Chapter 3

Synthesis of zinc orthotitanates by solvothermal method

3.1 Introduction

Research on nanoparticles includes synthesis and characterization with respect to structural, physical and chemical properties. Their assembly into 1-3D structures extending over several length scales with hierarchical construction principles and their application in various field. Many synthesis techniques gave access to nanomaterials with wide range of compositions, well defined and uniform crystallite size, astonishing and unique crystal shapes. Even though, gas phase synthesis techniques are well known for low cost production at large scale of nanomaterial, the liquid phase synthesis is more flexible with respect to controlled variation of structural, compositional and morphological features of the nanomaterials. Liquid phase synthesis route includes coprecipitation, aqueous and nonaqueous sol gel process, hydrothermal or solvothermal methods, template synthesis and biomimetic approaches.

In solvothermal synthesis, chemical reactions performed in closed reaction vessel at temperatures higher than the boiling point of the solvent used. If
water is used as solvent, it’s known as hydrothermal method. Solvothermal methods are mainly defined by chemical parameters such as nature of the solvent and reagents, temperature and pressure. Solvothermal technique has been fundamental branch of nanoparticle synthesis and processing. This technique consumes less energy due to moderate reaction temperature and commonly inexpensive solvents can be used for the synthesis. In solvothermal method only liquids having low boiling point can be used as solvents.

Solvothermal and hydrothermal technique for synthesis of nanostructured metal oxides are well known but not widely used for synthesis of multicomponent metal oxides. S. Iwatsuki et. al synthesized strontium titanate nanotubes by solvothermal method from strontium hydroxide and titanium tetraisopropoxide (TTISP) in mixture of ethanol and 2-methoxy ethanol at 240°C for 18 h. Apart from this, reports are available on synthesis of SrTiO3 by hydrothermal method, sol gel hydrothermal method. Hyun-Wook Lee et al. prepared nanosized barium titanate using solvothermal method at 200°C for 48 h using barium hydroxide, titanium butoxide in ethanol-ammonia-water mixed solvent and employing diethanolamine and triethanolamine to control the particle size. Xie, Yahong; et al synthesized Sn⁺² doped BaTiO₃ by microwave assisted solvothermal method.

Literature survey reveals that nanostructured Zn₂TiO₄ has been synthesized by various methods such as solid state, Ball milling, Polymeric precursor method, Co precipitation method, Chemical bath deposition method, sol gel method, Flame spray pyrolysis method. No reports are available on synthesis of Zn₂TiO₄ by hydrothermal or solvothermal method except reported by Cheng-Li Wang.

Cheng-Li Wang et al. synthesized zinc titanates by hydrothermal method without using dispersing agent at pH 7 in 25 % NH₃ at 150°C for 2 h followed by calcination at various temperature for 1 h. The author reported mixed phases of ZnO, TiO₂(a), Zn₂Ti₃O₈ at 600°C, ZnTiO₃ and ZnO at 700°C and ZnO, Zn₂TiO₄, TiO₂(r) and ZnTiO₃ at 900°C.
In this work glycothermal approach has been adopted for synthesis of zinc orthotitanates. Various attempts were performed using hydrothermal, solvothermal methods for desired synthesis.

3.2 Experimental

3.2.1 Optimization of synthesis method

The various trials were performed for the solvothermal synthesis of nanostructured zinc orthotitanates in aqueous as well as nonaqueous medium. These attempts are given below. Finally, zinc orthotitanates were synthesized by solvothermal method in ethylene glycol medium in presence of citric acid.

3.2.1.1 Hydrothermal synthesis by using zinc acetate and potassium titanyl oxalate

In this attempt, mixture of aqueous solutions of zinc acetate and potassium titanyl oxalate in the mole proportion 2:1 was filled in the teflon container which was enclosed in steel container. Then assembly was kept in autoclave at 150°C for 24 h. The product formed was washed with hot water followed by methanol and dried at 100°C. Thereafter product formed was thermally decomposed at 550°C for 3 h. The compound obtained after decomposition was characterized by XRD for confirmation of phase formation.

