Chapter-1

Introduction

1.1 Introduction

Luminescence and Energy are the two phenomenon that have captivated mankind since the ancient times. Sulphide compounds doped with suitable materials have been used in the field of Luminescence since long. In the past decades, Rare Earth Sulfides have gained much attention for their attractive physical and chemical properties. They were used as colors or pigments [1-2], Optical materials [3-6] and thermoelectric materials [7-10]. They are essential ingredients in a large variety of materials of vital technological, economic and ecological importance. This includes energy efficient lighting systems, plasma display panels, medical imaging, automotive catalysts, permanent magnets and pigments. These applications depend on the unique structural, electronic, optical, magnetic and chemical properties of Rare Earths [11].

In the present times, the fossil fuel resources have nearly attained its lower limit. They will soon get exhausted. In addition to the extended use of other renewable sources of energy, the suitable utilization of the wastage heat energy is the only means of obtaining further increase in the level of these resources. It means that a resource which had been discarded will now have be used and in this way the total efficiency of the energy system using fossil fuel will be raised. The enunciation of technologies which use recovery heat as effective energy will contribute to reducing the energy consumption of the social system as a whole. However, its contribution is not only limited to solving future energy problems, but also to solve environmental problems such as global warming. It can help in reduction of CO_2 in case thermoelectric power is generated using the heat energy of exhaust gases in automobiles. The consumption of fuel can also be reduced by converting the heat energy to electrical energy by a thermoelectric power generating system and reusing this energy. This has been successfully implemented in Japan where they have been able to reduce the percentage of CO_2 by 40 million tons per year with thermoelectric power generating systems with an efficiency of 20% [12]. Rare Earth Sulphides are a promising candidates for such thermoelectric conversions.

Advancement of materials which convert thermal energy to electrical energy with high efficiency (thermoelectric conversion materials) has been increasingly promoted using technologies that can really be applied. Even though many of these solid-state materials have been explored the old fashioned way (by accident), rational synthesis is now playing a growing vital role. The interaction between structural chemistry, physical measurement, and theory is today sufficiently refined so that it is possible to now make materials that have properties according to our requirements [13,14]. Even then, till today, the results of materials technologies and systems technologies have not approached a level that could support a thermoelectric power generation market, including cost effectiveness as compared with other power generating systems. Though the efficiency of the thermoelectric conversion systems is currently not high, the basic fact that heat can be converted to electrical energy itself can be of great value.

The existence and development of useful technologies often depend on the availability of materials with convenient physical and chemical properties. Just as the manufacturing of pure semiconductors as single crystals led to a full transformation of the electronics industry, the Rare Earth Sulphides which possess both luminescent and thermoelectric conversion properties may bring about important changes in the fields of communication, computing, transportation, thermoelectricity and chemical manufacturing.

In this study, we have made an attempt to synthesize Rare Earth Sulphides of Cerium, Gadolinium, Lanthanum and Yttrium doped with Europium, Terbium and Manganese by Solid State Reaction Method and Precipitation Method and study their optical and thermoelectric properties.

1.2 Rare-Earth Materials

The Rare Earth elements (Lanthanides) came into the existence 220 years ago from the year 1788, when the scientist Geijer reported that a black stone was found close to the Swedish town of Ytterby. The stone was named “Yttria”. After that Klaproth found stones which were called Ceria (1803). The lanthanides like Lanthanum, Cerium, Samarium, Europium, Gadolinium and Didymium were separated from the mineral Ceria. Actually, there is a scarcity of these elements that has led to the term Rare Earths. The first such mineral discovered was Gadolinite, a compound of Cerium, Yttrium, Iron, Silicon and other elements. This mineral was extracted from a mine in the village of Ytterby in Sweden. Several of the Rare Earth elements bear names derived from this location. After careful analysis that took many decades, finally it was concluded that these materials have different atomic numbers but are chemically very similar which made it difficult to isolate them. It has taken around 100 years to obtain all the Lanthanides in a pure state. Didymium was established as a mixture of Praseodymium and Neodymium. The mineral Yttria was found to make the elements like Terbium, Erbium, Ytterbium, Holmium, Thulium, Dysprosium and Lutetium. In the earth's crust, out of these elements Cerium is available in plenty and it is the 25th most abundant element at 68 parts per million. However, due to their geochemical properties, the Rare Earth elements are not often found in concentrated and economically exploitable forms. They are typically dispersed. The few economically absorbable deposits are known as Rare Earth minerals [15].

