5
Conclusion and Future Scope

5.1 Conclusion

Sulphides of transition metals with rare-earth doping have been used as luminescent materials since a very long time. The use of Rare-earth sulphides as host materials has not been investigated intensively and the studies so far have been limited to their synthesis and stabilization. In the last few years, Rare-earth sulphides have also emerged as useful materials for thermo-electric conversion.

In the present study, Lanthanum Sulphide (La_2S_3), Gadolinium Sulphide ((Gd_2S_3), Cerium Sulphide (Ce_2S_3) and Yttrium Sulphide (Y_2S_3) doped with Europium, Terbium and Manganese have been synthesized by the Solid State Method and Precipitation Method. Each sample has been doped with 1%, 2% and 3% of Eu, Tb and Mn dopants with the aim to study the photoluminescence and thermoelectric properties of the synthesized samples. The synthesized materials were characterized in the laboratory using X-Ray Diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and Field Emission Scanning Electron Microscopy (FESEM). Photoluminescence (PL) and Thermoelectric Properties (TEP) were studied.

Following are the important summary points drawn from the work:

1. The materials were synthesized by using the Solid State Method and Precipitation method. XRD patterns compared with the standard JCPDS database confirm the material structure and different phases.

- 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 much higher.

- The XRD results of samples of Gd_2S_3:Eu/Tb/Mn synthesized using solid state and precipitation methods confirm 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, as the intensity of XRD line depends on elemental composition of the sample and its preparation conditions.

- 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.

- EDAX analysis confirms the presence of elements in the samples.

2. The morphological analysis of the samples was carried out using FESEM. 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 show 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 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 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.

- Also the particle size is seen to reduce in samples synthesized by Precipitation method.

3. The lanthanide sulphides have attracted considerable interest for their potential luminescent properties. This study explains the luminescence characteristics of Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3 with Eu, Tb and Mn as dopants, which give different luminescence properties. The materials are found to have good luminescent properties and match with their characteristic excitation and emission wavelengths.

- The Photoluminescent study of the samples show the characteristic emissions of Eu and Tb in the red and green region respectively.

- The excitation 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 4f–4f transitions of Eu^{3+} ions. For Eu^{3+} doped samples, the maximum excitation intensity due to CTS transition is found to be 254 nm in Gd_2S_3 and Y_2S_3, while it is 274 nm in La_2S_3. In case of Ce_2S_3 synthesized by Precipitation method, the intensity of the

most intense excitation line changes from 372 nm to 365 nm to 358 nm for 1%, 2% and 3% of Eu doping respectively.

- In Eu doped samples prepared by Solid State method, the intensities of the most intense excitation line remain almost constant in case of Gd_2S_3 and Y_2S_3 for all doping percentages, while in case of La_2S_3, it increases from 1% to 2% and then decreases for 3% of Eu doping. In samples prepared by Precipitation method, the intensities of the most intense excitation lines are found to increase from 1% to 2% of Eu doping and then decrease with 3% of Eu doping in case of Ce_2S_3 and La_2S_3, while it remains almost same for Gd_2S_3 and increases with increase in doping percentage for Y_2S_3.

- The emission spectrum of Eu doped samples 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 emission spectra of samples synthesized by Precipitation method 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.

- For Eu doped samples prepared by Solid State method, the intensities of the emission lines are found to increase with increase in doping percentage from 1% to 2% while it decreases when Eu doping percentage becomes 3% for all the samples. This is not the case for samples prepared by Precipitation method. The intensities of the emission lines are found to increase with increase of Eu doping from 1% to 3% for all the samples except La_2S_3 for which the intensity increases with 1% to 2% Eu doping and then decreases for 3% of Eu doping.

- The excitation spectra of the samples synthesized by Solid State and Precipitation method for 1%, 2% and 3% of Tb doping show an intense peak due to the $4f^8 \rightarrow 4f^75d^1$ transition of Tb^{3+} ion while the series of other absorption lines can be attributed to the 4f–4f transitions of Tb^{3+} ions. The maximum intensity excitation wavelength is found to be 247 nm and 232 nm for Ce_2S_3 and La_2S_3 synthesized by Solid State method. Photoluminescence spectra for these two samples synthesized by Precipitation method

could not be obtained. The most intense excitation peak is found at 273 nm and 274 nm for Gd_2S_3 synthesized by Solid State and Precipitation method respectively, while it is obtained at 287 nm and 290 nm in Y_2S_3 for the respective methods. These values are found to remain the same for all doping percentages of Tb.

- In Tb doped samples synthesized by Solid State method, the intensity of the most intense excitation peak remains almost the same in case of Ce_2S_3 and Y_2S_3 for all doping percentages of Tb. The intensity of excitation line of Gd_2S_3 shows a steady decrease with increase in doping percentage while the intensity of La_2S_3 excitation line increases from 1% to 2% of doping and then decreases foe 3% of Tb doping. In samples prepared by Precipitation method, the intensities of the excitation peaks increase for doping percentage of Tb from 1% to 2% and then decreases for 3% of Tb doping for both Gd_2S_3 and Y_2S_3.

