The 4f\textsuperscript{n-1}5d \rightarrow 4f\textsuperscript{n} transitions of the rare earth ions have applications in the fields of lighting phosphors, cathode ray tube phosphors, UV and VUV laser crystals, inorganic scintillators, thin film electro-luminescent materials and plasma display panel phosphors. Understanding the properties of the 5d levels of the rare earth ions is very important. One method to study these states utilizes high pressure experiments. By applying external pressure, the inter-atom distance, the bonding angles and covalency of the materials are influenced by pressure. The relevant chemical, electrical, optical and magnetic properties of materials change with pressure. The diamond anvil cell (DAC) is a powerful tool for high-pressure optical spectroscopy. Generation of pressures by the DAC in the range 0.1-1.0 Mbar (10-100 GPa) has become a routine. The sample is placed between two opposed diamond anvils. When an external force is applied, the diamonds move together and the pressure on the sample is increased. Since the diamond anvils are transparent, the incident pumping source can be focused on the sample and the emission from the sample can be collected. In this dissertation, the DAC is used to study the 4f\textsuperscript{n-1}5d \rightarrow 4f\textsuperscript{n} emission of rare earth ions doped in different hosts under high pressure. Since the absorption edge of the diamond is at about 225 nm and the absorption of the 5d levels of most rare earth ions are at shorter wavelengths, a stepwise two-photon excitation process is utilized to populate
the 5d level of the rare earth ion. Three examples utilizing high pressure are presented in this
dissertation. These are the pressure dependence of electron phonon coupling of Ce\(^{3+}\), Pr\(^{3+}\) and
Nd\(^{3+}\) in LiYF\(_4\), the \(^1S_0\) and 4f\(^1\)5d\(^1\) state mixing of Pr\(^{3+}\) in BaSO\(_4\) under high pressure and an
investigation of the site distribution of Eu\(^{2+}\) in BaMgAl\(_{10}\)O\(_{17}\) (BAM).

INDEX WORDS: Rare earth ions, Ce\(^{3+}\), Pr\(^{3+}\), Nd\(^{3+}\) in LiYF\(_4\), BaSO\(_4\):Pr\(^{3+}\), BaMgAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\)
BAM, 4f\(^{n-1}\)5d \(\rightarrow\) 4f\(^n\) emission, High pressure, Diamond anvil cell, Two-photon excitation, Local compressibility, Electron-phonon coupling, State mixing, Site distribution
4f^{n-1}d \rightarrow 4f^n EMISSION OF RARE EARTH IONS UNDER HIGH PRESSURE

by

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$4f^{n-1}5d \rightarrow 4f^n$ EMISSION OF RARE EARTH IONS UNDER HIGH PRESSURE

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DEDICATION

For my seven years experiences in the Department of Physics and Astronomy at The
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I am very glad to have this page for my appreciations to those who contributed to make this dissertation possible.

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CHAPTER ONE
INTRODUCTION

The rare earth ions are characterized by a partially filled 4f shell. The 4f electrons are shielded by the outer completely filled 5s² and 5p⁶ orbitals. Therefore the optical transitions within the 4fⁿ configuration are not strongly affected by the electrostatic field of the host lattice. The spectra of 4fⁿ ↔ 4fⁿ transitions consist of narrow lines with line widths of typically 1 cm⁻¹ at liquid helium temperatures and 10 cm⁻¹ at room temperature. These intra-configurational 4fⁿ ↔ 4fⁿ (f-f) transitions have been studied for over a century. Most aspects of these transitions are understood well. Detailed theoretical models have been developed [1-3].

However, for the inter-configurational 4fⁿ ↔ 4fⁿ⁻¹5d (f-d) transitions the story is different. These transitions were studied widely only during the last two decades. The knowledge of these transitions is incomplete. One reason is that most of these transitions are in the ultraviolet (UV) and vacuum ultraviolet (VUV) region, where light sources for pumping are not easily available. In addition, the 5d orbitals are much more extended than the 4f orbitals resulting in much stronger host lattice interactions. The spectra of 4fⁿ ↔ 4fⁿ⁻¹5d transitions are broad with most of the intensity in vibronic sidebands, making the spectra more difficult to analyze. The research activities in understanding f-d transitions of rare earth ions have increased recently because of the potential applications of UV and VUV transitions.

The luminescent materials (phosphors) in mercury-free fluorescent lamps and plasma display panels (for flat panel TV) emit visible light by absorbing VUV radiation from a noble gas discharge (e.g. Xenon around 147 nm and 172 nm). The development of new phosphors is
needed in order to meet the goal of increasing energy efficiency [4, 5]. The \(4f^n \rightarrow 4f^{n-1}5d\) transitions of rare earth ions are parity allowed, and therefore suitable for efficient absorption of VUV radiation from the noble gas discharge. Blue lamp phosphors with \(\text{Eu}^{2+}\) (e.g. \(\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}\) (BAM)) are well-known phosphors with strong f-d absorption. Moreover, the absorption of one high energy VUV photon may make it possible to obtain two visible photons for one absorbed photon for some rare earth ions through the process of quantum cutting. The quantum yield (number of photons emitted per photon absorbed) can be higher than 1. For instance, Piper et al. found that the quantum yield for visible emission of \(\text{YF}_3:\text{Pr}^{3+}\) excited at 185nm is about 1.4 [6].

Other potential applications using \(4f^{n-1}5d \rightarrow 4f^n\) emission are for tunable VUV lasers and scintillator materials. Ehrlich et al. obtained laser emission from \(\text{LiYF}_4:\text{Ce}^{3+}\) in the 306nm-330nm region [7] and from \(\text{LaF}_3:\text{Ce}^{3+}\) at 286nm [8]. Wayant and Klein established the first solid state vacuum ultraviolet laser based on the d-f emission of \(\text{LaF}_3:\text{Nd}^{3+}\) [9]. For scintillation crystals, \(\text{Ce}^{3+}, \text{Pr}^{3+}\) and \(\text{Nd}^{3+}\) can act as the activator ions. \(\text{Ce}^{3+}\) is widely studied because of the short decay time of its d-f emission (usually in the UV). Due to the success of \(\text{Ce}^{3+}\) -doped materials, d-f emission of other rare earth ions are also studied [10]. \(\text{Pr}^{3+}\) and \(\text{Nd}^{3+}\) may show the required fast luminescence when the lowest 5d level does not relax by multi-phonon emission to lower lying 4f levels.

For the above applications, \(4f^n \leftrightarrow 4f^{n-1}5d\) transitions depend on the position of 5d bands relative to 4f levels. For instance, the quantum cutting process of \(\text{Pr}^{3+}\) ion occurs only when the lowest state of the \(4f^15d^1\) configuration lies above the \(^1S_0\) state. Therefore, understanding the 5d levels is essential. Dorenbos has summarized the 5d level positions of the trivalent lanthanides in
a very large number of inorganic compounds [11]. Van Pieterson et al. used an extension of the model for $4f^n$ levels to calculate the energies of $4f^{n-1}5d \rightarrow 4f^n$ transitions [12, 13].

High pressure techniques provide a powerful method to study luminescence properties of rare earth ions. The energies of the levels of rare earth ions are related to the surrounding environments and therefore depend on the host lattice. By applying pressure, the inter-atomic distances can be varied such that the energy levels and the resulting optical properties change. Studies of $4f^n \leftrightarrow 4f^{n-1}5d$ transitions of rare earth ions under high pressure can help understand the relationship between host lattice structure and the luminescence properties better. Especially with the development of the diamond anvil cell (DAC) [14, 15], the experimental study of rare earth crystal fields under high pressure can greatly aid our understanding of the high-lying 5d levels of rare earth ions [16, 17].

With a diamond anvil cell, the sample is loaded with a pressure transmitting media into a hole in the gasket placed between two opposite faces of the anvils made from diamonds. When an external force is applied, the anvils move together producing a pressure increase in the sample. Since diamond is the hardest material available, it can yield the highest pressures. In addition, low defect and low impurity diamond is transparent to most electromagnetic radiation over a wide range of wavelengths limited by its bandgap at 225 nm. Therefore, diamond anvils are also optical windows making possible photoluminescence measurement in the DAC. A laser beam is focused onto the DAC containing the sample then the emission is collected.

In the present dissertation, a DAC is used to study the $4f^{n-1}5d \rightarrow 4f^n$ emission of rare earth ions $\text{Ce}^{3+}$, $\text{Pr}^{3+}$, $\text{Nd}^{3+}$ and $\text{Eu}^{2+}$ in different hosts under high pressure. Chapter 2 reviews high pressure research. Chapter 3 gives the structure and the principle of the diamond anvil cell. Due to the cutoff wavelength of diamond and the high-lying 5d energy level of rare earth ion, the
two-photon excitation method has to be used to populate 5d level. Chapter 4 describes the principles and the experimental set-up for the two-photon excitation technique. Chapter 5 studies the $4f^{n-1}5d \rightarrow 4f^n$ emission of rare earth ions Ce$^{3+}$, Pr$^{3+}$ and Nd$^{3+}$ in LiYF$_4$ host under high pressure. The shifts of the lowest 5d levels of these ions due to pressure are presented, which is used to study the pressure dependence of the electron-phonon coupling of these materials, providing useful information about local compressibility of rare earth ions in the host lattice. The close proximity of the lowest $4f^15d^1$ state to the $^1S_0$ state of Pr$^{3+}$ leads to a mixing of these two states. Chapter 6 examines this state mixing of Pr$^{3+}$ in BaSO$_4$ under high pressure. As a function of pressure, both the time-resolved emission and the intensity ratio of the $^1S_0$ emission to the $4f^15d^1$ emission indicate that the state mixing is decreased with the increasing pressure, which is different from expectation. Chapter 7 is concerned with the sites that the rare earth ion could occupy in the host lattice as determined through the $4f^{n-1}5d \rightarrow 4f^n$ emission of the rare earth ion under high pressure. The well known and important luminescent material BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ (BAM) is studied. The Eu$^{2+}$ site distribution is discussed.

1.1 References


CHAPTER TWO
HIGH PRESSURE RESEARCH

As for the case of temperature, pressure is an important variable used to understand the physical and chemical properties of materials. Under high pressure, a material has its volume reduced. In other words, the microscopic effect of pressure is to decrease the distance between atoms or molecules and increase the overlap of the electronic orbitals. The electrical, magnetic, optical and chemical properties of a material, which are defined by the organization of atoms or molecules, are influenced by pressure. Consequently, the application of high pressure can produce phase transitions, frequency shifts, chemical reactions, and many other phenomena. Pressure provides scientists with a powerful tool with which to understand the properties of materials.

Perhaps the earliest experiment involving high pressure was the seventeenth-century Florentine Academy's attempts to determine whether water is compressible. However, unlike temperature, the studies of material properties as a function of pressure have been less popular historically. The major reason is that the procedure to attain high pressure is very complicated and time consuming. To produce significant physical changes, a system generating large pressure is required. Another problem is that it is difficult to ascertain exactly what pressure exists in an experiment. The increasing activity in the field of high pressure research is due, in large part, to the pioneering work of Professor P. W. Bridgman of Harvard University, who developed most of the important techniques and made a variety of measurements about electrical resistance and compressibility under pressure. The duration roughly from 1910 to 1950 is called the “Bridgman
era” [1]. Bridgman invented and developed the Bridgman anvil and the piston-cylinder device [2]. The pressure he reached was up to 100 kbar (10 GPa). Following Bridgman, H.G.Drickamer and his co-workers extended the pressure to 500 kbar with the development of the supported-taper anvil device. They discovered many new phenomena about the behavior of solids at high pressure [3, 4] and carried out a variety of measurements of optical absorption [5, 6], electric resistance [5, 6], x-ray diffraction [7] and the Mössbauer effect [8]. In the meantime, an improved version of the piston-cylinder device [9], the “belt” apparatus [10] and the multiple anvil devices [11] were developed and became powerful tools for high pressure research.

