Chapter - 3

The effect of fuel and fuel to oxidizer combinations on the properties of the ZnO nanoparticles
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It is well known that, solution combustion is the versatile technique used to synthesize nanocrystalline oxides through the redox reaction between an oxidizer and a fuel at a moderate low temperatures of around 350 – 500 °C within few minutes [1]. In this technique, the fuel to oxidizer (F/O) ratio plays a critical role in influencing the nature of combustion reaction or flame temperature. Selection of the suitable oxidizer and the fuel and their ratio controls the exothermicity of the reaction. It is well reported that, the F/O ratio of unity is known to produce highest exothermicity with complete combustion [1-3]. An arbitrary ratio of fuel to oxidizer (F/O ≠ 1) sometimes leads to the formation of intermediate phases or unreacted raw materials in the final product [4]. In addition, the SCT has greater advantages, as it produce fine, large surface area and sinter active particles by using different precursors and the fuels in as-synthesized form itself without any further heat treatment. This method has all the advantages of wet-chemical processes like homogeneity, control over stoichiometry, purity and incorporation of desired amount of impurity ions. In this regard, various fuels have been tested to synthesize nanocrystalline ZnO [5-6]. In this work, we report the synthesis of nanocrystalline ZnO powders by SCT using new, eco friendly and cost effective organic fuels, which have not been used and tested to synthesize ZnO and the effect of fuel and fuel to oxidizer combinations on the properties of the final product has been studied. The structure, morphology and the properties of the resulting powders were investigated and discussed with regard to the new fuels used by establishing correlation between adiabatic temperature (T_{ad}) obtained from thermodynamic theoretical calculations and characteristics of resulting powders.
3.1 Synthesis

Nanocrystalline ZnO particles were prepared by the SC1 using Znic Nitrate Hexahydrate (ZN) as an oxidizer and L-Valine, L-Glutamine and Leucine as fuels. The stoichiometric balanced equations used for the synthesis of ZnO as follows.

**ZN: L-Valine**

\[
\text{Zn (NO}_3\text{)\textsubscript{2}.6H}_2\text{O} + (\frac{10\Phi}{27}) \text{C}_3\text{H}_{11}\text{NO}_2 + (\frac{135\Phi}{54} - \frac{5}{2}) \text{O}_2 \rightarrow \\
\text{ZnO} + (\frac{50\Phi}{27}) \text{CO}_2\uparrow + (1 + \frac{5\Phi}{27}) \text{N}_2\uparrow + (6 + \frac{55\Phi}{27}) \text{H}_2\text{O}\uparrow \\
(7 + 4.074 \Phi \text{ moles gases produced}) \quad \text{......................... (3.1)}
\]

**ZN: L-Glutamine**

\[
\text{Zn (NO}_3\text{)\textsubscript{2}.6H}_2 + (\frac{10\Phi}{24}) \text{C}_5\text{H}_{10}\text{N}_2\text{O}_3 + (\frac{60\Phi}{24} - \frac{5}{2}) \text{O}_2 \rightarrow \\
\text{ZnO} + (\frac{50\Phi}{24}) \text{CO}_2\uparrow + (1 + \frac{10\Phi}{24}) \text{N}_2\uparrow + (6 + \frac{50\Phi}{24}) \text{H}_2\text{O}\uparrow \\
(7 + 4.583 \Phi \text{ moles gases produced}) \quad \text{......................... (3.2)}
\]

**ZN: Leucine**

\[
\text{Zn (NO}_3\text{)\textsubscript{2}.6H}_2\text{O} + (\frac{10\Phi}{33}) \text{C}_6\text{H}_{13}\text{NO}_2 + \frac{5}{2} (\Phi - 1) \text{O}_2 \rightarrow \\
\text{ZnO} + (\frac{50\Phi}{33}) \text{CO}_2\uparrow + (1 + \frac{5\Phi}{33}) \text{N}_2\uparrow + (6 + \frac{65\Phi}{33}) \text{H}_2\text{O}\uparrow \\
(7 + 3.94 \Phi \text{ moles gases produced}) \quad \text{......................... (3.3)}
\]
Where, $\Phi$ is fuel to oxidizer (F/O) ratio. The synthesis procedure of SCT is given in detail in experimental chapter. The F/O ratio ($\Phi$) was varied as $\Phi = 0.7$ (Fuel Lean), 1.0 (Stoichiometric), 2.0 (Fuel Rich) to synthesize ZnO nanoparticles.

