Zinc and Sulphur Ores

ZINC

Zinc, a metal, commonly known as spelter is a chemical element having symbol Zn and atomic number 30. It is the first element in group 12 of the periodic table. Its only oxidation state is +2 and it is the 24th most abundant element in the earth’s crust and has 5 stable isotopes (18).

ZINC ORE

Zinc carbonate, the commonly found chemical under zinc ore, occurs in a rounded, crystalline crusts with a luster that resembles a pearl. It occurs in two types of deposits namely primary zinc ore (also called as rakes) and secondary deposits. Primary zinc veins: This form of deposit is generally found in thin veins forming fissures through the rock. It either occurs as thin bands within the vein or as thin layers encrusting on the walls of the vein. Secondary zinc veins: Permeating oxygenated ground waters in the overhead parts of the vein splits the primary sulphide minerals. The presence of pyrite enriches this chemical reaction and on oxidation sulphuric acid is produced. Zinc is liberated from this oxidation of sphalerite with carbonate present in the host rock to form calamine (19).

PROPERTIES OF ZINC

Physical properties:

- This metal is heavy and hence it sinks in water
- The colour of zinc is bluish-white
- The melting point of zinc is 420° C
- It has a boiling point of 906° C
- On heating till 200° C, zinc loses its elasticity and the resultant is a grey powder
- Zinc has a high heat capacity and heat conductivity
- It is a considerably good conductor of electricity

Chemical properties:

Zinc, an efficacious element, dissolves in both acids and alkalis. Hydroxo-zincates are formed when the element reacts with alkalis

- Zinc carbonate is formed on reaction of zinc with moist air. The zinc carbonate prevents other reaction by the formation of a thin crust on the surface. When it burns in air, a bluish flame is produced. However, zinc does not react with oxygen in dry air
- Fumes of zinc oxide are formed when it burns in air with a bluish-green flame
- It reacts readily with acids, alkalis and other non-metals whereas intensely pure zinc reacts slowly at room temperature. Hydrochloric or sulphuric acids are strong acids and can remove the passivating layer and the consequential reaction with water releases hydrogen gas (20).

CRYSTAL STRUCTURE

Zinc has hexagonal crystal structure. Every zinc atom has 12 nearest neighbours.

SULPHUR

Sulphur is a chemical element (multivalent and non-metallic) with symbol S and atomic number 16. It is the fifth most common element on the earth. Sulphur usually occurs as sulphate minerals or sulphide but sometimes found in its pure form. Sulphur atoms with a chemical formula S_8 form cyclic octatomic molecules under normal conditions (21).

SULPHUR ORE

Sulphur ores containing more than 25% of sulphur are classified as rich ores, those ores containing 10%-25% are considered intermediate and those with 5%-10% are classified as lean. Sulphur deposits occur in the form of sheets, pocket formations and can be simple or complex (22).

PROPERTIES OF SULPHUR

Physical properties:

- Sulphur is non-metallic and is pale yellow in colour
- Rhombic, Amorphous and Prismatic are the different forms in which it exists
- It is odourless and tasteless
- It is insoluble in water
- It has several known allotropes
- The boiling point of sulphur is 444.6° C
- It is a poor conductor of heat and electricity

Chemical properties:

- On heating, sulphur reacts with metals which in turn forms the corresponding sulphides
- Most metals and non-metals combine directly with sulphur
- Sulphur burns in abundant exposure to air in a bright blue flame forming sulphur (IV) oxide and with less quantity of sulphur (VI) oxide (23).

STRUCTURE

It consists of S_8 rings of atoms. It has a higher melting and boiling point because of strong Vander Waals attractions. Rapid cooling of molten sulphur produces amorphous sulphur (24).

ZINC SULPHIDE

It is an inorganic compound with a chemical formula ZnS. It is naturally found in the more stable cubic form known as zinc blende or sphalerite. It is also found in the hexagonal form called as wurtzite. Zinc sulphide is one of the first semi-conductors discovered and has shown diverse applications including light emitting diodes (LEDs), sensors, lasers etc.

STRUCTURE OF ZnS

Zinc sulphide primarily has two available allotropes: one with a zinc blende or sphalerite structure and another one with a wurtzite structure. Zinc blende structure is stable at low temperature whereas wurtzite structure forms at high temperature (around 1296 K)

PREPARATION

Laboratory preparation:

Zinc sulphide is usually produced by igniting a mixture of zinc and sulphur. It can also be produced by a precipitation reaction as zinc sulphide is insoluble in water. Solutions encompassing Zn2+ salts readily form a precipitate ZnS in the presence of sulphide ions (example from H2S).

Zn2+ + S2? ? ZnS

This reaction is the basis of a gravimetric analysis for zinc (26).

PROPERTIES OF ZINC SULPHIDE:

Solubility: insoluble in alkalis and soluble in dilute mineral acids

- It is a white to yellow coloured powder or a crystal with molecular mass of 97.474 gmol-1 and density of 4.090 gcm-3
- Density: 4.04 g/cu cm (sphalerite); 4.09 g/cu cm (wurtzite)
- Stable if kept dry and when containing water it slowly oxidizes in air to sulphate

ZnS NANOPARTICLES

Nano ZnS possess anomalous physical and chemical properties such as the surface volume effect, enhanced surface to volume ratio etc when compared to bulk ZnS. Usually ZnS films can be prepared by numerous techniques such as molecular beam epitaxy (MBE), chemical vapour deposition (CVD), sputtering and chemical bath deposition (CBD). CBD has been proved to be the most suitable method to produce ZnS films for various applications because of its efficient, cost effective and large scale capability.

