RESEARCH PAPER

Defect-Engineered Tb^{3+}-Doped ZnO Nanoparticles via Mechanochemical Route: Correlating Structural Evolution, Optical Band Gap Modulation and Thermal Stability

Ratnamala T. More[1,3], Yogeshwar D. Kaldante[3], Suresh T. More[4], Dinesh N. Navale[5], Rashmi D. Pathrikar[2], Sunil R. Mirgane[1,2]*

Email- stm.vpmkchem@gmail.com

[1]Department of Chemistry, Jalna Education Society's R. G. Bagdia Arts, S.B. Lakhotia Commerce and R. Bezonji Science College, Jalna 431203 INDIA

[2]Rajarshi Shahu Arts, Commerce and Science College, Pathri, Chhatrapati Sambhaji Nagar – 431003 INDIA

[3]Department of Chemistry, PDEA's Annasaheb Waghire College, Otur, Pune, Maharashtra- 412409, INDIA.

[4]Department of Chemistry, VPMK's Appasaheb (Bhanushali) Arts Commerce and Science College Kinhavali, Thane, Maharashtra - 421403, INDIA.

[5]Vivekanand Education Society's College of Arts, Science and Commerce, (Autonomous), Chembur Mumbai-400 071, Maharashtra, INDIA

Abstract

Zinc oxide (ZnO) nanoparticles have attracted considerable attention due to their exceptional optical qualities, extraordinary structural stability, and several technological uses. However, deliberate alteration of their electronic structure is necessary to customise their physicochemical characteristics for improved performance. In this work, terbium (Tb^{3+})-doped Zinc oxide (ZnO) nanoparticles were successfully produced using a simple mechanochemical method and then calcined at 500 °C. The structural, morphological, optical, and thermal characteristics of ZnO nanoparticles were thoroughly examined concerning to rare-earth doping.

The efficient incorporation of Tb ions into the ZnO lattice was demonstrated by X-ray Diffraction (XRD) studies confirmed the formation of a single-phase. hexagonal wurtzite ZnO structure without identifiable secondary phases. Dopant ion-induced lattice deformation was indicated by a small shift in diffraction peaks. Surface hydroxyl groups and distinctive Zn–O the vibrational modes were analyzed through the application of a Fourier transform. infrared (FTIR) spectra. Energy dispersive spectroscopy (EDS) verified the presence of Zn, O, and Tb elements, during which scanning electron microscopy (SEM) pictures revealed nanoscale quasi-spherical particles with mild aggregation.

UV-visible diffuse reflectance spectroscopy (UV-DRS) analysis of optical characteristics revealed a change in the photosensitive band gap with Tb doping, which was explained by the introduction of defect levels and localised electronic states within the ZnO band structure. The efficiency of calcination at 500 °C in creating stable crystalline nanostructures was confirmed by thermogravimetric analysis (TG–DTG–DSC), which showed that the produced nanoparticles exhibit exceptional thermal stability beyond 400 °C.

The work emphasises that rare-earth doping in concurrence with mechanochemical production offers an effective method for adjusting the physical and optical characteristics of ZnO nanoparticles, making them attractive options for cutting-edge functional applications.

Keywords

ZnO nanoparticles; Terbium doping; Mechanochemical synthesis; Defect engineering; Band gap modulation; Thermal stability

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1. Introduction

Due to its exceptional physicochemical characteristics, which include a large direct band gap (~3.37 eV), a high exciton binding energy (~60 meV), outstanding chemical stability, and low toxicity, zinc oxide (ZnO) is a highly researched II–VI semiconductor material [1–4]. Because of these inherent qualities, ZnO is a very promising material for a range of uses, including gas sensors, optoelectronic devices, photocatalysis, and environmental remediation systems [5–7]. Because of their high surface-to-volume ratio, greater surface reactivity, and better charge transport characteristics,

nanoscale ZnO materials in particular perform noticeably better [8,9].