### 3.2 Thermodynamic calculations:

Solution combustion technique (SCT) is a well known conventional method to synthesize metal oxide nanoparticles. SCT is also known as self propagating high temperature synthesis, as the heat required to form nanoparticles is not supplied by an external source, rather it is self-generated during the exothermic reactions between the fuel and an oxidizer. The combustion reaction takes place within a short duration of time, involves rapid heating of the precursor mixture containing oxidizer and fuel with the release of enormous amounts of heat. Considering the complete combustion with no heat loss / dissipation in any form due to the short duration (~ few seconds) of the exothermic reaction / combustion flaming, the combustion reaction temperature equals to be adiabatic temperature ($T_{ad}$). To understand and account for the heat generated by the precursor during combustion flaming, the adiabatic flame temperature is estimated theoretically for different F/O ratio using the available thermodynamic data as given in table 3.1 [6-8]. Assuming the complete combustion would take place for the above stoichiometric equations (1-3), the $T_{ad}$ is calculated using the equation;

$$
\Delta H^o = - \int_{T_0}^{T_{ad}} \left( \sum n \cdot C_p \right)_{products} dT \\
\text{......................... (3.4)}
$$

Where, ‘$C_p$’ is the heat capacity of reaction products at constant pressure in kJ/mol K, ‘$n$’ is the number of the moles, $T_{ad}$ is the adiabatic temperature in K and $\Delta H^o$ is the standard enthalpy of reaction in kJ/mol.

$\Delta H^o$ can be calculated using the formula;

$$
\Delta H^o = (\sum n \cdot \Delta H_f^0)_{products} - (\sum n \cdot \Delta H_f^0)_{reactants} \\
\text{......................... (3.5)}
$$

Where, $\Delta H_f^0$ is the standard enthalpy of formation in kJ/mol.
The results obtained from the theoretical calculations, i.e. the obtained $T_{ad}$ and $\Delta H^\circ$ values for different fuels and F/O ratio’s are tabulated in table 3.2. It is observed that, $T_{ad}$, $\Delta H^\circ$ and the amount of gases evolved are varying linearly with F/O ratio.

3.3 X-ray Diffraction studies

The as-synthesized ZnO powders were characterized through powder XRD technique. The XRD patterns of the as-synthesized ZnO powders using different fuels and for various F/O ratios are depicted in Fig. 3.1. It is seen from the Fig. 3.1 that, all F/O combinations of the fuel-oxidizer mixture, the combustion reaction leads to the formation of nanocrystalline ZnO with hexagonal wurtzite structure. This indicates that, the nanocrystalline ZnO particles are directly formed after self propagating high temperature solution combustion of precursor gels without need of further heat treatment. The direct transformation of crystalline material, with higher degree of compositional homogeneity, from the gel after the combustion is due to the greater amount of heat generated from the exothermic reaction between nitrate and organic fuel. In combustion, during exothermic reaction, the large volume of gases is liberated due to the breakage of bonds leading to the formation of highly porous crystalline material. It is also observed that, the diffraction peaks are broadened with increase of F/O ratio (right insets of Fig. 3.1), suggesting a decrease in the crystallite size. As the combustion propagates rapidly forward once ignited, more and more gases are liberated. This leads to the breakup of agglomerates and more heat is carried from the system, thereby hindering particle growth, producing the final powder with less particle / crystallite size. It is seen from the equations (1-3) and Table 3.2, the total number of moles of gaseous products and $T_{ad}$ increase with increasing F/O ratio. Hence, as a result of the effect of combustion temperature and the number of moles of gases evolved, greatly influence the final particle size. In general, the increase in F/O ratio increases the $T_{ad}$ which further influences the release of the larger volume of gases (Table 3.2) resulting in the smaller crystallite size (Table 3.3) [9].
Table 3.1: The values of Standard enthalpy of formation ($\Delta H_f^o$) and heat capacity ($C_p$) used to calculate adiabatic temperature ($T_{ad}$) [6-8].