The Rare Earth elements (REEs) include the 15 Lanthanide elements from Z = 57 through Z = 71 and Yttrium (Z = 39). Most of them were originally segregated in the 18th and 19th centuries as Oxides from rare minerals. Rare Earth Elements are: 39-Yttrium(Y), 57-Lanthanum (La), 58-Cerium (Ce), 59- Praseodymium (Pr), 60-Neodymium (Nd), 61-Promethium (Pm), 62-Samarium (Sm), 63 Europium (Eu), 64-Gadolinium (Gd), 65-Terbium (Tb), 66-Dysprosium (Dy), 67-Holmium (Ho), 68-Erbium (Er), 69-Thulium (Tm), 70-Ytterbium (Yb), 71-Lutetium (Lu). The Lanthanide elements have been bifurcated into two segments: the light Rare Earth elements (LREEs)—Lanthanum through Europium (Z = 57 through 63) and the heavy Rare Earth elements (HREEs)—Gadolinium through Lutetium (Z = 64 through 71) [16]. Lanthanide elements with low atomic numbers are generally available in more abundance in the earth's crust as compared to those with high atomic numbers.

The global annual REE production and consumption was less than 5000 metric tons of Rare Earth Oxides (REO) before the 1950s and, until the 1960s, they were even rarely used in our daily life [17]. The abundance of the Rare Earth elements in the earth's crust as compared to Silicon is shown in the following figure-1.

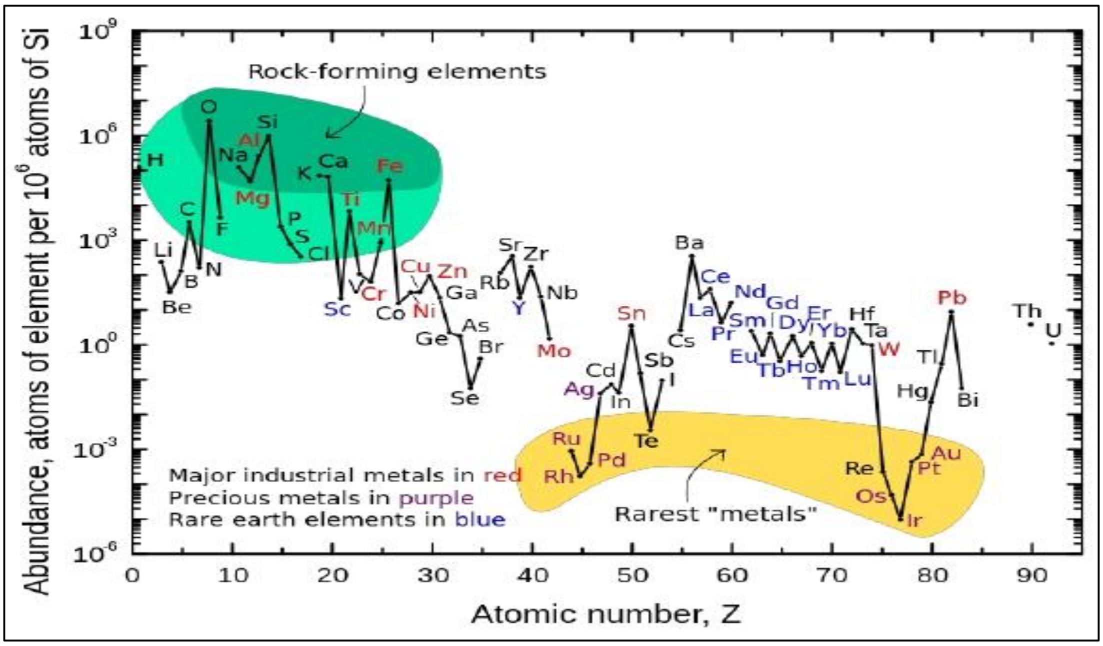

Figure 1-1: Earth's crustal abundance for "Rare Earth" elements shown by blue. Image courtesy of the U.S. Geological Survey [18]

Since the 1960s, Rare Earth applications gradually have expanded to everyday life, such as television screens, the petroleum industry, and computer systems. REE are now widely used in auto- and fluid catalysts, metallurgy, medical systems, high technology, clean energy, and military defense systems, and they are especially indispensable in emerging clean technologies, such as wind power turbines, electric vehicles, energy-efficient lighting, and catalytic converters [18,19]. A significant shift from traditional energy sources towards clean energy, such as electric vehicles, is occurring; wind turbines are becoming recognized on a global scale. This transition will lead to a continuous increase in demand for REE in the coming decades [20,21] and such an increasing demand puts forward a higher request for global production of REE, and requires a steady supply chain in the long run.

1.2.1 Properties of Rare Earth Materials

Rare Earths are usually found with non-metals, generally in the 3+ oxidation state. There may be tendency to valance variation. (Europium also has a valence of 2+ and Cerium also a valence of 4+). Though Yttrium is the lightest Rare Earth element, it is usually grouped with the heavy Rare Earth element to which it is similar in state chemically and physically. As the Rare Earth (RE) elements, which consists of the 14 elements of the Lanthanide series (Ln), Yttrium and Scandium have attracted huge interest, in both academic research and in the industry during the last decades, due to their unique physical and chemical properties [22,23].

