Structural microanalysis of green synthesized Al$_x$Zn$_{(1-x)}$O nanoparticles

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Abstract

In this article, environmentally compatible, low cost and easy green synthesized pure and Al-doped ZnO nanoparticles from the Azadirachta indica leaves extract were prepared. The greenly produced nanoparticles were mainly studied for structural properties. The x-ray diffraction data show that these were crystalline with the hexagonal wurtzite phase. The average crystallite size and some other important physical parameters such as stress, strain and energy density were estimated from the Williamson Hall analysis with the help of Rietveld refinement data. It was observed that with increasing Al-concentration, the crystallite size decreased but the other parameters like stress, strain and energy density increased. It was also seen that with increasing Al addition from 0%–15% the inter-planar spacing $d_{hkl}$ for each $hkl$ set of the samples first decreased and then increased, which indicates the influence of the smaller size of Al ion addition on the inter-planar distance.

1. Introduction

Zinc oxide (ZnO) has a hexagonal wurtzite crystal structure and belongs to an n-type II-VI semiconductor with a broad direct energy bandgap. For monocrystalline ZnO, this bandgap value at ambient temperature is between 3.1 to 3.3 eV. In the case of polycrystalline ZnO, the energy bandgap value is in the range of 3.28–3.30 eV [1]. It also shows a large exciton binding energy of 60 meV. Apart from that, ZnO has several advantages such as low cost, non-toxic, chemically stable, high availability in nature and can be used as a chemically additive material into other materials [2]. From this point of view, ZnO nanopowders perform well in many applications like in the fields of optoelectronic sensors, electronic sensors, gas sensors, solar cells, short-wavelength light-emitting devices and photo-catalyst with high chemical activity [3]. Due to its large optical bandgap, ZnO can transparent the light wave with a wavelength range from 400 – 700 nm and photocatalytic efficiency of only 5% of sunlight. By adding element as an impurity into the ZnO, the energy gap can be modified so that the transparency of the light wavelength range has to be changed. The addition of aluminium (Al) most effectively improves electrical properties. It was found that Al-doped ZnO nanoparticles (NPs) also have advantages such as high transparency beside the high conductivity and low resistivity [4]. Therefore, there is an inherent interest in synthesis, characterization, and understanding of the relationship between size, shape, crystal structure, energy, stress and strain, etc. of pure and Al-doped ZnO nanoparticles. There are so many technologies for the production of pure and doped ZnO nanoparticles such as sol-gel method [5], precipitation method [6], hydrothermal processes [7], magnetron sputtering method [8], pulsed laser deposition method [9], laser ablation in water [10] and spray pyrolysis [11], etc. Most of these methods, however, require difficult experimental conditions, including many complicated and problematic steps with expensive modern infrastructures [12]. Synthesis of nanoparticles by using plant extracts is so environmentally favored, fast, impurity-free, non-toxic, easy to handle reactants, simple reaction conditions, low-energy inputs and after all it is an inexpensive process [13, 14]. Most of the plant
extracts can act as both reducing and stabilizing agents in synthesizing nanoparticles. Different plant parts such as leaves, roots, stems, flowers, fruits and seeds have been used for the synthesis of nanoparticles. Due to its exclusive ability to produce phytochemicals, *Azadirachta indica* (AI) leaf extracts have many medical uses in Ayurveda \[15\]. So it can be a very attractive and valuable plant extract to produce nanoparticles for biomedical applications. On the other hand, the potential of medicinal plants for the production of nanoparticles should still be researched.

In this article, green synthesized \(\text{Al}_x\text{Zn}_{1-x}\) \(\text{O}\) nanoparticles using the AI leaf extracts were examined from the structural point of view. The influence of Al concentration on the lattice deformation, stress-strain relationship and strain as a function of energy density \(U\) was estimated by the modified form of Williamson Hall (WH), called the Uniform Deformation Model (UDM), Uniform Stress Deformation Model (USDM) and Uniform Deformation Energy Density Model (UDEDM). The Rietveld refinement analysis using Fullprof also helped to estimate the structural parameters more accurately.