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Compound $^a$</th>
<th>$\Delta H_f^o$ / (kJ / mol)</th>
<th>$C_p$ / (J / mol /K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc Nitrate Hexahydrate (ZnO(NO$_3$)$_2$.6H$_2$O) $^{(c)}$</td>
<td>- 2305.0</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>L-Glutamine C$_5$H$_9$N$_2$O$_3$ $^{(c)}$</td>
<td>- 826.4</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>L-Valine C$<em>5$H$</em>{11}$NO$_2$ $^{(c)}$</td>
<td>- 628.9</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>Leucine C$<em>6$H$</em>{13}$NO$_2$ $^{(c)}$</td>
<td>- 637.4</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>ZrO $^{(c)}$</td>
<td>- 350.46</td>
<td>$45.338 + 7.239 \times 10^{-3} , T$</td>
</tr>
<tr>
<td>6</td>
<td>CO$_2$ $^{(g)}$</td>
<td>- 393.51</td>
<td>$51.128 + 4.358 \times 10^{-3} , T$</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$O $^{(g)}$</td>
<td>- 241.83</td>
<td>$34.376 + 7.841 \times 10^{-3} , T$</td>
</tr>
<tr>
<td>8</td>
<td>N$_2$ $^{(g)}$</td>
<td>0</td>
<td>$30.418 + 2.544 \times 10^{-3} , T$</td>
</tr>
<tr>
<td>9</td>
<td>O$_2$ $^{(g)}$</td>
<td>0</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$ (c): crystalline, (g): gas
Table 3.2: Theoretically calculated Adiabatic Temperature ($T_{ad}$) and standard enthalpy of reaction ($\Delta H^\circ$) for different fuels, and F/O ratios.

<table>
<thead>
<tr>
<th>Fuel Name with chemical formula</th>
<th>$T_{ad}$ / (K) (<strong>a</strong>)</th>
<th>$\Delta H^\circ$ / (KJ/mol) (<strong>b</strong>)</th>
<th>Amount of gases produced / (No. of moles of gases / mol of ZnO) (<strong>c</strong>)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Phi = 0.7$</td>
<td>$\Phi = 1.0$</td>
<td>$\Phi = 2.0$</td>
</tr>
<tr>
<td>L-Valine ($C_3H_{11}NO_2$)</td>
<td>726.76</td>
<td>1239.46</td>
<td>2242.96</td>
</tr>
<tr>
<td>L-Glutamine ($C_4H_{10}N_2O_3$)</td>
<td>695.47</td>
<td>1187.63</td>
<td>2124.30</td>
</tr>
<tr>
<td>Leucine ($C_4H_{13}NO_2$)</td>
<td>746.29</td>
<td>1267.94</td>
<td>2295.10</td>
</tr>
</tbody>
</table>

(a) Calculated theoretically by thermodynamic data and Equation (3.4)
(b) Calculated theoretically from thermodynamic data and Equation (3.5)
(c) Obtained from Equations (3.1 - 3.3)
Fig. 3.1 XRD pattern of ZnO synthesized using various $\Phi$ combinations of ZN with fuels (a) L-Valine; (b) L-GLutamine and (c) Leucine.