- All the samples except Y_2S_3 give emission lines in both blue and green regions for all samples synthesized by both the methods. The blue emission peaks at 415 nm, 436 nm, 457 nm, 468 nm, 469 nm, 474 nm, 475 nm, 484 nm, 485 nm and 488 nm correspond 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 green emission peak at 545 nm is 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.

- In case of Y_2S_3, blue emission lines are absent in Solid State samples while in case of Precipitation samples, both blue and green emission lines are obtained.

- The intensities of emission lines of Tb doped samples prepared by Solid State method is found to increase with doping percentage from 1% to 2% and then decrease for 3% Tb doping for La_2S_3. It decreases with increase in doping percentage from 1%to 3% for Gd_2S_3 and remains almost constant for Ce_2S_3 and Y_2S_3. In case of all the samples prepared by Precipitation method, the intensities are found to increase with increase in Tb doping from 1%to 2% and then decreases when doping percentage becomes 3%.

- The overall emission intensity for samples synthesized by Precipitation method is less as compared to the emission intensities of samples synthesized by Solid State method for all doping percentages of Eu and Tb.

- Out of all the synthesized samples, the luminescence intensity is found to be highest in case of Gd_2S_3:Eu which suggests that it is a better material for Eu doped samples. Similarly, the luminescence intensity is found to be highest in case of Y_2S_3:Tb which suggests that it is a better material for Tb doped samples. This is true for samples synthesized by both the methods.

- The Manganese doped Rare earth sulphides of Cerium, Gadolinium, Lanthanum and Yttrium were dark in colour and did not give Photoluminescence spectra.

4. Thermoelectric properties of the materials Ce_2S_3, Gd_2S_3, La_2S_3 and Y_2S_3 were studied by obtaining their Resistance → Temperature curves in the temperature range of 308 K to 378 K (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 exhibits semiconducting properties with Negative Temperature Coefficient.

- 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 in undoped samples 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 and the resistance decreases in the order Eu → Tb → Mn doping. This is in agreement with theoretical results.

- In doped samples prepared by Solid State method, the resistance of Lanthanum Sulphide samples was found to be higher than Cerium Sulfide samples, which became the lowest in resistance, while in the doped samples prepared by Precipitation method, the sequence remained same as undoped samples.

- The resistance of the same samples prepared by Precipitation method is less than the ones prepared by Solid State method. This implies that preparation method affects the resistance of the material.

- The Temperature → Resistance curve displays three distinct regions. The values of Temperature Coefficient of Resistance in the almost linear region (higher temperature region) of Temperature → Resistance curve are the least for all the samples. This linear region of the curves can be utilized to develop temperature sensing devices. Of all the synthesized samples, Ce_2S_3 shows the best uniform characteristics and hence is a better candidate for temperature sensing.

- The Temperature → Resistance graphs can be fit to the power function **$f(x) = k\,x^n$** where k and n are real numbers. Using these equations, we can find the resistance of the material at any value of temperature.

- The current obtained at 35 ˚C is in the range of μA for all the samples. The resistance decreases by a factor of 10 or more, increasing the current by almost the same factor. The power obtained would be in the range of microwatt which may be used to operate various IOT (Internet of Things) devices like sensors, microprocessors and microchips which have found their way in lives. Many of such devices can function in the current range of nano and even up to pico amperes.

- These materials show a possibility to be utilized in thermoelectric applications like generation of power from waste heat in equipments and industries.

5.2 Limitations

- All the synthesized materials are not obtained in the pure phase as compared with the standard JCPDS database and a mixed phase is obtained for some samples because of process parameter limitations in the laboratory environment.

- This study is limited to the doping percentage of 1% to 3% in the various samples and out of these combinations, the best achievable results for Photoluminescence and Thermoelectric applications have been shown. The efficiencies of Luminescence can be improved further.

- Thermoelectric properties are quite sensitive to the composition and the crystal phase. This study focuses only on the synthesized rare earth-sulphides of Lanthanum, Gadolinium, Cerium and Yttrium and their scope of the work to achieve possible applications in the laboratory.

5.3 Future Scope

The Rare-earth sulphide materials have attracted tremendous interest in the industry and academia for their use in the different applications, most notably in electronic, optical, luminescence and thermoelectric conversion industry as emerging technology.

- The experimental method suggested in the work is low cost, simple and it is further suitable for its future application in mass production [1].
- Further experiments are suggested to do analysis with other combination of dopants which can gave better properties to develop suitable applications by utilizing rare-earth chalcogenide elements [2].
- The synthesised materials can be explored for their application in switching devices, superconducting devices, current controlled devices etc. [3].
- The materials can be investigated for the study of environmental pollution and in the characterization of trace amount of minerals bio-accumulated in the tissues [4].
- Trials can be made on these materials for generation of thermoelectric power to be used to operate various low power IOT (Internet of Things) devices like sensors, microprocessors and microchips etc. functioning in the current range of micro, nano and even up to pico amperes.

5.4 References

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