Study on Heating Profile of Liquid-mixing-synthesized ZnTiO₃

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Abstract. The synthesis of monophasic ZnTiO₃ powder has been reported as one of the challenges in material chemistry because under normal condition and as prepared by various synthesis methods, ZnTiO₃ phase readily decomposes to Zn₂TiO₄ and TiO₂ rutile phases. This is due to the temperature range of ZnTiO₃ phase formation was very narrow, i.e. 600 - 800 °C; above that temperature, the decomposition of ZnTiO₃ phase took place. This paper is intended to introduce a facile route, named liquid mixing method, to prepare ZnTiO₃ powder from Zn and Ti metal powders as the raw materials and HCl as the solvent. Via this route, ZnTiO₃ phase was formed at a temperature as low as 550 °C with particle size distributed homogeneously. The heating profile of ZnTiO₃ phase from 440 to 900 °C was studied based on TG/DTA, XRD and FTIR data. However, when a 'normal' stoichiometric ratio of Zn: Ti = 1: 1 was applied, TiO₂ rutile phase becomes dominant, while ZnTiO₃ phase is only a secondary phase. This affects to the crystallinity of the ZnTiO₃ phase. An effort to overcome the dominance of TiO₂ phase was also demonstrated in this paper.

1. Introduction
The synthesis of ZnO-TiO₂ nano composite usually results in the formation of poliphase compounds, ZnTiO₃ (hexagonal), Zn₂TiO₄ (cubic) and Zn₂TiO₈ (cubic) along with other secondary impurity phases, such as TiO₂ rutile. It has been reported that obtaining a single phase of either ZnTiO₃ is one of the challenges in material fabrication [1-4]. Various synthesis methods have been reported to produce ZnTiO₃, including the conventional solid-state reaction [3], sol-gel processes [2,4], a modified alcohohysis method [1]. However, pure hexagonal ilmenite type ZnTiO₃ was not obtained by those methods, due to the reason described above. The product of ZnTiO₃ has been useful, such as for catalytic sorbents for the desulfuration of hot coal gases, for ethanol, NO and CO gas sensor materials, for microwave resonator materials, and more preferably for low temperature co-fired ceramic [2].

A relatively new approach in fabricating ceramic powders, named liquid mixing method, has been successfully synthesise nearly single phase of MgTiO₃-based ceramic powder at low temperature [5-7] and the fabricated MgTiO₃-based ceramics exhibited excellent dielectric characteristics [6,8-9]. The liquid mixing method is to dissolve metal powders, as raw materials, separately in strong acid solvents until consistent aqueous solutions are obtained, mixing all the solutions homogeneously and drying the slurry. The dried powder is calcined to obtain the desired crystalline phase. Metal powder that has a high solubility level in strong acid solvents is very beneficial when combined with this simple synthesis method to accelerate the intimate mixing process between the metallic ions. By this way, the expected crystalline phase can be formed at low calcination temperatures and nano-sized powders was obtained.
However, when multiple raw materials is required, the stoichiometry of the materials tends to be relatively complicated. Occasionally this could interfere the intimate reactions; as a result, impurity phase might also be detected.

In this paper, the liquid mixing method was adopted to synthesise ZnTiO$_3$ powders due to simplicity of the process and the nature of crystalline phase formation at low temperature. The aims was to study the heating profile of ZnTiO$_3$ phase from 440 to 900 °C, to investigate the crystallinity and distribution of particle size in the samples. This paper also presents an effort to overcome the dominance of TiO$_2$ phase during preparation of ZnTiO$_3$ phase.

2. Experiment
ZnTiO$_3$ powder was prepared following the liquid mixing route given in Reff. [5,6]. Zn and Ti metal powders (Merck) were used as the starting materials and HCl 12 M as the solvent. The metal powders were weighed stoichiometrically (Zn: Ti = 1: 1) and dissolved individually in HCl using a stirring hotplate. The resulting ZnCl$_2$ and TiCl$_4$ liquid solutions were mixed homogeneously and the mixed liquid solution was heated at 110 °C to obtain dried powder. The powder was crushed manually for uniform particle size.