In the XRD patterns of fuel lean ($\Phi=0.7$) powders, an additional peak appeared (top left insets of Fig. 3.1) in the 20 range of 15-25°, is attributed to the un-burnt residues in the final product during the combustion [4]. It could be due to the insufficient fuel required to burn the oxidizer for the complete combustion reaction, which is evident from the grayish color of the final product. Whereas with $\Phi=1.0$, the complete combustion is observed and is evident from the expected whitish color of the final product (ZnO). However, for $\Phi=2.0$, though no residue is observed in the XRD pattern, but the final product showed the presence of carbonaceous materials indicating the presence of un-burnt fuel, as evident from the blackish color of the final product. In addition, the yield of the final product was very low, as the combustion reaction is too rapid and violent. Hence for the further studies, the $\Phi$ value is fixed to be unity.
The mean or average Crystallite size and strain are calculated using Williamson-Hall equation [10].

\[ \beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \quad (3.6) \]

where, \( \beta = \sqrt{(\beta_o^2 - \beta_i^2)} \) is the effective FWHM, \( \beta_o \) is the observed FWHM, \( \beta_i \) is the instrumental broadening, \( \theta \) is the Bragg angle, \( k \) is the Scherer’s constant (0.9), \( \lambda \) is the wavelength of the X-ray used, \( D \) is the mean crystallite size and \( \varepsilon \) is the strain present in the crystal. Synthesized micro-crystalline ZnO powder (~ 0.7 \( \mu \text{m} \)) was used for the estimation of the instrumental broadening.

Least Square Fit method was used to calculate the mean crystallite size and strain. From the plot of \( \beta \cos \theta \) along x-axis vs \( 4\varepsilon \sin \theta \) along y-axis, the slope gives the value of strain, \( \varepsilon \) and the intercept gives the value of \( k\lambda/D \), from which the actual size of the mean crystallites was calculated. After incorporating the instrumental broadening in \( \beta \), the obtained crystallite size and strain values are tabulated in table 3.3. It is observed that, as expected, the crystallite size and strain decreases with increase of F/O ratio and the size of crystallites are found to be in nano range, which is due to the fact that, the supply of enormous amount of heat (energy) by the fuel-oxidizer reaction during combustion with increase of F/O ratio (Fuel content). Detailed structural studies were carried out by Rietveld refinement using FullProf software [11]. The Rietveld refined (fitted) XRD patterns are depicted in Fig 3.2. The refined lattice parameters are found to be in agreement with the literature reported values and are tabulated in table 3.3. The XRD patterns of ZnO synthesized using different fuels exhibit a slight variation in FWHM. In general, for hexagonal crystal system, lattice parameters can be determined by using the following equation (7);

\[ \frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad \ldots \ldots \ldots \ldots (3.7) \]

Where, \((a = b \& c)\) are the lattice parameters and \( d \) is the inter-planar spacing and \((h, k, l)\) are the Miller indices.

\[ \text{Synthesis and studies on pure and doped ZnO nanomaterials and thin films} \]
(a) ZnO : L - Vlline

(b) ZnO : L - Glutamine
3.4 Thermal Analysis (TG-DTA) studies

The nature of the combustion process and the decomposition of gels are studied by thermal analysis (TG-DTA) of the dried gels. Prior to the combustion synthesis, the precursors (stoichiometric, $\Phi = 1$) were dried on hot plate to form the dried gel. The dried gel was then subjected to TG-DTA in the synthetic air atmosphere at the flow rate of 80 mL min$^{-1}$ for N$_2$ and 20 mL min$^{-1}$ for O$_2$ in the temperature range of 25 – 1000 °C, with heating rate of 10 °C/min. The TGA (mass loss) curves and DTA plots are depicted in Fig 3.3 (a) and (b) respectively. It is observed from the Fig. 3.3(a) that, all the gels show gradual mass loss of about 15% from room temperature to around 200 °C corresponding to the removal of the water content.
Table 3.3 Crystallite size, strain and lattice parameters of as-synthesized ZnO.

