As_2S_3:Er^{3+}: SPECTROSCOPY AND SPECTRAL HOLE BURNING

by

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(Under the direction of Uwe Happek)

ABSTRACT

Using spectral holes in Er doped Y_2SiO_2, stabilization of a semiconductor laser to 500 Hz at 1536 nm (i.e. 1 part in $2 * 10^{14}$) has been recently achieved. However, the stabilization could be maintained only for a period of 2 ms, since the spectral holes utilized for stabilization were non-persistent. Gated hole burning could provide persistent holes and long-term stabilization, but due to the large bandgap of the single crystalline host materials used in the experiments, this type of spectral hole burning could not be realized. Reported here are studies of Er^{3+} doped As_2S_3, a chalcogenide glass with a bandgap of about 2 eV, to explore the potential of this material as a persistent hole burning medium for the stabilization of NIR lasers. Samples were prepared by stirring molten As_2S_3 doped with Er_2S_3 powder for 8 hours in a sealed quartz tube. Subsequent quenching of the melt produced the bulk glass. The optical properties the As_2S_3:Er^{3+} samples were analyzed using emission and absorption spectroscopy.

INDEX WORDS: Spectroscopy, Hole Burning, Glass, Chalcogenide

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B.S., Georgia State University, 1999

A Thesis Submitted to the Graduate Faculty
of The University of Georgia in Partial Fulfillment
of the
Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2002

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December 2002

ACKNOWLEDGMENTS

First of all, I would like to thank my thesis advisor, Prof. Uwe Happek. Without his guidance and support, this accomplishment would not have been possible.

I would also like to thank my advisory committee, Prof.'s William Dennis and Gary Love. Thank you for the time and guidance you have given me.

Also, thank you to all of those who helped me develop early in my career. Dr. David Moore at Brookwood High School, Mr. James Weeks at Abraham Baldwin College, Prof. James Purcell at Georgia State University and Prof. Jeff Templon at UGA have all given me much support.

I would also like thank my all of my coworkers over my career for their friendship and support. Specifically, I thank Jay Fleniken, Paul Schmidt, Carl Liebig, Steve Cox, and Long Pham. Furthermore, I would like to thank everyone at the UGA Glassblowing Shop for their fantastic work on helping to prepare our samples.

Thank you, also, to all of my new friends in the ProSeed seed team, Specifically, Julie Darity, Laura Tweett, Pat Northcutt, Rhonda Taylor, Billy Means, and Russ Dean. You have provided me with a wonderful introduction into the world outside of academia and your friendship has made the difficult tasks of balancing work and school much easier.

Finally, I'd like to thank my family for all of their loving patience and support. You have always trusted in the decisions I've made. The pride you take in my accomplishments is profoundly important to me.

And now as I move on, looking into the future, all of my thoughts are with Angela…

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Chapter 1

Introduction

1.1 Purpose

Recently there has been much interest in spectral hole burning for use in many technical applications such as laser stabilization and optical data storage. For such applications, erbium seems to be a good choice. This is mainly because of its strong transition line at 1.5 μm, which is in the middle of the telecommunications band. Because the erbium transition is at such a technologically advantageous wavelength, much study has been done on it. One such study [1] has reported to have stabilized a laser to 200 Hz over 10-ms integration times in an erbium doped crystal using a hole burning technique called transient spectral hole burning. The disadvantage to using a transient spectral hole is that it can drift and thus cause destruction of the spectral hole itself. Two photon gated hole burning is another method of chemical hole burning that could solve the problem of frequency drift of the hole. The purpose of this study is to determine the feasibility of As_2S_3 doped with Er^{3+} as a candidate for this two photon gated hole burning process.

1.2 Persistent Spectral Hole Burning — Historical Overview

Persistent spectral hole burning [PSHB] is a high-resolution laser spectroscopic technique that provides a means of probing the microscopic dynamics of a solid through its interactions with optically active impurity molecules. In essence, the technique uses a narrow bandwidth laser to selectively reduce the optical absorption arising from the small subset of impurities that happen to be in resonance with the laser frequency. The resulting reduction in absorption strength in the narrow frequency region about the laser frequency is known as a “spectral hole” and if the lifetime of this hole is longer than any of the impurity excited state lifetimes, the hole is said to be persistent.

The earliest instances of persistent spectral hole burning involved electronic transitions of organic dyes in amorphous organic matrices. These first observations were reported in 1974 by Gorokhovskii et al. [2] for free-base phthalocyanine in a frozen n-octane matrix, and by Kharlamov et al. [3] for perylene and 9-aminoacridine in glassy ethanol matrices. Since these initial discoveries, numerous other examples of systems exhibiting PSHB for impurity electronic transitions have been discovered both in other organic systems [4] and in inorganic systems such as rare earth ions in silicate glasses [5]. In the course of these discoveries, it became clear that there were several mechanisms by which PSHB could occur. These mechanisms tend to fall within two broad categories: photochemical hole burning, in which the laser induces a change in the electronic properties of the impurity molecule or ion itself, breaking a bond for example, and non-photochemical hole burning, in which the impurity molecule or ion remains essentially unchanged but the host matrix around is altered. It is this former type of hole burning which will be relevant for this study of a rare earth element in a chalcogenide glass.

1.3 Motivation and Goals

A variety of uses have been found for persistent spectral hole burning. Hole burning can be used to find information on a variety of interactions, including excited state dephasing processes, host-guest dynamics, proton tunnelling, low frequency excitation in amorphous hosts, relaxation mechanisms for vibrational modes, photochemical mechanisms at liquid helium temperatures, and external field perturbation. In addition, the possibility that persistent spectral holes might be used to store digital information has led to the study of materials and configurations for frequency domain optical storage and related possible applications. And, as mentioned above, transient spectral hole burning using Er^{3+} has been used to stabilize a laser to 200 Hz over 10-ms integration times [1].

With these developments in mind, the aim of this work was to study a novel system, namely As_2S_3:Er^{3+}, to evaluate its suitability for spectral hole burning and use as a laser stabilization device. The proposed mechanism for spectral hole burning in this glass is a two photon gated hole burning process.

CHAPTER 2

BASIC CONCEPTS OF PERSISTENT SPECTRAL HOLE BURNING

2.1 OPTICAL LINESHAPES FOR DEFECTS IN SOLIDS

In order to understand persistent spectral hole burning and the information that it can provide, it is first necessary to review the factors which contribute to the optical lineshapes for defects in solids. First consider an ensemble of identical molecules experiencing identical local environments. An incident electromagnetic wave will set up a coherent superposition of the ground and excited states of these impurity molecules, with an associated oscillating dipole moment. The sum over all the impurities thus gives rise to an oscillating macroscopic polarization whose lifetime determines the width of the absorption line for this ensemble. This lifetime is governed by the rate at which the phase coherence among the individual molecule is lost, and hence is known as the dephasing time, usually denoted T_2. Two contributions determine the dephasing rate $1/T_2$. The first comes from the decay rates of the two states involved; since we will be dealing with the situation where the lower state is the ground state, with essentially infinite lifetime, only the excited state lifetime T_1 will appear. The second contribution originates in processes which interrupt the phase of the individual molecules, destroying the phase coherence and hence the macroscopic polarization, without altering the population of the energy levels. These are known as pure dephasing processes, and their characteristic time is denoted T_2^*. The total dephasing rate is given by

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*} \tag{2.1}$$

and the resulting Lorentzian absorption line has a width γ_h given by

$$\gamma_h = \frac{1}{\pi T_2} \tag{2.2}$$

known as the homogeneous width. The mechanisms for the pure dephasing contributions T_2^* depend on the system being studied. In crystalline solids, the dominant dephasing process is the scattering of phonons from the impurity. In the case of amorphous solids, the situation is more complicated, and is not as well understood. The most generally accepted models for impurity optical dephasing in glasses at low temperature involve the so-called "two-level systems" (TLS) originally proposed to explain the anomalous low temperature specific heat of glasses [6, 7]. The important point is that in solids, homogeneous lineshapes convey information about the dynamics of the host-defect system, with the defect acting as a microscopic probe of the host excitations.

The situation is not quite so simple in real solids, however, particularly in amorphus solids, because the defects in general *do not* experience identical local environments. Differences from site to site in the way the host couples to the impurity energy levels lead to different absorption frequencies for each molecule. In addition, these differences in coupling can result in variations in the homogeneous width at the various kinds of site. Thus, if one could look at only those defects within one certain type of host environment, one homogeneous absorption line would be observed. Likewise, a defect in a different host environment, would give rise to a homogeneous band with a different center frequency and width. What is actually observed in linear absorption spectroscopy, of course, is the sum over the entire distribution of possible environments, resulting in an absorption band many times wider (in glasses, typically by a factor of 10^3 to 10^5) than the homogeneous widths determined by dephasing rates. This is known as inhomogeneous broadening.

2.2 Basic Requirements for Persistent Spectral Hole Burning

The basic requirements for producing persistent spectral changes are that there exist at least two stable quasi-ground state configurations for the host-defect system, that relaxation between these ground states occurs on a much slower time scale than the defect excited state lifetimes, and that there exists an optical pumping pathway, involving an excited state of the defect, connecting the two ground states. The system is initially in a stable configuration which can be represented by the one well of a double-well potential. For those defects whose environments produce the proper energy level spacing in the impurity, the transition to the excited state can be made by absorption of a laser photon of energy $\hbar\omega_L$. After most absorption events, the defect simply relaxes back to its original ground state, with the system remaining in the one well. But there exists a finite probability that from the defect's excited state, the system can undergo a configuration change to the second well of the double well potential. With the system in the new configuration, the impurity's energy level spacing is changed and its absorption no longer lies at the laser frequency. Thus, at temperatures sufficiently low that thermal activation over the barrier is negligible, and with tunnelling between the wells sufficiently slow, centers absorbing at the laser frequency will gradually be removed from the one well and trapped in the other configuration, thus reducing the number of centers absorbing at that frequency. The result is a reduction in absorption strength, i.e. a spectral hole, centered at the laser frequency.

