

A Review on Pure and Metal Doped ZnO Nanoparticles Synthesized by Sol Gel Method: Assessment of crystallite Size and energy band Gap

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ABSTRACT

Pure and metal doped ZnO nanoparticles were produced by different synthesis routes like Physical, Chemical and Biological (Green route). There are many different synthesis methods like Co-precipitation, Sol gel, Solvothermal, Hydrothermal etc. in Chemical route. In this review, Sol gel synthesis method will be in focus. ZnO is N-type semiconductor having a wide energy band gap of nearly 3.37 eV at 300K. Variation of crystallite size and energy band gap of pure and metal doped ZnO via Sol gel synthesis method with different dopant metals in different solvents were surveyed and summarised in this review. Crystallite size and energy band gap may be also controlled by varying heat time and temperature. This study will improve our understanding of developments in doped ZnO and will assist in the creation of new ZnO based nanomaterials with improved structural, optical and photocatalytic properties.

Keywords: *Doped ZnO, sol gel, hydrothermal, semiconductor, optical.*

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Introduction

Zinc oxide is an inexpensive material, biodegradable and has a fairly low toxicity, which makes it an appropriate candidate for biomedical studies. ZnO is negative type semiconductor having a wide energy band gap of nearly 3.37 eV at 300K, high exciton binding energy of approximately 60 meV and a hexagonal unit cell with lattice constants of $a = b = 0.325$ nm, $c = 0.521$ nm. Recently Zinc oxide (ZnO) nanocrystals have evolved as one of the most potential research materials due to its unique properties and mesmerizing applications. ZnO nanocrystals can exhibit novel optical, electrical, chemical and mechanical properties when compared to their bulk form. Many different morphologies of ZnO, including nanowires, nanobelts, nanorods and many others, have been reported to demonstrate its adaptability for use in a variety of applications. Doped ZnO nanomaterials facilitate the production of free electrons because they are highly radiation-sensitive [1]. The modified morphology of the nanomaterials broadly recognizes the performance and behaviour of such devices [1].

Researchers have demonstrated that doping ZnO with certain elements augmented the emission and absorption power, which significantly enhanced the optoelectronic characteristics [1-4]. Doping ZnO with transition elements has proved an augmentation in the efficiency of laser diodes and LEDs due to the surface-plasmon effect (SPE) [1-4]. Due to these properties, transition metal-doped ZnO nanoparticles have potential applications in spintronic devices [5]. When zinc oxide (ZnO) nanostructures are synthesized with careful attention to the inclusion of metal dopants, they can significantly enhance light absorption, especially at the weak absorption edge. This meticulous approach not only improves the absorption efficiency at specific wavelengths but also enhances the overall optical absorption properties of the material. As a result, this enables its use in various applications, including photovoltaic and photo detector [6, 7]. Aluminium-doped zinc oxide (AZO) is widely seen as a substitute for indium tin oxide (ITO) because it has very low electrical resistance compared to other metal-doped

zinc oxide materials [8, 9]. Many studies have demonstrated the suitability of Al-doped ZnO in optoelectronic applications [8, 9]. Furthermore, the addition of manganese (Mn), strontium (Sr), cobalt (Co), magnesium (Mg) and europium (Eu) to zinc oxide nano particles (ZnO NPs) has been shown to improve their photocatalytic activity [10, 11]. Interestingly, even cationic dopants like Silver and Aluminium can enhance the photodegradation efficiency of ZnO nano particles [12, 13]. Al-doped ZnO nanoparticles have also demonstrated significant electron transport and injection properties in optoelectronic applications [14, 15]. ZnO-based nanoparticles can exhibit ferromagnetic behaviour when doped with transition metals such as titanium (Ti), cobalt (Co), iron (Fe), manganese (Mn) and nickel (Ni). In particular, Ti doping not only enhances the magnetic behaviour of ZnO but also improves its mechanical, optical and structural stability properties. The substitution of Zn atoms in the ZnO crystal lattice with Ti atoms alters the spin transport mechanism, thereby directly modulating the material's magnetic characteristics [16-22].

Many synthesis methods are developed and they can be divided into physical, chemical and biological methods (green route). Though compared to other synthesis techniques, chemical synthesis techniques (like co-precipitation, hydrothermal, solvothermal, sol-gel etc.) are less expensive, faster and produce pure crystals with a higher yield and stability. Multiple investigations have shown that "dual doping" may improve the electrical, optical, and antibacterial properties of ZnO [12-15]. Chemical synthesis methods-especially the sol-gel technique-play a key role in the production of ZnO-based DMS nanoparticles. The sol-gel method is preferred for its ability to enable controlled growth and uniform distribution of nanoscale particles at relatively low temperatures. The use of solvents such as monoethanolamine (MEA) and 2-propanol significantly contributes to the improvement of ZnO's crystal Structure, surface morphology and optical properties. The solvent environment determines the particle size and distribution, which in turn can indirectly influence the magnetic

performance of the material [23-28]. Here Sol gel synthesis method is mainly reviewed. When reaction conditions (precursor and their concentrations, solvent type, surfactant concentrations and temperature) in a specific synthesis route are controlled, it is possible to alter the size, morphology and energy band gap of ZnO nanostructures [29].

Co-precipitation synthesis method is one of the simplest, cost effective and highly efficient process used for the synthesis of doped zinc oxide nanoparticles. The precursors were mixed in a stoichiometric ratio and the solution is magnetically stirred with the addition of sodium hydroxide solution for 30 minutes. This mixture is held at constant temperature of 60°C for 5 hours until precipitate is formed. The solution is allowed to cool at room temp and precipitates were collected by centrifugation. The resulting precipitate was dried in an incubator at 80°C for 24 hours to remove moisture and annealed at 300°C for 5 hours [30, 31].