Despite these benefits, a number of inherent disadvantages frequently limit pure ZnO's usefulness. Rapid recombination of photogenerated electron-hole pairs is one of the main obstacles, which drastically lowers its performance in photocatalytic and optoelectronic applications [10–12]. Furthermore, ZnO's A wide band gap restricts its absorption to the UV spectrum, which inhibits its use when exposed to visible light [13–15]. The efficient application of ZnO in sophisticated functional systems is hampered by these restrictions.

Metal doping, non-metal doping, heterojunction creation, surface modification, and defect engineering are some of the methods for alteration that have been investigated to get beyond these restrictions [16–19]. Among these, doping with rare-earth elements has become a very successful strategy because of their special electronic configuration and capacity to add intermediate energy levels to semiconductor band structures [20–23].

Because their partially filled 4f orbitals are protected by outer orbitals, rare-earth ions can form localised energy states inside ZnO's band gap [24–26]. In order to decrease charge carrier recombination and increase carrier lifespan, these localised states serve as electron trapping centers [27–29]. Furthermore, rare-earth doping can induce lattice distortion, increase defect density and modify crystallinity, thereby significantly impacting the structural and optical characteristics of ZnO nanoparticles [30–32].

Terbium (Tb^{3+}), one of the rare-earth elements, has garnered a lot of interest because of its unique electronic structure and significant impact on defect chemistry [33–35]. The mismatch in ionic radii between Tb^{3+} and Zn^{2+} ions causes lattice distortion when Tb^{3+} ions are incorporated into the ZnO lattice [36–38]. Oxygen vacancies and defect states are created as a result of this replacement, and they are crucial for band gap modulation and optical property enhancement [39–41]. Tb doping is also a suitable dopant for ZnO-based nanomaterials because it enhances light absorption and facilitates effective charge separation [42–44].

The synthesis route is an prime factor in defining the structural and functional features of nanomaterials, aside from compositional change. Sol-gel, hydrothermal, and co-precipitation methods are examples of conventional synthesis techniques that frequently entail complicated processes, lengthy processing durations, and high energy usage [45–47]. On the other hand, mechanochemical synthesis has become a straightforward, economical, and eco-friendly method for creating nanomaterials [48–50].

High-energy grinding is used in mechanochemical processing, which facilitates uniform mixing at the atomic level, improves solid-state diffusion, and encourages defect development [51–53]. Benefits of this approach include shorter reaction times, less solvent use, scalability, and better doped system homogeneity [54–56]. Furthermore, The integration of mechanochemical synthesis with controlled calcination enhances the crystallinity and phase purity of the resulting nanoparticles [57–59].

The present study employed a mechanochemical approach to synthesize Tb^{3+}-doped ZnO nanoparticles, which were subsequently calcined at 500 °C. Techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy with energy dispersive spectroscopy (SEM–EDS) were utilized. UV–visible diffuse reflectance spectroscopy (UV–DRS), and thermogravimetric analysis (TG–DTG–DSC) were used to methodically examine the structural, morphological, optical, and thermal properties of the produced nanoparticles. In order to shed light on ZnO nanoparticles' potential for sophisticated functional applications, this study aims to demonstrate a direct relationship between rare-earth doping, defect formation, and the ensuing changes in their structural and optical characteristics.

2. Experimental Section

2.1 Materials

All chemicals used in this study were of analytical grade and did not need any further purification. The main The zinc precursor used was zinc acetate dihydrate ($Zn(CH_3COO)_2•2H_2O$, ≥99%, Merck, India). Terbium nitrate hexahydrate ($Tb(NO_3)_3•6H_2O$, 99.9%, Sigma-Aldrich), 99.9%, Sigma-Aldrich) were employed as dopants. Because of its potent chelating capacity and function in precursor production, oxalic acid dihydrate ($H_2C_2O_4•2H_2O$) was employed as a complexing/precipitating agent [60–62].