Thermogravimetric/differential thermal analysis (TG/DTA) was carried out to the powder from room temperature to 600 °C at the heating rate of 10 °C/min using a DTG-60 and DSC-60 plus Shimadzu to obtain information on any changes to physical and chemical parameters that occur due to heating and which can be measured as a function of temperature with constant heating rate. The powder was calcined at different temperatures as suggested by the TG/DTA curves using a Nabertherm furnace to study phases evolution during heating. Phase identification was monitored from the XRD spectra measured from 2$\theta$ = 20 – 65° using an X’Pert Diffractometer (Philips) with CuK$_\alpha$ radiation at the rate of 0.02 °/min. The crystallinity (%) was analysed from the XRD spectra according to the ratio between the intensity of the ZnTiO$_3$ peaks and that of all peaks, or from the ratio between the area of the ZnTiO$_3$ peaks and that of all peaks. FTIR measurement was performed using a Thermo-Scientific FTIR spectrometer from 4000 to 400 cm$^{-1}$. The distribution of particle size and the average value were examined using a particle size analyzer (PSA) Zetasizer Nano Series Software Version 7.0 (Malvern Instrument).

3. Results and Discussion

3.1 Heating profile
Figure 1 shows the TG/DTA curves of the dried ZnTiO$_3$ powder measured from room temperature (RT) to 600 °C at the rate of 10 °C/min. As shown, after the powder was heated constantly to 600 °C at the rate of 10 °C/min, the TG curve in Figure 1 recorded three different mass losses, i.e. A from RT to 243 °C, B from 243 to 440 °C and C from 440 to 600 °C. Within the A mass loss event, the DTA curve detected some minor thermal events, followed by a broad-endothermic peak. These thermal events indicate that a dynamic reaction took place within that temperature range; and the most probable produced compound is zinc chloride x-hydrates (ZnCl$_2$·xH$_2$O) [10,11] that unfortunately can not be detected by XRD. This hydrate component is presumed originally from the HCl used (i.e. 37 % HCl) which means that the rest content (63 %) is H$_2$O. The ZnCl$_2$·xH$_2$O compound is then decomposed into ZnCl$_2$·H$_2$O [11,12], accompanied by a release of the solvent used, in this case, H$_2$O. The calculated mass loss A in Figure 1 is 5.44 % which is 2.10 % lower than the experimental value, 7.54 %. This difference might be due to the presence of H$_2$O moisture in the sample which then evaporated with heating, or it is attributable to a compound containing Ti, probably TiCl$_4$ which later due to heating, the compound transformed into TiO$_2$ and HCl.
Within the temperature range 243 – 440 °C, the mass loss B is about 2.20 %. At the same time, the DTA curve recorded a noticeable endothermic peak at 315 °C which corresponds to the transition of 1 mol ZnCl2·H2O to zinc hydroxide chloride (Zn(OH)Cl) [13] followed by release of 1 mol HCl gas. The TiO2 compound remains unchanged. At the end of the B mass loss event, a very significant exothermic peak was recorded. Further heating from 440 to 600 °C also generates a massive mass loss C of 22.0 %. This substantial mass loss corresponds to the formation of ZnTiO3 phase and the release of 1 mol HCl gas as a result of the reaction between Zn(OH)Cl and TiO2 [14]. Figure 2 depicts the FTIR data of the powders calcined from 440 to 900 °C, while Figures 3 and 4 show the associated XRD spectra.
Within the 4000 to 400 cm$^{-1}$ range, the FTIR curves only detect four different absorption bands, namely a broad band A at the position of 3446.18 cm$^{-1}$, B at 1600.90 cm$^{-1}$, C at 494.09 cm$^{-1}$ and D at 418.02 cm$^{-1}$. The broad band A relates to an O-H stretching band in a lattice water [15]. The intended lattice water is most likely ZnCl$_2$·xH$_2$O as analysed on the TG curve in Figure 1; this broad band corresponds to the adsorbed H$_2$O [15].