A new era of high pressure research began with the appearance of the diamond anvil cell (DAC). Diamond is the hardest known substance. It has extremely high compressive strength and can stand higher forces than any other materials. Due to the cost of diamond, the weight of diamond used in experiments must normally be small. As a result, the size of samples must also be very small. Since the pressure is simply force per unit area, with higher force and small sample size, higher pressure can be attained. Lawson and Tang at the University of Chicago first used diamonds for high pressure studies in x-ray experiments [12]. The idea of an opposed diamond configuration for generating high pressure was developed independently and nearly simultaneously by workers at the University of Chicago [13] and the National Bureau of Standards (NBS) [14] with different versions. Since then, several modified versions of the DAC were developed [1]. A pressure of one Megabar (100 GPa) was first reached by Man and Bell [15]. Later they developed the beveled anvil which extended the pressure range well above one Megabar [16]. Xu and co-workers achieved pressures exceeding 5 Mbar [17]. Ruoff claimed that it would not be surprising to reach pressures over 1 TPa (10 Mbar) if the diamond tips are reduced to 5 µm in diameter [18]. Consequently, generation of pressures in the range 0.1-1.0 Mb
are becoming more routine. The improvement in pressure-generation capability has opened up a wide range of possible studies on the behavior of materials at these pressures.

During the evolution of DAC, several important new techniques must be mentioned. Van Valkenburg used a metal gasket with a hole to create a chamber that could be filled with a solid or liquid sample [19]. The most important function of the gasket is to reduce the magnitude of pressure gradients and provide an environment for hydrostatic pressure generation. The gasket also provides additional support for the anvils. In earlier years, there was no reliable method to determine the pressure generated inside the DAC. Direct calculation of the pressure from measurement of the applied force is not possible because the distribution of the force over the anvils is unknown and losses due to internal friction cannot be taken into account. This pressure calibration problem was overcome by the use of secondary standards. In 1972 Forman et al. first discovered that the R1 (694.2nm) and R2 (692.8nm) lines in the fluorescence spectrum of ruby shifted linearly with hydrostatic pressure up to 22 kbar [20]. Later the ruby scale was later calibrated against the compression of NaCl to a maximum pressure of 291 kbar [21] with the Decker equation of state [22]. The discovery allowed a convenient way to measure accurate pressures in the DAC. A large static pressure range became routinely available for the study of materials by a wide variety of experimental techniques. If the sample is a liquid or a gas at ambient conditions, it can be loaded directly. If the sample is solid, a fluid pressure transmitting medium is used. The function of the medium is to insure a homogeneous pressure distribution in the sample chamber by flowing or deforming in response to the applied pressure. Piermarini et al. found that a 4:1 methanol-ethanol mixture remains hydrostatic up to 104 kbar at room temperature [23]. Later Helium and other gases were found to be highly hydrostatic media up to pressures in the Megabar range [24, 25]. The development of gasket, pressure calibration and
pressure media turns the DAC into a quantitative tool for high pressure research. The DAC’s miniature size, portability, adaptability to other measurement apparatus and extreme pressure and temperature capabilities enable it to be modified appropriately for the particular experiment of interest. Finally scientists can use the pressure variable as they have used the temperature variable in the past. More details of the structure and the principle of the DAC will be given in the next chapter.

2.1 References


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CHAPTER THREE

DIAMOND ANVIL CELL

3.1 Basic Principle and Structure

The schematic diagram of the essential structure of a diamond anvil cell (DAC) is shown in figure 3.1. The basic principle of DAC operation is very simple. A metal gasket with a hole drilled in the center is placed between two small parallel diamonds in an opposed anvil configuration. The gasket hole provides a sample chamber which is loaded with the small sample and a ruby chip, which is the pressure calibrant used to monitor the pressure in the cell. A transparent pressure transmitting media is filled in the gasket hole to maintain hydrostatic conditions. When a force is applied to the diamond anvils, the diamonds move closer. The force is transmitted to the sample and the sample pressure increases.

There are several versions of the DAC widely used [1, 2]. The DAC used in our laboratory is the Merrill-Bassett type cell [3] with some modifications (figure 3.2 and figure 3.3). For the successful operation of the diamond cell, the two anvil surfaces should be accurately centered and set parallel to each other. This alignment is critical. Misaligned diamonds cause gasket failure and may break the diamonds due to shear stresses. The important modification from the original design is the use of a guide system to meet the alignment requirement. The cell in figure 3.2, which is obtained from the Department of Chemistry of Washington State University, uses three guide plates attached to the lower half of the cell to maintain the alignment. The cell in figure 3.3, which was purchased from High Pressure Diamond Optics, Inc., uses three guide pins to aid in alignment. Both cells use three screws to translate the halves of the cell. As the halves move together, the distance between the diamonds decreases and the sample pressure increases.
Figure 3.1 schematic diagram of the essential structure of a diamond anvil cell
Figure 3.2 DAC with guide plates.
Figure 3.3 DAC with guide pins
due to the reduction of the sample volume. The guide system also provides translational stability and increases the available pressure. The detailed structure of the cell in figure 3.3 is shown in figure 3.4. The miniature diamond cell of Merrill-Bassett type is one of the most compact, least expensive DAC and simplest to operate. The light weight and small size of the cell make it easy to be adapted to different experimental environments.

![Figure 3.4 Detailed structure of the DAC with guide pins](image)

3.2 Diamonds

The diamond anvil is a pressure generator and a very good optical window. The selection of diamond according to the mechanical properties and the optical quality is critical to high pressure experiments.

The diamond anvils are usually selected from brilliant-cut gem stones. The high pressure is due to the large force applied to the small area of the diamond culet. The maximum pressure is
limited by breakage of the diamond culet. Therefore the diameter of the diamond culet determines the maximum achievable pressure. There is no definitive relationship between the culet diameter and maximum pressure, but with well designed DAC one can typically expect to reach pressure of 100 kbar with 0.7 mm culet, 500 kbar with 0.4 mm culet and 1 Mbar with 0.2 mm culet [4]. The culet diameter of the DAC in our laboratory is about 0.6 mm. The pressure of 100 kbar should be easy to reach. However, the actual achievable pressure also depends on how the diamond anvil is mounted. For example, the diamond anvil of the DAC with guide pins is cemented to the supporting disc with super glue, and then a girdle of epoxy is sculpted around the diamond to produce a strong bond. When applying a too high pressure, the bonding between diamond and supporting disc can be broken and the cell has to be re-assembled and re-aligned completely. Therefore, the maximum pressure is lower than expected. The routine maximum pressure is about 70 kbar.

Natural diamonds are divided into two groups as type I and type II in relation to their absorption in the infrared, visible and ultraviolet regions [5]. Kaiser and Bond showed that type I diamonds contain appreciable amounts of nitrogen; whereas type II diamonds are nearly nitrogen free [6]. Cuters showed that a small proportion of type II diamonds are semi-conductors [7]. Type II diamonds are therefore further divided into the non-conducting type IIa diamonds and the semi-conducting type IIb diamonds. Type I diamonds show absorption starting at 330nm and increasing fairly rapidly at shorter wavelength. Type II diamonds transmit well in the ultraviolet down to the absorption edge at 225 nm [8, 9]. Since the absorption bands of the $4f^n \rightarrow 4f^{n-1}5d$ transitions of rare earth ions are in the range of violet, ultraviolet and vacuum ultraviolet, type II diamonds are more suitable for our research. Figure 3.5 shows the relative transmittance of type IIa diamond used in our DAC from 200nm to 450nm. This relative transmittance was obtained
Figure 3.5 Optical relative transmittance of type IIa diamond
by a Cary 14 recording spectrophotometer (Applied Physics Corporation) with a deuterium lamp as the light source. After the light passed through the diamond, the intensity, I, was detected by a photomultiplier tube (PMT) (RCA 1560078). Then the intensity of the background light source, \( I_0 \), was also obtained by the same PMT with the same optical path. The ratio of I to \( I_0 \) yields the transmittance of the diamond. Since the size of the light source is much larger than the size of the diamond, a lot of incident light does not pass through the diamond. Therefore, the resulting transmittance is only a relative value. The absolute transmittance \( T \) of a type IIa diamond can be expressed by [10]

\[
T = \frac{(1 - R)^2 \exp(-\alpha \cdot t)}{1 - R^2 \exp(-2\alpha \cdot t)}
\]

(3.1)

where, \( t \) is the thickness of the diamond (\( t = 2.3 \) mm for the diamond used in our lab), \( \alpha \) is the absorption coefficient at the corresponding wavelength, e.g. \( \alpha \approx 1.5 \text{ cm}^{-1} \) [11] at 300 nm and \( R \) is the reflectivity from two surfaces of the diamond given by

\[
R = \left( \frac{n-1}{n+1} \right)^2
\]

(3.2)

where \( n \) is the refractive index of the diamond at the corresponding wavelength, which can be obtained by [12]

\[
n^2 - 1 = \frac{0.3306 \cdot \lambda^2}{\lambda^2 - 175^2} + \frac{4.3356 \cdot \lambda^2}{\lambda^2 - 106^2}
\]

(3.3)

where \( \lambda \) is the wavelength in nm. For \( \lambda = 300 \) nm, \( n = 2.54 \), \( R = 0.19 \) and \( T = 0.47 \) with \( \alpha \approx 1.5 \text{ cm}^{-1} \). The absolute value of the transmittance is not necessary for experiments. Only the relative value is used to correct the wavelength dependence of the luminescence. The absolute transmittance as a function of wavelength can be estimated by normalizing the relative value of figure 3.5 at a wavelength where the absolute transmittance is known such as at 300 nm.
3.3 Gaskets

The development of the gasket makes the DAC a quantitative tool for high pressure research [13]. The gasket has two important purposes. First, the hole of the gasket provides a chamber for the sample, the ruby pressure calibration chip and for the pressure medium by which a hydrostatic pressure can be transmitted to the sample. The hydrostatic pressure is due to the frictional force between the gasket and the anvil. At high pressure, the gasket does not slide over the diamond but deforms with a stationary surface. Consequently, the pressure rise is linear inside the chamber. Second, when the gasket is squeezed between the diamond anvils, it deforms plastically and extrudes around the diamonds to act as a supporting ring, preventing breakage of the anvils due to stresses produced at the edge of the anvil culets.

Dunstan [14] developed a model for the operation of gaskets based on the theory for the plastic deformation of a disc between two anvils [15] and provided some practical implications for high pressure experiments, such as, the shear strength of the gasket, the friction coefficient between the gasket and the anvil faces, the gasket initial thickness, the size of chamber, the behavior of the gasket under high pressure and so on. For instance, the relative radii of the chamber and culet should be no larger than 1/2 and preferably 1/3. The gasket should be pre-indented; a gasket of thickness 0.1 mm, used with 0.6 mm diameter culets, and with a chamber diameter of 0.2 mm, can reach around 100kbar. These parameters are exactly the same as we used in our high pressure experiments.

Gaskets are usually made of stainless steel, such as Inconel, or beryllium copper. Rhenium is very good for megabar pressures or at high temperatures [16]. The gasket is prepared by cutting a raw sheet with 0.1-0.25 mm thickness to the required shape and size. For pre-indentation, the cell is assembled and progressively higher loads applied to the gasket to reach
the desired indentation thickness. A micrometer with small rounded measuring tip is used to measure the indentation thickness. After indentation, the gasket has the polygon impressions of both upper and lower diamonds. Then a hole is drilled in the center of the polygon. This makes sure that the gasket hole and the diamond culets are concentric, which is important for the stability of the experimental volume under pressure load.

3.4 Pressure calibration with ruby fluorescence

There are several techniques to determinate the pressure inside the DAC [17]. The most commonly used technique is the shift of the R lines (E^2 → A^2) emission from ruby (Al_2O_3:Cr^{3+}), for it is very rapid and quite precise. A small chip of ruby about 20 µm on its edge is placed in the gasket chamber with the sample and the fluorescence is excited by a laser. The R lines (R_1 and R_2 at 694.2 nm and 692.8 nm) are quite sharp (about 7.5 angstrom (Å)) and strong, but R_1, which is the stronger of the two, is generally used. Under pressure the R lines shift linearly to longer wavelengths. Figure 3.6 shows some representative spectra where the pressure values are obtained from equation 3.4 below. At room temperature the R_1 shift rate is linear up to 200 kbar (0.365 Å / kbar or -0.759 cm^{-1} / kbar)) [18]. Above 200 kbar, the shift becomes non-linear and has been quantified empirically [19, 20]. The range of 200 kbar is good enough for our experiments. The equation proposed for the R_1 line calibration can be expressed [18] by

\[ P = 2.746 \times (\lambda - \lambda_0) = 2.746 \times \Delta \lambda \]  

(3.4)

where, P in kbar and wavelength \( \lambda \) in Å. \( \lambda_0 \) is the R_1 line wavelength at ambient pressure.

