Tailoring structural and optical properties of ZrO_2 with nickel doping

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Abstract

Pure and nickel doped zirconium oxide (ZrO_2) samples namely N1, N2, N3, N4 have been synthesized by sol–gel method at different doping concentrations (0, 1, 3 and 5 molar percentage respectively). Energy dispersive X-ray spectroscopy (EDS) was used to confirm the elemental composition of samples. X-ray diffraction data following Rietveld refinement revealed the stabilization of tetragonal phase with some impurity of monoclinic phase. Unit cell volume and tetragonal-ity (c/a) ratio was found to be in good agreement with standard values. Results showed the increase in unit cell volume with the decrease in crystallite size. UV–visible spectroscopy, revealed the variation in optical band gap with increase in Ni dopant in ZrO_2 nano-crystals due to combined effect of quantum confinement and generation of interstitial sites.

Keywords Zirconium oxide · Nickel · XRD · Rietveld refinement · UV–visible spectroscopy

1 Introduction

Over the years, zirconium oxide and its doped counterparts attract considerable interest due to its structural behavior and various applications. Pure zirconia (ZrO_2) exist in three polymorphs; monoclinic, which remain stable up to 1447 K, then it transforms to tetragonal, which further transform to cubic phase above 2643 K. Cubic phase of zirconia is stable up to melting point (2953 K). Physical properties of zirconia is governed by nature of phase existed. The properties of zirconia, namely, low wear resistance, high hardness, high elastic modulus, chemical inertness, high transparency in ultra-violet and visible region, large optical band gap, high melting point, large dielectric constant, low coefficient of friction, low thermal conductivity and high melting temperature makes the material interesting candidate for applications such as piezoelectric devices, refractories, oxygen sensors and ceramic condensers [1–6]. Earlier, ZrO_2 was doped with rare earth metal oxides like Y_2O_3 , CaO , La_2O_3 , MgO , Ce_2O_3 , and Y_2O_3 [7–11]. Later, transition metal oxides like Cr_2O_3 , MnO_2 , NiO , CuO and Fe_2O_3 were used and could be well dislodged

in zirconia lattice with the perspective to elaborate the redox properties of these oxides [12–16]. These oxides have been doped to stabilize tetragonal or cubic phase of zirconia at low temperature. Stabilization of tetragonal or cubic phases at low temperature and phase transformation with the change in dopants and temperature of annealing have been explained by various reports [17–23]. The inconsistency with the zirconia literature and discrepancies in research reports is mainly in reference of alteration of structural properties, which alter with the doping of different atoms in lattice [24]. Several reports point out the stabilization of cubic phase [25–28], tetragonal phase [29, 30] and monoclinic phase [31]. Literature also showed the formation of low temperature stabilization of tetragonal phase without the addition of any dopant [32]. Further, zirconia have also being used in optical field including electro-optical devices and broadband filters due to excellent optical properties [33, 34]. Band structures of zirconia are highly influenced by crystallite sizes, crystal phases and nature of defects [35]. ZrO_2 is a photo-catalytic and active photon absorber having wide band gap with two direct band to band transitions at 5.2 eV and 5.79 eV

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[33]. Valence band of zirconia is mainly constructed by 2p states of oxygen with some amalgamate of 4p states of Zr and conduction band is primarily formed by 4p states of Zr with some mixing of 2p states of oxygen [36]. Optical band gap can be decreased or increased in comparison to the undoped host material. Widening of the band gap is due to the quantum confinement effect and blocking of the lowest states of the conduction band, known as Moss–Burstein effect. Reduction in the band gap is due to the lattice defects, which generate extrinsic energy levels between bands.