Persistent spectral hole burning in various systems has been attributed to the following mechanisms: (1) ionization of the defect with subsequent trapping of the electron [8, 9]; (2) internal rearrangement of the bonds in the defect molecule [14]; (3) reorientation of the defect with respect to the host [10]; (4) rearrangement of the local host structure around the defect. These mechanisms have traditionally been divided into two broad classes: Mechanisms (1) and (2) are examples of photochemical hole burning (PHB), in which laser radiation changes the electronic structure of the impurity molecule itself, typically resulting in a photoproduct molecule with optical absorptions far removed from the original frequency, outside the original inhomogeneous band. The other two mechanisms are examples of non-photochemical hole burning (NPHB), in which the impurity molecule remains intact, and the absorption is lost from the laser frequency through changes in the interactions between defect and host. A hallmark of this latter type of hole burning is the much smaller range of the redistribution of absorption strength; the hole-burned centers have their frequency shifted only by a small amount, so that the absorption strength from the hole is relocated nearby, inside the original inhomogeneous band. These two classes of mechanisms, however, are not absolutely distinct and systems with intermediate behavior exist, such as the $CN-{:}Na+$ defect in KBr, whose reorientational mechanisms would ordinarily be considered NPHB, but whose spectral signature suggests PHB [11, 12].

2.3 Two Photon Gated Hole Burning

One way to achieve persistent spectral hole burning via mechanism (1) above is through a process where two photons are used to put the defect into an excited state which is above the band gap of the host. In two photon hole burning, one laser photon is used to excite an electron from the ground state of the defect into an excited state still within the host band gap. A second photon is then used to further excite the electron from this intermediate state into a state which is out of the host material band gap (Figure 2.1). This method is useful to burn a spectral hole at an energy which is lower than that of the host material band gap. This also provides the advantage of possibly removing the electron into a distant trap, thus reducing the probability of it relaxing back to its ground state.

The keys to this two step process are a host with a sufficiently small band gap and a dopant with a long lived excited state. If the host has a wide energy gap then the photon energy will not be large enough to ionize the impurity through an excited state absorption process (Figure 2.1 (B)). In other words, if the photon is not sufficient to promote an electron into the conduction band, only intra-ion excitation can be achieved and the electron will relax rapidly back to its ground state. If this happens a persistent spectral hole cannot develop because the electrons will fall back into the same ground state from which it was excited originally. On the other hand, with a low band gap of the host, some of the electrons would be promoted into the conduction band (Figure 2.1 (A)). In the conduction band the electrons would be free to move around and some of them would get caught in traps. Once trapped, the hole would be persistent as long as the electron remained in the trap states.

2.4 TRIVALENT ERBIUM

Figure 2.2 shows the first four energy levels of trivalent erbium. These first four states of trivalent erbium can be determined by Hund's rule. The electron structure of Er^{3+} is [Xe]$4f^{11}$. According to Hund's rule, since several orbitals in the shell are available, electrons will first enter each orbital singly with parallel spins, then they will pair up in the orbitals. With seven orbitals available ($\ell = 3$), electrons will fill the orbitals leaving three unpaired electrons. The total orbital angular momentum (L) will then be six. The net spin (S) of these orbitals will be 3/2, giving a multiplicity ($2S + 1$) of 4. The total angular momentum ($J = L + S$) will then have values of $15/2 \cdots 9/2$. Since the shell is more than half-filled the lowest energy will correspond to the largest value of L, namely $J = 15/2$.

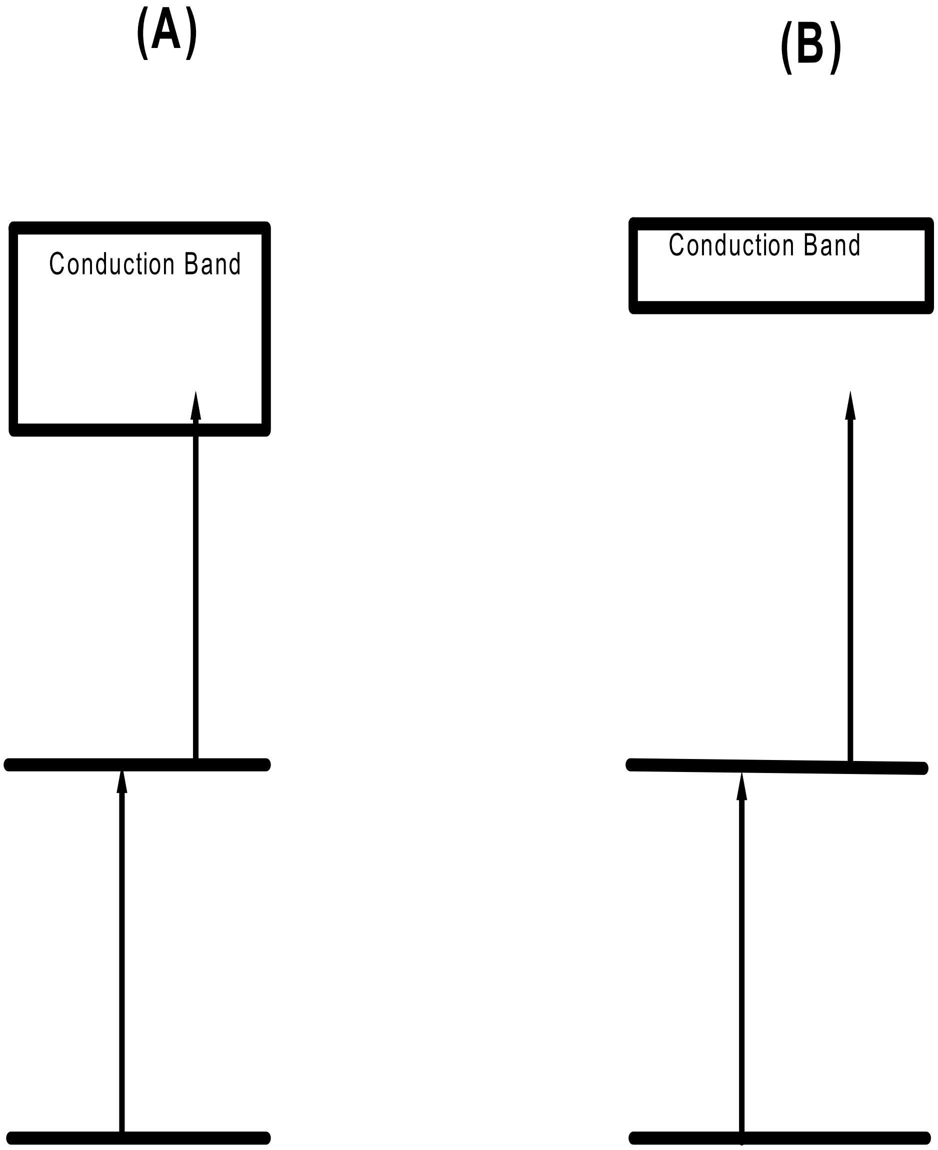

Figure 2.1: Excitation by two photons in a host glass with a small band gap (A) and a larger band gap(B)

