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To cite this article: F U Ermawati and S Suasmoro 2018 J. Phys.: Conf. Ser. 997 012005

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Dilatometric shrinkage study on magnesium titanate-based ceramic systems

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Abstract. The development of dielectric materials for applications in the microwave frequencies has been increasing with rapid progress in mobile and satellite communication systems. Magnesium titanate (MgTiO₃)-based ceramics have been the favourite candidates for such applications due to their excellent dielectric characteristics, *i.e.* a moderate level of dielectric constant together with a high-quality factor and high-temperature stability. These outstanding performance, however, can only be achieved when the ceramics are highly dense. The work reported in this paper discussed the study on the dilatometric shrinkage behaviour of pure and zinc-doped magnesium titanate (Mg_{1-x}Zn_xTiO₃ for x = 0-0.5) ceramic systems after the systems following the heating passage up to 1300 °C. The results were discussed based on the phase formation data recorded from powder X-ray diffraction (XRD). An additional 2 wt. % V_2O_5 to the MZT0.2 system has increased the shrinkage of the system, and hence the relative density. The V_2O_5 addition also prevented the grain growth and did not alter the structure. From 100 Hz to 20 MHz, the dielectric permittivity is constant; which varies from $(15.4 - 17.0) \pm 0.1$ % throughout the samples, these values are therefore frequency independent.

1. Introduction

Magnesium titanate (MgTiO₃) has been recognised to have a relative permittivity and other dielectric properties that are suitable for applications at high frequencies. Research on this dielectric ceramic material has been started since the last two decades, and the dielectric-performance reports on this ceramic in various microwave-frequencies have been available after that [1-4]. Many efforts have been taken to improve the characteristic of the ceramic [5-8]. One of the aspects to be considered in fabricating a good ceramic is the density. Ceramic with high relative density is advantageous as the measured permittivity represents the material permittivity without the inclusion of the vacuum permittivity.

The work reported in this paper is intended to study the dilatometric shrinkage on the magnesium titanate-based dielectric ceramics (Mg_{1-x}Zn_xTiO₃ for x = 0 - 0.5). The aim was to see the dielectric performance of the ceramics. This paper also presents the discussion on the similar shrinkage from another $Mg_{0.8}Zn_{0.2}TiO_3$ system after the inclusion of V_2O_5 . A fraction of V_2O_5 was added into the

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system as an effort to reduce the sintering temperature of the system. The resulting density, the structure, the microstructure and the relative permittivity of the developed ceramics were discussed.

2. Experiment

Six different compositions of $Mg_{1-x}Zn_xTiO_3$ powders for x = 0 - 0.5 (MZT0 – MZT0.5) were synthesised following the liquid mixing method [9-10]. The starting materials and the solvent were Mg, Zn and Ti metal powders (Merck) and hydrochloric acid (HCl). For each composition, each metal powder was weighed carefully according to the $Mg_{1-x}Zn_xTiO_3$ stoichiometry and dissolved individually in HCl using a magnetic stirring hotplate. The resulting liquids were homogeneously mixed and dried. The dried powder was crushed to produce homogeneous-grain-size powder. The zinc-doped MZT0.1 – MZT0.5 powders were subsequently calcinated at 550 °C for 2 hours at the heating rate of 10 °C/min using a Carbolite RHF-1400 furnace, while the zinc-free MZT0 powder was calcined at 700 °C for 2 hours.

Dilatometric shrinkage behaviour of MZT0 – MZT0.5 ceramics was investigated by preparing the green bodies of the respective calcined powders with the dimensions of $5 \times 5 \times 20$ mm³ using a rectangular uniaxial die and pressing at 100 MPa in the atmospheric environment using a hydraulic hand press. The green bodies were heated from room temperature to 1300 °C using an L76 Platinum Series Dilatometer (Linseis) at the heating rate of 10 °C/min. The shrinkage behaviour of another MZT0.2 system, i.e. the MZT0.2 system with the inclusion of 2 weight (wt.) % V₂O₅, was also examined. The addition of such a liquid agent into the system was intended to see the possibility of reducing the sintering temperature of the ceramic due to the formation of the liquid phase of V₂O₅ at the melting point which is below the sintering temperature. For that purpose, both MZT0.2 and V_2O_5 powders were weighed at the prescribed wt. % ratio and were mixed using zirconia balls for 2 hours in a planetary ball mill under ethanol environment. The ratio between the powder mass, the zirconia balls and the ethanol were 1: 5: 5/3. The mixed slurry was subsequently separated from the ethanol using a rotary evaporator operated at 20 rotations per minute for 1 hour and 90 °C. The powder product was stored in the oven for overnight to ensure that all ethanol evaporated. The dried powder was crushed manually using a mortar and pestle for gaining the homogeneous grain size powder. The resulting powder was then ready for the dilatometric shrinkage study.

