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Synthesis and characterization of Cobalt doped Zinc manganese Titanates

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ABSTRACT: - In the present research work, Cobalt doped Zinc Manganese Titanate ceramic compounds were prepared by conventional solid state reaction technique with calcinations at high temperatures. Crystalline structure and lattice parameters for the compound have been determined 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. 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 100 Hz to 100 KHz. The dielectric loss and dielectric constant increases gradually with an increase in temperature. At room temperature the AC conductivity value of Co doped ZnMnTiO3 is found to be $2.30X10^{-7}\Omega^{-1}cm^{-1}$ for the frequency 100 KHz. The activation energy is estimated from the slope of conductivity vs. inverse absolute temperature plot and found to be 1.05eV at higher temperature region for the frequency 10 KHz. These Co doped ZnMnTiO3 ceramic materials have wide range of applications in the field of Microwave devices etc.,

Keywords: *ZnMnTiO3, SEM, EDAX, XRD, Activation energy, Dielectric constant and dielectric loss*

1. INTRODUCTION

Zinc Manganese Titanate (ZnMnTiO3) are promising candidates for low temperature sintering dielectrics [1-2]. Hexagonal ZnTiO3 is unstable at higher temperatures and much work has been devoted to the synthesis of ZnTiO3 powder [3-4]. Dopents have been add to the reduced sintering temperature, but practical applications of partly restricted due to unstable dielectric properties originating from complex phase transitions [5]. Therefore many efforts have been made to prepare ZnMnTiO3 improved stability [6-9]. To achieve high stability divalent cations such as Mn^{2+}, Mg^{2+}, Co^{2+} etc., were introduced to ZnMnTiO3 and their stability were much better than that of ZnTiO3.

It is known that ZnTiO3 and MnTiO3 have the same crystal structure and

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both of them have close size of ionic radii (0.74A^o and 0.67A^o) for Zn^{2+} and Mn^{2+} respectively. It is possible to substitute zinc ion and manganese ion for each other to form ZnMnTiO3 by solid state reaction method, which might improve the stability and dielectric properties.

In the present work nominal compound of ZnMnTiO3 were prepared by solid state reaction method [10], and observed that the Dielectric properties were very poor in this case. So to enhancing the dielectic properties with the doping of divalent Cobalt ion.

2. EXPERIMENTAL WORK:

In recent time there are number of novel methods developed for the preparation of ceramics with fine particle size, homogeneity and high purity. Among these methods, solid state reaction method is the most commonly used one for the preparation of titanates. In the present study the high purity chemicals of Manganese Carbonate, Zinc oxide, Titanium dioxide, Cobalt Carbonate (all from Aldrich of 99.9%) were used as the raw materials. ZnMnTiO3 ceramic samples were prepared by conventional solid state reaction technique. High Purity chemicals of MnCO3, ZnO, TiO2 and CoCO3, (all from Aldrich of 99.9%) were used as the raw materials. Materials, first dried to eliminate any moisture present, were then weighed as per the stoichiometric. These powders were mixed thoroughly and ground to obtain fine powders .The powders were uniaxially pressed initially into a cylindrical disc of 1.2cm in diameter and about 2mm of thickness. This mixed powder was calcined in the temperature range of 1050-1150^{o}C for 10 hours. The powders were uniaxially pressed initially into a cylindrical disc of 1.2cm in diameter and about 2mm of thickness at a pressure of 10 Tons. These discs were sintered finally in the temperature range 1150-1250^{o}C for 2 hours in a crucible. The purpose of the sintering is to increase the mechanical strength of the pellet. These pellets were then annealed at ~300°C for about 2 hours under vacuum (10^{-2} torr) to remove the strain introduced due to mechanical stress.

Characterization of these Cobalt doped ZnMnTiO3 ceramic samples were studied with the help of XRD, SEM and EDAX [11-12] for structural characterization, for the conduction

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mechanism AC Conductivity, Thermoelectric power and activation energy experiments were carried and for the nature of the samples dielectric constant and dielectric loss were carried with the help of HIOKI 3532-50 LCR HI-TESTER.

3. RESULTS AND DISCUSSION

XRD patterns of ZnMnTiO3 and Co doped ZnMnTiO3 were shown in fig.1 and 2. The maximum peak intensities for the compound ZnMnTiO3 is found at an angle 35.60 (2θ) and Co doped ZnMnTiO3 is found at an angle 38.09 (2θ). When compare with the XRD pattern of ZnMnTiO3 the maximum peak intensity angle (2θ) shifted towards the higher angles in the Co doped ZnMnTiO3.

Fig.1 Shows the XRD of the Sample ZnxMn1-xTiO3 with x=0.5

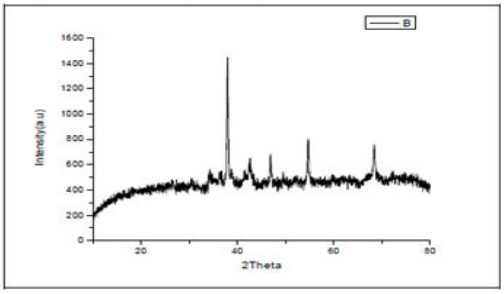
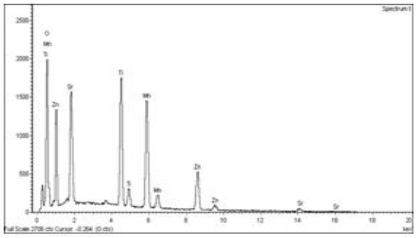


Fig.2 Shows the XRD plot of CoxZn1-x MnTiO5 with x= 0.5



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 A^o) and β is the full width at half maxima in radian.