3.5 Pressure media

The pressure medium plays a critical role in the success of DAC pressure experiments. It maintains a hydrostatic pressure environment in the sample chamber when loads are applied. The pressure media can be soft solids, liquids, or gases at ambient pressure [2, 21]. Liquid media can
Pressure values in kbar from left to right
0, 12, 21, 32, 44, 56, 65, 77

Figure 3.6 Ruby R lines shift to longer wavelengths with pressure increasing. The pressure values in figure are calculated by equation (3.1)
readily distribute force and eliminate pressure gradients by flowing. Methanol plus ethanol in a 4:1 ratio is the most widely used pressure medium and provides hydrostatic conditions at room temperature up to its glass transition at 104 kbar [22]. It becomes non-hydrostatic above the glass transition. Non-hydrostatic conditions are indicated by the change in the ruby line width because non-hydrostatic pressures lead to inhomogeneous broadening. In practice, using this mixture is challenging. Since the size of the sample and the ruby chip is so small, the medium has to be loaded by hypodermic syringe with a tiny drop, otherwise the sample and the ruby chip may flow away. When the medium is loaded, air bubbles are very likely formed and trapped in the sample chamber. Before the DAC is closed, bubbles must be removed. Due to the rapid evaporation of the medium, the DAC must be closed and tightened quickly. The process of loading the sample, the ruby and pressure medium often takes many trials before success.

3.6 References


CHAPTER FOUR
EXPERIMENTAL TECHNIQUE

4.1 Two-photon excitation

The 5d bands of trivalent rare earth ions are typically 40000-80000 cm\(^{-1}\) above the 4f ground state except for the Ce\(^{3+}\) ion. The lowest lying 5d level for Ce\(^{3+}\) ion in LiYF\(_4\) is at about 33400 cm\(^{-1}\) [1]. Since the absorption edge of type IIa diamond is about 225 nm (44444 cm\(^{-1}\), see figure 3.5), for a diamond anvil cell (DAC) conventional direct excitation of most rare earth ions is not possible in the high pressure experiments. This problem is solved by using stepwise two-photon excitation (also called excited state absorption or upconversion), which produces short wavelength emission from long wavelength pumping sources.

The principle of two-photon excitation was presented by Bloembergen in 1959 [2]. A more detailed discussion is given in reference [3]. The basic mechanism is shown schematically in figure 4.1. First, the ions are excited by the incident photons from the ground state (level 1) to a metastable intermediate state (level 2). After that, the excited ion may absorb a second pump photon to reach the higher excited state (level 3). When returning to ground state or low-lying excited states from level 3, emission with wavelength shorter than the excitation wavelength is produced. If the energy gap of the ground state absorption 1 \(\rightarrow\) 2 is the same as the energy gap of the excited state absorption 2 \(\rightarrow\) 3, one pumping source is enough for the two-photon excitation procedure. Otherwise, two different pumping sources are required for this stepwise two-photon excitation.

As an example, figure 4.2 shows the two-photon excitation scheme for LiYF\(_4\):Pr\(^{3+}\). Two pumping sources are required. One Ar\(^+\) laser with output at 476 nm (21008 cm\(^{-1}\)) pumps the Pr\(^{3+}\)
ions from the $^3\text{H}_4$ ground state to the $^3\text{P}_0$ metastable state (about 20860 cm$^{-1}$ [4]). This absorption occurs in the vibronic sideband of the $^3\text{P}_0$ level. Then a second Ar$^+$ laser with output at 364 nm (27473 cm$^{-1}$) pumps the ions from the $^3\text{P}_0$ state to the $4f^1 5d^1$ state. The first $4f^1 5d^1$ level is at around 46729 cm$^{-1}$ [1], while 20860 cm$^{-1}$ plus 27473 cm$^{-1}$ equals to 48333 cm$^{-1}$. Thus the $4f^1 5d^1$ band is populated and after rapid relaxation in the 5d states the resulting emission from the lowest $4f^1 5d^1$ state to the lower-lying states and ground state can be observed. Figure 4.3 shows the emission spectrum of LiYF$_4$:Pr$^{3+}$ after 476 nm plus 364 nm two-photon excitation. The transitions from $4f^1 5d^1$ to $^3\text{H}_4$ at 220 nm, to $^3\text{H}_5$ at 230 nm, to $^3\text{H}_6$, $^3\text{F}_2$ at 245 nm and to $^3\text{F}_{3,4}$ at 254 nm are observed. This emission spectrum is in reasonable agreement with that reported.
Figure 4.2. Energy levels and 476nm + 364nm two-photon excitation scheme for LiYF₄:Pr³⁺.
Figure 4.3 Emission spectrum of LiYF$_4$:Pr$^{3+}$ after 476nm + 364nm two-photon excitation.
previously by direct excitation at 157 nm [5]. All emission is in the range of 210-270 nm, which is shorter than any of the pumping wavelengths. This indicates that it is possible to study 4f^{5}5d^{1} → 4f^{2} emission of Pr^{3+} in LiYF_{4} using the DAC by two-photon excitation. Since the absorption edge of type IIa diamond is about 225 nm, only the transitions from 4f^{5}5d^{1} to {^{3}H_{6}, ^{3}F_{2}} at 245 nm and to {^{3}F_{3,4}} at 254 nm can be observed. The details of this high pressure study are presented in the next chapter (chapter five).

Figure 4.4 gives an example of two-photon excitation with only one pumping source. It shows the energy levels of Nd^{3+} ion in host LiYF_{4} and the two-photon excitation scheme. Nd^{3+} ions are excited to the 4f^{2}5d^{1} level with only one Ar^{+} laser operating at 351 nm (28490 cm^{-1}). The first photon excites the Nd^{3+} ion to the \(^{4}D_{5/2}\) state (about 28355 cm^{-1} [6]). The ion quickly relaxes to the \(^{4}D_{3/2}\) metastable state (about 28095 cm^{-1} [6]) due to rapid single or multiphonon emission. Basiev et al. have reported that the lifetime of \(^{4}D_{3/2}\) state was 1.1 µs [7]. The relatively long lifetime makes the excited state absorption possible and the second photon is absorbed by the excited ion to populate the 4f^{2}5d^{1} state. The lowest 4f^{2}5d^{1} level is about 56180 cm^{-1} [1], while 28095 cm^{-1} plus 28490 cm^{-1} equals to 56585 cm^{-1}. The emission spectrum after 351 nm two-photon excitation is shown in figure 4.5. The maximum of emission is at about 260 nm, which corresponds to the transition from 4f^{2}5d^{1} state to \(^{4}G_{5/2}\) state and is at a shorter wavelength than the 351 nm excitation wavelength. One can not observe the transition to the \(^{4}I_{9/2}\) ground state because of the wavelength cutoff of the diamond transmittance. One can also measure the power dependence of the emission intensity on the pumping laser to verify this transition is due to the sequential two-photon excitation. For a two-photon excitation process, the emission intensity should follow a quadratic power dependence on the pumping source [3, 8], i.e. \(I_{em} \propto P_{pump}^2\). We use a series of neutral density filters to attenuate the power of Ar^{+} laser and
Figure 4.4 Energy levels and two-photon excitation scheme for LiYF$_4$:Nd$^{3+}$. 
Figure 4.5 Emission spectrum of LiYF₄:Nd⁺³⁺ by sequential two-photon excitation at 351nm. Only transitions from 4f²5d¹ to ⁴G₅/₂, ⁴G₇/₂ and ⁴G₉/₂ are recorded due to the transmittance of type IIa diamond.
measure the corresponding intensities of the emission at 260 nm. It was found that the power dependence was $P^{1.88}$, which is in near agreement with the expected exponent of 2. Dooley et al. have reported similar results with two-photon excitation [8]. In the next chapter, the behavior of the emission at 260 nm under high pressure is investigated using the DAC.

4.2 Experimental setup

4.2.1 Sample preparation and diamond anvil cell operations

Since the diameter of the diamond anvil culet is about 600 µm and the diameter of the gasket hole is about 250 µm, the sizes of the sample and the ruby pressure calibrant also have to be small (around 50 µm diameter and 50 µm thick). Before the sample and the ruby chip are loaded in the DAC, it must be carefully aligned and clean. All procedures are performed under a binocular microscope. Appendix 1 presents the detailed operations on the DAC and the procedures of sample loading.

4.2.2 Layout of experimental equipments

Figure 4.6 shows the schematic experimental layout for high pressure spectroscopy measurement with two Ar$^+$ lasers as pumping sources. In order not to damage the diamond windows, cw lasers are used. One Ar$^+$ laser (Spectra-Physics, Model 2025, 3W) operates in the visible range with multi-line output. The required wavelength is selected by a Pellin-Broca prism. The other Ar$^+$ laser (Coherent, INNOVA 400) operates in the ultraviolet range. With various combinations of high reflectors and output couplers, and a prism, single line output is obtained. Laser outputs are tightly focused on the small sample with a X15 reflecting objective (Ealing Model 25-0555). Figure 4.7 shows the structure of the reflecting objective from Ealing. It is a Schwarzschild type microscope [9] with two curved mirrors, a concave primary mirror with a central hole, and a convex secondary mirror mounted with the same center as the primary mirror.
Figure 4.6. Experimental setup for high pressure spectroscopy measurement.
The laser beams are expanded and collimated to about 12 mm, which is the diameter of the entrance (secondary) mirror of the reflecting objective. The focused laser spot size can be estimated by viewing the emission through the reflecting objective and comparing the size of the fluorescent spot with the sample size (around 50 µm in diameter). One estimates, in their look, a spot size of about 20 µm in diameter. The fluorescence from sample is collected by the same reflecting objective. A neutral density filter acting as a beam splitter is placed before the reflecting objective. It transmits about 70% of the incident laser and reflects about 30% of the
fluorescence. The emission spectrum is recorded on a CCD camera (EG&G, Model 1530) at the focal plane of a Princeton Instruments 0.25 m spectrometer (EG&G, Model 1235). Appropriate filters are placed in the front of the entrance slit of the spectrometer to reduce the background due to the scattered exciting light. For the case of one pumping source in the two-photon excitation process, the layout is similar to the figure 4.6. Only one laser is expanded, reflected and focused. Then the emission spectrum is recorded.

For samples doped with Ce$^{3+}$ ion or samples that don’t need two-photon excitation, the 5d level can be excited directly by one pumping source. The experimental setup is similar to the figure 4.6 with only one Ar$^+$ laser.

We also measured the time-resolved emission under high pressure using a sapphire anvil cell. The detailed experimental setup is given in chapter 7 for the sample BaSO$_4$:Pr$^{3+}$.

4.3 References


CHAPTER FIVE

4f^{n-1}5d \rightarrow 4f^n EMISSION OF RARE EARTH IONS

IN LiYF_4 UNDER HIGH PRESSURE

5.1 Introduction

Lithium yttrium fluoride (LiYF_4) is a well known and commercially available crystal [1, 2]. It has the tetragonal crystal structure with space group C_{4h}^4 (I_4^1/a) and is isomorphic to scheelite (CaWO_4) [3, 4]. Since trivalent rare earth ions such as Ce^{3+}, Pr^{3+} and Nd^{3+} can substitute at Y^{3+} sites without charge compensation, LiYF_4 is a common host material for various rare earth ions in solid state laser applications and the doped materials have been studied for many years. LiYF_4:Ce^{3+} has ultraviolet laser emission in the region of 306-330 nm [5]. A blue laser transition at 479 nm at room temperature in LiYF_4:Pr^{3+} crystal has been reported by Esterowitz et al [6]. The near infrared emissions of LiYF_4:Nd^{3+} at 1047 and 1053 nm are widely used as laser lines [7, 8].

The interconfigurational 4f^{n-1}5d \rightarrow 4f^n transitions of rare earth ions in LiYF_4 are promising for high power tunable vacuum ultraviolet (VUV) and ultraviolet (UV) laser radiations [9]. Until now, only LiYF_4:Ce^{3+} has realized laser emission [5] due to the relatively simple energy level schema for both the ground state configuration and the first 5d^1 excited configuration of the Ce^{3+} (4f^3) ion. Several publications about 4f^{n-1}5d \rightarrow 4f^n emission of the rare earth ions in LiYF_4 have been reported [10, 11], but attempts at laser operation were not successful.