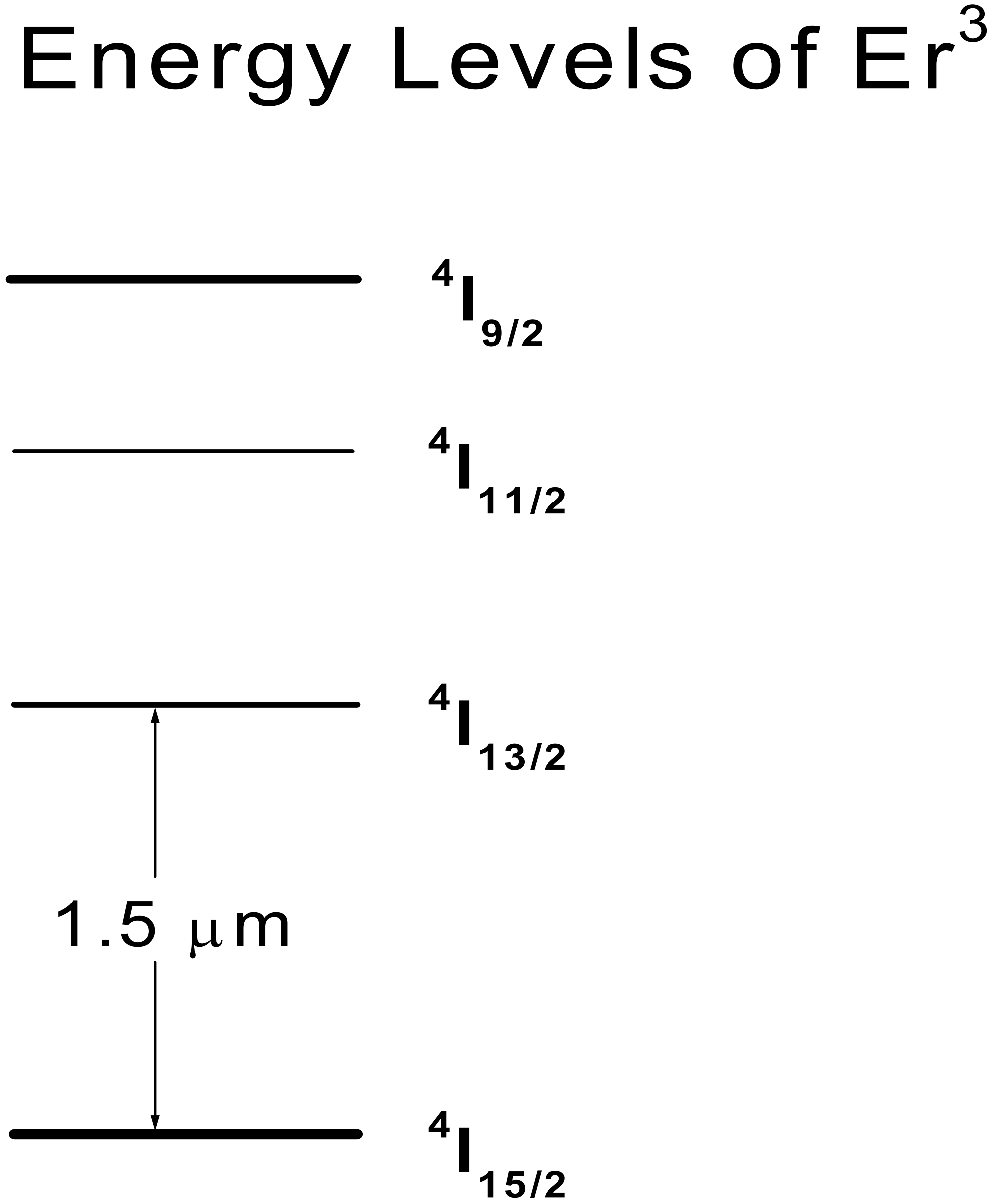

Figure 2.2: Energy levels of Er^{3+}.

It is also important to note that the transitions, since they are inter-f shell transitions, are forbidden. They are considered forbidden because they violate the dipole selection rule which requires that the initial and final states must have opposite parity.

One other characteristic of Er^{3+} that makes it a good choice for this study, is that one of its dominant transitions is around 1.5 μm. This is important for the usefulness of this material, especially in the telecommunications industry. Trivalent erbium is already in use in the telecommunications industry as an amplification medium for fiber optic communication because the transition at 1.5 μm is in the middle of the wavelength band used in this industry.

2.5 THE CHALCOGENIDE GLASSES

The name "chalcogenide glass" refers to the fact that these materials contain as one of their major constituents at least one of the chalcogens — members of that column of the periodic table which included S (brimstone), Se, and Te. The most widely studied chalcogenide glasses are arsenic trisulfide (As_2S_3), arsenic triselenide (As_2Se_3), and the glassy form of elemental Se. A hallmark of these chalcogenide compounds is their very strong glass-forming tendency. Indeed, glass forming is so strongly preferred by As_2S_3 that it is all but impossible to produce this material in crystalline form; until the recent synthesis of microscopic crystals of As_2S_3 [13], the only source of crystalline As_2S_3 was the naturally-occurring mineral called *orpiment*, resulting from slow annealing on geologic timescales.

The chalcogenides are semiconducting glasses, displaying the thermally activated d.c. electrical conductivity characteristic of semiconductors, and a large body of work has focussed on their electronic transport properties and electrically active defect states [15, 16, 17, 18]. A distinguishing hallmark of the chalcogenides arises from the electronic configuration of the chalcogen atoms. In its preferred bonding configuration, a chalcogen atom is covalently bonded to two neighboring atoms, so that two of its four p electrons go into bonding orbitals, while the two remaining unshared electrons form a non- binding ”lone-pair” orbital, while the anti-bonding states remain unoccupied. It was thus argued by Kastner [20] that in constructing the band structure of the solid from these states, the occupied lone-pair states form the valence band, while the unoccupied anti- bonding states form the conduction band. This is the key distinction between the chalcogenides and tetrahedrally bonded semiconductors such as Si and Ge, in which the valence band arises from bonding states and the conduction band arises from antibonding states. Because the electronic properties of the chalcogenides are dominated by the lone- pair band, Kastner [20] suggested that an apt name for them would be the *lone-pair semiconductors*, a term by which these materials are often called. Interactions between the lone-pair electrons are important in determining the structure of these materials. Lone- pair effects are also frequently invoked to attempt to understand some of the unusual phenomena unique to this class of materials, such as photo-darkening, a decrease in the optical band gap induced by the absorption of photons near the band gap energy.

2.6 LASER STABILIZATION USING SPECTRAL HOLES

One important application for persistent spectral holes is laser stabilization. 200 Hz Laser stabilization using regenerative transient spectral holes has been achieved in Er^{3+}:KTP by Cone *et al.*[1] Cone and his group were able to use a transient spectral hole in the strongest absorption site of the $^4I_{15/2} \rightarrow ^4 I_{13/2}$ Er^{3+} transition at 1536.87 nm to stabilize a InGaAsP/InP laser.

One limitation of using a transient spectral hole for this purpose is frequency shift and consequently laser drift since the laser is modifying its own reference. One possible solution to this is the use of the two photon hole burning described above because the laser used to create the spectral hole can be turned off, thus eliminating any drift of the hole.

Chapter 3

Experimental Details

3.1 Sample Preparation

3.1.1 Starting Materials and Doping Procedure

The samples used in these studies are ingots of bulk melt-quenched chalcogenide glass into which molecular impurities have been introduced. Each sample preparation begins with pieces of undoped starting material in bulk glass form. The use of starting material in the form of macroscopic chunks, rather than of the finer powder often obtained from chemical supply houses, greatly enhances the safety and convenience of handling these generally toxic materials. In addition, starting with material which has already been reacted and quenched to form a glass eliminates what would otherwise be the most time-consuming step of sample preparation — reacting the elemental constituents of the glass and ensuring that these constituents are microscopically dispersed isotropically throughout the sample.

Because As_2S_3 is in wide use as an infrared optical material, bulk samples of this glass can be obtained from many sources. High purity As_2S_3 starting material for the samples used in this study were obtained from *Alfa Æsar*, a chemical supply company.

The goal of preparing the sample was to create a substitutional impurity, where the erbium impurity atoms would replace some of the arsenic atoms inside the glass. The method used to insert the Er^{3+} impurity into the As_2S_3 consists of placing the bulk As_2S_3 in a sealed, evacuated quartz tube with Er_2S_3 powder. This tube is then heated in a furnace while being gently rocked to facilitate maximal surface area exposure to the impurity. Since Er_2S_3 melts at considerably higher temperature [1730 ^0C] than As_2S_3 the movement of erbium into the glass is due to surface reaction of molten As_2S_3 with Er_2S_3 powder. A main part of this study was to establish that the presence of single substitutional erbium ions instead of Er_2S_3 molecules.

Quartz tubes approximately 7-8" long with 0.270 " inner diameter are used to contain the sample and impurity during the melting process. Quartz is used because of its extremely high melting point while still being pliable in the glassblower's torch and because it is transparent, facilitating visual monitoring of the sample melting procedure. The tubes are prepared by the glass blowers to have a flat bottom in the interior of the tube. This is done to minimize the sanding and polishing necessary on that side of the sample, and also avoids some lensing loss if an infrared spectrum is desired of an unpolished sample.

The tubes are cleaned by soaking in medium strength nitric acid in order to remove any organic impurities. They are then rinsed in distilled water and soaked in acetone to remove other impurities. The tubes are dried in an oven for at least 10 minutes at 300 °C. Drying facilitates the removal of any atmospheric water molecules that have absorbed onto the silica surface.

Enough bulk As_2S_3 is loaded into the tube to create a 7 to 8 mm thick sample. The amount needed can be calculated using the density of As_2S_34, 3.43 g/cm^3. This allows for losses due to sanding away the meniscus and polishing, leaving a 1 to 2 mm thick polished sample which can be further reduced by sanding if necessary. The desired amount of Er_2S_3 was then determined by a ratio of molecular weight; higher concentration samples contained 0.5% Er_2S_3 and lower concentration samples 0.1% Er_2S_3.

The tube is then evacuated and valved off. The glass blowers seal the quartz tube at its halfway point by softening the glass at that point, which allows the tube to collapse on itself due to the pressure differential, forming a cone-shaped end. This method ensures that the tube's contents are never contaminated by the outside air or the flame. There is, however, usually some oxygen released into the tube when the flame warms the quartz enough to dissociate some of the SiO_2 in the quartz. A white ring of silicon formed near where the glass was molten is evidence that this process occurred.

The melting point of As_2S_3 is about 300 °C. However, since it is a glass, it has a pronounced viscosity change with temperature, getting progressively less viscous at higher temperatures. Thus in order to ensure good sample mixing, the samples must be heated well above their melting temperature so that they flow easily, typically to about 600 °C.

In order to facilitate this, a tube furnace was used to heat the samples. Figure 3.1 shows the furnace apparatus. The furnace is mounted so that it can either be laid horizontally on its side or stand vertically upright. Insulating doors close on both ends of the furnace. A stepper motor is attached to one end of the furnace, to which is attached a stainless steel oven insert (aluminum must be avoided due to the high temperature). The sample tube is placed in the oven insert, situated so that the furnace is upright; the sample falls to the flat bottom of the sample tube.

