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Characterization of ZnMnTiO3

M. Maddaiah, K.S.R. Chandrasekhar Rao, N. Ramakrishnaiah and T. Subba Rao

Dept.of Physics, S.K. University, Anantapur, 515 003 A.P. India.
Email: maddaiahphy@gmail.com

ABSTRACT

Zinc Manganese Titanate Zn0.5Mn0.5TiO3 ceramic compounds were prepared by solid state reaction route. Ceramic synthesis by calcinations at high temperatures 1200 C. The particle size found to be 6.06 A by X-Ray diffraction analysis (XRD). Bulk densities of the sintered ceramics was measured by the Archimedes's method with Xylene (density=0.87gm/cc) as the liquid media found to be 98-99% of the X-ray density. The sample density was determined as 5.24831 gm/cm3. Micro structural analysis using Scanning Electron Microscopy (SEM) supplemented with Electron Dispersive x-ray Analysis (EDAX) were Carried out to find the grain size as well as the chemical composition of the given compound . Dielectric constant (εr) and Dielectric loss (tanδ) as a function of temperature measured are studied from frequencies 100Hz to 1MHz. The Dielectric constant (εr) varies 107.80 to 0.30 with respect to temperature from 313K to 573K. And the Dielectric loss (tanδ) varies 4.15 to 0.45. The dielectric loss and dielectric constant increases gradually with an increase in temperature. At room temperature the AC conductivity value of (ZnMnTio3) is found to be 2.93x10-8 Ω-1cm-1, for the frequency 100Hz and 2.10X10-7 Ω-1cm-1 for 1MHz. The activation energies for Zn xMn1-x TiO3 (x=0.1 – 0.9) is found to be 1.125eV, 1.675eV, 0.8570eV, 1.25eV and 0.78eV respectively at 10 KHz. The lattice parameters are found to be a=b=4.8102 A and c=12.6489 A

Keywords: XRD = X-ray diffraction analysis: SEM = Scanning Electron Microscopy and EDAX = electron dispersive X-ray analysis

1.0 Introduction:

The growing importance of ceramic dielectrics for applications as microwave oscillators, filters, etc has led to great advances in the material research and development of dielectric ceramic systems. The ceramics were prepared by solid state reaction methods [1] Miniaturization of microwave circuits using low loss and temperature stable dielectric ceramic resonators has spurred the wireless communication industry enormously .Basically, a dielectric resonators a ceramic compact with high dielectric constant (€r>25), low dielectric loss or high quality factor (Q>2000) and good temperature stability (near-zero temperature coefficient of resonant frequency, sf) at microwave frequencies and bulk densities [2-5]. The ZntiO3 doped metal ions could be applied in luminescence proposed by Wang et al [6,7], Yamaguchi et al [8]. For high frequency applications and stability of the resonant frequency the low loss dielectric materials with limonite structures have been widely investigated for the microwave telecommunications systems (9). Zinc titanate (ZnMnTio3) are promising candidates for low temperature sintering dielectrics [10-11].Hexagonal Zntio3 is unstable at higher temperatures and much work has been devoted to the synthesis of Zntio3 powder [12-13]. Dopents have been add to the reduced sintering temperature, but practical applications of partly restricted due to unstable dielectric properties originating from complex phase transition[14]. Therefore many efforts have been made to prepare Zntio3 improved stability [15] to achieve high stability divalent cations such as Mn2+ ,Mg2+,Sr2+ etc., were introduced to Zntio3 and their stability were much better than that of Zntio3. It is known that Zntio3 and Mntio3 have the same crystal structure and both of them have close size of ionic radii (0.74A0 and 0.67Ao) for Zn2+ and Mn2+ respectively. It is possible to substitute zinc ion and manganese ion for each other to form ZnMnTiO3 by solid state reaction, which might improve the stability and dielectric properties.