Owing to their unique magnetic, optical, and catalytic properties, REEs can be used in a wide variety of products and technologies, including computing and defense systems and clean energy technologies [24,25]. They are particularly important for luminescent materials and permanent magnets, which are widely used in wind turbines, HEVs, all-electric vehicles, light-emitting diodes, and fluorescent lamps [26].

The Rare Earth Sulphides, Oxysulphides and Rare Earth dopants in different forms have been used in the field of luminescence since ancient times. Rare Earth Oxysulfide materials possess high luminescent efficiency and also exhibit excellent chemical stability. These materials are widely used as luminescent host materials of several commercially available phosphors such as red emitting phosphors for color television picture tube, X-ray phosphors, and long afterglow pigment. The Rare Earth Sulfides are definite promising agents for utilization as excellent temperature power conversion thermoelectric matter because of low lattice thermal conductivity and sublime chemical stability above 1000°C. Rare Earth Sesquisulfides (Ln_2S_3, Ln=Rare Earth) possesses some stimulant physical and chemical properties. Out of the many diverse sorts of Ln_2S_3, the high temperature γ-Ln_2S_3 phase is studied broadly because of its potential applications as heavy metallic free nontoxic pigments for plastics and paints [27], converters [28], n-type thermoelectric and optical material in IR transmission windows [29], lasers and magneto-optical devices [30]. It is known that Rare Earth Sulfides exist in different Crystal structures like α, β, γ, δ, and ε. The α-phase has an orthorhombic structure and is a low temperature phase of RE_2S_3 (RE: Rare Earth element). The β-phase has a tetragonal structure whereas the γ-phase has a cubic Th_3P_4 type of structure and is a high temperature phase of RE_2S_3.The δ -phase has a monoclinic structure, and the ε-phase has a rhombohedral structure [31].

1.3 Thermoelectric Properties

The Thermoelectric phenomena can be understood from the fundamental characteristics of thermal and electrical transport processes due to (1) heat transport by charge carriers and (2) scattering processes between charge carriers and other heat-carrying quasiparticles, e.g. phonons. Therefore, a flow of heat or charge generally induces both a temperature gradient and an electrical field.

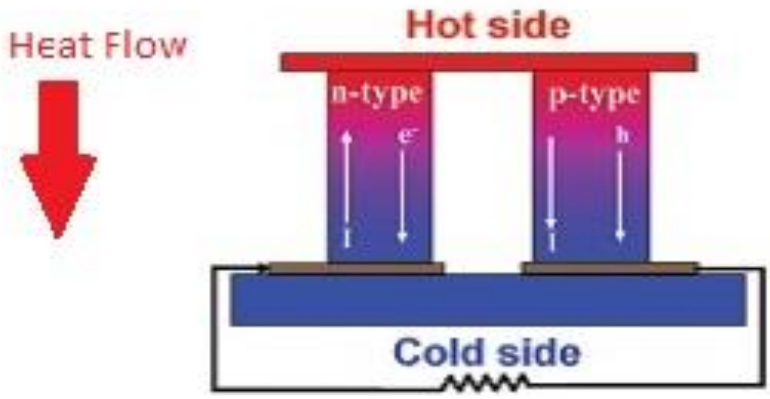

Figure 1-2: Thermoelectric Effect

The conversion of thermal energy to electrical energy is known as Thermoelectric Conversion (TEC). The TEC phenomenon can be used for the power generation and refrigeration. When a temperature gradient (ΔT) is applied to a thermoelectric material consisting of n-type (electron transporter) and p-type (hole transporter) elements, the mobile charge carriers at the hot end tend to diffuse to its cold end producing an electrostatic potential (ΔV). This characteristic is known as the Seebeck effect, where $\alpha = \Delta V/\Delta T$ is defined as the Seebeck coefficient and is the basis of TEC for power generation as shown in Figure 1. Conversely, when a voltage is applied to a TEC material, the carriers attempt to return to the electron equilibrium that existed before the current was applied by absorbing energy at one connector and releasing it at the other, an effect known as the Peltier effect. Thermoelectric and solid-state technology based on the TEC have several advantages consisting of no moving parts, reliable and scalable. This technology has therefore aroused worldwide interest in many fields, including waste heat recovery and solar heat utilization (power generation mode), temperature-controlled seats, portable picnic coolers and thermal management in microprocessors (active refrigeration mode) [32].

