Chapter 2

Synthesis of zinc orthotitanates by combustion method

2.1 Introduction

Zn$_2$TiO$_4$ alias zinc orthotitanate (ZOT) is the stable phase of ZnO-TiO$_2$ system which has been employed for various applications like microwave dielectrics, catalyst, photocatalyst, pigment, gas sensing material, antistatic films, anti-reflecting coating in solar cells.$^{1,2}$ ZnO-TiO$_2$ system can generate five compounds namely zinc orthotitanate (Zn$_2$TiO$_4$), zinc metatitanate (ZnTiO$_3$), Zn$_2$Ti$_2$O$_6$, Zn$_2$Ti$_3$O$_8$and Zn$_4$Ti$_5$O$_{16}$ but only ZnTiO$_3$, Zn$_2$TiO$_4$ and Zn$_2$Ti$_3$O$_8$ are found to be stable.$^{4,5,6}$ Phase formation temperature of zinc titanates varies with preparation method and Zn/Ti ratio of the precursors.$^{7,8,9,10}$ Many researchers have synthesized Zn$_2$TiO$_4$ from ZnO and TiO$_2$ by solid state reaction route.$^{11}$ The solid state reaction requires high temperature (1200°C) and longer sintering time (24 h). The nanostructured Zn$_2$TiO$_4$ is also been synthesized by ball milling method, Flame spray pyrolysis$^{12}$ and sol-gel method$^{13}$. Very limited literature is available on metal doped Zn$_2$TiO$_4$. Cu doped Zn$_2$TiO$_4$ has been reported with enhanced microwave dielectric properties as compared to Zn$_2$TiO$_4$.$^{14}$ Ceramic pigments of the spinal structure were obtained by synthesizing Co, Ni, and Mn doped Zn$_2$TiO$_4$ by polymeric precursor method.$^{15}$ Photoluminescence
properties of Cr$^{3+}$, V$^{5+}$ and Sn$^{4+}$ doped nanostructured Zn$_2$TiO$_4$ synthesized by polymeric precursor method was studied.$^1$

Zn$_2$TiO$_4$ has been effectively used for removal of multiple constituents of hot stream gases being an efficient adsorbent of gases at high temperature.$^{16}$ The regeneration of Zn$_2$TiO$_4$ was found to be fast with negligible loss as well as its thermal stability is higher than single metal oxides.

Combustion synthesis processes are generally characterized by high temperature, fast heating rate and short reaction time. These features make combustion synthesis an attractive, low cost method for manufacture of the nanomaterials. Other advantages are i) Use of simple equipment ii) Formation of high purity products iii) Stabilization of metastable phases iv) Formation of virtually any size and shape products.$^{17}$ In this method self sustained reaction of different oxidizers (metal nitrates) and fuels takes place. Fuels like urea, glycene, carbon hydrazides (CH), oxalylldihydradize (ODH), malonic acid dihydrazide (MDH), ammonium acetate, citric acid, ammonium citrate, etc. also can be used in combustion synthesis. The concept of mixed of fuel has also been attempted for synthesis of nanomaterials.$^{18,19}$ The complex fuel favours formation of nanosized particles but further calcination may be required for the removal of organic content which depends on the nature of the fuel. Many books and reviews have been published on combustion synthesis in recent years.$^{20,21}$ This technique has been applied for preparation simple metal oxides, multicomponent metal oxides such as titanates and many varieties of oxides.$^{20,21,22,23,24,25,26}$

In the present investigation, we have demonstrated the synthesis of nanostructured spinel Zn$_2$TiO$_4$ and Metal doped [Ag (I) and Co (II)] Zn$_2$TiO$_4$ by combustion method for the first time.

### 2.2 Experimental

#### 2.2.1 Optimization of synthesis method

Combustion method has been optimized with respect to precursor, fuel and temperature for the synthesis of the zinc orthotitanates.
2.2.1.1 Combustion method using potassium titanyl oxalate and zinc acetate

**A) Synthesis of the Intermediate by co precipitation method**

Intermediate has been prepared from potassium titanyl oxalate and zinc acetate by coprecipitation method. In this method, aqueous solutions of potassium titanyl oxalate and zinc acetate with desired stoichiometric amount (1:2 mole ratio) are prepared. The 3% H$_2$O$_2$ was added drop wise into the solution of potassium titanyl oxalate resulting intense orange colour to the solution. Zinc acetate solution has been added drop wise to this solution which produced yellow precipitate. The reaction mixture becomes colorless after the complete addition of zinc acetate solution. The reaction mixture was stirred overnight. The intermediate formed is filtered and washed with hot water and dried.