The sample tube is heated initially with the oven in the horizontal position. It is rotated at about 1 RPM by the stepper motor (8 Hz step rate). The sample tube insert is placed diagonally along the axis of the oven so that as the insert spins, alternating ends of the sample tube will be positioned lower than the opposite end. In this way, the sample material slowly flows from end to end inside the tube in order to provide sufficient mixing of the dopant with the glass. The rotation rate was empirically chosen to optimize this sloshing given the viscosity of the sample at

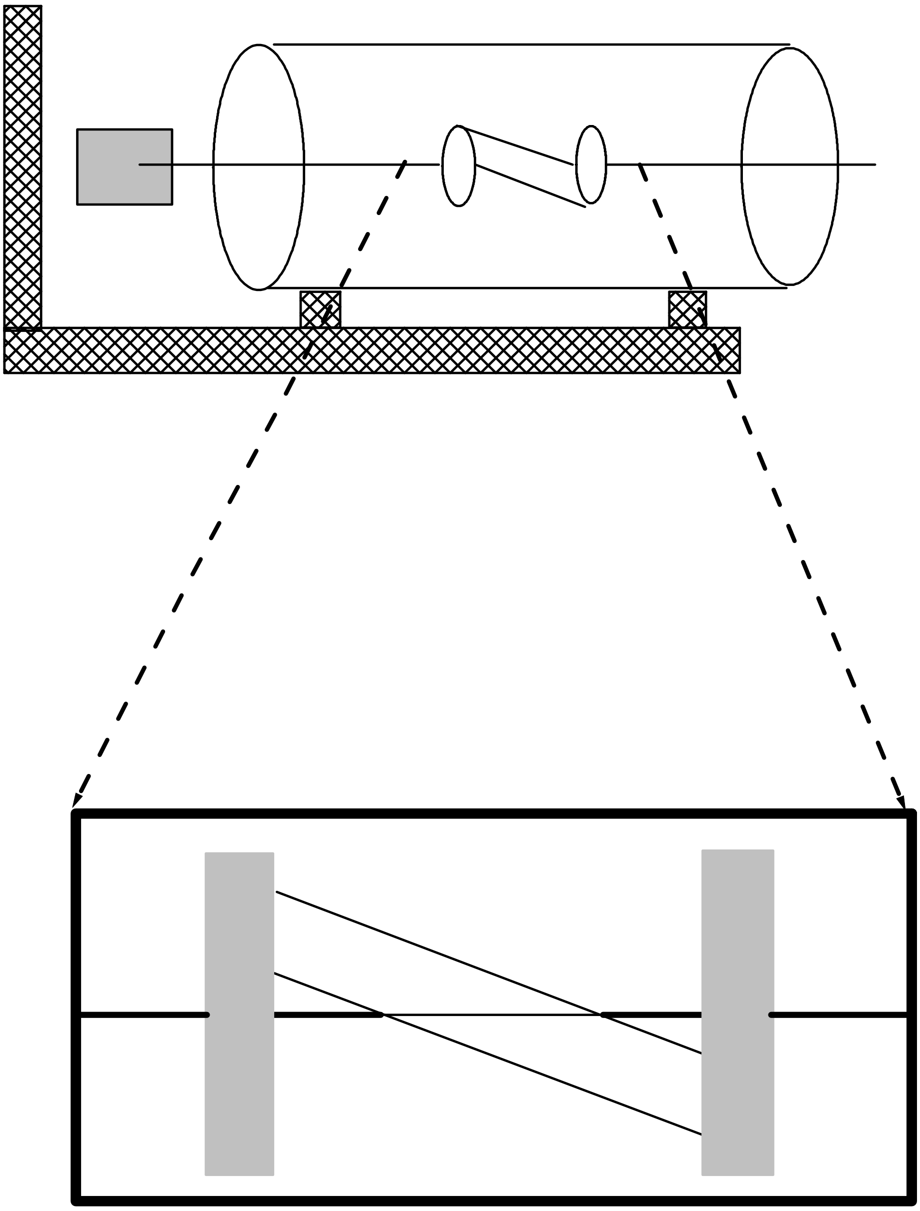

Figure 3.1: Schematic of furnace used to heat samples.

this temperature. This stirring technique is a great improvement over the standard technique that combines a rotating vial with a rocking mechanism for the entire furnace.

The sample is heated at least 8 hours at this temperature, whereupon the oven is turned upright and heated another 1 hour while the stepper motor remains running in order to facilitate sample flow. This allows the sample to drain to the bottom of the sample tube. Then the oven insert is removed through the oven top and the sample is immediately quenched in a water bath.

After about a minute the sample fully solidifies and forms a strong meniscus on top and a small one on the bottom. The sample is extracted from the tube by breaking the tube open in a fumehood and carefully breaking the tube away from the sample.

The sample is then hand sanded flat and parallel on both sides with fine sandpaper. It it is then polished with 3μm, 1μm, and finally 0.3μm polishing pads. This should produce an As_2S_3 sample that can easily be read through in bright light. The sample must be sanded and polished by hand because it is very brittle. Holding it by hand for the polishing pads tends to add some slight rounding and thus lensing to the sample, but avoids scratches and sample breakage. To keep dust to a minimum, mineral oil was used as a lubricant during the sanding and polishing steps. The mineral oil can be removed from the sample with an overnight toluene bath. After sanding and polishing, the sample is approximately 0.4 inches long. One example of an $As_2S_3{:}Er^{3+}$ sample is shown in Figure 3.2.

Great care has to be taken in the final steps of the sample preparation because the glass is very fragile. Samples can and do break easily when being removed from the quartz tube and during the sanding process. Also, it was found that quenching the sample too quickly can cause it to break inside of the quartz tube.

Figure 3.2: As_2S_3:Er^{3+} sample shown with a dime for size comparison.

In addition, a sample of KBr:Er_2S_3 was prepared for comparison purposes. This sample was prepared by mixing Er_2S_3 powder with KBr powder and then pressing the powder into a nearly transparent pellet.

3.1.2 Safety Considerations

In the course of preparing chalcogenide glass samples, it is important to keep in mind that these materials and many of their reaction products are very toxic, and should be handled accordingly. In particular, gaseous chalcogen compounds such as H_2S can be deadly if inhaled in sufficient concentrations. Accordingly, any operations which involves heating chalcogenide glasses should be carried out in a fume hood, even if the glass is in a sealed quartz tube; quartz tubes can and do break unexpectedly. In addition, the opening of the quartz tubes containing the finished doped glass should be carried out under a hood since the tube will contain the gaseous by-products of the doping process.

An appreciation of the toxicity of hydrogen sulfide can be gained from the following: A half-hour exposure to H_2S concentrations of 600 ppm are known to be fatal to humans [7]. When it is noted that death by hydrogen sulfide poisoning can occur even more rapidly than that following exposure to similar concentrations of the more infamous poison hydrogen cyanide, the need for caution becomes exceedingly clear. Fortunately, hydrogen sulfide provides a warning in the form of a strong unpleasant rotten egg odor which becomes apparent at concentrations well below those which would be immediately lethal, but it should be noted that the ability to detect this odor rapidly diminishes due to olfactory fatigue. Thus a prudent criterion would be that detection by smell should be sufficient reason to immediately evacuate the room.

The chalcogenide glasses themselves, especially when in the form of macroscopic pieces of glass, are not quite so hazardous as their gaseous by-products, but care is still required. Arsenic compounds such as As_2S_3 can give rise to both acute and chronic poisoning through either ingestion or inhalation. These compounds are also suspected carcinogens. The most likely route by which the careless experimentalist may expose himself to a dangerous dose of these materials in their solid form is through inhalation of dust. Thus the opening of containers, which usually contain a considerable amount of fine dust regardless of what form the bulk material is in, should be performed in a fume hood.

The cutting and polishing steps necessary for producing optical quality surfaces on the samples are problematical because, by their very nature, they produce a large amount of fine dust. The use of lubricant during cutting and polishing safely eliminates airborne chalcogenide dust, but care must be taken to ensure that the sample, polishing pad, and anything else contaminated with the dust, is coated with oil at all times until all polishing materials can be safely disposed of. Protective plastic gloves should be worn during any polishing operation to avoid accumulation of toxic dust on the skin and under fingernails.

3.2 Linear Spectroscopy

One method used to characterize the samples is linear absorption spectroscopy. This is accomplished using a Bruker IFS66v Fourier Transform Infrared (FTIR) Spectrometer. FTIR is a method of resolving the spectrum of light incident on the spectrometer by encoding the spectrum by way of a Michelson interferometer into its Fourier transform. As the variable length arm of the interferometer goes through its full motion, the full spectrum of light is recorded as an interferogram (Figure 3.3). The Fourier transform of this yields the spectrum of the incident light. The ratio of the spectrum of the incident light that has passed through the sample to the bare infrared source yields the absorption spectrum of the sample.

