The Use of Liquid Mixing Method to Prepare Ilmenite Structure-Based Ceramic Powders

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Abstract. Ilmenite structure-based ceramics such as MgTiO₃, ZnTiO₃ and FeTiO₃ have become important materials in ceramic industries. One of them is for microwave dielectric resonator and oscillator applications on radar systems for MgTiO₃ and ZnTiO₃, and for spintronic device applications for the wide band gap antiferromagnetic semiconductor FeTiO₃. The conventional solid-state reaction method has been widely utilized to prepare the ilmenite ceramic powders due to its practicability in industrial applications. In spite of its recognition, this method still has some shortcomings. Some of these are requiring high calcination temperatures (> 1000 °C), the use of very intensive milling causes granules of powder to coagulate with varying sizes in several micrometers that gives rise to inhomogeneity in the final product. The co-presence of intermediate phases such as Mg₂TiO₄, MgTi₂O₅, and Zn₂TiO₄ on the calcined MgTiO₃ and ZnTiO₃ powders may inhibit the dielectric properties of the ceramics, thus detrimental in industrial applications. As an alternative, a facile route of liquid mixing method was introduced to synthesize the ilmenite MgTiO₃, FeTiO₃ and ZnTiO₃ powders at much lower calcination temperatures, i.e. 340 and 500-550 °C and that of free of intermediate phase presence. This paper reports the performance of liquid mixing method on synthesis of the above three ilmenite ceramic powders as examined using TGA-DTA and XRD data.

1. Introduction
Ilmenite structure-based ceramics with crystal stoichiometry of ABO₃, where A and B are cations while O is anion as found in MgTiO₃, FeTiO₃ and ZnTiO₃ have been favourite materials for technological applications in industrial ceramics. For instance, MgTiO₃ that exhibits moderate dielectric constant (εᵣ), high quality factor (Qᵣ) and near zero temperature coefficient of resonance frequency (τₑ) becomes paramount candidate dielectric materials for using in radar systems as microwave dielectric resonator and oscillator, in wireless technologies, global positioning systems and antenna, and in capacitor systems as high-frequency capacitor, chip capacitor and temperature compensating capacitor [1], [2]. FeTiO₃ as a wide band gap (2.8 eV) antiferromagnetic semiconductor material is also potential for applications in spintronics [3].

Various ceramic dielectrics based on ilmenite structure have been fabricated and the dielectric characteristics have also been reported [1], [4], [5]. MgTiO₃-, ZnTiO₃- and FeTiO₃-based ceramic powders have been prepared using different methods, not only limited to solid state reaction method [6], sol-gel method [7] [3], solution combustion method [8] and coprecipitation method [9]. Each method has its own advantages and disadvantages. An alternative method named liquid mixing method was
introduced to prepare the ilmenite ceramic powders at quite low temperature and of free of intermediate phase [1], [10-15].

What is meant by the liquid mixing method is dissolving metal powders in hydrochloric acid to obtain liquid solutions; mixing the solutions homogeneously, drying it and heating it for gaining the desired crystalline phase. This paper is devoted to report the preparation of MgTiO\(_3\), ZnTiO\(_3\) and FeTiO\(_3\) based ceramic powders using the facile liquid mixing method and examined the phase formation based on TGA/DTA and XRD data.

2. Experiment

Each of (Mg\(_{0.9}\)Zn\(_{0.1}\))TiO\(_3\), ZnTiO\(_3\) and FeTiO\(_3\) dried powder systems was prepared by liquid mixing method using Mg, Zn, Ti and Fe metal powders (Merck) as raw materials and HCl 12 M as solvent. Each of the metal powders was weighed based on the stoichiometric ratio of the intended system and dissolved separately in HCl to gain homogeneous MgCl\(_2\), ZnCl\(_2\), FeCl\(_2\) and TiCl\(_4\) liquid solutions. In order to prepare (Mg\(_{0.9}\)Zn\(_{0.1}\))TiO\(_3\) powder system, the required MgCl\(_2\), ZnCl\(_2\) and TiCl\(_4\) solutions were mixed uniformly and heated to obtain dried sediment. For preparing ZnTiO\(_3\) powder, another ZnCl\(_2\) and TiCl\(_4\) liquid solutions were mixed homogeneously before being heated for dried sediment. Likewise, to prepare FeTiO\(_3\) powder, the FeCl\(_2\) and TiCl\(_4\) liquid solutions were also mixed and heated to obtain similar dried sediment. The dried sediment of each system was crushed manually so that it turned to be powders with uniform grain sizes.