Hydrothermal synthesis technique is simple and convenient method that imparts good control over homogeneity, composition, size, phase, and morphology [32-34]. In this process the precursors are dissolved in a suitable solvent like deionised water in a beaker and the mixture is put in to a sealed vessel mainly a Teflon – lined autoclave inside a stainless steel reactor and heated. The mixture undergoes heterogeneous reactions under high temperature and pressure to dissolve the recrystallized materials insoluble under normal conditions. The metal oxide is produced during this process, which is typically carried out below 300 °C and can be thought of as an electrostatic reaction between metal ions and hydroxyl ions. After reaction, the autoclave is left to cool naturally to room temperature. The precipitated is separated by centrifugation and the separated metal oxide product is washed several times with deionised water. Then after the product is dried and the dried product is calcined to remove residual moisture and organic materials and the product metal oxide has improved crystallinity. [32, 33].

The sol-gel method is one of the most extensively used techniques for producing ZnO nanoparticles because of its good homogeneity

[35,36], simplicity of composition control, low processing temperature, large-area coating, cheap equipment cost and excellent optical qualities [37]. The term “sol-gel” is a combination of “solution” and “gelation.” Before reaching the gel state, the system is a liquid form, consisting of a mixture of colloidal oligomers and very small macromolecules, as well as different partly hydrolysed monomers, depending on the intensity of the polymerization reaction. The steady dispersion of colloidal particles inside a liquid is called a “sol.” The size of the solid particles, which are denser than the liquid, must be small enough that gravity does not overpower the forces responsible for dispersion. The gel is composed of an oxide network swollen by the solvent, with chemical bonds maintaining mechanical cohesion and giving the material a rigid and non-deformable nature. The gel is equivalent to a three- dimensional network of Vander-Waals bonds. The time it takes for a “sol” to convert into a “gel” is referred to as the gelation time (or gelation point) The sol-gel method begins with a homogeneous solution of the precursors; a coordinating agent (ethylene glycol) added to the solution produces a sol, after the solution condenses to form a gel, the solvent is dried to create the nanoparticles [38, 39]. This method is particularly well suited for producing doped zinc oxide nanoparticles with good control over size and shape, and it can produce crystalline nanoparticles using ambient temperatures for sol and gel preparation [38]. To increase the crystallinity of the resulting nanoparticles, the majority of these processes seek for an additional calcination step [40-42].

Advantages of Sol gel method for synthesis of ZnO and metal doped ZnO

There is no need for special or expensive equipment.

- **Better chemical homogeneity:** High purity due to mixing of metal ions (dopants) at molecular/ ionic level in precursor solution.
- **Versatile:** Good control of the structure, including porosity and particle size; the possibility of incorporating nanoparticles and organic materials into sol-gel-derived oxides.
- **Extended composition ranges:** It allows the fabrication of any oxide composition, but also some non-oxides, as well as the production of new hybrid organic-inorganic materials, which do not exist naturally
- **Less energy consumption:** There is no need to reach the melting temperature since the network structure can be achieved at relatively low temperatures near glass transition temperature (T_g).

Disadvantages of Sol gel method for synthesis of ZnO and metal doped ZnO

- Cost of precursors.
- Shrinkage of a wet gel upon drying often leads to fracture due to the generation of significant capillary stresses, making the attainment of large monolithic pieces difficult.
- Preferential precipitation of a particular oxide during sol formation (in multicomponent glasses) due to the different reactivity of the alkoxide
- Difficult to avoid residual porosity and OH groups.

The steps involving in synthesis of Pure ZnO nanoparticles via Sol gel method has been shown in Fig-1.

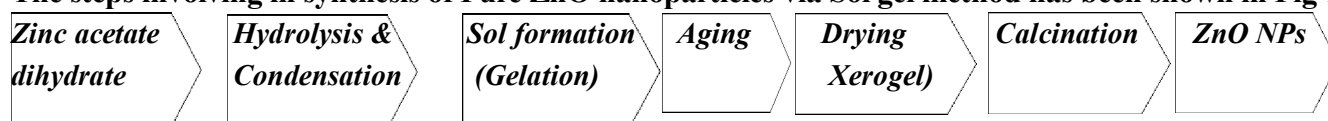
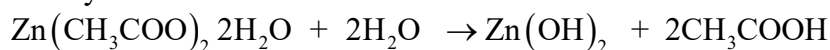


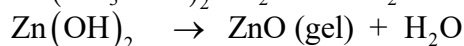
Fig -1: Sol gel synthesis of pure ZnO nanoparticles

Chemical reaction occurring in the synthesis of pure ZnO nanoparticles are given below:

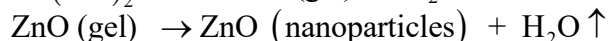
1. Hydrolysis of precursor Zinc acetate dehydrate



2. Condensation (gel formation)



3. Calcination



Synthesis of pure ZnO nanoparticles/nanopowders via Sol gel method

A Modric et al. synthesized ZnO powder via the sol-gel method at temperatures of 25°C and 60 °C. They dissolved Zinc acetate dihydrate and sodium hydroxide separately in deionized water and mixed for several minutes at room temperature using a magnetic stirrer. The sodium hydroxide solution was then added to the zinc acetate solution and stirred continuously. Two batches were prepared: the first batch was mixed at room temperature (25°C), while the second batch was mixed at temperature 60°C.

XRD analysis confirmed high crystallinity with a pure hexagonal wurtzite structure, with average crystallite sizes of approximately 20 nm at 25°C and 38 nm at 60 °C. Both SEM and TEM techniques established needle-like nanorods at 25°C and nanoflower-like structures at 60 °C [43].

