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# Synthesis of $Zn_2TiO_4$ and $ZnTiO_3$ nanocomposites by the CBD method

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$Zn_2TiO_4/ZnTiO_3$ nanopowders were synthesized via CBD method. $TiCl_4$, $ZnCl_2$ and NaOH were used as precursors. The effect of temperature was investigated on morphologies and compositions of final product. The calcinations of the samples were carried out at 630 ºC. The structures and morphologies of the products were studied by X-ray diffraction and scanning electron microscopy. The results show that the best temperature for fabrication of the compounds without ZnO is 25 ºC.

Key words: *$Zn_2TiO_4$; $ZnTiO_3$; nanopowder; composite; chemical bath deposition*

## 1. Introduction

Because of interesting optical and electrical properties of ZnO, this material has extensively been studied. Low cost of precursors, simplicity and high efficiency of its chemical synthesis encourage scientists to investigate on nano-ZnO. ZnO obtained under various conditions has different nanomorphologies, in turn affecting properties of this metal oxide. Also, $TiO_2$ is one of the most extensively studied oxides because of its remarkable optical and electrical properties.

Zinc titanates are promising candidates as dielectric materials [1–3]. It has been reported that three compounds exist in $ZnO–TiO_2$ system, including $Zn_2TiO_4$ (cubic), $ZnTiO_3$ (hexagonal), and $Zn_2Ti_3O_8$ (cubic) [4–6]. Among these compounds, ilmenite

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type hexagonal $ZnTiO_3$ has been reported to have superior electrical properties: the dielectric constant of 19, high quality factor $Q$ = 3000 (at 10 GHz), and the temperature coefficient of resonance frequency $\tau_f$ = –55 ppm/ºC, very similar to those of other ilmenite type titanates [3, 7, 8]. Li et al. [9] reported the formation of a new $ZnTiO_3$ (cubic) phase as a precipitate inside the $Zn_2TiO_4$ matrix having the same structure and lattice parameter with $Zn_2TiO_4$ phase. Zinc orthotitanate, $Zn_2TiO_4$, can be easily prepared via the conventional solid-state reaction of $2ZnO{\cdot}TiO_2$.

According to XRD patterns of CBD synthesis of ZnO, upon increasing temperature, the particle size and morphology of ZnO can be changed. As noticed in related papers, in dropwise CBD synthesis, if aqueous solutions of $ZnCl_2$ and NaOH were used as precursors, nano-ZnO flakes are observed at ambient temperature. On the other hand, in reaction between $TiCl_4$ and NaOH, amorphous $TiO_2$ particles are formed, which convert to rutile at about 600 ºC, according to DTA diagram. One of the main procedures for producing mixed oxides is to arrange conditions for diffusion of oxides into each other [10, 11]. Due to dependence of the diffusion coefficient of oxides on their structure, surface area, etc., the crystallography and physical properties of the obtained particles can be changed by changing their morphology and particle sizes.

Although rich literature exist on the synthesis of oxide nanocomposite powder, very little attention has been paid to the effect of synthesis conditions such as synthesis temperature on the morphology and particle size distribution of these nanocomposites. Furthermore, no previous studies have been conducted on the influence of synthesis temperature on the diffusion processing of oxide particles ( ZnO and $TiO_2$) into each other. It is interesting to know how the morphology and size distribution of the obtained particles change with the variation of temperature. Therefore, the purpose of this paper is to present results of such studies for chemical bath deposited $Zn_2TiO_4$ and $ZnTiO_3$ nanocomposites.

We obtained nanocomposites of crystalline ZnO with amorphous $TiO_2$ before calcination processing. After calcination, nanocrystalline $Zn_2TiO_4$ and $ZnTiO_3$ from $ZnO–TiO_2$ (1:1 mol %) were prepared.

## 2. Experimental

The starting materials, $TiCl_4$, and NaOH purchased from Merck and $ZnCl_2$ purchased from Fluka were used without further purification.