3.2.1.2 Solvothermal synthesis by using zinc acetate and titanium isopropoxide in methanol

In this attempt, Solvothermal reaction was carried out using precursors zinc acetate and titanium tetraisopropoxide (2:1 mole proportion) in methanol medium. Zinc acetate was dissolved in methanol and TTISP in mixture of isopropanol–methanol. The mixture was filled in teflon container which then enclosed in steel container. The container was kept in autoclave at 150°C for 24 and 48 h. The product formed was washed with hot methanol and dried at 100°C and characterized by XRD for the confirmation of the desired phase formation.
3.2.1.3 Solvothermal synthesis in ethylene glycol medium (Glycothermal)

In this attempt, solvothermal reaction was carried out in ethylene glycol medium following the same procedure described in section 3.2.1.2. Trials were performed at 150ºC for 12, 24 and 36 h. The solvothermal process has been performed in presence and absence of citric acid. The product formed were further washed with methanol and dried at 100 ºC and thermally decomposed at 550 ºC and 650 ºC for 6 h. The compounds obtained after thermal composition were characterized by XRD to confirm the formation of Zinc orthotitanate. It is observed that zinc orthotitanate has been formed after thermal decomposition. So, this method is adopted and synthesis of zinc orthotitanates (undoped and metal (Ag and Co) doped) have been carried out in presence of citric acid.

3.2.2 Characterization

The compounds synthesized during optimization of the method as per procedure described in sections 3.2.1.1-3.2.1.3 were characterized XRD for confirmation of desired phase formation. The intermediates produced during the solvothermal process were characterized by TG-DTG-DSC analysis wherever necessary.

The zinc orthotitanates synthesized by optimized method as described in section 3.2.1.3 were characterized by XRD, FTIR, FESEM, TEM, EDXRF, BET-BJH, UV-Vis-DRS and PL spectroscopy. Details of the instruments used are given in the chapter 2. (Section 2.2.2)

3.3 Results and Discussion

3.3.1 Optimization of synthesis method

3.3.1.1 Hydrothermal method:

The weight of the product obtained after the hydrothermal process was found to be higher than the expected weight of the Zn2TiO4. So, thermogravimetric analysis of the intermediate was performed to find out the decomposition temperature. Thermogram shown in the figure 3.1 shows that decomposition takes place in two stages and complete decomposition takes place at 415ºC. Therefore intermediate was decomposed at 550ºC for 6 h.
Figure 3.1: TG-DTG of the intermediate synthesized by hydrothermal method: a) TG and b) DTG

XRD pattern of the intermediate and thermally decomposed product is shown in the figure 3.2. XRD of the intermediate indicates that it is neither mixture of ZnO – TiO₂ nor zinc orthotitanate.
Figure 3.2 : XRD pattern of the hydrothermal product a) at 550°C b) intermediate

XRD peaks of the thermally decomposed product indicate presence of ZnO and absence of peaks due to TiO$_2$ depicts amorphous nature of TiO$_2$. This confirms that, after decomposition of the intermediate composite of the ZnO-TiO$_2$ has been formed.

The intermediate obtained was thermally decomposed at 900°C. Major peaks observed in the XRD pattern of the product obtained (Figure 3.3) were found to be in agreement with Zn$_2$TiO$_4$ along with minor peaks due to TiO$_2$ and ZnO.
Thus, it can be concluded that, zinc orthotitanate cannot be synthesized directly by hydrothermal method or followed by thermal decomposition at 550°C.

3.3.1.2 Solvothermal method

A) In alcoholic medium

Solvothermal reaction in methanol (alcoholothermal) medium has been attempted to perform at 150°C for 24 h. The product obtained was characterized by XRD to confirm the formation of zinc orthotitanate. XRD pattern of the compound as shown in figure 3.4a indicates existence of ZnO. Peaks corresponding to TiO$_2$ are not observed indicates its existence in amorphous form. The product obtained has been annealed at 550°C for 3h. XRD of the calcined product is shown in figure 3.4b which indicates no change in the nature of the compound even after annealing.
Solvothermal reaction has been also carried out at $150\,^\circ C$ for 48 h and at $180\,^\circ C$ for 24 h. XRD pattern of the compounds obtained at respective conditions shown in the figure 3.5 depicts same nature of the products as obtained at $150\,^\circ C$ for 24 h. Hence, in all the cases mixture of ZnO (crystalline) and TiO$_2$ (amorphous) has been formed.
Figure 3.5: XRD pattern of the compound obtained at a) 150°C (24 h) b) 150°C (48 h), c) 180°C (24 h)

Figure 3.6: XRD pattern of the Zn$_2$TiO$_4$ obtained by solvothermal (in methanol medium) method followed by annealing at 900°C.
When compound obtained by solvothermal method in methanol medium (150 °C for 24 h) calcined at 900 °C for 3 h, it produces single phase Zn₂TiO₄ (Figure 3.6). Traces of ZnO observed may be due to stoichiometric error occurred during synthesis. XRD pattern of the Zn₂TiO₄ is in good agreement with cubic phase.