. Proper material selection is achieved by the thermoelectric parameters such as Figure of merit (Z), coefficient of performance (β), maximum cooling (Th-Tc), efficiency (ψ) and input power to control the device which finally depends on the physical data such as thermoelectric power or Seebeck coefficient(S) electrical resistivity(ρ), thermal conductivity (k) and temperature(T) [33]. Good thermo-electrical properties are often seen in materials those are electrical conductors and thermal insulators with high Seebeck coefficient [33]. The higher Seebeck coefficient for common metallic-alloy thermocouples is demonstrated by chrome-constantan. By Using these values also by using the classical value of the Lorenz number, $L=2.43 \times 10^{-8}$ W-ohm/deg $^{-1}$, the values for $ZT = (a^2/L)$ can be Observed and calculated, Although the Lorenz numbers (L) for different metals are very close to the predicted value, in practice, L varies for different metals and ranges between 1.55×10^{-8} to 2.64×10^{-8} W-ohm deg^{-1} for Ni and Cd, respectively. The values of ZT for chrome-constantan are, therefore, only approximate. The fields of applications are Photo-luminescence, thermoelectric generator, solid state refrigeration heat pumps and infrared detectors [33]. The efficiency of passive cooling in solid state refrigerators depends upon the proper selection of material [34]. Extrinsic alloy semiconductors are known to possess great thermal power as compare to other kind of materials.

From the study of Thermo-electric transport properties of Rare-Earth compounds containing Ce, Eu, and Tb, it is found that at low temperatures these systems usually exhibit enhanced thermo powers as compared to normal metals. In combination with low thermal conductivities, large thermo power values are desirable for materials used in thermoelectric applications. Further, thermo power of Rare-Earth systems provide valuable information on the characteristic electronic energy scales.

1.4 Photoluminescence

The light obtained can be categorized in two ways; first one is incandescence and the other one is luminescence. The phenomenon “Incandescence” is the light glare by the heating of the materials and a bright light is produced. Luminescence is a collective term for the phenomena in which the light is emitted by a substance that has not been heated as in fluorescence and phosphorescence. This definition is also described by the term "cold light". The materials which possess this phenomenon are known as ‘Luminescent materials’ or ‘Phosphors’ meaning ‘light bearer’ in Greek language. The term ‘phosphor’ was coined in 17th century by an Italian alchemist named Vincentinus Casciarolo of Bologona [35,36] with the discovery of the “Bolognian stone” in Italy. This stone had the property of emitting red light in the dark after exposure to sun light. Similar findings were briefed and reported from many places in Europe and these light emitting stones were given the name phosphors that means, “Light bearer” in Greek language. The word Phosphorescence was derived from the word phosphor, which means light emission from an element after the exciting radiation process has extinguished. The word fluorescence was proposed to notify the insensible short afterglow of material after the excitation process. In 1888, a German physicist named Eilhardt Wiedemann used the word “luminescence” which included both mechanisms of fluorescence and phosphorescence. This word originates from the Latin language word “lumen” which means light.

The phenomenon of luminescence can be classified into various categories depending on the mode of excitation. (A) Photoluminescence phenomenon, when the stimulation is by electromagnetic radiation or photons. (B) Cathodoluminescence phenomenon, when the stimulation is by energetic electrons or cathode. (C) Electroluminescence phenomenon is light emission stimulated by electric influences. (D) Radioluminescence phenomenon, when the stimulation is by high-energy X-rays. (E) Sonoluminescence phenomenon, when the stimulation is by ultrasonic waves. (F) Triboluminescence phenomenon may precede when a material is mechanically treated. (G) Chemiluminescence phenomenon is light emitted during chemical reactions. H). Bioluminescence phenomenon is the form of chemiluminescence occurred from living organisms. (I). Thermoluminescence phenomenon, also known as thermally stimulated luminescence, is the Luminescence activated thermally after primary irradiation by other means such as alpha, beta, and gamma, UV or X-rays. It is not to be confused with thermal radiation: the thermal stimulation only stimulates the release of stored energy.

Each of the processes mentioned above have their own significance and advantages in the field of science and technology. In the present work emphasis is been given to the study of photoluminescence (PL) of phosphors that exhibit strong emission in the visible regions. Moreover, before proceeding into detail, it is good to know and understand, the procedure leading to luminescence and its various characteristics.

1.4.1 Luminescence characteristics

In the progression of luminescence, the excited atoms can return to the ground state by two processes: one radiative and the other non-radiative. The first is the one through which the luminescence process occurs. The second one does not have any role to play in the process of luminescence; however, it occurs along with radiative emission due to the photons which are converted to lattice vibrations that transport energy in the form of extent heat. The one in which radiative transitions dominate over the nonradioactive ones is called an efficient radiative transition but, in practice, the situation is more complex. [37-39].

