

# Use of Domestic Microwave Oven in the Preparation of Nanostructured Materials

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## Abstract

Preparation and characterization of nanostructured materials, possessing the structural features between those of atoms and the bulk materials, have attracted the attention of several researchers. A simple and highly useful method to prepare a variety of nanostructured materials is the microwave assisted solvothermal method. In that, use of domestic microwave oven is an interesting feature. In this article is made a nearly comprehensive review of various reports available on the preparation of nanostructured materials using the domestic (commercially available) microwave oven.

**Keywords:** Nanostructured materials; Nanopowders; Synthesis of nanomaterials; Solvothermal method; Characterization; Physicochemical properties

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## Introduction

Nanoscience is concerned with small-sized materials and systems or small structures with at least one dimension in the nanometer range whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes because of their small nanoscale size.

Ultrafine microstructures having an average phase (or grain or particle or crystallite) size in the order of a nanometer ( $\times 10^{-9}$  m) are classified as *nanostructured materials* or simply nanomaterials. That is, any solid material that contains grains or clusters below 100 nm, or layers or filaments of that dimension, can be considered to be nanostructured. Nanoparticle which is mostly crystalline is called *nanocrystal*.

Nanostructured surfaces (or coatings) are one dimensional in the nanoscale, *i.e.* only the thickness of the surface of an object is between 1 (0.15 after considering graphene) and 100 nm. Nanotubes are two dimensional in the nanoscale, *i.e.* the diameter of the tube is between 1 and 100 nm, its length could be much greater. Spherical nanoparticles are three dimensional in the nanoscale, *i.e.* the particle between 1 and 100 nm in each spatial dimension.

Owing to the *small size* of the building block (crystallite/particle/grain/phase) and *high surface-to-volume ratio*, these materials are expected to demonstrate unique mechanical, optical, electronic and magnetic properties. In general, the properties of nanostructured materials depend on: (i) fine grain size and size distribution (<100 nm); (ii) the chemical composition of the constituent phases; (iii) the presence of interfaces, more specifically, grain boundaries, heterophase interfaces, or the free surface; and (iv) interactions between the constituent domains.

So, preparation and characterization of nanostructured materials have attracted the attention of a large number of researchers for more than three decades. Nanomaterials, in general, have been prepared either by way of a top-down approach (a bulk material is reduced in size to nanoscale pattern) or a bottom-up approach (larger structure is built or grown atom by atom or molecule by molecule) <sup>[1-4]</sup>. A variety of nanomaterials have been prepared by the microwave assisted solvothermal method, a simple and highly useful method <sup>[5-23]</sup>.

The present author (along with his co-workers) has introduced the use of domestic microwave oven to further simplify the microwave assisted solvothermal method as well as to improve the quality of the nanomaterials prepared; and, there are now several reports available in the literature on the preparation of various nanostructured materials (as reaction products from suitable precursors in solution) by using the domestic (commercially available) microwave oven [24-58]. A nearly comprehensive review of these reports is made in this article.

### **Importance of Nanostructured Materials** [4,25,34,35,42-45,52,53,56,57]

Engineered nanomaterials, either by way of a top-down approach or a bottom-up approach, go beyond just a further step in miniaturization. They have broken a size barrier below which quantization of energy for the electrons in solids becomes relevant. The so-called *quantum size effect* describes the physics of electron properties in solids with great reductions in particle size. When the reduction from the bulk material (in three dimensions) is in all three dimensions, the material reduces to a point which is well known as *quantum dot*. It is called a nanoparticle or cluster and the state of matter around this size is referred to as *mesoscopic state*. A *nanoparticle* is considered as the one whose dimensions are large enough to exhibit properties that are significantly different from those in the bulk state.

Nanoscience is concerned with small-sized materials and systems or small structures with at least one dimension in the nanometer range, whose structures and components exhibit novel and significantly improved properties (physical, chemical and biological). Nanotechnology is the application of nanoscience to useful devices. Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form; but, material in nanometer scale may exhibit properties distinctively different from those of a single atom (molecule) and bulk matter with the same chemical composition. For example, crystals (crystallites) in the nanometer scale have a low melting point (the difference can be as large as 1000 °C) and reduced lattice constants. Crystal structures which are stable at elevated temperatures are stable at much lower temperatures in nanometer sizes; also, ferroelectrics and ferromagnetics may lose their ferroelectricity and ferromagnetism when the material particles are shrunk to the nanometer scale. Although bulk gold does not exhibit catalytic properties, Au nanocrystals demonstrate to be an excellent low temperature catalyst.

Nanoscience and nanotechnology have grown explosively in the last about three decades, because of the increasing availability of methods of synthesis of nanostructured materials as well as tools of characterization and manipulation. Basic structures of nanostructured materials are: *Nanoparticles* (Ultrafine solid particles on a nanoscale including nanopowders and nanocrystals); *Nanotubes* (Hollow nanoscale particles including nanotubes, nano horns and nano capsules); *Nanostructured materials* (Materials made of structural elements with dimensions in the nano range and which may form films or be free standing); and *Nanocomposites* (Mixtures of components with at least one of which has nanoscale dimensions). Interesting nanostructures including cube, rod, disk, wire, sphere, triangle, hollow sphere, core-shell structure, flower and dendrites, have been observed in transition metals, alloys, metal-oxides or semiconducting materials.

The nanometer sizes of materials make them with the following attributes:

#### (1) *Large fraction of surface atoms*

When a particle decreases in size, more atoms are found at the surface as compared with those inside. For example, a palladium cluster measuring 7 nm in size possesses 35 % of its atoms on its surface, at 5 nm in size 45 % of its atoms on its surface, and at 1.2 nm 76 % of its atoms on its surface. Hence nanomaterials have an extremely large surface area to volume ratio, resulting in more “surface”-dependent material properties. When the sizes of nanomaterials are comparable to the Debye length, the entire material will be affected by the surface properties of nanomaterials. Surface atoms are chemically more active as compared with interior atoms because they usually

have fewer adjacent coordinate atoms and more unsaturated or dangling bonds. For example, metallic nanoparticles can be used as very active catalysts.

### (2) *Spatial confinement or quantum effect*

A particle behaves as if it was free when the confining dimension is large as compared with the wavelength of the particle. The band gap remains at its original energy due to the continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically at the nanoscale, the energy levels become discrete. As a result, the band gap becomes size dependent. This ultimately results in a blue shift in optical illumination as the size of the particles decreases. For example, CdSe nanoparticles with different sizes possess different colors.

### (3) *Reduced imperfections*

Nanostructures and nanomaterials favour a self purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. The chemical stability may be enhanced and the mechanical properties of nanomaterials will be better than that of the bulk material. For example, carbon nanotubes have been reported to have a Young's modulus of  $1.8 \pm 0.9$  TPa, which is much higher than that of high-strength steel of  $\sim 200$  GPa.

