STRUCTURAL AND DIELECTRIC PROPERTIES OF ZINC DOPED MANGANESE TITANATES (Zn\textsubscript{x}Mn\textsubscript{1-x}TiO\textsubscript{3}, x=0.1, 0.3, 0.5, 0.7 & 0.9)

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ABSTRACT

In the present investigation the Zinc doped Manganese titanate ceramics were prepared by using solid state reaction route with equal molar ratio. We studied the variation of properties with the variation of zinc composition. The characterization of the target samples were carried out with XRD for Structural, SEM with EDAX for micro structural and HIOKI 3532-50 LCR Hitester for dielectric measurements. We found that the structure of the ceramic sample was ilmenite hexagonal and the particle size of the samples were studied from the XRD. From the dielectric measurements the dielectric constant and dielectric loss were studied.

KEYWORDS: Solid State Reaction Route, XRD, SEM, EDAX, Dielectric Measurements, Thermal Studies

INTRODUCTION

MnTiO\textsubscript{3} ceramics have the ilmenite structure, which is the derivative of the hexagonal structure. The ilmenite structure results from equal amounts of divalent and tetravalent cations, which are ordered at the octahedral sites and alternate along the c-axis of the unit cell. For high frequency applications and stability of the resonant frequency, the low loss dielectric materials with ilmenite structure such as MnTiO\textsubscript{3} have been widely investigated for the microwave telecommunication systems [1]. It is known that ZnTiO\textsubscript{3} and MnTiO\textsubscript{3} are the same crystal structure of rhombohedral symmetry with a space group of \textit{R}\textsuperscript{3}, and both of them have close size of ionic radii (0.740 and 0.67 °A for Zn\textsuperscript{2+} and Mn\textsuperscript{2+}, respectively). It is possible to substitute zinc ion and manganese ion for each other to form (Zn, Mn)TiO\textsubscript{3} solid solution, which might improve the thermal stability and dielectric properties [2]. Manganese Titanate has attracted much attention for its strong absorption in visible region which may be propitious to utilization of solar energy [3]. The incorporation of metal ion into the titanate ceramics can significantly extend the absorption by the photocatalysts into visible range. The effect of doping is to change the equilibrium concentration of electrons or holes [4–6]. Microwave resonators, filters, oscillators or capacitors [7-9] play an important role in industrial or commercial electronic systems. The required materials to fabricate these components must exhibit a high dielectric constant, a low dissipation factor, a small temperature coefficient of the dielectric constant (\(\varepsilon'\)) [10,11], and that at high and hyper frequencies range. In the present study, the author have attempted to reveal the influence of the milling conditions on structural and dielectric properties of sintered Zinc doped MnTiO\textsubscript{3} at different compositions and we report the characterization of Zinc doped MnTiO\textsubscript{3} with XRD, SEM with EDAX, HIOKI 3532-50 LCR Hitester.

EXPERIMENTAL DETAILS

Materials

Titanium dioxide (TiO\textsubscript{2}) powder (P-25), Zinc Oxide (ZnO) and Manganese Corbate (MnCO\textsubscript{3}) were purchased from Aldrich Chemical (USA) with purities above 99.9%. Poly Vinyl Alcohol (PVA) as binder to prepare the pellets.
Preparation of Zinc Doped MnTiO$_3$ Samples

Ceramic samples were prepared by the conventional Solid State Reaction Route [12] from oxide powders with purities above 99.9%. The starting materials were mixed in ethanol by Ball Milling for 24h with Zirconia balls in polyethylene jars and dried at 150°C. The mixed powders were calcined at 1200°C for 24h. The obtained grained powders were mixed with 2.5 wt% of Polyvinyl Alcohol (PVA) solution as binder and then pressed into discs 10mm diameter and thickness of 2mm under hydrostatic pressure about 10Kg/cm$^2$. The resultant pellets were sintered at 1250°C for 6h.

Characterization Techniques

The structural characterizations were carried out with XRD [13] and the surface morphology [14-16] was examined by scanning electron microscopy (JEOL J. SM-35, Japan). Differential scanning calorimetry measurements were carried out in HT-DSC (SDT Q 600 (TA Instruments) equipment in order to investigate the phase formation in Zinc doped MnTiO$_3$. The porosity were measure by the Archimedes techniques [17] using water immersion. The dielectric constant, loss tangent, ac conductivity were measured using HIOKI 3532-50 LCR HiTester (imported from Japan) with variation of temperature and frequency (upto 1MHz).

