γ^{em}) , the red shift (D(2+1,A)), centroid shift (ϵ_c) , and Stokes shift $(\Delta S = E^{ex} - C^{em})$; all values in cm⁻¹ and at 80 K.

Host	\mathbf{E}^{ex}	E^{em}	Γ^{em}	D(2+,A)	$\epsilon_c(300K)$	ΔS
$Rb_2CaP_2O_7$	25,000	15,474	2,400	9,036	$5,\!115$	9,475
$Rb_2SrP_2O_7$	25,648	16,940	3,022	8,388	4,920	8,366

where E^{free} is the energy differences between the ground state and the Eu^{2+} 4f⁶[⁷4F₀]5d¹ excited level in the free ion (34,036 cm⁻¹:4.22 eV). The red shift is calculated 9,036 cm⁻¹ and 8,388 cm⁻¹ for Rb2CaP₂O₇ and Rb₂SrP₂O₇, respectively. The red shift in Rb₂CaP₂O₇ exceeds that in Rb₂SrP₂O₇ (Table 4.2) mainly due to larger crystal field splitting of the Eu²⁺ 4f⁶5d¹ electronic configuration[2]. The larger red shift is responsible of the energetically lower Eu^{2+} emission in Rb₂CaP₂O₇ (15,474 cm⁻¹) relative to that in Rb₂SrP₂O₇ (16,940 cm⁻¹). The value for the Rb₂CaP₂O₇ is the lowest reported frequency for the Eu emission in any phosphate.

5.4 Temperature Dependence of the Eu^{2+} Lifetime

Life time curves were collected for every 25 K between at 80 K and 525K. All data show single exponential character for both sample. Figures (5.5) and (5.6) show lifetime data at three different temperature for both sample, with the red curves representing single exponential fits.

The relaxation time of Eu^{2+} emission and in general of any luminescence center is temperature dependent. The temperature dependence of the emission lifetimes of $Rb_2SrP_2O_7$ and $Rb_2CaP_2O_7$ are shown in figures (5.7) and (5.8):

The activation energy (ΔE) for the thermal quenching of the Eu²⁺ emission in Rb₂SrP₂O₇ and Rb₂CaP₂O₇ were determined by measuring the temperature dependence of the Eu²⁺



Figure 5.5: Flouresence transition for $Rb2CaP_2O_7:Eu^{2+}$ at three different temperatures. The red curves are the single exponential curve fits with background to the data.



Figure 5.6: Flouresence transition for $Rb2SrP_2O_7:Eu^{2+}$ at three different temperatures.



Figure 5.7: Relaxation time for $Rb_2CaP_2O_7$ as a function of temperature. The red curve is the Arrhenius fit (Eq. 5.7) to the data.



Figure 5.8: Relaxation time for $Rb_2SrP_2O_7$ as a function of temperature. The red curve is the Arrhenius fit Eq. (5.7) to the data.
emission lifetime(Figs 5.7 and 5.8). The following Arrhenius equation was used to fit the lifetimes :

$$\tau(T) = \frac{1}{\Gamma_0 + \Gamma_{NR} e^{-\Delta E/kT}}$$
(5.10)

From the fit, the values are $\tau_0=1.18 \ \mu s$ and 1.45 μs and $\Delta E=3,845 \ cm^{-1}$ and 3,158 cm⁻¹ for the Rb₂CaP₂O₇ and Rb₂SrP₂O₇, respectively. The quenching temperature T_{0.5} is defined as the temperature where the emission intensity and lifetime has decreased to 50 percent of the low temperature value. (T_{0.5}) is about 385 K for the Rb₂CaP₂O₇ and 380 K for the Rb₂SrP₂O₇. The complete quenching of the Eu²⁺ emission occurs around 525 K for both sample. These values are compiled in Table(5.3).

Table 5.3: The Values of the parameters used in fitting the temperature dependence of the lifetime data, the activation energy for thermal quenching ΔE , and the thermal quenching temperature $T_{0.5}$.

