Contribution of Relaxation Effect to the Permittivity of Mg$_{1-x}$Zn$_x$TiO$_3$ Ceramics

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Abstract. This work reported the investigation on the effect of relaxation to the permittivity ($\varepsilon'$) characteristic of Mg$_{1-x}$Zn$_x$TiO$_3$ ceramics for $x = 0$ – 0.5 (MZT0 – MZT0.5) measured from 1 Hz to 330 MHz. Within that frequency range, the relaxation effect that consists of the space charge (SC) and the dipolar (D) polarization mechanisms were identified. The contribution of the D relaxation in MZT0 – MZT0.2 systems extents overall from about 100 Hz to 330 MHz, while that in MZT0.3 – MZT0.5 systems is from 50 kHz to 330 MHz. The remaining frequencies, i.e. from 1 to 90 Hz for MZT0 – MZT0.2 and from 1 Hz to 50 kHz for MZT0.3 – MZT0.5, are attributed to the SC relaxation. The D polarization mechanism provides constant $\varepsilon'$ values which vary from (15.4 – 17.0) ± 0.3 throughout the samples. Contribution of the SC polarization mechanism to the characteristic is supported by the simultaneous presence of different content and level of resistivity of the secondary phase of (Mg$_{1-x}$Zn$_x$)$_2$TiO$_4$ in MZT0 – MZT0.2 systems and of (Zn$_{1-x}$Mg$_x$)$_2$TiO$_4$ in MZT0.3 – MZT0.5, along with the presence of the main Mg$_{1-x}$Zn$_x$TiO$_3$ phase, as a result of the variation of zinc content in the systems.

Keywords. Dielectric ceramic, dipolar polarization, Mg$_{1-x}$Zn$_x$TiO$_3$, permittivity, and space charge polarization.

1. Introduction
Magnesium titanate (MgTiO$_3$) with ilmenite structure has been a favorite dielectric ceramic candidate for using as electronic components in various applications in communication systems operating at microwave frequencies such as resonators, filters, and antennas for global positioning systems [1, 2], as well as type I capacitors [3, 4]. These are due to characteristics of the dielectric met the important criteria for using in the microwave frequencies, i.e. a high relative permittivity ($\varepsilon'$) to reduce the size of the components, especially when miniaturization of microwave circuits has been a concern in wireless communication industry, a high-quality factor ($Q\times\nu$) to increase the frequency selectivity, and a good temperature stability ($\tau$) to ensure the performance stability at high temperatures [4].

Polarization processes in ceramic dielectrics due to the application of electric field occurs via relaxation and resonance effects. Dielectric relaxation refers to the relaxation response of a dielectric
medium to an external, oscillating electric field. Such response, which is due to space charge (SC) and dipolar (D) polarizations, is often described in terms of permittivity as a function of frequency in the range below $10^{10}$ Hz; and for ideal systems this response can be described by the Debye equation [5]. On the other hand, dielectric sonance results from the distortion related to ionic and electronic polarizations that shows the behavior of the resonance type at optical frequencies since the resonances of electrons in atoms and of ions in crystals occur at optical frequencies (about $10^{15}$ Hz and $10^{13}$ Hz respectively) [5]. Information on how the relaxation and the resonance effects contribute to the nature of permittivity of dielectric material is therefore advantageous. As far the author's concern, however, the number of reports to discuss this matter is very limited.

This paper is devoted to reporting the study on the characteristic of real part of the relative permittivity ($\varepsilon'$) of Mg$_{1-x}$Zn$_{x}$TiO$_3$ dielectric ceramic systems measured from 1 Hz to 330 MHz, to identify the relaxation effect within that frequency range in the form of SC and D polarization mechanisms, and to investigate the contribution of those polarization mechanisms to the $\varepsilon'$ characteristic. Analyses were related to the structural data and the electrical property of the identified phases in the systems.