Applications of nanostructures and nanomaterials are mainly based on their peculiar physical properties, their huge surface area, and the small size that offers additional possibilities for accommodating multiple functionalities, *e.g.*, nanomaterials for drug delivery. Catalysts are among the first industrial nanotechnologies applications. Nanoparticles and nanostructured materials offer new ways of designing and controlling catalytic functions, including the provision of enhanced activity and selectivity for target reactions. The number of atoms increases as the surface area increases and more electrons/ions are available for catalytic reaction.

The most important and flexible energy technology is the direct conversion of sunlight to electrical energy by the use of nanostructured photovoltaic devices. Existing photovoltaic devices are limited by low conversion efficiency and high cost. But, the use of nanostructured quantum dots have a potential for cost effectiveness. They absorb the light in broader wavelength of the spectrum. Heterostructured absorber layers will increase the efficiency of the cell, which leaves us an option of using lesser quality materials and thus reducing the cost.

Photoexcitation of the electrons in photoactive semiconductors mainly occurs at the surface. Therefore nanomaterials are more reactive than bulk materials in catalytic processes. Nanostructured materials find application in generation of hydrogen by the photocatalytic conversion of oxygen and hydrogen by using nanostructured catalyst or nanoscale additives. Also, they find applications in flexible solar cells, portable fuel cells and lithium ion batteries which are used in cell phones and PCs, and in cordless power tools, proving the technology to power hybrid and electric vehicles.

Other application of nanotechnology includes the use of nanomembranes, zeolites and nanoporous polymers for water purification and desalination. Many technologies have been explored to fabricate nanostructures and nanomaterials. Different fabrication and processing techniques may be grouped into top-down and bottom-up approaches, and spontaneous and forced processes.

## **Microwave Assisted Synthesis of Nanoarchitectures** [7,14,22]

One of the simple methods to prepare a variety of nanostructured materials is the microwave assisted solvothermal (including the use of water solvent) method. It is well known that the interaction of dielectric materials, liquids or solids with microwave leads to what is generally known as dielectric heating. The frequencies allotted for microwave assisted heating are 918 MHz and 2.45 GHz with the latter frequency being most often used. The latter is also applied in domestic (commercially available in a great number of shops with low cost) microwave ovens.

Compared with conventional heating methods (like that involving the use of an electric furnace or oil bath, which heats the walls of the reactor and then the reactants by convection or conduction), microwave assisted heating (rapid volumetric heating) presents a more rapid and simultaneous environment for the formation of nanoparticles due to the rapid and homogeneous heating effects of microwave irradiation. Therefore, microwave assisted heating method has the advantages of short reacting time, high energy efficiency, and the ability to induce the formation of particles with small size, narrow size distribution, and high chemical (phase) purity. Moreover, microwave-assisted methods can be considered as a promising green strategy to prepare the nanostructured materials and architectures.

When materials are irradiated with microwaves they absorb energy from the microwave field. Power absorbed,  $P$ , is given as:

$$P = 2\pi f \epsilon_0 \epsilon_r (\tan\delta) |E_i|^2$$

The frequency ( $f$ ) and amplitude ( $|E_i|$ ) of the microwaves are instrumental parameters (controllable) while the dielectric constant ( $\epsilon_r$ ) and dielectric loss tangent ( $\tan\delta$ ) are material parameters. In a given experimental setup (where  $|E_i|$  and  $f$  are held constants),  $P$  is determined by  $\epsilon_r$  and  $\tan\delta$ . Therefore, when a mixture of two materials A and B of different dielectric constants ( $\epsilon_A$  and  $\epsilon_B$ ) is exposed to the microwave field, the material with higher value of  $\epsilon_r$  absorbs energy preferentially and gets heated rapidly compared to the other.

A precursor material can be chosen such that it has a high value of  $\epsilon_r$  and decomposes by preferential microwave absorption to yield the desired material. The liquid chosen should be one which does not decompose before the normal boiling temperature. Also, the resulting material (product) should not be soluble in it. The insoluble material product, however, should be prevented from growing into large particles. This is accomplished by the addition of a suitable capping agent (or surfactant) to the initial solution. Also, it is necessary to control the microwave power so that the solvent does not boil violently.

The  $\tan\delta$  and  $\epsilon_r$ , in combination, can show the ability of a solvent molecule to convert the electromagnetic energy into thermal energy at a given microwave frequency and temperature; which is an immediate estimation of heat at a specific level of polarization. Water has a very high dipole moment which makes it one of the best solvents for the microwave assisted reactions. During the formation of the nanoparticles under microwave irradiation, the solvents have important influence on the size and morphology of the final products. In different solvents, the collision rate between reactant molecules, the heating rate, and the temperature of the reaction are different. As a result, nanoparticles with different sizes and morphologies could be obtained by using different solvents. Availability of several solvents and their smart combinations will provide maximum freedom for the fast synthesis of a great number of nanostructured materials; and can control over the chemical composition, structure, size, morphology, and self-assembly.

The exact interaction mode of microwave radiation with reaction materials is not yet perfectly understood. However, the parameters like material's dielectric properties, emissivity, intensity of applied microwave field, volume of reaction material, geometry of reaction vessel and reaction time can decide the dimension of microwave heating. It is believed that the reaction material acknowledges the microwave energy followed by the electronic relaxation; and this phenomenon involves the dipolar polarization or ionic conduction mechanism, which relies upon the material and the reaction solvent; therefore a rapid heating of reaction mixture takes place.

Materials with mobile electric charges (like polar molecules or conducting ions in a solid/solvent) can be heated, in general, using microwaves. The polar molecules (like water molecules), during microwave heating, try to orientate with the alternating electric field (which is rapidly changing). The heat is generated by the dipolar polarization mechanism (that is, by the friction, rotation, and collision of molecules). The ions present in the solution, based on the electric field orientation, will move through the solution in constantly changing directions; and, due to friction and collision, this will cause a local temperature rise.

Microwave heating can be done in two ways: pulsed microwave heating and continuous microwave heating. It is possible that the quality of nanoparticles prepared by using pulsed microwave heating can be better than that prepared by using continuous microwave heating. Shen *et al.* [59] have investigated the difference between these two microwave heating modes with the preparation of WC nanoparticles using  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$  in mixed solvents of 2-propanol and water. The pulsed microwave heating produced WC nanoparticles with an average particle size of 21.4 nm with a 15s-on and 15s-off heating mode for 20 times; however, the particle size increased to 35.7 nm by the continuous microwave heating for 5 min.

### ***The Actual Method Using a Domestic Microwave Oven***

This method can be adopted by using a simple domestic microwave oven (normally with pulsed microwave) also. The present author and his group of researchers have proposed this simple way of doing it and have successfully prepared several high quality nanoparticles (as reaction products from suitable precursors) and reported [24-58]. The following is the actual method of doing it.