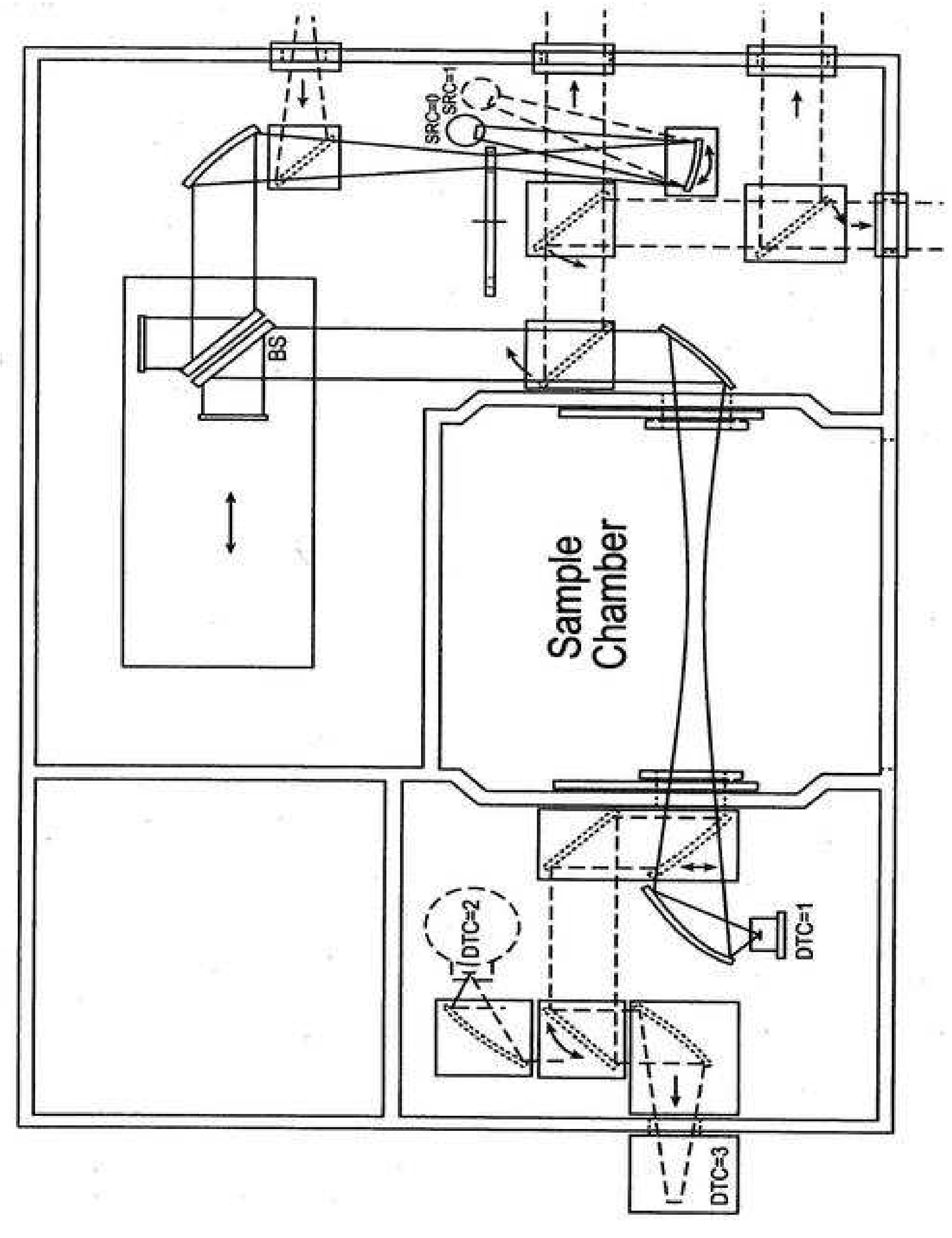

Figure 3.3: Bruker Interferometer.

For all transmission measurements reported in this work, the spectra are taken using a tungsten source, CaF_2 beamsplitter, and Ge detector. All absorption spectra have a minimum of 3 cm^{-1} resolution and were taken with the entire beam path under vacuum. The low temperature measurements were made using an Oxford continuous flow cryostat inserted in the sample chamber of the spectrometer.

The other method used to characterize the samples is emission spectroscopy. This was accomplished using the same Bruker IF66v Fourier Transform Spectrometer. For the emission spectra, the spectrometer measures the full spectrum of light that is emitted from the sample that is being excited by an incident laser. The bench set-up for finding the emission spectra is shown in Figure 3.4.

For all emission measurements reported in this work, the spectra were taken with an 803 nm laser as the excitation source. The CaF_2 beamsplitter, Ge detector and Oxford cryostat were again utilized. The resolution of all of the emission spectra was 3 cm^{-1}.

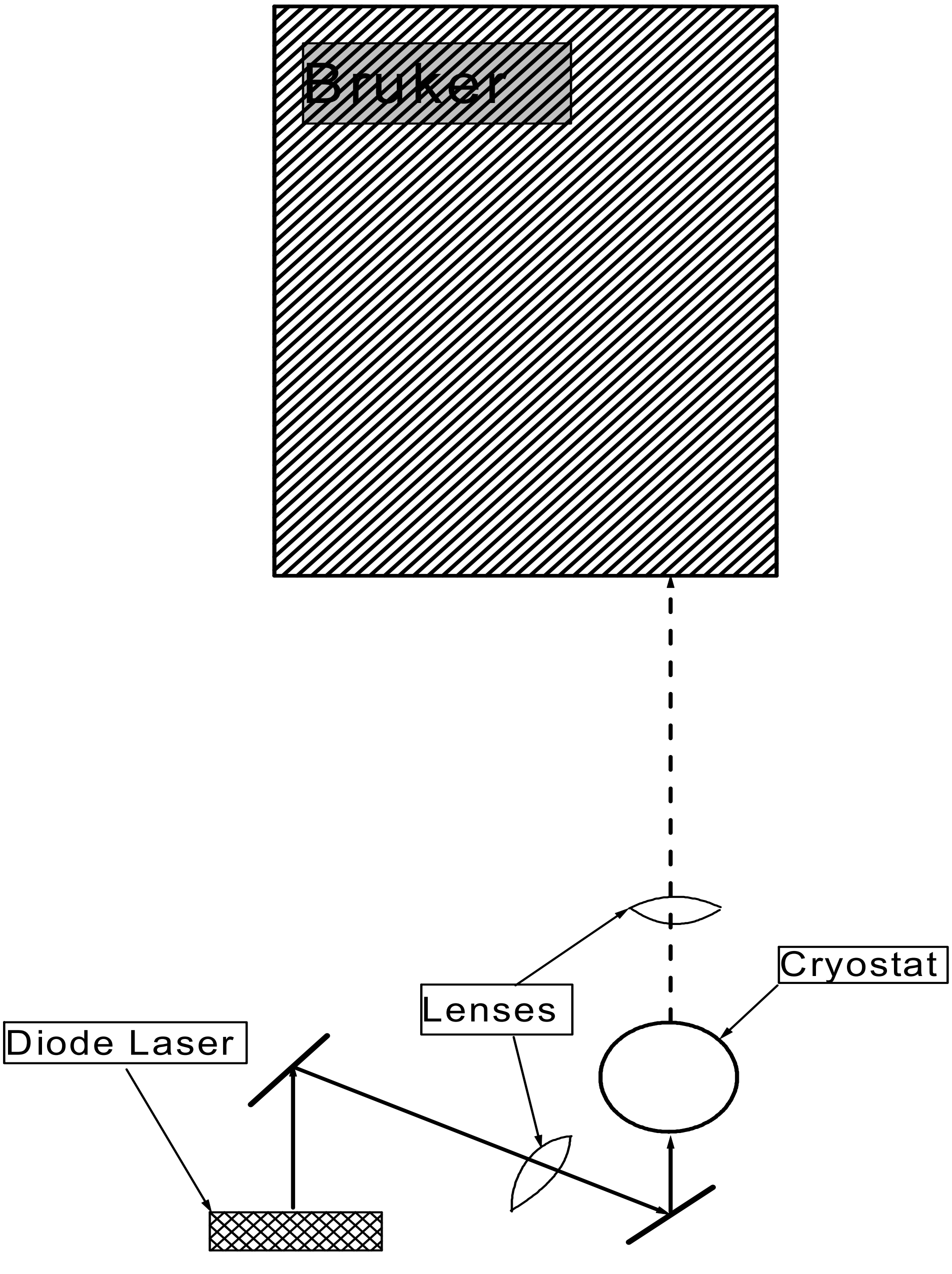

Figure 3.4: Set-up for taking emission spectra.

CHAPTER 4

RESULTS

4.1 TRANSMISSION

The first step in characterizing the As_2S_3:Er^{3+} was to measure its transmission spectra. The spectra of the As_2S_3:(0.1%)Er^{3+} sample were taken at temperatures of 8.4 K, 25 K, 50 K, and 75 K. The transmission at these temperatures is shown in Figure 4.1. The resolution was 3 cm^{-1}.

The line at 6505 cm^{-1} corresponds to the well-known Er^{3+} transition at 1.54 μm. This is the transition from the lowest state of the $^4I_{15/2}$ manifold to the lowest state of the $^4I_{13/2}$. It can also be noted that some of the lower energy lines "freeze" out at the lower temperatures. This is due to the omission of some of the thermally accessible states within the ground state. Also, a very strong line exists at 6675 cm^{-1}. This line is most probably due to transmission from two nearby defect sites as will be shown in Section 4.4.

4.2 EMISSION

Next the As_2S_3:(0.1%)Er^{3+} sample was characterized by measuring its emission spectra. The emission spectra were measured at temperature of 45 K, 100 K, 150 K, 200 K, and 250 K. The resolution was 3 cm^{-1}. The emission spectra at these temperatures are shown in Figure 4.2.