2.0. Experimental details:

The present investigation involves the detailed study of structural, electrical, and dielectric properties of mixed titanate dioxide compounds. The samples are prepared through solid stare reaction methods [16–18]. Samples used in the present investigation were Manganese Carbonate, Zinc oxide, titanate, were synthesized in air by the high temperature solid-state reaction.. Raw Materials of reagent grade (Purity of Powders were Higher than 99%) TiO2, MnCO3, ZnO, were weighed in an electronic single pan balance and the weighed materials were transferred into ball mill to ground the mixture for over two hours, dried and calcined The ground mixture was taken in an Alumina Crucible and is kept in an electrical Silicon carbide furnace that can be heated up to 1000°C. The furnace was made from a four SiC rods. The temperature was varied from 30°C to 1000 0C (~10 OC per minute). X-ray diffraction profile was recorded at room temperature with Seifert X-ray diffractometer using Ni-filtered Cu-Kα radiation (λ = 1.54056Å) at a rate of 2°/min. in the range of 10°-90°. W.L. Bragg showed that the X-ray reflected from a lattice plane and the effect associated with it could be derived by the equation,

$n\lambda = 2d \sin\theta$ (Bragg's Law)

Surface morphological studies (grain size, twin boundaries, stress, strain, dislocation etc.) are routinely carried out by Scanning electron microscopy (SEM) with energy dispersive analysis of X-rays (EDAX). The scanning electron microscopy is used in determining the surface structure and EDAX is used in studying the composition of the ceramic titanates. The interfacial losses may be understood on the basis of the polarization mechanism. This model assumes the existence of anon-homogeneous structure where in the crystallite core is a better conductor than the surface layer; the later together with inter-granular layers, acts as an inter-crystallite barrier. This mechanism was analyzed in the Maxwell-Wagner capacitor model and in Volger's [17] and Krotzsch's [18] development of it.From the equality of conductance activation energy and that of the temperature dependence of frequency corresponding to maximum tan δ, it would follow that relaxation is due to the jump motion of carriers. This idea was put forward in an earlier paper of Kamiyoshi [19]

The thermal behavior of the precursor powders were studied by thermo gravity metry, Diffrential thermal analysis (DSC-TGA). With this analysis we are able to find weight loss and other parameter of exo or endow thermic nature also be analyzed.

The impedance measured is useful tool for electrical and dielectric characterization of ceramic materials. The dielectric parameters such as dielectric permittivity ($\acute{\varepsilon}$) ac conductivity (σac) and dielectric loss tangent ($\tan\delta$) of these compounds where measured using a HIOKI 3532-50 LCR meter in the frequency range of 100Hz to 100 KHz at different temperatures. The ac electrical conductivity for all the compounds was calculated from the conductivity relation.

$\sigma ac = \omega \acute{\varepsilon} \varepsilon 0 \tan\delta$, Where eo is the vacuum dielectric permittivity and w is the angular frequency. The ac conductivity increases with an increase of temperature shown in figure 4.The activation energy is estimated from the slope of ln σac verses 1000/T K -1, which is known as Arrhenius plots shown in figure 5, using the conductivity relation

$\sigma = \sigma 0 \exp(-Ea/ KB\ T)$, Where KB is the Boltzmann's constant.

3.0 Results and Discussion:

XRD pattern of ZnMnTiO3 is shown in figure 1. The maximum peak intensities for the compound ZnMnTiO3 is found at an angle 35.610(2θ). The lattice parameters are found to be a=b=4.8102 Ao and c=12.6489 A0. From the XRD data using the Debye Scherer formula

$D=0.9^* \lambda / \beta \cos\theta$

Where' D' is the average crystalline size, λ is the X-ray wavelength (1.5404 A0) and β is the full width at half maxima in radian Bulk density of the sintered ceramic is measured by the Archimedes's method with Xylene (density=0.87 gm/cc) as the liquid media having 5.24831 gm/cm3 and found to be 98-99 % of X-ray density. Surface micro structure of sintered compound is typical of the ceramic material based on hexagonal layered compound with preferential grain growth in the crystalline plain forming non-rounded shaper of plate like aggregate crystals shown in figure 2.Similar grain morphology was observed in ZnMntio3 prepared by other methods . The scanning electron micrograph reveals that the grain size is in the range of 2-3 μm. Figure 3 shows that EDAX plot with elemental analysis of ZnMnTiO3.