RESULT AND DISCUSSIONS

XRD

The structural characteristics of the samples were studied with the help of XRD plots which are shown in Fig. 1 at different compositions of Zinc (0.1, 0.3, 0.5, 0.7 & 0.9). From the following plots the maximum intensity (at x=0.3) of the peak shifted towards the higher angles as the composition of the Zinc were increased because of the Zinc ions replaces the position of the manganese ion sites. The particle sizes (8.07-6.18) of the sample were decreased because of smaller Zn$^{2+}$cation is introduced then the lattice parameters and volume were decreased with the increase of Zn composition. The structure of the sample might be observed with the help of XRD patterns were ilmenite hexagonal.

Figure 1: Shows the XRD Plots for the Zn$_x$Mn$_{1-x}$TiO$_3$ at x=0.1, 0.3, 0.5, 0.7 & 0.9
SEM & EDAX

The following fig. 2 depicts the scanning electron micrographs of Zinc doped Manganese Titanate at different Zinc compositions with sintering temperature of 1250°C. The grain size is more in the composition of Zinc at x=0.5 because of the atomic radii of Zinc and Manganese is almost similar nature. The average grain size is in the order of 1-2 µm, which was slightly increased with increase of composition zinc. The density of the compound were increased with the increase of zinc composition. The porosity of the samples was studied with the help of Scanning morphology and we found that the lower porosity because of the density was higher at higher composition. As the zinc compositions were increased into the perovskite structure lattice promotes the grain growth. From the EDAX analysis, we found that the elemental composition of the each element in the sample and the samples were well stochiometric.

![SEM Micrographs](image)

**Figure 2: Shows the Scanning Electron Micrographs of Zn\textsubscript{x}Mn\textsubscript{1-x}TiO\textsubscript{3} at x=0.1, 0.3, 0.5, 0.7 & 0.9**

Dielectric Measurements

For dielectric measurements the powder form of the sample is grained for 24h and taken 1 gram of the sample then add small amount of PVA as a binder and prepare the pellet by pellet making machine with diameter 1.2cm and thickness 2mm with the application of hydraulic pressure of 10 Tons per square centimeter. These pellets were sintered at 1250°C for 6h. Then these pellets were used for the dielectric measurements with the help of HIOKI 3532-50 LCR Hitester (Imported from Japan) at different frequencies and different temperatures.

From fig. 3, the dielectric constant variation with frequency and we found that the dielectric constant is maximum at composition x=0.3 and the decreased at all frequencies because which might be the smaller ionic polarizability of manganese than that of zinc.
Figure 3: Shows the Dielectric Constant Variation with Composition of Zinc in MnTiO$_3$

The dielectric constant variation with temperature of Zn$_x$Mn$_{1-x}$TiO$_3$ ($x=0.1, 0.3 \& 0.5$) at different frequencies are shown in fig.4. The dielectric constant variation with temperature at different frequencies with the composition of zinc $x=0.1, 0.3, 0.5, 0.7 \& 0.9$ and we observed that the dielectric constant were increased with temperature and decreased with frequency because of the off-center ion displacement of the Zn$^{2+}$ at the Mn$^{2+}$ ion site in the manganese titanate ceramics.

Figure 4: Shows the Variation of Dielectric Constant vs. Temperature of Zn$_x$Mn$_{1-x}$TiO$_3$ at $x=0.1, 0.3, 0.5, 0.7 \& 0.9$
The dielectric losses of the material were studied with respect to temperature at different frequencies which are shown in fig.5. Fig.5. shows that a small hump at 370K were observed and then further increased with respect to temperature at all frequencies at x=0.1. Similar results were observed in remaining compositions of Zinc, which were shown in fig.5. The dielectric loss tangent (δ) was relatively high because of the magneto resistive effect of manganese content.

**CONCLUSIONS**

The Zinc doped manganese titanate ceramic samples were prepared by using solid state reaction method at sintering temperature of 1250°C. From structural studies the sample exhibits the Hexagonal ilmenite type and particle sizes were decreased with increase of the zinc composition. The thermal stability of Manganese titanate ceramics were increased with the doping of zinc composition which might be benefit for the applications of zinc-based titanate microwave ceramics. The dielectric constant were increased with the amount of Zinc upto x=0.3 and afterwards decreased. The loss tangent were varied with temperature and frequency were reported. The dielectric constant and dielectric loss increased with temperature. Both the dielectric constant and the loss tangent decreased with increasing the measured frequencies.
REFERENCES


