Role of Zn Substitution on Improvement of Electromagnetic and Microwave Absorption Characteristics of BaTi\(_{1-x}\) Zn\(_x\)O\(_3\) (x= 0; 1/3; ½; 2/3; 1)

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Abstract. In the current study, we have explored the electromagnetic and microwave absorption characteristics, especially the permeability, permittivity and reflection loss of magnetoelastic BaTi\(_{1-x}\)Zn\(_x\)O\(_3\) with x = 0; 1/3; ½; 2/3; 1. The composition was selected to include the effect of structural change when Ti is substituted with Zn in BaTi\(_{1-x}\)Zn\(_x\)O\(_3\) material system. When x = 0, the Zn free BaTiO\(_3\) possesses a tetragonal phase with lattice parameters a = b = 3.996361 Å and c = 4.029751 Å. The lattice parameters changed when x > 0 and phase transformation as well as material structure change occurred when x = 1. In addition, the effect of the geometric effect of replacing Ti ions with Zn which has a bigger ion radius will increase the absorption of electromagnetic waves.

1. Introduction

Microwave Absorbing Materials (MAM) are currently being explored by researchers for applications in high-speed wireless communication systems to reduce electromagnetic waves that affect human health [1-3]. For military applications MAM is usually used to avoid radar detection [1, 2]. Good candidates that meet the requirements of MAM are those materials that have high complex electrical permittivity (\(\varepsilon' - j\varepsilon''\)) and complex magnetic permeability (\(\mu' - j\mu''\)) which contribute to increasing the reflection loss value (RL) [3]. Property like complex permittivity and permeability reflect the electromagnetic waves absorption characteristics of MAM.

Research on electromagnetic wave absorbing materials based on BaTiO\(_3\) is very unique considering that this material has perovskite structure and poor ferromagnetic properties [4]. A good MAM is to tune the combination of these two properties [5, 6] in obtaining a matching impedance which provides a better absorption effect. The preparation methods employed for the fabrication of BaTiO\(_3\) based material, mostly are a sol gel, coprecipitation, conventional ceramic techniques, In-situ chemical oxidative polymerization and there are still few using solid state reaction [6].

Barium titanate (BaTiO\(_3\)) is a dielectric compound and has a small complex permeability. Despite dielectric constant pertaining in BaTiO\(_3\) relatively large, its performance for MAM is found still relatively low [4]. In this study, we report results of our current studies on the improvement of
absorbing capability of zinc doped barium titanate of BaTi\((1 - x)\)Zn\(_x\)O\(_3\) (BTZ). The x is selectively selected being 0; 1/3; ½; 2/3; 1.

2. Experimental method

Stoichiometry quantities of standard research-grade BaCO\(_3\), TiO\(_2\), ZnO precursors were mixed and wet milled in a high energy milling (Shaker Mill), with the addition of alcohol until 60 % volume for 10 hours. All mixed precursors were mechanically alloyed produced heavy deformed powder materials. The powder materials of BaTiO\(_3\) composition were then dried and sintered at 1200 °C for 3 hours. Whereas dried powders of BaTi\(_{2/3}\)Zn\(_{1/3}\)O\(_3\) and BaTi\(_{1/2}\)Zn\(_{1/2}\)O\(_3\) compositions were sintered at 1100 °C and those of BaTi\(_{1/3}\)Zn\(_{2/3}\)O\(_3\) and BaZnO\(_3\) compositions were sintered at 1000 °C. The BaTi\(_{1 - x}\)\(_x\)Zn\(_x\)O\(_3\) compound has been prepared using solid state reaction.

The characterization of polycrystalline samples was characterized by X-Ray Diffraction (Bruker D8 Advance). XRD data of polycrystalline samples were refined by GSAS for structural analysis. Microwave absorption properties were measured by Vector Network Analyzer (Advantest R3770 300 kHz - 20GHz). While complex permittivity (\(\varepsilon' - j\varepsilon''\)) and permeability (\(\mu' - j\mu''\)) values were calculated by Nicolson-Ross-Weir (NRW) method.