**B) Combustion of the intermediate**

The as synthesized intermediate was mixed with glycene, urea and starch in methanol kept overnight to form the uniform paste. Combustion was performed in the tublar furnace. Decomposition of intermediate was carried out at 650, 700 and 800 °C for 3 h. The obtained products were characterized by XRD to find out the phases.

2.2.1.2 Synthesis of zinc orthotitanates by using zinc acetate and Titanium tetraisopropoxide (TTISP)

Zinc acetate, titanium tetraisopropoxide (TTISP), citric acid, ammonium nitrate were taken in 1:0.5:5:5 mole proportions along with 2.5 g starch. The homogeneous paste was prepared in isopropanol and methanol. Paste was kept overnight to obtain uniform mixture. Paste was dropped stepwise into preheated tubular furnace at 650 °C and 750 °C and heating continued for 3 h after completion of dropping. The product obtained is further characterized by XRD to confirm the formation of Zn$_2$TiO$_4$ phase.

2.2.1.3 Synthesis of zinc orthotitanates by optimized method

From XRD of the product obtained at 650 °C, formation of Zn$_2$TiO$_4$ was confirmed. Therefore undoped and doped Zn$_2$TiO$_4$ were synthesized by method described in section 2.2.1.2 at 650 °C by heating for 3 h
For synthesis of Ag and Co doped zinc orthotitanates, AgNO$_3$ and Cobalt acetate were taken in stoichiometric proportion for synthesis of Zn$_{1.9}$Ag$_{0.2}$TiO$_4$ and Zn$_{1.9}$ Co$_{0.1}$TiO$_4$ respectively. The zinc orthotitanates synthesized are further characterized using sophisticated techniques.

### 2.2.2 Characterization

The UV-vis absorption spectra of the as synthesized compounds were recorded on Perkin Elmer UV-Vis spectrophotometer in 300-900 nm range using pure BaSO$_4$ as reference. Photo Luminance spectra were recorded on PL-Shimadzu (RF-5301 PC) at room temperature in aqueous dispersion state at excitation wavelength 300 nm. XRD patterns of the as synthesized compounds were recorded in ambient air at room temperature on D-8 Advanced X-ray diffractometer using K$_\alpha$ radiation ($\lambda = 0.15418$ nm) at the scan rate of 0.1$^\circ$/min in the 20 range 20-80$^\circ$. FTIR spectra were recorded on Perkin Elmer IR spectrophotometer in the range 350-4000 cm$^{-1}$. Field Emission Scanning Electron Microscopy (FESEM) images were obtained on HITACHI 4800 instrument. The powder sample was dispersed in methanol and ultrasonicated for 10 min and loaded on Al foil. Transmission Electron Microscopy (TEM) micrographs were obtained by using instrument Philips CM-200 at 80 KV. Copper grid coated with holey carbon support films was used to prepare samples for TEM. The powder sample was dispersed in ethanol and ultrasonicated for 10 min before loading on Cu-grid. Surface area of the synthesized compounds was measured from Nitrogen adsorption-desorption isotherm at 77 K. The Brunaur Emmett Tellor (BET) method (Make/model Micromeritics, ASAP 2010) was used for surface area determination. Pore diameter and pore volume was determined by Barrete-Joyner-Halenda (BJH) method. Elemental analyses of the compounds were performed by EDXRF (ARL QUANT’X, Thermofischer) analyses.

### 2.3 Results and Discussion

#### 2.3.1 Optimization of synthesis method

Combustion method has been attempted for the synthesis of the zinc orthotitanates for the first time. Prior to combustion method described in the section 2.2.1.2 for the synthesis of the zinc orthotitanates, various trials have been attempted for the synthesis of zinc orthotitanates.
2.3.1.1 Combustion method using potassium titanyl oxalate and zinc acetate

The thermogravimetry (TG) analysis of the intermediate was performed to know the stages and the temperature of the decomposition at which oxide formation takes place. According to TG analysis, intermediate completely decomposes at 400 °C (Figure 2.1).