2. Materials and methods
The six different compositions of Mg$_{1-x}$Zn$_x$TiO$_3$ dried powders for $x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5 (MZT0 – MZT0.5) were synthesized from Mg, Ti and Zn metal powders (Merck©) following the dissolved-metals-mixing procedure reported in [6, 7]. The MZT0 – MZT0.5 green bodies were prepared using a uniaxial die in the form of a disc and to press at 100 MPa using a Weber-hand hydraulic press. A Carbolite RHF-1400 furnace was occupied to sinter the bodies. Sintering was performed in the atmospheric environment and at the heating rate of 10 °C/min. The bulk density was measured following the Archimedes technique. Structural characterization of the sintered ceramics was performed using X’Pert Diffractometer (Philips) with CuKα radiation. Dielectric property in the form of real part of the relative permittivity ($\varepsilon'$) were measured from 1 Hz to 32 MHz using SI 1260 Impedance/Gain-Phase Analyzer (Solartron Analytical), followed by from 1 kHz to 330 MHz using HP 4291A RF Impedance/Material Analyzer and HP 16453A Dielectric Test Fixture (Agilent). All the measurements were performed at room temperature (23 ± 2) °C.

3. Results and discussion
3.1. The Origin of Space Charge and Dipolar Polarization Mechanisms
Polarization processes in ceramic dielectric systems are related to the resonance and relaxation effects. The first effect is in the form of electronic and ionic polarizations that takes place at optical frequencies (about $10^{15}$ Hz and $10^{13}$ Hz, respectively). The second effect, i.e. the effect that was under investigation in this work, consists of the dipolar (D) and the space charge (SC) polarizations that occur at lower frequencies, below $10^{10}$ Hz [5]. The SC relaxation involves a limited transport of charge carriers, in this case, in the form of distribution of thermally excited electrons above 0 K in the Fermi-Dirac statistic. Such transport will be stopped at a potential barrier, possibly in the form of a grain boundary or an inter-phase boundary. The applied electric field polarizes the distribution of thermally excited electrons following the orientation of crystal lattices. Meanwhile, the D polarization is due to the presence of permanent electric dipoles in the crystal lattices, could be the oscillation of cations or cation-anion bonds in the system. In the case of the MZT0 – MZT0.5 dielectric ceramics under investigation, the intended permanent dipoles are therefore addressed to the oscillation of Ti$^{4+}$ and Mg$^{2+}$ cations in MZT0 system and of Ti$^{4+}$ and (Mg$_{1-x}$Zn$_x$)$^{2+}$ cations in MZT0.1 – MZT0.5 systems, or the oscillation of TiO$_6$ and MgO$_6$ bonds in the crystal lattices of MZT0 and of TiO$_6$ and (Mg$_{1-x}$Zn$_x$)O$_6$ bonds in the crystal lattices of MZT0.1 – MZT0.5 as a result of the ABO$_3$ stoichiometry of the ilmenite structure of the systems, where A and B are cations while O is anion.
3.2. Dielectric Characteristic: Real Part of Relative Permittivity

Figure 1 provides characteristics of the real part of relative permittivity ($\varepsilon'$) of MZT0 – MZT0.5 ceramic systems after the systems were sintered at 1400 °C for 8 h and that were measured from 1 Hz to 330 MHz using SI 1260 Impedance/Gain-Phase Analyzer (Solartron Analytical), HP 4291A RF Impedance/Material Analyzer and HP 16453A Dielectric Test Fixture (Agilent).