Required amounts of the precursors are dissolved in the solvent and kept in the domestic microwave oven. The oven is operated normally with a frequency of 2.45 GHz and power 800/840 W. Microwave irradiation is done till the solvent is evaporated completely. The colloidal precipitate obtained is cooled and washed several times with distilled water and then with acetone to remove the organic impurities present, if any. The sample is then dried in atmospheric air and collected as the yield. If necessary, annealing at the required temperature for the required duration can be done to achieve the required result. X-ray diffraction analysis and thermogravimetric analysis can be carried out (respectively) to understand the phase purity and crystallinity, and to fix the temperature for annealing (if required).

### ***X-ray Powder Diffraction Analysis*** [60,61]

Recording the X-ray diffraction (XRD) pattern using an automatic X-ray powder diffractometer allows us to deduce the distribution of atoms in a crystalline material by using the Bragg's law:  $2d \sin\theta = n\lambda$ , where  $d$  is the inter planar spacing and  $\lambda$  is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle  $2\theta$  and the specimen's orientation. Average particle size ( $D$ ) can also be estimated from the peak width using the Scherrer's formula:  $D = K\lambda/(\beta \cos\theta)$ , where  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum (FWHM) of the X-ray reflection intensity expressed in radians,  $K$  is the Scherrer's constant (0.96) and  $\theta$  is the diffraction angle. A comparison of the recorded XRD pattern and the available XRD database, namely, JCPDS File provides the phase identity. Crystal structure, lattice parameters and particle/crystallite size can be determined by using the powder X-ray diffraction technique. For further details about X-ray diffraction analysis, the books by Cullity [60] and Ladd, and Palmer [61] can be referred.

### ***Thermogravimetric Analysis*** [62]

A thermogravimetric (TG/DTA) analyzer is used to measure the amount and rate of weight change in a sample material as a function of time or temperature in inert or oxidative atmosphere. This measurement is used for determining the conditions of melting, crystallization, glass transition temperature, polymorphism, kinetic studies, curing reaction, *etc.* Endothermic and exothermic effects and isothermal cure kinetics studies can also be made to understand the melting point, decomposition, structural phase transition, *etc.* This is used to determine the temperatures of endothermic and exothermic transitions at temperatures up to 1500 °C. Analysis is normally carried out by raising the temperature of the sample gradually and plotting weight percentage against temperature. Further details about thermogravimetric analysis can be had from the book by Brown [62].

The simple solvothermal method using the domestic microwave oven (SSM-DMO, mentioned as Mahadevan's method in some reports <sup>[58,63]</sup>), described above, have been used to prepare several simple compound nanocrystals, several two-component (single phased as well as multiphased) nanocomposites and prominent nanophases of ferric oxide and nickel sulfide. Doped nanocrystals and nanocomposites, in many cases, have also been prepared by this method and characterized.

### Simple Compound Nanocrystals

Pure (un-doped) and doped (in many cases) simple compound nanocrystals like ZnS, CdS, ZnO, Cd(OH)<sub>2</sub>, CdO, Ni(OH)<sub>2</sub>, NiO, Mn<sub>3</sub>O<sub>4</sub>, CdCO<sub>3</sub>, PbS, PbO, CdSe, MnCO<sub>3</sub>, CuS, CuO, SnO<sub>2</sub>, MnS<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -NiS have already been reported to be prepared by the SSM-DMO. The authors have found that this SSM-DMO is an economical, suitable and scalable one to prepare these proposed nanocrystals with reduced size, phase purity and homogeneity.

The present author and his co-workers <sup>[28,32-35,37-39]</sup> have prepared pure and Mn<sup>2+</sup>/Mg<sup>2+</sup> doped ZnS nanocrystals by the SSM-DMO using different precursors (zinc acetate or zinc chloride as the Zn<sup>2+</sup> source; sodium sulfide or thiourea as the S<sup>2-</sup> source; manganese(II) acetate for Mn<sup>2+</sup> doping; and magnesium sulfate heptahydrate for Mg<sup>2+</sup> doping) and different solvents (distilled water or ethylene glycol) and have characterized the as-prepared samples structurally, optically and electrically; the as-prepared samples have shown homogeneity, phase purity and reduced crystallite size up to about 2 nm. Saravanan *et al* <sup>[39]</sup> have presented a comparative analysis of the ZnS quantum dots (QDs) synthesized by using the conventional and microwave heating (SSM-DMO) methods using zinc acetate and sodium sulfide reactants; the crystallite sizes observed by them have indicated the superiority of the SSM-DMO (the crystallite size of QDs prepared by the SSM-DMO is at least 30 times smaller than that of QDs prepared by the conventional heating method).

The present author and his co-workers <sup>[26,27,34,37,38,40,41]</sup> have prepared pure and Mn<sup>2+</sup> doped CdS nanocrystals by the SSM-DMO using different precursors (cadmium chloride or cadmium acetate as the Cd<sup>2+</sup> source; thiourea or sodium sulfide as the S<sup>2-</sup> source; and manganese(II) acetate for Mn<sup>2+</sup> doping) and different solvents (distilled water or ethylene glycol) and have characterized the as-prepared samples structurally, optically and electrically; the as-prepared samples have shown homogeneity, phase purity and reduced crystallite size up to about 4 nm. Priya *et al* <sup>[40]</sup> have studied the effect of using excess of S<sup>2-</sup> source (thiourea) in the preparation of CdS nanocrystals (with the precursors, *viz.* cadmium chloride and thiourea dissolved in distilled water in different molar ratios, *viz.* 1:1, 1:2 and 1:3); and have found that increase of crystallite size, optical bandgap energy and sulfur content are possible with the increase of thiourea concentration in the preparation of CdS nanocrystals. Pure and Pb<sup>2+</sup> doped CdS nanocrystals have also been prepared by the SSM-DMO using cadmium acetate (Cd<sup>2+</sup> source), thiourea (S<sup>2-</sup> source) and lead(II) acetate (for Pb<sup>2+</sup> doping) as the precursors and ethylene glycol as the solvent; the average crystallite sizes observed to be varied from 5.52 to 6.27 nm <sup>[63]</sup>. The electrical measurements made on pelletised samples have indicated that the polarization mechanism is mainly contributed by the space charge polarization <sup>[63]</sup>.

The present author and his co-workers <sup>[24-28,32,33,35,55,56]</sup> have prepared pure and Mn<sup>2+</sup>/Mg<sup>2+</sup> doped ZnO nanocrystals by the SSM-DMO using different precursors (zinc acetate or zinc chloride as the Zn<sup>2+</sup> source; urea as the O<sup>2-</sup> source; manganese(II) acetate for Mn<sup>2+</sup> doping; and magnesium sulfate heptahydrate for Mg<sup>2+</sup> doping) and ethylene glycol as the solvent; and the as-prepared samples annealed at 100/200 °C (to improve ordering and phase purity) have been characterized structurally, optically and electrically. The crystallite sizes obtained have been found to be lower when compared to that observed for the ZnO nanocrystals prepared by many other methods.