Pressure studies are very useful to understand the characteristics of the 4f^{n-1}5d states of the rare earth ions. External pressure decreases the distance between the rare earth ion and the surrounding ligands. This leads to an increasing interaction between the rare earth ion and its
local environment. Therefore, the pressure variations can smoothly control the crystal field strength and the electron-lattice interactions. With high pressure spectroscopy of the $4f^{n-1}5d \rightarrow 4f^n$ emission, one can analyze the influence of pressure on the crystal field and the electron-phonon coupling (or electron-lattice coupling) and understand the details of the electronic and vibronic structure of rare earth ions.

In this chapter, studies of the $4f^{n-1}5d \rightarrow 4f^n$ emission of Ce$^{3+}$, Pr$^{3+}$ and Nd$^{3+}$ in LiYF$_4$ under high pressure using a diamond anvil cell (DAC) are presented. A standard crystal field method and a single configurational coordinate model are used to explain the effects of pressure on the electronic energies of the $4f^{n-1}5d$ states and the electron-phonon coupling. The study of a series of rare earth ions offers the opportunity to investigate the systematics of these interactions. The information about the local compressibility of rare earth ions is also obtained.

5.2 Theory

To analyze the pressure dependence of the emission spectra, a single configurational coordinate model [12] is used. The diagram for the model is shown in figure 5.1a. The lattice potentials are presented by the parabolas. This model is based on harmonic potential well approximation for the lattice vibrational potentials and the vibrational sublevels are separated by phonon energy $\hbar \omega$, where $\omega$ is the frequency of the phonon. The single configurational coordinate model assumes that the rare earth ion interacts with a single, totally symmetric vibrational mode. From figure 5.1a, the energies of the ground state and the excited state are given by

$$E_g(Q) = E_g^0 + \frac{1}{2} k(Q - Q_g)^2$$ (5.1)

$$E_e(Q) = E_{eabs} - \frac{1}{2} k(Q_e - Q_g)^2 + \frac{1}{2} k(Q - Q_e)^2 = E_{eabs} + \frac{1}{2} k(Q - Q_g)^2 - k(Q_e - Q_g) \cdot (Q - Q_g)$$ (5.2)
Figure 5.1 (a) Single configurational coordinate model (b) The first $4f^{n-1}5d$ level of rare earth ion in the host is lowered relative to the free ion energy by depression energy $E_{dep}$.
where $E^0_g$ is the pure electronic energy of the ground state. $Q$ is the configurational coordinate proportional to the average distance between the rare earth ion and the surrounding ligands, which oscillates about the equilibrium value. $Q_g$ and $Q_e$ are the equilibrium configurational coordinates of the ground state and the excited state, respectively. $k$ is the force constant, which is assumed the same for all states in the single configurational coordinate model. $E_{abs}$ is defined in figure 5.1a, which corresponds to the absorption energy. Since

$$E_e(Q) - E_g(Q) = E_{abs}^0 - k(Q_e - Q_g) \cdot (Q - Q_g)$$ \hspace{1cm} (5.3)

is linear in $(Q - Q_g)$, this is referred to as the linear coupling. From figure 5.1a, the stokes shift $E_s$ (difference in energy between absorption $E_{abs}$ and emission $E_{em}$) is given by

$$E_s = E_{abs} - E_{em} = 2S \hbar \omega$$ \hspace{1cm} (5.4)

where $S$ is the Huang-Rhys parameter [13]. The value of $S$ is a measure of the strength of coupling of the rare earth ion to the surrounding lattice. $\hbar \omega$ is called the electron-lattice coupling energy or the lattice relaxation energy [14], which is defined by

$$\hbar \omega = \frac{1}{2} k \cdot (Q_e - Q_g)^2$$ \hspace{1cm} (5.5)

When the rare earth ion is doped in a host crystal, the energy of the first dipole-allowed $4f^n \rightarrow 4f^{n-1}5d$ transition is reduced relative to its free ion energy by amount called as the depression energy $D$ [15] (see figure 5.1b), which is given by

$$D = E_{cen} + E_{cr}$$ \hspace{1cm} (5.6)

where $E_{cen}$ is called the 5d centroid shift, which is used to measure the lowering of the average position of the 5d levels (the centroid or barycenter) relative to the position of the $4f^n$ ground state of the free ion due to the nephelauxetic effect. Morrison used the ligand polarization model to show that $E_{cen}$ depends on the average distance between the rare earth ion and the surrounding
ligand, \( E_{\text{cen}} \propto Q^m \) and the value of \( m \) is 6 [16, 17]. \( E_{\text{cr}} \) is called the crystal field shift, which is due to crystal field and spin-orbit splitting. In a cubic crystal field, \( E_{\text{cr}} \) is proportional to the crystal field strength \( Dq \) [16]. Since in a point charge model \( Dq \propto Q^n \) with \( n = 5 \), \( E_{\text{cr}} \) is also proportional to \( Q^n \) (\( n = 5 \)).

From figure 5.1b, the absorption energy can be written as

\[
E_{\text{abs}} = E_{5d}^0 - E_{4f}^0 - D = E_{5d}^0 - E_{4f}^0 - (E_{\text{cen}} + E_{\text{cr}}) \tag{5.7}
\]

where \( E_{5d}^0 \) and \( E_{4f}^0 \) are the energies of the first 5d state and the ground state of the free rare earth ion. From equation (5.4)

\[
E_{\text{em}} = E_{5d}^0 - E_{4f}^0 - (E_{\text{cen}} + E_{\text{cr}}) - 2Sh\omega \tag{5.8}
\]

Therefore, the pressure derivative of emission can be written as

\[
\frac{dE_{\text{em}}}{dP} = \left( \frac{dE_{\text{cen}}}{dP} + \frac{dE_{\text{cr}}}{dP} + 2 \frac{dSh\omega}{dP} \right) \tag{5.9}
\]

The isothermal compressibility, \( K_T \), which is the reciprocal of the isothermal bulk modulus of the host material, \( B_0 \), is used to indicate the sensitivity of the material to pressure, and is defined as

\[
K_T = \frac{1}{B_0} = -\frac{1}{V} \left( \frac{dV}{dP} \right) = -\frac{3}{a} \frac{da}{dP} \tag{5.10}
\]

where \( V = a^3 \) is the unit cell volume. Under external pressure, the distance between rare earth ion and the surrounding ligands is decreased with pressure. One can define a local compressibility, \( K_{\text{loc}} \), similar to equation (5.10) as

\[
K_{\text{loc}} = \frac{1}{B_{\text{loc}}} = -\frac{3}{Q} \frac{dQ}{dP} \tag{5.11}
\]
where $B_{loc}$ is the bulk modulus associated with the volume involved in the variation with pressure. Therefore, one obtains a relation

$$K_Q = \frac{K_{loc}}{K_T} = \frac{dQ}{Q} \left/ \frac{da}{a} \right.$$

(5.12)

$K_Q$ is an indication of the variance of the local environment of the rare earth ion relative to the host lattice due to macroscopic external pressure. The three cases $K_Q = 1$, $K_Q < 1$ and $K_Q > 1$ correspond to the conditions in which the local compression of the ligands surrounding the rare earth ion in the excited state is equal to, relatively smaller than and relatively larger than the bulk compressibility, respectively.

Considering the configuration coordinate as a function of pressure, the derivative with respect to pressure can be expressed as

$$\frac{dQ}{dP} = \frac{dQ}{da} \cdot \frac{da}{dP} = -\frac{a}{3B_0} \cdot \frac{dQ}{da}$$

(5.13)

Therefore, one can obtain the following relations.

$$\frac{dE_{cen}}{dP} = \frac{dE_{cen}}{dQ} \cdot \frac{dQ}{dP} = -\frac{mE_{cen}}{3B_0} \cdot \left( \frac{dQ}{Q} \left/ \frac{da}{a} \right. \right) = \frac{mE_{cen}}{3B_0} \cdot K_Q$$

(5.14)

$$\frac{dE_{cr}}{dP} = \frac{dE_{cr}}{dQ} \cdot \frac{dQ}{dP} = \frac{nE_{cr}}{3B_0} \cdot \left( \frac{dQ}{Q} \left/ \frac{da}{a} \right. \right) = \frac{nE_{cr}}{3B_0} \cdot K_Q$$

(5.15)

$$\frac{dE_{em}}{dP} = -\frac{K_Q}{3B_0} \cdot (mE_{cen} + nE_{cr}) - \frac{dSh\omega}{dP} = -\frac{nK_Q}{3B_0} \cdot \left( \frac{m}{n} E_{cen} + E_{cr} \right) - 2 \cdot \frac{dSh\omega}{dP}$$

(5.16)

Equation (5.16) can be used to calculate $K_Q$ if the pressure induced changes in emission and electron lattice coupling energy are observed experimentally. Assuming that $\frac{m}{n} \approx 1$, and with $n = 5$, the relation (5.16) can be simplified as
\[
\frac{dE_{em}}{dP} = -\frac{nK_o}{3B_0} \cdot (E_{cen} + E_{cr}) - \frac{dS\hbar\omega}{dP} = -\frac{5K_o}{3B_0} \cdot D - 2 \cdot \frac{dS\hbar\omega}{dP} \tag{5.17}
\]

The error of the approximation is about 10%, which is within the accuracy of estimation of \(K_o\).

Since the pressure dependence of absorption energy cannot be observed experimentally due to the absorption of the diamond window and the high-lying 5d energy levels of the trivalent rare earth ions, in calculations we assume it is equal to the pressure dependence of emission energy. In other words, we assume that the electron-lattice coupling energy is pressure independent,

\[
\frac{dS\hbar\omega}{dP} = 0 \tag{5.18}
\]

and,

\[
\frac{dE_{em}}{dP} = -\frac{5K_o}{3B_0} \cdot D \tag{5.19}
\]

If one knows \(B_0\) and \(D\) then one can use the pressure dependence of the emission to determine \(K_o\). In practice, the pressure shift of the absorption energy could be larger or smaller than the pressure shift of the emission energy, depending on whether the electron-lattice coupling energy decreases or increases with pressure, respectively [14].

5.3 Experimental results

The sample was loaded into a type IIa diamond anvil cell (DAC) with 4:1 mixture of methanol plus ethanol as pressure transmitting medium. A 0.08 wt.% ruby chip was also loaded in the cell for pressure calibration by the shift of the ruby R-lines with pressure. To pump the 5d levels of Pr\(^{3+}\) and Nd\(^{3+}\), a two-photon excitation method was used due to the cutoff edge of the diamond window (around 225 nm). The principle of two-photon excitation was presented in last chapter (chapter 4). For Pr\(^{3+}\) doped LiYF\(_4\), two Ar\(^+\) lasers operating at 476 nm and 364 nm respectively were used. The experimental setup is shown in figure 4.6. For Nd\(^{3+}\) doped LiYF\(_4\),
one Ar\textsuperscript+ laser, operating at 351 nm, was used to realize two-photon excitation. The experimental setup is similar to figure 4.6 with only one pumping source required. Since the first 5d level of Ce\textsuperscript{3+} ion in LiYF\textsubscript{4} is at about 33400 cm\textsuperscript{-1} (299 nm) [18], it can be pumped directly without using two-photon excitation. An Ar\textsuperscript+ laser operating at 275 nm was used. The experimental setup is similar to that of figure 4.6 with only one pumping source.

5.3.1 LiYF\textsubscript{4}: Ce\textsuperscript{3+}

The energy levels of Ce\textsuperscript{3+} in LiYF\textsubscript{4} are very simple. The 5d configuration is split into five crystal field levels with the first 5d level at about 33400 cm\textsuperscript{-1} (299 nm) [18]. There are only two energy multiplets in the 4f\textsuperscript{1} configuration due to spin-orbit splitting, the \( ^2F_{5/2} \) ground state and the \( ^2F_{7/2} \) excited state. Since the influence of the crystal field on the 4f states is much smaller than the spin-orbit splitting, the Stark splitting due to the crystal field is small and not resolved in these transitions. Figure 5.2a shows the configurational coordinate diagram of the three lowest states of the LiYF\textsubscript{4}:Ce\textsuperscript{3+} system. Absorption and emission transitions are indicated by arrows.

The room temperature emission spectrum of LiYF\textsubscript{4}:Ce\textsuperscript{3+} at ambient pressure excited with a 275 nm Ar\textsuperscript+ laser is shown in figure 5.2b. Two broad bands are observed with maxima at 305 and 325 nm due to the transitions from the lowest 5d state to the \( ^2F_{5/2} \) and \( ^2F_{7/2} \) levels, respectively. The spectrum is in reasonable agreement with that reported previously [18].