Thermo gravimetric and differential thermal analyses (TG/DTA) examination on the as prepared powders was conducted using a Star\(^\text{e}\) System TG/DTA Mettler Toledo from room temperature to 600 °C at the heating rate of 10 °C/min. The aim was to study thermal events in the systems during heating. The powders were calcined at the same heating rate (10 °C/min) using a Nabertherm furnace at the temperature suggested by the TG/DTA curves. X-ray diffraction (XRD) measurement on the calcined powders was conducted using an X\(^\text{P}\)ert Diffractometer (Philips) with CuK\(_\alpha\) radiation from 2\(\theta\) = 15-65° and the rate of 0.02°/min to monitor the phase formation in the systems.

3. Results and Discussion

3.1 Phase formation in (Mg\(_{0.9}\)Zn\(_{0.1}\))TiO\(_3\)

Figure 1 shows TG/DTA curves of the as prepared (Mg\(_{0.9}\)Zn\(_{0.1}\))TiO\(_3\) powder after heating from temperature (RT) to 600 °C at the rate of 10 °C/min using Star\(^\text{e}\) System TG/DTA Mettler Toledo. Figure 2 shows the associated XRD patterns, both as prepared (pattern labelled RT) and after calcination at different temperatures as dictated on the TG/DTA curves in Figure 1. The XRD pattern labelled RT contains the phases of MgCl\(_2\)-6H\(_2\)O (PDF #25-0515), TiO\(_2\) rutile (PDF #21-1276) and ZnCl\(_2\) (PDF #15-0452). As seen in Figure 1, there are three different mass loss regions on the TG curve of (Mg\(_{0.9}\)Zn\(_{0.1}\))TiO\(_3\) sample, i.e. A is from RT to 220 °C, B is between 220 – 380 °C and C is 380 – 500 °C. Above 500 °C, the TG curve is horizontal indicating that no further mass loss was recorded on the sample. Within the A region, the DTA curve recorded some dynamic thermal events; however, the produced phases cannot be identified by XRD. Further scrutiny on the TG and XRD patterns reveals that about 5 mol H\(_2\)O gas was released following dehydration of 0.9 mol MgCl\(_2\)-6H\(_2\)O. The calculated mass loss was 25.3 %, while the experiment loss was 29.3 %. The loss difference (4.0 %) was assumed due to the presence of H\(_2\)O moisture in the system which then evaporates during heating. Another possible cause of this mass loss difference was due to the presence of an amorphous phase containing Ti, which might be Ti(OH)\(_4\), and this turns to be TiO\(_2\) rutile and H\(_2\)O with heating. This argument was based on the XRD data in Figure 2 telling that TiO\(_2\) rutile phase existed on the pattern labelled RT and the presence has continued up to the pattern labelled 600.

Within the B region, the mass loss measured on the TG curve was only 5.6 % which corresponds to the transformation of (Mg\(_{0.9}\)Zn\(_{0.1}\))Cl\(_2\)-H\(_2\)O to form (Mg\(_{0.9}\)Zn\(_{0.1}\))(OH)Cl, followed by HCl gas releases. No significant DTA curve was recorded on this region. An interesting fact is that the only ZnCl\(_2\) peak
recorded at $2\theta = 18.5^\circ$ on the XRD pattern labelled 220 in Figure 2 was disappeared. This peak was detected on the pattern labelled RT. The disappearance of the ZnCl$_2$ peak indicates that the Zn$^{2+}$ ions have entered the positions of Mg$^{2+}$ ions in the $(\text{Mg}_{0.9}\text{Zn}_{0.1})\text{Cl}_2.\text{H}_2\text{O}$ structure mentioned above as a result of the similarities in coordination number and ionic radius between those two ions. Both ions have the same octahedral coordination and the radius is 0.074 Å for Zn$^{2+}$ and 0.072 Å for Mg$^{2+}$. The inclusion of Zn$^{2+}$ ions occurs at 220 ºC.