![Figure 2.1: TG-DTA of the intermediate prepared by coprecipitation method](image)

Combustion of the intermediate was performed in the tubular furnace at 650, 700 and 800 °C for 3h. The phases formed were determined from the XRD of the product obtained at respective temperature. Figure 2.2 shows the XRD of the compounds formed at 650, 700 and 800 °C by combustion method. Decomposition leads to the formation of composite of ZnO and TiO₂ at 650 °C. Zn₂TiO₄ phase formation begins at 700 °C. The zinc orthotitanate (Zn₂TiO₄) has been formed with trace amount of ZnO (Figure 2.2).
Figure 2.2: XRD pattern of compounds formed at a) 650 °C  b) 700 °C and  c) 800 °C

Hence, it is confirmed that formation of Zn$_2$TiO$_4$ could be possible above 800 °C. Below this temperature, mixed phases of Zn$_2$TiO$_4$ and ZnO may be observed. So, combustion method by using above mentioned precursors and fuel could not synthesize Zn$_2$TiO$_4$ at lower temperature, which was one of the objectives of the research work.

2.3.1.2 Synthesis by using zinc acetate and Titanium tetraisopropoxide (TTISP)

In this attempt paste of the precursors is prepared with the fuels and oxidizer and combustion was performed at 650 and 750 °C for 3h. XRD of the product obtained is depicted in the figure 2.3
Figure 2.3: XRD pattern of the product obtained at a) 650 and b) 750 °C.

From the XRD pattern of the compound obtained at 650 and 750 °C, it reveals that Zn$_2$TiO$_4$ phase has been formed along with ZnO and there is no much reduction in extent of ZnO at 750 °C. So, combustion reaction at 650 °C has been preferred over 750 °C. Hence, undoped and doped zinc orthotitanates were synthesized by combustion method at 650 °C by heating for 3h. Precursors taken for the silver and cobalt doping were silver nitrate and cobalt acetate, respectively. The as synthesized zinc orthotitanates were characterized and employed for waste degradation.

2.3.2 Characterization of the undoped and doped zinc orthotitanates

Zn$_2$TiO$_4$ has been synthesized by combustion method using titanium tetraisopropoxide (TTISP) and zinc acetate precursors and citric acid and starch as fuel and ammonium nitrate as an oxidizer. We have used complex fuel system because it favours formation of nanosized particles. When ammonium nitrate decomposes, it releases oxygen which can be used by fuel i.e. citric acid and starch. Citric acid forms complex with Zinc(II) and Ti(IV) which facilitates homogeneous mixture in the gel as well as they are the source of C and H which produce CO$_2$ and H$_2$O accompanied by liberation of heat. Hence due to high exothermicity the phase formation is obtained.
at low temperature as compared to solid state reaction (>1000 °C).\textsuperscript{30,31,32,33} Mixture of ZnO and TiO$_2$ has been formed when the combustion was performed at 550-600 °C. After several trials, we found desired phase formation at 650 °C. It is quite understood that due to liberation of huge amount of gases during thermal shock at 650 °C, the nanocrystalline product is formed.\textsuperscript{34}

In combustion technique employed, the chelating agents like citric acid forms complex with the metal cations which upon thermal decomposition forms carbonaceous matrix. Carbonaceous matrix formed act as substrate for homogeneous distribution of metal oxide phase. Extensive distribution of mesoporous carbonaceous matrix which provides large number of well separated nucleation sites for oxide to form. This helps in obtaining particles with lower size distribution. Following chemical reaction is taking place during the combustion at 650 °C.\textsuperscript{35}

\[
2\text{Zn(CH}_3\text{COOH)}_2\cdot2\text{H}_2\text{O} + \text{Ti(CH}_3\text{CH}_2\text{COO)}_4 + 10\text{NH}_4\text{NO}_3 + 10\text{C}_6\text{H}_8\text{O}_7 + \text{x(C}_6\text{H}_{10}\text{O}_5)\text{n} + (59+6\text{n}x)\text{O}_2 \rightarrow \text{Zn}_2\text{TiO}_4 + [80+6\text{n}x]\text{CO}_2 + [82+5\text{n}x]\text{H}_2\text{O} + 10\text{N}_2
\]

Where ‘n’ is number of monomers in starch and ‘x’ is number of moles corresponding to amount of starch taken.

