Structural, Electrical & Dielectrical properties of $ZnCaTiO_3$

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Abstract

Zinc calcium titanate pellets were prepared by solid state reaction method and studied its structural, electrical and dielectrical properties. $ZnCaTiO_3$ Pellets of 2.37mm size were prepared at an annealing temperature of 900°C under pressures of 12 tons for the analysis. The density was determined as 4.608 at room temperature 36°C with Xylene relative comparison. The Lattice parameters a=b=c=9.215A°.The sample has a rhombohedral in space group R-3 (148) at room temperature. The Particle size was determined as 0.74µm from the XRD of the sample. The grain size of the particle was found to be 0.25µm by the SEM Profile of the pellets. The Seebeck coefficient (S) values are determined at 350K,450K and 550K are 706µV/K, 556µV/K, and 560 µV/K and Charge carrier densities were 4.44E15, 1.27E15 and 1.59E15 respectively. The Activation energies are calculated as 1.44, 1.03 and 1.92 eV at 350K, 550K and 750K respectively. The dielectric constant (K) investigated and calculated for 10KHz, 1MHz and 10MHz are 11.2, 5.6 and 14.4 and dielectric losses (tanδ) 0.433, 0.953 and 0.520 at 450K.These parameters are suitable for the construction of resonators, filters and other key components in microwave communications.

Key words: XRD = X-ray diffraction, SEM = Scanning Electron Microscope, EDAX = Energy dispersive analysis of X-rays, €$_a$ = Activation energy. TEP = Thermo electric Power.

1.0. Introduction:

Much attention is paid because of its diverse electrical and other properties, leading to the wide applications in sensors

microelectronics and high performance catalysts (1, 2). Recently the Zinc titanate ciramics have been promisingly reported as microwave dielectric materials due to their stable and proper dielectric properties (3, 4). The stable formation of $ZnTiO_3$ phase was known to be complicated, mainly due to the decomposition of $ZnTiO_3$ into Zn_2TiO_4 and rutile at about 945°C (5). Several reports evident in the literature on the characteristics of $ZnTiO_3$ powder prepared by solid state reaction (6-8). Kim et al and researchers (9-12) also try to obtain suitable dielectric properties by controlling composition in ZnO- TiO_2 binary system and /or substituting Zinc with Barium, Calcium, Strontium and Magnesium. Most of those studies involve only bulk system. As ceramic material $CaTiO_3$ has been widely used in electronic devices and it is a key component of Synroc (type of synthetic rock used to store nuclear waste) (13). $CaTiO_3$belongstotheimportantgroupofcompoundswithperovskitetypestructure.$CaTiO_3$exhibits an orthorhombic structure with space group Pbnm below1380K.Theunconventional space group Pnma is designed to the "orthorhombic" structure. In temperatures between 1380 and 1500K occurs a phase transition and changes the space group for Cmcm. At 1500K, the orthorhombic structure transforms to "tetragonal" structure with space group I4/mcm. Above 1580K, this material exhibits "cubic" structure with space group $Pm3^{-}m$ [14]. Lemanov et al (15) measured the dielectric properties of $CaTiO_3$ at low temperature and classified this pervoskite as an incipient Ferro electric or Quantum Para electric.

The development of microwave dielectric ceramics resonators for communication systems such as cellular telephones and global positioning systems has been rapidly growing in the past decades (16). This type of materials is usually used as compensators of the temperature coefficient of resonant frequency (τ_f) due to its high ϵ_r (~ 170) and large τ_f (~ $8X10^{-4}$ / C°). However the sintering temperature of pure calcium titanate is very high (≥1400 C°) and it has relatively low QXf value (~ 3500GHz) by the traditional solid state preparation process. The effect of Zinc substitution site on sintering temperature and dielectric properties was investigated. It was observed that the sintering temperature was decreased due to addition of Zinc.

2.0.Experimental procedure: The Zinc calcium titanate ceramic pellet was prepared by a solid state reaction method using ZnO (99.9%), CaO(99.9%)

and TiO_2 (99.9%) raw powders. These powders were approximately weighed to meet the Stoichio-metric ratio 1: 1: 1 and then grinded using agate mortar for 5-6 hours and milled with Ball Miller (PM 200). Mixtures were dried and calcined at 900°C for 10 hours. After re milling and drying the calcined powders, those were mixed with poly vinyl alcohol (PVA) solution as a binder and pressed into pellets of 1.316cms diameter and with thickness 2.37mm using iso-static press. The pellet was sintered at 950°C for six hours. The crystal structure of the calcined and sintered ceramic pellet was analyzed by X-ray diffracto meter. These grown and annealed pellets were characterized with XRD, SEM and EDAX. For measuring electrical properties silver nitrate was applied as a ohmic- contact. The prepared pellet was investigated for the recording of XRD and other necessary parameters studied. Figure.1 gives XRD profile of the recording of $ZnCaTiO_3$. The figure.2 indicates the SEM pictures of the sample for 5K and 10K magnifications. Figure .3 represents the composition of the pellet from the EDAX findings.