![Figure 1. TG/DTA curves of the as prepared $(\text{Mg}_{0.9}\text{Zn}_{0.1})\text{TiO}_3$ powder recorded from room temperature to 600 ºC at the rate of 10 ºC/min using Star® System TG/DTA Mettler Toledo](image)

Within the C region, the experimental mass loss was 22.0 %. The DTA curve on this region recorded a significant endothermic peak. The corresponding XRD data reveals that the peak intensities of $(\text{Mg}_{0.9}\text{Zn}_{0.1})\text{Cl}_2.\text{H}_2\text{O}$ reduced constantly with the increase of calcination temperature, the width broadens and unresolved before being vanish. On the pattern labelled 500, the emerging phase was $(\text{Mg}_{0.9}\text{Zn}_{0.1})\text{TiO}_3$ solid solution that can be indexed as MgTiO$_3$ phase. Further analysis on the DTA curve discloses that the intended significant endothermic peak was due to the formation of $(\text{Mg}_{0.9}\text{Zn}_{0.1})\text{TiO}_3$ solid solution that was started at 420 ºC. The Equations (1) below summarise the reactions described above.

\[
\begin{align*}
\text{RT} - 220^\circ\text{C} & : \quad 0.9\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 0.1 \text{ZnCl}_2 + \text{TiO}_2 \rightarrow (\text{Mg}_{0.9}\text{Zn}_{0.1})\text{Cl}_2 \cdot \text{H}_2\text{O} + \text{TiO}_2 \cdot x \text{H}_2\text{O} \\
220 - 380^\circ\text{C} & : \quad (\text{Mg}_{0.9}\text{Zn}_{0.1})\text{Cl}_2 \cdot \text{H}_2\text{O} + \text{TiO}_2 \rightarrow (\text{Mg}_{0.9}\text{Zn}_{0.1})\text{OHCl} + \text{TiO}_2 + \text{HCl} \\
380 - 500^\circ\text{C} & : \quad (\text{Mg}_{0.9}\text{Zn}_{0.1})\text{OHCl} + \text{TiO}_2 \rightarrow (\text{Mg}_{0.9}\text{Zn}_{0.1})\text{TiO}_3 + \text{HCl} \\
\end{align*}
\]
Figure 2. XRD patterns of (Mg$_{0.9}$Zn$_{0.1}$)TiO$_3$ powders at different calcination temperatures recorded using X’Pert Diffractometer (Philips), CuK$_\alpha$ radiation at the rate of 0.02°/min. The peaks with $hk\ell$ indices = MgTiO$_3$, a = MgCl$_2$·6H$_2$O, b = ZnCl$_2$, c = TiO$_2$ rutile.

3.2 Phase formation in ZnTiO$_3$

Figure 3. TG/DTA curves of the as prepared ZnTiO$_3$ powder recorded from room temperature to 600 °C at the rate of 10 °C/min using Star® System TG/DTA Mettler Toledo.
Figure 3 depicts the TG/DTA curves of the as prepared ZnTiO$_3$ powder after heat treating from RT to 600 °C at the same rate as in (Mg$_{0.9}$Zn$_{0.1}$)TiO$_3$ powder using Star² System TG/DTA Mettler Toledo. Figure 4 showing the XRD patterns of ZnTiO$_3$ powders after calcination at various temperatures.