### 2. Experimental details

In this case, the necessary chemicals such as zinc acetate dihydrate (ZAD), aluminium nitrate nonahydrate (ANN) and ethylene glycol (EG) with analytical grade were used to produce \(\text{Al}_x\text{Zn}_{1-x}\) \(\text{O}\) \((x = 0.00, 0.05, 0.10\) and 0.15\) nanoparticles. A suitable amount of ZAD and ANN were completely dissolved in 50 ml and 20 ml doubled distilled water respectively in two glass beakers separately and stirred for \(\frac{1}{2}\) hour at room temperature to obtain homogeneous solutions. The ANN solution was mixed dropwise with the ZAD solution and stirred again for \(\frac{1}{2}\) hour. After that, 5 ml of EG was added and stirred to obtain a clear solution. Finally, 10 ml of AI leaf extracts were added. After mixing and stirring for 1 h with a magnetic stirrer, a golden yellow precipitate was obtained. AI leaf extract contains flavonoids and phenolic acid compounds that help the bio-reduction reactions. The presence of some terpenoid derivatives in the leaf extract also acts as a capping agent to form a complex molecule with \(\text{Zn}^{2+}\) ion (shown in figure 1) and stabilizes the \(\text{ZnO}\) NPs in solution \[16\]. Precursor solutions made by stoichiometry amount of Al and Zn-salts can also be reduced by the same reaction pathways. All these steps were carried out at room temperature. Later, the solutions were dried and powder samples were obtained. The samples were called \(\text{Al}_0, \text{Al}_5, \text{Al}_10\) and \(\text{Al}_15\) based upon the nominal Al contents.

For structural analysis, data were recorded by X-ray powder diffraction (XRPD) with Cu-K\(_\alpha\) radiation \((\lambda = 1.5406\) Å) using the Bruker D8 Advanced instrument. The structural parameters of the powders were obtained from Rietveld’s analysis (using Fullprof) of the XRPD data. The surface morphologies of the powder samples were studied using a field emission scanning electron microscope (FE-SEM) with the help of Zeiss Ultra Plus 4095, 20 kV machine. The chemical compositions of the samples were determined using an energy dispersive x-ray spectrometer (EDX) equipped with the FE-SEM.
3. Results and discussion

Figure 2(a) shows the XRPD patterns of Al0, Al5, Al10 and Al15 powder samples at room temperature. All detectable peaks could be indexed as the hexagonal wurtzite structure with the $P6_3mc$ space group. No additional impurity peaks were observed which reveals that Al$^{3+}$ ions have completely been incorporated into the ZnO lattice and no new crystalline phases have been formed [4]. Initially, the Bragg reflections shift to higher $2\theta$ values and gradually shift towards lower $2\theta$ values with increasing Al concentrations from 0% to 15%. The shifting of Bragg’s reflection is clear from figure 2(b). The Bragg reflections moving towards higher angles suggest the formation of nanoparticles with reduced lattice parameters and vice versa. The XRPD data of the prepared samples have been analyzed by the Rietveld refinement method using Fullprof suit. The fitted outputs are shown in figure 3. The red circles represent the observed data and black solid lines represent the fitted data, respectively. The blue lines represent the difference between the observed and the fitted data. All plots show that the refined XRPD patterns are in very good agreement with the measured data. From the Rietveld refinement analysis, it is also confirmed that no secondary crystalline phase was formed. The wurtzite lattice parameters $a = b$ (3.248 ± 0.000 Å, 3.234 ± 0.001 Å, 3.237 ± 0.002 Å and 3.245 ± 0.005 Å) and $c$ (5.205 ± 0.000 Å, 5.177 ± 0.001 Å, 5.186 ± 0.003 Å and 5.191 ± 0.008 Å), $c/a$ ratio (1.603 ± 0.000, 1.601 ± 0.001, 1.602 ± 0.001 and 1.600 ± 0.003), unit cell volume ($v = 47.539$ ± 0.005 Å$^3$, 46.899 ± 0.026 Å$^3$, 47.048 ± 0.042 Å$^3$ and 47.336 ± 0.131 Å$^3$) and atomic packing fraction ($\text{APF} = 75.45$ ± 0.00%)
75.54 ± 0.02%, 75.47 ± 0.06% and 75.59 ± 0.16% of Al₀, Al₅, Al₁₀ and Al₁₅ powders were estimated from the Rietveld refinement data with the help of lattice geometry relations [17]. The angle, $\phi$ was calculated between the planes (112) and (201) for all the samples using the well known reported relation [18]. Also, the Zn–O bond length ($L$) has been deduced by the following equation [19].

$$L = \sqrt[3]{\frac{a^2}{3} + \left(\frac{1}{2} - \mu\right)c^2} \quad (1)$$

The parameter $\mu$ is defined by the equation: $\mu = a^2/3c^2 + 1/4$, $a$ and $c$ are lattice parameters. The distortion parameter ($\varepsilon_v$) of a unit cell as well as the cell distortion degree ($R$) were calculated from the following relationships [20].