The zinc orthotitanates obtained at 650 °C were used for further characterization.

2.3.2.1 Structural study

XRD analyses

Figure 2.4 represents XRD pattern of the compound synthesized, which contains peaks due to Zn$_2$TiO$_4$ and ZnO. The XRD pattern shows the existence of spinel structure of Zn$_2$TiO$_4$. Peaks due to Zn$_2$TiO$_4$ are in good agreement with tetragonal phase (a= 6.006 °A, b=8.415 °A)\textsuperscript{27} as well as cubic phase of Zn$_2$TiO$_4$ (a=8.469 °A)\textsuperscript{36}. The presence of two phases has been discussed thoroughly by Robert Millard et al.\textsuperscript{31} According to their findings, tetragonal phase Zn$_2$TiO$_4$ along with cubic phase exists in the temperature range 490-555 °C and extent of cubic phase increases with increase in temperature. Hence, cubic phase can be formed at higher temperature and mixed phases at lower temperature which is quite justifiable in our case. However, it is quite difficult to obtain single phase in case of zinc orthotitanate at lower temperature.\textsuperscript{37} The further evidences have been discussed in optical properties.
Comparative XRD of Zn$_2$TiO$_4$ and Ag@Zn$_2$TiO$_4$ is shown in the figure 2.5. XRD pattern of Ag@Zn$_2$TiO$_4$ depicts additional peaks due to Ag (cubic, a=4.086 Å) element along with the peaks of Zn$_2$TiO$_4$ and ZnO (hexagonal, a=3.253 Å, c=5.213 Å) indicate formation of composite of Ag-ZnO-Zn$_2$TiO$_4$. It means, AgO is not formed during the combustion, instead of this elemental Ag has been formed by reduction of Ag$^+$ during combustion. This may be because of citric acid used during combustion which generally creates reductive atmosphere. It is quite well known that, silver oxide decompose to silver at high temperature. XRD peaks shows very marginal shift at 20 max indicates doping silver in Zn$_2$TiO$_4$. Hence, the XRD pattern shows the existence of spinel structure of Zn$_2$TiO$_4$ even in Ag@Zn$_2$TiO$_4$. The isolated sharp Ag peaks in XRD indicates presence of Ag on surface of the Zn$_2$TiO$_4$.

![Figure 2.4: XRD pattern of zinc orthotitanate (Zn$_2$TiO$_4$)](image-url)
Figure 2.5: Comparative XRD pattern of a) Zn$_2$TiO$_4$ and b) Ag@Zn$_2$TiO$_4$

Figure 2.6: Comparative XRD pattern of a) Zn$_2$TiO$_4$ and b) Co@Zn$_2$TiO$_4$
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Figure 2.6 depicts the XRD pattern of Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$. XRD of Co@Zn$_2$TiO$_4$ (Figure 2.6b) indicates no additional peaks due cobalt oxide. It means that Co$^{2+}$ ions have replaced Zn$^{2+}$ ion in the Zn$_2$TiO$_4$ lattice and no shifting in 20 of any peaks is observed due to equivalent ionic size of Zn$^{2+}$ (74 pm) and Co$^{2+}$ (74.5 pm) ions. Thus, as synthesized Co@Zn$_2$TiO$_4$ will have molecular formula Zn$_{1.9}$Co$_{0.1}$TiO$_4$. The XRD pattern shows the existence of spinel structure of Zn$_2$TiO$_4$ in case of Co@Zn$_2$TiO$_4$. Soraia C Souza et. al. synthesized Co doped Zn$_2$TiO$_4$ by polymeric precursor method and reported that single phase Zn$_{2-x}$Co$_x$TiO$_4$ can be formed up to x=0.4. Hee Kwon Jun et al. observed that Co replaces one of the zinc metals in Zn$_2$TiO$_4$ followed by ZnCoTiO$_4$ formation.

General phenomena of the metals are that Metal ions having same oxidation number and nearly the same ionic radius do not affect on XRD pattern. Hence, it is impossible to distinguish between the spinel structure of Zn$_2$TiO$_4$ and ZnCoTiO$_4$ by XRD analysis. The average crystallite size of Zn$_2$TiO$_4$ has been observed to be 13 nm while, average crystallite size of Zn$_2$TiO$_4$ in Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ is 19 and 18 nm respectively. The crystallite size of Ag in Ag@Zn$_2$TiO$_4$ is 21 nm. It was observed that doping leads to an increase in short-range disorder and an increase in crystallite size.