Unit cell and optical band gap of ZrO_2 can be varied with the addition of cation as dopant depending upon the ionic radius of element [37, 38]. Pure ZrO_2 also contain some intrinsic defects such as O vacancies, Zr vacancies and interstitial Zr [33]. Generally dopants used are of smaller size with lower valency (lower than Zr^{4+}), which may result in generation of holes and decrease the crystallite size. Structural and optical properties of ZrO_2 can be tailored by suitable doping of cobalt, zinc, iron, nickel and copper. Nickel (Ni) dopant is gaining great interest because of its inhibition inside the ZrO_2 matrix, capacity of grain development, eco-friendly nature, good optical and electrochemical properties and being economical [39–42]. By introducing extrinsic dopant Ni, having smaller ionic radius ($0.69 \text{ \AA}$) as compared to Zr^{4+} ($0.84 \text{ \AA}$) [43] may affect the defect environment, which will play an important role in tuning the structural and optical properties of ZrO_2 . Ahmed et al. [44] examined the narrowing of optical band gap of Ni doped SnO_2 nanoparticles. Rajesh et al. [45] explored the structural and optical properties of Ni doped ZrO_2 nanoparticles. Moreover, literature survey revealed that majority of the work concentrates on Ni doped SnO_2 [46], Ni doped ZnO [47], Ni doped TiO_2 [48]. Although, little study have been reported to scrutinize deeply into the structural and optical properties of Ni doped ZrO_2 [45, 49]. So, it is quite worthy to investigate the effect of Ni doping on the structural and optical properties of ZrO_2 . There is possibility of the replacement of Zr^{4+} ions with Ni^{2+} ions, which will results in change in concentration of oxygen vacancies and have vital role in obtaining feasible applications of ZrO_2 .

2 Experimental

Powder of pure and Ni doped ZrO_2 (0%, 1%, 3% and 5%) were synthesized by using sol–gel method. All the precursors are of analytical grade and used without further purification. Precursor solution was prepared by using zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 2-butanol, ethanol, acetylacetone, nitric acid and water in a desired ratio.

Ethanol and 2-butanol were mixed in the ratio of 1:1 and one-third of this mixture was used to dissolve zirconium oxide salt and remaining two-third of mixture was used to dissolve Ni salt. Oxide solution was stirred for 60 min and then nitric acid: acetylacetone: water was added into the stirring solution in the ratio of 0.4:5:15. Then Ni solution having desired concentration was added into the oxide solution slowly and stirring continuously for next 100 min till the formation of clear solution. Then filtered solution is evaporated to obtain powders of pure and Ni doped ZrO_2 . All the powder samples then annealed at 500°C for further characterization. Structural properties of synthesized samples were investigated through X-ray diffraction (Panalytical's X'pert Pro). Energy dispersive spectroscopy (Hitachi SU-8010) was employed to confirm elemental composition and optical properties was investigated through UV–visible spectroscopy (Shimadzu UV-1800).

3 Results and discussion

3.1 Elemental composition

Figure 1a show the EDS of pure ZrO_2 powder, which represent the composition of zirconium and oxygen in the synthesized sample. Doping of Ni was also confirmed by EDS in 5% Ni doped ZrO_2 as shown in Fig. 1b. Effective doping for Ni doped sample was found to be 4.39%.

Fig. 1 Energy dispersive X-ray spectroscopy of **a** pure and **b** 5% Ni doped ZrO_2

Fig. 2 X-ray diffraction of pure and Ni-ZrO₂ (1%, 3%, 5%) powders

3.2 Structural analysis

Figure 2 shows the X-ray diffraction (XRD) patterns of pure and Ni doped ZrO₂ powders synthesized by sol-gel method. The diffraction peaks are associated with (hkl) planes having tetragonal orientation along (101), (002), (110), (102), (112), (103), (211), (202), (220), (213), (310) (ICSD card number 01-80-0965) and monoclinic orientation along (110), ($\bar{1}11$), (111) and ($\bar{1}20$) (ICSD card number 00-37-1484). However, there were no Ni/NiO peaks observed in the doped samples emphasizing that the dopant was well dissolved in the ZrO₂ crystal lattice.