In 2011, Somayeh Nazerdeylami et al. synthesized ZnS: Mn+2 nanoparticles capped with PVP in aqueous solution by chemical method. Prepared samples were characterized by using UV-Visible spectroscopy, XRD and PL studies. The UV data reveals that the synthesized nanoparticles show absorption near 292 nm and also that the concentration of Mn does not alter the bang gap of nanoparticles. XRD studies show that the average particle size is 2 nm and ZnS nanoparticles cubic structure. PL studies performed at room temperature show the orange-red emission at 594 nm and its intensity increases with increase in Mn+2 ion concentration.

In 2010, Manoj et al. reported the study of energy transfer mechanism using different capping agents to intrinsic luminescent vacancy centers of ZnS. Co-precipitation method was used to synthesize nanoparticles of capped and uncapped ZnS. Sterically stabilized NPs were obtained using organic polymers: poly vinyl pyrrolidone, thioglycerol and 2-mercaptoethanol. TEM observation revealed that Monodispersed NPs were observed for both capped and uncapped ZnS nanopowders. Though, tendency of forming nanorod like structures existed for nanopowders of uncapped ZnS. X-ray diffraction pattern gave the size in between 1.95-2.20 nm for capped nanostructures and 2.2 nm for uncapped nanostructures. Emission intensity and Band gap were observed to be increased on addition of different capping agents in comparison to uncapped ZnS NPs. Overall result revealed that Capped ZnS NPs showed more pronounced energy transfer from capping layer to photoluminescent.

In 2010, Ram Kripal et al., prepared ZnS: Mn+2 by co-precipitation method and conducted their photo luminescent and photoconductivity properties. UV- visible spectra shows blue shift as compared to bulk counterpart. PL spectra show orange emission that varies with Mn+2 concentrations. The XRD studies estimated the size of nanoparticles to be around 2-4 nm. The TEM images overestimates the larger nanoparicle size due to drying step in sample preparation. The time resolved rise and decay of photocurrent indicates the anomalous behaviour during steady state illumination.

In 2010, Srivastava et al., made an attempt to study the photoconductivity and dark-conductivity characteristics of doped ZnS nanoparticles. Photoconductivity and dark-conductivity are measured at room temperature under visible illumination. The Mn-doped ZnS nanoparticles synthesized by co-precipitation technique are found to exhibit anomalous behaviour of photocurrent which decreases with increased intensity of illumination. At 5000 lux of illumination photocurrent is found to be even lower than the dark-current. The variation of photocurrent with applied voltage is super-linear. Structural studies using XRD and TEM have been performed.

In 2006, Ghosh et al. synthesized Polyvinyl Pyrrolidone (PVP) encapsulated Zinc Sulphide (ZnS) nanoparticles by adding measured amount of zinc acetate, thiourea and PVP into N, N-Dimethyl Formamide (DMF) medium with consistent stirring at 150 rpm. The resulted TEM image of ZnS NPs explained the effect of capping on size separation. It exhibited that PVP capped ZnS nanoparticles were mono dispersed in nature. Their size ranging within 2-3 nm matches with of XRD results. Whereas uncapped nanoparticles on the other hand were aggregated and were larger in sizes than capped ones. This explains the use of PVP as capping agent. Also Blue shift in absorption edge as compared to bulk ZnS clearly explained the quantum confinement effect within ZnS nanoparticles.

In 2006, Sarika Pandey et al. prepared Manganese doped ZnS nanoparticles capped with histidine molecule by co-precipitation reaction from the homogenous solution of zinc and manganese salts. The PL spectrum shows the emission peak of doped nanoparticles at around 590 nm. The XRD results calculated the average particle size of ZnS nanophosphor by Debye Scherrer’s formula to be of the order of 5-6 nm. A small angle X-ray study shows the maximum uniform particle size distribution of 3.5 nm for the prepared sample.

In 2006, Gilbert et al. combined real space Pair Distribution Function (PDF) analysis of nanoparticle structure with the particle size analysis (zetasizer) and FTIR to point out that the nature of surface solvent or ligand interactions will have an effect on the interior crystallinity of nanoparticles. The availability of particles with a variety of crystallinity provides a model system during which it’s possible to see the interior disorder effects of nanoparticle, where properties like mechanical stiffness and fluorescent quantum yield are affected. PDF analysis showed that samples of ZnS nanoparticle with similar mean diameters (3.2-3.6 nm) however synthesized and treated differently possess a dramatic range of interior disorder

In 2004, Manzoor et al. studied multi color emitting doped ZnS nanocrystals by making use of pyridine (P-ZnS) or Polyvinyl Pyrrolidone (PVPZnS) as capping agents via wet chemical methods. The PL studies showed that the emission related to dopant from P-ZnS nanocrystals are due to energy transfer during band-to-band excitation of the host lattice. Although, in the case of PVP-ZnS, sig