Though, single phase Zn₂TiO₄ is obtained, this method is not used for synthesis of nanoparticles since, aim of the work is synthesis of visible light nanostructured oxide photocatalyst at lower temperature.

B) In ethylene glycol medium

i) In absence of citric acid: Intermediates obtained at 12, 24 and 36 h reaction were neither composite of ZnO and TiO₂ nor Zn₂TiO₄, so decomposed at 550 °C for 6 h. reaction. XRD pattern of the compounds formed after decomposition of the intermediates obtained by glycothermal reaction at 12, 24 and 36 h is shown in the figure 3.7. Decomposition of intermediate formed from 12 h reaction gives mixture TiO₂ (tetragonal) (JCPDS card No. 89-4203) and ZnO after thermal decomposition at 650 °C for 3 h. While, Zn₂TiO₄ has been formed after thermal decomposition of intermediates obtained in 24 and 36 h. From the XRD pattern, it is observed that trace amount of ZnTiO₃ has also been formed along with Zn₂TiO₄. Hence, optimum period for hydrothermal reaction is 24 h for synthesis of Zn₂TiO₄. Since, Ag doped Zn₂TiO₄ could not be formed; this method was not adopted for the synthesis of zinc orthotitanates.

ii) In presence of citric acid: Intermediate formed at 24 and 36 h reaction produces Zn₂TiO₄ along with trace amount of ZnO and ZnTiO₃ after thermal decomposition at 650 °C. While, intermediate obtained at 12 h results into mixture of Zn₂TiO₄ and ZnTiO₃ (JCPDS card No. 85-0547) after thermal decomposition at 650 °C for 3 h. Hence optimum period for synthesis of Zn₂TiO₄ by solvothermal reaction in presence of citric acid is 24 h. Figure 3.8 shows XRD pattern of the compounds obtained after thermal decomposition of the intermediate synthesized at 12, 24 and 36 h.
Figure 3.7: XRD pattern of the compounds obtained by glycothermal method at 1500°C for a) 12 h b) 24 h and c) 36 h duration.

Figure 3.8: XRD pattern of the compounds obtained at a) 12 h b) 24 h c) 36 h duration.
iii) Thermal Analysis of the intermediate

The intermediates obtained by solvothermal reaction ($150^\circ \text{C}, 24 \text{ h}$) for synthesis of zinc orthotitanates were thermally analysed to determine decomposition temperature and effect of doping on the intermediate. Figures 3.9-3.11 show TG-DTG-DSC thermograms of undoped intermediate and doped intermediates (Ag and Co).

*Figure 3.9: Thermograms of undoped intermediate A) TG and DTG B) DSC*
Figure 3.10: Thermograms of Ag doped intermediate  A) TG and DTG  B) DSC
Figure 3.11: Thermograms of Co doped intermediate A) TG and DTG B) DSC

TG-DTG curves of the undoped and doped intermediate given in the figures 3.9A-3.11A show complete decomposition in three stages. The major weight loss takes place in first two stages and minor weight loss in third stage (TableNo.3.1). The decomposition at first stage may be attributed to loss of water while second and third stage to decomposition of organic part of the complex. 21 These findings conclude that intermediates obtained are the complexes of the Zn, Ti and doped
metal (Ag and Co). The complete decomposition of all intermediates was observed to be at ~ 550 °C. DSC curve of the undoped and doped intermediate shows (Figure 3.9B-3.11B) major exothermic peaks in the range 350-400 °C. In case of undoped intermediate, temperature is slightly lowered. Similar TG-DTG pattern obtained shows same type of complex formation. Though decomposition completes at ~ 550 °C, phase formation does not take place at 600°C. Hence, intermediates were thermally decomposed at 650°C. Table 3.1 gives details of the decomposition stages.