All the pure and Ni doped samples have broader diffraction peak as compared to that of standard XRD data, which confirms the smaller crystallite size of the synthesized particles in the nanometer range. Crystallite size of the particles have been evaluated by using Scherrer's formula [50].

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

Here D , k , λ , β and θ are average crystallite size in nm, Scherrer's constant (0.9), wavelength of X-rays (1.5406 Å), full width at half maximum (FWHM) in radians, and Bragg's diffraction angle respectively. Average crystallite size for pure ZrO₂ (N1) was found to be ~21.6 nm and for Ni doped samples 1% (N2), 3% (N3) and 5% (N4) are approximately 11.4 nm, 14.1 nm and 15.4 nm respectively. Decrease in crystallite size for N2 sample was due to the contraction of lattice of ZrO₂ because of smaller ionic size of Ni (0.69 Å) as compared to that of Zr (0.84 Å) [43]. With the increase in Ni doping beyond 1%, there was increase in crystallite size. This increase in crystallite size is due to the increase in abundance of Ni in the host material, which leads to the large grain growth of Ni doped ZrO₂ [51] and agglomeration of grains around dopant material [36].

It can be seen that monoclinic phase of ZrO₂ increases in sample N4. Increase in monoclinic phase at lower temperature as compared to pure ZrO₂ (N1) can be attributed to the modified chemistry of inner-volume interfaces [52]. Increase in tetragonal grain size and concentration of oxygen vacancies in the presence of dopant can play significant role in the generation of monoclinic phase [53, 54]. With Ni doping, increase in oxygen vacancies at the surface of tetragonal phase favors structural rearrangement, ionic reorganization and bond rupture for monoclinic phase. It is already well accepted that the rate of transformation from tetragonal to monoclinic is strongly influenced by the concentration of oxygen vacancy [54].

XRD patterns of the samples have been fitted with Thompson-Cox-Hastings pseudo-voigt axial divergence asymmetry function of peak shape for Rietveld refinement analysis using fullprof software [55, 56]. Because of considerable line broadening and overlapping of X-ray reflections, actual structure can only be observed by Rietveld refinement. Refinement fitting of pure and Ni-doped ZrO₂ is shown in Fig. 3. Chi square (χ^2) of refinement, R-factors and S ($= R_{wp}/R_{exp}$) are listed in Table 1. Goodness of fit is represented by 'S' parameter. Value of 'S' parameter adjacent to unity shows the quality of fitting. Values of lattice parameters of pure and doped ZrO₂ derived after refinement are listed in Table 2 and Fig. 4. Variation in 'c' is in accordance with unit cell volume and contraction in 'a' is noticed up to 3% doping and increases with

Fig. 3 Rietveld refinement analysis experimental data (open black squares), fitted data (red) and residue (blue) of pure and doped ZrO₂ samples

Table 1 R-factors (R_p , R_{wp} and R_{exp}), chi square (χ^2) and goodness of fit (S) after Rietveld refinement

Sample ID	R-factors			S ($=R_{wp}/R_{exp}$)	χ^2
	R_p	R_{wp}	R_{exp}		
N1	17.10	13.70	11.29	1.213	1.48
N2	11.00	10.30	9.73	1.059	1.11
N3	16.20	14.30	11.34	1.261	1.59
N4	12.20	10.60	10.47	1.012	1.03

