ABSTRACT

- Rare Earth Sulfides have gained much attention for their attractive physical and chemical properties. Sulphide compounds doped with suitable materials have been used in the field of Luminescence since long. The fossil fuel resources will soon get exhausted. In addition to other renewable sources of energy, the technologies which convert wasted heat energy into electrical energy are being increasingly promoted in present times. Rare Earth Sulphides are a promising candidates for such thermoelectric conversions. 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. 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. It is a practice to use Hydrogen Sulphide (H_2S) or Carbondisulphide (CS_2) or an inert gas atmosphere of Argon (Ar) in conventional Solid State synthesis. In our study, none of the above toxic gases were used and successful synthesis of rare earth sulphides has been achieved by a simple high temperature heating reaction. The synthesized materials were characterized using X-Ray Diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and Field Emission Scanning Electron Microscopy (FE-SEM). The optical properties of the materials were studied using Photoluminescence Spectroscopy (PL) and its thermoelectric properties were studied by calibrating the Resistance → Temperature curve. XRD patterns of the synthesized materials 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. 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. Field Emission Scanning Electron Microscopy shows a wide variation of the grain size and different morphologies are obtained for the samples. 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. 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. 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. 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 $4f^8 \rightarrow 4f^7 5d^1$

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. 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 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. 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 and 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. 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 materials can be utilized to develop temperature sensing devices. With current obtained in the range of μA, the power obtained would be in the range of microwatt which may be used to operate various IOT (Internet of Things). These materials show a possibility to be utilized in thermoelectric applications like generation of power from waste heat in equipments and industries.