3. Results and discussion

All samples with BaTi\((1 - x)\)Zn\(_x\)O\(_3\) compositions were successfully characterized by X-ray diffraction (XRD). Figure 1 compares all diffraction patterns of mechanically alloyed BaTi\((1 - x)\)Zn\(_x\)O\(_3\) powders which show typical of crystalline sample. Obviously, the diffraction pattern of all samples indicates a similar pattern, but with an additional indication that the diffraction peaks are shifted due to partial substitution of Zn.

![Figure 1](image.png)

**Figure 1.** (a) XRD spectrum of BaTi\((1 - x)\)Zn\(_x\)O\(_3\) \((x = 0; 1/3; ½; 2/3; 1)\) and (b) Shift in peak intensity of BaTi\((1 - x)\)Zn\(_x\)O\(_3\) \(x = 0; 1/3; ½; 2/3; 1\).

The formation of a single phase is confirmed from peaks identification of the pattern which match well with ICSD number 98-007-8876 that all patterns correspond to BaTiO\(_3\) phase. Figure 1, (b) compares a diffraction peak of (1 2 1) which clearly shown peaks shifting when Zn partially substituted Ti ion in BaTiO\(_3\) phase. With increasing the Zn ratio, the peaks shifted to the right direction because the lattice parameter changes. The change must be due to the different in ionic radius between Zn\(^{2+}\) (74 pm) and Ti\(^{4+}\) (53 pm) [7].
Table 1. Lattice data parameters of BaTi\(_{(1-x)}\)Zn\(_x\)O\(_3\).

| No. | x   | BaTi\(_{(1-x)}\)Zn\(_x\)O\(_3\) Sample | Lattice Parameters |
|-----|-----|--------------------------------------|-------------------|
|     |     |                                      | a (Å)  | b (Å)  | c (Å)  | \(\alpha, \beta, \gamma\) (degree) |
| 1   | 0   | BaTiO\(_3\)                          | 3.996  | 3.996  | 4.030  | \(\alpha = \beta = \gamma = 90^\circ\) |
| 2   | 1/3 | BaTi\(_{2/3}\)Zn\(_{1/3}\)O\(_3\)     | 4.009  | 4.009  | 4.032  | \(\alpha = \beta = \gamma = 90^\circ\) |
| 3   | 1/2 | BaTi\(_{1/2}\)Zn\(_{1/2}\)O\(_3\)     | 4.047  | 4.047  | 4.042  | \(\alpha = \beta = \gamma = 90^\circ\) |
| 4   | 2/3 | BaTi\(_{1/3}\)Zn\(_{2/3}\)O\(_3\)     | 5.843  | 11.801 | 11.940 | \(\alpha = \beta = \gamma = 90^\circ\) |
| 5   | 1   | BaZnO\(_3\)                          | 5.833  | 11.376 | 12.585 | \(\alpha = \beta = \gamma = 90^\circ\) |

All data of the diffraction patterns are then refined by GSAS in which the refined pattern is determined by Goodness of Fit (GOF) and weighted profile R-factor (Rwp) as the acceptance indicators. Analysis of refined data have resulted in lattice parameters and crystal system of BaTi\(_{(1-x)}\)Zn\(_x\)O\(_3\) as summarized in Table 1. In addition, the dimension of cell allows for calculation of the cell volume of BaTi\(_{(1-x)}\)Zn\(_x\)O\(_3\) which then plotted in Figure 2. Data in Table 1 indicate that there is a limit of the Zn to substitute Ti while still maintaining the shape of the tetragonal structure. Since the ionic radii of Zn\(^{2+}\) is much higher than that of Ti\(^{4+}\), the a and c parameters changed with x. However, at x = 2/3 and 1 the crystal structure changes from the tetragonal to orthorhombic.

