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Electrical resistivity of Nano-Hgs under high pressure and temperature

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ABSTRACT

β-HgS nanoparticle plays a vital role in many areas of science and technology. It has proven and promising application in the fields like electronic, optical and environmental remediation. Such technologically important nanosized mercury sulphide (β-HgS) was prepared by eco-friendly micro wave assisted method and characterized. Electrical resistivity studies of synthesized nano HgS were carried out by four probe method using Bridgman Opposed Anvil High Pressure Device (OAHPD) under high pressure and high temperature of 10 GPa and 300° C respectively. On application of pressure the nano HgS undergoes a transition from semimetal to conductor and thereby resistivity decreases. The transition pressure shifts to the lower value on increase of temperature.

KEY WORDS: Nanoparticles, mercury sulphide, resistivity, phase transition, high pressure and temperature.

1. INTRODUCTION

Nanocrystalline materials with dimension less than 100 nm show remarkable revolution in the area of research in Physics, Chemistry and Engineering (Gleiter, 2000). The metallic nanoparticles and their sulphide derivatives have become important components in various fields like catalysis (Ansari, 2009), environmental remediation (Lukhele, 2010), gene therapy (Andreu, 2008), imaging (Lee, 2006) drug delivery (Akin, 2007), biomarkers (Ranzomi,2012), sensors (Fan, 2010) and energy storage (Ryu, 2010). The unique properties of nanoparticles like large surface area, high magnetism and high chemical activity (Akbarzadeh, 2012) paved way for the above said applications. These properties can be altered by the size and shape of the nanoparticles (Tao, 2008). Sulphide semiconductors have been the focus of many researchers in recent years due to the quantum size effect (Gorer, 1994; Empedocles, 1999). Among the semiconductor nanoparticles, Mercuric Sulphide (HgS) is a technologically important semiconductor and is widely used for application in ultrasonic transducer (Tokyo, 1975,1978), electrostatic image material (Tokyo, 1975), photoelectric conversion devices (Charkraborty, 2005; Kershaw, 2000; Roberts, 1969), acousto-optical materials (Sapriel, 1971) and infrared sensing (Higginson, 2002). Meta – cinnabar (β- HgS) is an insulator which can be used for low power consumption electronic devices (Virot, 2011). Research has been employed for the remediation of mercury and β- HgS is a promising nanoparticle to remove the toxicity of the mercury from the contaminated environment.

For this purpose β- HgS must be synthesized in various forms with high purity of controlled size and shape for stabilizing surface modification. Though we have a number of methods to prepare metal sulphide (HgS) it is still a challenge to synthesize nanosized β- HgS particle by a practical and facile route. The microwave assisted route is a novel method which is faster and energy efficient. This method is used for synthesizing metal sulphide (Wang, 2001; Ding, 2003). It is a fast, convenient, mild, energy – efficient and environmentally friendly route for synthesing β- HgS. The prepared product was characterized by XRD, TEM and XPS. According to TEM observations the HgS nanoparticles are mostly spherical in shape with an average size of 15 – 20 nm (Ding, 2003).

High pressure plays a vital role to explore the phase transformation and possible path to expand the range of available solid state materials for applications. β- HgS being an II-VI semiconductor, the electrical transport property of HgS under high pressure is very important and useful. In our present work, *insitu* electrical resistivity measurement is carried out under high pressure and high temperature.

2. EXPERIMENTAL PROCEDURE

The high – pressure electrical resistivity studies for β- HgS has been carried out using the standard four probe method by using Bridgman opposed anvil device. The sample is placed between the two anvils face using a gasket material Pyrophillite of 10 mm in diameter with 2mm hole drilled at the centre. The steatite is used as pressure transmitting medium and Bismuth as pressure calibrant. The overall thickness of the sample cell is about 0.5mm. Four copper leads of thickness 0.1mm are used to measure the resistivity. The resistivity measurements are carried out up to a pressure of 10 GPa. The schematic of the experimental set up is made as reported (Freny, 2004, 2006). For high temperature, a circular heating coil made up of Kanthal wire overlaid by brass shield is used externally. The temperature is measured with the K- type thermocouple and a temperature controller is used to maintain the temperature. The heating coil is heated with 220 V power supply and the experiment is carried out for different pressures up to a temperature of 300°C.