Monika et al. added 15.7 gm of Zinc Nitrate in 500 ml of double distilled water and the solution is continuously stirred to dissolve completely. The solution

was heated to 50°C and 700 ml of alcohol (ethanol) was added slowly with continuous stirring and pH of solution is adjusted near about 5.4. After this, 6 ml of H_2O_2 was added drop wise to the above solution and mixed it by using a magnetic stirrer until to get a clear solution. After adding H_2O_2 the pH of solution was increased from 5.4 to 9 (Alkaline Condition) of the solution. After formation of gel, the gel is transferred into Centrifuge tubes and centrifuged at 10000 rpm for 5 min. Then after the sample was washed with distilled water. The above steps were repeated 2-3 times. The sample allowed to dry at 80°C until the samples become dry then annealed the sample at 500°C for 1 h in muffle furnace, crushed the annealed sample of ZnO nanoparticles with Mortar and Pestle [44].

Average size of crystal recorded by XRD data was 21.28 nm, the crystallinity of ZnO refers to a wurtzite hexagonal structure which was result of penetration of two hexagonal lattices. SEM morphology of ZnO Particle and image taken at 30,000 magnifications were spherical in shape and having smooth surface [44].

The steps involving in synthesis of metal doped ZnO nanoparticles via Sol gel method has been shown in Fig-2.

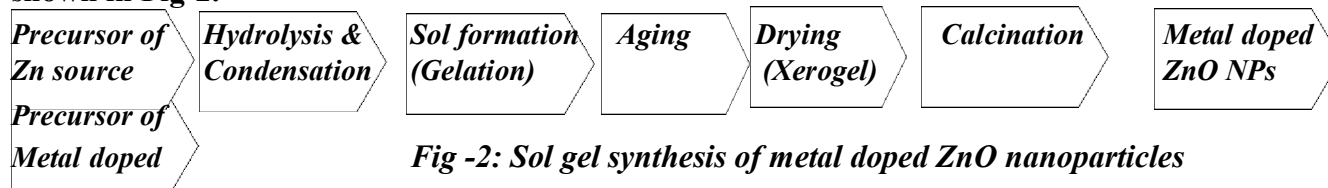


Fig -2: Sol gel synthesis of metal doped ZnO nanoparticles

Synthesis of metal doped ZnO via Sol gel method and study of crystal size and energy band gap

Sidra et al. synthesized $Zn_{1-x}Mn_xO$ ($x = 0M, 0.03, 0.04$) nanoparticles using $Zn(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, Sodium hydroxide, Ethylene glycol, Citric acid & Ammonia via Sol gel method. They take required amount of $[Zn(NO_3)_2 \cdot 6H_2O]$ in a beaker containing 312 ml water placed on a hot plate. After stirring the solution for 25 min, the required amount of $[Mn(NO_3)_2 \cdot 4H_2O]$ was added in the beaker, followed by constant Stirring for 20 min more to get better results. The required amount of citric

acid and ethylene glycol were added as a catalyst. For maintaining the pH of solution between 9 and 10, some amount of ammonia was added. The temperature of solution is set to 80 °C for 2 h then after temperature was raised to 120 °C and the solution changed to a gel form. After some time, the gel Started burning, which assured that the sample was synthesized successfully. Then, the sample was dried in an oven at 80 °C for 2 h. After drying, the sample was ground to change it into fine powder. After that, the sample was annealed at 300°C for 3 h in a box furnace under air. After annealing, the samples were ready for different characterization techniques [45].

Table-1

Synthesis technique, crystal size and optical properties of pure and Mn doped ZnO [45].

Sample	ZnO	Zn _{0.99} Mn _{0.01} O	Zn _{0.97} Mn _{0.03} O	Zn _{0.96} Mn _{0.04} O	Synthesis Method & Precursors for Mn doped ZnO
Average crystallite size D(nm)	38.42	35.61	29.23	27.54	Sol gel auto combustion Zn(NO ₃) ₂ ·6H ₂ O, Mn(NO ₃) ₂ ·4H ₂ O Sodium hydroxide, Ethylene glycol, acid and Ammonia
Optical band gap (eV)	3.25	3.02	3.16	2.62	
FWHM(?)(deg)	0.3576	0.4831	0.5656	0.6053	

Structural analysis and phase determination were done by X ray and a hexagonal wurtzite structure was exhibited with disparate micro structures.

Debye Scherer's equation determines the average crystal size:

$$\text{Average crystal size (D)} = 0.9\lambda / \beta \cos \theta$$

Where θ is the Bragg's angle, λ is the Full Width at half- maximum and λ is the wavelength of the incident light which is $1.45 \text{ \AA}$.

From table-1, Average crystallite size of pure ZnO is 38.42 nm but its decrease to 27.54 nm on doping Mn to ZnO upto 4% concentration. Full width at half maxima increases from 0.3576 degree to 0.6053 degree on doping Mn to ZnO from ZnO to Zn_{0.96}Mn_{0.04}O but energy band gap for pure ZnO is 3.25 eV and it reduces to 2.62 eV on doping of Mn to ZnO up to 4% concentration.

Deepak et al. fabricated ZnO NPs via sol-gel route. 0.2 M zinc acetate dihydrate solution was prepared in double-distilled Water (DDW). In this, 0.02 M of sodium dodecyl sulfate (SDS) was added to the solution with constant stirring for 15 min. In this homogenous solution, ammonium hydroxide was

mixed drop wise until pH reaches to the basic condition, i.e., 8.0 ± 0.1 . The formation of zinc hydroxide sol takes place that placed at 80°C for 9 h for gelation. This obtained gel was dried to get the powder and further calcinated at 400°C for 3 h in a muffle furnace. Similarly, Mn-doped ZnO (Mn-ZnO) NPs were prepared by taking manganese acetate tetrahydrate in similar zinc acetate dihydrate solution as per calculated doping amounts of 1%, 3% and 5% wt. composition [46].