Scanning electron microscopy studies were preformed using an OXFORD Leo 440i microscope. The size measurements were carried out with an Able Image Analyzer v3.6. Powder X-ray diffraction studies were carried out using a Philips (PW3710) diffractometer with CuKα radiation source ($\lambda$ = 0.154178 nm). Quantitative analyses were performed by X-ray fluorescence (XRF) using an XRF- 8410 RH operated at 60 kV. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed in the powder samples with a thermal analyzer system model STA 1640.

Two separate aqueous solutions of $ZnCl_2$ (1 M, 100 ml) and NaOH (6 M, 100 ml) were prepared. Due to high chemical reactivity of $TiCl_4$ with water, it was used without being dissolved in water. After preparation of the solutions, a separate $ZnCl_2$ solution and $TiCl_4$ were added dropwise to the NaOH solution simultaneously. This procedure lasted 30 min at various temperatures, as shown in Table 1. Then the samples were kept for 2 h at the same operating conditions. The obtained precipitates were centrifuged and then washed with distilled water and absolute methanol for several times. Finally, the precipitates were dried at about 50–60 ºC for 24 h.

Table 1. Conditions of syntheses

| Sample | Temperature [ºC] | Stirring time [h] |
|---|---|---|
| I | 25 | 2.5 |
| II | 55 | 2.5 |
| III | 75 | 2.5 |

All synthesized powders were calcined at about 630 ºC for 4 h and then naturally cooled to room temperature. The structures and morphologies of the powders were investigated by XRD and SEM, respectively.

## 3. Results and discussion

### 3.1. Synthesis of crystalline ZnO/amorphous $TiO_2$ nanocomposite powder

XRD patterns of ZnO–$TiO_2$ nanocomposite powder without calcination treatment are shown in Fig. 1. ZnO peaks were identified while amorphous $TiO_2$ particles were detected by XRF. Percentages of components are given in Table 2.

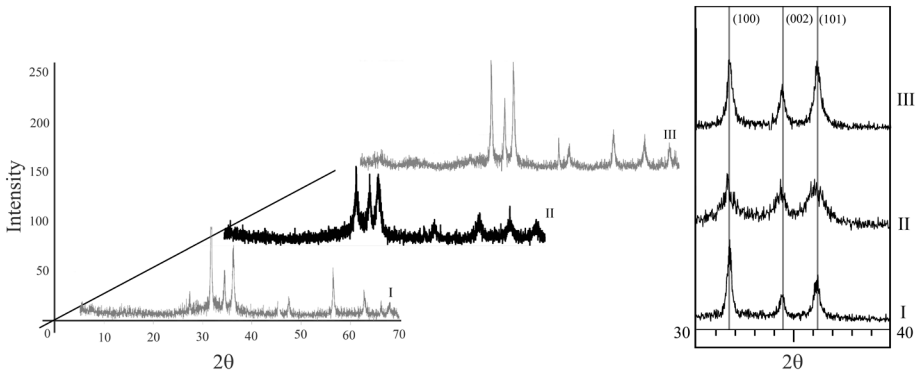


Fig. 1. XRD patterns of samples I (25 ºC), II (45–50 ºC) and III (70–75 ºC) without calcination

With the increasing reaction temperature, the intensity of ZnO XRD peaks increased. Also with increasing temperature, the sizes of obtained nanoparticles decreased and their morphologies tended to form semi-spherical particles which affected the XRD peaks of obtained nano-ZnO. This well agrees with reported observations of pure ZnO synthesis.