For dielectric property characterisation, the green bodies of all the samples were prepared using a uniaxial die in the form of a disc and the hydraulic hand press. The powders were pressed at the same pressure (100 MPa) and sintered using a Carbolite RHF-1400 furnace at the temperature suggested by the dilatometric shrinkage curves. Sintering was performed in the atmospheric environment and at the same heating rate (10 °C/min). The bulk density of the ceramics was measured following the Archimedes technique. The structural analysis was performed using a Philips X'Pert Multi-Purposes Diffractometer System with CuK_{α} radiation. The microstructural data was recorded using a scanning electron microscope (SEM) CARL ZEISS EVO MA 10. The dielectric property in the form of real part of the relative permittivity (ε'_r) was measured at room temperature from 1 Hz to 20 MHz using an SI 1260 Impedance/Gain-Phase Analyzer (Solartron Analytical).

3. Results and Discussion

3.1. Dilatometric shrinkage of green bodies

The following subsubsections provide the dilatometric shrinkage data measured from all the samples $(MZT0 - MZT0.5 \text{ and } MZT0.2 + 2 \text{ wt. } \% \text{ V}_2\text{O}_5)$ recorded using the L76 Platinum Series Dilatometer (Linseis) and the analyses.

3.1.1. MZT0 - MZT0.5. Figure 1 shows the intended shrinkage curves ($\Delta L/Lo$) as a function of temperature recorded from MZT0 - MZT0.5 samples. As observed, all the curves experience contraction as indicated by dropping of the curves, starting at 800 - 850 °C and this lasts up to 1300

°C. The total shrinkage varies from 12.8 - 14.0 %. At the temperature around 1100 °C, the shrinkage rate slows down as signified by the presence of a dip on the curves. This particular concave-shaped curve is seen in the samples containing zinc (MZT0.1 - MZT0.5), but not for the one without zinc (MZT0).



To understand the dip co-presence in Figure 1, the MZT0.2 (without V_2O_5) was sintered at two different temperatures, each at 900 °C (*i.e.* before the dip position in Figure 1) and at 1300 °C (after the dip) for 8 hours. Figure 2 depicts the XRD patterns of the intended MZT0.2 after sintering at 900 and 1300 °C.



IOP Conf. Series: Journal of Physics: Conf. Series **997** (2018) 012005 doi:10.1088/1742-6596/997/1/012005

 $Mg_{0.8}Zn_{0.2}TiO_3$, * = Mg_2TiO_4 , a = $MgTi_2O_5$, b = TiO_2

In Figure 2, the 900 °C pattern consists of the main Mg_{0.8}Zn_{0.2}TiO₃ phase (the peaks labelled '+') accompanied by MgTi₂O₅ ('a') and TiO₂ rutile ('b') as the minor phases. The identified MgTi₂O₅ phase coincides with the powder diffraction file (PDF) No. 35-0792, while the TiO₂ phase agrees with the PDF No. 21-1276. The detected Mg_{0.8}Zn_{0.2}TiO₃ phase matches the MgTiO₃ (PDF No. 06-0494). The X-ray diffractometer also identified the Mg_{0.8}Zn_{0.2}TiO₃ phase on the 1300 °C pattern. The accompanying secondary phase on this particular pattern, however, is different, *i.e.* Mg₂TiO₄ (the peaks labelled '*'). This crystalline phase matches the PDF No.25-1157. The fact is that, after sintering at 1300 °C, the X-ray diffractometer only detected the minor Mg₂TiO₄ phase, while the MgTi₂O₅ and TiO₂ phases were not. This fact gives a strong indication that during the sintering process, a reaction between TiO₂ and an amorphous 'phase' containing magnesium oxide took place to form the secondary Mg₂TiO₄ phase, possibly via the process of 2MgO + TiO₂ \rightarrow Mg₂TiO₄. This side reaction is considered to be detrimental because this has slowed the shrinkage rate, and the loss is indicated as the concave-shaped curve at 1100 °C in Figure 1. Based on this result, all the samples were subsequently sintered at 1400 °C for 8 hours using the Carbolite RHF-1400 furnace at the heating rate of 10 °C/min.