As shown in Figure 3, on the TG curve, three different mass losses, i.e. A (RT to 243 °C), B (243 – 440 °C) and C (440-600 °C) were recorded. On the A loss event, the DTA curve measured insignificant thermal events and a broad endothermic peak from 200 to 243 °C. This peak corresponds to the formation of zinc chloride penta hydrates compound (ZnCl$_2$)$\cdot$5H$_2$O in the system [15]. During heating, the hydrate component of this compound was slowly broken and released as H$_2$O gas, and leaving behind (ZnCl$_2$)$\cdot$H$_2$O. The experimental mass loss was 7.54 % which is 2.10 % higher than the calculated loss. The loss difference was believed due to the presence of TiCl$_4$ compound in the system which then during further heating, this compound decomposed into TiO$_2$ rutile and HCl gas. The only phase detected on the XRD patterns at RT and at 243 °C (which were not shown in Figure 4) is TiO$_2$ rutile, the same as the major phase on the XRD pattern labelled 440 in Figure 4.

The B mass loss on the TG curve in Figure 3 was quite small, i.e. 2.2 %. Meanwhile, the DTA curve also measured a small endothermic peak at 315 °C. This particular peak coincides with the transition of the resulting ZnCl$_2$.$\cdot$H$_2$O compound into zinc hydroxide chloride, Zn(OH)Cl and HCl gas [15]. At the end of the B mass loss temperature range, TiO$_2$ phase was reserved as proven on the XRD pattern labelled 440 in Figure 4. As also seen, a small peak ZnTiO$_3$ was also detected on the pattern, suggesting that via the liquid mixing method, the desired ZnTiO$_3$ phase was produced at low temperature, i.e. 440 °C.

The C mass loss recorded on the TG curve was very massive, i.e. 22.0 %. This loss agrees with the formation of ZnTiO$_3$ phase (PDF #26-1500) after the reaction between the resulting Zn(OH)Cl compound and TiO$_2$ rutile [15]. This analysis was in line with the XRD patterns labelled 500 and 600 in Figure 4. As shown, the TiO$_2$ rutile peaks was dominant while the ZnTiO$_3$ peak was less dominant. However, on the pattern labelled 600 Zn 1.05, the situation changed, i.e. the (104) ZnTiO$_3$ peak at 2θ = 32.8° turns to be dominant. This was due to the addition of stoichiometry excess of Zn during synthesis,
in this case the mole ratio between Zn and Ti = 1.05: 1. The peak intensities however, was slightly declined. Equations (2) recapitulate the analysis given above.

$$\text{RT} - 243 \text{C}: \quad \text{ZnCl}_2 \cdot 5\text{H}_2\text{O} + \text{TiCl}_4 \rightarrow \text{ZnCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}^{\uparrow} + \text{TiO}_2 + 4\text{HCl}^{\uparrow}$$

$$243 - 440 \text{C}: \quad \text{ZnCl}_2 \cdot \text{H}_2\text{O} + \text{TiO}_2 \rightarrow \text{Zn(OH)}\text{Cl} + \text{TiO}_2 + \text{HCl}^{\uparrow} \quad (2)$$

$$440 - 600 \text{C}: \quad \text{Zn(OH)}\text{Cl} + \text{TiO}_2 \rightarrow \text{ZnTiO}_3 + \text{TiO}_2$$

3.3 Phase formation in FeTiO₃

![Figure 5. TG/DTA curves of the as prepared FeTiO₃ powder recorded from room temperature to 600 °C at the rate of 10 °C/min using Star System TG/DTA Mettler Toledo.](image)

Figure 5 presents the TG/DTA curves of the as prepared FeTiO₃ powder after following the heating passage from RT to 600 °C at the rate of 10 °C/min using the Star System TG/DTA Mettler Toledo. Figure 6 shows the XRD patterns of the FeTiO₃ powders at various calcination temperatures as noted on the label of each pattern.
The XRD patterns of the as prepared FeTiO$_3$ powder, and that after calcination at 170, 340, 500 and 600 °C. a = FeTiO$_3$, b = TiO$_2$ rutile, c = FeCl$_2$·H$_2$O, d = TiCl$_4$.