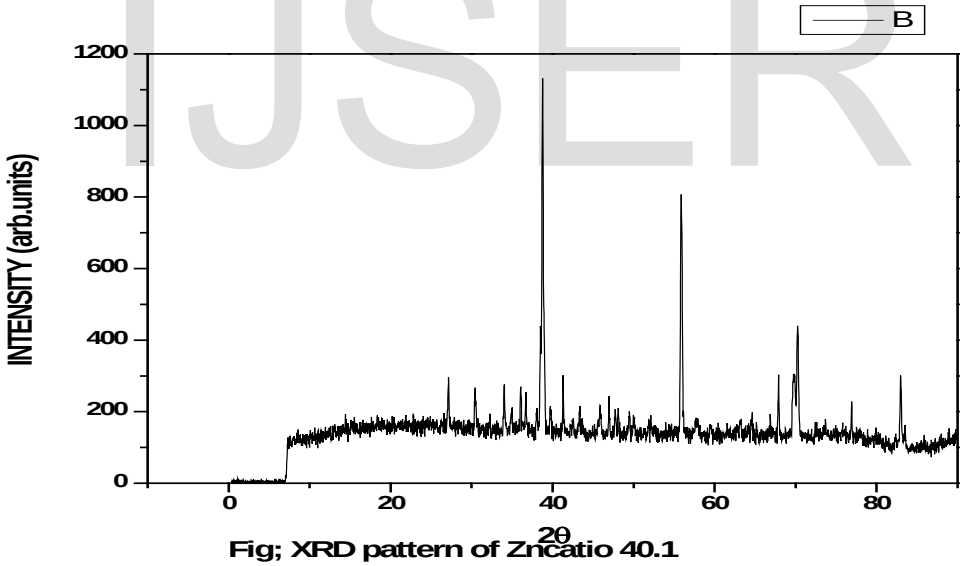
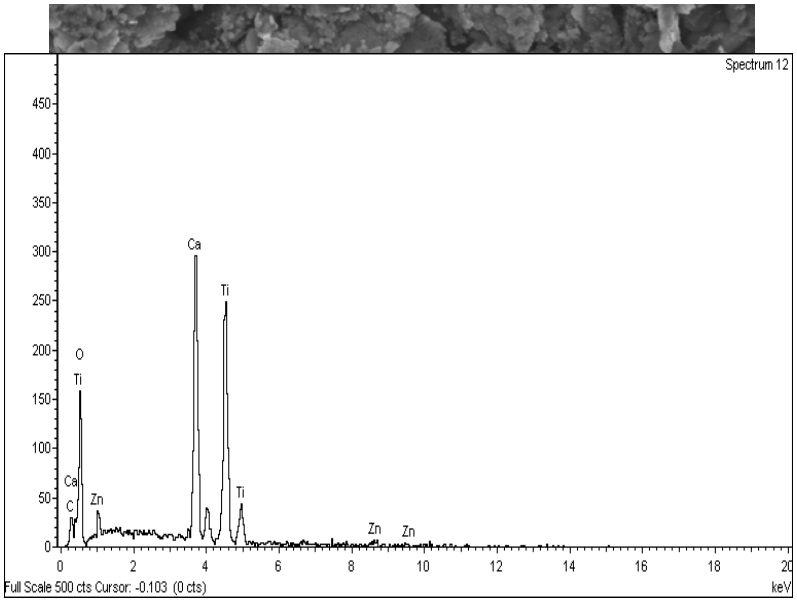
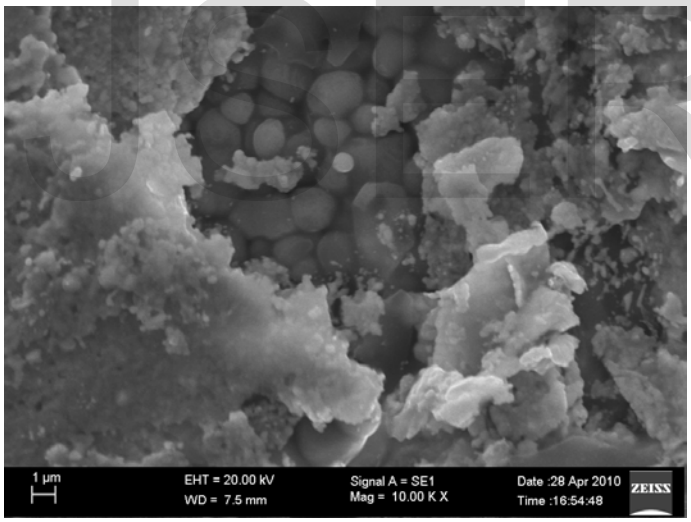