The crystallite size was found to be 7.093 A^o. The scanning electron micrograph reveals that the grain size is in the range of 2-3 μm. Fig. 3 shows that the structural analysis of Co doped ZnMnTiO3 and we observed that the grain size was increased. From fig.4 shows that the EDAX Plot for the Co doped ZnMnTiO3 for the identification of the chemical composition in the ceramic samples.

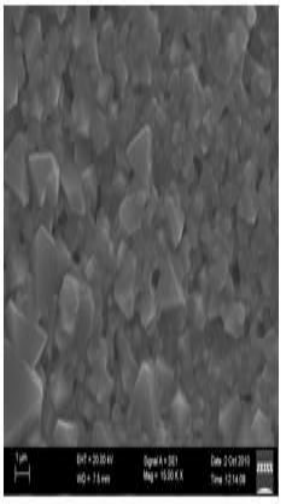


Fig.3. SEM photograph of Co doped ZnMnTiO3

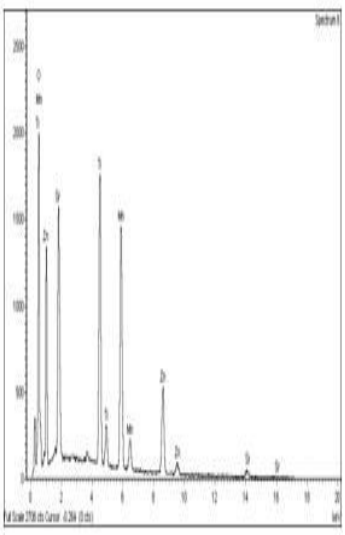


Fig. 4. EDAX of Co doped ZnMnTiO3

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The ac electrical conductivity for all the compounds were calculated from the conductivity relation.

$$\sigma ac = \omega \varepsilon \varepsilon o \tan\delta$$

Where εo is the vacuum dielectric permittivity and ω is the angular frequency. The ac conductivity increases with an increase of temperature shown in fig. 5. The activation energy is estimated from the slope of ln σac verses 1000/T K^{-1}, which is known as Arrhenius plots shown in fig. 6, using the conductivity relation

$$\sigma = \sigma o \exp (-Ea/KBT)$$

Where KB is the Boltzmann's constant [13-15]. From the AC Conductivity and ln σac verses 1000/T K^{-1} were increases with temperature and frequency.

Dielectric measurements are carried out from room temperature to 573 K in the frequency range from 100Hz to 100KHz. Dielectric constant increases with an increase of temperature is shown in fig. 7. Dielectric loss (tanδ) also increases with increase of temperature. In $ZnMnTiO_3$ the dielectric constant and dielectric loss were high because of the magnetoresistive effect of the manganese. So for the increase of dielectric constant and low dielectric loss we were dope the Co with different compositions and we were observed that the dielectric constant were raised from 0.30 to 2.77 at 1 MHz frequency.

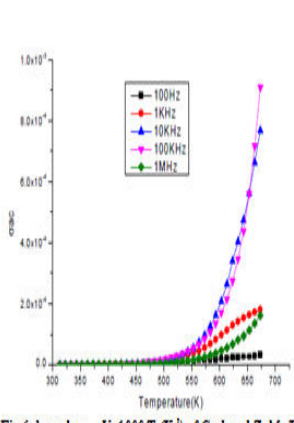

Fig.6 shows ln σ_{ac} Vs 1000/T (K^{-1}) of Co doped $ZnMnTiO_3$

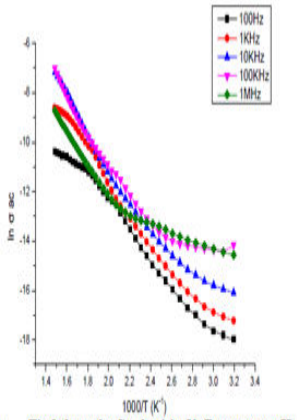

Fig.5 shows the Conductivity Vs Temperature (K) plot of Co doped $ZnMnTiO_3$

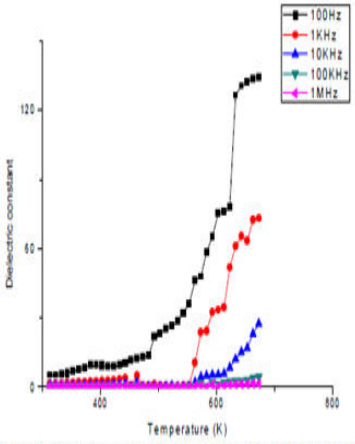

Fig.7 shows the Dielectric constant Vs Temperature (K) of Co doped ZnMnTiO3

4. CONCLUSION:

Co doped Zince Manganese Titanate ceramic materials were prepared by Solid state reaction method. In this work we found

that the structures of the sample unit cell were ilmenite hexagonal structure. With the doping of Co in the ZnMnTiO3 ceramic sample, we found that the dielectric constant was raised from 0.30 to 2.77 at 1 MHz frequency. AC conductivity and activation were studied and we observed the AC conductivity increases with temperature and frequency. These ceramic compounds were widely used to fabrication of electronic components such as boundary layer capacitors.

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