Figure 5.3 displays the emission spectra of LiYF\textsubscript{4}:Ce\textsuperscript{3+} at different pressures. All spectra are represented in an emission lineshape versus energy. The spectral lineshape \( L(\omega) \) as a function of the emission frequency is related to the number of photons \( N(\omega) \) observed experimentally by the formula [19]

\[
L(\omega) \sim N(\omega) \cdot (\omega)^3
\]

(5.20)

where \( \omega \) is the emission frequency. The reason for the adjustment is that for vibronic transitions
Figure 5.2 (a) Configurational coordinate diagram of the energy levels of Ce$^{3+}$ in LiYF$_4$ (b) Room temperature emission spectrum of LiYF$_4$:Ce$^{3+}$ at ambient pressure excited at 254 nm
Figure 5.3 Emission spectra of LiYF₄:Ce³⁺ at different pressures.
consisting of a number of components, the radiative rates of those transitions emitting at higher frequency are enhanced by the frequency-dependent photon density of states. It is these adjusted spectra that can then be fit to Gaussian line shapes [20]. Another advantage of such a representation is that the maxima of the lineshapes are directly related to the energies of the Franck-Condon transitions in the configurational coordinate model.

From figure 5.3, one can observe that the emission peak energies shift to lower energy with increasing pressure. The spectra in figure 5.3 can be fitted by two Gaussian functions with each Gaussian represented by

\[
G_i(E) = \frac{A_i}{\sqrt{w_i (\pi / 2)}} \exp \left[-2 \times \left( \frac{E - E_i}{w_i} \right)^2 \right]
\]  

(5.21)

where \(E_i\), \(A_i\) and \(w_i\) represent the energy peak, amplitude and width, respectively. The resulting energy peaks of the \(5d \rightarrow ^2F_{5/2}\) and \(5d \rightarrow ^2F_{7/2}\) transitions at different pressures are shown in figure 5.4. By the least squares fits, the rates of the red shifts for the \(5d \rightarrow ^2F_{5/2}\) and \(5d \rightarrow ^2F_{7/2}\) transitions are -12.7 ± 0.4 cm\(^{-1}\)/kbar and -13.9 ± 0.5 cm\(^{-1}\)/kbar, respectively. The pressure shifts are different for the two transitions. Gryk et al. indicated that one possible reason for this is due to a pressure induced change in the spin-orbit coupling within the 4f configuration [21].

The pressure shifts for LiYF\(_4\):Ce\(^{3+}\) can be compared with other high pressure luminescence studies of Ce\(^{3+}\) systems. Table 5.1 shows the pressure induced red shifts of 5d emission of the Ce\(^{3+}\) in several systems.

5.3.2 LiYF\(_4\):Pr\(^{3+}\)

The energy levels of Pr\(^{3+}\) in LiYF\(_4\) are shown in figure 4.2. Figure 5.5a displays the configurational coordinate diagram for the energy levels involved in the process of two-photon excitation and emission. Figure 5.5b shows the ambient pressure emission spectrum, which is
Figure 5.4 Emission peak energies of LiYF₄:Ce³⁺ as a function of pressure. Solid lines represent data for linear least-squares fits.

E(\[^2F_{5/2}\]) = 32728 - 12.7 \, P \,(\text{cm}^{-1})

E(\[^2F_{7/2}\]) = 30722 - 13.9 \, P \,(\text{cm}^{-1})
<table>
<thead>
<tr>
<th>Materials</th>
<th>Red shift rate (cm(^{-1})/kbar)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiYF(_4)::Ce(^{3+})</td>
<td>-12.7 ± 0.4 ((^2)F(_{5/2}))</td>
<td>this chapter</td>
</tr>
<tr>
<td></td>
<td>-13.9 ± 0.5 ((^2)F(_{7/2}))</td>
<td></td>
</tr>
<tr>
<td>Y(_3)Al(<em>5)O(</em>{12})::Ce(^{3+}) (YAG)</td>
<td>-12.5 ± 0.7 ((^2)F(_{5/2}))</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>-11.8 ± 0.7 ((^2)F(_{7/2}))</td>
<td></td>
</tr>
<tr>
<td>Gd(_3)Sc(_2)Al(<em>3)O(</em>{12})::Ce(^{3+}) (GSAG)</td>
<td>-8.3 ± 0.5 ((^2)F(_{5/2}))</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>-7.5 ± 0.5 ((^2)F(_{7/2}))</td>
<td></td>
</tr>
<tr>
<td>Lu(_2)SiO(_5)::Ce(^{3+}) (LSO)</td>
<td>-13 ± 1</td>
<td>[23]</td>
</tr>
<tr>
<td>Lu(_2)S(_3)::Ce(^{3+})</td>
<td>-30 ± 3</td>
<td>[24]</td>
</tr>
</tbody>
</table>

Table 5.1 Pressure induced red shifts for several Ce\(^{3+}\) systems.

obtained with 476 nm plus 364 nm two-photon excitation at room temperature. Four peaks are observed, corresponding to the transitions from the lowest 4f\(^{1}\)5d\(^{1}\) state to the states of \(^3\)H\(_5\), \(^3\)H\(_4\), \(^3\)H\(_6\) and \(^3\)F\(_2\), and \(^3\)F\(_{3,4}\), respectively. The spectrum is in reasonable agreement with that reported previously [25].

The emission spectral lineshape as the function of pressure are shown in figure 5.6. Due to the transmittance of the type IIA diamond window, the high energy transitions from 4f\(^{1}\)5d\(^{1}\) to \(^3\)H\(_5\) and \(^3\)H\(_4\) are cut off. Only the low energy transitions from 4f\(^{1}\)5d\(^{1}\) to \(^3\)H\(_6\), \(^3\)F\(_2\) and \(^3\)F\(_{3,4}\) are observed. However, part of the transition of 4f\(^{1}\)5d\(^{1}\) → \(^3\)H\(_5\) starts to show up on the high energy side of figure 5.6 because of the red shifts of the emission spectra with increasing pressure. The shifts depend linearly on pressure with a slope of -13.5 ± 0.6 cm\(^{-1}\)/kbar for the transition of 4f\(^{1}\)5d\(^{1}\) →
Figure 5.5 (a) Configurational coordinate diagram of the energy levels of Pr$^{3+}$ in LiYF$_4$
(b) Room temperature emission spectrum of LiYF$_4$:Pr$^{3+}$ at ambient pressure by 476 nm
and 301 nm two-photon excitation
Figure 5.6 Emission spectra of LiYF$_4$:Pr$^{3+}$ at different pressures.
Figure 5.7 Emission peak energies of LiYF₄:Pr³⁺ as a function of pressure. Solid lines represent data for linear least-squares fits.
The energy levels of \( \text{Nd}^{3+} \) in \( \text{LiYF}_4 \) are shown in figure 4.4. The \( 4f^2 5d^1 \) levels are excited by the sequential two-photon excitation at 351 nm. The diamond window blocks the highest energy transitions; only the emission around 260 nm (\( 4f^2 5d^1 \rightarrow 4G_{5/2} \)) is observed (see figure 4.5). The shoulder between 270 nm and 280 nm in figure 4.5 most likely arises from transitions to the \( 4G_{7/2} \) and \( 4G_{9/2} \) multiplet levels. This is in agreement with the spectrum reported by Thøgersen, who used three-photon excitation at 532 nm [27]. Figure 5.8 shows the emission spectral lineshapes at different pressures. The peak at 260 nm shifts to lower energy with the slope of \( 11.5 \pm 0.3 \text{ cm}^{-1}/\text{kbar} \) as the pressure is increased (figure 5.9).

5.4 Calculations and conclusions

The site symmetry of the \( \text{Y}^{3+} \) sites in \( \text{LiYF}_4 \), for which the rare earth ions substitute, is \( S_4 \), which is a slightly distorted dodecahedron site described by a point group \( D_{2d} \) [28] and can be interpreted reasonably as a distortion from cubic [18]. Therefore, one can use equation (5.19) to calculate the local compression of \( \text{Ce}^{3+} \), \( \text{Pr}^{3+} \) and \( \text{Nd}^{3+} \) ions in \( \text{LiYF}_4 \) with the experimentally observed emission shifts. The values of the depression energies \( D \) for each sample are obtained from reference [29] and the isothermal bulk modulus of the host material, \( B_0 \), is obtained from reference [30]. The resulting values of \( K_Q \) are listed in table 5.2. For comparison, values of \( K_Q \) for other systems are also listed.

From table 5.2, the values of \( K_Q \) for all materials are smaller than unity. In other words, the local compressibility of rare earth ions is smaller than the bulk compressibility of the host
Figure 5.8 Emission spectra of LiYF$_4$:Nd$^{3+}$ at different pressures.
Figure 5.9 Emission peak energies of LiYF₄:Nd³⁺ as a function of pressure. Solid line represents data for linear least-squares fit.
Table 5.2 Data for calculating $K_Q$ and results.

<table>
<thead>
<tr>
<th>Material</th>
<th>$dE_{el}/dP$ (cm$^{-1}$/kbar)</th>
<th>$D$ [29] (cm$^{-1}$)</th>
<th>$B_0$ (kbar)</th>
<th>$K_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiYF$_4$:Ce$^{3+}$</td>
<td>-12.7±0.4</td>
<td>15093</td>
<td>810 [30]</td>
<td>0.4</td>
</tr>
<tr>
<td>LiYF$_4$:Pr$^{3+}$</td>
<td>-13.5±0.6</td>
<td>14632</td>
<td>810 [30]</td>
<td>0.45</td>
</tr>
<tr>
<td>LiYF$_4$:Nd$^{3+}$</td>
<td>-11.5±0.3</td>
<td>15282</td>
<td>810 [30]</td>
<td>0.37</td>
</tr>
<tr>
<td>YAG:Ce$^{3+}$</td>
<td>-12.5±0.7 [22]</td>
<td>27570 [22]</td>
<td>1870 [31]</td>
<td>0.51</td>
</tr>
<tr>
<td>YAG:Pr$^{3+}$</td>
<td>-14.1±0.1 [26]</td>
<td>26860</td>
<td>1870 [31]</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Material. One possible reason of this is due to the size difference between the rare earth ion and the host ion. In general, the size of the rare earth ion is greater than that of the host ion. The radii of Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$ and Y$^{3+}$ are 1.15 Å, 1.13 Å, 1.123 Å and 1.04 Å, respectively. When the rare earth ion substitutes for the Y$^{3+}$ ion, the bonding strength is possibly enhanced between the rare earth ion and ligands compared with that between the host ion and ligands in the pure lattice. The coupling of the rare earth ion to the lattice is possibly tighter and hence the compressibility is decreased. However, since the local compressibility of Y$^{3+}$ is unknown, the above argument is not confirmed. Grinberg concludes that the rare earth doping contributes additional localized states in the band gap and one needs more energy to compress the rare earth ion site than for the pure lattice site [32]. Therefore, the local compressibility is smaller than the bulk compressibility.

Although we expected to find some trends of the local compressibility and the electron-lattice coupling by studying a series of rare earth ions doped in the host LiYF$_4$, it seems there is no general trend found. However with the single configurational coordinate mode, the
information of the local compression modulus can be obtained by the experimentally observed pressure induced redshift in the peak energy of emission band. Equation (5.17) and (5.19) can be used for prediction of the pressure dependence of the electron lattice coupling.

5.5 References

[10] P. S. Peijzel, P. Vergeer and A. Meijerink, $4f^{n-1}5d \rightarrow 4f^n$ emission of Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Er$^{3+}$, and Tm$^{3+}$ in LiYF$_4$ and YPO$_4$. Physical Review B 71 (2005) 045116


[25] P. S. Peijzel, P. Vergeer, A. Meijerink, M. F. Reid, L. A. Boatner and G.W. Burdick, 4f$^{n-1}$5d $\rightarrow$ 4f$^n$ emission of Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Er$^{3+}$, and Tm$^{3+}$ in LiYF$_4$ and YPO$_4$. Physical Review B 71 (2005) 045116


CHAPTER SIX
MIXING OF THE 4f^2(^1S_0) AND 4f^15d^1 STATES OF Pr^{3+}
IN BaSO_4 UNDER HIGH PRESSURE

6.1 Introduction

Trivalent praseodymium ion (Pr^{3+}) doped inorganic materials have been widely investigated. The ultraviolet (UV) 4f^{1}5d^{1} → 4f^{2} emission of Pr^{3+} was studied for the applications in scintillators [1] and tunable UV lasers [2, 3]. Moreover, in some hosts the highest 4f^{2} state of Pr^{3+}, ^1S_0 state, which is located at about 47000 cm^{-1}, exhibits photon cascade emission (PCE) or quantum cutting phenomenon [4, 5]. This process involves two-step transitions ^1S_0 → ^1I_6, ^3P_J followed by ^3P_0 → ^3F_J, ^3H_J or ^1S_0 → ^1D_2 followed by ^1D_2 → ^3H_J (see figure 6.1). These emission spectra show narrow lines compared with the broad 4f^{1}5d^{1} → 4f^{2} emission. Quantum cutting with efficiency higher than 100% has been demonstrated in YF_3 and it can be used in plasma display panels (PDP) and mercury-free fluorescent lamps.