Figure. 1.depicts the XRD profile of $ZnCaTiO_3$





Figure; 2 depicts the SEM profiles of $ZnCaTiO_3$ for 5K and 10K

Composition of the $ZnCaTiO_3$

Element	Weight%	Atomic%
C K	2.80	5.52
O K	48.07	71.15
Ca K	8.76	5.17
Ti K	26.68	13.19
Zn K	13.69	4.96
Totals	100.00	

Figure: 3.depicts the EDAX results of $ZnCaTiO_3$

3.0 Results & Discussions: After careful examination of the XRD and SEM pictures it was confirmed that the material consisting rhombohedral structure with space group of R-3 (148).By the parameters studies implies that the prepared material is single phase formed with perfect Frenkel grain

boundaries. It was observed that the particle size ranges between 0.7 to 1.4μm. The average grain size calculated as 0.26 μm. The crystal boundaries are very clear and perfectly matched. These structural parameters made to come to a conclusion that the new material formed.

The electrical conductivity and thermo electric Power recordings were studied from room temperature to 600K. The compound to be P-type conducting and conductivity increases with increase of temperature. Figure.4 shows the temperature variation of electrical conductivity. Electrical conductivities are in the range of $6X10^{-9}$ to $5X10^{-10}$ mho/cm. Figure.5 depicts the temperature variation of activation energy of the Pellet. It was observed the activation energy decreases as temperature increases.Figure.6 shows the temperature variation of the thermoelectric power (TEP). It was observed that the TEP decreases with increase of temperature from 900 to 500 μV/K. This indicates that the saturated position indicates the material is stable one.

The figure 7 & 8 depicts the experimental observation of variation dielectric constant (K) and dielectric losses (Tanδ) with temperature for the various frequencies of the sample. From these the dielectric constant decreases with increase of temperatures. It was observed that the dielectric losses decrease at high frequencies. At lower temperatures the dielectric constant is stable and constant with temperature.

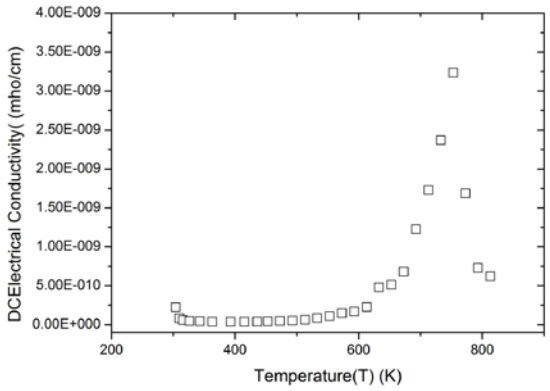
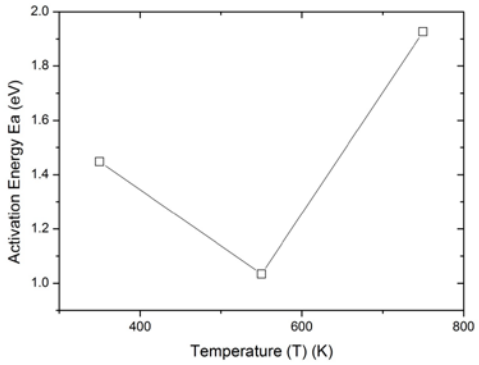


Figure.4 depicts variation of electrical conductivity with temp.



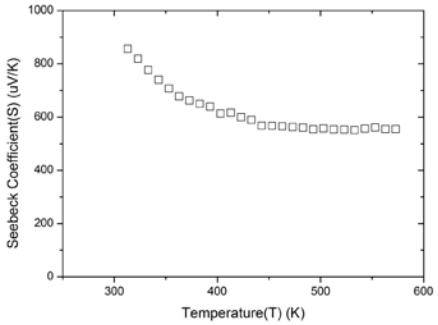


Figure.5 & 6 depicts the variation of the Activation energy and TEP with Temp.