2.2 Synthesis of Tb^{3+}-Doped ZnO Nanoparticles (Mechanochemical Route)

Mechanochemical and thermal treatment were used to create Tb^{3+}-doped ZnO nanoparticles. A well-known solid-state method that facilitates effective mixing,

improved diffusion, and defect creation in nanomaterials is mechanochemical processing [65–69].

First, stoichiometric amounts of terbium nitrate and zinc acetate dihydrate were precisely weighed, where x stands for dopant concentration. To help create a homogenous precursor complex, Oxalic acid dihydrate was incorporated. as a chelating and precipitating agent in a 1:2 proportion of moles to the zinc precursor [60–62].

To assure uniform mixing and efficient mechanical activation, the precursor mixture was vigorously mashed for around 45 minutes using an agate mortar and pestle. Repeated fracture and cold welding procedures during grinding improved solid-state diffusion and encouraged the creation of a homogeneous intermediate precursor phase [65,67,70].

To eliminate moisture and volatile ingredients, the resulting paste-like mixture was dried for an hour under an infrared (IR) lamp. After the dried bulk was further crushed into a fine powder for fifteen minutes, it was subjected to an hour of secondary infrared drying.

After that, the precursor powder was moved to a ceramic crucible and calcined for several hours at 500 °C temperature in a muffle furnace. The fabrication of crystalline Tb^{3+}-doped ZnO nanoparticles and the breakdown of oxalate-based precursor complexes were made easier by this heat treatment [71–74]. Additionally, phase stability and crystallinity are enhanced by calcination [75,76].

Following calcination, the samples were left in the boiler to naturally cool to ambient temperature. The finished product was gathered, ground, and kept in airtight receptacles.

2.3 Characterization Techniques

Using a variety of sophisticated analytical methods, the structural, morphological, optical, and thermal properties of the produced Tb^{3+}-doped Zinc oxide (ZnO) nanoparticles were methodically examined.

X-ray diffraction (XRD) analysis was utilized to examine the crystalline structure, phase purity, and lattice characteristics of the synthesized nanoparticles. The diffraction patterns were recorded using Cu Kα radiation (λ = 1.5406 Å) over an appropriate 2θ range. The Debye–Scherrer equation was employed to estimate the average crystallite size, and the corresponding diffraction peaks were indexed to ascertain the crystal structure. XRD remains an essential technique for phase identification and crystallographic analysis of nanomaterials [77,78].

Fourier Transform Infrared (FTIR) spectroscopy was utilized to investigate the functional groups and chemical bonds present in the synthesized nanoparticles. To identify specific vibrational modes associated with the Zn–O interaction and surface hydroxyl groups, the spectra were collected within the wavenumber range of 4000–400 cm^{-1}. FTIR analysis offers valuable insights into the surface chemistry of oxide nanoparticles and the bonding between metal and oxygen [79,80].

Scanning electron microscopy (SEM) was utilized to analyze the surface features of the nanoparticles, their particle size distribution, and their microstructural properties. Additionally, Energy Dispersive Spectroscopy (EDS) connected to the SEM apparatus was used to corroborate the elemental composition and distribution of constituent elements, allowing for qualitative and semi-quantitative examination of Zn, O, and Tb elements. For the morphological and compositional characterisation of nanostructured materials, SEM-EDS is frequently used [81,82].

Using UV–Visible Diffuse Reflectance Spectroscopy (UV–DRS) in the 200–800 nm wavelength range, the optical characteristics and light absorption behaviour of the produced nanoparticles were examined. Assuming a direct allowed transition characteristic of ZnO, the optical band gap energy was calculated using the Kubelka–Munk function and Tauc plot method. A trustworthy method for assessing optical transitions and band gap energy in semiconductor nanomaterials is UV-DRS analysis [83,84].

Thermogravimetric Analysis (TGA) in conjunction with Derivative Thermogravimetric (DTG) and Differential Scanning Calorimetry (DSC) techniques were used to assess the thermal stability and decomposition behaviour of the produced nanoparticles. In order to evaluate the material's weight loss patterns, phase transitions, and thermal stability, measurements were conducted under controlled settings throughout a broad temperature range. Understanding the stability and breakdown behaviour of nanostructured oxides requires the use of thermal analytical techniques [85,86].