In order to obtain quantum cutting, Pr^{3+} must be located at a site with a very low crystal field so that the lowest state of the 4f^{1}5d^{1} configuration lies above the ^1S_0 state. Then, nonradiative transition populates the ^1S_0 state following the excitation of the 4f^{1}5d^{1} state. Otherwise the parity allowed 4f^{1}5d^{1} → 4f^{2} emission will be observed instead. For instance, LiYF_4:Pr^{3+} [4] only shows the broad band UV emission due to the 4f^{1}5d^{1} → 4f^{2} transitions as presented in chapter five. It was reported that the quantum cutting process occurs in Pr^{3+} doped barium sulfate (BaSO_4) [6]. Figure 6.1 displays the energy levels of Pr^{3+} in BaSO_4 as well as the
Figure 6.1 Schematic representations of energy levels, two-photon excitation and quantum cutting of Pr$^{3+}$ in BaSO$_4$. 
quantum cutting process. This is different from the schema of LiYF\(_4\):Pr\(^{3+}\) shown in figure 4.2 because the \(^1S_0\) level of 4f\(^2\) lies below the 4f\(^1\)5d\(^1\) levels.

Figure 6.2 shows the room temperature emission of BaSO\(_4\):Pr\(^{3+}\) around 250nm after 476 nm plus 301 nm two-photon excitation at ambient pressure. The emission consists of a sharper feature sitting atop a broad one. The sharper feature corresponds to the parity forbidden \(^1S_0\rightarrow^3F_{3,4}\) transitions within the 4f\(^2\) configuration of Pr\(^{3+}\). The broader features are the parity allowed emission from the lowest 4f\(^1\)5d\(^1\) component to the \(^3F_{3,4}\) (250 nm), \(^3H_5\) (230 nm) states. The fact that both features appear at room temperature and are nearly resonant indicates that the splitting between the lowest 4f\(^1\)5d\(^1\) state and the \(^1S_0\) states is very small. It was reported that the energy gap between the \(^1S_0\) state and the lowest 4f\(^1\)5d\(^1\) state is only 323 cm\(^{-1}\) [7]. Therefore, a strong mixing between the \(^1S_0\) state and the 4f\(^1\)5d\(^1\) state could occur. This state mixing has been considered by Huang et al. for Pr\(^{3+}\) in SrAl\(_{12}\)O\(_{19}\) [8].

In this chapter, we examine the state mixing of BaSO\(_4\):Pr\(^{3+}\) using hydrostatic pressure to tune the energy gap and obtain the relative intensity of the \(^1S_0\) to the 4f\(^1\)5d\(^1\) emission as well as the \(^1S_0\) lifetime. These are quite sensitive to the mixing since the emission from the lowest 4f\(^1\)5d\(^1\) state is parity allowed while emission from \(^1S_0\) is parity forbidden.

We had expected that pressure would cause a decrease in the 4f\(^1\)5d\(^1\) energy by reducing the energy gap. Instead we found that both the relative intensities and lifetimes indicate an increase in the splitting between the 4f\(^1\)5d\(^1\) and \(^1S_0\) states. Using a simple model to calculate the relative intensities and lifetimes we have been able to measure this gap as a function of pressure.

6.2 Experimental techniques

Barium sulfate (BaSO\(_4\)), known as barite, has an orthorhombic crystal structure with space group P\(_{nma}\) (No. 62) [6]. The Ba\(^{2+}\) site in BaSO\(_4\) has the C\(_{1h}\) point symmetry [9], coordinated by
Figure 6.2 Emission of BaSO₄:Pr³⁺ around 250 nm after 476 nm + 301 nm two-photon excitation. 4f⁵5d¹ → 4f² as well as ¹S₀ → 4f² emission is observed at the same time.
twelve $O^{2-}$ ions. Since the trivalent praseodymium ion ($Pr^{3+}$) is introduced on a divalent cation site, sodium ion ($Na^{+}$) is co-doped for charge compensation.

$BaSO_4$:Pr$^{3+}$ powder was loaded into a type IIa diamond anvil cell (DAC). Excitation of the $4f^1 5d^1$ state of Pr$^{3+}$ was obtained by stepwise two-photon excitation with one Ar$^+$ laser operating at 476 nm and another UV enhanced Ar$^+$ laser operating at 301 nm. The principle of two-photon excitation was presented in chapter 4 and the experimental setup was shown in figure 4.6.

In order to measure the time-resolved emission spectrum as a function of pressure, a sapphire anvil cell is used. The sapphire is transparent from 144 nm to 6500 nm [10]. Therefore, the $4f^1 5d^1$ states of Pr$^{3+}$ can be excited directly by UV or vacuum UV (VUV) pumping sources with a single photon. Figure 6.3 shows the experimental setup for measuring the time-resolved emission spectrum of $BaSO_4$:Pr$^{3+}$. A pulsed (10 ns pulse width) ArF excimer laser (GAM LASER, Model EX5/250-125, 1.5W) operating at 193 nm was used to excite the $4f^1 5d^1$ state. The 193 nm laser line was separated from the background emission from the discharge using a Pellin-Broca prism. Pressures up to 89 kbar were applied until the sapphire anvils broke. The laser beam is focused on the small sample in the sapphire cell through the front window and the luminescence from the back window is collected. A monochrometer (Jarrell Ash, Model 82-410) was used to select the luminescence wavelength and the time resolved emission was recorded using a photomultiplier tube (PMT) (Hamamatsu, Model 943-02) and a digital oscilloscope (Tektronix TDS 460A).

6.3 Experimental results and discussions

The emission spectra of $BaSO_4$: Pr$^{3+}$ near 250 nm under different pressures by two-phonon excitation are shown in figure 6.4. As the pressure is increased the relative intensity of the sharp ($^1S_0$) transition increases with respect to the broad ($4f^1 5d^1$) transition and the $^1S_0$ peak shifts to
Figure 6.3 Experimental setup for high pressure time-resolved spectroscopy measurement
Figure 6.4 Emission spectra of BaSO₄: Pr³⁺ near 250 nm under different pressures at room temperature (T = 293 K) by 476 nm + 301 nm two-photon excitation.
lower energy with the rate of about $3\pm0.5$ cm$^{-1}$/kbar (see figure 6.5). The increase in the relative intensity of the $^1S_0$ emission indicates that the relative population of that state increases with pressure as would occur if the energy gap increases with pressure.

The representative time-resolved emission as a function of pressure is presented in figure 6.6. The lifetime of the $^1S_0$ level at ambient pressure is $82\pm10$ ns which is somewhat longer than the 56 ns value obtained by Vink et al. [7] at room temperature. My fellow student, Yi Zhou, measured the lifetime of the $^1S_0 \rightarrow ^1I_6$ transition at 411 nm of BaSO$_4$:Pr$^{3+}$ with a F$_2$ excimer laser operating at 157 nm at different temperatures (see table 6.1). He found that the lifetime is 68 ns at room temperature, which is in reasonable agreement with our results. As the pressure is increased, the lifetime increases to about 240 ns by 89 kbar.

<table>
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<th>Temperature (K)</th>
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</tr>
<tr>
<td>98</td>
<td>640</td>
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<td>289</td>
<td>70</td>
</tr>
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<td>293</td>
<td>68</td>
</tr>
</tbody>
</table>

Table 6.1 Lifetime of the $^1S_0 \rightarrow ^1I_6$ transition at 411 nm of BaSO$_4$:Pr$^{3+}$ at different temperatures at the ambient pressure.
Figure 6.5 $^1S_0$ emission peak energies as a function of pressure. Solid lines represent data for linear least-squares fits.
Figure 6.6 Time-resolved emission at 410nm after excitation at 193 nm as a function of pressure.
Both the relative emission intensities and lifetimes depend on two factors:

(1) The relative population of the \( ^1S_0 \) and \( 4f^15d^1 \) states

(2) The transition probabilities of the \( ^1S_0 \) and \( 4f^15d^1 \) states.

The relative population of the states depends on the energy gap and temperature (assuming thermal equilibrium). The relative intensities depend both on the relative population and the relative transition probabilities, both of which are a function of pressure. Because of the state mixing, the \( ^1S_0 \) lifetime depends on the transition probabilities of both unmixed states and on the relative populations which determine the time fraction that the excitation spends in each of the two states. A calculation must therefore consider both the relative populations and the mixing of the two states, factors which each depend on the energy gap.

We therefore model the behavior by considering two basis states, a pure \( 4f^2 (^1S_0) \) state and a single \( 4f^15d^1 \) state, separated by energy \( \Delta E \). The states are assumed to be mixed according to the Hamiltonian

\[
H = H_0 + H_{\text{odd-crystal}} + \alpha \cdot P
\]  

(6.1)

where \( H_0 \) describes the free-ion and even parity crystal field terms that determine the unmixed states. \( H_{\text{odd-crystal}} \) describes the coupling between the even parity \( 4f^2 \) states and odd parity \( 4f^15d^1 \) states by the odd components of the crystal field resulting in only off-diagonal elements. The third term linear in the pressure contributes only to the diagonal elements of the coupling matrix. The Hamiltonian is diagonalized and the matrix elements are obtained by a best fit to the data for the pressure dependence of both the relative intensities and \( ^1S_0 \) lifetime.

The Hamiltonian matrix is represented as

\[
H = \begin{pmatrix}
E(^1S_0) & H_{12} \\
H_{21} & E(4f^15d^1)
\end{pmatrix}.
\]  

(6.2)
The diagonal matrix elements are
\[
E(1S_0) = \langle \psi(1S_0) | H | \psi(1S_0) \rangle,
\]
\[
E(4f5d) = \langle \psi(4f5d) | H | \psi(4f5d) \rangle = E(1S_0) + \Delta E_0 + \alpha P.
\]
(6.3)

where, \(\psi(1S_0)\) and \(\psi(4f5d)\) are the unmixed basis states, \(\Delta E_0\) is the diagonal splitting at zero pressure. The off-diagonal elements, assumed to be real, are
\[
H_{12} = \langle \psi(1S_0) | H_{\text{odd-crystal}} | \psi(4f5d) \rangle = H_{21} = \alpha \psi(1S_0) + \Delta + \psi(4f5d)
\]
(6.4)
and are assumed independent of pressure. The two mixed states are described by
\[
\Phi_1 = a_1 \psi(1S_0) + a_{12} \psi(4f5d)
\]
\[
\Phi_2 = a_{21} \psi(1S_0) + a_{22} \psi(4f5d)
\]
(6.5)

From the orthonormal property of base states and mixed states, one obtains relations
\[
\begin{cases}
    a_{11}a_{21} + a_{12}a_{22} = 0 \\
    a_{11}^2 + a_{12}^2 = 1 \\
    a_{21}^2 + a_{22}^2 = 1
\end{cases}
\]
(6.6)

The matrix (6.2) is diagonalized as
\[
\begin{pmatrix}
    E(1S_0) + E(4f5d) - \sqrt{(\Delta E_0 + \alpha P)^2 + 4C^2} \\
    0
\end{pmatrix}^{\frac{1}{2}}
\]
\[
\begin{pmatrix}
    0 \\
    E(1S_0) + E(4f5d) + \sqrt{(\Delta E_0 + \alpha P)^2 + 4C^2}
\end{pmatrix}^{\frac{1}{2}}
\]
(6.7)

Let \(E_1\) and \(E_2\) be the energies for the states \(\Phi_1\) and \(\Phi_2\) respectively, the energy splitting of the mixed states is
\[
E_2 - E_1 = \Delta = \sqrt{(\Delta E_0 + \alpha P)^2 + 4C^2}
\]
(6.8)

Since \(H\Phi_1 = E_1\Phi_1\) and \(H\Phi_2 = E_2\Phi_2\), with relation (6.6), the mixing coefficients \(a_{ij}\) can be represented as
\[ a_{11} = a_{22} = \left[ 1 + \frac{(\Delta E_0 + \alpha P)^2}{4C^2} \right]^{-1/2} \left( 1 - \sqrt{1 + \frac{4C^2}{(\Delta E_0 + \alpha P)^2}} \right) \]  

(6.9)

\[ a_{12} = -a_{21} = \frac{(\Delta E_0 + \alpha P)}{2C} \left( 1 - \sqrt{1 + \frac{4C^2}{(\Delta E_0 + \alpha P)^2}} \right) \]  

(6.10)

The transition probabilities of the mixed states are expressed as

\[ W_1 = a_{11}^2 W(1^1 S_0) + a_{12}^2 W(4f5d) \]

\[ W_2 = a_{21}^2 W(1^1 S_0) + a_{22}^2 W(4f5d) = a_{12}^2 W(1^1 S_0) + a_{11}^2 W(4f5d) \]  

(6.11)

where \( W(1^1 S_0) \) and \( W(4f5d) \) are the radiative transition probabilities of the bare unmixed states and are assumed independent of pressure.