The specific absorption peak was recorded on the FTIR curves labeled 440 1h, 500 1h, 600 1h, 600 2h and 600 3h in Figure 2. The peak intensities are gradually weaken with heating temperature; and this peak totally disappeared on the curves labeled 700 1h, 800 1h and 900 1h. This fact implies that the x-value in the ZnCl$_2$·xH$_2$O compound was quite big and therefore a high temperature was required to completely remove the hydrate content in the compound.

The sharp B band at 1600.90 cm$^{-1}$ in Figure 2 was identified as an O-H deformation or bending vibration band [15]; in this work, this particular band corresponds to Zn(OH)Cl, the hydrolysis product of ZnCl$_2$·H$_2$O. Similar to the previous A band, this B band was also traced on the FTIR curves labeled 440 1h, 500 1h, 600 1h, 600 2h and 600 3h and the peak disappeared afterward. The C band at 494.09 cm$^{-1}$ and the D band at 418.02 cm$^{-1}$ are respectively identified as a Ti-O stretching vibration band and a Zn-O vibration band [15]. Unlike the previous A and B absorption peaks, the peaks of Ti-O and Zn-O remain detected on all FTIR curves, starting from the curves labeled 440 1h to 900 1h. These Ti-O and Zn-O bands show the fact that two independent phases containing Ti and Zn are present in the samples, presumably TiO$_2$ and ZnTiO$_3$. The XRD spectra in Figures 3 and 4 clarify this argument.

![Figure 3](image_url)

**Figure 3.** The associated XRD spectra of the calcined powders in Figure 2.

As shown in Figure 3, at 440 °C, TiO$_2$ rutile (Powder Diffraction File - PDF #21-1276) is the only phase detected. Further heating to 550 °C, some peaks belong to ZnTiO$_3$ phase (PDF #04-0836) were also recorded along the TiO$_2$ peaks. This suggests that using the liquid mixing method, ZnTiO$_3$ phase was initially formed at 550 °C. Kong et al. [1] reported that some XRD peaks of ZnTiO$_3$ was originally recorded at 600 °C for 2 h after being prepared by a modified alcoholysis method using Zn(Ac)$_2$·2H$_2$O and Ti(OC$_6$H$_5$)$_4$ as the raw materials, ethylene glycol as reagent/solvent and acetylacetone as stabilizer. Chai et al. [2] occupied sol-gel method and zinc acetate and ethylene glycol as the starting materials to prepare ZnTiO$_3$ powder. He found that the ZnTiO$_3$ peaks were identified at first at 700 °C for 6 h. Chang
et al. [3] prepared ZnTO$_3$ powder from the conventional solid-state reaction using 99.99% pure ZnO and TiO$_2$ powders as the raw materials; he recorded the ZnTiO$_3$ peaks at 700 $^\circ$C for 24 h in air. By following the sol-gel method, using the raw materials of zinc acetate dihydrate, titanium tetraisopropoxide and oxalic acid, and by experimenting various Zn:Ti precursor molar ratio to prepare zinc titanates, Nolan et al. [4] recorded the ZnTiO$_3$ peaks at temperatures of 600 – 900 $^\circ$C. Based on these literatures, the liquid mixing method adopted in this work was a prospective method to synthesise ZnTiO$_3$ at a lower calcination temperature.