$$\varepsilon_v = \left(\frac{a^2c}{a_0^2c_0} - 1\right) \quad (2)$$

and

$$R = 2\sqrt[3]{\frac{2}{3}\left(\frac{a}{c}\right)} \quad (3)$$

where $a_0$ and $c_0$ are the crystal parameters as per the standard JCPDS database (card no. 05–0664) while $a$ and $c$ are the calculated values. All the crystal parameters ($a, b$ and $c$) including $c/a$ ratio, volume, density, APF, interplanar angle, bond length, distortion parameter, etc. for Al₀, Al₅, Al₁₀ and Al₁₅ nanoparticles obtained from Rietveld refinement analysis are listed in table 1. For the case of structural parameters, it is found that the lattice parameters, unit cell volume as well as the Zn–O bond length of Al₅ nanoparticles are slightly reduced because of the smaller Al³⁺ radius than that of Zn²⁺ ($r_{{Al}^{3+}} = 0.63\text{Å}, r_{{Zn}^{2+}} = 0.74\text{Å}$). However, these parameters increase for Al₁₀ and Al₁₅ samples, which may be due to the inclusion of other factors such as defect, strain and distortion, etc. It is also clear from the XRPD data that the intensities of the peaks decrease with increasing broadening due to higher Al mixing in the case of Al-doped samples. The peak intensity helps to determine the texture coefficient ($TC_{hkl}$) values, which gives a quantitative idea about the preferred crystal orientation. It can be defined as [21–24],

$$TC_{hkl} = \frac{I_{hkl}}{I_{0hkl}} = \frac{1}{N\sum_{N} I_{hkl}} \quad (4)$$

where $I_{hkl}$ is the measured intensity of x-ray diffraction peak on the (hkl) plane; $I_{0hkl}$ is the intensity of corresponding x-ray diffraction reference of the randomly oriented grains as per the JCPDS database and $N$ is the number of diffraction peaks considered in the analysis. If the texture coefficient is unity, the nanoparticles are randomly oriented crystallite just like JCPDS reference. Higher than unity i.e. $TC_{hkl} > 1$ indicates the abundance...
Table 1. Crystal parameters of Al₀, Al₅, Al₁₀ and Al₁₅ nanoparticles, estimated from the Rietveld refinement data.

| Sample ID | \( a = b \) (Å) | \( c \) (Å) | \( c/a \) | Vol (V) (Å³) | Density (\( \rho \)) (g cm\(^{-3}\)) | APF (%) | \( \epsilon \) (Unitless) | R (Unitless) | L (Å) | \( \mu \) (Unitless) | \( \cos \phi \) |
|-----------|----------------|-------------|---------|-------------|-----------------|--------|----------------|--------------|------|----------------|-------------|
| Al₀       | 3.248          | 5.205       | 1.603   | 47.539      | 5.742            | 75.45  | -0.0014        | 1.0189       | 1.977| 0.3797         | 0.847365    |
| Al₅       | 3.234          | 5.177       | 1.601   | 46.899      | 5.773            | 75.54  | -0.0200        | 1.0201       | 1.968| 0.3801         | 0.847370    |
| Al₁₀      | 3.237          | 5.186       | 1.602   | 47.048      | 5.763            | 75.47  | -0.0153        | 1.0192       | 1.970| 0.3799         | 0.847366    |
| Al₁₅      | 3.245          | 5.191       | 1.600   | 47.336      | 5.757            | 75.59  | -0.0082        | 1.0208       | 1.974| 0.3802         | 0.847337    |
of grains in a given \(<hkl>\) direction while \(0 < T_C(hkl) < 1\) indicates the lack of grains orientation in that direction. So the value of \(T_C(hkl)\) gives the information about the preferential growth of the crystallites in the perpendicular direction to \((hkl)\) plane [25, 26]. Since the Rietveld fit shown in figure 3, clearly shows that except for (102) and (110) reflections, all others are almost fitted properly. Therefore, the reflections corresponding to (102) and (110) have been taken into account for the calculation of \(T_C(hkl)\). The \(T_C(hkl)\) values for the (102) peak are 0.870, 0.915, 1.020, 0.983 and for the (110) peak are 0.964, 1.006, 1.414, 1.051 for Al0, Al5, Al10 and Al15 nanoparticles respectively. With the increasing amount of Al from 0% to 10%, it was found that the grain of grains in a given perpendicular direction to \(d\) direction. So the value of \(\theta_{TC(hkl)}\) gives the information about the preferential growth of the crystallites in the perpendicular direction to \((hkl)\) plane [25, 26]. Since the Rietveld fit shown in figure 3, clearly shows that except for (102) and (110) reflections, all others are almost fitted properly. Therefore, the reflections corresponding to (102) and (110) have been taken into account for the calculation of \(T_C(hkl)\). The \(T_C(hkl)\) values for the (102) peak are 0.870, 0.915, 1.020, 0.983 and for the (110) peak are 0.964, 1.006, 1.414, 1.051 for Al0, Al5, Al10 and Al15 nanoparticles respectively. With the increasing amount of Al from 0% to 10%, it was found that the grain orientation increases, but with 15% Al doping there is the opposite tendency i.e. less oriented crystallite for both (102) and (110) reflections. It may be due to the substitution of divalent Zn by trivalent Al which may help to create lattice defects and affect the intensity distribution of the x-ray diffraction lines. The distance between neighboring planes \((d_{fl})\) has been obtained from the XRPD data and the percentage of deviation from the standard \(d_0\) value (taken from ICPODS data) for major six different peaks (100, 002, 101, 102, 110 and 103) are listed in table 2. It can be seen that with increasing Al addition from 0% to 15% the inter-planar distance \(d_{fl}\) for each \((hkl)\) set of the samples first decreased and then increased, which indicates the influence of Al addition on the inter-planar distance similar to lattice parameters.

