XRD and EDX Analyses on the Formation of MgTiO$_3$ Phase in (Mg$_{0.6}$Zn$_{0.4}$)(Ti$_{0.99}$Sn$_{0.01}$)O$_3$ Powders Due to Calcination Temperature Variations

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Abstract. MgTiO$_3$-based dielectric ceramics have been recognized as functional materials in the microwave telecommunications industry. Research and development on MgTiO$_3$ dielectric ceramics has therefore developed rapidly. This paper reports x-ray diffraction (XRD) and energy dispersive x-ray (EDX) analyses on the formation of MgTiO$_3$ phase in (Mg$_{0.6}$Zn$_{0.4}$)(Ti$_{0.99}$Sn$_{0.01}$)O$_3$ powder due to variations in calcination temperature from 550 to 700°C for 2 h. The powder was synthesized via the dissolved metal mixing course using magnesium, zinc, titanium and tin metal powders (Merck) as starting materials. The Rietveld refinement on the XRD patterns of the samples revealed that increasing the calcination temperature reduces the molar% content of MgTiO$_3$ phase of from (97.91±1.51) at 550°C to (87.81±1.29) at 700°C and causes a decrease in the diffraction peak intensity. The remaining % belongs to TiO$_2$ rutile. The calcination temperature also enlarged the size of MgTiO$_3$ unit cell volume. The EDX data on the atomic% ratio of the elements confirmed the presence of the phases. Discussion of these results is presented in detail in this paper.

1. Introduction
Geikielite MgTiO$_3$ based dielectric ceramics have been recognized as their main functional material for various applications in the satellite telecommunications industry, including global positioning systems, resonator dielectrics and high frequency capacitors [1–8]. Fabrication of Geikielite MgTiO$_3$-based dielectric ceramics has developed rapidly by creating various compositions and designs with the aim of obtaining superior dielectric characteristics that can meet industrial needs [1–3, 9,10]. In each of these compositions, the presence of the MgTiO$_3$ as the main phase is very important to ensure these superior properties. This paper reports the analysis of the formation of the MgTiO$_3$ phase in the new composition, namely (Mg$_{0.6}$Zn$_{0.4}$)(Ti$_{0.99}$Sn$_{0.01}$)O$_3$ powder prepared by dissolved metal mixing method as a function of the calcination temperature based on the XRD and EDX measurements. The aim is to ensure that in the new composition, whether the MgTiO$_3$ phase can be formed as the main phase, and at what calcination temperature the content of the MgTiO$_3$ phase reaches its maximum value.

2. Method
The new composition of (Mg$_{0.6}$Zn$_{0.4}$)(Ti$_{0.99}$Sn$_{0.01}$)O$_3$ powders (abbreviated to MZTS) were prepared from magnesium, zinc, titanium and tin high purity metal powders (Merck). Each metal powder was weighed according to the expected stoichiometry and dissolved homogeneously in 12 molar
hydrochloric acid using a magnetic stirring hotplate. The four liquid solutions were then mixed consistently, dried and crashed to obtain an amorphous powder with a uniform particle size. The resulting powder was then calcined at temperatures of 550, 600, 650 and 700 °C for 2 h using a BWS furnace with a heating step of 10 °C/min. The temperature of 550 °C was chosen because the thermo gravimetric analysis/differential thermal analysis (TGA/DTA) on the (Mg$_{0.8}$Zn$_{0.2}$)TiO$_3$ powder reported in [11] revealed that the diffraction peaks belonging to the MgTiO$_3$ phase were formed at 500 °C and the powder was calcined at 550 °C. Ermawati et al in [3] also calcined (Mg$_{1-x}$Zn$_x$)TiO$_3$ powders for $x = 0.1 – 0.5$ at 550 °C. In this study, as already mentioned, the powder was calcined at temperatures of 550, 600, 650 and 700 C in order to study the effect of variations in calcination temperature on the formation of the MgTiO$_3$ phase in the new composition, MZTS powders.