Crystal size for pristine ZnO is 43nm and decreased to 36nm on doping of Mn (5%) to ZnO. The band gap for ZnO measured to be 3.16 eV seems to lesser because of the oxygen vacancies and defects at the surface of ZnO nanocrystals. Energy band gap values for 1, 3 and 5% Mn-ZnO are 2.788, 2.782 and 2.805 eV respectively. The band gap decreases up to 3% Mn doping, while it is then slight increases for 5% Mn doping. This decrease in band gap of doped ZnO NPs was because the d-electron of Mn (t_{2g} levels) can easily overlap with ZnO valence band. While 5% doping shows slight increase because of Burstein—Moss effect initiated by excess of charge carriers that pushes the Fermi level to higher energy [46].

Table-2

Results calculated from XRD, SEM data [46]

Samples	Crystal size D (nm)_XRD	Lattice Parameters a=b(nm) c(nm)		Energy Band Gap (eV)	Synthesis method & Precursors
Pure ZnO	43	0.3250	0.5207	3.16	Sol gel Zinc acetate dihydrate and Manganese acetate tetrahydrate as precursors sodium dodecyl sulphate, ammonium hydroxide and double distilled water
Zn _{0.99} Mn _{0.01} O	42	0.3251	0.52	2.788	
Zn _{0.97} Mn _{0.03} O	38	0.3253	0.5207	2.782	
Zn _{0.95} Mn _{0.05} O	36	0.3253	0.5207	2.805	

A.K. Azfar et al. synthesized materials Ag and Ni doped ZnO nanoparticles at different stoichiometry (x= 1%, 3%, 7% and 10%) via sol gel method. Zinc acetate dihydrate and silver acetate/nickel (II) acetate were dissolved under absolute ethanol and was stirred for 2 h to gain a homogeneous mixture. Base (ammonium hydroxide) was added to increase the pH value to 9 and this was followed by a heating process at 80°C. The materials underwent slow drying process and grey precursors were obtained within 24 h. For comparison, a control sample (undoped ZnO) was prepared by mixing zinc acetate dihydrate with absolute ethanol and processed with the similar procedure as above. The precursor were annealed at 400°C for 3 h. Next, structural studies on crystallinity were carried out after the annealing process [47].

S. Al Arikki et al. prepared a homogeneous solution by dissolving 9.9163 g of zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ as zinc oxide source and 6.4041g of Citric acid anhydrous ($\text{C}_6\text{H}_8\text{O}_7$) in de-ionized Water (80ml) for pure ZnO nanopowder. For preparation of Ni-ZnO nanopowders, 9.9163 g

of zinc nitrate hexa hydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, 6.4041 g of citric acid anhydrous ($\text{C}_6\text{H}_8\text{O}_7$) and nickel nitrate hexa hydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ as Ni source were dissolved in de-ionized water (80ml) and Ag with ZnO (AgZnO) nanopowders were synthesized using the same technique described for Ni-ZnO, except AgNO_3 was used as Ag source instead of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Different molar ratios (0, 1, 3 and 5% mole) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AgNO_3 , Were Chosen to prepare Ni-ZnO and Ag-ZnO nanopowders, respectively. The prepared solutions were stirred separately by a magnetic stirrer for 3 h and heated at 42 °C. They were kept at room temperature for 24 h. “the resulting solutions were stirred for another 1.5h and heated at 72 °C for 48h. Within the third day, the reaction mixtures were stirred for 1h and heated at 92 °C until gels were obtained. The prepared materials were dried at 120 °C for 4 h in an oven and then ground for 10 min. The resulting powders were heat-treated at 450 °C for 6 h in a furnace.[48]

Hexagonal structure maintain for both NiZnO and AgZnO by XRD [48].

Table-3

Average crystallite Size, Optical band gap and average FWHM of pure ZnO, Ni doped ZnO and Ag doped ZnO nanopowders [48].

Sample	ZnO	$\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$	$\text{Zn}_{0.97}\text{Ni}_{0.03}\text{O}$	$\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$	Synthesis Method & Precursors for Ni doped ZnO
Average Cristalight Size D (nm)	19.13	18.47	21.67	17.77	Sol gel $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{AgNO}_3 \cdot 6\text{H}_2\text{O}$, citric acid anhydrous & deionised water
Optical band gap (eV)	3.10	3.05	2.95	3.00	
FWHM (deg)	0.4259	0.4581	0.3793	0.4697	
Average Critallite Size D (Mn)	19.13	19.95	22.21	25.63	
Optical band gap (eV)	3.10	2.90	2.00	1.80	
FWHM	0.4259	0.4214	0.3612	0.3134	

From table-3, the average crystallite size was 19.13 nm for pure ZnO. A Slight decrease in the average crystallite size of Ni-ZnO was observed in comparison to the pure ZnO. Ni-ZnO also showed a smaller crystallite sized compared to Ag-ZnO. The average crystallite sizes were between 17 and 22 nm for Ni-ZnO and between 19 and 26 nm for Ag-ZnO. The band gap energy of pure ZnO was 3.1 eV. The doped samples exhibited better optical properties in comparison with pure ZnO, A slight decrease in the band gap energies of Ni-ZnO was observed in comparison to the pure ZnO. Ag-ZnO exhibited a higher decrease in the band gap energies than Ni-ZnO.