Nanocrystals of Cd(OH)<sub>2</sub> and CdO (pure and doped/co-doped with Mn<sup>2+</sup> and Pb<sup>2+</sup>) have been prepared by the SSM-DMO by the present author and his co-workers <sup>[24,25,30,31,47,56]</sup> using cadmium acetate (Cd<sup>2+</sup> source), urea ((OH)<sup>-</sup>/O<sup>2-</sup> source), manganese(II) acetate (for Mn<sup>2+</sup> doping) and lead(II) acetate (for Pb<sup>2+</sup> doping) as the precursors and ethylene glycol as the solvent; the as-

prepared sample has been found to be  $\text{Cd}(\text{OH})_2$ , and annealing the as-prepared sample at  $450\text{ }^\circ\text{C}$  has been found to be required to get the  $\text{CdO}$  nanocrystals with high phase purity. The  $\text{CdO}$  nanocrystals prepared have shown homogeneity, phase purity and reduced crystallite size (up to about 27 nm); the average crystallite size observed for the  $\text{Cd}(\text{OH})_2$  nanocrystals is up to about 11 nm [24,25,31,56].

Nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ) and nickel oxide ( $\text{NiO}$ , Bunsenite) nanocrystals have been prepared by the SSM-DMO using nickel acetate ( $\text{Ni}^{2+}$  source) and urea ( $(\text{OH})/\text{O}^{2-}$  source) dissolved (in 1:3 molar ratio) in ethylene glycol [44]. The as-prepared sample has been found to be phase pure  $\text{Ni}(\text{OH})_2$  (with an average crystallite size of 1.7 nm); and the phase pure  $\text{NiO}$  (with an average crystallite size of 8.9 nm) could be got from the above as-prepared sample ( $\text{Ni}(\text{OH})_2$ ) on annealing at  $300\text{ }^\circ\text{C}$  [44].

Pure and  $\text{Zn}^{2+}/\text{S}^{2-}$  doped  $\text{Mn}_3\text{O}_4$  (Hausmannite) nanocrystals have been prepared by the SSM-DMO using manganese(II) acetate ( $\text{Mn}^{2+}$  source), urea ( $\text{O}^{2-}$  source), zinc acetate (for  $\text{Zn}^{2+}$  doping) and thiourea (for  $\text{S}^{2-}$  doping) dissolved (in 1:3 molar ratio) in ethylene glycol [36,42-44,47,58]. High phase pure  $\text{Mn}_3\text{O}_4$  (with an average crystallite size of 14.5 nm) could be obtained from the as-prepared sample, on annealing at  $400\text{ }^\circ\text{C}$  [44].

Pure and  $\text{S}^{2-}$  doped  $\text{CdCO}_3$  (Otavite) nanocrystals have been prepared by the SSM-DMO using cadmium acetate ( $\text{Cd}^{2+}$  source), urea ( $(\text{CO}_3)^{2-}$  source) and thiourea (for  $\text{S}^{2-}$  doping) dissolved (in 1:3 molar ratio) in ethylene glycol [43,58]. The three samples prepared have been found to exhibit diamagnetism and the average crystallite sizes observed are: 6.58 nm for the pure  $\text{CdCO}_3$ , 6.37 nm for the 2.5 wt.%  $\text{S}^{2-}$  doped  $\text{CdCO}_3$ , and 8.85 nm for the 5 wt.%  $\text{S}^{2-}$  doped  $\text{CdCO}_3$  [43,58].

Saravanan *et al* [54] have prepared the nanocrystals of  $\text{PbS}$  doped/co-doped with  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  by the SSM-DMO using lead(II) acetate ( $\text{Pb}^{2+}$  source), thiourea ( $\text{S}^{2-}$  source), manganese(II) acetate (for  $\text{Mn}^{2+}$  doping) and cadmium acetate (for  $\text{Cd}^{2+}$  doping) as the precursors and ethylene glycol as the solvent; the average crystallite sizes observed are within 18 – 33 nm, and the optical bandgap energies observed are within 2.025 – 2.235 eV. They have found that the electrical conductivities observed exhibit the Arrhenius behavior with two different activation energies, and the electrical conduction is the combined effect of thermionic emission across the grain boundaries and bipolaron hopping [54].

Pure and  $\text{Mn}^{2+}$  doped  $\text{PbO}$  nanocrystals have been prepared by the SSM-DMO using lead(II) acetate ( $\text{Pb}^{2+}$  source), urea ( $\text{O}^{2-}$  source) and manganese(II) acetate (for  $\text{Mn}^{2+}$  doping) as the precursors and ethylene glycol as the solvent; the as-prepared samples were annealed at  $100\text{ }^\circ\text{C}$  to improve the ordering; and the average crystallite sizes have been observed to be within 29.5 – 34.5 nm [29]. The optical bandgap energy has been observed to be reduced on doping; and the photoconductivity and dielectric measurements made on pelletised samples have indicated positive photoconductive nature and the importance of space charge contribution in the polarizability and charge transport process [29].

Nanostructured hexagonal cadmium selenide ( $\text{CdSe}$ ) has been prepared by the SSM-DMO using cadmium acetate ( $\text{Cd}^{2+}$  source) and sodium selenite ( $\text{Se}^{2-}$  source) taken in 2:1 molar ratio as the precursors and mixture of distilled water and ethylene glycol as the solvent, and annealing the as-prepared sample at  $100\text{ }^\circ\text{C}$ ; the average crystallite size has been observed to be 10 nm [64]. The optical bandgap energy has been observed to be 3 eV (blue shifted) and photoluminescence (PL) emission spectrum exhibits sharp intense peaks at 425 and 466 nm; also, the material is thermally stable up to  $650\text{ }^\circ\text{C}$  [64].

Madhu and Mahadevan [46] have investigated the difference in considering two different molar ratios (1:1 and 1: 3) of the precursors (manganese chloride and urea dissolved in ethylene glycol solvent) used for the preparation of  $\text{MnCO}_3$  nanocrystals by the SSM-DMO. They have observed the crystallite sizes as 29 nm for the 1:1 ratio sample and 20 nm for the 1:3 ratio sample; also, observed higher dielectric parameters (dielectric constant, dielectric loss factor and AC

electrical conductivity) observed for the 1:3 ratio sample than that observed for the 1:1 ratio sample <sup>[46]</sup>.

Pure and Mn<sup>2+</sup> doped CuS (hexagonal phase) and CuO (monoclinic phase) have been prepared by the SSM-DMO using copper(II) acetate (Cu<sup>2+</sup> source), urea (O<sup>2-</sup> source), thiourea (S<sup>2-</sup> source) and manganese(II) acetate (for Mn<sup>2+</sup> doping) as the precursors and distilled water as the solvent; and the as-prepared samples were annealed at 200 °C to improve the ordering and phase purity <sup>[65-67]</sup>. The samples prepared have been found to be paramagnetic; and the electrical measurements made on pelletised samples have shown the importance of space charge polarization and occurrence of nanoconfined states contributing substantially to the electrical properties <sup>[65-67]</sup>.