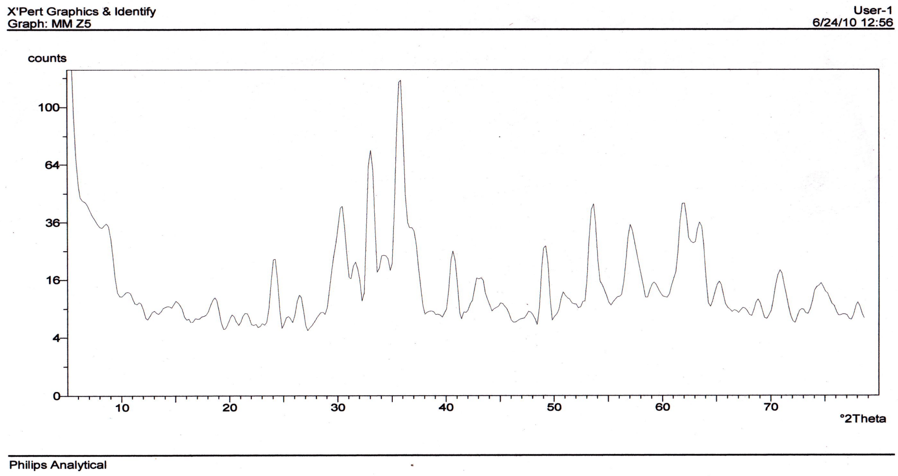


Figure. 1. XRD profile of Zn0.5 Mn 0.5 TiO3

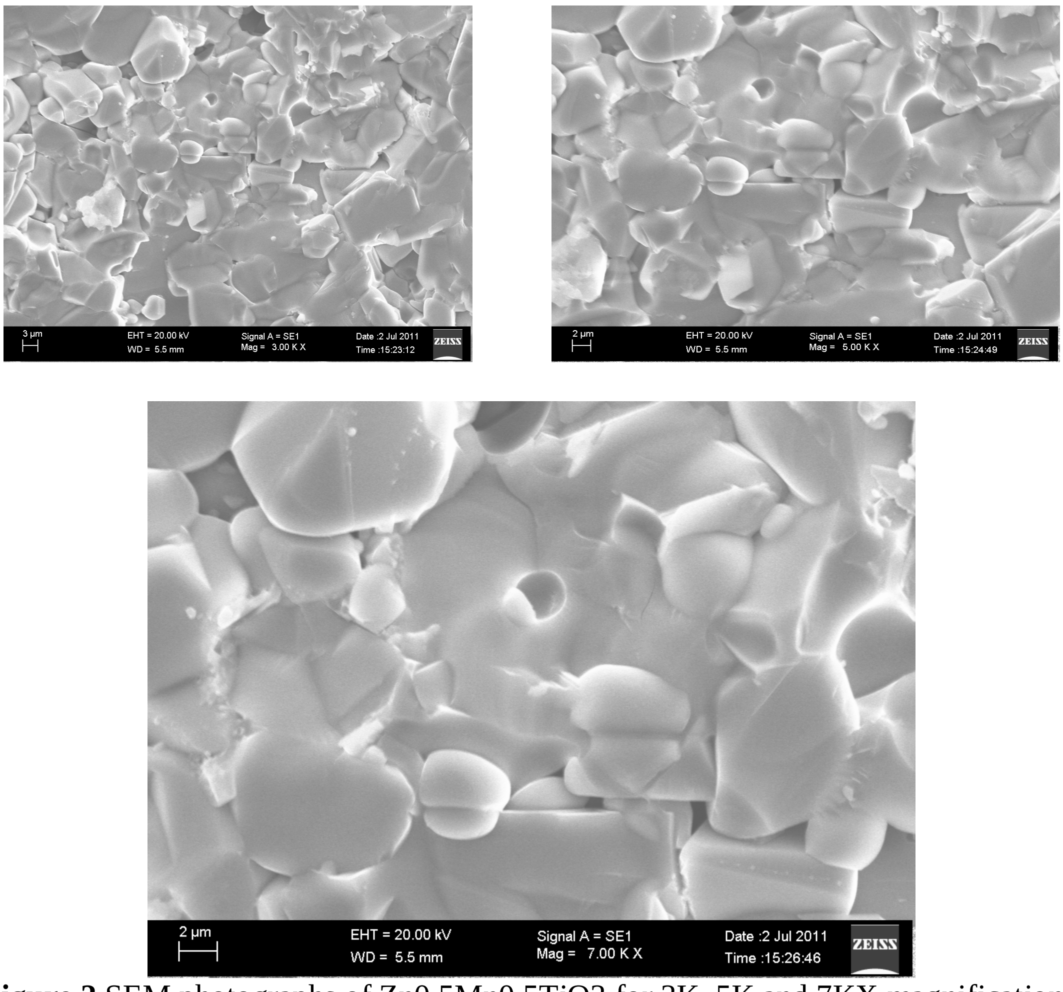
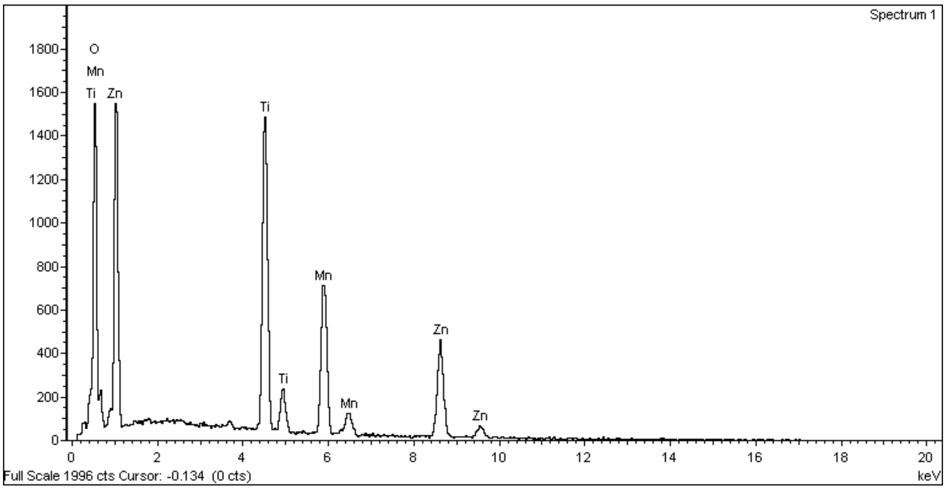


Figure.2 SEM photographs of Zn0.5Mn0.5TiO3 for 3K, 5K and 7KX magnifications



Element	Weight%	Atomic%
O K	41.02	70.90
Ti K	18.90	10.91
Mn K	15.25	7.67
Zn K	24.84	10.51
Totals	100.00	

Figure. 3 . plot of Zn0.5Mn0.5TiO3 EDAX profile.