Table 2. XRF results of samples I, II and II

| Sample | Percentage of oxides [wt. %] | | | Percentage of elements [wt. %] | | | |
|---|---|---|---|---|---|---|---|
| | $TiO_2$ | ZnO | Na | Cl | Ti | Zn | Other |
| I | 39.7 | 42.2 | 18.1 | 14.1 | 30.2 | 48.6 | 5.3 |
| II | 39.9 | 42.4 | 17.7 | 12.6 | 31.7 | 48.3 | 6.9 |
| III | 34.8 | 44.8 | 20.4 | 10.2 | 31.3 | 51.2 | 6.2 |

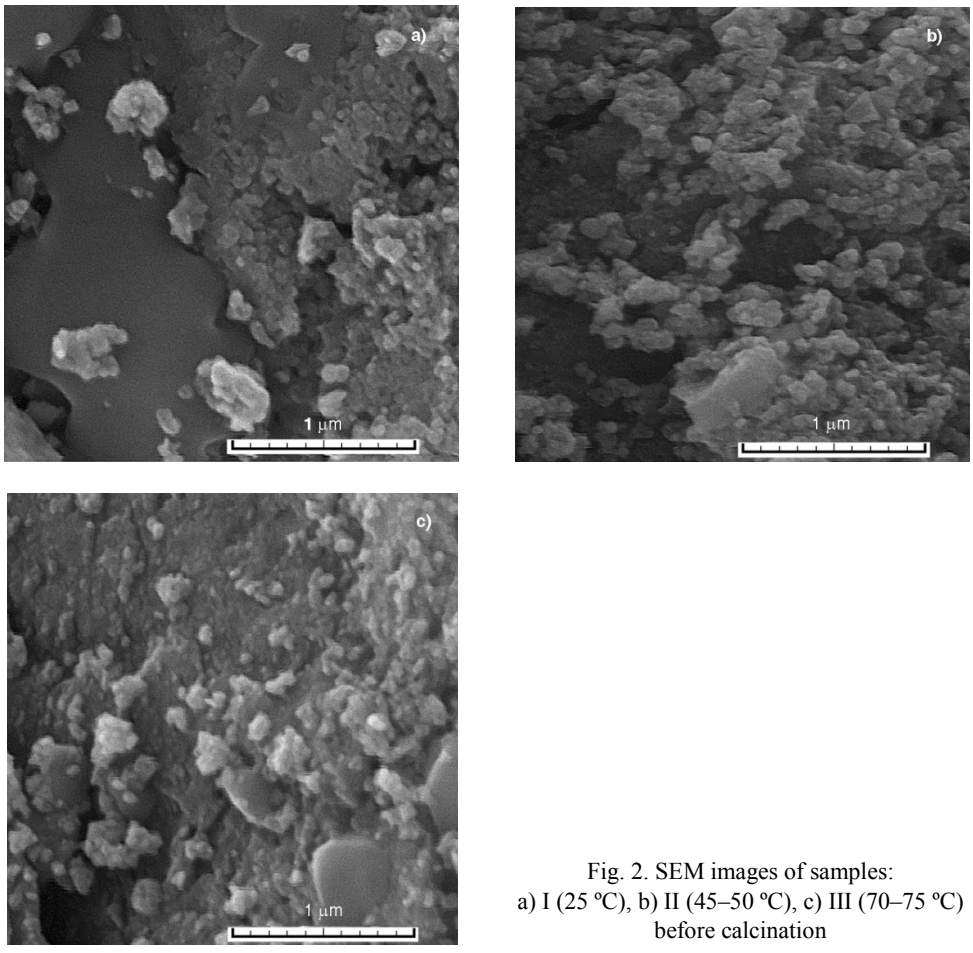


Fig. 2. SEM images of samples:
a) I (25 ºC), b) II (45–50 ºC), c) III (70–75 ºC)
before calcination

Figure 2 shows SEM images of the samples before calcination. EDAX analysis of sample I (Fig. 3) indicates that the uniform areas are $TiO_2$ flakes. These flakes become finer upon increasing temperature.