S. Siva et al. prepared Cu doped ZnO [$Zn_{1-x}Cu_xO$] (where $x = 0, 0.03, 0.06$) nanoparticles via sol gel method using Zinc nitrate hexa hydrate [$Zn(NO_3)_2 \cdot 6H_2O$], Copper (II) nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$] and sodium hydroxide (NaOH). For

undoped ZnO nanoparticles, they dissolved [$Zn(NO_3)_2 \cdot 6H_2O$] in 50 ml deionised water in a beaker. After completing homogeneous solution, a molar ratio of 1:2 NaOH solution of 50 ml was added drop wise under vigorous stirring. After 2h of continuous stirring the solution, a white precipitate was obtained. A similar procedure was used to prepare Cu doped ZnO [$Zn_{1-x}Cu_xO$] (where $x = 0.03, 0.06$) nanoparticles using appropriate amount of Zinc nitrate hexa hydrate [$Zn(NO_3)_2 \cdot 6H_2O$], Copper (II) nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$] and sodium hydroxide (NaOH). The final products were left overnight then after they were hot aired oven at 80°C for 2h. The dry products were crushed into a fine powder using an agate mortar. Finally the powdered products were annealed in a muffle furnace at 500°C for 2h to thermally decompose all the hydroxide molecules [49].

Table-4.

Average crystallite Size of pure ZnO and Cu doped ZnO nanoparticles [49].

Sample	Crystallite size D (nm)	Energy band gap (eV)	Synthesis method Precursors	References
Pure ZnO	25.87	3.27	Sol gel method Zinc nitrate	
Zn _{0.97} Cu _{0.03} O	23.46	3.39	hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$],	[49]
Zn _{0.94} Cu _{0.06} O	22.51	3.44	Copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$] Sodium hydroxide (NaOH) and deionised water.	

On increasing doping % from 0 to 6, crystallite size decreases from 25.87 nm to 22.51 nm while energy band gap increases for 3.27 eV to 3.44 eV.

Pallavi et al., dissolved Zinc nitrate and copper nitrate in 100 ml distilled water to get a homogeneous solution for 30 min by using magnetic stirrer. Citric acid had been dissolved separately in 100 ml distilled water for 30 min and add to the nitrate solution. Then the solution was stirring and continuously heating at 90°C until water gets evaporated, thus the sol is converted in to gel. The gel subsequently in to bulge form and it get strong Self combustion reaction to give the fine powder. All the samples are ground by pestle and mortar and powdered samples were annealed at 600°C for 6h in

muffle furnace. The final powder of pure ZnO was in white colour and Cu^{2+} doped ZnO was in moss green colour [50] The average crystallite size of doped and undoped ZnO nanoparticles were estimated using the Debye- Scherrer's Eq. Average crystal size (D) = $0.9\lambda/\beta \cos\theta$ Where θ is the Bragg's angle, β is the Full Width at half- maximum and λ is the wavelength of the X rays. The crystallite size of Cu^{2+} doped ZnO nanoparticle is smaller than those of the pure ZnO nanoparticles shown in Table 1. The decreasing crystallite size is due to the distortion in ZnO lattice by the presence of Cu^{2+} reduces nucleation and interference growth rate of ZnO nanoparticles. Crystallite size D of $Zn_{1-x}Cu_xO$ is 21nm for $x = 0$ and 19nm for $x = 0.05$ [50].

Table-5:
Hexagonal wurtzite structure: Crystallite size and energy band gap of Zr doped ZnO Nanoparticles [51].

Sample	Crystallite size D(nm)	Energy band gap (eV)	Synthesis method Precursors	References
Pure ZnO	15.1	3.32	Sol gel method Zinc nitrate hexa hydrate	
Zn _{0.985} Zr _{0.015} O	17.2	3.36	[Zn(NO ₃) ₂ 6H ₂ O], zirconyl nitrate	
Zn _{0.97} Zr _{0.03} O	18.8	3.39	monohydrate [Zr(NO ₃) ₂ H ₂ O],	
Zn _{0.955} Zr _{0.045} O	20.3	3.51	sodium hydroxide (NaOH) and urea	[51]

Asad et al. prepared Zr doped ZnO [Zn_{1-x}Cu_xO] (where x = 0, 0.015, 0.03, 0.045) nanoparticles via sol gel method using Zinc nitrate hexa hydrate [Zn(NO₃)₂6H₂O], zirconyl nitrate monohydrate [Zr(NO₃)₂H₂O], sodium hydroxide (NaOH) and urea. They prepared by dissolving stoichiometric amounts of Zinc nitrate hexa hydrate [Zn(NO₃)₂6H₂O] and zirconyl nitrate monohydrate [Zr(NO₃)₂H₂O] in double distilled water. When both precursors were fully dissolved in solvent then regulated amount of urea are added in molar ratio of 1:1 (precursors and urea). NaOH was added to solution to adjust their pH around 7. The solutions were continuously stirred on hot plate at 140°C until gel was formed. The formed gel was dried at 200°C in an open environment. The dried gel was grinded to make powder and the powder was annealed at 400°C for 4h to improve phase ordering [51]. From table -5,

it is clear that on increasing doping % from 0 to 4.5, crystallite size increases from 15nm to 20nm and energy band gap increases from 3.32 eV to 3.51 eV.

E. Jackcina et al. prepared Zr(IV) doped ZnO photocatalyst using Zinc acetate dehydrate, oxalic acid dehydrate, zirconium oxychloride, and ethanol via Sol gel method. Zinc acetate dehydrate (1.8 g) was dissolved in 50 ml of ethanol under continuous stirring at 60°C for 30min. Similarly, oxalic acid (2. I g) was dissolved in ethanol at 40°C. The dopant Zr(IV) (zirconium oxychloride) was dissolved in distilled water. The molar ratio of Zr(IV) with ZnO is 1, 2,3 and 4 M ratio. The oxalic acid and dopant Zr(IV)) were added simultaneously to the warm ethanolic solution of Zinc acetate slowly under stirring condition. A white colour xerogel was formed and it was kept for drying at 60°C. The xerogel was calcinated in a muffle furnace at 500°C for 2 h [52].