Pure and Cu<sup>2+</sup> doped SnO<sub>2</sub> nanocrystals have been prepared by the SSM-DMO using stannous chloride (Sn<sup>2+</sup> source), urea (O<sup>2-</sup> source) and cupric acetate (for Cu<sup>2+</sup> doping) as the precursors and ethylene glycol as the solvent; the ordering and phase purity have improved on annealing the as-prepared samples at 500 °C <sup>[68-70]</sup>. The samples prepared have been characterized structurally, optically and electrically; shifting of PL emission peak positions have been observed due to Cu<sup>2+</sup> doping and coupled with the variation of optical bandgap energies <sup>[68-70]</sup>.

Pure and Zn<sup>2+</sup>/O<sup>2-</sup> doped MnS<sub>2</sub> have been prepared by the SSM-DMO using manganese(II) acetate (Mn<sup>2+</sup> source), thiourea (S<sup>2-</sup> source), zinc acetate (for Zn<sup>2+</sup> doping) and urea (for O<sup>2-</sup> doping) as the precursors and ethylene glycol as the solvent; the nanopowders obtained are spherical in shape and well crystalline <sup>[42,45]</sup>. The prepared samples have been characterized structurally, optically, electrically and magnetically; and all the samples have been found to be paramagnetic <sup>[42,45]</sup>.

Pure and Sn<sup>2+</sup>/Pb<sup>2+</sup> doped Cr<sub>2</sub>O<sub>3</sub> nanocrystals have been prepared by the SSM-DMO using chromium acetate (Cr<sup>3+</sup> source), urea (O<sup>2-</sup> source), stannous chloride (for Sn<sup>2+</sup> doping) and lead(II) acetate (for Pb<sup>2+</sup> doping) as the precursors and ethylene glycol as the solvent; the as-prepared samples have been annealed at 700 °C to improve the ordering and phase purity; and the average crystallite size has been found to be reduced from 24 nm (for the pure Cr<sub>2</sub>O<sub>3</sub> nanocrystal) to 10 nm by Sn<sup>2+</sup> doping whereas it is increased to 29 nm by Pb<sup>2+</sup> doping <sup>[71,72]</sup>. The antibacterial activity (against *Klebsiella Pneumonia*) of the pure Cr<sub>2</sub>O<sub>3</sub> nanocrystal has been observed to be higher than that observed for the Pb<sup>2+</sup> doped Cr<sub>2</sub>O<sub>3</sub> nanocrystals <sup>[72]</sup>.

Pure and Zn<sup>2+</sup>/Cd<sup>2+</sup>/Mn<sup>2+</sup>/Ni<sup>2+</sup> doped Co<sub>3</sub>O<sub>4</sub> nanocrystals have been prepared by the SSM-DMO using cobalt acetate (single source material for Co<sub>3</sub>O<sub>4</sub>), cadmium acetate (for Cd<sup>2+</sup> doping), zinc acetate (for Zn<sup>2+</sup> doping), manganese(II) acetate (for Mn<sup>2+</sup> doping) and nickel acetate (for Ni<sup>2+</sup> doping) as the precursors and ethylene glycol as the solvent <sup>[52]</sup>. As prepared pure Co<sub>3</sub>O<sub>4</sub> nanocrystalline sample was calcined at 100, 200, 300 and 400 °C to understand the phase evolution; olive green colored as-prepared nanopowder, on calcination, changed to black colored powder depending on the calcination temperature; and the XRD, Fourier transform infrared (FTIR) and Raman spectral analyses have confirmed the good crystallinity and phase purity of the sample calcined at 400 °C <sup>[52]</sup>.

Transmission electron microscopic (TEM) image of Co<sub>3</sub>O<sub>4</sub> nanopowder calcined at 400 °C shows well faceted particles without amorphous secondary phases segregated at the grain boundaries; and the average particle size observed through TEM analysis is 33.59 nm <sup>[52]</sup>. The higher optical bandgap energies observed (the low and high values are 1.55 and 2.46 eV, respectively) (blue shifted) have indicated the entry of this sample into the quantum confinement regime which allows to have a fine tuning on their material properties; the magnetic study has confirmed the antiferromagnetic Co<sub>3</sub>O<sub>4</sub> nanoparticles possessing considerable magnetization below and above Neel temperature <sup>[52]</sup>. Zn<sup>2+</sup>/Cd<sup>2+</sup>/Mn<sup>2+</sup>/Ni<sup>2+</sup> doped (with 2.5 and 5.0 wt. %) Co<sub>3</sub>O<sub>4</sub> nanoparticles (the as-prepared calcined at 400 °C) have been found to tune significantly the optical (optical absorption and PL emission), magnetic and electrical properties; and the particle sizes decrease on doping with these transition metal ions <sup>[52]</sup>.

Ramya and Mahadevan<sup>[48,50,51,57]</sup> have prepared spherical shaped pure and Mn<sup>2+</sup>/Co<sup>2+</sup>/Cu<sup>2+</sup>-doped (with two concentrations in each case: 1 and 2 at.%)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Hematite) nanocrystals by the SSM-DMO using ferric chloride (Fe<sup>3+</sup> source), urea (O<sup>2-</sup> source), manganese(II) chloride (for Mn<sup>2+</sup> doping), cupric chloride (for Cu<sup>2+</sup> doping) and cobaltous chloride (for Co<sup>2+</sup> doping) dissolved (in 1:3 molar ratio) in ethylene glycol; high phase purity could be obtained by annealing the as-prepared sample at 700 °C. Grain size has been found to increase from 36 - 42/46/43 nm as a result of increase in the Mn<sup>2+</sup>/Co<sup>2+</sup>/Cu<sup>2+</sup> content from 0 – 2 at.% indicating the presence of Mn<sup>2+</sup>/Co<sup>2+</sup>/Cu<sup>2+</sup> ions in hematite. It has been found that the iron content increases while the oxygen content decreases indicating the creation of oxygen vacancies due to Mn<sup>2+</sup>/Co<sup>2+</sup>/Cu<sup>2+</sup>-doping<sup>[50,57]</sup>.

Their XRD, energy dispersive X-ray absorption (EDX), TEM and FTIR analyses have indicated that hematite nanocrystals prepared are with good crystallinity, morphological homogeneity, reasonably reduced grain size and high phase purity; their optical absorption and diffuse reflectance spectral analyses have indicated that the Mn<sup>2+</sup>/Co<sup>2+</sup>/Cu<sup>2+</sup>-doped hematite nanocrystals have higher ability to reflect light and lower ability to absorb visible light than do the pure hematite nanocrystals which could be understood as mainly due to the anisotropic effects due to Mn<sup>2+</sup>/Co<sup>2+</sup>/Cu<sup>2+</sup>-doping<sup>[50,57]</sup>. Their magnetic measurements made at room temperature have indicated significant improvement in the ferromagnetic order which could be understood as due to the creation of oxygen vacancies and the magnetocrystalline anisotropic effects due to doping; their AC electrical measurements made at various temperatures (40 -130 °C) and frequencies (100 Hz - 1 MHz) have indicated a normal electrical behavior; and it has been understood that space charge contribution plays an important role in the charge transport process and polarizability in the case of almost all the seven nanocrystals studied by them<sup>[50,57]</sup>.

