Synopsis of the Thesis entitled

Study of Optical and Thermoelectric Properties of Rare Earth Based Nanosulphides

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by

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Introduction

Emission of energy as Luminescence is a phenomenon that has captivated mankind since the ancient times. Sulphide compounds doped with suitable materials have been used in the field of Luminescence since long [1-2]. 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 [3-4], Optical materials [5-8] and thermoelectric materials [9-12]. 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 [13]. In the present times, the fossil fuel resources have nearly attained its lower limit. They will soon get exhausted. Apart from the extensive use of other renewable sources of energy, the suitable utilization of the wasted energy is another means of obtaining further increase in the level of utilization 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. Rare earth sulphides are promising materials for such thermoelectric conversions. 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 and thermoelectricity.

Motivation

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 La_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 is also a source of motivation for the study.

Objectives

- To synthesize 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 properties of the synthesized rare earth sulphides.

The thesis addresses the 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. 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 [29], converters [30], n-type thermoelectric and optical material in IR transmission windows [31], lasers and magneto-optical devices [32]. This chapter also describes the properties of Cerium sulphide (Ce_2S_3), Gadolinium sulphide (Gd_2S_3), Lanthanum sulphide (La2S3) and Yttrium sulphide (Y2S3) which have been synthesized in this work.

This chapter also gives the overview of process methods. Development and synthesis of applied materials with desired properties is of utmost important in experimental condensed matter physics and research. The samples can be synthesized using various methods like the Solid State Reaction (SSR), Vapor Phase Transport (VPT), Precipitation, Sol - Gel, Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Pulsed Laser Deposition (PLD), Chemical Solution Deposition (CSD), Metal-Organic Chemical Vapor Deposition (MOCVD), Sputtering, Flux Growth Technique, Electrochemical Methods etc. Choice of selection of the Methods depend upon the suitability of the materials and its properties to achieve applications in the field of the research. Low cost process with desired characteristics of the materials is prime need of the industry and market devices. Keeping these facts in view, the Solid State Method and Precipitation Method were used for synthesis of samples.

❖ Chapter 2: Literature review and Fundamentals

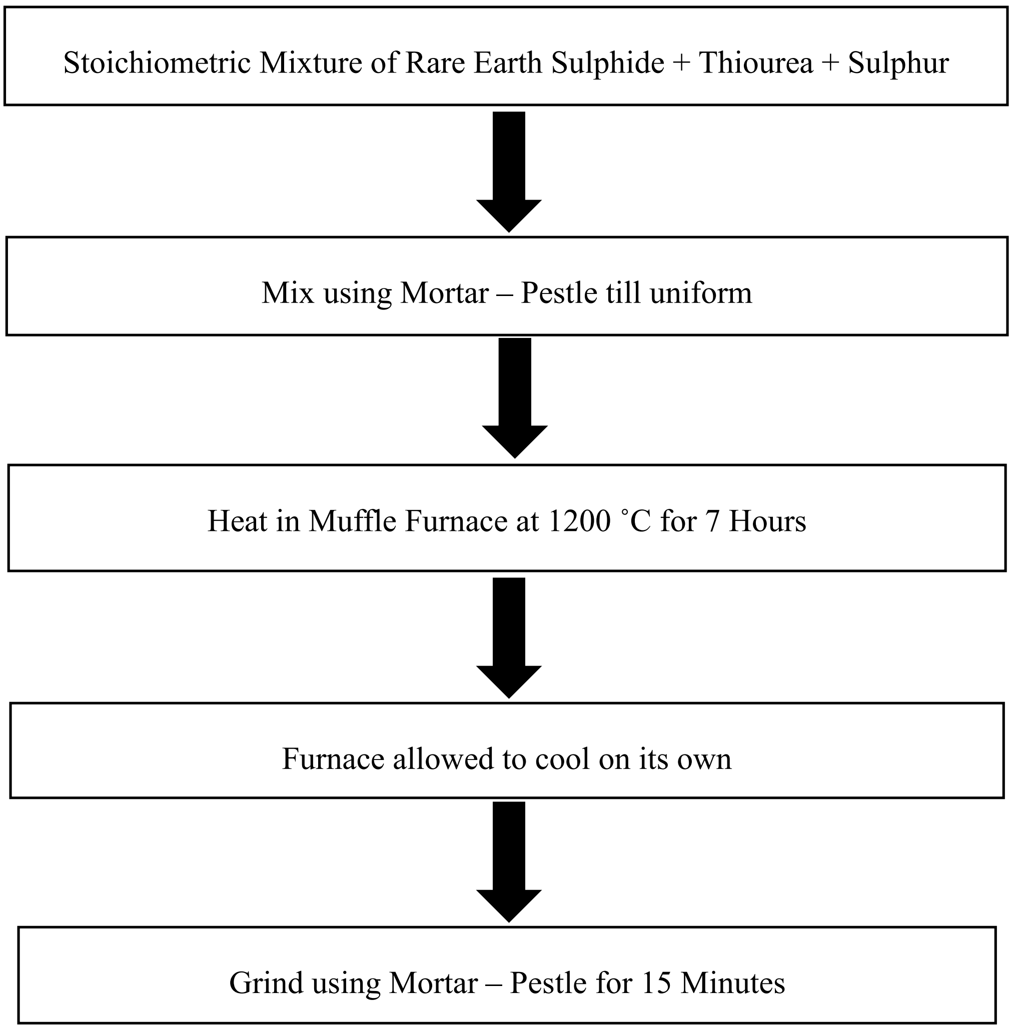
It describes the fundamental concepts and literature review of the present and past studies of the work. The Thermoelectric phenomena can be understood from the fundamental characteristics of thermal and electrical transport processes due to (1) heat transport by charge carriers and (2) scattering processes between charge carriers and other heat-carrying quasi-particles, e.g. phonons. The basic phenomenon of Thermoelectric properties like Seebeck