A dielectric relaxation response usually consists of relative permittivity ($\varepsilon_r$) recorded from two different zones. The first zone located in the low-frequency region is signified by an exponential decrease of $\varepsilon_r$-values and high loss factor ($\tan \delta$). These exponential decrease and the high loss factor characteristics were considered due to the presence of SC polarization as a result of the accumulation of mobile charges at structural surfaces and interfaces. The second zone is located at the frequencies which are higher than that of the first zone. Such zone is marked by a relatively constant $\varepsilon_r$ due to the presence of permanent dipoles in the crystal structure. All the features described in the two different zones are recorded on the curves in Figure 1. As shown, the $\varepsilon_r'$ curves reach the maximum values at 1 Hz and then decline exponentially before being constant thereafter. The decline exponential part is therefore justified as the SC polarization contribution, while the constant and the frequency independent part is contributed by the D polarization. Figure 1 also depicts that in MZT0 – MZT0.2 curves, the $\varepsilon_r'$ values at 1 Hz are all similar, i.e. (76.0 ± 1.0) for MZT0, (69.4 ± 1.0) for MZT0.1 and (89.5 ± 1.2) for MZT0.2. Another similarity of the $\varepsilon_r'$ values at 1 Hz are also shown in MZT0.3 – MZT0.5 curves, i.e. (11,372.0 ± 110.0) for MZT0.3, (16,261.0 ± 130.0) for MZT0.4 and (122.0 ± 1.5) for MZT0.5. The three later values, on average, are 1000 times higher than the three former values. This significant difference is believed mainly due to the population number difference of the charge carriers that are successfully passing through the potential barriers existed in the systems. In this case, the number of existing populations in MZT0.3 – MZT0.5 ceramics are about 1000 times higher than that in MZT0 – MZT0.2 ceramics. In a polycrystalline and mixed-phase ceramic, the SC polarization is predominantly arising from the difference between the conductivity of the phases present. Analysis on the conductivity of the phases present in MZT0 – MZT0.5 ceramics is provided in the following paragraphs and the data was supported by the phase identification result on the XRD spectra shown in Figure 2 and the Rietveld analysis in Figure 3.
Figure 2. The XRD spectra (CuKα radiation) of: (a) MZT0 – MZT0.2 and (b) MZT0.3 – MZT0.5 ceramics sintered at 1400 °C for 8 h. The indexed peaks = Mg1-xZnxTiO3, a = (Mg1-xZnx)2TiO4 and b = (Zn1-xMgx)2TiO4.

Figure 2 shows the XRD spectra of MZT0 – MZT0.5 ceramics after sintering at 1400 °C for 8 h. On each spectrum, two different phases are identified: 1) MgTiO3 (PDF No. 06-0494) as the main phase, i.e. peaks with hkl and 2) the peaks labeled ‘a’ and ‘b’ as the secondary phase. The phase identification analysis on these secondary ‘a’ and ‘b’ phases reveals that the 2θ position and the variation of relative intensity of the ‘a’ peaks recorded in the MZT0 – MZT0.2 spectra corresponds to the 2θ position and the variation of relative intensity of Mg2TiO4 phase (PDF No. 25-1157). Meanwhile the 2θ position and the variation of relative intensity of the ‘b’ phase detected in the MZT0.3 – MZT0.5 spectra matches the 2θ position and the variation of relative intensity of Zn2TiO4 (PDF No. 77-0014). Based on the Rietveld analysis data in Figure 3, the intended main phases are Mg1-xZnxTiO3 solid solution that can be indexed as MgTiO3, while the secondary phases are (Mg1-xZnx)2TiO4 and (Zn1-xMgx)2TiO4 solid solutions that can be indexed as Mg2TiO4 and Zn2TiO4 respectively; in this case, the α-values are unknown. The porosity data in Figure 3B was 1 – RD, where RD is the fraction of relative density. The relative density is the ratio between the bulk density and the theoretical density. The theoretical density is the output of the Rietveld analysis.

Kumar [8] reported that Mg2TiO4 dielectric exhibits the characteristic of AC conductivity which varies from 5.0×10^4 (Ω·cm)^-1 at 75 kHz to 1.5×10^4 (Ω·cm)^-1 at 20 MHz. Meanwhile, Obadovic [9] measured the characteristic of resistivity of Zn2TiO4 dielectric of 1.02 Ωm at 4 MHz. This value corresponds to a conductivity of approximately 0.98 (Ω·m)^-1. These two-conductivity data confirmed that the (Mg1-xZnx)2TiO4 phases detected in the MZT0 – MZT0.2 ceramics are very resistive as compared to the (Zn1-xMgx)2TiO4 phases recorded in the MZT0.3 – MZT0.5 ceramics. Filipovic [10] measured the electrical resistivity of 0.38 MΩ·m at 5 MHz from the MgTiO3 dielectric. This value is equivalent to a conductivity of about 2.63 (µΩ·m)^-1. Based on this literature, MZT0.3 – MZT0.5 ceramics were justified to be more conductive than MZT0 – MZT0.2 ceramics. Potential barriers in conductive dielectrics are much lower than the height of the same barriers in resistive dielectrics. As a result, the motion of charge carriers passing through the barriers in MZT0.3 – MZT0.5 ceramics should be easier and smoother than when the similar charge carriers going through the barriers in MZT0 – MZT0.2 ceramics. The population number of the charge carriers at the boundaries in MZT0.3 – MZT0.5 ceramics are therefore much greater than the similar number found at the boundaries in MZT0 – MZT0.2 ceramics. Bigger population numbers mean a larger polarization and, hence, a higher permittivity value. For that reason, at 1 Hz, the εrı values in MZT0.3 – MZT0.5 ceramics should be higher than the values in MZT0 – MZT0.2 ceramics; that is what is shown in Figure 1.
Figure 3. (a) Unit cell volume of the \((\text{Mg}_{1-x}\text{Zn}_x\text{TiO}_3), (\text{Mg}_{1-x}\text{Zn}_x)_2\text{TiO}_4\) and \((\text{Zn}_{1-x}\text{Mg}_x)_2\text{TiO}_4\) solid solutions. (b) The volume fraction of the three phases and of the porosity present in the systems.