FTIR analysis

Figure 2.7: FTIR spectra of Zn$_2$TiO$_4$, Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ A) in the range 4000-350 cm$^{-1}$ B) magnified in the range 1000-350 cm$^{-1}$

Figure 2.7 shows FTIR spectra of the zinc orthotitanates in the region 4000-350 cm$^{-1}$ and 1000-350 cm$^{-1}$. Bands in the spectral region 1200-4000 cm$^{-1}$ are due to vibration
frequencies of organic residue and water adsorbed. FTIR spectra of Zn₂TiO₄, Ag@Zn₂TiO₄ and Co@Zn₂TiO₄ indicates that bands appeared at ~ 3470 and ~ 1630 cm⁻¹ are due to weak physical adsorption of water molecules being originated due to stretching and bending vibrations. In this case, existence of the hydroxyl groups are detected even at higher temperature. T. Ivavova et al. also observed presence of hydroxyl group at high temperature in case of thin film of Zn₂TiO₄ system at 600 °C.² Bands in the range 1200-4000 cm⁻¹ show trace of carbon content even at 650 °C. For complete removal of carbon content, sintering at 1000 °C is required. However, at 1000 °C particle size will increase leading to formation of macro particles.⁴⁵ Trace amount of carbon content has not reflected in XRD of Zn₂TiO₄ and M@Zn₂TiO₄. Broad band at ~ 710 and weak band at ~ 586 cm⁻¹ are due to stretching vibration in TiO₆ group present in the Zn₂TiO₄.² These peaks are clearly seen in the FTIR spectra in the range 1000-350 cm⁻¹ as shown in the figure 2.7b. Band around 420 may be due to ZnO₈ polyhedron which appears in all zinc titanates.⁴⁶ Presence of absorption bands 575 (b), 475(w), 420(w) and 400 (w) indicates tetragonal phase of Zn₂TiO₄.⁴⁷ Bands due to M-O (M= Ag and Co(II) ) are not observed may be because of very less % of metal dopant in Zn₂TiO₄. Bands due to anatase and amorphous TiO₂ are also not observed in IR spectra of all synthesized compounds. It is very difficult to confirm the absence of TiO₂ and ZnO on the basis of IR frequencies appeared in the range 1000-350 cm⁻¹ because, bands due to Zn₂TiO₄, ZnTiO₃, ZnO and TiO₂ appears in the same region with minor variation.

**EDXRF Analyses**

The elemental analyses of the synthesized compounds has been performed by Energy Dispersive X ray Fluorescence (EDXRF) analyses technique. The data given in table 2.1 shows that % Zn and Ti observed in all synthesized samples is in good agreement with expected values.
Table 2.1: EDXRF data for elemental analyses of zinc orthotitanates

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound</th>
<th>Elements (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn (Ti)</td>
<td>M (Co/Ag)</td>
<td></td>
</tr>
<tr>
<td>01</td>
<td>Zn₂TiO₄</td>
<td>73.2 (73.2)</td>
<td>26.8 (26.8)</td>
</tr>
<tr>
<td>02</td>
<td>Zn₁.₉Co₀.₁TiO₄</td>
<td>71.4 (69.8)</td>
<td>25.4(26.9)</td>
</tr>
<tr>
<td>03</td>
<td>Zn₁.₉Ag₀.₂TiO₄</td>
<td>64.3 (64.1)</td>
<td>24.9(24.7)</td>
</tr>
</tbody>
</table>

Figures in the parenthesis indicates expected % of the elements

2.3.2.2 Morphological study

Morphological study was performed by FESEM and TEM analyses

FESEM study

FESEM images of Zn₂TiO₄ given in the figure 2.8 shows formation of web like morphology consisting of pot holes. Spherical nanoparticles of the size around 50 nm are self-aligned to form web like morphology. The web like morphology with pot holes may be formed due to evolution of gases during synthesis of Zn₂TiO₄ by combustion method. The evolution of gases favours formation of web like morphology.²¹

Figure 2.8: FESEM images of Zn₂TiO₄ magnified at a) 10 K  b) 100 K magnification.
In case of Ag@Zn$_2$TiO$_4$ (Figure 2.9) stacking of layers has been observed with larger pot holes. Increase in crystallite size due to doping and stacking of layers indicates lower surface area with respect to Zn$_2$TiO$_4$.