Table-6
Crystallite size of Zr doped ZnO nanoparticles

Samples	Crystal size D (nm)_XRD	Synthesis method & Precursors	References
Zn _{0.99} Zr _{0.01} O	42.66	Sol gel	[52]
Zn _{0.98} Zr _{0.02} O	58.97	Zinc acetate dehydrate, oxalic acid	
Zn _{0.97} Zr _{0.03} O	69.78	dehydrate, zirconium oxychloride and	
Zn _{0.96} Zr _{0.04} O	73.76	ethanol	

Estimated mean crystallite sizes of ZnO and Zr(IV) doped ZnO are given in Table 12 with respect to various percentages of dopant. The average crystallite size of Zr(IV) doped ZnO nanocomposites increases with increase in the percentage of doping of Zr(IV) as shown in table-1. Because of Zr⁺ ion substitution into Zn⁺ site.

Pooja et al. [53], prepared pure and Al doped ZnO nanoparticles using Zinc acetate dihydrate [Zn (CH₃COO)₂ 2H₂O], aluminium acetate [Al(CH₃COO)₃] as a precursor and ethanol (CH₃CH₂OH) as a solvent and distilled water

and Sodium hydroxide (NaOH) as medium via sol gel route. To get a homogeneous solution, ethanol (about 2 mL) was added drop wise along with continuous magnetic stirring. Keeping the stoichiometry in mind, a 2-gm batch of zinc oxide was prepared. After that, the obtained residue was dried in an oven for about 4 h at a temperature of 200 °C. The obtained samples were calcinated at 500 °C, 700 °C, and 750 °C. Finally, yellowish-white ZnO nanomaterial in the form of powder was obtained [53].

For preparing AZO nanopowder, they dissolved different amounts of aluminium acetate $[Al(CH_3COO)_3]$ in a solution of zinc acetate dihydrate and polyethylene glycol to obtain concentrations of 0%, 2%, 4%, and 6% AZO (g/mL) respectively. The prepared materials were dried at 500 °C for a few minutes in an oven and then ground for 10 min. The resulting powders were heat-treated at 700 °C and 750 °C in a furnace. The synthesized ZnO and AZO nanopowder was taken out and subjected to the characterization process [53].

Table 7.

Variation in crystallite size and energy band gap of pure and capped ZnO at different temperatures

Synthesis Method & Precursors	Pure ZnO & Growth Temperature (°C)	Crystallite Size (nm) (From Scherrer Formula)	Energy Band Gap (Eg) (eV)	Reference
Sol gel Zinc acetate dihydrate [Zn (CH ₃ COO) ₂ 2H ₂ O], ethanol (CH ₃ CH ₂ OH), Distilled water and NaOH	Uncapped 500	14.19	2.97	[53]
	Capped 700	28.50	2.90	
	Capped 750	34.17	2.84	

Table 8.

Variation in crystallite size and energy band gap of AZO with different Al concentrations.

Synthesis Method & Precursors	Al Content (%) in AZO Nanopowder at 500 °C	Crystallite Size (nm) (From Scherrer Formula)	Band Gap (Eg) (eV)	Reference
Sol gel Zinc acetate dihydrate [Zn (CH ₃ COO) ₂ 2H ₂ O], Aluminium acetate [Al(CH ₃ COO) ₃], Polyethylene glycol and NaOH	0% (Uncapped)	35.05	3.10	[46]
	2% (capped)	24.03	3.02	
	4% (capped)	24.57	3.08	
	6% (capped)	18.89	3.09	

From table - 8, it is clear that crystal size and energy band gap of pure ZnO depends on annealing temperature. On increasing annealing temperature, crystal size increases but energy band gap shrinks.

Emine et al. synthesized Ti doped ZnO nanoparticles (Zn_{1-x} Ti_xO) with (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05) using precursors zinc acetate dihydrate and titanium(IV) butoxide either in solvents methanol and monoethanolamine (MEA) or in 2 - propanol via sol gel synthesis technique [54].

Table 9

Comparison of crystal size and lattice parameters of ZnO and Ti doped ZnO nanoparticles prepared With MEA and 2- Propanol solvents [54].

Solvent type	Samples	D (nm)	a (Å)	c (Å)	c/a	Synthesis method & Precursors
MEA	Pure ZnO	24.12	3.24	5.19	1.60	Sol gel zinc acetate dihydrate and titanium (IV)butoxide as precursors Methanol and monoethanolamine (MEA) as solvents
	Zn _{0.99} Ti _{0.01} O	15.64	3.23	5.19	1.60	
	Zn _{0.98} Ti _{0.02} O	16.07	3.21	5.19	1.60	
	Zn _{0.97} Ti _{0.03} O	13.78	3.24	5.19	1.60	
	Zn _{0.96} Ti _{0.04} O	14.27	3.24	5.19	1.60	
	Zn _{0.95} Ti _{0.05} O	16.27	3.23	5.17	1.60	
2-Propanol	Pure ZnO	35.01	3.25	5.20	1.60	Sol gel zinc acetate dihydrate and titanium(IV) butoxide as precursors 2-Propanol as solvent
	Zn _{0.99} Ti _{0.01} O	24.67	3.24	5.18	1.59	
	Zn _{0.98} Ti _{0.02} O	20.36	3.24	5.21	1.60	
	Zn _{0.97} Ti _{0.03} O	24.07	3.24	5.20	1.60	
	Zn _{0.96} Ti _{0.04} O	22.12	3.24	5.20	1.60	
	Zn _{0.95} Ti _{0.05} O	27.88	3.21	5.17	1.61	