**Table 3.1: Thermal analysis of doped and undoped zinc orthotitanates.**

<table>
<thead>
<tr>
<th>Intermediate/Stages</th>
<th>I (°C)</th>
<th>II (°C)</th>
<th>III (°C)</th>
<th>Exothermic Peak temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped complex</td>
<td>50-200 (14.1 %)</td>
<td>300-475 (41.1 %)</td>
<td>500-550 (1.7 %)</td>
<td>401</td>
</tr>
<tr>
<td>Ag-doped complex</td>
<td>50-200 (12.9 %)</td>
<td>300-475 (30.2 %)</td>
<td>500-550 (1.7 %)</td>
<td>360</td>
</tr>
<tr>
<td>Co-doped complex</td>
<td>50-225 (15.7 %)</td>
<td>300-475 0°C (41.4 %)</td>
<td>500-550 (1.3 %)</td>
<td>380</td>
</tr>
</tbody>
</table>

( ) : Figures in parenthesis indicates % weight loss at respective stage.

**3.3.2 Structural study**

**3.3.2.1 XRD analysis:**

XRD pattern of the zinc orthotitanate (Zn₂TiO₄) as shown in the figure 3.12a indicates formation of Zn₂TiO₄ along with trace quantity of ZnO.²² XRD peaks demonstrated in figure are in good agreement with cubic phase as well as tetragonal phase.²³ XRD pattern of Ag@Zn₂TiO₄ (figure 3.12b) consist of major peaks due to Zn₂TiO₄ and elemental Ag.
On the contrary, there are no peaks due to metal oxides of cobalt in the XRD of Co@Zn$_2$TiO$_4$ (Figure 3.13) which indicates substitutional doping in lieu of Zn$^{+2}$ ions. XRD of Co doped zinc titanate includes peaks due to Zn$_2$TiO$_4$ and ZnO. In this case, extent of ZnO is found to be increased as compared to that of in undoped Zn$_2$TiO$_4$. 

Figure 3.12: XRD pattern of the (a) Zn$_2$TiO$_4$ and (b) Ag@Zn$_2$TiO$_4$
Figure 3.13: XRD pattern of (a) Zn$_2$TiO$_4$ and (b) Co@Zn$_2$TiO$_4$

Crystallite size calculated from Sherrer’s formula has been observed to be 19.8, 14.8 and 18.8 nm in Zn$_2$TiO$_4$, Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ respectively. Crystallite size of Ag nanoparticles was observed to be 34.3 nm in Ag@Zn$_2$TiO$_4$.

3.3.2.2 FTIR analysis

FTIR spectra of undoped and doped zinc orthotitanates in the range 4000-500 cm$^{-1}$ is shown in the figure 3.14. According to FTIR spectra, all zinc orthotitanates don’t show band due to –OH group which may arise due to adsorbed water or hygroscopic nature. Broad band in the range 700-500 cm$^{-1}$ is attributed to TiO$_6$ group in Zn$_2$TiO$_4$ and Band at ~ 500 cm$^{-1}$ may be due to tetragonal phase of Zn$_2$TiO$_4$. Absence of major bands in the region 2000-1000 cm$^{-1}$ indicates formation of organic matter free zinc orthotitanates.
Figure 3.14 : FTIR spectra of zinc orthotitanates a) Zn$_2$TiO$_4$ b) Ag@Zn$_2$TiO$_4$ c) Co@Zn$_2$TiO$_4$

3.3.2.3 EDXRF Analysis:

Elemental composition (Table 3.2) of as synthesized zinc orthotitanates determined by EDXRF technique is in agreement with stoichiometric composition of Zn$_2$TiO$_4$ and Ag and Co doped Zn$_2$TiO$_4$.

Table 3.2 Elemental analyses of zinc orthotitanates.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound</th>
<th>Zn</th>
<th>Ti</th>
<th>Doped Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Zn$_2$TiO$_4$</td>
<td>73.1(73.2)</td>
<td>26.9 (26.8)</td>
<td>-</td>
</tr>
<tr>
<td>02</td>
<td>Co@Zn$_2$TiO$_4$</td>
<td>69.6 (69.8)</td>
<td>27.02(26.9)</td>
<td>3.2(3.3)</td>
</tr>
<tr>
<td>03</td>
<td>Ag@Zn$_2$TiO$_4$</td>
<td>65.2(64.1)</td>
<td>24.9(24.7)</td>
<td>9.9 (11.2)</td>
</tr>
</tbody>
</table>