3. Results and Discussion

3.1 X-ray Diffraction (XRD) Analysis

Figure 1 displays the X-ray diffraction (XRD) pattern of ZnO nanoparticles doped with Tb^{3+}, which were synthesized through the mechanochemical method and

subsequently calcined at 500 °C. The observation of diffraction peaks at specific 2θ values related to the crystallographic planes (100), (002), (101), (102), (110), (103), (200), (112), and (201) confirms the formation of ZnO with a hexagonal wurtzite crystal structure [87–89]. The exceptional match of the resulting diffraction pattern with reference JCPDS card No. 36-1451 indicates the high phase purity of the synthesized material.

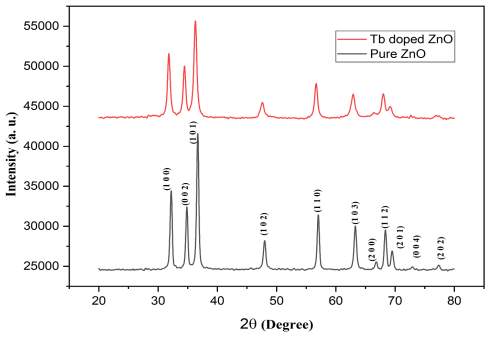

Figure 1. XRD pattern of Tb^{3+}-doped ZnO nanoparticles synthesized via mechanochemical route and calcined at 500 °C.

Crucially, no extra diffraction peaks that correspond to terbium oxide or additional impurity phases are identified, indicating that Tb^{3+} The ions are seamlessly incorporated into the ZnO lattice without creating distinct crystalline phases [90,91]. This supports earlier findings on rare-earth doped ZnO systems by confirming the efficient substitutional or interstitial integration of Tb ions into the ZnO matrix.

The addition of Tb^{3+} ions causes lattice deformation, which results in a minor change in peak sets when compared to pure ZnO [92,93]. The arrangement of atoms in a crystal structure. experiences strain due to the ionic radius mismatch between Tb^{3+} and Zn^{2+}, which causes slight modifications in lattice properties. The electrical structure and defect states of ZnO nanoparticles are recognized to be affected by such structural deformation.

The diffraction peaks exhibit clarity and sharpness, which signifies the high crystallinity of the produced nanoparticles [94]. The average crystallite size (D) was determined using the Debye–Scherrer formula.:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, D = Crystallite size (nm)

0.9 = Shape factor (constant, typically 0.89–0.94)

λ (lambda) = Wavelength of X-ray (e.g., Cu Kα = 0.15406 nm)

β (beta) = Full Width at Half Maximum (FWHM) in radians

θ (theta) = Bragg angle

The calculated crystallite size confirms that the synthesized Tb-doped ZnO nanoparticles are in the nanometer range. The nanoscale crystallite size provides a higher surface area and enhanced surface activity, which is beneficial for various functional applications [95].

3.2 Analysis using Fourier Transform Infrared (FTIR)

Figure 2 displays the Fourier Transform Infrared spectra of Tb^{3+}-doped ZnO nanoparticles found in the 4000–400 cm^{-1} region. The spectrum offers important details on the chemical bonds and vibrational properties of the produced substance. The stretching vibration of hydroxyl (–OH) groups, which are connected to adsorbed water molecules or surface hydroxyl species, is represented by a wide absorption band seen at about 3400 cm^{-1} [96,97]. These -OH groups are known to contribute to the reactivity of the nanoparticles and play a significant part in surface-related processes.

The absorption band around ~1600 cm^{-1} is attributed to the bending vibration of adsorbed water molecules (H–O–H), indicating the presence of residual moisture on the nanoparticle surface [98]. Such features are commonly observed in oxide nanomaterials synthesized via mechanochemical or wet chemical methods.