Identification of the crystalline phases formed in the MZTS powders was carried out using a Match! Software on the MZTS’s x-ray diffraction (XRD) pattern. The XRD measurement was accomplished using XPert MPD (Philips) with Cu K$_\alpha$ radiation at a diffraction angle (2$\theta$) range of 15-70° and at the step size of 0.017 °/min. Analysis on the composition of the identified phases was performed using the Rietveld method implemented in Rietica software. Elemental composition of the MZTS calcined powders was examined via energy dispersive x-ray (EDX) technique using EDAX$^{\text{TSL}}$ (AMETEX). Figure 1 shows the flowchart of all the experimental stages above.

![Figure 1. The experimental stages carried out in this work](image)

3. Results and Discussion

3.1. XRD Analysis

Figure 2 shows the XRD patterns of the MZTS powders calcined at 550, 600, 650 and 700 °C for 2 h.

![Figure 2. XRD patterns of MZTS powders calcined at 550, 600, 650 and 700 °C for 2 h. a = MgTiO$_3$ (PDF #06-0494), b = TiO$_2$ rutile (PDF #21-1276)](image)
As shown in Figure 2, the diffraction patterns of the four samples were identified as belonging to the MgTiO$_3$ phase (PDF #06-0494), namely peaks with the label "a" above them. However, three extra peaks at $2\theta = 27.44^\circ$, $36.08^\circ$ and $54.32^\circ$ belonging to TiO$_2$ rutile phase (PDF #21-1276), i.e. the peaks with the label "b", were also identified. The identification of these phases was completed using the Match! Software. As the calcination temperature increases from 550 to 700 °C, the intensity of the highest diffraction peak belonging to the MgTiO$_3$ phase at $2\theta = 32.87^\circ$ (i.e. the peak with $hkl = 104$) decreases. At the same time, the intensity of the diffraction peak belonging to the TiO$_2$ rutile phase at $2\theta = 27.44^\circ$ (i.e. the peak with $hkl = 110$) is increasing. The decrease in the intensity of the (104) peak might be closely related to the vibration of the atoms in the sample as the temperature increases. In addition to the decrease in the intensity of the (104) peak followed by peak broadening, it turns out that the $2\theta$ position of the peak also shifts towards a smaller $2\theta$ value as the calcination temperature increases, as shown in Figure 3. The facts in Figures 2 and 3 will then be discussed in the following paragraphs based on the theoretical review and confronted with the XRD quantitative data obtained in this work and that was presented in Figures 4-9. So far, the ordered expanses of atoms in a crystal have often been thought to lie at fixed points in the lattice. The truth is that the atoms undergo thermal vibrations at their average position, even at absolute zero temperature. The amplitude of the thermal vibration will increase along with the increase in temperature, resulting in a shift in the position of the atoms from their average position. Theoretically, Cullity [12] explained that the increase in atomic thermal vibration due to an increase in temperature can cause the following, namely: a) the size of the unit cell volume becomes larger so that the periodicity of the distance between the closest crystal planes ($d$) changes, and therefore the $2\theta$ position of the diffraction peak also shifts from its original position; b) the intensity of the diffraction peak is reduced, and c) the intensity of the background scattering between the diffraction peaks increases.

![Figure 3. The shift in the $2\theta$ position of the (104) peak belonging to the MgTiO$_3$ phase as a function of the calcination temperature. The data is taken from Figure 2](image)

Figures 4, 5, 6, and 7 provide the results of the refinement of the x-ray diffraction pattern of the four samples in Figure 2 using the Rietveld method and Rietica software. Figures of merit (FoM) values of the refinement that consist of the goodness of fit ($GoF$), the profile factor ($R_p$) and the weighted profile factor ($R_{wp}$) are also given for each refinement. In Figures 4-7, the +++ spectrum represents the experimental pattern, the red line is the model pattern generated based on the crystallographic data of the identified MgTiO$_3$ and TiO$_2$ rutile phases (i.e. PDF #06-0494, PDF #21-1276, ICSD #65794 and ICSD #64987). The green line is the difference in intensity height between the experimental pattern and the model pattern. The small vertical blue lines are the Bragg peaks positions of the identified MgTiO$_3$
and TiO$_2$ rutile phases. Figures 8-9 show the variation of unit cell volume of MgTiO$_3$ phase and the Molar% of MgTiO$_3$ and TiO$_2$ phases as a function of calcination temperature.