5% doping due to the increase in monoclinic phase [57]. Unit cell volume and tetragonality (c/a) ratio was found to be approximately $66\text{--}67 \text{ \AA}^3$ and 1.44, which is in good agreement with standard value of 66.9 nm^3 and 1.4429 (ICSD card number 80–0965). It was found that unit cell volume increases with 1% Ni doping (N2), which is in good agreement with already published study that the unit cell volume increases with decrease in crystallite size [58, 59]. Expansion in the unit cell volume with the decrease in crystallite size was attributed to the larger number of dangling bonds in smaller crystals. Ni doping may displace Zr atoms toward coordinated axis, which in turn produce surface defect dipoles. Expansion of unit cell volume is due to the increase in negative pressure because of interaction as compared to positive pressure due to surface curvature effect up to some critical crystallite size [59]. Further with the increase in doping concentration to 3% (N3), decrease in unit cell volume is observed with the increase in crystallite size. With the increase in doping to 5% (N4), increase in unit cell volume was observed. This increase in unit cell volume is due to the increase in monoclinic phase with Ni doping, which is in accordance with already published report showing increase in unit cell volume due to tetragonal to monoclinic transformation in ZrO_2 [60]. Tetragonal distortion leads to two distinct bond lengths; one along shorter side and other along longer side [61], which can be clearly seen from Table 2.

Growth orientation of synthesized nanostructures is provided by texture coefficient. Higher the deviation of texture coefficient from unity, higher will be the preferred orientation of that particular plane. Texture coefficient, $TC(h_i k_i l_i)$ was determined using Harris's formula [62–64] from the XRD patterns given by

Fig. 4 Variation of lattice parameters with Ni doping derived from Rietveld refinement**Table 3** Texture coefficient of pure and Ni doped ZrO_2 nanopowders

Crystal planes (hkl)	Texture coefficient, $TC(h_i k_i l_i)$			
	N1	N2	N3	N4
(101)	0.9977	0.9479	0.9792	0.9533
(112)	0.9970	1.0857	1.0284	1.0647
(211)	1.0052	0.9664	0.9923	0.9819

$$TC(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_o(h_i k_i l_i)} \left[\frac{1}{n} \sum_{i=1}^n \frac{I(h_i k_i l_i)}{I_o(h_i k_i l_i)} \right]^{-1}$$

Here $TC(h_i k_i l_i)$, $I_o(h_i k_i l_i)$, $I(h_i k_i l_i)$ and n are the texture coefficient corresponding to plane specified by miller indices $(h_i k_i l_i)$, standard diffraction peak intensities, specimen diffraction peak intensities and number of different peaks taken into account, respectively. Preferred orientation of pure ZrO_2 is along (211) plane. Upon introducing the Ni dopant nanostructures are oriented along (112) plane as shown in Table 3 and Fig. 5. This behavior may be attributed to the incorporation of Ni dopant in ZrO_2 lattice, which produce defects in crystal lattice. So, this can be inferred that Ni doping causes distortion in the crystal lattice, which leads to preferred orientation along (112) plane.

Table 2 Unit cell lattice parameters of pure and Ni-doped ZrO_2 nanocrystals derived after Rietveld refinement

Sample	Lattice parameters		c/a	Cell volume ($\text{\AA}^3$)	Bond length (Longer)	Bond length (Shorter)
	a	c				
N1	3.6018	5.1751	1.437	67.136	2.3464	2.1016
N2	3.6011	5.1801	1.438	67.175	2.3974	2.0631
N3	3.5981	5.1619	1.435	66.826	2.2960	2.1375
N4	3.5997	5.1756	1.438	67.065	2.3872	2.0686

Fig. 5 Texture coefficients of pure and Ni doped ZrO_2 nano-crystals

3.2.1 Unit cell representation of pure and Ni doped ZrO_2

Figure 6 represents the unit cell of pure and Ni doped ZrO_2 modeled by Visualization for Electronic and Structural Analysis (VESTA) version 3.4.7 using lattice parameters and atomic positions from Rietveld refinement. ZrO_2 crystal belongs to the tetragonal structure with two molecules per unit cell ($Z=2$) having point group symmetry (D_{4h}^{15}) and space group (P42/nmc) number 137 in the International Tables of Crystallography [65]. In these unit cell Zr atoms or Ni atoms are co-ordinated to eight oxygen atoms establishing square anti-prism type polyhedral having distorted deltahedral [ZrO_8]/[NiO_8] clusters. Mendes et al. [66]

reported similar results of cluster formation with yttrium (Y) doping in ZrO_2 nanocrystals. From the Fig. 6 it can be verified that bonds between Zr-O-Zr/Ni-O-Ni were projected out of the unit cell. Each deltahedral showed the presence of 8 vertices (V), 10 faces (F) and 16 edges (E). Number of V, F and E present in distorted ZrO_8 or NiO_8 can also be confirmed by using Euler's polyhedral formula given by $V - E + F = 2$.