Pure and Cd<sup>2+</sup>/Fe<sup>3+</sup>/O<sup>2-</sup> doped  $\alpha$ -NiS nanoparticles have been prepared by the SSM-DMO using nickel chloride (Ni<sup>2+</sup> source), thiourea (S<sup>2-</sup> source), cadmium chloride (for Cd<sup>2+</sup> doping), ferric chloride (for Fe<sup>3+</sup> doping) and urea (for O<sup>2-</sup> doping) as the precursors and ethylene glycol as the solvent; and the structural, optical, electrical and magnetic properties of the as-prepared nanoparticles annealed at 700 °C (to get the high phase pure nanoparticles) have been investigated<sup>[49,53]</sup>. Scanning electron microscopic (SEM), TEM and atomic force microscopic (AFM) analyses have indicated that the nanoparticles formed are agglomerative, spherical in shape and homogeneous; the particle sizes obtained are within 15 - 20.7 nm; and the EDX spectra have indicated the incorporation of impurities added in the host matrix of doped samples. UV-Vis absorption peaks have been found to blue-shift when compared to that of the bulk NiS (band gap energy, E<sub>g</sub> = 2.1 eV) as well as exhibit grain size dependence; decrease of particle size increases the E<sub>g</sub> of nanoparticles indicating the quantum confinement effect<sup>[53]</sup>.

Doping increases the PL yield (O<sup>2-</sup> doping increases in a better way than the others); doping leads to reduction of ferromagnetic order, which is understood as due to improvement in coordination of surface spins caused by doping (Fe-doping retains some ferromagnetic order when compared to others). All the electrical parameters have been found to increase with increase in doping concentration at all temperatures and frequencies for all the three dopants considered; and the variation of electrical parameters (X =  $\sigma_{dc} / \epsilon' / \epsilon'' / \tan\delta / \sigma_{ac}$ ) can be stated as: X (Pure) < X (Cd-doped) < X (Fe-doped) < X (O-doped). The results observed have indicated that O<sup>2-</sup> (anionic) doping makes it a better electrochemical sensing performer than the Cd<sup>2+</sup> and Fe<sup>3+</sup> (cationic) doping<sup>[53]</sup>.

When grain size is smaller than the electron mean free path, grain boundary scattering dominates and hence the electrical resistivity is increased; higher electrical resistivity observed indicates that grain boundary scattering may play an important role in the charge transport process; and low dielectric constant values observed for nanocrystals indicate that the polarization mechanism in nanocrystals considered can be mainly due to the space charge polarization. It is generally accepted that smaller the particle size higher the lattice defects, and it is suggested that the lattice defects form acceptor or donor like levels in the forbidden energy gap and act as trapping

centers for the charge carriers which affect the electrical behavior; so, the nickel vacancies and interstitial sulfur act as acceptors while the sulfur vacancies and interstitial nickel act as donors <sup>[53]</sup>.

### Two-component Nanocomposites

Pure and doped (in many cases) two-component nanocomposites like ZnO-CdO, ZnO-CdS, ZnS-ZnO, ZnS-CdS, MnS<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub>, CdCO<sub>3</sub>-Mn<sub>3</sub>O<sub>4</sub>, Ni(OH)<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub>, CdS-MnS<sub>2</sub>, CdO-Mn<sub>3</sub>O<sub>4</sub>, CuO-CuS and SnO<sub>2</sub>-ZnO have already been reported to be prepared by the SSM-DMO and characterized. In all these cases, the authors have found that this SSM-DMO is an economical, suitable and scalable one to prepare their proposed nanocomposites with reduced size, phase purity and homogeneity. In the case of non-isomorphous systems, multiphased nanocomposites could be obtained.

The present author and his co-workers <sup>[24,25]</sup> have prepared ZnO-CdO nanocomposites (Zn<sub>x</sub>Cd<sub>1-x</sub>O with x = 1.0, 0.8, 0.6, 0.4, 0.2 and 0.0) by the SSM-DMO and characterized. Zinc acetate (Zn<sup>2+</sup> source), cadmium acetate (Cd<sup>2+</sup> source) and urea (O<sup>2-</sup> source) were used as the precursors and ethylene glycol as the solvent; the as-prepared samples were annealed up to 450 °C to have good phase purity and ordering. The average crystallite (grain) sizes of the nanocomposites prepared have been found to be within the range of 27.03 – 46.28 nm; and the optical bandgap energies are within the range of 2.24 – 3.06 eV, which indicates a significant reduction in bandgap energy when compared to that observed for thin films <sup>[24]</sup>.

(ZnO)<sub>x</sub>(CdS)<sub>1-x</sub> (with x = 1.0, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.0) nanocrystals have been prepared by the SSM-DMO and the as-prepared samples were annealed at 100 °C (to improve the ordering); zinc acetate (Zn<sup>2+</sup> source), cadmium acetate (Cd<sup>2+</sup> source), urea (O<sup>2-</sup> source) and thiourea (S<sup>2-</sup> source) were used as the precursors and distilled water as the solvent <sup>[26,27]</sup>. The average crystallite sizes observed are within the range of 1.49 – 13.25 nm; the AC electrical measurements made on pelletised samples at different temperatures (in the range of 40 – 150 °C) with a fixed frequency of 1 kHz have indicated that all the seven nanocrystals prepared exhibit the possible occurrence of nano-confined state <sup>[26]</sup>. The optical bandgap energies have been observed to be in the range of 2.53 – 4.69 eV; photoluminescence emission spectra have shown five prominent peaks; and the samples have been found to exhibit positive photoconductive nature <sup>[27]</sup>.

Un-doped and doped (with Mn<sup>2+</sup>/Mg<sup>2+</sup>) nanocrystals of ZnS<sub>x</sub>O<sub>1-x</sub> (with x = 1.0, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.0) have been prepared by the SSM-DMO using zinc acetate (Zn<sup>2+</sup> source), manganese(II) acetate (for Mn<sup>2+</sup> doping), magnesium sulphate heptahydrate (for Mg<sup>2+</sup> doping), urea (O<sup>2-</sup> source) and thiourea (S<sup>2-</sup> source) as the precursors and ethylene glycol as the solvent; the as-prepared samples were annealed at 200 °C to improve the ordering <sup>[32,33,35]</sup>. The average crystallite sizes observed are within the range of 1.44 – 17.31 nm; the AC and DC electrical measurements made on pelletised samples at various temperatures (in the range of 40 – 150 °C) have indicated the importance of space charge contribution in the polarizability and charge transport process <sup>[32,33,35]</sup>.