In Figure 3, however, the intensities of the XRD spectrum labeled 600, 1h diminished due to unknown reasons. By increasing the calcination holding time to 2 and 3 h, the numbers of ZnTiO$_3$ peaks and the intensities increased considerably. The increase of TiO$_2$ peak intensities was also noted. Further heating to 700 $^\circ$C for 1 h caused the intensities of ZnTiO$_3$ and TiO$_2$ peaks continued to increase. The increase in the peak intensities of ZnTiO$_3$ and TiO$_2$ phases, however, slowed down when the sample was calcined at 800 for 1 h. At that temperature, the peak intensities of the two phases declined. Heating up to 900 $^\circ$C, the intensities of TiO$_2$ went up again, but that of ZnTiO$_3$ weakened; and even some ZnTiO$_3$ peaks with the Miller indices of (012) at 2$\theta$ position of 23.92$^\circ$ and (214) at 62.80$^\circ$ are missing at 900 $^\circ$C. At the same time, three new peaks at 2$\theta$ = 29.93$^\circ$, 35.25$^\circ$ and 63.18$^\circ$ appeared. These three new peaks were identified as belonging to Zn$_2$TiO$_4$ phase (PDF #77-0014), each with Miller indices of (220), (311) and (440). These findings suggested that within 800 – 900 $^\circ$C, some parts of ZnTiO$_3$ phase were decomposed into Zn$_2$TiO$_4$ via the reaction of 2ZnTiO$_3$ $\rightarrow$ Zn$_2$TiO$_4$ + TiO$_2$. That is the reason why at 900 $^\circ$C: the intensities of TiO$_2$ increased as compared to that at 800 $^\circ$C, the intensities of ZnTiO$_3$ diminished and simultaneously, some Zn$_2$TiO$_4$ peaks started to appear (see Figure 4). Equations 1-5 recapitulate the chemical reactions explained above.

![Figure 4. The similar XRD spectra in Figure 3, but only the spectra labeled 600, 2h up to 900, 1h.](image-url)
\[ \text{RT} - 243 \, ^\circ C: \quad \text{ZnCl}_2 \cdot 5\text{H}_2\text{O} + \text{TiCl}_4 \rightarrow \text{ZnCl}_2 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O}^+ + \text{TiO}_2 + 4\text{HCl} \uparrow \]  
\[ 243 - 440 \, ^\circ C: \quad \text{ZnCl}_2 \cdot \text{H}_2\text{O} + \text{TiCl}_2 \rightarrow \text{Zn(OH)Cl} + \text{TiO}_2 + \text{HCl} \uparrow \]  
\[ 440 - 600 \, ^\circ C: \quad \text{Zn(OH)Cl} + 2\text{TiO}_2 \rightarrow \text{TiO}_2 + \text{ZnTiO}_3 + \text{HCl} \uparrow \]  
\[ 600 - 700 \, ^\circ C: \quad \text{TiO}_2 + \text{ZnTiO}_3 \rightarrow \text{TiO}_2 + \text{ZnTiO}_3 \]  
\[ 800 - 900 \, ^\circ C: \quad \text{TiO}_2 + 2\text{ZnTiO}_3 \rightarrow \text{Zn}_2\text{TiO}_4 + 2\text{TiO}_2 \]  

3.2 Crystallinity and particle size distribution

Figure 5 depicts the crystallinity of ZnTiO\textsubscript{3} phase as a function of calcination temperature from 600, 2h to 900 °C, 1h calculated from the ratio of peak intensity and of peak area of ZnTiO\textsubscript{3} phase with respect to that of the other phases present in the spectra in Figure 4. Since ZnTiO\textsubscript{3} is not the major phase, the crystallinity of the phase is limited as compared to that of the main phase of TiO\textsubscript{2} rutile. At 600, 2h in Figure 5, the crystallinity of ZnTiO\textsubscript{3} is 36 and 41 %. By prolonging the calcination holding time to 3 h, the crystallinity increased to 38 and 46 % before reaching to the maximum, 45 and 50 %, at 700 °C. Further, owing to the decomposition process of ZnTiO\textsubscript{3} into Zn\textsubscript{2}TiO\textsubscript{4} and TiO\textsubscript{2} at higher temperatures, the crystallinity of ZnTiO\textsubscript{3} phase was affected. The values went down significantly to 27 and 35 % at 800 °C and 11 and 20 % at 900 °C.