The relative population is given by a Boltzmann distribution at temperature \( T \)

\[ \frac{N(\Phi_2)}{N(\Phi_1)} = \exp \left( -\frac{\Delta}{kT} \right) = \exp \left( -\frac{\sqrt{(\Delta E_0 + \alpha P)^2 + 4C^2}}{kT} \right) \]  

(6.12)

where \( k \) is Boltzmann’s constant, \( N(\Phi_1) \) and \( N(\Phi_2) \) are the number of electrons occupying the mixed states \( \Phi_1 \) and \( \Phi_2 \) respectively. The observed lifetime \( \tau \) is obtained from

\[ \tau^{-1} = W = \left( \frac{N(\Phi_1)}{N_T} \right) \cdot W_1 + \left( \frac{N(\Phi_2)}{N_T} \right) \cdot W_2 \]  

(6.13)

where \( W \) is the total transition probability and \( N_T = N(\Phi_1) + N(\Phi_2) \) is the total number of electrons. From equation (6.12), equation (6.13) can be expressed as

\[ \tau^{-1} = W = \frac{W_1 + W_2 \cdot \exp(-\Delta / kT)}{1 + \exp(-\Delta / kT)} \]  

(6.14)
Equation (6.14) can also be used to fit the data of the temperature dependence of lifetime shown in table 6.1. At temperature $T = 80$ K, the decay time of the $^1S_0$ level was measured as 700 ns (see table 6.1), corresponding to the transition probability $W_1 = 1.43 \times 10^6$ s$^{-1}$ at ambient pressure because the emission is almost from the mixed state $\Phi_1$ at low temperature. Therefore, this value must be consistent in all calculations.

In calculating the relative intensities it is important to note that transitions from the mixed states contribute to both the broad and to the sharp spectral features. The mixed state $\Phi_1$ is in the 4$f^2$ configuration. The electron lattice coupling is weak. Therefore the transition from $\Phi_1$ is characterized by a strong sharp line with a weak vibronic sideband on the lower energy side. On the other hand, the mixed state $\Phi_2$ belongs to 5$d$ configuration and undergoes strong electron lattice coupling. The transition from $\Phi_2$ is a broad band with weak zero phonon line on the higher energy side. In the emission spectrum (see figure 6.4), the zero phonon line due to the transition from $\Phi_2$ can not be observed. Thus the sharp feature is only due to the transition from state $\Phi_1$ and the broad feature, which is mostly due to the transition from state $\Phi_2$, includes the vibronic sideband of state $\Phi_1$ as well. Under the assumption of thermal equilibrium at 293 K and negligible contributions from non-radiative relaxation in either state, the relative intensity $R$ of the broad to sharp feature in the spectrum is expressed as

$$R = \frac{I(\Phi_2)}{I(\Phi_1)} = \frac{W_1 a_{12}^2 N(\Phi_1) + W_2 a_{21}^2 N(\Phi_2)}{W_1 a_{11}^2 N(\Phi_1)} = \frac{W_1 a_{12}^2 + W_2 a_{21}^2 \exp(-\Delta/kT)}{W_1 a_{11}^2}$$

(6.15)

During the calculation, all parameters should be determined by obtaining a simultaneous best fit to the pressure dependent data for both the relative intensities and lifetimes and maintaining consistency with the temperature dependence of the lifetime at ambient pressure (data in table 6.1). Table 6.2 lists a set of results of the model calculation. These results are
Table 6.2 Results of the model calculation, which are compared with experiment shown from figure 6.7 to figure 6.10 for different values of C.

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<td>60</td>
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<td>1.43</td>
<td>1.43</td>
<td>1.43</td>
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</tr>
<tr>
<td>$W(4f5d)$ (base state)</td>
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<td>236</td>
<td>158</td>
<td>$10^6$ s$^{-1}$</td>
<td></td>
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<td>$W_2$ (mixed state) ($P = 0$)</td>
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<td>280</td>
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<td>$10^6$ s$^{-1}$</td>
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<td>5.6</td>
<td>5.3</td>
<td>5.1</td>
<td>cm$^{-1}$/kbar</td>
</tr>
</tbody>
</table>

compared with experiment shown from figure 6.7 to figure 6.10. In the figures shown the experimental intensity ratio $R$ against pressure at temperature $T = 293$ K, the amplitude of the emission is assumed to consist of a sharp feature of about 2 nm half-width sitting atop a broad feature. The height of the broad feature is estimated from the amplitude just beyond the wings of the sharp feature and the height of the sharp feature can be obtained using the amplitude of the broad feature as the base upon which it sits (see figure 6.4). As seen from figure 6.7 to 6.10, for $C \leq 40$ cm$^{-1}$, the experimental results are described fairly well by this simple model using these best fit parameters. With $C = 60$ cm$^{-1}$, although one can vary the parameters to fit the pressure dependence of the intensity ratio and lifetime, the fit for the temperature dependence of lifetime is not as good as that for $C \leq 40$ cm$^{-1}$. Therefore, to best fit to the experiment, the value of $C$ is in the range of $0 \sim 40$ cm$^{-1}$; the energy splitting of the mixed states at the ambient pressure is in
Figure 6.7 Comparison of experiment with the results of the model calculation of column 1 in table 6.2. There is no state mixing.
Figure 6.8 Comparison of experiment with the results of the model calculation of column 2 in table 6.2, where $C = 20$. 
Figure 6.9 Comparison of experiment with the results of the model calculation of column 3 in table 6.2, where $C = 40$. 
Figure 6.10 Comparison of experiment with the results of the model calculation of column 4 in table 6.2, where C = 60.
the range of 595 ~ 630 cm$^{-1}$; $W_1 = 1.43 \times 10^6$ s$^{-1}$ (700 ns) and $W_2$ is in the range of 235 x $10^6$ ~ 280 x $10^6$ s$^{-1}$ (3.6 ~ 4.3 ns). It can be seen that the state mixing is small. These parameters are quite different from the results obtained by Vink et al (Energy splitting is 323 ± 48 cm$^{-1}$, $W_1' = 6.24 \times 10^6$ s$^{-1}$ and $W_2' = 62.24 \times 10^6$ s$^{-1}$ at ambient pressure) [7]. They used the Deutsches Electronen Synchotron (DESY) to measure the time-resolved spectrum of BaSO$_4$:Pr$^{3+}$ with 200 ns time interval between bunches of photons (FWHM = 130 ps). This setup made their lifetime measurements at lower temperature inaccurate because the lifetime was much larger than 200 ns according to Zhou’s measurements (see table 6.1). Thus their energy splitting, $W_1$ and $W_2$ are severely in error.

From the results of the fit to the data it is concluded that the energy of the lowest 4f$^1$5d$^1$ state of Pr$^{3+}$ increases with pressure. The energy gap is found to increase with a rate in the range of 5.3 ~ 5.9 cm$^{-1}$ kbar$^{-1}$ based on the best fit to the data. The energy of the $^1S_0$ state decreases by about $3$ cm$^{-1}$ kbar$^{-1}$ (see figure 6.5) implying that the lowest component of the 4f$^1$5d$^1$ increases with increasing pressure. This is in contrast to the expectation that the 5d states of rare earth ion generally decrease in energy with pressure as the compression increases the crystalline field. Based on emission in YAG, the lowest 5d levels of Pr$^{3+}$ and Ce$^{3+}$ have been found to decrease at rates of 14.1 [11] and 12.5 cm$^{-1}$/kbar$^{-1}$ [12], respectively.

The conclusion that the lowest component of the 4f$^1$5d$^1$ state of Pr$^{3+}$ in BaSO$_4$ increases in energy with pressure does not necessarily imply that the energy of the centroid of the 4f$^1$5d$^1$ state increases with pressure. It may be that the compression resulting from the application of hydrostatic pressure affects the crystal field in such a way that the lowest component of 4f$^1$5d$^1$ moves in energy opposite to that of the centroid. Also, pressure induced changes in the electron
phonon coupling can, for example, cause the emission to shift differently under pressure than the absorption [13]. However, the specific cause for this unusual behavior in BaSO$_4$:Pr$^{3+}$ is unknown.

6.4 References


CHAPTER SEVEN

LUMINESCENCE OF BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ UNDER HIGH PRESSURE:

THE Eu$^{2+}$ SITES

7.1 Introduction

Barium magnesium aluminate (BaMgAl$_{10}$O$_{17}$) doped with divalent europium ions (Eu$^{2+}$), also known as BAM, is a well known blue-emitting commercial phosphor [1]. The 4f$^6$5d $\rightarrow$ 4f$^7$ transition of Eu$^{2+}$ in this phosphor leads to a broad band emission with the maximum at about 450nm. It is widely used in three-color fluorescent lamps and plasma display panels (PDP) under Hg or vacuum ultraviolet (VUV) excitation due to its high efficiency and good chromaticity [2-4]. However, BAM phosphor degrades more rapidly than the red and green emitting phosphors used to produce the full color spectrum [5, 6]. A good understanding of the location and environment of the Eu$^{2+}$ luminescent center might help improve the stability of BAM.

BAM has a crystal structure similar to the hexagonal $\beta$-alumina structure of NaAl$_{11}$O$_{17}$ [7]. It has a layered structure with a series of spinel blocks of composition [MgAl$_{10}$O$_{16}$] separated by mirror planes of composition [BaO]. Ba$^{2+}$ ion is located in the mirror plane at the Beevers–Ross site. Within the spinel block, Al$^{3+}$ ions are located at a tetrahedral site or an octahedral site. Mg$^{2+}$ ions are tetrahedrally coordinated. Generally BAM is synthesized with the replacement of Ba$^{2+}$ by Eu$^{2+}$. Although there is only one crystal site of Ba$^{2+}$, the location of Eu$^{2+}$ is not precisely known. Eu$^{2+}$ ions may occupy the Beevers–Ross (BR) site, the anti-Beevers–Ross site (a-BR) or the mid-oxygen (mO) site, or even the tetrahedral site inside the spinel block by substitution of Mg$^{2+}$ ions. Several researchers have reported that there exist multiple sites as locations of Eu$^{2+}$ [8-10]. Zhang et al. presented a broad absorption feature from 210 nm to 410 nm in the
excitation spectrum of BAM while the emission spectrum is broad and asymmetric [11]. Figure 7.1 shows the emission spectra of BAM with different excitation wavelengths. The emission spectrum of BAM is not very dependent on excitation wavelength. The method of site-selective excitation (fluorescence line narrowing) [12] can not be applied to provide answers about the Eu$^{2+}$ site location or whether multiple sites are occupied. A number of attempts have been made using other means to address this question. Boolchand et al. [8] measured the Mössbauer spectroscopy of BAM:Eu$^{2+}$ and identified three Eu$^{2+}$ sites and based on calculations of the nuclear quadrupole coupling constants, these were identified as the Beevers–Ross (BR) site, the anti-Beevers–Ross site (a-BR) and the mid-oxygen (mO) sites in the $\beta$-alumina structure. Calculations using a scattered wave model for the electronic structure of these different potential Eu$^{2+}$ sites yielded an excitation spectrum that is consistent with the existence of these three sites [9]. A spectroscopic study of BAM samples doped with Sm$^{2+}$, which exhibits sharp line emission within the $4f^6$ configuration, indicated the presence of either two or three sites for Sm$^{2+}$ which, because of its similarity to Eu$^{2+}$ implied a similar conclusion for BAM:Eu$^{2+}$ [10].