3. RESULTS AND DISCUSSION

HgS is semimetallic in nature and called as zero band gap semiconductors. At ambient conditions, the resistivity of mercury sulphide is in the range of ohms. Initially, the resistivity of HgS is found to ρ_o = 2.006 x $10^3 \Omega$m. As the pressure is increased, the resistivity decreases upto 5.7 GPa and becomes almost constant upto 10 GPa. This shows that the mercury sulphide becomes conductor with very low resistance. The value of resistivity falls to ρ = 0.0201 x 10^2 Ωm. When the high pressure resistivity studies are carried at different temperatures the transition pressure shift towards the lower pressure. Figure 1 shows the high pressure and high temperature resistivity measurements of nano sized β-HgS.

The nanoparticles are very sensitive to the thermo dynamical parameters and they are very unstable. Phase transitions under the application of pressure present most important and interesting results as they lead to sharp changes on both crystal lattice and electron transportation. On application of pressure, the electrical resistivity changes and discontinuities appears at 5.4 GPa, 14.6 GPa and 25 GPa representing the phase transformation of bulk β-HgS from Zinc blende to cinnabar and then to rock salt structure (Jing, 2015). The bulk β-HgS shows a discontinuity of conductivity at 5 GPa and a corresponding phase transition from β- phase to α- phase from 5 GPa to 20 GPa and at 27GPa it becomes metallic (Hao, 2007). According to the result obtained nanoparticle β-HgS shows a remarkable enhancement in the electrical transportation property. Nano sized β-HgS becomes metallic at 5.7 GPa whereas its bulk counterpart showed metallic nature at 27 GPa. Thus the phase transition from semiconductor to metallic is enhanced on application of pressure and due to the tremendous reduction of particle size. These differences from the bulk help to determine a new phase diagram of nanocrystallites as a function of temperature and pressure. It provides way for met stabilization of new crystalline forms at ambient pressure and temperature to exploit various physical properties for applications. The surface to volume ratio and the probability of monodomain crystallites formation is inversely proportional to the size of the nanocrystallite. The difference in the transition pressure between the bulk and the nanoparticle is comprised by three main factors (Tolbert, 1995; Jinag, 2004) such as (i) difference of surface energy of the phase under investigation, (ii) difference of the internal energy at the crystallite site, (iii) difference in the volume of the bulk and the nanoparticle. The surface energy play a major role in the enhancement of transition pressure and phase transformation dynamics. By taking high pressure diffraction pattern we have confirmed that there is no structural distortion upto 15 GPa and the results have been reported (Freny Joy, 2006).

From the resistivity values obtained at high temperature and high pressure we infer that the β-HgS is semi-metallic at normal conditions. In the present work, the resistivity decreases and the conductivity increases on application of pressure. The value of conductivity of β-HgS for a maximum temperature of 300°C and pressure 10 GPa is 4.975x10^3 Ω^{-1}m^{-1}. Due to the application of pressure the charge carrier concentration increases and decreases the electrical resistivity of the material under consideration. Moreover the mobility of charge carriers also plays an important role in the reduction of resistivity values. For Hg chalcogenides the mobility of charge carries decreases on application of pressure and is limited due to ionized impurity scattering and polar optical scattering (Jing, 2015). According to the present work the reduction of mobility occurs on application of pressure and temperature and not due to the presence of impurity as the sample prepared is of high purity according to the results obtained (Ding, 2003).