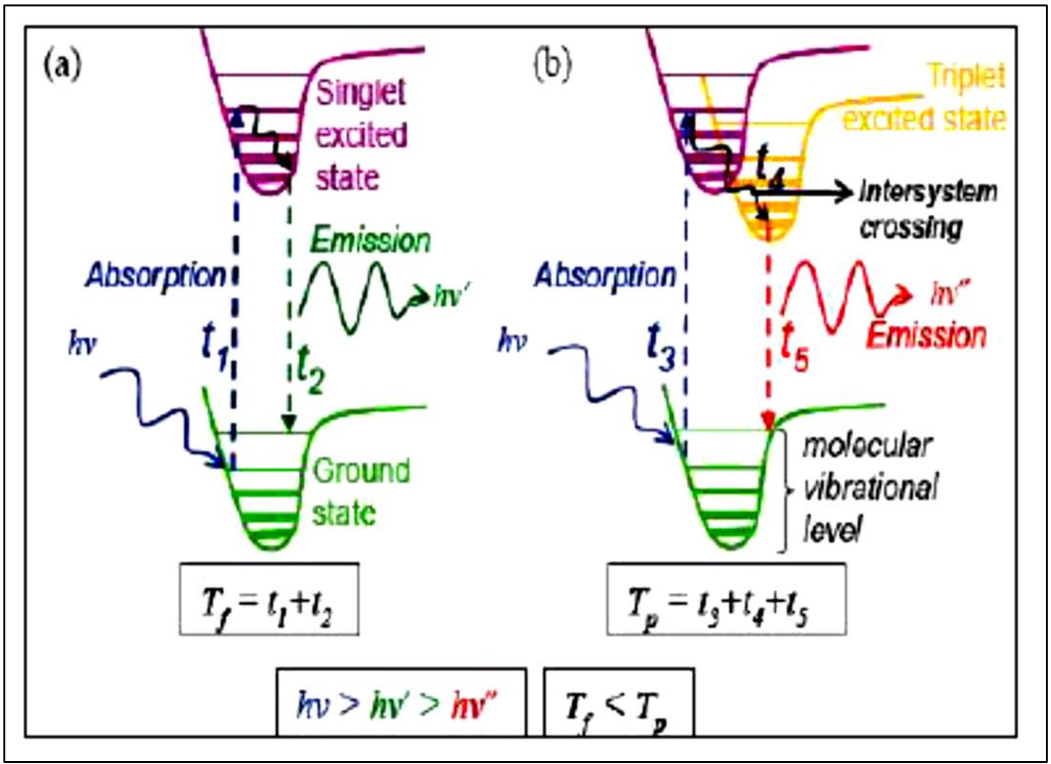

Figure 1-3: Principle of Photoluminescence

Depending on the time duration of the emission process, luminescence has been further sub divided into:

(a) Fluorescence: During this process, the material releases light immediately on absorption of radiation and on expulsion of excitation, the light disappears. There is an exponential afterglow that does not depend upon the excitation intensity and their temperature having a lifetime duration less than 10^{-8} seconds. It involves singlet-singlet transition.

(b) Phosphorescence: During this process, the material does not stop the radiation process immediately on the expulsion of excitation. There is a delay between absorbing light and release of light; hence, there occurs another phenomenon of afterglow in which the decay is very slow with complex kinetics. It is rarely dependent on the intensity of excitation but is very strongly temperature-dependent, having lifetime duration of more than 10^{-8} seconds, sometimes lasting for a few seconds. It involves the singlet-triplet transition in which intersystem crossing takes place which quantum is mechanically forbidden.

Photoluminescence addresses to the luminescence stimulated by the excitation process of solid material by using light of another wavelength, typically ultraviolet (UV), visible or infrared light. Photoluminescence analysis is non-destructive technique which requires very small sample manipulation or environmental control. The basic limitation of PL analysis is its dependence on radiative events. The materials having poor radiative efficiencies like low quality indirect semiconductors, are very difficult to study via ordinary Photoluminescence. Accordingly, the identification of impurity and defect states depends on their optic activity [40]. The main use of photoluminescent phosphors is in fluorescent lamps and it is bifurcated into two major types, namely intrinsic photoluminescence and extrinsic photoluminescence. The intrinsic photoluminescence is shown by the materials which have no impurity atoms while extrinsic photoluminescence results from intentionally added impurities, in many of the cases metallic impurities or intrinsic defects.

After the invention of the incandescent lamps more than a century ago, many new technology lamps have been promoted out of which many are discharge lamps with far higher efficacies (lumen per watt) than the incandescent lamps. Different lamps have different significance and possibilities with consideration to wattage, efficacy size, performance and color temperature. At present an addition of halo phosphate and troposphere mixture is used in many lamps as conciliation between performance cost and the lamp manufacturing cost. The induction of trichromatic fluorescent lamps is the corner stone in the lighting industry. The introduction of Rare-Earth phosphor systems for lamp applications has changed the industry for it addressed to the major issues concerning the lamp performance through higher lumen output (90-100 lumens/W), higher wall load factor and better color rendition index (Ra=90). In particular, the high wall load –factor empowered this phosphor system to be applied in compact fluorescent lamps in which stability against high-load of UV is the tough requirement for the successful lamp performance. Entertainingly, the triband phosphor system performing near the physical limit leaves no scope for further improvement in the luminous efficiency. Because of that reason the new ways are used to being focused on the design of in-expensive phosphors system without compromising the performance and effectively harnessing the influence of impurities to achieve the ultimate efficiency.