Sample	$ au_0 \ (\mu s)$	$\Delta E (cm^{-1})$	$T_{0.5}$ (K)
$Rb_2CaP_2O_7$	1.45	3,160	385
$Rb_2SrP_2O_7$	1.18	3,840	380

5.5 Discussion

The Rb₂(Ca,Sr)P₂O₇ have very interesting emission and excitation spectra. The Eu²⁺ emission spectra are centered at 645 cm⁻¹ and 590 cm⁻¹ for Rb₂CaP₂O₇ and Rb₂SrP₂O₇, respectively. These values are the farthest red-shifted emission peaks that have been reported in the literature concerning Eu²⁺ doped phosphate compounds.[4] Both samples have very large Stokes shift (Δ S \rangle 1 eV) of the emission which is uncharacteristic of the normal Eu²⁺ 4f⁶5d¹ \rightarrow 4f⁷ emission transition in solids.[2] These large Stokes shifts are often an indication of anomalous emission (for example, CaCsF₃).

5.6 EXCITATION SPECTRA

The absorption transition for free Eu^{2+} is observed at 33,800 cm⁻¹. The free energies for lanthanide ions are schematically represented in figure(4.9).

In an octahedral symmetry, the 5d excited level of the Eu^{2+} splits into two bands. The lower-energy band t_{2g} is three fold degenerate and corresponds to electronic wavefunction occupying the position off axis with respect to ligands. The high-energy band e_g is two fold degenerate and those state arise from excitation along ligand axis.

In Rb₂SrP₂O₇ and Rb₂CaP₂O₇, the octahedrally crystal field splitting are estimated 16,260 cm⁻¹ and 17,570 cm⁻¹. In XMP₂O₇(X=Cs,Ra) and (M=Ca,Sr) samples the crystal field splitting are increased with a decrease in bond length by due to the smaller M cations; $Dq\approx 1/R^5$ where R is the bond length between a center ion and ligand ions[5]. The rule is confirmed XMP₂O₇ (X=Cs,Ra) and (M=Ca,Sr) samples. As it is seen from table

$$10Dq_{Rb_2CaP_2O_7} > 10Dq_{Rb_2SrP_2O_7}$$
 (5.11)

and

$$10Dq_{Cs_2CaP_2O_7} \rangle 10Dq_{Cs_2SrP_2O_7} \tag{5.12}$$

Table 5.4: The octahedrally crystal field splitting increases with decreases size of the divalent cation.

Sample	$10 \text{ Dq } (\text{cm}^{-1})$
$Rb_2CaP_2O_7$	$17,\!570$
$Cs_2CaP_2O_7$	18,200
$Rb_2SrP_2O_7$	16,260
$Cs_2SrP_2O_7$	17,387

Some of the observed splitting in the excitation spectra of $Rb_2MP_2O_7$ (M=Ca,Sr) may be due to a distortion of the octahedral symmetry, either because of the non-ideal octahedral site



Figure 5.9: The energy level scheme of the free divalent lanthanide. The solid curve (a) connects the locations of the first $4f^{n-1}5d$ level[11]

symmetry (the Ca/Sr octahedral site is slightly distorted [1]) or to spontaneous symmetry reduction due to a Jahn-Teller distortion.

5.7 Emission Spectra

In previous chapter, we discussed the Eu^{2+} broadband emission. We can distinguish between the normal d-f emission and anomalous emission. We also described five criteria for anomalous type emission.Now, we can evaluate what type of emission $Rb_2MP_2O_7$ sample have according to above five criteria.

5.7.1 The Stokes Shift

The stokes shift of $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$ are abnormally large. The Stokes shift are estimated 8,708 cm⁻¹ and 9,525 cm⁻¹ for $Rb_2SrP_2O_7$ and $Rb_2CaP_2O_7$, respectively. The large stokes shift is normally an indication of anomalous emission. However, the large Stokes shift can be indicative of sustainable geometric distortion (either because of the non-ideal octahedral site symmetry or to spontaneous symmetry reduction due to a Jahn-Teller distortion) around the Eu^{2+} in the excited state.

S.H.M. Poort and G. Blasse gave an explanation for large Stoke shift with a long wavelength emission[7]. The long wavelength Eu^{2+} emission with large Stoke shift is observed in host lattice in which large cations from linear chains in the lattice. The divalent Eu^{2+} in these chains experiences positive charge due to cation neighbors in the chain direction. In addition to this effect, the negative charges of the nearest anion neighbor also effect Eu^{2+} ion. The positive charge can orient one d-orbital preferentially. This will lower its energy and therefore result in the Eu^{2+} emission at longer wavelengths. Since such d-orbital will be more delocalized than without preferential oriention, the Stokes shift of the emission will be also larger. This effect has been observed $BaAl_2O_4:Eu^{2+}$, $Sr_3(P_2O_4)_2:Eu^{2+}$. Γ_{em} in the Rb₂CaP₂O₇ and Rb₂SrP₂O₇ samples are relatively narrow (2,400cm⁻¹ and 3,022 cm⁻¹ respectively). These two values are less than the value of 3,000 cm⁻¹, which is indication of anomalous emission.