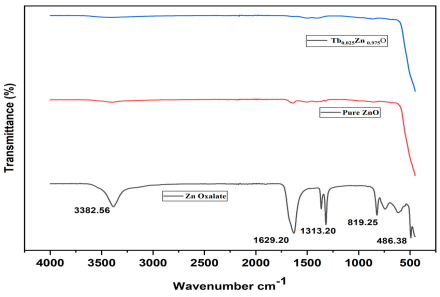

Figure 2. FTIR spectrum of Tb^{3+}-doped ZnO nanoparticles showing Zn–O stretching vibrations

The creation of the ZnO lattice is confirmed by the most prominent peak in the lower wavenumber band (~450–550 cm^{-1}), which corresponds to Zn–O stretching vibrations [99,100]. For ZnO nanostructures, this distinctive band acts as a fingerprint.

The lack of extra peaks associated with organic contaminants or precursor residues suggests that

calcination at 500 °C successfully eliminates intermediate chemicals, producing pure Tb-doped ZnO nanoparticles.

3.3 SEM–EDS Analysis

SEM analysis was conducted to examine the surface morphology and microstructural features of the synthesized Tb^{3+}-doped ZnO nanoparticles; the obtained micrographs can be seen in Figure 3. The SEM images reveal that the nanoparticles exhibited nanoscale dimensions and displayed a morphology that ranged from nearly spherical to quasi-spherical.

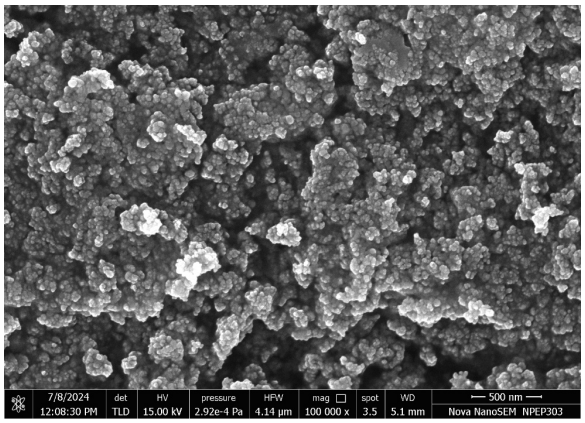

Figure 3. SEM micrographs of Tb^{3+}-doped ZnO nanoparticles showing quasi-spherical morphology and particle agglomeration.

The particles seem to be fairly uniform in size, although some agglomeration is present. This agglomeration can be attributed to the strong interparticle interactions that arise from the high surface energy of nanoparticles during the calcination process [101,102]. Nanoparticles of metal oxides synthesized through solid-state or mechanochemical techniques commonly demonstrate this type of aggregation behavior.

Since SEM shows aggregated particle size rather than individual crystallites, the particle size seen in SEM is somewhat greater than the crystallite size determined by XRD analysis.

As illustrated in Figure 4, EDS analysis was employed to further confirm the elemental composition of the synthesized nanoparticles.

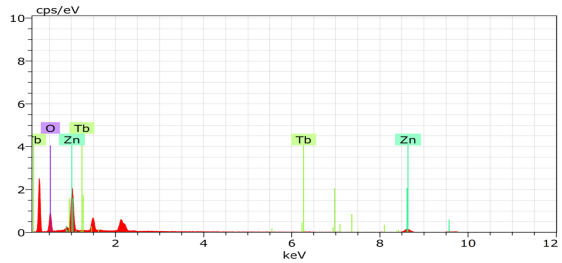

Figure 4. EDS spectrum of Tb^{3+}-doped ZnO nanoparticles confirming the presence of Zn, O and Tb elements.

The efficient incorporation of terbium into the ZnO matrix is confirmed by the EDS spectra, which clearly shows the presence of Zn, O, and Tb elements [103,104]. The EDS spectrum shows no impurity peaks, demonstrating the synthetic material's great purity. The effective doping of Tb into ZnO nanoparticles and consistent morphology are confirmed by the combined SEM–EDS measurements.