From table -9, it is clear that crystal size of Ti doped ZnO is larger in the case of solvent 2-Propanol than in the case of solvent monoethanolamine (MEA). These findings clearly demonstrate that the choice of solvent is a critical parameter which directly influences the structural properties of Ti -doped ZnO systems. Z. A. Sandhu et al. used sol gel synthesis method for the synthesis of Ca doped ZnO (Zn_{1-x}Ca_xO) (where x = 0, 0.01, 0.02, 0.03, 0.04) nanoparticles. For preparing pure ZnO nanoparticles, 2 grams of Zinc nitrate is dissolved in 50 ml water and the solution is stirred continuously for 30 min then after 1g citric acid is gradually added to the solution and stirred constantly for 15 min. Ammonia solution (NH₄OH) is poured to mixture to maintain the pH at 9. The solution was stirred continuously for 6 hrs and then heated to 1400C until a thick gel formed. The gel was washed with deionised water three times to reduce its pH to 7. The gel is dried and crushed into powder and the powder is annealed at 5000C for 2 hrs. In similar way, Ca doped ZnO nanopowder was obtained by using appropriate amount of Ca(NO₃)₂ [55].

Table-10

Hexagonal wurtzite structure: Crystallite size and energy band gap of Ca doped ZnO nanoparticles [55].

Sample	Crystallite size D(nm)	Energy band gap (eV)	Synthesis method Precursors	Reference
Pure ZnO	42.17	3.22	Sol gel method Zinc nitrate, Calcium nitrate, Citric acid, Ammonium and deionised water	[55]
Zn _{0.99} Ca _{0.01} O	24.15	3.09		
Zn _{0.98} Ca _{0.02} O	22.66	3.00		
Zn _{0.97} Ca _{0.03} O	19.07	2.88		
Zn _{0.96} Ca _{0.04} O	15.86	2.95		

From table-10, on increasing doping % of Ca, Crystallite size decrease continuously. On increasing doping % of Ca from 0 to 3, energy band gap decreases but from 3% to 4%, energy band gap begins to increase.

Roghayeh et al. prepared Mg doped ZnO nanoparticles using $\text{Zn}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and citric acid via sol-gel method. Citric acid was added drop wise to the mixture of $\text{Zn}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$. The molar ratio of metal ions to citric acid was maintained as 1:1 and the molar ratio of Mg^{2+} to Zn^{2+} was also maintained as 1:1. They raised temperature of solution slowly to 600C using water bath. The solution is transformed to hydrogel in 1 hr at 600C. The gel was dried at 800C for 48hrs in a vacuum oven. The resulting xerogel is calcinated at 5000C for 1hr for obtaining Mg doped ZnO nanoparticles [56].

Mg doped ZnO possessed a hexagonal wourtzite crystal structure. Average particle size of pure ZnO NPs was 161.2nm which decreased to 93.4nm on doping with Ca to ZnO NPs. Energy band gap decreased from 3.23 eV for pure ZnO to 3.18 eV for Mg doped ZnO [56].

Behnam et al. prepared pure ZnO, monometallic Mg/ZnO and La/ZnO and bimetallic Mg-La/ZnO nanoparticles using zinc acetate di-hydrate, $\text{Mg}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$ as precursors via sol-gel method. For the co-doped ZnO nanoparticles with 5-6 wt.% Mg and 4-5 Wt. % La, at first zinc acetate di-hydrate was slowly dissolved in 100 mL ethanol at 600C (with thermal controlling) and ongoing stirring for 30 min until homogeneous solution was obtained. Then, appropriate amounts of $\text{Mg}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$ dissolved in 20 mL ethanol at 600C were used which were continuously stirred for 30 min until homogeneous solution was obtained and was added drop by drop to the ethanolic solution of zinc acetate (Where temperature was controlled). The oxalic acid, dissolved in ethanol (40ml) at 600C, was added drop by drop to the ethanolic solution. The mixture was stirred for 2 h. The obtained white colloidal semi-gel dried at 90 0C for 12 h in the oven. The dried xerogel was calcinated at 4000C for 2 h in the electric Furnace. It was powdered by mortar. Doped Mg/ZnO and La/ZnO nanoparticles with 1-6 wt. % and bare ZnO were also prepared by the similar procedure [57]

Table-11.

Sample	ZnO	Zn0.95Mg0.05 ^o	Zn0.96La0.04 ^o	Zn0.90Mg0.05	Zn0.90Mg0.06
Average crystallite	14.28	7.25	10.79	7.45	7.33
Size D (nm)					
Average particle size(nm)	28.55	17.62	23.71	16.06	13.38
Optical band					
gap (eV)	3.11	3.183	3.150	--	3.175

Saumaya et al. prepared pure, doped and co-doped ZnO NPs by a modified sol-gel route. Mg doped ZnO NPs were prepared by dissolving 16 g of zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] in 112 ml of methanol under magnetic stirring at an ambient temperature. Then an adequate quantity of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) corresponding to a ratio $[\text{Mg}]/[\text{Zn}]$ of 0.01(1at.%) was added under magnetic stirring until total dissolution. The same

protocol was used to prepare Al-doped ZnO NPs. The Al precursor was the aluminium isopropoxide ($\text{C}_9\text{H}_{21}\text{AlO}_3$) and the $[\text{Al}]/[\text{Zn}]$ atomic ratio was 0.05 (5 at.%). The Al-Mg co-doped sample was also prepared by the same adopted protocol. The magnesium and aluminium precursors were introduced simultaneously after dissolving zinc precursor (1 at.% Mg and 5 at.% Al). At the end, the gained nanopowders were annealed, in a muffle furnace, at 400 °C in air for 2 h. [58].