As the frequency in Figure 1 increases, the SC polarization effect to the \(\varepsilon'_r\) values of the ceramics become less important and the role was replaced by the D polarization. Based on the above analysis, it is obvious that the values of \(\varepsilon'_r\) at 1 Hz in MZT0.3 – MZT0.5 ceramics will decay within a wide frequency range, *i.e.* by order of about 1 kHz of the similar frequency range observed in MZT0.1 – MZT0.2 ceramics. The D interaction response to the \(\varepsilon'_r\) values is frequency independent, as shown in Figure 1. The region between SC and D polarizations is called the transition area. Table 1 lists the location of the SC and the D polarization regions and their transition area, as well as the frequency independent \(\varepsilon'_r\) values recorded in the D polarization region recapitulated from Figure 1. As observed, in general, the \(\varepsilon'_r\) values in the D polarization region increase with the zinc content.

### Table 1. Space charge and dipolar polarization regions and their transition area and the frequency independent \(\varepsilon'_r\) values in MZT0 – MT0.5 dielectric ceramic systems.

| Sample    | The SC polarization region (± 0.1 %) | The transition area (± 0.1 %) | The D polarization region (± 0.1 %) | The \(\varepsilon'_r\) values in the D polarization region |
|-----------|-------------------------------------|------------------------------|-------------------------------------|---------------------------------------------------------------|
| MZT0      | \((1.0 – 12.2)\) Hz                 | \((13.0 – 80.0)\) Hz         | \((120.0 \text{ Hz} – 330.0 \text{ MHz})\) | \(15.4 \pm 0.3\)                                              |
| MZT0.1    | \((1.0 – 7.0)\) Hz                  | \((8.0 – 80.0)\) Hz          | \((127.0 \text{ Hz} – 330.0 \text{ MHz})\) | \(16.2 \pm 0.3\)                                              |
| MZT0.2    | \((1.0 – 10.4)\) Hz                 | \((20.0 – 30.5)\) Hz         | \((80.0 \text{ Hz} – 330.0 \text{ MHz})\) | \(15.1 \pm 0.3\)                                              |
| MZT0.3    | \(1.0 \text{ Hz} – 15.7 \text{ kHz}\) | \((32.0 – 80.0)\) kHz       | \((120.0 \text{ kHz} – 330.0 \text{ MHz})\) | \(16.3 \pm 0.3\)                                              |
| MZT0.4    | \(1.0 \text{ Hz} – 18.3 \text{ kHz}\) | \((20.0 – 30.0)\) kHz       | \((32.5 \text{ kHz} – 330 \text{ MHz})\)  | \(16.2 \pm 0.3\)                                              |
| MZT0.5    | \(1.0 \text{ Hz} – 1.5 \text{ kHz}\) | \((2.0 – 4.0)\) kHz         | \((5.0 \text{ kHz} – 330 \text{ MHz})\)   | \(17.0 \pm 0.3\)                                              |

4. Conclusions

Dielectric characteristic of the real part of the relative permittivity \(\varepsilon'_r\) in \(\text{Mg}_{1-x}\text{Zn}_x\text{TiO}_3\) \((x = 0 – 0.5)\) ceramic systems from 1 Hz to 330 MHz has been analyzed based on the phase composition data and the electrical properties of the identified phases. Contribution of the space charge and the dipolar polarization mechanisms to the characteristic were confirmed and the \(\varepsilon'_r\) values were justified. Variation of the zinc content in the systems has classified the systems into two different sub-systems, each with different conductivity level.
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