Figures in the parenthesis indicates expected % of the elements
3.3.3 Morphological study

Morphological study was performed by FESEM and TEM analyses

3.3.3.1 FESEM analyses

Figure 3.15 shows micrographs of the Zn$_2$TiO$_4$ obtained by glycothermal method indicating formation uniform spheres having size ~ 500 nm. Careful examination of the micrographs shows trapping of small spheres into the cavity of the large sphere (Figure 3.15a). Some spheres are observed to be opened which also indicates hollowness of the spheres. (Figure 3.15b) All these spheres are formed by self-alignment of ~50 nm size spherical nanoparticles as seen in the figure 3.15b.

![Figure 3.15: FESEM micrograph of Zn$_2$TiO$_4$ at a) 10 K and b) 100 K magnification](image)

Morphology of the Ag@Zn$_2$TiO$_4$ found to be disturbed as compared to that of Zn$_2$TiO$_4$. Figure 3.16a shows formation of spheres with size ~ 500 nm as well as some irregular shape objects. Agglomeration of the particles has been observed to be more as compared to that of in Zn$_2$TiO$_4$. There is also appearance of scattered nanoparticles (Figure 16b) having size in the range of 50-100 nm. Similar effect of Ag doping on morphology has also been reported many researches$^{26,27}$.
Figure 3.16: FESEM micrographs of Ag@Zn$_2$TiO$_4$ at A) 9k and b) 50 K

Figure 3.17 (a-c) shows spherical morphology having size of the spheres ~ 500 nm. Figure 3.17d shows opened sphere in which small bunch of nanoparticles has been suspended. This indicates that these spheres are not hollow. Careful observation reveals small nanoparticles of the size ~ 50 nm are assembled to form large sphere.

Figure 3.17: FESEM micrographs of Co@Zn$_2$TiO$_4$ at a) 10 K b) 25 k c) 50K and d) 100 K
3.3.3.2 TEM Analyses:

TEM images of Zn$_2$TiO$_4$ are shown in the figure 3.18 (a-c). Uniform size particles with some extent of agglomeration are seen in the figure 3.18a. The size of the particles has been observed to be in the range 10-25 nm from figure 3.18b and 3.18c. Shape of the particle cannot be clearly identified due to overlapping, but cubical shape of the some particles can be seen in figure 3.18b and 3.18c.

![Figure 3.18: TEM images of Zn$_2$TiO$_4$ at a) 200 nm b) 20 nm, c) 20 nm scale and d) ED pattern](image)

Concentric rings observed in the ED pattern (Figure 3.18d) are corresponding to the 100, 111, 102 and 210 planes of tetragonal structure and 111, 220, 311 and 222 planes of f.c.c. structure. Most of the planes in cubic and tetragonal structure are common except 100 plane ($2\theta = 14.75^\circ$) which belongs to tetragonal structure only. The peak at $14.75^\circ$ has not been appeared in XRD pattern of Zn$_2$TiO$_4$ (Figure
3.12a). Appearance of concentric ring corresponding to 100 plane of tetragonal phase is evidence for mixed phases of Zn$_2$TiO$_4$. All crystal planes indexed from ED pattern are in agreement with JCPDS data.

TEM images of Ag@Zn$_2$TiO$_4$ shows more agglomerated particles (Figure 3.19a) as compared to observed in Zn$_2$TiO$_4$. Particle size has been observed to be in the range 20-50 nm (Figure 3.19b and 3.19c). Figure 3.19b shows appearance of some cubical and tetragonal particles along with some irregular shapes are observed in figure 3.19c.

![Figure 3.19: TEM images of Ag@Zn$_2$TiO$_4$ at a) 100 nm, b) 50 nm, c) 20 nm scale and d) ED pattern](image-url)
Spotty ring pattern has been observed for Ag@Zn2TiO4 (Figure 3.19d). ED pattern shows rings corresponding to cubic and tetragonal structure. Concentric ring corresponding to 100 plane \( (2 \theta = 14.75^\circ) \) of tetragonal structure has also been observed in Ag@Zn2TiO4. Concentric ring corresponding to ZnO (002 plane) has been observed in the ED pattern.