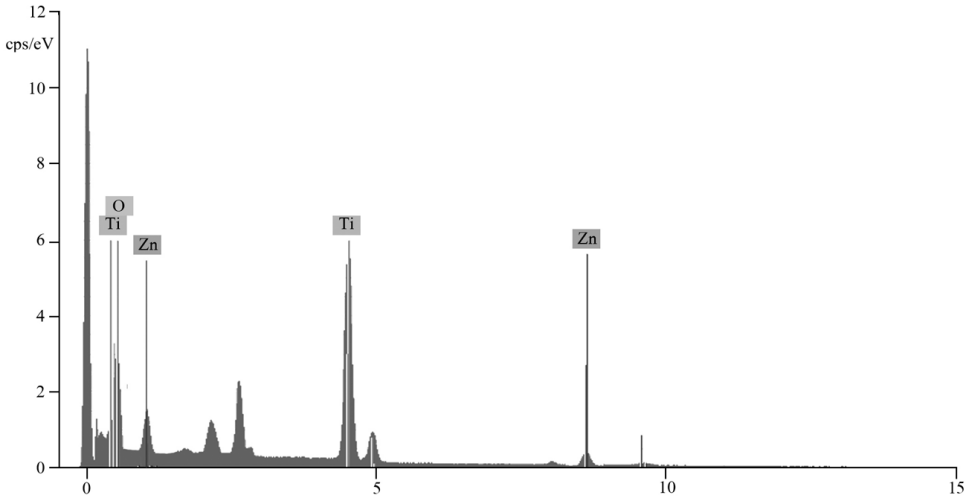


Fig. 3. EDAX result of flakes in sample I

Based on the DTA results of pure $TiO_2$ reported in literature [12, 13], the transformation from amorphous $TiO_2$ to crystalline $TiO_2$ is exothermic. Consequently, the temperature of 630 ºC is selected for crystallization of amorphous $TiO_2$. All three samples were calcined for 4 h at this temperature.

### 3.2. Formation of ZnO–$ZnTiO_3$–$Zn_2TiO_4$ nanocomposite powders

Figure 4 shows TGA/ DTA curves of the nanocomposite powders produced by the CBD method. As can be seen, there is an undulating shape in the TGA curves (Figs. 4a–c). The undulating shape of the TGA curves occurs at $T > 350$ ºC. Also, a broad exothermic peak is clearly visible in the DTA curves close to temperature initializing the undulating behaviour of TGA curves. The undulating shape of the TGA curves is due to the diffusion of ZnO and $TiO_2$. Because of the diffusion of ZnO and $TiO_2$ phases, the compounds such as $ZnTiO_3$ and $Zn_2TiO_4$ may be formed. A broad exothermic peak observed at 350 ºC $< T <$ 600 ºC in the DTA curves corresponds to atomic diffusion and therefore no considerable mass loss was detected in this region. No sharp exothermic peak was also observed at ~ 630 ºC in Figs. 4b, c. This peak corresponds to a phase transformation process of $TiO_2$ from amorphous to a crystalline state.

After calcination for 4 h at 630 ºC, XRD patterns indicate that ZnO coexists with $ZnTiO_3$, $Zn_2TiO_4$ and $Ti_3O_5$ (Fig. 5a). In the XRD pattern of sample I synthesized at 25 ºC, $ZnTiO_3$ and $Zn_2TiO_4$ phases can be detected, and the intensity of ZnO and $Ti_3O_5$ phases is negligible (Fig. 5a). It can be observed from these patterns that in-

creasing the synthesis temperature decreases the amount of $ZnTiO_3$ and $Zn_2TiO_4$ phases and increases that of ZnO and $Ti_3O_5$ phases.