The crystallite sizes \((D)\) were calculated from the full width at the half maximum (FWHM) for six prominent peaks (100), (002), (101), (102), (110) and (103) using the Scherrer and the Modified Debye–Scherrer (MS) equations, respectively. Using the Scherrer method we determined the crystallite size from the slope of the \(1/\beta\) versus \(\cos \theta\) diagrams (not shown) for each sample. The Modified Debye–Scherrer is the new approach to the Scherrer equation and in this case, the least square method is used to minimize the sources of errors. Crystallite sizes \((D_{MS})\) for all samples were obtained from the Y-intercept of \(\ln \beta\) versus \(\ln (1/\cos \theta)\) of figure 4 [27, 28]. The values of \(D_{MS}\) \((D_{MS})\) corresponding to Al0, Al5, Al10 and Al15 nanoparticles are 21.52 ± 0.85 nm (21.12 ± 15 nm), 14.55 ± 0.53 nm (14.33 ± 0.11 nm), 12.44 ± 0.62 nm (12.10 ± 0.13 nm) and 5.33 ± 0.41 nm (5.04 ± 0.11 nm) respectively. It is clear that the crystallite size reduces due to Al-doping. Again, the dislocation density \((\delta)\) is the indicator of lattice defects. It is directly related to crystallite size and is defined as the length of the dislocation lines per unit volume of the crystal and is calculated using the relation \(\delta = 1/D^2\) [29, 30].

According to Scherrer and Modified Scherrer methods, the values of \(\delta (\times 10^{-4})\) \((\delta_{MS})\) in nm \(^{-2}\) are 21.59 ± 0.04 and 22.42 ± 0.01 for Al0, 47.24 ± 0.12 and 48.70 ± 0.03 for Al5, 64.62 ± 0.26 and 68.30 ± 0.06 for Al10, 35.20 ± 5.08 and 39.37 ± 1.70 for Al15 respectively. Therefore, it can be said that due to more doping of a small Al element in the ZnO lattice, more lattice defects have been developed.

Table 2. The \(d_{fl}\) values of neighboring planes and the percentage of deviation of inter-planar spacings for the major six peaks corresponding to all samples.