In the recent years, keen attention has been targeted to the development of material science for various commercial applications in many fields like color television, fluorescent tube, X-ray phosphors, and scintillators [41,42]. Lately various phosphor materials have been vigorously calibrated to enhance their luminescent properties, applications and to meet the sustainable development of different demonstration and luminescence devices. Many Inorganic compounds doped with Rare Earth ions form a good class of phosphors because they possess a few important characteristics like they exhibit sublime chemical stability, very high luminescence efficiency, and different emission colors react with different activators [43,44]. A great dimensional growth is made in the development of new colour emitting phosphor elements. It shows the merger of thermal and chemical stability in air while reacting with high emission quantum yield at room temperature. The luminescent properties were observed, to mainly depend on, size of particle, size distribution and morphology of particle. These relationships can be used in current interest, and it may take to new fabrication processes to yield high-quality luminescent materials.

Use of technology and research in phosphors needs a peerless combination of interdisciplinary methods and techniques. Agglutination and preparation of inorganic phosphors depends on physical and inorganic chemistry. Luminescence mechanism are illustrated and elucidated based on solid state physics. The research and development of all major and minor applications of phosphors pertains to the field of illuminating engineering and electronics and image engineering. Mainly, there are four parameters, viz. excitation type and spectrum, emission intensity and the emission spectrum, relaxation to emitting state and decay time, which have laid down a stepping stone in the utility of Rare Earth doped phosphors. All these parameters are further dependent and change under temperature and concentration. This dependence is equally vital in concern of the utility of the phosphors in various photoluminescence applications.

1.5 Motivation and Objectives

Though sulphides have been extensively studied in the past, most of the investigations were performed mainly on doped Alkaline Earth Sulphides and doped Rare Earth Oxysulphides. Most of the studies have focused on Rare Earths as dopants. The use of Rare Earth Sulphides as host materials began much later and is still in the investigation stages. Few studies on Rare Earth Sulphides have been undertaken but mostly on the Lanthanum Sulphides and their stabilization. Also, some preliminary studies have been undertaken for preparation of

Ln_2S_3. As the technology has advanced from colour LCD to LED, there is always a need to develop the materials which have enhanced luminescent properties. Rare Earth compounds are chemically much more stable than other transition compounds. The fact that the thermoelectric properties of these materials has not been widely explored and well-studied also is a source of motivation for the study.

The objectives of the study are:

- To synthesis Rare Earth Sulphides of Lanthanum, Cerium, Yttrium and Gadolinium doped with Europium, Terbium and Manganese.
- To characterize the synthesized samples.
- To study the optical and thermoelectric properties of the synthesized materials.
- To compare the bulk/nano optical properties of the synthesized Rare Earth Sulphides

1.6 Thesis organization

The Rare Earth based Sulphide materials have been explored in the present studies to understand the different aspects of their luminescent and thermoelectric properties. The purpose of these studies is to provide a comprehensive overview and in depth understanding of the current state of the art, with special focus on the commonly employed synthesis methods and functionalization strategies of Rare Earth based materials for their different properties. These materials have attracted attention due to Rare Earth and relatively low cost, and therefore are prospective candidates in the development of future applications.

The present thesis addresses above mentioned aspects of material and the work has been presented in five chapters as summarized below:

Chapter 1: Introduction

It gives an introduction, background and overview of the area and the origin of the issue along with the different properties of Rare Earth elements. It describes the invention and basic properties of Rare Earth materials. The Rare Earth Oxysulphides and Rare Earth dopants in different forms have been used in the field of luminescence since ancient times. The Rare Earth Sulfides are definite promising agents for utilization as excellent thermoelectric conversion materials because of low lattice thermal conductivity and sublime chemical stability at high temperatures. Rare Earth Sesquisulfides (Ln_2S_3, Ln=Rare Earth) possesses some stimulant physical and chemical properties. This chapter also gives the basic fundamentals of Thermoelectric properties and Photoluminescence and its present scenario. It also highlights the motivation behind research and research objectives. Lastly, it describes the organization of this thesis.

Chapter 2: Literature review

This chapter describes the detail literature review of the present and past studies of the work. It discusses several aspects of the materials and major reports in the field of area. It also discusses about solutions of the problems and ongoing work towards benefits from this studies. It also describes the properties of the chosen Rare Earth materials which have been considered for this study. Most of the work done so far in the field of luminescence is based on the use of Rare Earth Oxysulphides of Y_2O_2S, La_2O_2S and Gd_2O_2S. Some studies are based on the synthesis and stabilization of different phases of Rare Earth Sulphides of La_2S_3 and Ce_2S_3. The thermoelectric properties of the γ phase of La_2S_3 has been studied. Gd_2S_3 has been studied from the point of view of its preparation, characterization and optical and thermoelectric properties but more emphasis is found to be on Gd_2S_4 and GdS_2. Ce_2S_3 has been studied for its stabilization, electronic transport and optical properties. Photoluminescence spectra of these materials have not yet been reported except that for γ - Gd_2S_3. The optical and thermoelectric properties of Y_2S_3 have not been studied so far. Only studies regarding its synthesis and phase diagram have been reported. The thermoelectric properties of Y_2S_3 are still to be explored.