![FESEM micrographs of Ag@Zn$_2$TiO$_4$ at a) 10 K b) 100 K magnification.](image)

**Figure 2.9:** FESEM micrographs of Ag@Zn$_2$TiO$_4$ at a) 10 K b) 100 K magnification.

Figure 2.10 shows formation of large and thick clusters due to agglomeration of nanoparticles in the case of Co@Zn$_2$TiO$_4$. Very few pot holes are observed on the cluster (Figure 2.10a) as compared to that of in Zn$_2$TiO$_4$ and Ag@Zn$_2$TiO$_4$. Agglomerated spherical particle of the size around 50 nm are clearly seen in figure 2.10a and 2.10b. Crystallite size also found to be increased with respect to Zn$_2$TiO$_4$ but equivalent to Ag@Zn$_2$TiO$_4$.

![FESEM micrographs of Co@Zn$_2$TiO$_4$ at a) 10 K and b) 100 K magnification](image)

**Figure 2.10:** FESEM micrographs of Co@Zn$_2$TiO$_4$ at a) 10 K and b) 100 K magnification.
Overall impression, lower surface area may be due to agglomeration of nanoparticles in the form of cluster. In conclusion it seems that doping of Ag and Co disturbs the morphology of doped Zn$_2$TiO$_4$ as well as lowers the surface area when synthesized by combustion method.$^{44, 48, 49}$

**TEM analysis**

![TEM images of Zn$_2$TiO$_4$](image)

**Figure 2.11:** TEM images of Zn$_2$TiO$_4$  
(a) 100 nm scale and Inset ED pattern  
(b) 50 nm scale  
(c) 10 nm scale  
(d) magnified portion of figure 2.11c showing lattice fringes with d$_{211}$=0.250 nm

TEM images of Zn$_2$TiO$_4$ are shown in figure 2.11. Diffused particles of irregular shape in the range of 10 nm size are observed in figure 2.11b. Very fine particles diffused in such a way that their shape and size cannot be identified. Lattice fringes observed in figure 2.11c are clearly seen in magnified image shown in figure 2.11d which shows lattice fringes corresponding to 211 plane (d$_{211}$=0.250 nm). Uniform and continuous ring pattern observed in ED pattern (inset of figure 2.11b) is
due to randomly oriented nanocrystals. The d spacing determined from ED pattern are in good agreement with XRD results.

Figure 2.12: TEM images of Ag-Zn$_2$TiO$_4$ a) 100 nm scale b) 50 nm scale and inset ED pattern

TEM images of Ag@Zn$_2$TiO$_4$ shown in the figure 2.12 indicate formation of nanoparticles in the range 30-50 nm. Small particles having size in the range 5-10 nm are found to be embedded into the large particles as seen the figure 2.12a and 2.12b. These may be the silver nanoparticles as detected by XRD. ED pattern shows ring pattern consisting of very fine spots indicating polycrystalline nature and random alignment of nanocrystals. From d spacing calculated from rings observed in ED pattern (inset of figure 2.12b) reveals the appearance of rings corresponding to 002 plane of ZnO and 100, 220, 200 planes of Ag along with planes of Zn$_2$TiO$_4$. These observations are in agreement with XRD pattern of Ag@Zn$_2$TiO$_4$.
Figure 2.13: TEM images of Co@Zn$_2$TiO$_4$ at a ) 1 µm b ) 100 nm c ) 50 nm scale and d) ED pattern

TEM image of Co@Zn$_2$TiO$_4$ shows alignment of nanoparticles of the size ~ 25 nm to form 2-D sheet as shown in figure 2.13a and 2.13b. High magnification image shows (figure 2.13c) nanoparticles of uneven shape and size in the range 25-50 nm with pattern. The ED pattern (figure 2.13d) shows bright spotty ring pattern indicating polycrystalline nature of the sample. The d spacing calculated from ED pattern and XRD pattern are in agreement with each other. ED pattern doesn’t show rings due to any form of cobalt oxide which supports interpretation led by XRD pattern of Co@Zn$_2$TiO$_4$. It reveals from the ED pattern that, more spotty ring pattern has been observed for Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ as compared to that of Zn$_2$TiO$_4$ indicating increasing polycrystalline nature as well as size of the crystal. The increase in polycrystalline nature is may be due to doping.
2.3.2.3 Surface study