| \(hkl\) planes | Al% | \(d_{fl}\) (Å) | \(d_0\) (Å) | % of deviation |
|---------------|-----|---------------|--------------|---------------|
| 100           | 0   | 2.813         | 2.816        | 0.11          |
|               | 5   | 2.801         |              | 0.54          |
|               | 10  | 2.803         |              | 0.45          |
|               | 15  | 2.810         |              | 0.20          |
| 002           | 0   | 2.603         | 2.602        | −0.02         |
|               | 5   | 2.589         |              | 0.52          |
|               | 10  | 2.593         |              | 0.35          |
|               | 15  | 2.596         |              | 0.25          |
| 101           | 0   | 2.475         | 2.476        | 0.06          |
|               | 5   | 2.463         |              | 0.51          |
|               | 10  | 2.466         |              | 0.40          |
|               | 15  | 2.471         |              | 0.19          |
| 102           | 0   | 1.910         | 1.911        | 0.04          |
|               | 5   | 1.901         |              | 0.53          |
|               | 10  | 1.904         |              | 0.39          |
|               | 15  | 1.907         |              | 0.23          |
| 110           | 0   | 1.624         | 1.626        | 0.12          |
|               | 5   | 1.617         |              | 0.55          |
|               | 10  | 1.619         |              | 0.46          |
|               | 15  | 1.623         |              | 0.22          |
| 103           | 0   | 1.477         | 1.477        | 0.02          |
|               | 5   | 1.469         |              | 0.53          |
|               | 10  | 1.471         |              | 0.38          |
|               | 15  | 1.473         |              | 0.24          |
In many cases, x-ray diffraction patterns are influenced not only by the size of the particles but possibly also by the lattice defects and lattice strain. The W-H method is applied to investigate the possible strain-induced broadening arising from crystal imperfections as well as distortions. The induced strain is related to the relationship, \( \varepsilon \approx \beta / \tan \theta \). The W-H method does not follow \( 1 / \cos \theta \) dependency as in the Scherrer equation but varies with \( \tan \theta \). The individual contribution to the line broadening of Bragg reflection can be written as, \( \beta_{hk} = \beta_s + \beta_d \). Where \( \beta_{hk} \) is the FWHM of XRPD peaks, \( \beta_s \) and \( \beta_d \) are the widths due to the size and strain effects, respectively. If the strain is uniform in the entire crystallographic direction, combining the Scherrer equation with \( \varepsilon \approx \beta / \tan \theta \), we get a relationship as \( \beta_{hk} \cos \theta = (K\lambda/D) + 4\varepsilon \sin\theta \) which is known as UDM. Here, \( D \) and \( \varepsilon \) are the values of the crystallite size and strain, respectively. The diagrams were drawn with \( \beta_{hk} \cos \theta \) on the y-axis and \( 4\sin\theta \) on the x-axis (shown in figure 5). The strain was calculated from the slope of the fitted line and the crystallite size was determined from the Y-intercept. The increasing of strain (\( \varepsilon \times 10^{-3} \)) value (1.44 \( \pm \) 0.23, 1.80 \( \pm \) 0.32, 3.11 \( \pm \) 0.54 and 10.97 \( \pm \) 2.13 for Al0, Al5, Al10 and Al15 nanoparticles, respectively) may be due to the defects enhancement by Al doping.

The stress (\( \sigma \)) is assumed to be uniform in the case of USDM. The UDM equation can be modified by replacing \( \varepsilon = \sigma / Y_{hk} \) and is represented by \( \beta_{hk} \cos \theta = (K\lambda/D) + (4\sigma \sin\theta / Y_{hk}) \). Here, \( Y_{hk} \) is Young’s modulus in the direction normal to the set of \((hkl)\) planes. The plots \( \beta_{hk} \cos \theta \) versus \( 4\sin\theta / Y_{hk} \) have drawn in figure 6 and the crystallite size was easily evaluated from the Y-intersection. Here crystallite size also follows the decreasing trend with Al addition like Scherrer and UDM. Accordingly, the slope represents the uniform stress.

The strain can also be measured when \( Y_{hk} \) of hexagonal ZnO is known. For samples with the wurtzite hexagonal
phase, Young’s modulus $Y_{hkl}$ is related to their elastic compliances $S_{ij}$ as \[ \frac{Y_{hkl}}{S_{ij}} = \beta_{hkl} \cos \theta \] where $s_{11}$, $s_{13}$, $s_{33}$, and $s_{44}$ are the elastic compliances of ZnO and their values are $7.858 \times 10^{-12}$ m$^2$N$^{-1}$, $-2.206 \times 10^{-12}$ m$^2$N$^{-1}$, $6.940 \times 10^{-12}$ m$^2$N$^{-1}$ and $23.57 \times 10^{-12}$ m$^2$N$^{-1}$, respectively [34]. The average calculated value for $Y_{hkl}$ is $\sim 127$ GPa. With adding Al, the values of $\sigma$ (156.60 ± 29.28 MPa, 214.12 ± 39.89 MPa, 337.12 ± 69.09 MPa and 1193.26 ± 270.53 MPa for Al$_0$, Al$_5$, Al$_{10}$ and Al$_{15}$ nanoparticles, respectively) is increased.