TEM image of Co@Zn2TiO4 shows cluster formed due to assembly of spheres (Figure 3.20a). These spheres are formed from particles of the size in the range 25-50 nm as observed in figure 20b and 20c.

Figure 3.20: TEM images of Co@Zn2TiO4 at a) 200 nm  b) 20 nm, c) 20 nm and d) ED pattern
ED pattern shows (Figure 3.20d) concentric rings corresponding to cubical as well as tetragonal structure. Ring corresponding to 100 plane of tetragonal structure is also observed in ED pattern. Spotty ring pattern has been observed in case of Co@Zn$_2$TiO$_4$ similar to observed in Ag@Zn$_2$TiO$_4$.

3.3.4 Surface Area analysis

Nature of the surface of the zinc orthotitanates can be determined from the nitrogen-adsorption isotherms and pore size distribution. The shapes of hysteresis loop of all zinc orthotitanates are of H3 type (Figures 21a-21c). H3 type of hysteresis loop is associated with mesopores present on the surface $^{28}$. The broad pore size distribution has been observed for Zn$_2$TiO$_4$, Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$. Nature of pore size distribution in case of Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ seems to be similar kind.

![Figure 3.21: Nitrogen adsorption desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution plot (inset) a) Zn$_2$TiO$_4$ b) Ag@Zn$_2$TiO$_4$ and c) Co@Zn$_2$TiO$_4$](image)
The average surface area, pore volume and pore diameter has been decreased considerably upon incorporation of Ag into Zn$_2$TiO$_4$ as compared to Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$. BET Langmuir surface area of undoped Zn$_2$TiO$_4$ has found to be largest as compared to surface area of Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$. The surface area of the Ag@Zn$_2$TiO$_4$ has been found to be lowest. The increase in pore volume and lower crystallite size of Zn$_2$TiO$_4$ may be responsible for high surface area. Pore volume depends on the pore diameter as well as depth of the pores. So, their variation cannot be correlated. Form the trend of pore volume and surface area it can be concluded that porosity as well as surface area decreases due to doping. But BJH pore diameters are not in accordance with the BET pore diameter. This is because BET method determines surface area of any shape and porosity while BJH assumes pores have cylindrical shape. Hence, BET surface area and BJH pore diameter are in agreement with each other. Plausible explanation regarding decrease in surface area may be given on the basis of morphology and crystallite sites of undoped and doped zinc orthotitanates. Highest surface area of Zn$_2$TiO$_4$ is because of hollow spheres (Figure 3.15b) and less agglomeration and smaller particle size (Figure 3.18) as compared to observed in Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$. In case of Ag@Zn$_2$TiO$_4$ spheres observed are more compact than observed in Co@Zn$_2$TiO$_4$ and hence, surface area of Ag@Zn$_2$TiO$_4$ is even less than Co@Zn$_2$TiO$_4$. The phenomena of decrease in surface area upon doping have also been reported in previous studies.

Table 3.3: Surface area, pore volume and pore diameter of zinc orthotitanates

<table>
<thead>
<tr>
<th>Compound</th>
<th>BET (m$^2$/g)</th>
<th>Pore Volume cm$^3$/g (Pores &lt; 77.1 nm)</th>
<th>Pore diameter nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$TiO$_4$</td>
<td>17.44</td>
<td>0.076</td>
<td>17.46 (25.59)</td>
</tr>
<tr>
<td>Ag@Zn$_2$TiO$_4$</td>
<td>6.50</td>
<td>0.0277</td>
<td>17.02(30.37)</td>
</tr>
<tr>
<td>Co@Zn$_2$TiO$_4$</td>
<td>11.14</td>
<td>0.062</td>
<td>22.17(27.01)</td>
</tr>
</tbody>
</table>
3.3.5 Optical Studies

3.3.5.1 UV-Vis DRS analysis:

Figure 3.22A represents absorbance plot of Zn$_2$TiO$_4$ and Ag@Zn$_2$TiO$_4$. Band gap of Zn$_2$TiO$_4$ observed to be at 3.23 and 3.74 eV which corresponds to tetragonal and cubic phase of Zn$_2$TiO$_4$. Band gaps in Ag@Zn$_2$TiO$_4$ has been observed at 3.16 eV and 1.68 eV with respect to Zn$_2$TiO$_4$ and elemental Ag.