3.3 Optical analyses

Figure 7 shows the absorption spectroscopy of pure and Ni doped nano-crystals. It is observed that optical absorbance increased with the increase in Ni doping. Being a 3d atom, Ni doping generate new absorption peak which is due to $d \rightarrow d$ transition [67–69] and increase in absorption intensity is due to increase in crystallite size from 1 to 5% (N2–N4) of doping because absorption increases with the increase in crystallite size [70].

Optical band gap of pure and Ni doped ZrO_2 was determined by using UV–Vis spectroscopy. Band gap was calculated by using the Tauc's relation given by [71]

$$\alpha h\nu = \beta (h\nu - E_g)^n$$

Here h is Planck's constant, ν is frequency of incident beam, E_g is optical band gap, n is exponent which can take value 1/2, 2, 3/2, 3 for direct, indirect, forbidden direct and forbidden indirect transitions respectively. α is optical

Fig. 6 Schematic representation of tetragonal unit cell corresponding to ZrO_2 crystal illustrating deltahedral [ZrO_8] clusters

Fig. 7 Absorption spectroscopy of pure and Ni doped ZrO_2 nano-crystals

absorption coefficient given by $a = \ln(1/T)/d$, T is transmittance and d is thickness of absorbing media.

Energy band gap (E_g) is determined by extrapolating the linear portion of $(\alpha h\nu)^2$ and $h\nu$, which intersect photon energy axis as shown in Fig. 8. Pure ZrO_2 (N1) nano-crystals have optical band gap of 5.69 eV. With the increase in doping concentration to 1% (N2), band gap increases to 5.91 eV. This increase in band gap is due to the effect of quantum confinement [31, 72], which is in accordance with XRD results showing decrease in crystallite size with 1% Ni doping (N2). Further, with the increase in doping from 3 to 5% (N3–N4), decrease in band gap is observed,

but it remains large as compared to pure ZrO_2 (N1). This variation in band gap is due to the combined effect of quantum confinement and formation of interstitial sites with the increase in Ni concentration in host material. In addition, band gap also greatly depends on crystalline phases. Larger band gap of 5% Ni doped material (N4) as compared to pure ZrO_2 (N1) may also be due to increase in monoclinic phase, which was also reported by French et al. [73], who demonstrated the band gap of 5.78–6.62 eV for tetragonal phase and 5.83–7.09 eV for monoclinic phase using vacuum ultraviolet spectroscopy (VUV). Another absorption peak can be seen for samples N2, N3 and N4, in the range 4–5.5 eV, which may be due to the generation of defect states in between the band gap of ZrO_2 with Ni doping.

4 Conclusions

Nanocrystals of pure and Ni doped ZrO_2 have been synthesized by using sol–gel method. EDS confirms the Ni doping percentage in ZrO_2 nano-crystals. XRD results showed the variation in crystallite size from approximately 11–22 nm with the increase in doping. Rietveld refinement confirmed the increase in cell volume with the decrease in crystallite size due to dangling bonds in small crystals. Unit cell representation modeled using VESTA showed the formation of Ni cluster for 3% and 5% doping. UV–visible studies represent the increase in optical band gap for 1% Ni doping due to quantum confinement effect. With the

Fig. 8 Variation of energy band gap with Ni doping in ZrO_2 nano-crystals

increase in Ni dopant to 3–5%, band gap decreases due to generation of oxygen vacancies and interstitial sites between valence band and conduction band.

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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