Chapter 3: Synthesis and Characterization Methods

It describes the preparation of samples, experimental methods and process and the different characterization techniques which are deployed for the data collection and analysis. The present thesis deals with the synthesis of Rare Earth materials La_2S_3, Gd_2S_3, Ce_2S_3, Y_2S_3, doped with Europium, Terbium and Manganese by the method of Solid-State Reaction and Precipitation which are low cost processes. Each of the host material has been doped with 1%, 2% and 3% of dopants. Thus, a total of 80 samples, 40 by Solid State Method and 40 by Precipitation method have been synthesized.

The different characterization techniques have been described. The material characterization techniques like X-Ray Diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and Field Emission Scanning Electron Microscopy (FE-SEM) were used for material characterization and are described in this chapter. The optical properties of the materials were studied using Photoluminescence Spectrography (PL) and its thermoelectric properties were studied by plotting the Resistance → Temperature curve.

Chapter 4: Result and discussion

This chapter describes the results obtained by characterization of La_2S_3, Gd_2S_3, Ce_2S_3, Y_2S_3, doped with Eu, Tb, Mn by Solid-State Reaction and Precipitation method.

The XRD results of samples of La_2S_3:Eu/Tb/Mn confirm the presence of the material in the mixed orthorhombic and tetrahedral phase with high degree of matching with JCPDS file no. 71-2349 (α-phase) and 43-0340 (β-phase). The results obtained for samples synthesized by precipitation method also show matching with the same JCPDS files but the amount of β-phase is found to be higher.

The XRD results of samples of Gd_2S_3:Eu/Tb/Mn synthesized using solid state and precipitation methods confirms the presence of the material in the orthorhombic phase with high degree of matching with JCPDS file no. 76-0265 (α-phase).

The XRD results of samples of Ce_2S_3:Eu/Tb/Mn synthesized using solid state and precipitation methods confirms the presence of the material in the orthorhombic phase with high degree of matching with JCPDS file no. 43-0799 (α-phase).

The results of samples of Y_2S_3:Eu/Tb/Mn synthesized using solid state and precipitation methods confirms the presence of the material in the monoclinic phase with high degree of matching with JCPDS file no. 79-2250 (δ-phase). Though both the methods give the same phase of synthesized samples, there is a variation in hkl values and intensity. This can be attributed to the change in orientation of the material due to different synthesis methods because the intensity of XRD line depends on elemental composition of the sample and its preparation conditions.

EDAX analysis was carried out to confirm the presence of the respective elements.

The Field Emission Scanning Electron Microscopy shows a wide variation of the grain size. Different morphologies are obtained for the samples. The particles of Cerium Sulphide (Ce_2S_3) prepared by Solid State Method are arranged in scattered regions but are somewhat spherical in shape. The FESEM images of Gadolinium Sulphide (Gd_2S_3) synthesized by Solid-State Method show the particles blooming and rolling over each other and have an elongated rounded edge structure. The Lanthanum Sulphide (La_2S_3) samples prepared by the Solid-State Method have arrangement like a rock formation and seem to have cuboidal structures bonded with each other. Yttrium Sulphide (Y_2S_3) samples prepared by the Solid-State Method shows formation similar to lumps of the particles in the form of elongated rounded structures that are closely spaced to each other.

The Cerium Sulphide (Ce_2S_3) samples prepared by the Precipitation method can be seen in the form of kinks of the particles which are closely spaced to each other. The nano particles are smooth and have vivid shapes but are mostly cuboidal. As compared to the SEM images of samples synthesized by Solid State Method, these images are more smooth and distinct. The images of Gadolinium Sulphide (Gd_2S_3) synthesized by Precipitation method shows formation of material in the cuboidal bunch form. The particles are smooth and are very close to each other. As compared to the SEM images of Solid State Method, these images are more distinct, more rounded and show almost no pores on the surface. The morphology of the Lanthanum Sulphide (La_2S_3) prepared by Precipitation method was like a conglomeration of nano size particles bonded together to form different shapes and sizes. All the particles are arranged in scattered regions showing rock formation and this scattering is much more as compared with their Solid State counterpart. The Yttrium Sulphide (Y_2S_3) samples prepared by the Precipitation are seen somewhere in the form of rounded nano agglomerates while somewhere they are in the form of elongated structures. As compared to its Solid State material, the precipitation sample is more distinctly separated and shows some order. Thus, the FESEM images obtained in case of samples synthesized by Precipitation method are more clear, distinct and specific as compared to those synthesized by Solid State method.