Figure 5. Crystallinity of ZnTiO\textsubscript{3} phase in the powders in Figure 4 after heat-treated at various temperatures from 600 to 900 °C.

Chai et al. [2] also reported the crystallinity of ZnTiO\textsubscript{3} phase calculated using the same approach, i.e. by taking the ratio of XRD peak intensities and of peak area of ZnTiO\textsubscript{3} phase relating to that of the other phases (TiO\textsubscript{2} rutile and α-Zn\textsubscript{2}TiO\textsubscript{4}). Within the same temperature range, from 600 to 900 °C, Chai et al. [2] obtained that the crystallinity of ZnTiO\textsubscript{3} increased from 77 and 83 % at 600 °C to 92 and 93 % at 800 °C. These values slightly declined to 90 and 91 % at 900 °C. In the Chai et al. case, ZnTiO\textsubscript{3} was the main phase. In the liquid mixing method, as seen in Figures 3 and 4, TiO\textsubscript{2} rutile phase has been formed since the beginning of the reaction. The presence of TiO\textsubscript{2} phase dominates even when the
calcination temperature increases and this inhibits the formation of ZnTiO₃ phase. To overcome this, an attempt was initiated, i.e. by adding the stoichiometrically excess of Zn during the synthesis process.

Figure 6 shows the effect of the addition of stoichiometrically excess of Zn, in this case Zn: Ti = 1.05: 1, to the reduction of TiO₂ rutile phase dominance, as well as to the formation of ZnTiO₃ as the main phase in the system. The powder sample in Figure 6 was calcined at 600 °C for 3 h. As seen, by testing the ratio of Zn: Ti = 1.05: 1, the intensity of the highest peak belonging to the TiO₂ phase at $2\theta = 27.5^\circ$ ($hkl = 110$) in Figure 6 becomes lower than the intensity of the highest peak belonging to ZnTiO₃ phase at $2\theta = 32.8^\circ$ ($hkl = 104$). In other words, the (110) peak of TiO₂ phase in Figure 6 is not dominant anymore. This fact is very contrary to the result shown in Figure 4 labeled 600, 3h, where the TiO₂ peak intensity at $2\theta = 27.5^\circ$ is much higher than the ZnTiO₃ peak intensity at $2\theta = 32.8^\circ$. Reducing the dominance of TiO₂ phase was also detected at the peak at $2\theta = 36.1^\circ$ with $hkl = (101)$. At the same time, ZnTiO₃ peak at $2\theta = 35.3^\circ$ with $hkl = (110)$ becoming dominant. The addition of stoichiometrically excess of Zn has driven the formation of ZnTiO₃ phase; further addition of stoichiometrically excess of Zn potentially has further diminished TiO₂ phase and increased the formation of ZnTiO₃ phase. Figures 7a-c show the distribution of particle size in the powders in Figure 4 labeled 700, 800 and 900, 1 h.

![XRD Pattern](image)

**Figure 6.** The XRD pattern of ZnTiO₃ powder with the addition of stoichiometrically excess of Zn, i.e. Zn: Ti = 1.05: 1. The powder was calcined at 600 °C, 3 h.
Figures 7a-b. Particle size distribution in ZnTiO$_3$ powder in Figure 4 labeled: (a) 700, 1h and (b) 800, 1h.
Figure 7c. Particle size distribution in ZnTiO₃ powders in Figure 4 labeled 900, 1h.