3.4 UV–Visible Diffuse Reflectance Spectroscopy (UV–DRS) Analysis

UV-DRS was used to examine the optical characteristics of the Tb^{3+}-doped ZnO nanoparticles; Figure 5 displays the corresponding spectrum. ZnO semiconductor materials are characterised by a prominent absorption edge in the ultraviolet portion of the spectrum.

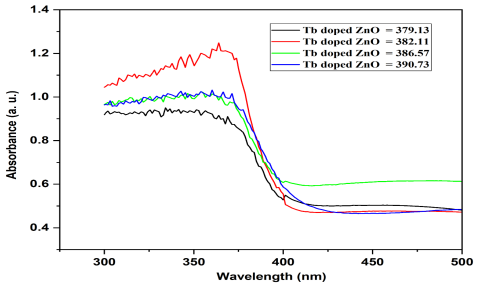

Figure 5. UV–DRS spectrum of Tb^{3+}-doped ZnO nanoparticles.

Electrons moving from the valence band to the conduction band are represented by the absorption edge [105,106]. The absorption edge's sharpness suggests that the produced nanoparticles have a well-defined electrical structure and good crystallinity.

As seen in Figure 6, the Tauc plot was used to determine the optical band gap energy using the following relation:

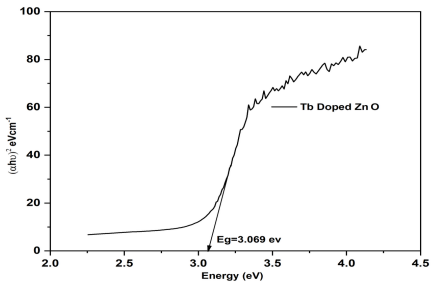

Figure 6. Tauc plot of Tb^{3+}-doped ZnO nanoparticles for determination of optical band gap.

(αhν)2=A(hν−Eg)(\alpha h\nu)^2 = A(h\nu - E_g)(αhν)2=A(hν−Eg)

The calculated band gap value shows a little deviation from pure ZnO, indicating that Tb doping modifies ZnO's electrical structure [107–109]. This change results from the introduction of defect states and localised energy levels within the band gap, which improve the material's functional characteristics by influencing optical transitions and acting as charge carrier trapping centers.

4. Conclusion

Tb^{3+}-doped ZnO nanoparticles were successfully produced in this research through a simple mechanochemical technique and subsequently calcined at 500 °C. The utilized synthesis method proved to be simple, cost-effective, and environmentally friendly, enabling the formation of nanostructured materials with high phase purity and crystallinity.

The effective integration of Tb^{3+} ions into the ZnO lattice was confirmed through X-ray diffraction analysis, which substantiated the formation of a singular-phase hexagonal wurtzite ZnO structure devoid of any secondary impurity phases. The structural effects of rare-earth doping were illustrated by the noted peak shifts, indicating lattice distortion caused by the mismatch in ionic size between Tb^{3+} and Zn^{2+}.

The ZnO framework's formation and the presence of active surface species were validated through FTIR analysis, which also indicated the existence of surface hydroxyl groups and specific Zn–O stretching vibrations. Meanwhile, EDS analysis confirmed the elemental composition and uniform integration of terbium within the ZnO matrix, while SEM images revealed quasi-spherical nanoparticles with nanoscale sizes and slight aggregation.

The formation of localized defect states and impurity energy levels within the ZnO band structure has led to a notable alteration in the band gap energy as observed through optical measurements using UV-DRS with Tb doping. These states induced by defects play a crucial role in enhancing functional performance and modifying optical characteristics.

The present research demonstrates a significant relationship between defect creation, doping with rare-earth elements, and the resulting structural and optical variations in ZnO nanoparticles. Using the mechanochemical method along with Tb doping allows for the effective and scalable engineering of ZnO-based nanomaterials with tunable properties, making them promising candidates for advanced applications in photocatalysis, optoelectronics, and environmental cleanup.

5. References

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