Effect and Peltier Effect have been described in this chapter. The phenomenon of luminescence can be classified into various categories depending on the mode of excitation. In the present work emphasis has been given to the study of photoluminescence (PL) of phosphors that exhibit strong emission in the visible regions. The basic aspects of the theory of Fluorescence and Phosphorescence have been mentioned. This chapter discusses several aspects of literature review of the materials and major reports in the field of 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 Methods and characterization Techniques

It describes the preparation of samples, experimental methods and processes and the different characterization techniques which are deployed for the data collection and analysis.

The thesis deals with the synthesis of rare earth materials La_2S_3, Gd_2S_3, Ce_2S_3 and Y_2S_3 doped with Eu, Tb and Mn by the method of solid-state 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 flow chart of the Solid State method is shown below:



The Precipitation method was also used to synthesize the samples. Its flow chart is as shown below:

Solution A: Stoichiometric amount of Sodium Nitrate was dissolved in 10 ml Methanol under constant stirring for 30 Min at Room Temperature

↓

Solution B: Stoichiometric amount of Rare Earth Nitrate was dissolved in 30 ml Methanol under constant stirring for 1 Hour at Room Temperature

↓

Solution A was added to Solution B drop by drop using addition funnel under continuous stirring for 2 Hours

↓

Solution C: Stoichiometric amount of Sodium Nitrate was dissolved in 30 ml Methanol under constant stirring for 30 Min at Room Temperature

↓

Solution C was added to above solution drop by drop using addition funnel under continuous stirring for 5 Hours at 60˚C

↓

Precipitates were filtered and washed with Petroleum Ether

↓

The filtered precipitates were dried in oven at 50 ºC for 1 hour and allowed to cool.

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 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 just a little higher as compared to those of Precipitation method. This implies that the material integrity of rare-earth sulphides does not depend much 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 outcomes of the future scope.

Following are the important summary points drawn from the thesis experimental work:

(1) XRD analysis confirms the synthesis of Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3 and EDAX results provide proof for the same. The results of samples synthesized by the Solid State method are much better as compared to those synthesized by Precipitation method in terms of sharpness of peaks and intensity.

(2) The morphological analysis of Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3 using FESEM show a dispersive and cluster growth with a medium coverage in nano-dimensions. The FESEM images obtained in case of samples synthesized by Precipitation method are more clear, distinct, ordered and specific as compared to those synthesized by Solid State method.

(3) The synthesized samples of Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3 doped with the Eu and Tb exhibit good luminescent properties and show sharp peaks at the characteristic wavelengths of Eu and Tb in the red and green emission regions. The intensity of the spectra increases from 1% to 2% doping and then decreases for 3% doping for all the samples. Mn doped samples do not give PL. The PL spectra of samples synthesized by Solid State method are much better than those synthesized by Precipitation method in terms of intensity.

(4) The Resistance → Temperature plots of Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3 show a decrease in

resistance with an increase in temperature in the range of 35°C to 105 °C under laboratory conditions. The resistance decreases with doping in all the samples. There is a very little variation in the resistance of samples synthesized by Solid State and Precipitation methods. Thus, they are found suitable for the thermo-power conversion applications.

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Publications:

[1] ***Exploring Lanthanum Sulphide Characteristics for its Physical Properties*, Kavita R. Kolte, Kevil Shah, B. S. Chakrabarty, (International Journal of Scientific & Technology Research (2019), Vol. 8, Issue 11, pp. 957-961)**

❖ Conference Presentations:

1. Oral presentation on "**Synthesis, Characterization and Optical Properties of Lanthanide Complexes with Sulphur containing New Ligand**" at National Conference titled "Current Trends in Chemical, Biological and Allied Sciences" organized by Association of Chemists & Biologists in Patan on 27-28 July 2019.
2. Poster Presentation on "**Impact of Artificial Light on Environment**" at National Conference titled "Contemporary Issues in Environment" organized by Swami Vivekanand Govt. P. G. College, Neemuch (MP) on 23-24 February 2016.

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