![Absorbance Plot](image1.png)  
![Tauc Plot](image2.png)

Figure 3.22: A) UV-Vis DRS spectra in absorbance mode  B) Tauc Plot of Zn$_2$TiO$_4$ and Ag@Zn$_2$TiO$_4$

Comparative absorption and tauc plots of Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ are given in the figure 22B. Band gap of Co, doped Zn$_2$TiO$_4$ has been observed to be at 2.72 eV, which indicates shifting of band gap (Red shift) into visible region. Red shift observed is result of the substitualional doping of Co(II).
Figure 3.23: A) UV-Vis DRS spectra in absorbance mode B) Tauc plot

Absorption plot of Co@Zn$_2$TiO$_4$ shows major extent of tetragonal form of the zinc orthotitanate as compared to undoped zinc orthotitanate. This also indicates that Co doping favours tetragonal phase formation.

3.3.5.2 PL studies: PL of the as synthesized zinc titanates consists of three prominent peaks at 330, 365 and 467 nm. Peak at 365 nm is sharp with maximum intensity while peak at 330 nm is very small and at 467 nm is broad. There is no shifting of peaks observed at 365 and 467 nm due to Ag and Co(II) doping. The weak peak emission peak has been observed at 330 nm. This can be referred as near band edge emission which is closed to band gap observed at 335 nm in UV-vis spectra. The emission peak observed at 467 nm indicates that defects exists in the crystalline ordered mesostructured Zn$_2$TiO$_4$. The existence of intrinsic defects such as O$^{2-}$ and Zn$^{2+}$ vacancies may be responsible for the emission.

Effect of doping can be interpreted form Relative Intensity (RI) of peak observed at 467 nm. There is no effect of doping on peak observed at 365 nm and 330 nm. RI of the peak in Ag@Zn$_2$TiO$_4$ has been slightly increased (0.65) with respect to observed in undoped Zn$_2$TiO$_4$. While, RI of the peak has been markedly increased in Co@Zn$_2$TiO$_4$. 

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Figure 3.24: Photoluminescence spectra: a)Ag@Zn$_2$TiO$_4$ b) Zn$_2$TiO$_4$ and c) Co@Zn$_2$TiO$_4$

Increase in intensity of the peak at 467 nm due to doping indicates increase in crystal defects as compare to undoped Zn$_2$TiO$_4$.

3.4 Summary

Zinc orthotitanates were synthesized by glycothermal method in presence of citric acid followed by thermal decomposition of the intermediate at 650 °C. XRD analyses show negligible presence of ZnO in Zn$_2$TiO$_4$ and Ag@Zn$_2$TiO$_4$. But extent of ZnO has been increased unexpectedly in Co@Zn$_2$TiO$_4$. XRD pattern of Zn$_2$TiO$_4$ is in agreement with tetragonal as well as cubic crystal structure (fcc). UV DRS study supports appearance of tetragonal as well as cubic phase. XRD pattern of Ag@Zn$_2$TiO$_4$ reveals existence of elemental Ag while XRD pattern of Co@Zn$_2$TiO$_4$ confirms substitutional doping. FESEM study indicates formation self assembled spheres of nanoparticles in all zinc orthotitanates. But in case of
Zn$_2$TiO$_4$ hollow spheres has been observed. TEM investigation depicts formation of nanoparticles in the range 10-20 nm in Zn$_2$TiO$_4$ and 25-50 nm particles in Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$. Spherical cluster has been observed in case of Co@Zn$_2$TiO$_4$. Surface analyses shows decrease in surface area due to doping. Surface area of Ag@Zn$_2$TiO$_4$ is observed to be lowest amongst all zinc orthotitanates synthesized. FTIR study shows absence of -OH group in all zinc orthotitanates. UV DRS study shows band gap due to tetragonal and cubic phase of Zn$_2$TiO$_4$. In case of Ag@Zn$_2$TiO$_4$ additional band gap due to elemental silver has been observed. In case of Co@Zn$_2$TiO$_4$ shifting of band gap of Zn$_2$TiO$_4$ observed towards visible region which clearly indicates substitutional doping. PL study shows increase in intrinsic defects in Co@Zn$_2$TiO$_4$ as compared to observed in Zn$_2$TiO$_4$ and Ag@Zn$_2$TiO$_4$. The as synthesized zinc orthotitanates have been employed for photocatalytic degradation of Acid Orange -8 and Rhodamine –B under sunlight.
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