**Figure 4.** The Rietveld refinement on the XRD pattern of MZTS powder calcined at 550°C for 2 h. GoF = 1.62, $R_p$ = 10.81 and $R_{wp}$ = 12.78

**Figure 5.** The similar Rietveld refinement result as in Figure 4, but this is for MZTS powder calcined at 600°C for 2 h. GoF=1.76, $R_p$=10.73 and $R_{wp}$=10.56

**Figure 6.** The similar Rietveld refinement result as in Figures 4-5, but this is for MZTS powder calcined at 650°C for 2 h. GoF=1.99, $R_p$=9.68 and $R_{wp}$=9.92
Figure 7. The similar Rietveld refinement result as in Figures 4-6, but this is for MZTS powder calcined at 700°C for 2 h. GoF=1.50, $R_p=11.37$ and $R_{wp}=11.11$

Figure 8. Variation of the unit cell volume of MgTiO$_3$ phase in MZTS powders as a function of calcination temperature. The data was the output of the Rietveld refinement in Figures 4-7

Figure 9. Variation of Molar % of MgTiO$_3$ and TiO$_2$ rutile phases in MZTS powders as a function of calcination temperature. The data was also the output of the Rietveld refinement in Figures 4-7
As shown in Figures 4-7, all the diffraction peaks belonging to the MgTiO$_3$ and TiO$_2$ phases can be modelled and their positions coincide with the positions of the Bragg peaks. In addition, the difference in intensity between the experimental peaks and the model peaks is almost all low, as evidenced by the GoF values which are less than 2.00 [3,11,13,14]. As a result, the output of the Rietveld refinement, in this case the unit cell volume of the MgTiO$_3$ phase in Figure 8 and the molar % of the two phases in Figure 9, can be used for further analysis. In Figure 8, when the calcination temperature was increased from 550 °C to 650 °C, the unit cell volume of the MgTiO$_3$ phase increased significantly from (30.72±0.08) nm$^3$ to (32.81±0.09) nm$^3$. When the temperature was raised to 700 °C, however, the volume of the unit cell actually decreases slightly to (32.75±0.08) nm$^3$. The decrease is still well above the value at 550 °C. The fact in Figure 8 is consistent with the shift of the (104) peak position in Figure 3, i.e. the increase in temperature from 550 °C to 650 °C causes the peak to shift towards the smaller 2θ value, but at 700 °C the peak shifts slightly in the opposite direction of 2θ. The reason why the phenomenon of 2θ shift direction changes between 650 - 700 °C occurs, unfortunately cannot be explained yet. Perhaps further calcination of the sample at 800 °C could provide an answer to this phenomenon. Nevertheless, the facts in Figs. 3 and 8 are all in accordance with the theory, especially at the points a) and b). The point c) seems also to appear, in Figures 4-7.

In Figure 9, an increase in the calcination temperature from 550 °C to 700 °C also resulted in a molar % change of the MgTiO$_3$ phase in the sample, but with the opposite direction of the change in the unit cell volume in Figure 8. At 550 °C, the molar % of the MgTiO$_3$ phase is (97.91±2.21). The value then dropped to (78.81±2.28) at 650 °C before rising to (87.81±2.29) at 700 °C. The remaining % molar belongs to the rutile TiO$_2$ phase. As far as the researcher is concerned, there are no publications reporting on this composition so no comparisons can be made. However, the closest composition ever reported was Mg(Ti$_{1-x}$Sn$_x$)O$_3$ with a variation of $x = 0, 0.01, 0.02, 0.03$ and 0.04 but with a calcination temperature of 800 °C [15]. It was reported that for all these $x$ variations, the MgTiO$_3$ phase was detected as the main phase accompanied by TiO$_2$ rutile as the impurity phase. The composition with $x = 0.01$, i.e. Mg(Ti$_{0.99}$Sn$_{0.01}$)O$_3$ contained (97.03±2.52) molar % of MgTiO$_3$ phase and the unit cell volume of (30.72±1.13) nm$^3$.