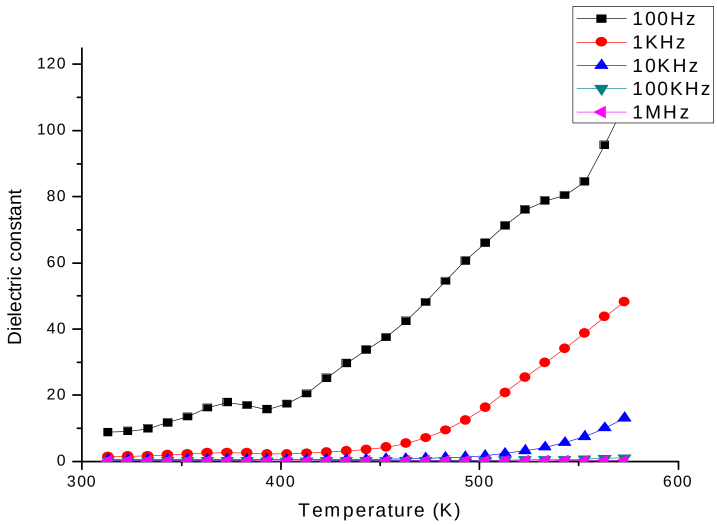


Figure.4 shows Dielectric constant plot

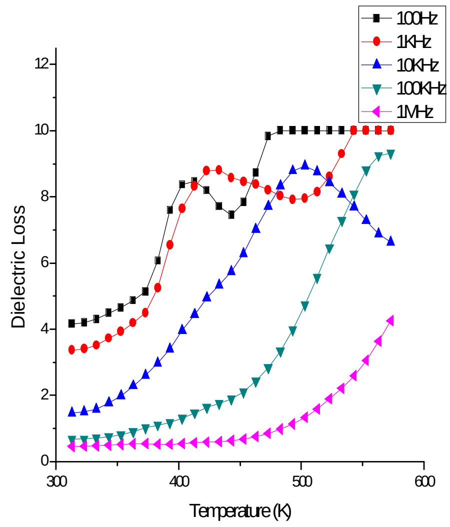


Figure.5 shows Dielectric loss tanδ

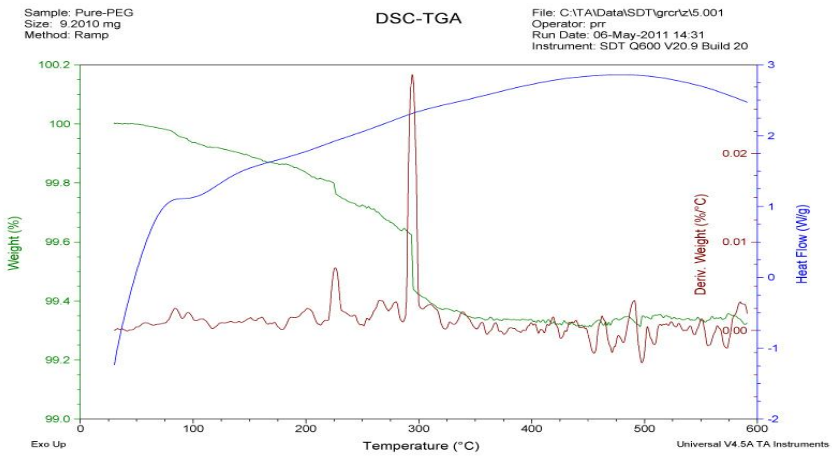
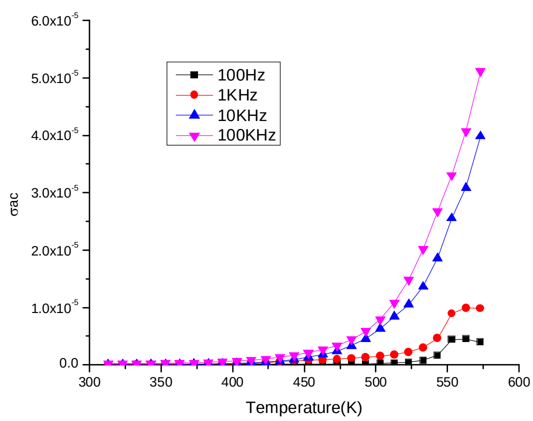
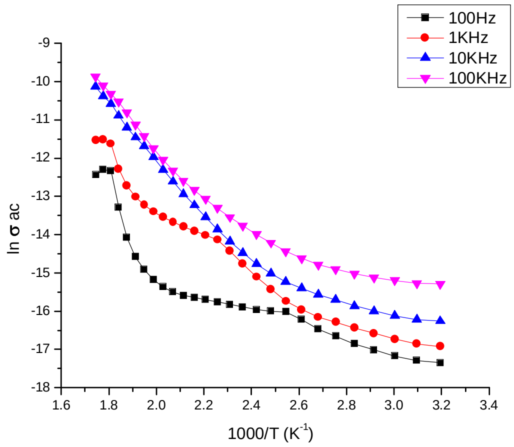