The three different mass losses on the TG curve in Figure 5 was recorded, i.e. A between RT – 170 °C, B is between 170 and 340 °C and C is between 340 and 500 °C. Within the A mass loss region, the DTA curve recorded a wide endothermic peak. As found on the previous ilmenite samples, this particular endothermic peak corresponds to the formation of iron chloride penta hydrates (FeCl$_2$·5H$_2$O) in the as prepared powder. As before, the hydrates component in FeCl$_2$·5H$_2$O compound was gradually broken and releases as H$_2$O gas after further heating, the remaining compound was FeCl$_2$·H$_2$O, as confirmed on the XRD pattern labelled RT and 170. The experimental mass loss was 3.60 %. The co-presence of TiCl$_4$ compound on the XRD patterns labelled RT and 170 in Figure 6 remains stable up to 170 °C. However, some of TiCl$_4$ seemed to be decomposed into TiO$_2$ and HCl gas as shown on the pattern. The similar happening was also noted on the FeCl$_2$·H$_2$O compound. Above 170 °C, both TiCl$_4$ and FeCl$_2$·H$_2$O peaks have completely disappeared.

The total mass loss on B in Figure 5 was 11 %. The DTA curve recorded a massive peak. This peak coincides with two different chemical reactions, i.e. first, within 170-220 °C, the transition of FeCl$_2$·H$_2$O becomes Fe(OH)Cl and TiO$_2$ followed by release of 1 mol HCl gas. The experimental mass loss within this temperature range was 7.0 %. Second, within 220-340 °C, the reaction between Fe(OH)Cl and TiO$_2$ to initiate the formation of FeTiO$_3$ phase at 340 °C (see the ‘a’ symbols on the XRD pattern labelled 340 in Figure 6 to represent FeTiO$_3$ peaks). The experimental mass loss on this second temperature range was 4.0 %. Based on this analysis, it can be concluded that the massive endothermic peak was due to the initial formation of FeTiO$_3$ phase (PDF #75-1207) that took place on that temperature range.

The C mass loss on the TG curve in Figure 5 was very small, i.e. 0.23%. At the same time, the DTA curve detected a minor exothermic peak. This peak is thought to be the release of residual HCl gas during the formation of the FeTiO$_3$ phase. Equations (3) review the analysis given above.

\[
\begin{align*}
\text{RT – 170 C:} & \quad \text{FeCl}_2 \cdot 5\text{H}_2\text{O} + \text{TiCl}_4 \rightarrow \text{FeCl}_2 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O}^\uparrow + \text{TiO}_2 + 4\text{HCl}^\uparrow \\
170 – 220 \, \text{C:} & \quad \text{FeCl}_2 \cdot \text{H}_2\text{O} + \text{TiO}_2 \rightarrow \text{Fe(OH)Cl} + \text{TiO}_2 + \text{HCl}^\uparrow \\
220 – 340 \, \text{C:} & \quad \text{Fe(OH)Cl} + 2\text{TiO}_2 \rightarrow \text{FeTiO}_3 + \text{TiO}_2 + \text{HCl}^\uparrow \\
340 – 600 \, \text{C:} & \quad \text{FeTiO}_3 + \text{TiO}_2 \rightarrow \text{FeTiO}_3 + \text{TiO}_2
\end{align*}
\]
4. Conclusion
The work to prepare the ilmenite \((\text{Mg}_{0.9}\text{Zn}_{0.1})\text{TiO}_3\), \(\text{ZnTiO}_3\) and \(\text{FeTiO}_3\) powders using the liquid mixing method has been completed. The results confirmed that this simple method can produce the desired phase at very low temperatures, i.e. 340 °C for \(\text{FeTiO}_3\) and 500-550 °C for \((\text{Mg}_{0.9}\text{Zn}_{0.1})\text{TiO}_3\) and \(\text{ZnTiO}_3\) without accompanied by any intermediate phase. The co-presence of \(\text{TiO}_2\) rutile on the final product can be reduced by adding the stoichiometry excess of the cations.

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