3.2. EDX Analysis

Figures 10-13 depict the EDX analysis on the elemental compositions of the MZTS powders calcined at 550, 600, 650 and 700 °C for 2h using EDAX$^{TSL}$ (AMETEX).
Figure 10. EDX elemental analysis on the MZTS powder calcined at 550 °C in the red square areas
**Element** | Wt.% | At.%
--- | --- | ---
OK | 22.70 | 44.86
MgK | 12.08 | 15.72
SnL | 00.59 | 00.16
TiK | 45.35 | 29.94
ZnK | 19.29 | 09.33
Matrix Correction ZAF

**Element** | Wt.% | At.%
--- | --- | ---
OK | 35.35 | 58.96
MgK | 12.71 | 13.95
SnL | 00.53 | 00.12
TiK | 40.23 | 22.41
ZnK | 11.18 | 04.56
Matrix Correction ZAF

**Figure 11.** The similar EDX elemental analysis as in Figure 10, but this is for the powder calcined at 600°C

In Figures 10-13, the EDX measurements were performed at three different spots in the red boxes. The weight % and atomic % data along with the spectra for each element are also shown. Overall, the atomic % data of each element is relatively consistent between the three spots. By taking the atomic % data in one of spots, in Figure 10, the ratio of

\[
(Mg_{0.6}Zn_{0.4}) : (Ti_{0.95}Sn_{0.05}) : O = (24.03 + 0.25) : (17.65 + 0.10) : 57.97 = 24.28 : 17.75 : 57.97
\]  
(1)

The ideal atomic % ratio is \( \approx 19.33 : 19.33 : 57.97 = 1 : 1 : 3 \)  
(2)

By comparing the data in Equations (1) and (2), it is seen that the % of Ti atoms in Figure 10 is less than it should be. In other words, the % of Ti atoms in Equation (1) is mainly for the MgTiO\(_3\) phase. This hypothesis is in accordance with the data presented in Figures 2 and 9 for the 550 °C where the TiO\(_2\) phase is trivial, i.e. only (2.09±1.77) molar %. With the same analysis, in Figure 11, the ratio of

\[
(Mg_{0.6}Zn_{0.4}) : (Ti_{0.99}Sn_{0.01}) : O = (15.72 + 9.33) : (29.94 + 0.16) : 44.86 = 25.05 : 30.01 : 44.86
\]  
(3)

The ideal atomic % ratio is \( \approx 14.95 : 14.95 : 44.86 = 1 : 1 : 3 \)  
(4)

Therefore the % of Ti atoms in Equation (3) is excessive. This means that apart from the MgTiO\(_3\) phase, some of the Ti belongs to another phase, presumably TiO\(_2\) rutile. The hypothesis also fits the data in Figures 2 and 9 for 600 °C.
**Figure 12.** The similar EDX elemental analysis as in Figures 10-11, but this is for the powder calcined at 650°C

With the same analysis, in Figures 12 and 13, the ratio of \((\text{Mg}_{0.6}\text{Zn}_{0.4}) : (\text{Ti}_{0.99}\text{Sn}_{0.01}) : \text{O}\) are given in Equations (5) and (7), while the ideal atomic % ratio are given in Equations (6) and (8).