Figure.6.shows the plot of DSC –TGA of Zn0.5Mn0.5TiO3



Conductivity Vs Temperature (K) plot of $Zn_{0.5}Mn_{0.5}TiO_3$



ln σ_{ac} Vs 1000/T (K^{-1}) of $Zn_{0.5}Mn_{0.5}TiO_3$
Figure 7. Shows the ac conductivity & ln σ ac of Zn0.5Mn0.5TiO3

x=0.5 composition of ZnxMn1-xTiO3 the maximum intensity peak at angle 2θ of 35.61^o. From this XRD profile the calculated particle size was determined through Sherer formula 6.06 A^o . By the witness of the single peak it was determined that the compound formed at this peak. In the figure.2 the different magnifications and grain boundaries shows that there is a clear phenomena of forming new compound. The over lappings of the grain boundaries are compared with ASTM tables and confirmed that the compound has special characteristics. The composition of the sample is analyzed and tabulated. From this figure.3 we conclude our self that this has special identity in composition mixing properties. The results are reported in the above figure3. The compound was analyses for dielectric properties and the results are reported in the figures.4 & 5. From the plot it was observed that as the temperature increases the dielectric constant (€r) increases linearly from 313K to 573K .similarly the same linearity was also observed in the case of Dielectric losses (tanδ)plot . We witnessed that for 10 KHz plot linearity was terminated at 600K suddenly and falling continuous up to 673K. This is an anomalous behavior. This property can be used for the fabrication of microwave applications. The steep peak of the figure.6 represents that Zn0.5Mn0.5TiO3 is belongs to exothermic category. The complicated process involved dehydration of the bonded water removal of excess organic substances. The figure.7 shows the conductivity verses temperature and ln σ ac Vs 1000/T (K-1) of Zn0.5Mn0.5TiO3. It was observed that as the temperature increases the ac conductivity also increased. The Activation energies are calculated as 1.125eV, 1.675eV, 0.857eV, 1.25Ev and 0.78eV.It was observed that at 100Hz frequency the energies are lowered. The relaxations are also observed in dielectric laws verses temperature plots the behavior of the parameters suggest that by increasing calcinations, temperature and sintering time the microstructure is improved. Since the grain boundary electrical characteristic are more affected in bulk properties [20-24]

4.0 Conclusions:

The sample Zn0.5Mn0.5TiO3 particle size was determined as be 6.06 A^o The grain size of the sample measured and found to be 1-3µm . The chemical compositions of the sample are in good agreement with the estimated values found in EDAX analysis. The sample density was determined as 5.24831 gm/cm^3. The Dielectric constant (εr) varies 107.80 to 0.30 with respect to temperature from 313K to 573K. And the Dielectric loss (tanδ) varies 4.15 to 0.45. The dielectric constant and dielectric losses are increasing with respect to temperatures. The peak of the DSC –TGA of Zn0.5Mn0.5TiO3 implies that the sample was exothermic. Miniaturization of microwave circuits using low loss and temperature stable dielectric ceramic resonators has spurred the wireless communication industry enormously. Similar synthesized materials are used in sensor applications and varistors capacitor multifunctional component widely.

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