Table-12

Crystallite size from XRD data and optical band gap of pure, doped and co doped ZnO [58].

Sample	ZnO	Zn _{0.99} Mg _{0.01} ^o	Zn _{0.95} Al _{0.05} ^o	Zn _{0.94} Mg _{0.01}	Synthesis method Al _{0.05} ^o & Precursors Modified Sol gel Zn(CH ₃ COO) ₂ 2H ₂ O, MgCl ₂ 6H ₂ O, aluminium isopropoxide (C ₉ H ₂₁ AlO ₃)
Average crystallite size D (nm)	36	57	35	27	
Optical band gap (eV)	3.24	3.25	3.17	3.19	

From table -12, it seems that Mg is responsible for the small enhancement in energy gap and Al is responsible for the shrinkage of energy gap. K. Omri et al. dissolved the major precursor, zinc acetate dihydrate in 70 millilitres of methanol (CH₃OH). In order to dope, appropriate amounts of Copper (II) acetate monohydrate [Cu(CH₃COO)₂.H₂O] and gallium(III) nitrate monohydrate were added with constant stirring until total dissolution. To create powder aerogels, the resultant transparent solution was dried under supercritical ethanol conditions at 2500C at a rate of 450C/hr. The samples ZnO-Cu, ZnO-Ga, and ZnO-Cu/Ga were assigned to these Cu (1 at.%) doped ZnO, Ga (4 at.%) doped ZnO, and Cu(1 at.%) Ga(4 at.%) doped ZnO powders, respectively [20].

Table-13

The band gap and average size of nanoparticles samples [20].

Sample	ZnO	ZnO-Cu	ZnO-Ga	ZnO-Cu/Ga	Synthesis method & Precursors	Reference
Average crystallite size D (nm)	32	36	45	39	Sol gel Zn(CH ₃ COO) ₂ H ₂ O, Cu(CH ₃ COO) ₂ H ₂ O, Ga(NO ₃) ₃ H ₂ O & methanol	(20)
Optical band gap (eV)	3.34	3.29	3.06	3.11		

Average crystallite size is 32nm which is least for pure ZnO and it increases on doping

Average crystallite size is 32nm which is least for pure ZnO and it increases on doping either with Cu or Ga but crystallite size is increased more in the case of Ga doping. Energy band gap is 3.34 eV for undoped ZnO and it decreases on doping either with Cu or Ga but in the case of Ga doping, it shrinks more. M.D. Alshahrani et al. dissolved 4.38 g of zinc nitrate and 1.05 g of glycine in 100 mL of distilled water, where glycine acted as a fuel and complexing agent. The solution was stirred at 750 rpm for 5 min and then heated on a hot plate to

approximately 300°C under continuous stirring. As the water evaporated, the solution gradually formed a viscous gel. After around 1 hour and 45 min, the gel began to dry and then underwent an exothermic combustion reaction, generating gases such as CO₂, H₂O vapour and N₂. This resulted in the formation of an off white ZnO powder, which was ground into fine particles using a mortar and pestle. The use of glycine not only facilitates gel formation but promotes uniform particle morphology and better thermal decomposition. For the synthesis of Zn_{0.99-x}Cr_xMn_{0.01}O samples (x = 0, 0.01, 0.02), the procedure remained the same, with the addition of precise dopant amounts to the solution: For Mn doping (fixed

at 0.01), 0.040 g Of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was used, and for Cr doping, 0.080 g ($x = 0.01$) and 0.160 g ($x = 0.02$) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used, The dopants were dissolved along with the Zinc nitrate and glycine during the initial solution preparation step. Following combustion. All the resulting powders were subjected

to post synthesis heat treatment in a muffle furnace at 600°C for two hours to phase purity and crystallinity [59]. The crystal Structure and purity were examined using X-ray diffraction (XRD). The morphology and grain size were analysed using a SEM.

Table -14

Crystalline Size, micro-strain and dislocation density were calculated using XRD data [59].

Samples	Crystal size D (nm) XRD	C axis of cell Parameters	Dislocation densit	Microstrain	Synthesis method Precursors
Pure ZnO	44.53	5.210	0.000504	0.000795	Sol gel Zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, glycine $\text{C}_2\text{H}_5\text{NO}_2$, Chromium nitrate nonahydrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and manganese(II) nitrate tetrahydrate $(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
$\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$	43.79	5.2097	0.000521	0.000808	
$\text{Zn}_{0.98}\text{Cr}_{0.01}\text{Mn}_{0.01}\text{O}$	43.58	5.2075	0.000526	0.000813	
$\text{Zn}_{0.97}\text{Cr}_{0.02}\text{Mn}_{0.01}\text{O}$	42.65	5.2066	0.00055	0.00083	

Pure ZnO and $\text{Zn}_{0.99-x}\text{Cr}_x\text{Mn}_{0.01}\text{O}$ nanoparticles possessed hexagonal wurtzite structure from XRD. On increasing doping concentration, crystal size decreases from 44.53nm to 42.65nm.

Conclusion:

In this review, pure and metal doped ZnO nanoparticles and nanopowders were synthesized using different precursors, solvents and their concentration via Sol gel method. Structure and energy band gap of pure and metal doped ZnO nanoparticles or nanopowders can be tuned by changing precursors, solvents, heat time and temperature etc. It has been also found that morphology and energy band gap can be changed by changing concentration of precursors and dopants. Structural, Optical, electrical, magnetic and catalytic properties by changing either concentration of precursors or solvent type or heat time or annealing temperature can be changed. This study will improve our understanding of developments in doped ZnO and will assist in the creation of new ZnO based nanomaterials with improved structural, optical and photocatalytic properties.

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