In this chapter, a study of the emission spectrum under various pressures is reported in an attempt to further elucidate the site distribution problem. The emission is studied at a number of excitation wavelengths (275, 300, 336, 350 and 363 nm) as a function of pressure from ambient up to 150 kbar. It was expected that the $4f^65d \rightarrow 4f^7$ Eu$^{2+}$ transition of each site would shift differently under pressure. As a result, the positions of the emission peaks associated with the different sites would move relative to one another as a function of pressure. At any pressure there should be an emission peak associated with each occupied emitting site whose sum should yield the observed spectrum. At a given pressure, the spectra for different excitation wavelengths would always be a sum of these same peaks but with different relative amplitudes. By carrying
Figure 7.1 Emission spectra of BAM with different excitation wavelengths.
out this process over a large number of pressures, it was hoped that a self-consistent picture would emerge whereby the transition energies of each site could be followed as a function of pressure. Furthermore, based on the observed differences in the transition energy sensitivity to pressure in conjunction with an examination of the possible sites and their expected response to pressure, it seemed possible that specific spectroscopic features might be associated with particular sites.

7.2 Experimental results and discussions

Commercial powder samples of BAM:Eu$^{2+}$ were loaded into the high-pressure diamond anvil cell (DAC) with a silicone dimethylosiloxane oil solution as pressure transmitting medium. Emission was excited with the single lines of a UV-enhanced Ar$^+$ laser. The experimental setup is similar to figure 4.6 but using only one pumping source to excite the 5d band directly. The luminescence spectra were corrected by calibrating the wavelength-dependent response of the spectrometer and CCD camera using a calibrated FEL tungsten lamp traceable to a NIST (National Institute of Standards and Technology, former National Bureau of Standards, NBS) calibrated standard lamp.

The spectra obtained under different excitation wavelengths and at different pressures are shown in figures 7.2 to 7.6. All spectra are presented in spectral lineshape against energy for the reason mention in chapter five (see section 5.3.1) and reference [13]. The corrected spectra are then fit to Gaussian line shapes.

We consider that the emission is a result of the transition from the lowest state of the excited 4f$^6$5d$^1$ electronic configuration to the ground state of the 4f$^7$ electronic configuration of Eu$^{2+}$ in BAM. The spectra excited at 275 (figure 7.2), 336 (figure 7.4), 350 (figure 7.5) and 363 nm (figure 7.6) are very similar when compared at the same pressures; only for 300 nm (figure
Figure 7.2 Emission lineshapes of $4f^65d \rightarrow 4f^7$ Eu$^{2+}$ transition under excitation at 275 nm. The lineshapes are decomposed into two Gaussian functions labeled by s1 and s2.
Figure 7.3 Emission lineshapes of $4f^65d \rightarrow 4f^7$ Eu$^{2+}$ transition under excitation at 300 nm. The lineshapes are decomposed into three Gaussian functions labeled by s1, s2 and s0.
Figure 7.4 Emission lineshapes of $4f^65d \rightarrow 4f^7$ Eu$^{2+}$ transition under excitation at 336 nm. The lineshapes are decomposed into two Gaussian functions labeled by s1 and s2.
Figure 7.5 Emission lineshapes of $4f^65d \rightarrow 4f^7$ Eu$^{2+}$ transition under excitation at 350 nm. The lineshapes are decomposed into two Gaussian functions labeled by $s1$ and $s2$. 
Figure 7.6 Emission lineshapes of $4f^65d \rightarrow 4f^7$ Eu$^{2+}$ transition under excitation at 363 nm. The lineshapes are decomposed into two Gaussian functions labeled by s1 and s2.
7.3) excitation are marked differences observed. For the fitting, each Gaussian is represented by
the following function:

\[
G_i(E) = \frac{A_i}{\sqrt{w_i}(\pi/2)} \exp \left[ -2\times \left( \frac{E - E_i}{w_i} \right)^2 \right]
\]  

(7.1)

where \( E_i, A_i \) and \( w_i \) represent the energy peak, amplitude and width, respectively. In performing
the fitting, no constraints were placed on the parameters.

Except for 300 nm excitation, the spectra can be decomposed into two Gaussian bands
labeled as s1 (site 1) and s2 (site 2). The fits, along with the two Gaussians which add up to yield
this fit, are shown for each pressure. The fits reproduce the spectrum very well and attempts to
add a third Gaussian do not significantly improve the results. We assign these two Gaussian
bands to two different sites of Eu\(^{2+}\).

Under excitation at 300 nm the spectra are significantly different as seen in figure 7.3 and
attempts to fit the spectra require an additional Gaussian in the higher energy region. Thus, we
have decomposed the emission under excitation with 300 nm into three bands; s1 and s2 that
have already been observed under other excitation wavelengths and an additional band s0 which
peaks at higher energies. The intensity (amplitude) of this band decreases with pressure and
disappears for pressures greater than 100 kbar.

The pressure dependence of the peak energy, the line width and the normalized amplitude
of the Gaussian bands used in fitting the spectra are shown in figure 7.7, figure 7.8 and figure 7.9,
respectively. Different symbols identify the excitation wavelengths and emitting sites. One sees
that a self-consistent picture emerges in that the parameters behave smoothly with pressure and
are relatively independent of excitation wavelength. The energies of the maxima of the bands s0,
s1 and s2 all decrease at similar rates with pressure. The results of the least-squares fitting are
Figure 7.7 Energies of the peaks corresponding to individual Gaussian bands s0, s1 and s2. The symbols identify the site and excitation wavelength yielding that data point.
Figure 7.8 Line widths corresponding to individual Gaussian bands s0, s1 and s2. The symbols identify the site and excitation wavelength yielding that data point.
Figure 7.9 Amplitudes corresponding to individual Gaussian bands s0, s1 and s2. The symbols identify the site and excitation wavelength yielding that data point.
Table 7.1 Resulting peak positions and pressure dependent energy shifts as a function of excitation wavelengths for the three sites in BAM.

<table>
<thead>
<tr>
<th>$\lambda_{\text{exc}}$</th>
<th>300 nm cm$^{-1}$</th>
<th>275 nm cm$^{-1}$</th>
<th>336 nm cm$^{-1}$</th>
<th>350 nm cm$^{-1}$</th>
<th>363 nm cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$ kbar</td>
<td>cm$^{-1}$ kbar</td>
<td>cm$^{-1}$ kbar</td>
<td>cm$^{-1}$ kbar</td>
<td>cm$^{-1}$ kbar</td>
</tr>
<tr>
<td>Site0</td>
<td>23369</td>
<td>-6.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site1</td>
<td>21888</td>
<td>-10.20</td>
<td>22108</td>
<td>-6.50</td>
<td>22072</td>
</tr>
</tbody>
</table>

summarized in table 7.1. Whereas the energy of the s1 band is almost independent of excitation wavelength, with differences of less than 300 cm$^{-1}$, the energies of the s2 band show a larger dependence of up to 500 cm$^{-1}$. The widths of the two bands are quite different; the s2 band is much wider than that of the s1 band. The amplitude of s2 increases, whereas the amplitude of s1 decreases with pressure. The widths of the three Gaussian bands are distinct and quite different and are relatively pressure independent. The width of s2 is quite large. It is possible that a width of more than 3000 cm$^{-1}$ as obtained for pressures below 100 kbar under excitation at 300 nm may be unphysical.

While, it is expected that the peak energies and widths of the emission of each site should be independent of excitation wavelength since they represent emission from the same site, it is somewhat surprising that the amplitudes are relatively independent of excitation wavelength. This may indicate that the excitation spectra of site s1 and site s2 are relatively similar. Site s0 behaves differently and has a much narrower excitation band width yielding excitation only
around 300 nm. It is also possible that energy transfer among the sites plays an important role in
determining the relative intensities of the three sites.

7.3 Conclusions

The spectroscopy under high pressure supports the claim for three distinct sites of Eu$^{2+}$ in
BAM based on attempts to fit the observed emission spectra of BAM as a function of pressure
and excitation wavelength. While two of the sites appear in all spectra, the third site appears only
for excitation at 300 nm. The parameters of the Gaussian bands describing the three sites vary
smoothly with pressure and are fairly independent of excitation wavelength. Site 1 dominates the
spectra. While this may indicate that it has the largest occupancy, it may also indicate a larger
absorption strength. It is also possible that energy transfer from the higher energy to lower
energy sites occurs during the $\sim$1 µs lifetime. The three sites have different peak energies and
bandwidths. These distinct properties of the three sites may provide evidence for the identity of
the site responsible for each band but such a connection has not been attempted in this work.

7.4 References

fluorescent lamps, combining an efficacy of 80 lumens/W or more with a color rendering index

H. Pyun and G.Y Hong, Phosphors for plasma display panels. Journal of Alloys and Compound,
311 (2000) 33-39


APPENDIX A

OPERATIONS OF DIAMOND ANVIL CELL

A.1 Diamond mounting

The diamond anvil is glued to the support disc. Then the disc is inserted into the supporting plate and clamped by three set screws.

A.2 Diamond alignment

Precise diamond alignment is most important in obtaining high pressure. The diamond culets must have the same diameters, must be concentric and must be parallel. Misaligned diamonds result in gasket failure before reaching the desired high pressure, and may damage the diamonds. Normally the DAC should be well aligned by the manufacture. However new cells must be checked before use.

The axial alignment is easy checked by looking through the optical access hole of the diamond supporting plate with a binocular microscope. If adjustment is needed, three set screws are used to adjust the lateral position of the diamond anvils. Checking the parallelism of diamond anvils is a little bit tricky. If the diamond culets are not parallel, with white light transmitting through two closely approached diamond culets, the optical interference fringes are formed, which can be seen under the microscope. There should be only one fringe when the diamond culets are parallel to each other. More than one fringe indicates that the diamond is tilted. The three screws for force loading are used to tilt the supporting plate to remove the fringes. Then a micrometer is used to measure the relative heights of the top plate at the positions close to the three loading screws. The heights are then used as the future reference values for the parallelism of the diamond culets. Details of the alignment procedure are well described by Jephcoat et al. [1]
and Dunstan and Spain [2]. An alternative method of checking the parallelism is to let a Helium Neon laser beam passes through the diamond culets; the reflective beams from two culets should be overlap if the culets are parallel. Otherwise, the supporting plate is tilted to make the beams overlap.

Note that aligned diamonds will generally remain aligned unless the diamonds get loose or broken and need to be re-assembled and re-aligned. When checking the alignment or making adjustments, never let the bare faces of the diamond culets touch since they may be chipped or broken by contact. A spacer is always placed between the two diamonds (gasket or other materials) to keep them separated.

A.3 Procedures of sample loading

After the DAC is well aligned, the procedures of sample loading in the DAC are as follows. Since the dimensions of all components are so small, almost all the procedures are performed under a binocular microscope.

1. Clean both diamond anvils by wiping alcohol across the culets using tissue paper twisted into a pointed tip moistened with alcohol. However, do not use too much alcohol because the glue for diamond mounting will be dissolved.

2. Make reference marks on the gasket for referencing the angular orientation of the gasket. Pre-indent the gasket to the desired thickness. Drill a hole as close to the center of the indentation as possible with a micro drill. Remove any rough borings around the hole. Clean the gasket with alcohol.

3. Clean the culets again. Carefully put the above prepared gasket in the same position on the lower diamond anvil as during pre-indentation by using reference marks.
4. Load the sample, ruby chip and pressure medium. Close the cell and tighten the screws. Observe the chamber hole with microscope to make sure the sample, ruby chip and pressure medium are loaded. As mentioned before, several attempts may be needed.

5. Measure and record the height. Make the culets parallel using the reference height values for parallelism.

After loading the sample, put the DAC into the path of the experimental setup. Apply the force progressively and measure the pressure using the ruby luminescence for each step to be sure the cell is sealed. If the cell is not sealed, the ruby lines won’t shift to the longer wavelength. One can also check the cell condition under microscope. When the cell is not sealed, the pressure medium will flow away or evaporate and the chamber hole of the gasket will be collapsed.

A.4 References