The Photoluminescent study of the samples show the characteristic emissions of Eu and Tb in the red and green region respectively. The PLE spectra of the samples synthesized by Solid State and Precipitation method for 1%, 2% and 3% Eu doping shows an intense

peak due to the charge transfer (CTS) transition of Eu^{3+} ions while in some cases, there are additional small peaks due to the forbidden 4f–4f transitions of Eu^{3+} ions.

The emission (PL) spectrum of Eu doping shows an intense peak between 612 nm to 618 nm for all the samples corresponding to the transition $^5D_0 \rightarrow {}^7F_2$ and additional peaks at 535 nm, 535 nm, 582 nm 583 nm, 588 nm, 593 nm, 595 nm, 625 nm and 630 nm which can be associated to the transitions $^5D_1 \rightarrow {}^7F_0$ (534 and 535 nm), $^5D_0 \rightarrow {}^7F_0$ (582 and 583 nm) $^5D_0 \rightarrow {}^7F_1$ (588 nm) and $^5D_0 \rightarrow {}^7F_2$ (593, 595, 625 and 630 nm) of Eu^{3+} ions. The PL spectra of samples synthesized by Precipitation method also show some additional peaks corresponding to transitions $^5L_7 \rightarrow {}^7F_1$ (371 nm), $^5L_6 \rightarrow {}^7F_0$ (393 nm), $^5D_3 \rightarrow {}^7F_3$ (451 nm), $^5D_2 \rightarrow {}^7F_0$ (467 nm, 468 nm and 474 nm) and $^5D_1 \rightarrow {}^7F_0$ (513 nm) in addition to the above mentioned peaks. It can be seen that intensity increases with Eu doping from 1% to 2% and then decreases for 3% of Eu doping.

The PLE spectra of the samples synthesized by Solid State and Precipitation method for 1%, 2% and 3% Tb doping shows an intense peak due to the spin allowed $4f^8 \rightarrow 4f^7 5d^1$ transition of Tb^{3+} ion while the series of other absorption lines from can be attributed to the forbidden 4f–4f transitions of Tb^{3+} ions.

The emission (PL) spectrum consists of two sets of lines, the blue emission lines at shorter wavelengths, and a strong green emission line at longer wavelengths. The emission peaks at 415 nm, 436 nm, 457 nm, 468 nm, 469 nm, 474 nm, 475 nm, 484 nm, 485 nm and 488 nm give blue emissions corresponding to the $^5D_3 \rightarrow {}^7F_5$ (415 and 436 nm), $^5D_3 \rightarrow {}^7F_4$ (457, 468, and 469 nm), $^5D_3 \rightarrow {}^7F_3$ (474, and 475 nm), $^5D_3 \rightarrow {}^7F_1$ (484 and 488 nm) and $^5D_4 \rightarrow {}^7F_6$ (488nm) transitions while the sharp and intense peak at 545 nm gives green emission associated with the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} ions. The other peaks associated with green emissions are attributed to the transitions $^5D_4 \rightarrow {}^7F_5$ (544, 547, 548, 551, 552 and 553 nm) and $^5D_4 \rightarrow {}^7F_4$ (585, 586, 589, 592, 596 and 597 nm). Some peaks are also seen at 613 nm, 616 nm, 619 nm and 624 nm corresponding to the $^5D_4 \rightarrow {}^7F_3$ transitions. The luminescent intensity increases from 1% to 2% of Tb doping and decreases when doping percentage becomes 3%.

The Manganese doped Rare Earth Sulphides of Cerium, Gadolinium, Lanthanum and Yttrium were almost black in colour and hence the Mn doped samples did not give Photoluminescence spectra.

The Thermoelectric properties of the samples synthesized by Solid State and Precipitation method were studied by plotting the Resistance → Temperature curve. The change in resistance of Rare Earth Sulphides was studied with an increase in temperature in the range of 35°C to 105 °C under laboratory conditions. The resistance is in the order of 10^5 Ω which decreases significantly with increase in temperature. Thus, the Rare Earth Sulphides of Cerium, Gadolinium, Lanthanum and Yttrium exhibit semiconductor and Negative Temperature Coefficient Thermistor like properties. It is seen that the resistance of the samples decreases in the order of Gd_2S_3 to Y_2S_3 to Ce_2S_3 to La_2S_3 which can be understood on the basis of their Electronic Configuration and Ionization energies. It is also seen that the resistance of the samples doped with Mn, Eu and Tb have less resistances as compared to their undoped samples. This is in agreement with theoretical results. The results obtained in case of Solid State method are higher as compared to those of Precipitation method. This implies that the material integrity of Rare-Earth Sulphides depends on variation of laboratory conditions. These results can be interestingly used in the future possible applications of power conversion in industries for the recovery of waste heat from different equipment.

Chapter 5: Conclusion

It summarizes the current studies and possible outcome of the future scope.

1.7 References

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