![Figure 2. Plot lattice data parameters of BaTi\(_{(1-x)}\)Zn\(_x\)O\(_3\).](image)

![Figure 3. Reflection Loss of BaTi\(_{(1-x)}\)Zn\(_x\)O\(_3\).](image)
Values of RL, which were calculated from the relation $RL = 20 \log\left|\frac{Z_m - Z_0}{Z_m + Z_0}\right|$ [6, 8], in the frequency range 7 – 13 GHz for BaTi$_{(1-x)}$Zn$_x$O$_3$ (x = 0; 1/3; ½; 2/3; 1) samples are compared in Figure 3. $Z_m$ and $Z_0$ are respectively impedance of the sample and electromagnetic wave in air. The absorption spectrums clearly indicate that the incoming electromagnetic waves entering the samples were absorbed partially in which the RL values are below 0 dB in the frequency range but at a certain frequency, the RL value even reduced further. The RL value at peak frequencies 8.29 GHz, 8.86 GHz, 9.19 GHz, 10.06 GHz, 11.32 GHz and 12.55 GHz increases with a decrease in x from x = ½ to x = 0. However, a significant increase in RL was obtained in samples with x = 2/3 and 1 where the crystal system has changed from cubic to orthorhombic. The change in the crystal system must also be followed by a change in dielectric constant since there is a discrepancy in ionic size between Zn$^{2+}$ and Ti$^{4+}$.

The RL value of BaTi$_{(1-x)}$Zn$_x$O$_3$ and BaZnO$_3$ are 20.69 dB and 27.20 dB respectively at a frequency 10.06 GHz being the largest value within the frequency range. Hence, the highest microwave absorption up to 95.64% was obtained in BaZnO$_3$ at a frequency 10.06 GHz. The presence of Zn as a doping agent increases permittivity value [9]. This might be the reason for such RL enhancement. In Table 3, the electromagnetic characteristics of BaTi$_{(1-x)}$Zn$_x$O$_3$ samples are summarized which including the value of complex permittivity and permeability calculated based on NRW. The RL value is determined by both the magnetic and dielectric properties in addition to resistivity which overall determine the total impedance of material. BaTi$_{(1-x)}$Zn$_x$O$_3$ sample with x = 2/3 and x = 1 must have the great dielectric value, because in the electric field the frequency of the dielectric constant can increased the electrical energy loss [4]. It is also worthy to note that BaTi$_{(1-x)}$Zn$_x$O$_3$ possesses the negative value of imaginary permeability ($\mu^*$) due to the substitution effects that enhance the level of the microwave absorption [10].

| No. | x     | Frequency 10.06 (GHz) | Frequency 11.32 (GHz) |
|-----|-------|-----------------------|-----------------------|
|     |       | ε ($\varepsilon_r$)  | μ ($\mu_r$)           | Absorption (%)  | ε ($\varepsilon_r$)  | μ ($\mu_r$)           | Absorption (%)  |
| 1   | x=0   | 1.87+j2.10           | 4.31-j1.35            | 78.47           | 0.30+j1.87           | 2.53-j0.20            | 60.51           |
| 2   | x=1/3 | 1.80+j2.07           | 4.26-j1.42            | 78.85           | 0.43+j1.67           | 2.18-j0.29            | 56.45           |
| 3   | x=1/2 | 1.02+j1.74           | 3.64-j2.47            | 68.17           | 0.56+j1.36           | 1.78-j1.41            | 44.54           |
| 4   | x=2/3 | 2.21+j0.10           | 2.92-j1.64            | 89.30           | -0.83+j1.68          | 1.48-j2.07            | 71.09           |
| 5   | x=1   | 2.05-j0.01           | 2.82-j1.06            | 95.64           | 1.36-j0.35           | 1.00-j1.35            | 91.49           |

4. Conclusion
The role of Zn substitution in BaTi$_{(1-x)}$Zn$_x$O$_3$ with composition x = 0; 1/3; ½; 2/3; 1 is to change both phase and dielectric properties. The BaTi$_{(1-x)}$Zn$_x$O$_3$ with x = 0, 1/3 and ½ are a single phase material with a tetragonal crystal system which change to an orthorhombic crystal system at x = 2/3 and 1. The change of crystal system brought the change in dielectric constant and microwave absorption characteristics of the BZT. The microwave absorption characteristics are found improved in BZT from which the absorption of more than 89 and 95 % is respectively obtained in samples with x = 2/3 and 1.

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