Again, the well-known $^4I_{15/2} \rightarrow ^4 I_{13/2}$ Er^{3+} is evident at 6505 cm^{-1}. Also, it can be noted that the intensity of the emission increases at lower temperatures. This is

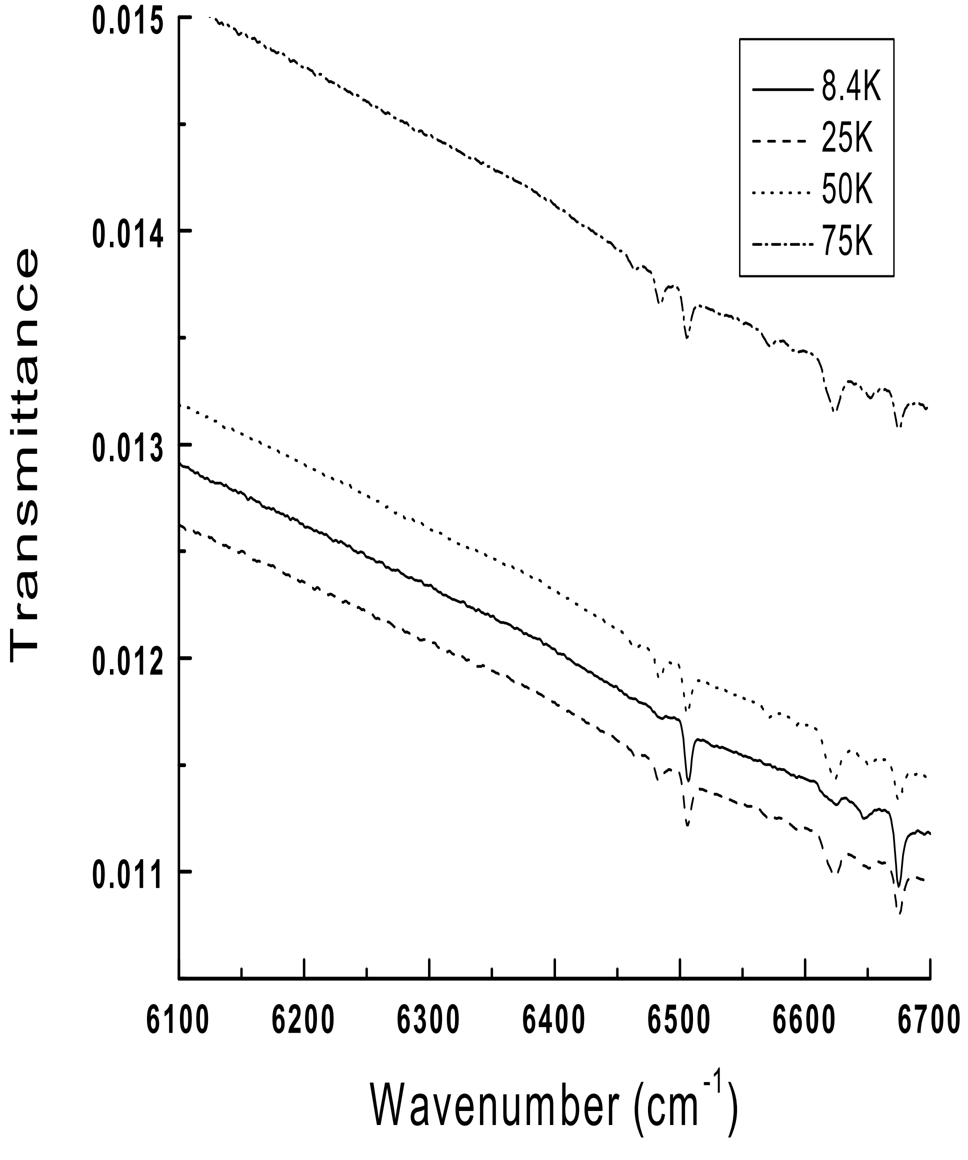

Figure 4.1: Transmission Spectra of As_2S_3:Er^{3+}.

due to the lower non-radiative decay back to the ground state. If the total decay Γ_T is given by

$$\Gamma_T = \Gamma_R + \Gamma_{NR}, \tag{4.1}$$

where Γ_R and Γ_{NR} are the radiative and non-radiative decay, then the intensity of the decay would follow the form:

$$I \propto \frac{\Gamma_R}{\Gamma_R + \Gamma_{NR}}. \tag{4.2}$$

4.3 Comparing the Transmission and Emission

A comparison of the emission spectrum and transmission spectrum at room temperature is shown in Figure 4.3. The most noticeable difference between these two spectra is the splitting of the 6505 cm^{-1} peak in the emission spectrum that is not present in the transmission spectrum. Also, the peak at 6675 cm^{-1} in the transmission spectrum is not evident in the emission spectrum. This is due to the fact that, because of different experimental set-ups, it was not possible excite the same spot on the sample when measuring the two different spectra. We interpret this as an indication of spectral hole burning.

4.4 Evidence of Nearby defect Sites

As mentioned earlier evidence was found that, in some regions of the sample, two defect sites lie close to one another in the glass structure. This was assumed to be responsible for the transition line in Figure 4.1 at 6675 cm^{-1}. Figure 4.4 shows further evidence of this by comparing the emission of a sample containing 0.1% Er^{3+} with one containing 0.5% Er^{3+}. The higher concentration sample again contains the transition line at 6675 cm^{-1} while the lower concentration sample does not. Since it

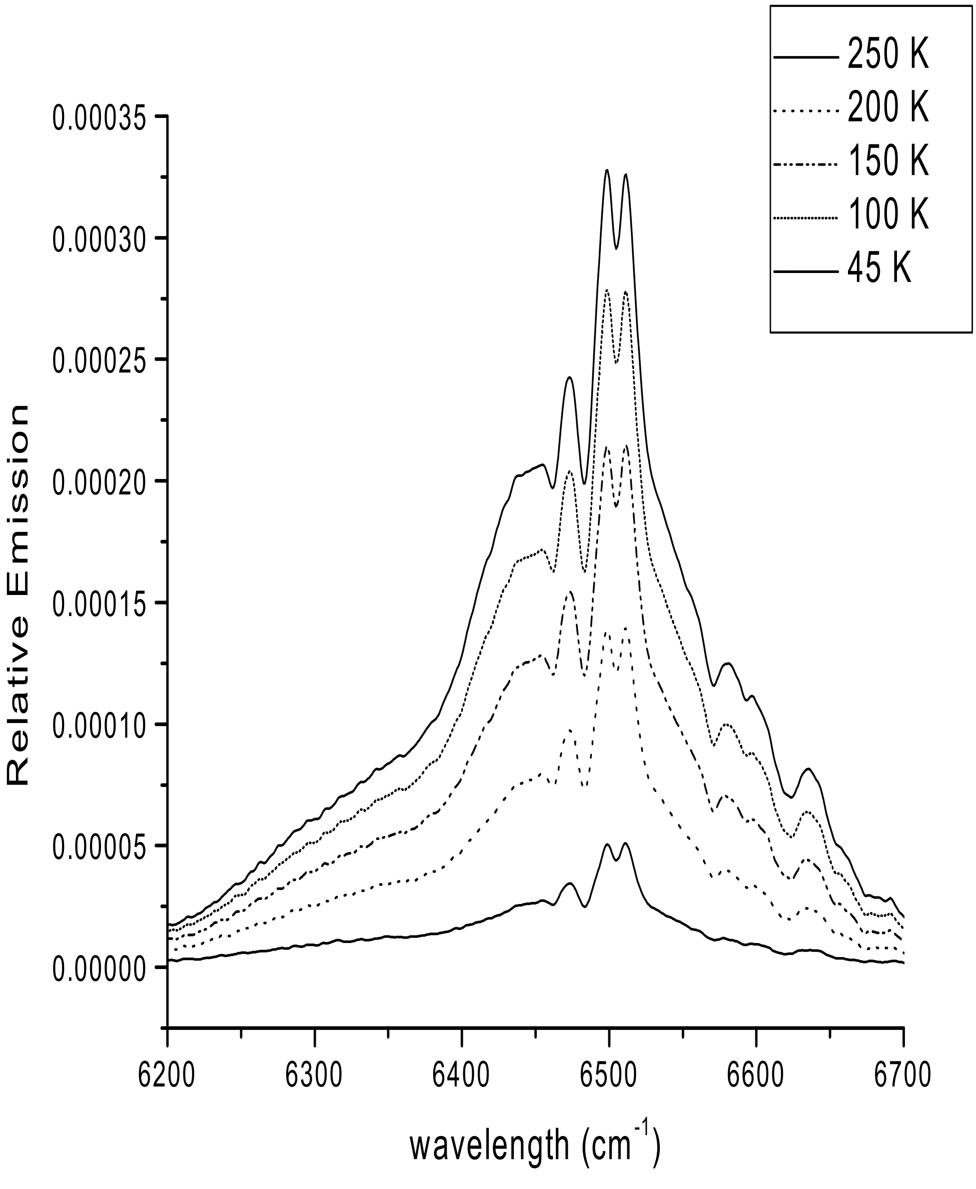

Figure 4.2: Emission Spectra of As_2S_3:Er^{3+}.