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 2.14a, 2.14b and 2.14c). H3 type of hysteresis loop is associated with mesopores present on the surface.\(^\text{50}\) The pore size distribution obtained from the isotherm shows broad pore size distribution for Zn\(_2\)TiO\(_4\), Ag@Zn\(_2\)TiO\(_4\) and Co@Zn\(_2\)TiO\(_4\), respectively.

![Figure 2.14](image)

**Figure 2.14 : BET adsorption isotherms and pore size distribution shown inset for a) Zn\(_2\)TiO\(_4\), b) Ag@Zn\(_2\)TiO\(_4\) and c) 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 increase in pore volume and lower crystallite size of Zn\(_2\)TiO\(_4\) may be responsible for high surface area. The FESEM images and TEM images indicate that depth of the pores is more in case of Zn\(_2\)TiO\(_4\) as compared to Ag and Co doped Zn\(_2\)TiO\(_4\). 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.\textsuperscript{51,52} Hence, BET surface area and BET 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 size of pristine and doped zinc orthotitanates. Stacking of layers in case of Ag@Zn\textsubscript{2}TiO\textsubscript{4} and compact cluster formation in case of Co@Zn\textsubscript{2}TiO\textsubscript{4} as well as increase in crystallite size may also be the possible factors behind decrease in surface area. The phenomena of decrease in surface area upon doping have also been reported in previous studies.\textsuperscript{44}

Table 2.2: BET Surface area, pore volume and pore diameter of zinc orthotitanates

<table>
<thead>
<tr>
<th>Compound</th>
<th>BET (m\textsuperscript{2}/g)</th>
<th>Pore Volume cm\textsuperscript{3}/g (Pores &lt; 77.1 nm)</th>
<th>Pore diameter nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn\textsubscript{2}TiO\textsubscript{4}</td>
<td>12.24</td>
<td>0.040</td>
<td>13.1 (22.7)</td>
</tr>
<tr>
<td>Ag@Zn\textsubscript{2}TiO\textsubscript{4}</td>
<td>08.88</td>
<td>0.026</td>
<td>11.9 (30.8)</td>
</tr>
<tr>
<td>Co@Zn\textsubscript{2}TiO\textsubscript{4}</td>
<td>08.31</td>
<td>0.031</td>
<td>13.9 (29.5)</td>
</tr>
</tbody>
</table>

( ): BJH pore volume

2.3.2.4 Optical study

Optical characterization of the compounds synthesized were performed by UV-Vis DRS and Photoluminescence analyses

UV-Vis DRS analyses

Figure 2.15A represents the UV DRS spectra of Zn\textsubscript{2}TiO\textsubscript{4} and Ag-doped Zn\textsubscript{2}TiO\textsubscript{4} in absorbance mode and respective tauc plots (figure 2.15B). Band gap of the compounds has been determined from tauc plot and first derivative of Absorbance Vs energy plot.\textsuperscript{53,54} Absorption edge of Zn\textsubscript{2}TiO\textsubscript{4} is appeared to be at 385 nm and 335 nm with corresponding band gap 3.22 eV and 3.70 eV, respectively. Band gap observed for as synthesized Zn\textsubscript{2}TiO\textsubscript{4} is higher than reported in literature (3.11 eV) indicating nanocrystalline nature.\textsuperscript{30,55} In absorption spectra of Zn\textsubscript{2}TiO\textsubscript{4} two absorption edges are
observed which indicates presence of Zn$_2$TiO$_4$ in two phases. Band gap 3.22 eV is attributed to tetragonal phase while 3.7 eV to cubic phase. Many researchers synthesized Zn$_2$TiO$_4$ having tetragonal phase with Band gap 3.11 eV and cubic phase with band gap 3.7 eV. In absorption spectra of Ag@Zn$_2$TiO$_4$ cut off observed at 387 nm is due to Zn$_2$TiO$_4$ while cut off at 738 nm is due to nano Ag particles with corresponding band gap 3.20 and 1.68 eV respectively.