<table>
<thead>
<tr>
<th>ZnO: Fuel Combination</th>
<th>Fuel combination</th>
<th>D$_{wh}$ / (nm)</th>
<th>D$_{TEM}$ / (nm)</th>
<th>Strain $\varepsilon$ / (%)</th>
<th>Lattice parameters</th>
<th>XRD</th>
<th>SAED</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Valine (C$<em>{8}$H$</em>{11}$NO$_{2}$)</td>
<td>$\Phi = 0.7$</td>
<td>31.7</td>
<td>--</td>
<td>0.1854</td>
<td>XRD</td>
<td>3.2507 (1)</td>
<td>5.2060 (2)</td>
</tr>
<tr>
<td></td>
<td>$\Phi = 1.0$</td>
<td>29.5</td>
<td>33</td>
<td>0.1575</td>
<td>XRD</td>
<td>3.2511 (1)</td>
<td>5.2069 (2)</td>
</tr>
<tr>
<td></td>
<td>$\Phi = 2.0$</td>
<td>16.2</td>
<td>--</td>
<td>0.0434</td>
<td>XRD</td>
<td>3.2524 (2)</td>
<td>5.2034 (3)</td>
</tr>
<tr>
<td>L-Glutamine (C$<em>{5}$H$</em>{10}$N$<em>{2}$O$</em>{3}$)</td>
<td>$\Phi = 0.7$</td>
<td>23.8</td>
<td>--</td>
<td>0.0903</td>
<td>XRD</td>
<td>3.2508 (2)</td>
<td>5.2085 (4)</td>
</tr>
<tr>
<td></td>
<td>$\Phi = 1.0$</td>
<td>21.2</td>
<td>20</td>
<td>0.0755</td>
<td>XRD</td>
<td>3.2506 (2)</td>
<td>3.2084 (3)</td>
</tr>
<tr>
<td></td>
<td>$\Phi = 2.0$</td>
<td>19.4</td>
<td>--</td>
<td>0.0151</td>
<td>XRD</td>
<td>3.2515 (1)</td>
<td>5.2100 (2)</td>
</tr>
<tr>
<td>Leucine (C$<em>{6}$H$</em>{13}$NO$_{2}$)</td>
<td>$\Phi = 0.7$</td>
<td>25.4</td>
<td>--</td>
<td>0.1557</td>
<td>XRD</td>
<td>3.2508 (1)</td>
<td>5.2056 (2)</td>
</tr>
<tr>
<td></td>
<td>$\Phi = 1.0$</td>
<td>20.5</td>
<td>19</td>
<td>0.1369</td>
<td>XRD</td>
<td>3.2509 (1)</td>
<td>5.2069 (2)</td>
</tr>
<tr>
<td></td>
<td>$\Phi = 2.0$</td>
<td>12.8</td>
<td>--</td>
<td>-0.0091</td>
<td>XRD</td>
<td>3.2526 (2)</td>
<td>5.2094 (3)</td>
</tr>
</tbody>
</table>
The gels show a drastic mass loss at around 200 °C with varied amount of mass loss as shown in table 3.4, corresponding to the initiation of the combustion reaction with the removal of all the gaseous products leaving behind the final ZnO residue. The amount of residue (final product, ZnO) is measured and tabulated in table 3.4. The gel prepared with L-Glutamine show high mass loss due to the evolution of large amount of gases. For comparision, among all the gels, the gel prepared with Leucine has high yield, about 15 % compared to that of other gels due to the less amount of gases evolved during the combustion (Table 3.2). These results suggest that the dried gels of the ZN-Valine, ZN-Glutamine and ZN-Leucine decomposes exothermically in a single step at about 25 - 400 °C. The observed mass loss in the temperature range 25 - 400 °C was measured and tabulated in table 3.4. After 400 °C, no weight loss is observed. The corresponding high exothermic peaks in the DTA curves (Fig 3.3(b)) are observed and attributed to the exothermicity of these nitrate-fuel gels. In DTA curves, a sharp exothermic peak around 220 °C is attributed to the evolution of gases, whereas a broad hump around and above 400 °C corresponds to the evaporation of carbonaceous material left out with the combustion product.

Table 3.4 Mass loss and the yield of the samples

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Temperature Range / (°C)</th>
<th>Mass loss / (%)</th>
<th>Yield of the product / (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Valine</td>
<td>25 - 400</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>L-Glutamin</td>
<td>25 - 400</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>Leucine</td>
<td>25 - 400</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

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Fig. 3.3 (a) TGA and (b) DTA curves for the precursor of nitrate-fuel mixtures with $\Phi = 1.0$
3.5 Transmission Electron Microscopy Studies

The High Resolution-Transmission Electron Microscope (HR-TEM) images of ZnO prepared with L-Valine, L-Glutamine and Leucine as fuels are depicted in Fig. 3.4, Fig. 3.5 and Fig. 3.6, respectively. The detailed analysis of the particle size, structure and morphology of as synthesized ZnO samples are as follows.