\[
(\text{Mg}_{0.6}\text{Zn}_{0.4}) : (\text{Ti}_{0.99}\text{Sn}_{0.01}) : \text{O} = (14.23 + 5.60) : (32.48 + 0.23) : 47.46 = 19.83 : 23.71 : 47.46 \quad (5)
\]

The ideal % atomic ratio is \(\approx 15.82 : 15.82 : 47.46 = 1 : 1 : 3\) \quad (6)

\[
(\text{Mg}_{0.6}\text{Zn}_{0.4}) : (\text{Ti}_{0.99}\text{Sn}_{0.01}) : \text{O} = (15.64 + 6.16) : (27.52 + 0.32) : 50.36 = 21.80 : 27.84 : 50.36 \quad (7)
\]

The ideal % atomic ratio is \(\approx 16.79 : 16.79 : 50.36 = 1 : 1 : 3\) \quad (8)

Based on the % of Ti atoms data in Equations (5) and (7), it turns out that the % of Ti atoms at 650 and 700 °C is excessive so that the presence of other phases containing Ti besides MgTiO\(_3\) becomes clear. As is the case at 550 and 600 °C, the intended phase may be TiO\(_2\) rutile. Again, this hypothesis corresponds to data in Figure 9 for 650 and 700 °C.
Element | Wt.% | At.%
------- | ------ | ------
OK      | 30.15  | 53.51  
MgK     | 12.74  | 14.88  
SnL     | 01.16  | 00.28  
TiK     | 44.37  | 26.30  
ZnK     | 11.59  | 05.03  
Matrix  | Correction | ZAF

Figure 13. The similar EDX elemental analysis as in Figures 10-12, but this is for the powder calcined at 700°C

4. Conclusion
A series of analyses on the formation of the MgTiO$_3$ phase in (Mg$_{0.6}$Zn$_{0.4}$)(Ti$_{0.99}$Sn$_{0.01}$)O$_3$ powders with a calcination temperature of 550-700°C using XRD and EDX data have been completed. The two types of data support each other, i.e. the MgTiO$_3$ phase was formed as the main phase accompanied by TiO$_2$ rutile as the impurity phase. The increase in calcination temperature causes the MgTiO$_3$ content to decrease. The temperature of 550°C gives the most optimum MgTiO$_3$ molar %.

References
[1] Zhang J, Yue Z, Luo Y, and Li L 2018 Ceram. Int. **44** 21000
[2] Wu H T, Jiang Y S, Cui Y J, Zhang X H, Jia X, and Yue Y L 2012 J. Electron. Mater. **42** 445
[3] Ermawati F U, Pratapa S, Suasmoro S, Hübert T, and Banach U 2016 J. Mater. Sci. Mater. Electron. **27** 6637
[4] Kadarosman A and Ermawati F U 2021 J. Neutrino **13** 67
[5] Ermawati F U 2021 J. Phys. Conf. Ser. **1805** 012039
[6] Izza L and Ermawati F U 2021 J. Ilmu Fis. **13** 62
[7] Samyuktha V S, Subbarao T, Suvarna R P, and Kumar A G 2017 J. Ovonic Res. **13** 33
[8] Hsu C H and Chang C H 2015 Ceram. Int. **41** 6965
[9] Zhang M, Li L, Xia W, and Liao Q 2012 J. Alloys Compd. **537** 76
[10] Xue X, Yu T, and Xu G 2013 J. Mater. Sci. Mater. Electron. **24** 1287
[11] Ermawati F U, Suasmoro S, and Pratapa S 2015 *Adv. Mater. Res.* **1112** 47
[12] Cullity D and Stock S R 2014 *Elements of X-Ray Diffraction 3rd Edition* (New York: Pearson)
[13] Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65
[14] Post J E and Bish D L 2018 *Rietveld Refinement of Crystal Structures Using Powder X-Ray Diffraction Data in: Modern Powder Diffraction* (USA: De Gruyter) p 277
[15] Ermawati F U, Ahfa M H, and Supardiyono 2019 *J. Phys. Conf. Ser.* **1171** 012038