The present author and his co-workers <sup>[34,37,38,41]</sup>, by the SSM-DMO, have prepared the quantum dots of Zn<sub>1-x</sub>Cd<sub>x</sub>S (un-doped and doped with Mn<sup>2+</sup>) with x = 0.0, 0.25, 0.5, 0.75 and 1.0. Zinc acetate (Zn<sup>2+</sup> source), cadmium acetate (Cd<sup>2+</sup> source), manganese(II) acetate (for Mn<sup>2+</sup> doping) and thiourea (S<sup>2-</sup> source) were used as the precursors and ethylene glycol as the solvent; and the as-prepared samples were annealed at 100 °C to improve the ordering. The average crystallite sizes observed are within the range of 1.283 – 1.508 nm; the optical bandgap energies observed are within the range of 2.442 – 3.878 eV, nearly matching with the DC activation energies obtained (within the range of 2.413 – 3.748 eV) <sup>[34,37]</sup>. The dielectric constant and charge confinement properties of the prepared quantum dots have been shown to have fine tuned by choosing the appropriate composition and crystallite size as required for specific applications <sup>[34,38]</sup>. It has been found that the Zn<sub>1-x</sub>Cd<sub>x</sub>S nanocrystals offer high luminescent quantum yields with narrow emission spectral widths; the optical emission properties can be tuned from 440 nm (blue emission) to 575 nm (orange emission). Moreover, the electrical impedance analysis indicates that the Zn<sub>1-x</sub>Cd<sub>x</sub>S

nanocrystals exhibit negative temperature coefficient of resistance; the AC electrical conductivities of the three mixed systems (nanocomposites) have been found to be higher than that of ZnS and CdS nanocrystals<sup>[41]</sup>.

CdO and Mn<sub>3</sub>O<sub>4</sub> are non-isomorphous systems and thereby preparation of monophased nanocomposite based on these systems may not be possible. Deepa and Mahadevan<sup>[47]</sup> could prepare the multiphased (CdO)<sub>0.5</sub>(Mn<sub>3</sub>O<sub>4</sub>)<sub>0.5</sub> nanocomposite by the SSM-DMO using cadmium acetate (Cd<sup>2+</sup> source), manganese(II) acetate (Mn<sup>2+</sup> source) and urea (O<sup>2-</sup> source) as the precursors and ethylene glycol as the solvent; they found that the as-prepared sample requires annealing at 300 °C to attain high phase purity and homogeneity of the particle morphology. The average crystallite size has been found to be 8.15 nm.

Pure and Zn<sup>2+</sup> doped (MnS<sub>2</sub>)<sub>x</sub>(Mn<sub>3</sub>O<sub>4</sub>)<sub>1-x</sub> (with x = 0.0, 0.25, 0.5, 0.75 and 1.0) nanocomposites (multiphased) have been prepared (by the SSM-DMO) using manganese(II) acetate (Mn<sup>2+</sup> source), urea (O<sup>2-</sup> source), thiourea (S<sup>2-</sup> source) and zinc acetate (for Zn<sup>2+</sup> doping) as the precursors and ethylene glycol as the solvent; the nanopowders obtained are spherical in shape and well crystalline, and the average crystallite sizes obtained are within the range of 19 – 43 nm<sup>[42]</sup>. The optical bandgap energies observed are higher and within the range of 3.36 – 6.37 eV (indicating a blue shift); the photoluminescence (PL) emission spectra observed exhibit prominent peaks within 420 – 550 nm. Magnetic measurements have indicated that all samples prepared are paramagnetic; the electrical measurements have shown that space charge polarization and occurrence of nanoconfined states may substantially contribute to the electrical properties<sup>[42]</sup>.

Pure and S<sup>2-</sup> doped (Mn<sub>3</sub>O<sub>4</sub>)<sub>x</sub>(CdCO<sub>3</sub>)<sub>1-x</sub> (with x = 0.0, 0.25, 0.5, 0.75 and 1.0) nanocomposites (multiphased) have been prepared by the SSM-DMO using manganese(II) acetate (Mn<sup>2+</sup> source), cadmium acetate (Cd<sup>2+</sup> source), urea (O<sup>2-</sup> source) and thiourea (for S<sup>2-</sup> doping) as the precursors and ethylene glycol as the solvent<sup>[43,58]</sup>. The average crystallite sizes obtained are within the range of 6.37 – 28.95 nm; the optical bandgap energies observed are within the range of 1.55 – 3.25 eV. It has been found that the prepared samples (other than pure and doped CdCO<sub>3</sub>) exhibit paramagnetism at room temperature; the pure and doped CdCO<sub>3</sub> exhibit diamagnetism. The electrical measurements made on pelletised samples have indicated the importance of space charge contribution in the transport process and polarizability<sup>[43,58]</sup>.

Multiphased nanocomposites of pure and S<sup>2-</sup> doped (Mn<sub>3</sub>O<sub>4</sub>)<sub>x</sub>(Ni(OH)<sub>2</sub>)<sub>1-x</sub> (with x = 0.0, 0.25, 0.5, 0.75 and 1.0) have been prepared by the SSM-DMO using manganese(II) acetate (Mn<sup>2+</sup> source), nickel acetate (Ni<sup>2+</sup> source), urea (O<sup>2-</sup> source) and thiourea (for S<sup>2-</sup> doping) as the precursors and ethylene glycol as the solvent<sup>[44]</sup>. The as-prepared nanopowders have been found to be well crystalline, spherical shaped, homogeneous and of considerable phase purity; the average crystallite sizes range from 1.7 – 20.7 nm. The optical bandgap energies observed range from 2.25 to 3.84 eV and it could be understood that major tuning of optical bandgap can be done by changing the composition and minor tuning by changing the S<sup>2-</sup> doping concentration. Electrical measurements have indicated that these nanocomposites are interesting and useful for electrochemical sensing applications; magnetic measurements have indicated the presence of paramagnetic nature<sup>[44]</sup>.

Pure and O<sup>2-</sup> doped multiphased nanocomposites of (CdS)<sub>1-x</sub>(MnS<sub>2</sub>)<sub>x</sub> (with x = 0.0, 0.25, 0.5, 0.75 and 1.0) have been prepared by the SSM-DMO using cadmium acetate (Cd<sup>2+</sup> source), manganese(II) acetate (Mn<sup>2+</sup> source), thiourea (S<sup>2-</sup> source) and urea (for O<sup>2-</sup> doping) as the precursors and ethylene glycol as the solvent; average crystallite sizes obtained range from 5.633 to 13.890 nm; and SEM images observed show agglomerated cluster like patterns<sup>[45]</sup>. Optical bandgap energies have been found to range from 2.721 to 3.273 eV; and the PL emission spectra recorded show prominent peaks within 420 – 550 nm. Magnetic measurements have indicated the pure and O<sup>2-</sup> doped CdS samples as diamagnets and the other samples prepared as paramagnets; the electrical measurements have shown the importance of the space charge contribution to the electrical

properties, and the  $O^{2-}$  addition has been found to increase the dielectric constant value for all the samples except for the samples with equimolar composition [45].