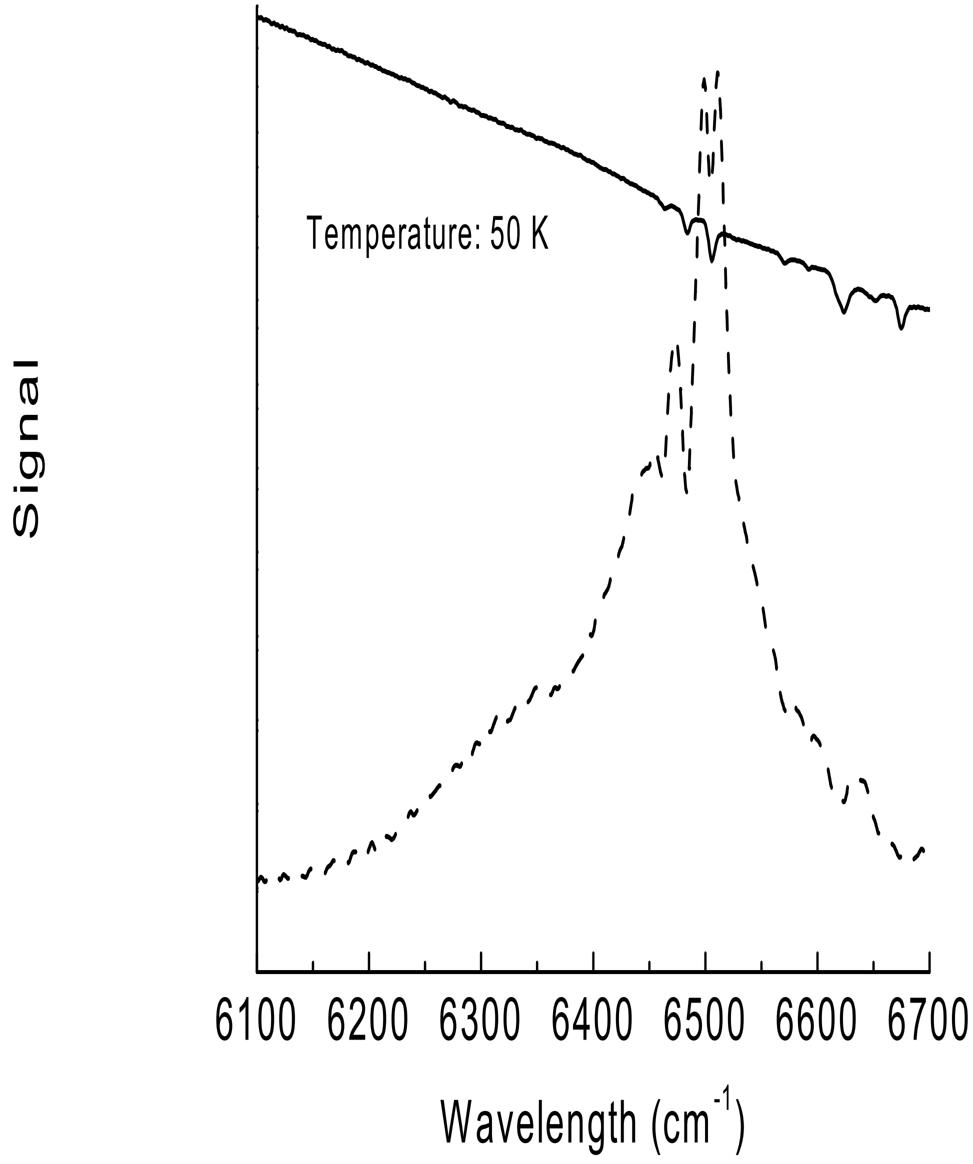

Figure 4.3: Comparison of the transmission spectrum and emission spectrum for As_2S_3:Er^{3+} at room temperature.

is more likely that the erbium atoms will be closer together as their concentration increases, any changes in the spectrum due to two nearby erbium atoms should be more pronounced as concentration increases. These changes will arise since the local field will be different when two erbium atoms couple as opposed to when an erbium atom couples with an arsenic atom.

One other explanation for this transition at 6675 cm^{-1} could be that the Er_2S_3 was not fully dissolved in the glass and therefore the spectrum has some signature of the transitions of Er_2S_3. To eliminate this as a possibility, Er_2S_3 powder was mixed with KBr powder and pressed into a pellet. The emission spectrum of the pellet was then measured and compared to the emission of As_2S_3:Er^{3+}. As can be seen from Figure 4.5, the two emission spectra both show the transition at 6505 cm^{-1} but are dissimilar enough to conclude that there was not a significant amount of Er_2S_3 in the glass.

To summarize, a comparison of the low and high doped As_2S_3 samples with the optical properties of Er_2S_3 containing pressed pellet shows that we have been successful in preparing Er^{3+} doped As_2S_3.

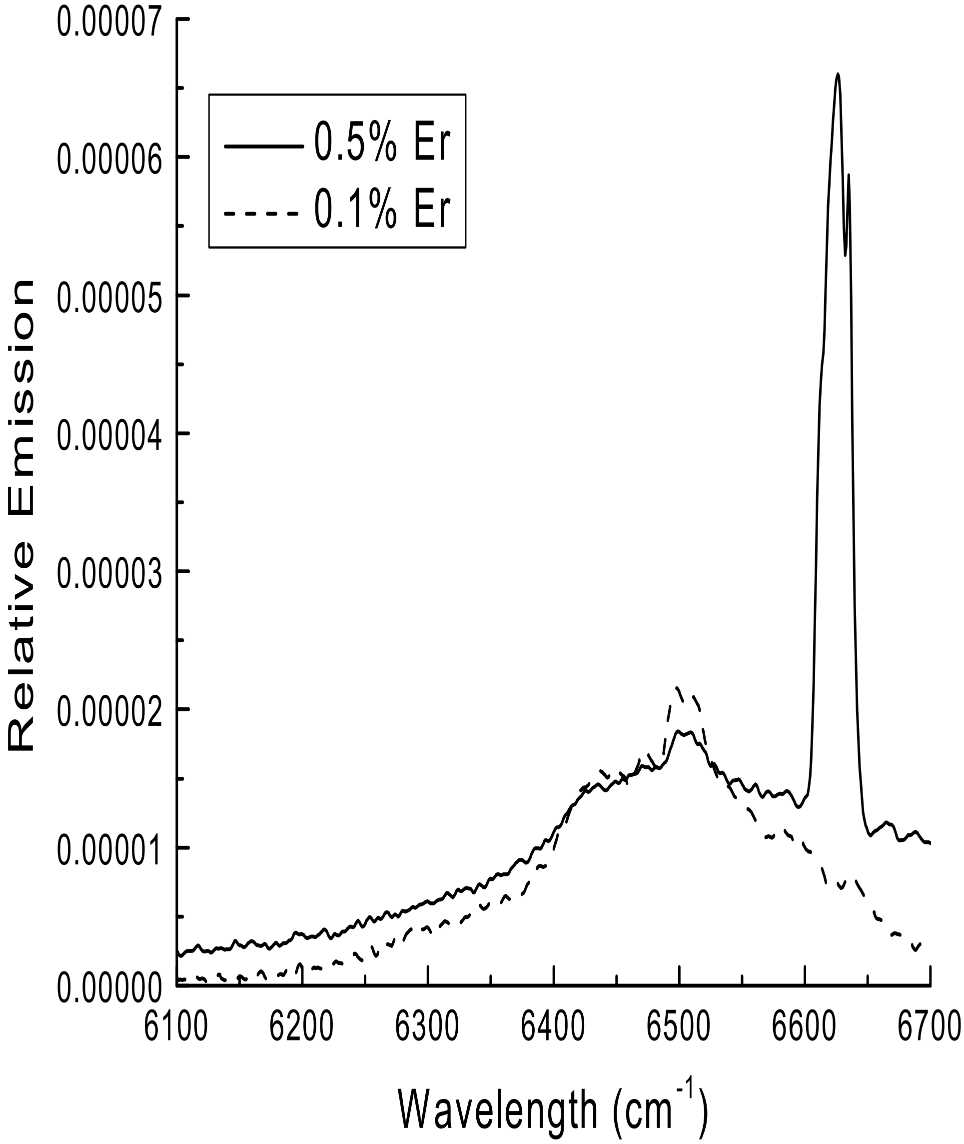

Figure 4.4: Emission spectra of As_2S_3:(0.5%)Er^{3+} and As_2S_3:(0.1%)Er^{3+}

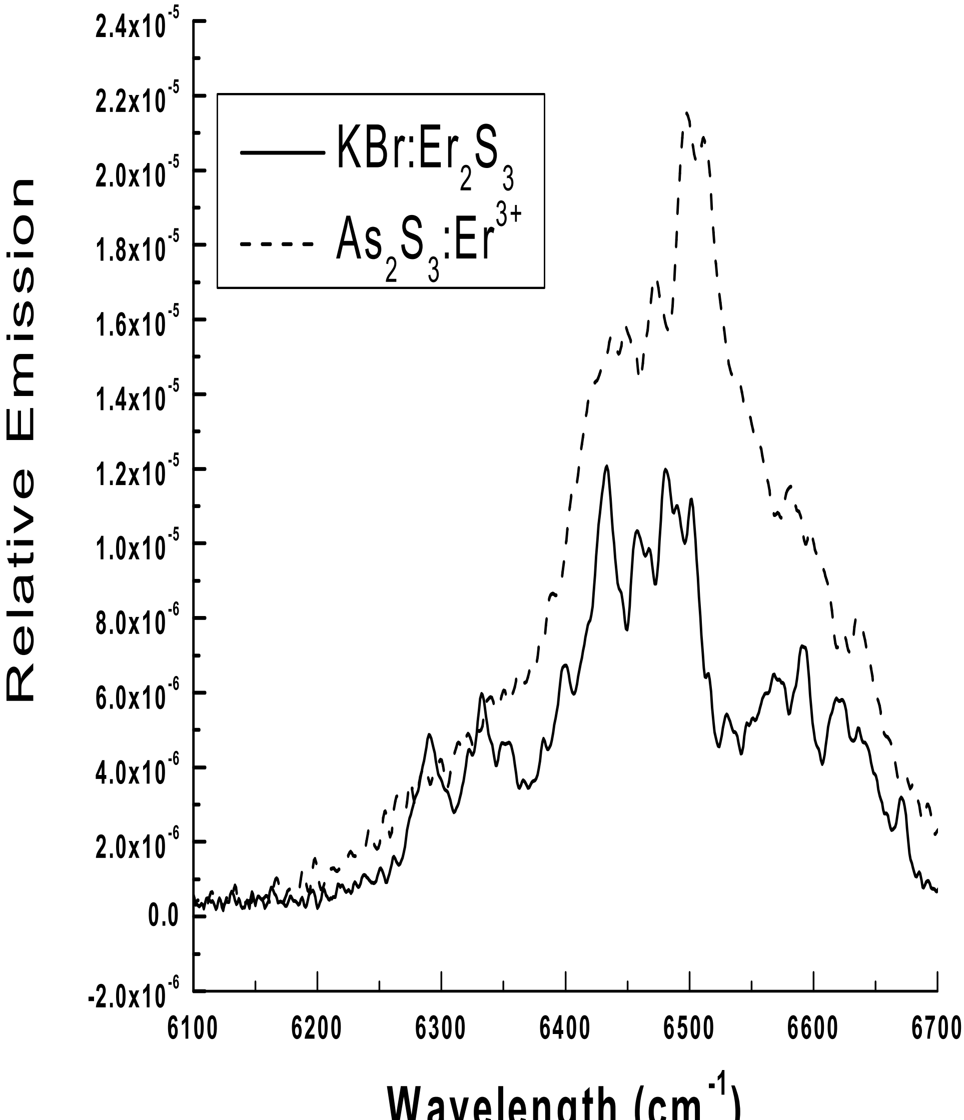

Figure 4.5: Comparison of the emission spectrum of As_2S_3:Er^{3+} and KBr:Er_2S_3 at room temperature.