The particle size distribution in Figures 7a-c are all normal-single mode ranging from 295 – 1280 nm at 700 °C, 190 – 615 nm at 800 °C and 91 – 2304 nm at 900 °C. The average particle size at 700 °C is 683 nm, at 800 °C is 370 nm and at 900 °C is 709 nm, each with deviation of around 4 %. Using the fact that the distribution curves are single modes and the deviation of the average size is diminutive, it can be concluded that the particles in the above samples are all homogeneously distributed. Chai et al. [5] measured the particle size of the ZnTiO₃ powders directly from TEM image and obtained that the average size were about 30 nm after heating at 800 °C for 6 h.

4. Conclusion
The liquid mixing method has been demonstrated as a promising synthesis route to produce ZnTiO₃ phase because the desired phase can be formed at a temperature as low as 550 °C. Besides, particles in the samples are all homogeneously distributed with diminutive deviation for the average particle size. The problem faced by this method is when using the ‘normal’ stoichiometric ratio of Zn: Ti = 1: 1; TiO₂ rutile phase was formed as the main phase while the ZnTiO₃ phase is only a secondary phase. This situation causes limited crystallinity of ZnTiO₃ phase; the value is no more than 50 % and that was achieved when the powder was calcined at 700 °C. Above 700 °C, the crystallinity of ZnTiO₃ phase dropped significantly because some of the ZnTiO₃ phase decomposed into Zn₂TiO₄ and TiO₂ phases. The practical best solution to encourage the formation of ZnTiO₃ phase as the main phase is by adding the stoichiometrically excess of Zn during the synthesis process. The experiment using the ratio of Zn: Ti = 1.05: 1 has proved it.

5. References
[1] Kong J-Z, Li A-D, Zhai H-F, Li H, Yan Q-Y, Ma J and Wu D. 2009 J. Haz. Mat. 171 918-23
[2] Chai Y-L, Chang Y-S, Chen G-J and Hsiao Y-J. 2007 Mater. Res. Bull. 43 1066-73
[3] Chang Y-S, Chang Y-H, Chen I-G, Chen G-J, Chai Y-L, Fang, T-H and Wu, S. 2004 Ceram. Int. 30 2183-89
[4] Nolan N T, Seery M K and Pillai S C. 2011 Chem. Mater. 23 1496-1504
[5] Ermawati F U, Suasmoro S and Pratapa S. 2015 Adv. Mater. Res. 1112 47-52
[6] Ermawati F U, Pratapa S, Suasmoro S, Hübert T and Banach U. 2016 J. Mater. Sci. Mater. El. 27 6637-45
[7] Ermawati F U, Suasmoro S and Pratapa S. 2017 Omega: Jurnal Fisika dan Pendidikan Fisika. 3 15-22
[8] Ermawati F U and Suasmoro S. 2018 J. Phys: Conf. Ser. 997 012005
[9] Ermawati F U, Supardi Z A I, Suasmoro S, Pratapa S and Hübert T. 2018 IOP Conf. Ser.: Mater. Sci. Eng. 367 012003
[10] Hennings E, Schmidt, H and Voigt, W. 2014 Acta Crystallogr. Sect. E. E70 515–18
[11] Haghighi, H, Chapoy, A and Tohidi, B. 2008. Ind. Eng. Chem. Res. 47, 3983–89.
[12] Sutton, L. E and Truter, M R 2007. Molecular Structure by Diffraction Methods, Volume 5 (Great Britain: Royal Society of Chemistry) p 173
[13] Brauer, G and Herrmann, W A. 2011 Synthetic Methods of Organometallic and Inorganic Chemistry: Catalysis, Volume 10 (The University of Carolina: Thieme) p 123
[14] Zhou, S, Patty, A and Chen S. 2015 Advances in Energy Science and Equipment Engineering: Proceedings of the International Conference on Energy Equipment Science and Engineering, (ICEESE 2015), May 30-31, 2015, Guangzhou, China. (Great Britain: CRC Press) p 31-34
[15] George S. 2001 Infrared and Raman Characteristic Group Frequencies: Tables and Charts. 3rd Ed. (West Sussex, England: John Wiley and Sons) p 322-26

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