

# Synthesis of Nano Crystalline Compound $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ By Solvent Matrix Method

C. P. Gupta

Department of Chemistry, St. Andrew's P.G. College Gorakhpur India  
cpgupta673@gmail.com

**Abstract:** New complex of the type  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  has been synthesized in solid state in presence of sun light by the interaction of  $\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$  with  $\text{Pr}_6\text{O}_{11}$  at ambient temperature. Characterization of the parent compound  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ , has been done by elemental analysis, TGA, DTA and X – ray powder diffraction pattern. Doping occurs in parent compound with  $\text{Cr}^{+3}$  ion forming dark green nano crystalline compound  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ . The doped complex of  $\text{Pr}^{+3}$  ion is paramagnetic. The doped complex of  $\text{Pr}^{+3}$  ion is also hexagonal structure with lattice constant,  $a = 4.141\text{Å}$  and  $c = 7.601\text{Å}$ . The UV – visible spectrum of  $\text{Cr}^{+3}$  ion shows peak at 380 and 450 nm. New peaks at 490 and 600 nm occur due to  $f-d$  and  $f-f$  transition for  $\text{Cr}^{+3}$  and  $\text{Pr}^{+3}$  ions respectively in compound,  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ . Nanoparticles of  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  were prepared in ethylene glycol indicating the particle size 50-100nm in TEM photograph.

**Keywords:** Nano crystalline compound  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ , paramagnetic, hexagonal structure, UV – visible spectrum, SEM

## 1. Introduction

A literature survey [1-8] indicated no evidence of studies on the interaction of  $\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$  with lanthanon oxides in the presence of sun light. There is considerable interest in doping of rare earth ions in lattice of  $\text{Cr}_2\text{O}_3$  and vice versa. Doping of  $\text{Cr}^{+3}$  ion in place of  $\text{Pr}^{+3}$  ion in lattice of new complex  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ , may result in an interesting material since radii of  $\text{Cr}^{+3}$  ion is smaller than  $\text{Pr}^{+3}$  ion. It has also been reported that during the process of doping [9] of  $\text{Mn}^{+2}$  ion in ZnS, the formation of nano particles occurs. The synthesis of the parent compound  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ , mono aqua hydroxyl mercaptyl Pr(III) and its characterization by elemental and IR spectral analysis, TGA, DTA and X – ray powder diffraction pattern has been already been reported [9] by Lakshmi et al. Synthesis of nanocrystalline compound, CdS by chemical technique [10,11] tempted us to prepare nano crystalline material by solvent method. Al. L. Eros et.al. [12] have prepared thin film of CdS on glass. Cerium molybdate and iron titanium oxide hollow nanoparticles have been prepared by I.A, Kartosonakis et al. [13]. Similarly we have synthesized thin film of the complex,  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  from parent compound  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ . This thin film of nano crystalline material has been characterized by SEM (scanning electron microscope) indicating crystalline size 50 – 100 nm.

## 2. Experimental

Reactants were sodium sulfide,  $\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$  (Emerk, 99.9%) and the oxide of the praseodymium,  $\text{Pr}_6\text{O}_{11}$  (BDH, 99.9%). Parent compound was prepared in the solid state in the presence of sunlight. No reaction occurs when reactants are confined in darkness in solid state for a period of 4 -5 days.  $\text{Pr}_6\text{O}_{11}$  (black solid, m.p.980 0c) and  $\text{Na}_2\text{S} \cdot 7\text{H}_2\text{O}$  (yellow solid, m.p.11680c) confined in sun light react at ambient temperature within a period of about 35 min. and yield the compound  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ . The compound is insoluble in acetone, dichloromethane,

chloroform, DMSO, dimethyl ether but is soluble in methanol, HCl, DMF and ethane diol.

The complex  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  was dissolved in ethane diol and stirred by magnetic stirrer for 3hrs. A green solution of complex was obtained. The green solution was poured in three test tubes and 1, 2 and 3 specks of  $\text{K}_2\text{Cr}_2\text{O}_7$  were added gently to three test tube without disturbing the solvent matrix. After 3- days a dark green color developed in each test tube in near vicinity of  $\text{K}_2\text{Cr}_2\text{O}_7$ . The contents were stirred thoroughly and kept for 15 – days. Solution becomes completely dark green in each test tube. Thin films were prepared on glass slides from the content of three tubes and left over for one month for nucleation of nano particle.