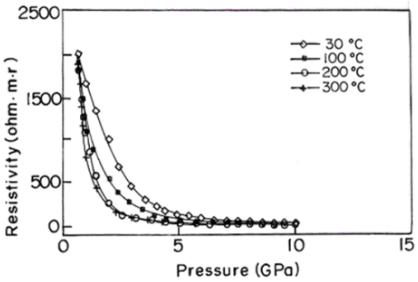

Figure.1. Pressure Vs Resistivity graph at various temperature for nano β-HgS

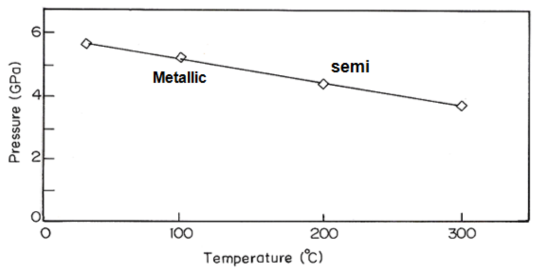

Figure.2. Pressure – Temperature phase diagram for nano β-HgS

The temperature is increased up to 300°C in steps of 100°C. The pressure – temperature phase diagram is shown in Fig. 2. The transition is an irreversible phase transition on release of pressure. The transition pressure for different temperature is clearly known from the graph and it shifts towards the lower values of pressure. The high – pressure behaviour on nanocrystallites material shows a remarkable difference with respect to bulk and their study not only provides information of fundamental importance but also helps to determine new nanomaterials phases whose properties can be tuned with the size of the particle.

4. CONCLUSION

In situ electrical resistivity measurements are carried out under high pressure and high temperature for nano β-HgS. We conclude that on applying pressure the semiconductor nanocrystal undergoes an electrical phase transition from semiconductor to metallic nature and the transition is irreversible on release of pressure. The conductivity of the nanomaterial has drastically increased and the phase stability is obtained. This physical property makes nano β-HgS a promising material for environmental remediation to remove toxic mercury contamination and to promote hazardous free environment.

REFERENCES

Akbarzadeh A, Samiei M and Davaran S, Magnetic nanoparticles, preparation, physical properties and application in biomedicine, Nanoscale Res. Lett, 7, 2012, 144-156.(b)Chirita M and Grozescu L, Fe_2O_3 – Nanoparticles, physical properties and their photochemical and photoelectrochemical applications, Chem. Bull. 54, 2009, 1-8.

Akin D, Sturgis J and Ragheb K, Bacteria-mediated delivery of nanoparticles and cargo into cells, Nature Nanotech, 2, 2007, 441-449.

Andreu A, Fair weather N and Miller AD, Clostridium neurotoxin fragments as potential targeting moieties for liposomal gene delivery to the CNS, Chem Bio Chem, 9, 2008, 219-231.

Ansari F, Grigiriev P and Labor S, DBT degradation enhancement by decorating Rhodococcus erythropolis IGST8 with magnetic Fe_3O_4 nanoparticles, Biotech Bioeng, 102, 2009, 1505 -1512.

Charkraborty I, Mitra D and Moulik S P, Spectroscopic studies on Nanodispersions of CdS, HgS their Core –shells and Composites prepared in Micellar Medium, J. Nanopart. Res, 7, 2005, 227-236.

Ding T and Zhu J, Microwave heating synthesis of HgS and PbS nanocrystals in ethanol solvent, Mater. Sci, Eng, 100, 2003, 307-313.

Ding T, Zhang j R, Long S and Zhu J J, Synthesis of HgS and PbS nanocrystals in a polyol sovent by microwave heating, Microelectron Engg, 66, 2003, 46.

Empedocles SA, Influence of Spectral Diffusion on the line shapes of Single CdSe nanocrystallite Quantum Dots, J. Phy. Chem, 103(11), 1999, 1826-1830.

Fan Y, Xu S and Schaller R, Nanopaticle decorated anodes for enhanced current generation in microbial electrochemical cells, Biosens Bioelectron, 26, 2010, 1908 – 1912.

Freny Joy K M, Victor Jaya N and Zhu J.J, Structural Transformation in PbS and HgS Nanocrystals under high Pressure, 20, 2006, 963-970.