Chapter 5

Spectral Hole Burning?

An unexpected result of this thesis is the observation of a double peak in the emission of As_2S_3:Er^{3+}. We will first summarize the characteristics of the observed splitting, followed by a discussion of the possible origins of this phenomenon.

The splitting is observed in all samples studied. In some experiments a simple splitting of the main emission line is observed, in others we find a breakup into several peaks.

The splitting can be observed in the temperature range between 8 K and 300 K.

The dip in the emission line does not coincide with the peak in the absorption spectrum 5.1.

As a possible cause for the splitting we consider the following mechanisms:

a) Sample inhomogeneities.

b) Re-absorption of the emitted radiation within the sample.

c) Physical spectral hole burning

d) Chemical spectral hole burning

Option (a) can be ruled out because we do not observe any splitting in the absorption spectrum, or even a shift in the main absorption maximum for samples synthesized under different conditions, or for samples cut from different parts of an ingot.

Option (b) is a phenomenon that has been observed in samples with extremely sharp and strong absorption features (i.e. the zero phonon line of Eu^{2+} in CaF_2

[21]) In the samples investigated for this study, the absorption is very weak, which reflects the small matrix element for the forbidden $f \rightarrow f$ transition. Typically, we find an absorption coefficient on the order of $\alpha = 0.02$ cm^{-1}, thus we can rule out this higher-order process as well.

Physical spectral holeburning (c) has been observed in As_2S_3 for vibrational transitions of small molecules [22]. In this case, we would assume the excitation of the ion and the subsequently released energy causes a re-arrangement of the defect site around the resonantly pumped Er ion. Surprising in this case is the persistence of the hole even at room temperature.

More likely for the origin of the splitting is chemical hole burning in which the pump laser excites a subset of the Er ions, and ionization occurs from either the $^4I_{9/2}$, $^4I_{11/2}$ or $^4I_{13/2}$ levels. Support for this explanation is provided by the fact that the hole does not coincide with the absorption peak, that multiple holes have been observed (the laser wavelength shifts when the power is adjusted - however, no systematic studies have been carried out due to the limited time available), and we do observe spectral holes not only in the main emission line, but also in the weaker transitions.

While the distinction between physical and chemical hole burning has to be sorted out, we like to point out the novel aspect that a hole is burned in one transition, while the hole is observed in another. A number of additional experiments are planned, including pumping the $^4I_{11/2}$ level, using tunable and narrow-band semiconductor lasers, and conducting studies to quantify the persistence of the holes.

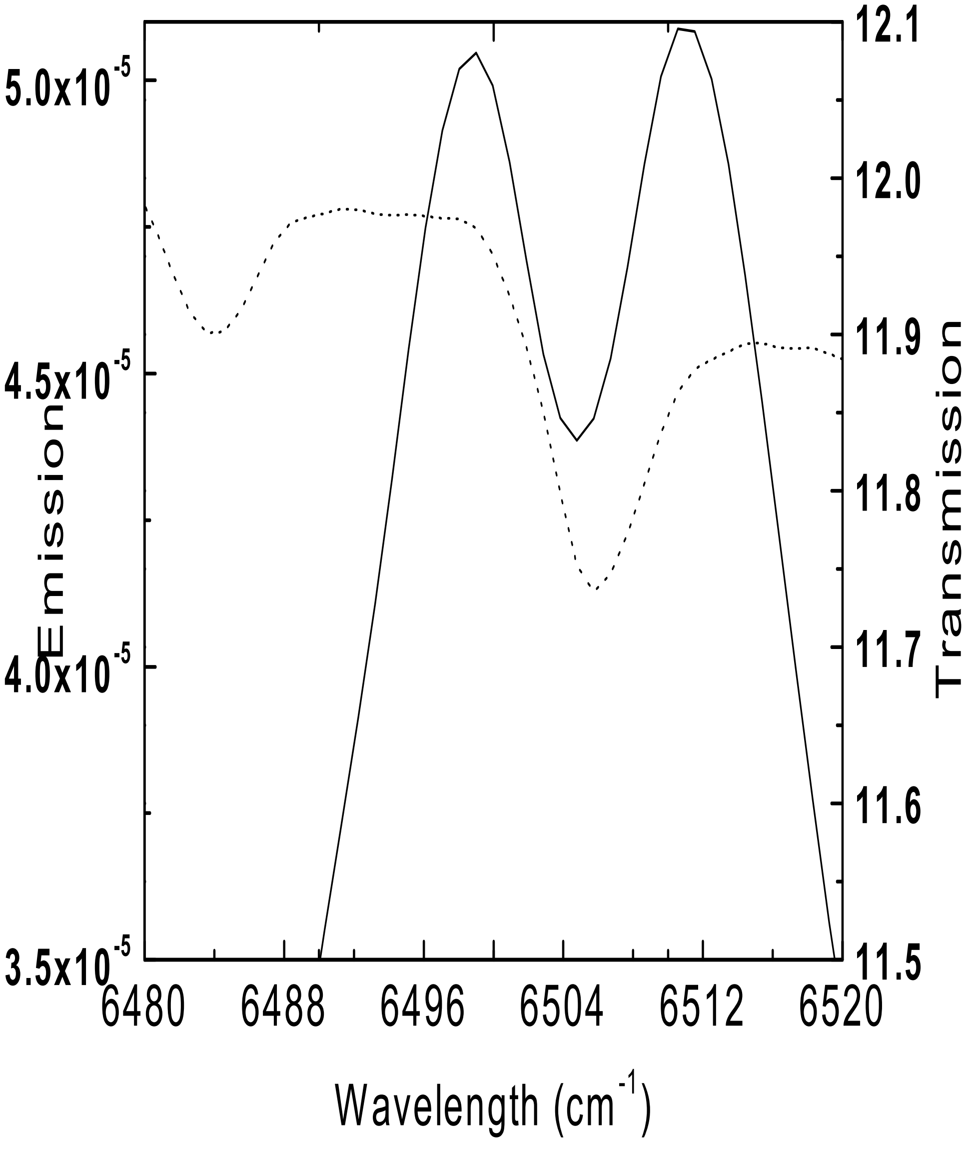

Figure 5.1: Evidence of a spectral hole at 6504 cm^{-1}.

Chapter 6

Conclusion

The purpose of this study was to optically characterize As_2S_3:Er^{3+} in order to evaluate the potential of this system for persistent spectral hole burning. As_2S_3:Er^{3+} was chosen because of the small bandgap of the host, which would facilitate the occurrence of chemical hole burning. Also, since the $f \rightarrow f$ transitions in Er^{3+} are forbidden, these transition are long lived which results in efficient excited state absorption processes, necessary to promote an impurity electron into the conduction band.

One of the main obstacles was the synthesis of high quality samples that contain single Er sites. A large number of attempts were made, with varying growth conditions (temperature, heating period, and quenching conditions) and different impurity concentrations.

Since no earlier work on the characterization of bulk As_2S_3:Er^{3+} could be found in the literature, the next step in determining the viability of As_2S_3:Er^{3+} as a spectral hole burning material was to produce a sample that could be used in the study. This was done by preparing the samples in a manner that others had used to produce similar samples [19]. This proved to the most time consuming part of the study because the glass produced was softer and more brittle than expected. This meant that, until a suitable technique for handling the samples was determined, many samples broke and were unusable.

Finally, the samples were characterized using linear spectroscopy. In order to determine if the samples produced were suitable for spectral hole burning, they were characterized by using emission and transmission spectroscopy. The results from this part of the study showed that, although the some erbium defect sites lie close together, the sample produced was the intended type and quality of material.

A surprising by-product of our study was the observation of non-linear processes during the optical characterization experiments. Serendipitously, we burned spectral holes while pumping the Er^{3+} $^4I_{15/2} \rightarrow ^4 I_{9/2}$. The holes were observed in the $^4I_{13/2} \rightarrow ^4 I_{15/2}$, which, to our knowledge, is a novel and exciting result. This is an exciting result because spectral holes have not previously been observed in this material.

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Appendix

Outlook

This thesis is just the first part of a work in progress. Due to the unforseen time and energy required in the preparation of the samples, there was not enough time to continue with this study before this thesis had to be submitted.

The next step taken will be to attempt to do the gated hole burning in this material and to measure the lifetime of the hole. If this is successful, laser stabilization using the burned hole will follow.

This material will be of considerable importance to many scientific fields and industries if spectral hole burning is successful. It is for this reason that this study will continue and spectral hole burning will be attempted.