In order to characterize the nano compound the IR spectrum was run in the range of  $4000 - 400 \text{ cm}^{-1}$  using KBr discs on a Perkin Elmer FT – IR spectrophotometer. The X – ray powder diffraction pattern of the compound was carried on a Phillips Analytical X – ray B. V. diffractometer PW 3710, using CuK $\alpha$  radiation with  $2\theta = 5 - 80^\circ$ . The room temperature magnetic susceptibility was measured on a Cahn Faraday electro balance using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as calibrant. Electronic spectrum of doped compound was recorded on a Shimadzu 160A spectrophotometer in methanol and ethane diol ( $10^{-2}\text{M}$  molar). SEM photograph have been produced from scanning electron microscope JEOL – 840, JEOL Corporation Japan. Thin film was cut to appropriate size (10mm approx.) and coated with gold to avoid charge accumulation on the surface of film.

## 3. Results and Discussion

The parent compound has been characterized as  $[\text{Pr}(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  [11,14-18] by elemental, IR spectral analysis, TGA, DTA and X – ray powder diffraction pattern. The doped complex of  $\text{Pr}^{+3}$  ion obtained from parent compound is also paramagnetic with magnetic moment  $\mu = 3.67\text{BM}$ . The doped complex of  $\text{Pr}^{+3}$  ion also

has a hexagonal structure with lattice constant  $a = 4.141\text{Å}^0$  and  $c = 7.601\text{Å}^0$  [Table-1]. As radius of  $\text{Cr}^{+3}$  ion ( $0.62\text{Å}^0$ ) is smaller than radius of  $\text{Pr}^{+3}$  ion ( $1.01\text{Å}^0$ ), doping occurs with  $\text{Cr}^{+3}$  ion forming dark green compound  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$ . Doping occurs also due to reducing character of ethane diol. Solvent ethane diol reduces  $\text{Cr}^{+6}$  ion to  $\text{Cr}^{+3}$  ion. Perhaps, during this process formation of nanoparticle takes place. The UV – visible spectrum of  $\text{Cr}^{+3}$  ion shows peaks at 380, 450 nm due to d – d transition  ${}^4\text{A}_2 \rightarrow 4\text{T}_1$  and  ${}^4\text{A}_2 \rightarrow 4\text{T}_2$  respectively. New peaks at 490 and 600 nm in compound  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  appear due to f – d transitions  ${}^3\text{H}_4 \rightarrow {}^4\text{A}_2$  and f – f transitions  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2, {}^3\text{P}_1$  respectively. The transition  ${}^3\text{H}_4 \rightarrow 3\text{P}_0$  is most probably marked by f – d transition as shown in figure 1.

Hoyer et. al.[10] have confirmed nano crystalline nature of CdS thin film from its optical absorption spectrum showing a shift from 515 to 417 nm for nanocrystalline CdS. The energy difference between two peaks is 0.47 ev in CdS. This difference depends on the crystalline size [12]. The energy difference, between two peaks at 490 nm and 600 nm as calculated from UV – visible absorption spectrum of our doped compound is 0.46 ev. This is comparable to the energy difference 0.47 ev found by Hoyer et al for CdS having crystalline size 20 nm [11]. TGA and DTA have been carried out to show the thermal stability and phase changes. Fig.2. Thermal stability [19, 20] of oxides has been reported as  $\text{CdO} > \text{HgO}$  ie  $700^\circ\text{C}$  for CdO and  $360^\circ\text{C}$  for HgO. Similar order of stability in TGA might be for  $\text{CdS}(\text{H}_2\text{O})_3 > \text{HgS}(3\text{H}_2\text{O})$  which follows the sequence  $481.70^\circ\text{C}$  and  $391.2^\circ\text{C}$  respectively. While the doped compounds  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  prepared in solid state show  $365.2^\circ\text{C}$ .

Therefore, exists the possibility that the compound  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$  is nanocrystalline compound. This argument has been supported by SEM photograph (Fig. 2) showing growth of particles ( slide- 1, and 2, containing 1, and 2 specks of  $\text{K}_2\text{Cr}_2\text{O}_7$  doped in content of test tube 1 and 2) in regular patterns in nano range (50 - 100nm). Sridhar Komarneni et al and other workers [21 – 23] have also used ethane diol for the synthesis of nanoparticles.