There is another model that has been used to determine the energy density of nanocrystals called the UDEDM. This model assumes that crystals are homogeneous and isotropic. For any elastic systems which follow the Hook’s law, the anisotropic energy density can be calculated using the relationship, $U = \frac{\varepsilon^2 Y_{hkl}}{2}$. Now, using this equation in UDM we can rewrite the expression as $\beta_{hkl} \cos \theta = \left( \frac{K \lambda}{D} \right) + 4\sin \theta \left( \frac{2U}{Y_{hkl}} \right)^{1/2}$. Plots of $\beta_{hkl} \cos \theta$ against $4\sin \theta \left( \frac{2U}{Y_{hkl}} \right)^{1/2}$ have been drawn and the data fitted to straight lines (figure 7). The $U$ value has estimated from the slope of the lines and crystallite size from the Y-intercept. The $U$ values corresponding to the samples are summed up in table 3. It is cleared from table 3 that $U$ moves to the higher values with the addition of Al. This change is similar to both the dislocation density, stress and strain. The $U$ value is likely to increase probably due to the increase in some factors of lattice defects, strain, stress and a decrease in crystallite size due to
Table 3. Crystallite size and elastic parameters (ε, σ and U) of Al₀, Al₅, Al₁₀ and Al₁₅ nanoparticles.

| Parameters          | Al₀  | Al₅  | Al₁₀ | Al₁₅ |
|---------------------|------|------|------|------|
| Dₛ (nm)             | 21.52| 14.55| 12.44| 5.33 |
| Dₘ₃₅ (nm)           | 21.12| 14.33| 12.10| 5.04 |
| Dₜₐ₄ (nm)           | 29.98| 19.30| 19.02| 10.76|
| ε × 10⁻³ (no unit)  | 1.44 | 1.80 | 3.11 | 10.97|
| σ (MPa)             | 156.60| 214.12| 337.12| 1193.26|
| U (KJ m⁻³)          | 113.85| 188.24| 529.92| 6617.82|

Figure 8. Variation of crystallite size (D) and dislocation density (δ) with increasing Al-doping.

Figure 9. FE-SEM images of Al₀, Al₅, Al₁₀ and Al₁₅ nanoparticles.
the increase of Al doping. Variation of $D$ and $\delta$ values have been calculated using different methods such as Scherrer, Modified Scherrer and W-H with different amounts of Al-doping portrayed in figure 8.

The surface morphology of all samples (Al0, Al5, Al10 and Al15) synthesized using Al leaf extract has carried out using FESEM (shown in figure 9). In this case, we have measured the dimension of the nanoparticles from side to side for the visible particles in two-dimensional figures, which is sometimes not the exact value due to the lack of perpendicular view. Each sample has large agglomerates. Figure 9 also shows that with an increasing amount of Al in ZnO, the growth of the nanograins is influenced and they are randomly oriented. Depending on the amount of Al, the nanoparticles have different shapes and sizes. Al0 grains have solid conical shape with an average height of 181 nm and an average base radius of 91 nm. Al5 grains have dry-date like structures with an average dimension of 227 nm. Al10 grains have scale-like structure with a dimension of 85 nm. And Al15 grains have almost disc-like shape. The measured mean diameter of Al5 nanodiscs is 127 nm with a width of 13 nm.

The EDX data is recorded (not shown) to determine the elemental composition of the nanoparticles produced. It is ensured that no peaks other than zinc and oxygen have been determined for pure ZnO nanoparticles and additional peaks for Al in the Al-doped ZnO samples are available.

4. Conclusion

Samples of pure ZnO and Al-doped ZnO nanoparticles have been successfully synthesized by a green method using Azadirachta indica leaf extracts. XRPD data have been collected for Al0, Al5, Al10 and Al15 samples and analyzed using the Rietveld refinement technique. It is confirmed that all samples have hexagonal wurtzite structure with the P63/mmc space group. The lattice parameters (a, c) and the unit cell volume (v) reach their minimum value and increase again with Al doping. The XRPD data of the nanoparticles show that the slight lattice contraction leads to the peak shifting in the higher angle. We have found that lattice strain, stress and energy density increase with increasing Al-content. The surface morphology is also strongly dependent on the doping concentration of Al. It can be concluded that the line broadening of pure and Al-doped ZnO nanoparticles is due to small crystallite size and lattice strain. The crystallite size estimated by the Scherrer, Modified Scherrer and WH methods agrees well and is strongly correlated.

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