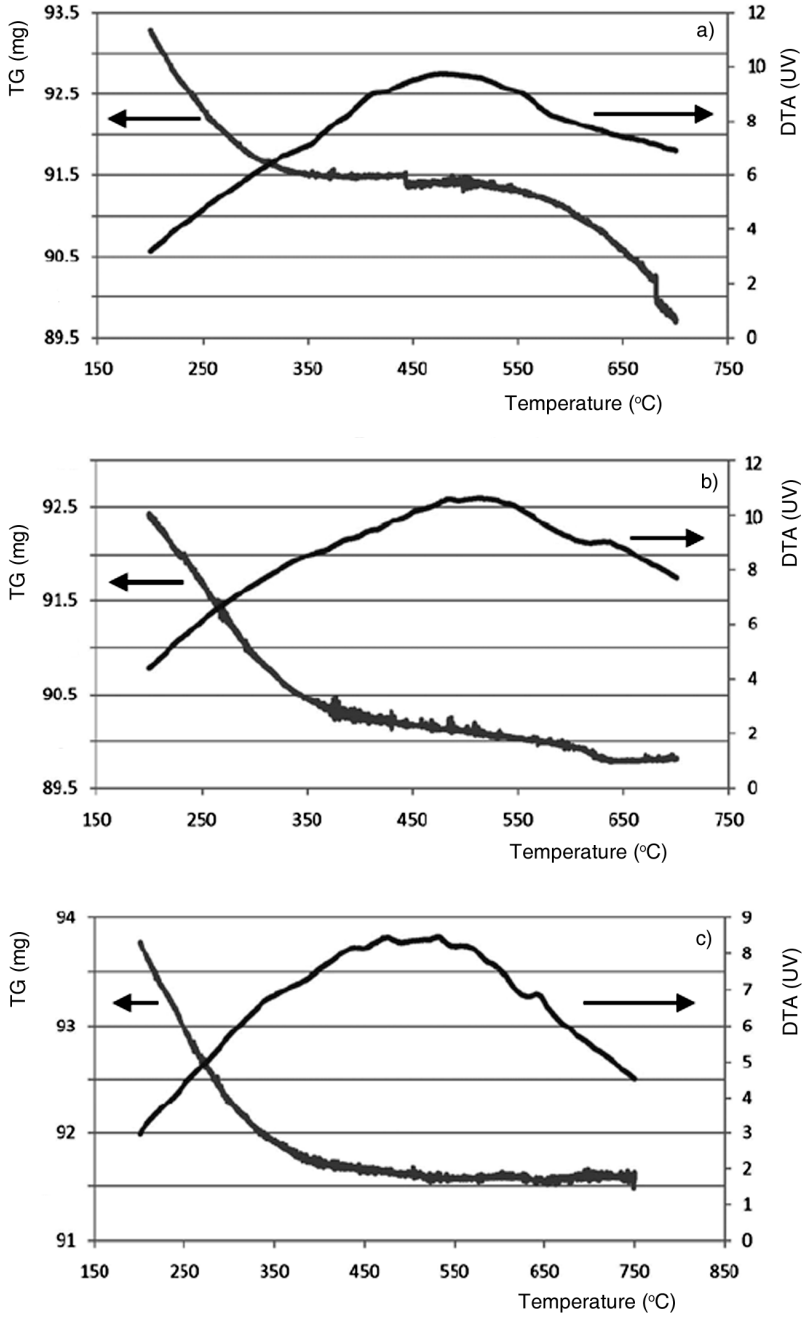


Fig. 4. TGA/DTA curves of the samples: a) I, b) II, c) III

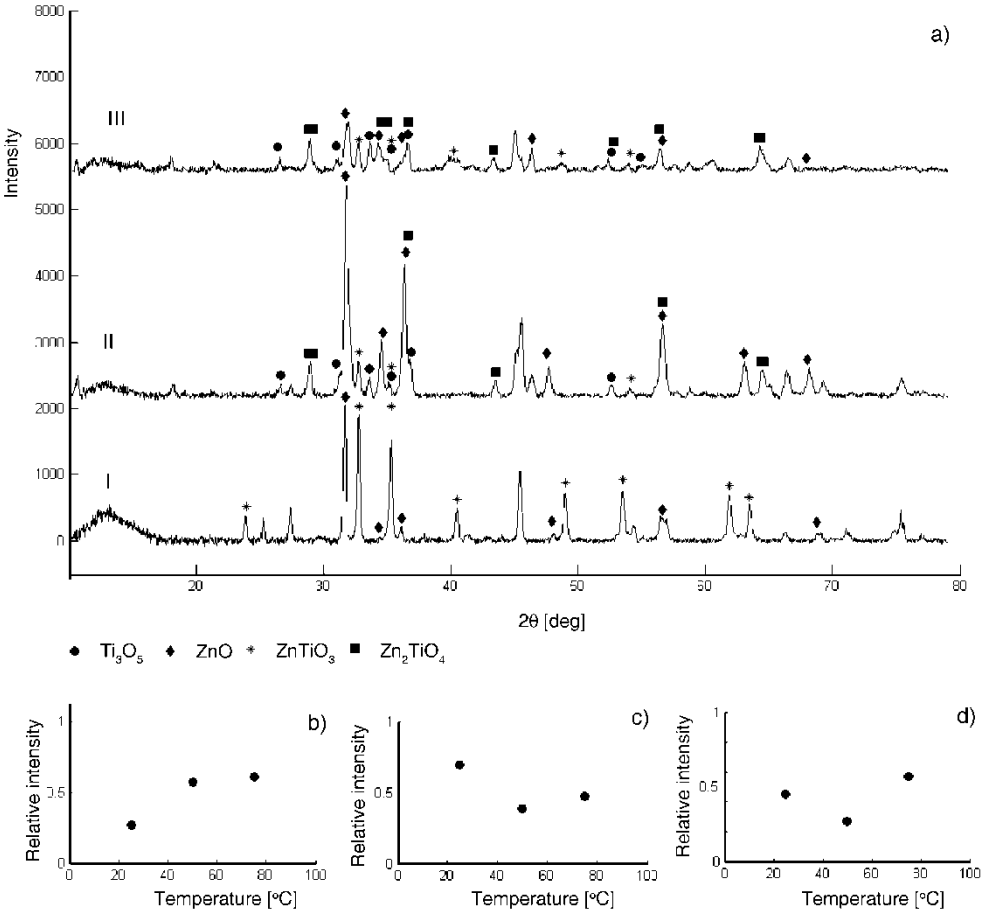


Fig. 5. XRD patterns of samples calcined at 630 ºC (a) and the relative intensity of (101) peak for ZnO (b), (104) peak for $ZnTiO_3$ (c), and (211) peak for $Zn_2TiO_4$ (d) vs. the synthesis temperature

Relative intensities of the peaks corresponding to (104) plane of $ZnTiO_3$ and (211) plane of $Zn_2TiO_4$ decreased with increasing synthesis temperature and that of the peak belonging to (101) plane of ZnO increased with increasing the synthesis temperature. Figures 5b–d show the dependence of relative intensities of ZnO ( $I_{(101)}/(I_{(100)} + I_{(002)} + I_{(101)} + I_{(110)} + I_{(103)} + I_{(102)})$), $ZnTiO_3$ ($I_{(104)}/(I_{(110)} + I_{(104)} + I_{(012)} + I_{(024)} + I_{(116)})$), and $Zn_2TiO_4$ ($I_{(211)}/(I_{(103)} + I_{(211)} + I_{(112)} + I_{(200)} + I_{(220)} + I_{(321)} + I_{(224)})$) with the synthesis temperature. As is shown in Fig. 5b, the relative intensity of ZnO decreased after synthesizing at 55 ºC (Fig. 5b), whereas those of $ZnTiO_3$ and $Zn_2TiO_4$ phases decrease with increasing the synthesis temperature up to 55 ºC and then gradually increase (Figs. 5c, d). It can be concluded that the optimum temperatures of synthesis in which ZnO and $ZnTiO_3/Zn_2TiO_4$ can be considerably formed are 55 ºC and 25 ºC, respectively. Also, it can be observed from Fig. 5 that the appropriate temperature of synthesis for producing the $ZnO/ZnTiO_3/Zn_2TiO_4$ nanocomposite powder is in the range

between 25 ºC and 55 ºC. It is believed that the most intensive peaks are caused by the minimization of internal stress and surface energy.