Fig. 3.4 (a) and (a’) shows the distribution of particles and their corresponding histogram of ZnO nanoparticles respectively. Fig. 3.4 (b) shows the TEM micrograph taken with dark field imaging, left inset shows the single particle spherical in shape and the corresponding particle distribution estimated from the dark field TEM micrograph are depicted in Fig. 3.4 (b’). Fig. 3.4 (c) is their corresponding HR-TEM image and (c’) shows the SAED pattern of ZnO nanoparticles. It is found from the TEM micrographs that; the particles are agglomerated, having wide size distribution ranging from 15-50 nm with an estimated average particle size of 33 nm. These values are in agreement with the crystallite size obtained from XRD studies. It is seen that, a few particles appear to be larger in size, due to the aggregation of smaller particles during the evolution of enormous amount of gases during combustion reaction (Table 3.2). From the HR-TEM image, the fringe width (d-spacing) is determined and found to be ~ 0.260 nm for (002) and ~ 0.245 nm for (101) planes. The (002) and (101) planes are assigned after comparing the measured d-spacing values with those from the standard JCPDS pattern (# 36-1451). This indicates that, the particles (ZnO crystallites) are having orientations along (002) and (101) planes. The corresponding SAED pattern is shown as inset of Fig. 3.4 (c’). In SAED pattern, clear ring patterns are seen represents the polycrystalline nature of the sample. All the ring patterns are indexed to the JCPDS pattern # 36-1451, which confirms the formation of ZnO wurtzite nano structure.

Fig. 3.5 is the TEM images of ZnO prepared using L-Glutamine as fuel. Fig 3.5 (a) is the TEM micrograph showing the particles distribution and the corresponding histogram of size distribution is shown in Fig. 3.5 (a’). From Fig. 3.5 (a & a’), it is seen that, the particles are agglomerated with wide size distribution in the range 12 -30 nm with an average particle size is 20 nm. Fig 3.5 (b) is the HR-TEM image, from which the d-spacing is determined and found to be ~ 0.263 nm corresponds to (002) plane, indicating that, more (major) number of crystals
are orienting along (002) directions. Along with nano particles, few nano plates with an average size of 25 nm x 10 nm in dimensions are observed (Fig 3.5 (c)). The enlarged image of such a single nano plate is given as an inset of Fig. 3.5 (c). The rapid and high exothermic reaction between the fuel (L-Glutamine) and the oxidizer (Zinc Nitrate) vigorously supplies high temperature, which further influences the evolution of large volume of gases. As a result, preferentially grown crystals along (002) plane segregates and condense to form a single grain along one direction, resulting in the formation of nano plates. The SAED pattern of ZnO is depicted in Fig. 3.5 (d). All the diffraction fringes (rings) are indexed to the JCPDS card no. 36-1451, belongs to ZnO wurtzite crystal structure. From the obtained SAED pattern, it is confirmed that, ZnO has polycrystalline nature.