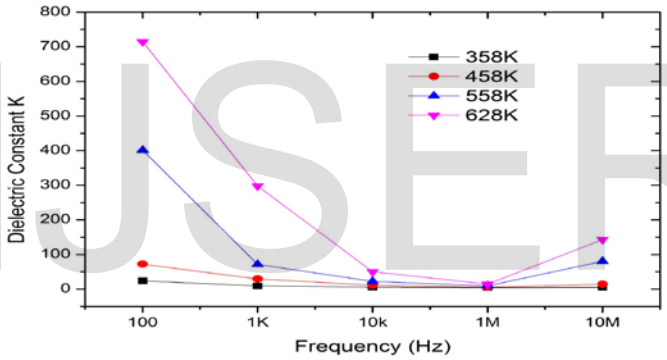


Figure.7 depicts variation dielectric constant with Temp.

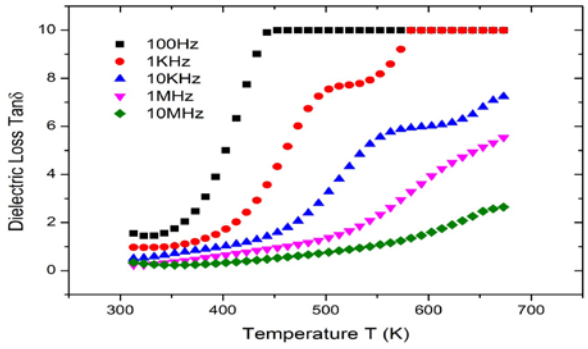


Figure.8 depicts variation of dielectric losses with Temp.

4.0 Conclusions:

The pellet was synthesized by the solid state reaction method and studied the transport properties and dielectrical properties. The particle size and average grain size are determined as 0.74μm and 0.25 μm respectively. The Lattice parameters were a=b=c=9.215A°. The crystal structure was determined as rhombohedral with space group R-3(148). Electrical conductivities are in the range of $6X10^{-9}$ to $5X10^{-10}$ mho/cm for the sample. The thermo electric power varies between 900 to 500 μV/K. The dielectric constant (K) s investigated and calculated for 10KHz, 1MHz and 10MHz are 11.2, 5.6 and 14.4 and dielectric losses (tanδ) 0.433, 0.953 and 0.520 at 450K.These parameters emphasizes the need for the construction of the resonators, key components in microwave communications.

5.0 References:

1. H.Obayashi, Y.Sakurai, T.Gejo, J.Solid.state.chem. 17 299(1976)
2. Z.X.Chen, A.Derking. W.Koot, M.P. Van Dijk, J.catal. 161 730(1996)
3. H.T. Kim, Mat.Res. Bull. 33 963 (1998)
4. A. Golov chasky, H.T.Kim, Y.H.Kim, J. Kor. Phyys.Soc. 32 1167 (1998)
5. F.H.Dulin.,D.E.Rase., J.Am.ceram.Soc. 43 125 (1960)
6. E.Hosono, S.Fujihara, M.Onuki, T.Kimoura, J.Am.Ceram. Soc. 87 1785 (2004)
7. H.T.Kim, Mater.Res.Bull. 33 975 (1998)
8. Y.S. Chang, Y.H.Chang, I.G. Chen, G.J.Chen, Y.L. Chai, J. Crystl.Growth 243 319 (2002)
9. H.T.Kim, Mater.Res.Bull. 33 963 (1998)
10. A.Golovchansky, H.T.Kim, Y.H.Kim, J.Kor.Phys. Soc. 32 1167 (1998)
11. Y.S. Chang, Y.H.Chang, J. Alloys Compd. 354 303 (2003)
12 Y.S. Chang, Y.H.Chang, Solid.state Commun. 123 203 (2003)
13 A.E. Ringwood, S.E. Kesson, K.D. Reeve, D.M. Levins, E.J. Ramm, in: W. Lutze,R.C. Ewing (Eds.), Radioactive Waste Forms for the Future, Elsevier, Amsterdam, 1988, p. 233.
14. B.J. Kenndey, C.J. Howard, B.C. Chakoumakos, Phase transitions in perovskite atelevated temperatures—a powder neutron diffraction study, J. Phys.: Conden.Matter 11 (1999) 1479–1488.
15. V.V. Lemanov, A.V. Sotnikov, E.P. Sminova, M. Weihnacht, R. Kunze, Perovskite$CaTiO_3$ as an incipient ferroelectric, Solid State Commun. 110 (1999) 611–614.
16. Wersing W. Curr. Opin. Solid state Material.Sci., 1996, 1 (5): 715-731.