Freny Joy K.M, High Pressure studies on nanocrystalline Aurivillius Oxides, Lead and Mercury Chalcogenides, Chapter 5, 2006, 124-148.

Freny Joy K.M, Jaya Arun T K, Victor Jaya N and Castro A, High pressure and high temperature phase transition in nanocrystalline Aurivillius oxide, Physica E, 23, 2004, 188 – 192.

Gleiter H, Nanostructured Materials, Basic Concept and Microstructure, Acta Materialia, 48(1), 2000, 6243 – 6248.

Gorer S and Hodes G, Quantum size effects in the study of chemical solution deposition mechanism of semiconductor films, J. Phys. Chem, 98(20), 1994, 5338-5346.

Hao A, Gao C, Li M, Chunyuan He, Huan X, Zhang D, Yu C, Liu H Ma Y and Tian Y, A study of the electrical properties of HgS under high pressure, J. of Phys, Cond. Matt. 19, 2007, 425222.

Higginson K A, Kuno M, Bonevich J, Qadri S B, Yousuf M and Mattoussi H, Synthesis and Characterization of Colloidal β-HgS Quantum Dots, J. Phys. Chem B, 106, 2002, 9982-9985.

Jinag J.Z, Phase transformation in nanocrystals, J. Mater, Sci, 39, 2004, 5103-5110.

Jing T, Yan X, Xue Fei L, Wang J S, Yang J H and Gao C X, In situ electrical resisitivity and Hall Effect measurement of β-HgS under high pressure, Chin. Phys. Letters, 32, 2015, 016402-016403.

Kershaw S V, Harrison M, Rogach A L and Kornowski A, Development of IR- Emitting Colloidal II-VI Quantum dots Materials, IEEE J. Sel. Top. antum Electron, 6, 2000, 534-543.

Lee J. H, Huh Y M and Jun Y W, Artificially engineered magnetic nanoparticles for ultra-sensitive imaging, Nature Med, 13, 2006, 95 – 99.

Lukhele L.P, Bhekie BM, Momba MNB and Krause RWM, Water disinfection using novel cyclodextrin polyurethanes containing silver nanoparticles supported on carbon nanotubes, J. Appl, Sci, 10, 2010, 65 – 70.

Ranzomi A, Sabatte G, Van Ijzendoorn I J and Prins M W, One step homogenous magnetic nanoparticle immunoassay for biomarker detection directly in blood plasma, ACS Nano, 6, 2012, 3134 – 3141.

Roberts G G, Lind E L and Davis E A, Photoelectronic properties of Synthetic Mercury Sulphide Crystals, J. Phys. Chem Solids, 30, 1969, 833-844.

Ryu J, Kim S W, Kang K and Park C B, Synthesis of diphenylalanine/cobalt oxide hybrid nanowires and their application to energy storage, ACS Nano, 4, 2010, 159 – 64.

Sapriel J, Cinnabar (α-HgS), a Promising Acousto-Optical Material, Appl. Phys. Lett, 19,1971, 533-535.

Tao A R, Habas S and Yang P, Shape control of colloidal metal nanocrystals, Small, 4, 2008, 310-325.

Tokyo N and Aziko K, Jpn. Kokai Pat.7855478 (Cl. C23C15/00), 1978.

Tokyo N, Jpn Kokai Pat.75130378 (Cl. H011L. C01b), 1975.

Tolbert S.H and Alivisatos, The wurtzite to rock salt structural transformation in CdSe nanocrystals under high pressure, J. Chem. Phys, 102, 1995, 4642

Virot F, Hayn R, Richter M and Vanden Brink J, Metacinnabar (β-HgS), A strong 3D topologicalInsulator with highly Anisotropic surface states, J. Phys. Review Letter, 106, 2011, 236806-1-4.

Wang H, Zhang J R and Zhu J J, A Microwave assisted heating method for the rapid synthesis of sphalrite –type mercury sulfide nanocrystals with different sizes, J. Cryst. Growth, 233, 2001, 829-831.