Fig. 3.6 is the TEM micrographs of ZnO prepared using Leucine as fuel. Fig. 3.6 (a) is the TEM micrograph showing the particles distribution and (c”) represents the histogram of size distribution. It is found that, the particles are agglomerated and highly dense, due to the large exothermicity of the fuel (Leucine)-oxidizer, which results in coalesce of particles. The wide distribution of particle size is observed in the range 14-26 nm (Fig. 3.6 (a”)) with an average particle size of 19 nm. The right inset of Fig. 3.6 (a) show the typical size of single ZnO particle. Though much agglomeration is observed, the pores are seen on the surface of the agglomerated ZnO, due to evolution of large amount of gases during the combustion synthesis. The typical average size of pores is found to be 4-8 nm in diameter (Fig. 3.6 (d)). Fig. 3.6 (b) is the HR-TEM image of ZnO particles, from which the d-spacing value is determined. The d-spacing value is found to be ~ 0.26 nm corresponding to (002) plane, indicating that, more (major) number of crystals is oriented along (002) direction. Inset of Fig. 3.6 (b) shows a single particle larger in size due to the agglomeration of smaller sized particles. The polycrystalline nature of the material is confirmed from the SAED pattern. The SAED pattern of ZnO is depicted in Fig. 3.6 (c). Due to the fact of wide, dense and high crystalline particles, diffraction rings with bright dots are seen in SAED pattern. All the diffraction fringes (rings) are indexed to the JCPDS card no. 36-1451, belongs to ZnO wurtzite crystal structure.
Fig. 3.4 (a, b) TEM micrographs, (b’, c’) histogram of particles size, (c) HRTEM image and (c’) shows SAED pattern of ZnO prepared using L-Valine as fuel.
Fig. 3.5 (a) TEM micrograph showing the particles distribution and (a’) is its histogram; (b) HR-TEM image showing the d-spacing; (c) TEM micrograph, showing particles and plates, the zoomed part of single plate is shown as an inset; (d) SAED pattern of ZnO prepared with L-Glutamine.

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Fig. 3.6 (a) TEM micrograph showing the particles distribution, inset is the single particle image; (a’) is the histogram showing particle size distribution; (b) HR-TEM image showing the d-spacing, inset is the large particle indicating the agglomeration of smaller sized particles; (c) SAED pattern; (d) HR-TEM micrograph showing pores on its surface of ZnO prepared with Leucine.

Synthesis and studies on pure and doped ZnO nanomaterials and thin films
Further, lattice parameters are estimated using TEM-SAED patterns. The Bragg angle (2θ) is determined from the inter-planar d-spacing which is obtained from SAED patterns using the formula, \( n \lambda = 2d \sin \theta \). The lattice parameters are estimated through unit cell program [12] having known \((h \ k \ l)\) and 2θ values and are tabulated in the table 3.3. It is observed that, the estimated lattice parameters from TEM-SAED patterns are in agreement with those obtained from Rietveld refinement of XRD data and the estimated particle sizes from HR-TEM micrographs.

### 3.6 Conclusions

In the present investigation, new fuels such as L-Valine, L-Glutamine and Leucine are explored in the preparation of ZnO nanoparticles by solution combustion technique and the effect of fuel to oxidizer combinations on the properties of ZnO nanoparticles was studied. It was observed in all the cases, the nanocrystalline ZnO resulted from the combustion process in as-synthesized form. The decomposition of the nitrate-organic fuel precursors is investigated by TG-DTA studies and the compositional dependent exothermicity (T_{ad}) and the amount of evolution of gases for the different fuel-oxidizers were estimated through thermodynamic theoretical calculations. The correlations were established between the nature of the combustion synthesis characterized by the exothermicity (T_{ad}) and the amount of gases liberated with the characteristics of as-formed ZnO powders. It was found that, the compositional dependent exothermicity (T_{ad}) influences the amount of gases liberated with increase of F/O ratio, which results in the smaller size particles from the combustion synthesis. Further, the lattice parameters obtained from the structure refinement by Rietveld refinement of XRD data are in agreement with the literature reported values. Nano sized particles and the different morphology of as-synthesized ZnO powders were observed through TEM images, which is dependent on the exothermicity of the fuel-oxidizer used and also a wide size distribution of nano sized ZnO particles are observed due to the agglomeration of particles. These agglomerations were attributed to the nature of combustion reaction due to the evolution of enormous amount of gases during combustion process. In addition, nanoplates are observed in samples prepared using L-Glutamine as a fuel, whereas agglomerated morphology of
nanoparticles are observed in case of other fuels. The structural investigation was carried out to understand the effect of fuel on the structure of the as-formed ZnO and it is found that, the estimated lattice parameters from TEM-SAED patterns are in agreement with those obtained from Rietveld refinement of XRD data.
REFERENCES