5.7.3 LIFETIME MEASUREMENTS

The spectra of Eu²⁺ doped compounds are generally due to parity-allowed electric dipole transitions, $4f^6 5d^1 \rightarrow 4f^7$. The decay times of these transitions are usually in the range from 0.2 to 2 μ s [6] The characteristic lifetime of Eu²⁺ is around 1.2 μ s.[1]

The low temperature relaxation times of 1.16 μ s for Rb₂SrP₂O₇ and 1.44 μ Rb₂CaP₂O₇ are within the typical range found for divalent europium.

5.7.4 Thermal Quenching of the Eu^{2+} Emission

The quenching temperature $T_{0.5}$ is the temperature at which the emission intensity has dropped to 50 percent of the low temperature value. The low quenching temperature is one of the indication of anomalous emission. However, it is not the sole indicator for an impurity trapped exciton level. The normal emission of the Eu₂₊ may quench at relatively low temperatures if the excited $4f^{6}5d^{1}$ level is located close to the conduction band. Table (5.5) shows the quenching temperature $T_{0.5}$ of Eu²⁺ 5d \rightarrow 4f emission M=Sr,Ca site in inorganic compounds.[8]

The quenching temperatures in $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$ are 385 K and 380 K respectively.

5.7.5 Emission Wavelength as a Function of Temperature

In the previous chapter, we said that for anomalous emission, the emission peak shifts on the order of 100 nm towards shorter wavelengths from low to high temperature. The emission spectra of Eu^{2+} in $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$ do shift by 13 nm and 6 nm, respectively,

Compound	$T_{0.5} (K)(Sr)$	$T_{0.5}$ (K)(Ca)	Reference
MP_2O_7	470	407	[8(1)]
$M_2B_5O_9Cl$	480	460	[8(23)]
MGa_2S_4	470	440	[9,10]
M ₃ SiO ₅	400	360	[8(2)]

Table 5.5: The quenching temperature $T_{0.5}$ of Eu^{2+} 5d \rightarrow 4f emission M=Sr,Ca site in inorganic compounds.[8]

to shorter wavelength when the temperature is increased from at 77 K to 300 K. However, this is a slight change relative to that of anomalous emission and is expected due to the decreasing crystal field strength with increasing temperatures.

As a result of five criteria, we conclude that the very large Stokes shift for these materials is in conflict with the general experience of the normal Eu^{2+} luminescence. Generally, a large Stokes shift is associated with anomalous emission related to self trapped excitons. However, based on the evidence of normal radiative lifetimes and the normal range of the full width half maximum values, the Eu^{2+} emission in $Rb_2MP_2O_7$ originates from the lowest t_{2g} state of the $4f^65d^1$ electronic configuration and is a normal $d\rightarrow f$ emission.

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Chapter 6

CONCLUSION

In this dissertation, we investigate the luminescence properties of Eu^{2+} doped in CsCaF₂ and in Rb₂MP₂O₇ (M=Ca,Sr) samples.

The emission spectra of Eu^{2+} doped in CsCaF₂ behaves uniquely with increasing temperature. The peak of emission spectrum shifts by 135 nm for a temperature change of 250 K. Our experiments indicate that the low temperature emission is due to an impurity bound exciton, Based on this model, we derived an equation that describes the temperature dependence of the relaxation time in this system. Fitting the experimental data with this equation allows us to determine crucial system parameters, such as excitonic relaxation time and an activation energy.

In $Rb_2MP_2O_7$ phosphors, the experimental results can support both normal and anomalous emission. However, based on the our data,i.e., the full width half maximum values, radiative life time and centroid of emission shift of $Rb_2MP_2O_7$ sample, it is concluded that the Eu^{2+} emission in $Rb_2MP_2O_7$ originates from lowest level of the $4f^{6}5d^{1}$ electronic configuration, i.e. it is a normal, albeit extreme case of dipole allowed d-f emission.