Pure and  $Mn^{2+}$  doped  $CuS_xO_{1-x}$  (with  $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0$ ) nanocomposites (multiphased with the monoclinic phase of  $CuO$  and the hexagonal phase of  $CuS$  co-existing) have been prepared (by the SSM-DMO) using copper (II) acetate ( $Cu^{2+}$  source), urea ( $O^{2-}$  source), thiourea ( $S^{2-}$  source) and manganese(II) acetate (for  $Mn^{2+}$  doping) as the precursors and distilled water as the solvent, and the as-prepared samples were annealed at  $200\text{ }^\circ\text{C}$  to improve the ordering and phase purity; the nanopowders obtained are well crystalline and the average crystallite sizes obtained are within the range of  $27.04 - 43.04\text{ nm}$  [65-67]. The magnetic measurements made at room temperature have indicated that all the samples prepared are paramagnetic; and the electrical measurements made on pelletised samples have shown that space charge polarization and occurrence of nanoconfined states may substantially contribute to the electrical properties [65-67].

Multiphased nanocomposites of pure and  $Cu^{2+}$  doped  $(SnO_2)_{1-x}(ZnO)_x$  (with  $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0$ ) have been prepared by the SSM-DMO using stannous chloride ( $Sn^{2+}$  source), zinc acetate ( $Zn^{2+}$  source), urea ( $O^{2-}$  source) and cupric acetate (for  $Cu^{2+}$  doping) as the precursors and ethylene glycol as the solvent; the as-prepared samples were annealed at  $500\text{ }^\circ\text{C}$  to improve the ordering and phase purity; and all the samples prepared have been characterized structurally, optically and electrically [68-70]. The electrical measurements made on pelletised samples have indicated the occurrence of space charge polarization, and that the variation of AC electrical conductivity with frequency and temperature is due to the hopping of electrons; the optical measurements have indicated shifting of PL emission peak positions due to  $Cu^{2+}$  doping and coupled with the variation of optical bandgap energies [68-70].

### Nanophases of Ferric Oxide and Nickel Sulfide

$Fe_2O_3$  (ferric oxide) has four prominent phases with different crystal structures:  $\gamma\text{-}Fe_2O_3$  (maghemite) has a spinel structure,  $\varepsilon\text{-}Fe_2O_3$  has an orthorhombic structure,  $\beta\text{-}Fe_2O_3$  has a bixbyite structure and  $\alpha\text{-}Fe_2O_3$  (Hematite) has a corundum structure [57]. Ramya and Mahadevan [48,51,57] have attempted to prepare all the four nanophases in their pure form by the SSM-DMO. They have found that the method followed is an effective one for the preparation of  $\gamma\text{-}$ ,  $\varepsilon\text{-}$ ,  $\beta\text{-}$  and  $\alpha\text{-}Fe_2O_3$  nanophases with good purity, stoichiometry, homogeneity and physical (optical, magnetic and electrical) properties; their transmission electron microscopic (TEM) analysis has shown that the average particle sizes are  $19, 24, 29$  and  $33\text{ nm}$  respectively for the  $\gamma\text{-}Fe_2O_3$  (in the amorphous condition),  $\varepsilon\text{-}Fe_2O_3$  (crystalline),  $\beta\text{-}Fe_2O_3$  (crystalline) and  $\alpha\text{-}Fe_2O_3$  (crystalline) nanophases prepared [48,57].

They have considered ferric chloride ( $Fe^{3+}$  source) and urea ( $O^{2-}$  source) as the precursors and ethylene glycol as the solvent for the preparation of the above nanophases. The as-prepared sample (found to be very poor crystalline or amorphous  $\gamma\text{-}Fe_2O_3$  phase) was calcined at different temperatures, *viz.*  $400\text{ }^\circ\text{C}$  (for crystalline  $\varepsilon\text{-}Fe_2O_3$  phase),  $600\text{ }^\circ\text{C}$  (for crystalline  $\beta\text{-}Fe_2O_3$  phase) and  $700\text{ }^\circ\text{C}$  (for crystalline  $\alpha\text{-}Fe_2O_3$  phase) and cooled naturally to the room temperature. The optical bandgap energies have been found to be red-shifted, and in the range of  $1.76 - 1.87\text{ eV}$ ; the magnetic measurements have indicated superparamagnetism for the  $\gamma\text{-}$  phase and weak ferromagnetism for the other three phases [48,57]. The AC electrical measurements made with pelletized samples at various temperatures and frequencies have indicated low AC electrical conductivities showing the occurrence of nano confined states; the exciton Bohr radii obtained (from the dielectric constant) have indicated a strong quantum confinement; and non-ideal behavior have been exhibited by the impedance spectra [51,57].

Nickel sulfide ( $NiS$ ) exhibits three prominent crystalline phases: the non-stoichiometric  $NiS_{1.03}$  with hexagonal crystal structure, the low temperature  $\beta\text{-}NiS$  (Millerite) with rhombohedral crystal structure and the high temperature  $\alpha\text{-}NiS$  with hexagonal crystal structure; and amorphous  $NiS_{1.03}$  can be considered as the fourth phase [53]. Nagaveena and Mahadevan [49,53] have developed

the SSM-DMO and prepared all the above four nanophases successfully with high purity, reduced particle size, homogeneity, and useful optical, magnetic and electrical properties; the average particle sizes obtained (through TEM analysis) are 15, 17, 18 and 20 nm respectively for the amorphous NiS<sub>1.03</sub>, crystalline NiS<sub>1.03</sub>, crystalline  $\beta$ -NiS and crystalline  $\alpha$ -NiS phases.

They have considered nickel chloride (Ni<sup>2+</sup> source) and thiourea (S<sup>2-</sup> source) as the precursors and ethylene glycol as the solvent; the as-prepared sample (found to be the amorphous NiS<sub>1.03</sub>) was calcined at different temperatures, viz. 300 °C (for crystalline NiS<sub>1.03</sub>), 500 °C (for crystalline  $\beta$ -NiS) and 700 °C (for crystalline  $\alpha$ -NiS) and cooled naturally to the room temperature. The optical bandgap energies for the NiS nanophases were observed to be in the range of 3.81 – 4.52 eV, and a maximum photoluminescence yield was observed for the crystalline  $\alpha$ -NiS. The AC electrical measurements have shown the importance of space charge contribution in the charge transport process and polarizability; and the magnetic measurements have indicated ferromagnetism for all the four nanophases prepared [49,53].

## Conclusion

In effect, various studies made in the past have indicated that the method adopted (SSM-DMO) is found to be an effective, scalable and economical one for preparing a number of nanomaterials in powder form with high chemical purity, reduced particle (or grain or crystallite) size, homogeneous morphology and useful physical properties. Moreover, studies have indicated that this method of preparation could be adopted to prepare successfully the prominent nanophases of ferric oxide and nickel sulfide; and is expected to be suitable for preparing (in the future), at a cheaper cost, the prominent nanophases of other such materials in the pure form.

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## Conflict of Interest

The author declares that this article was prepared in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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