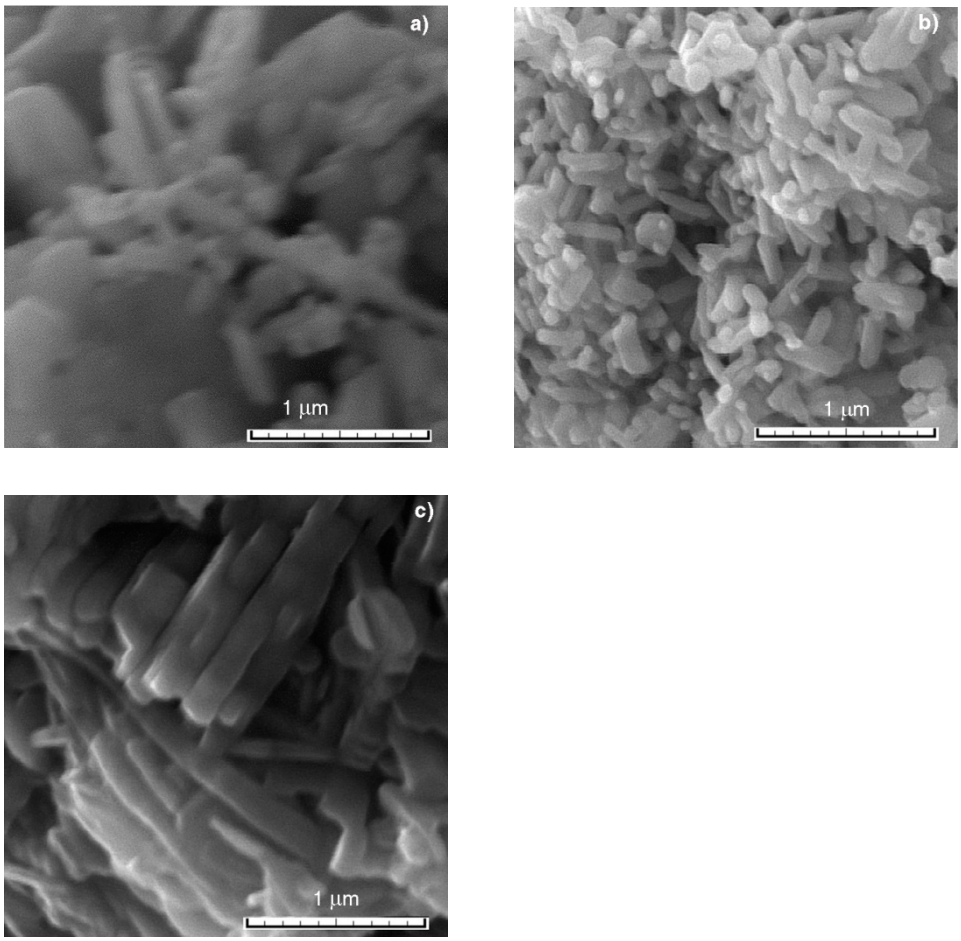


Fig. 6. SEM micrographs of samples: a) I, b) II, c) III

In Figure 6, the SEM images of samples I, II and III calcined at 630 ºC are shown. They have the same morphology and particle sizes.

## 4. Conclusion

Nanosized $ZnTiO_3/Zn_2TiO_4$ in CBD processing have been synthesized. The best temperature for fabrication of these compounds without ZnO is 25 ºC. Also, the appropriate temperature of synthesis $ZnO/ZnTiO_3/Zn_2TiO_4$ nanocomposite powders is in the range between 25 ºC and 55 ºC. From the thermal analysis, it can be concluded

that the diffusion process is the main factor playing a key role in synthesizing $ZnTiO_3$ / $Zn_2TiO_4$ nanocomposite powders.

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