![Figure 2.15](image1.png)

**Figure 2.15** A) UV vis -DRS absorption plot of Zn$_2$TiO$_4$ and Ag-Zn$_2$TiO$_4$ B) tauc plot of Zn$_2$TiO$_4$ and Ag-Zn$_2$TiO$_4$.

![Figure 2.16](image2.png)

**Figure 2.16.** A) UV-DRS of Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ in absorbance mode and B) tauc plot.

Figure 2.16A represents UV DRS absorbance plot of Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ in absorption mode and Figure 2.16B represents corresponding tauc plots. Optical spectra clearly shows shifting of adsorption edge towards visible region at 2.67 eV due to Co
doping. In general absorption edge around 400 nm was ascribed to the band transition from O 2p to Zn 4s. In case of Co doped Zn$_2$TiO$_4$ new absorption edge has been observed at 2.67 eV. The absorption of Co doped Zn$_2$TiO$_4$ samples was based on transition from Co $e_g$ to Co 4s transition. In this case inter band may exist between the conduction band and valence band of Zn$_2$TiO$_4$.\(^{30}\)

**PL analysis**

The room temperature PL spectra of the Zn$_2$TiO$_4$ (Figure 2.17a) shows weak band at 330 nm, strong and sharp peak at 363 nm and broad and weak peak at 468 nm. The weak emission peak observed at 330 nm is because of band to band transition. This can be referred as near band edge emission which is closed to band gap observed at 335 nm in UV-Vis spectra.\(^{60}\)

![Figure 2.17: PL spectra of (a)Zn$_2$TiO$_4$, (b)Ag@Zn$_2$TiO$_4$ and (c) Co@Zn$_2$TiO$_4$.](image)

The emission peak observed at 468 nm indicates that defects exists in the crystalline ordered mesostructured Zn$_2$TiO$_4$.\(^{61,62}\) The existence of intrinsic defects such as O$^{2-}$ vacancies, Zn$^{+2}$ vacancies may be responsible for the emission.\(^{63}\) Ag composite and Co doping affects on the intensity of emission spectra observed on 468 nm peak and
no effect on peak at 363 nm. It is observed that relative intensity (RI) of peak at 468 nm (RI = 0.26) for Ag@Zn$_2$TiO$_4$ (Figure 2.17b) is lowest which shows complete diminishing of peak due to composite formation with Zn$_2$TiO$_4$. However, in case of Co@Zn$_2$TiO$_4$ (Figure 2.17c) it has been reduced to 0.46. Decrease in intensity of the peak at 468 nm due to doping indicates minimization of crystal defects as compare to undoped Zn$_2$TiO$_4$.64

2.4 Summary

The nanostructured zinc orthotitanate and doped (Ag and Co) zinc orthotitanates were synthesized using combustion method using multiple fuel system for the first time. The structural and optical analysis shows the existence of cubic and tetragonal phases. The appearance of ZnO phase has been observed in all the cases. Ag doping leads to existence of additional phase due to formation of Ag while substitutional doping of Co(II) at the site of Zn(II) ions and produces single phase Zn$_{0.9}$Co$_{0.1}$TiO$_4$. Doping of Ag and Co causes increase in crystallite size, decrease in surface area, increases in agglomeration and diffuses morphology. Morphological study by FESEM reveals the formation of web like structure along with pot holes by self assembly of spherical nano particles of ~ 50 mm size. Further, TEM investigations reveal diffused and uneven shaped nanoparticles in the range of 10-25 nm. BET surface area measurements show decrease in surface area due to doping. The as synthesized zinc orthotitanates shows two band gaps i.e. 3.2 (tetragonal phase) and 3.7 (cubic phase). The Ag@Zn$_2$TiO$_4$ shows band gap at 1.67 eV due to the nanosized Ag metal along with a band gap of zinc orthotitanate while, Co@Zn$_2$TiO$_4$ shows shifting of the band gap of Zinc orthotitanates towards the visible region (2.67 eV). These Zinc orthotitanates were used for photocatalytic dye degradation (Acid Orange -8 and Rhodamine –B) under natural sunlight between 11.00 am to 3.00 pm on clear sunny days as well as for Photocatalytic H$_2$S splitting to produce H$_2$ under visible light source.
Chapter 2

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