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$$\text{Hexagonal } a = 4.141\text{Å}^0, c/a = 1.633, c = 7.601\text{Å}^0 \\ \text{Sin}^2 \theta = \lambda^2/4a^2[4/3 (h^2 + k^2 + kh) + l^2 a^2/c^2], \lambda = 1.539\text{Å}^0$$

**Table 1:** XRD pattern of the complex  $[\text{Pr}_{1-x}\text{Cr}_x(\text{SH})(\text{OH})_2(\text{H}_2\text{O})]$

$\theta$	$\text{Sin } \theta$	$\text{Sin}^2 \theta$	$d(\text{Å}^0)$	$I/I_0$	(h, l, k)
8.0	0.1391	0.0194	5.55	120 strong	(001) hexa
14.0	0.2419	0.0585	3.201	90 strong	(002) hexa
14.5	0.2503	0.0627	3.077	110 strong	(101) hexa
15.5	0.2672	0.0714	2.901	40 weak	(100) tetra
16.25	0.2798	0.0783	2.765	30 weak	(002) tetra
20.50	0.3502	0.1226	2.215	90	(011) tetra
24.5	0.4147	0.1720	1.847	45	(103) hexa
25.0	0.4226	0.1786	1.817	60 weak	(120) tetra
26.0	0.4384	0.1922	1.751	35	(020) hexa
29.0	0.4848	0.2350	1.596	35 weak	(201) tetra

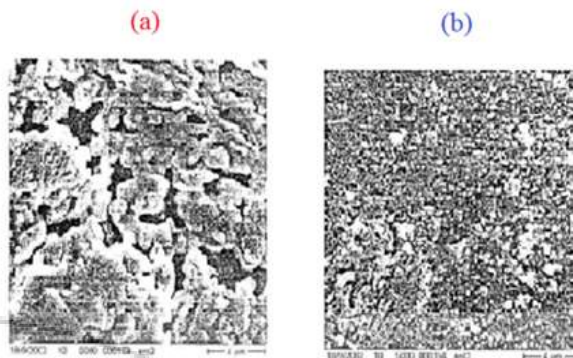
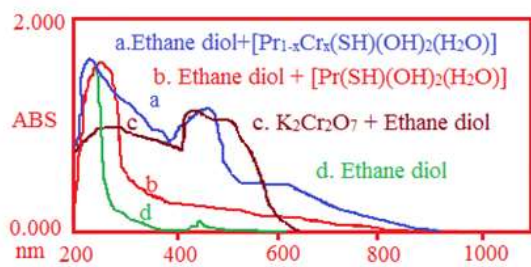


Fig.3. SEM Photograph of (a) undoped  $[Pr(SH)(OH)_2(H_2O)]$  and (b) doped  $[Pr_{1-x}Cr_x(SH)(OH)_2(H_2O)]$

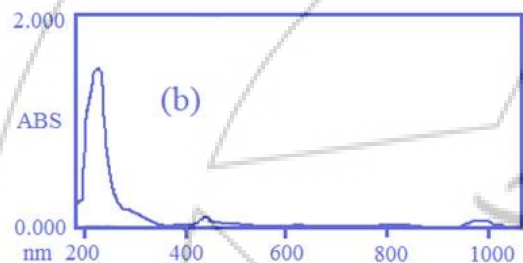
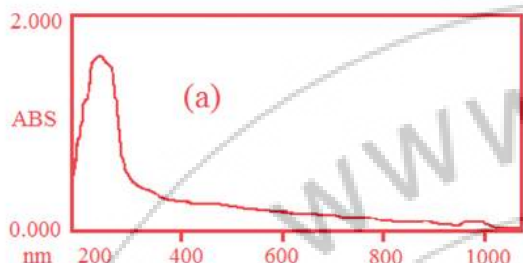


Fig.1. Adsorption spectra of (a) undoped  $[Pr(SH)(OH)_2(H_2O)]$  and (b) doped  $[Pr_{1-x}Cr_x(SH)(OH)_2(H_2O)]$

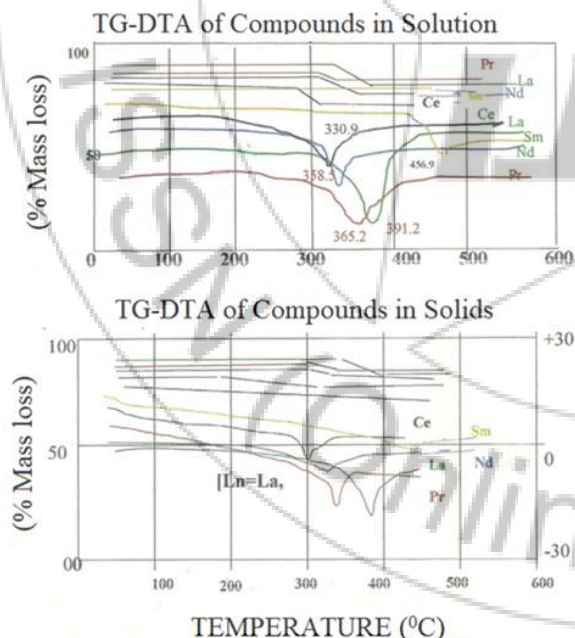


Fig.2. TG-DTA of Compounds of  $[Ln(SH)(OH)_2(H_2O)]$   
Ln =La, Ce, Pr, Nd,Sm