3.1.2 MZT0.2 with V_2O_5 addition. Figure 3 shows the shrinkage curve of MZT0.2 + 2 wt. % V_2O_5 sample, together with that of the MZT0.2 without V_2O_5 addition (in Figure 1). As observed, both curves started to shrink at the similar temperature, 800 °C. Above that temperature, the curve with V_2O_5 experiences a total shrinkage of up to 14.4 %. This percentage is higher than that of the curve without V_2O_5 (12.8 %). During heating, V_2O_5 with low melting point (656 - 690 °C) formed a liquid phase. The presence of such liquid caused the capillary force to attract fluid into the pores. This attraction gave rise the grains to rearrange the positions to be more stable. In the areas where the capillary pressure is high, *i.e.*, in the places where the particles are close together, the atoms were likely to enter the solution and resided in the areas with a lower chemical potential. The smaller particles moved toward the solid-solution structure and stayed on the larger particles causing compaction. This compacting process spread throughout the system. Due to the presence of V_2O_5 , the shrinkage process occurred more quickly and the total percentage is, therefore, higher as depicted in Figure 3. Based on that, the MZT0.2 sample with V_2O_5 addition was subsequently sintered at 1100 °C for 4 hours. The subsection 3.2 provides the density, the structure, the microstructure and the dielectric characteristic data on this particular ceramic, together with that of the other ceramics without V_2O_5 .



3.2. Ceramic density, structure, microstructure and dielectric characteristic

Figure 4 depicts the relative density of MZT0 – MZT0.5 ceramics after sintering at 1400 °C for 8 hours and of MZT0.2 with V_2O_5 after sintering at 1100 °C for 4 hours. As shown, the relative density of the MZT0 – MZT0.5 ceramics, in general, increases with the zinc content, *i.e.* from 90.0 % of the theoretical density in MZT0 to 92.4 % in MZT0.5. The zinc content has increased the relative density of the systems. In Figure 4, the percentage of the MZT0.2 with V_2O_5 addition is 94.5 % which is considerably higher than that of the same ceramic without V_2O_5 (89.9 %). The V_2O_5 content in MZT0.2 has played a role in increasing the density.



The content of V_2O_5 was not found to alter the structure of the MZT0.2 system, as depicted in Figure 5. As observed, the two patterns consist of the same phases, *i.e.* MgTiO₃ (the peaks with *hkl*) and Mg₂TiO₄ (the peaks labelled '*'). There is no phase containing zinc or vanadium was recorded on the patterns. This disappearance suggested that the zinc ions entered the magnesium sites because the radius of magnesium and zinc ions are similar, and the resulting phase is Mg_{0.8}Zn_{0.2}TiO₃. The vanadium ions, as mentioned before, has turned to be the liquid phase at its melting point and might remain as an amorphous phase at higher temperatures.

doi:10.1088/1742-6596/997/1/012005



Figure 6 compares the XRD patterns recorded from all the samples (MZT0 – MZT0.5 and MZT0.2 with V₂O₅). As depicted, the spectra are composed of the diffraction peaks derived from the two phases, *i.e.* Mg_{1-x}Zn_xTiO₃ (the peaks with *hkl*) and Mg₂TiO₄ ('*'). This result confirmed that variation of the zinc content (*x*-values) in the Mg_{1-x}Zn_xTiO₃ without V₂O₅ and the inclusion of 2 wt. % V₂O₅ in the Mg_{0.8}Zn_{0.2}TiO₃ does not change the structure of Mg_{1-x}Zn_xTiO₃ ceramics. Instead, the co-presence of Zn and V₂O₅ improved the density of the systems.



with $(hkl) = MgTiO_3$, * = Mg₂TiO₄.

Figure 7 provides the microstructure of MZT0.2 ceramic with and without V_2O_5 addition recorded from the SEM CARL ZEISS EVO MA 10. As observed, the morphology and the grain size of the two samples are different. The grains in the sample containing V_2O_5 (Figure 7a) elongate in one direction with the thickness of about 1 μ m. The tiny grains are also pictured. In the sample without V_2O_5 (Figure 7b), however, the grains had grown, and the size is almost uniform, *i.e.* 3-5 μ m. The grain boundaries are visualised. The grain growth is due to the high sintering temperature (at 1400 °C). In addition, to reducing the sintering temperature, the co-presence of V_2O_5 in the MZT0.2 system was confirmed to prevent the grain growth.



Figure 8 shows the characteristic of real part of permittivity (ε'_r) of MZT0 – MZT0.2 and MZT0.2 with V₂O₅ addition measured from 1 Hz to 20 MHz using the SI 1260 Impedance/Gain-Phase Analyzer. All samples display the similar character, *i.e.* at 1 Hz, the ε'_r values reach the maximum before declining exponentially and constant afterwards. The maximum ε'_r at 1 Hz varies from 72 ± 0.1 % in MZT0.2 with V₂O₅ addition. From 100 Hz to 20 MHz, the ε'_r values are constant (15.4 to 17.0) ± 0.1 % throughout the samples. These findings are showing that the dielectric characteristics of the developed ceramics are similar to each other.

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4. Conclusion

The dilatometric shrinkage study on the $Mg_{1-x}Zn_xTiO_3$ dielectrics has been carried out. The use of V_2O_5 is very significant in increasing the density of the ceramics and preventing the grain growth. This particular liquid agent does not alter the structure of the ceramics as well as the dielectric characteristic of the ceramic systems.

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