



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>

INTERNATIONAL JOURNAL  
OF ADVANCED RESEARCH

## RESEARCH ARTICLE

## Dielectric properties of $ZnO_{99-x}Bi_2O_3_{0.5}CoO_{0.25}Cr_2O_3_{0.25}Ce_6O_{11}_x$ ceramics

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### Manuscript Info

#### Manuscript History:

Received: 17 August 2015  
Final Accepted: 26 September 2015  
Published Online: October 2015

#### Key words:

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### Abstract

Mixtures of ZnO doped with  $Ce_6O_{11}$ ,  $Bi_2O_3$ , CoO and  $Cr_2O_3$  as additive were prepared by solid state reaction from the calcined oxides with the following proportions  $Ce_6O_{11}$  (0.05, 0.1, 0.2 and 0.4 mol%),  $Bi_2O_3$  (0.5 mol%), CoO (0.25 mol%) and  $Cr_2O_3$  (0.25 mol%). SEM and AFM revealed the presence of inter-granular phase. Additives present in grain boundaries between ZnO grains. XRD showed that no binary compound was formed. The conductivity and the dielectric constant are highly dependent on the microstructure of conducting grains surrounded by this insulating oxide barrier. Microstructure had been studied with SEM and AFM.

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## INTRODUCTION

Varistors have wide spread applications in protecting power and signal level of electrical circuits against dangerous voltage surges [1]. Many researchers have reported the sintering behavior of several doped ZnO systems, such as  $Bi_2O_3$ -doped ZnO [2],  $Sb_2O_3$ -doped ZnO [3] and  $Al_2O_3$ -doped ZnO [4]. The electrical properties of ZnO varistors are obviously related to the composition and microstructure, such as grain size, density, morphology and the distribution of second phases. As a consequence, the nonohmic properties of these materials are strongly dependent on the fabrication process, which in turn regulates the defect chemistry in the depletion region and in the vicinity of the grain boundary. Microstructurally, the excellent nonlinear properties are attributed to the electrostatic potential barrier at the grain boundaries containing many interface states. The semiconducting n-type ZnO grains and the thin insulating intergranular layers surrounding them can be considered as structural units that correspond to micro-varistors [5, 6]. Several conduction mechanisms for the varistor have been proposed based on this ceramic microstructure[7-9] which has led to varistor behavior being widely interpreted as resulting from the series-parallel network formed by the ZnO-intergranular-phase junctions[9,10]. Capacitance measurements as a function of voltage have supported the model of Schottky barriers at grain boundaries [11]. This property is related to conduction mechanism in the inter- granular phase. Conduction mechanism is related to electronic structure in the vicinity of the grain boundaries. It is assumed that oxygen will be at ZnO grain boundaries. This oxygen is responsible for the generation of the electronic interface states out the grain boundaries. Schottky barriers are formed on both sides of the grain boundary where a depletion layer is formed as a result within the ZnO grains [12].This depletion layer controls varistor action. Therefore ,conduction paths are located between grains in the region of closest contact over the Schottky barrier as well as through bulk inter-granular material at grain corners .The former may show a thermally activated temperature leakage conduction related to barrier height while the latter is thermally sensitive but is governed by different additives. The amounts of additives affect the coefficient of non-linearity and breakdown voltage. [13,14]. The aim of this paper is to study the effect of the addition cerium oxide on dielectric properties of ZnO bodies.

## 2. Materials and methods:

Sintered polycrystalline samples were prepared by conventional ceramic fabrication procedures. Reagent – grade ZnO,  $Ce_6O_{11}$  , CoO , $Cr_2O_3$  and  $Bi_2O_3$  powders were mixed by wet ball – milling using deionized water . Three series

of mixes were proposed in table. 1. Disc specimens with the following dimensions ,diameter either 1.2cm or 5cm and thickness 0.3cm were processed under a force of 70 KN , dried and then fired at 1150<sup>0</sup>C for 30 minutes . Specimens were first polished with different grades of diamond past thoroughly washed in an ultrasonic bath dried then ,thermally etched at 1000<sup>0</sup>C for 30 minutes. Microstructure developed was examined under SEM type Philips XL 30 provided with EDS after sputtering with gold. The surface morphology was investigated by the atomic force microscopy (AFM, Bruker Dimension Icon) using the Peak Force Tapping and silicon nitride probes with sharp tips (a tip radius: 2 nm).The PM6304 programmable automatic RCL meter was used for precise measurements of resistance, capacitance and inductance. The capacitance and resistance at frequency from 1 kHz to 20kHz were measured at different temperatures between 313 to 523 K and the respective permittivity [ $\epsilon'$ ] and conductivity [ $\sigma$ ] were calculated according to the following relations :

$$\epsilon' = C.d / \epsilon_0 A$$

Where C = capacitance in Farad

d = thickness of specimen in m

$\epsilon_0$  = dielectric constant of vacuum = 8.85x10<sup>-12</sup> F/m

A = area of specimen in m<sup>2</sup>

Also, from the values of resistance [R] the resistivity [ $\rho$ ] and conductivity[ $\sigma$ ] were calculated from the following relation:

$$\text{Resistivity } [\rho] = RA / d$$

where R = resistance

### 3.Results and Discussion :

The XRD patterns of the respective mixes fired at 1150<sup>0</sup>C for 30 min , showed a shift in the d spacing equivalent to [ 0.03 – 0.04 ] Å<sup>0</sup> in the main ZnO peak indicating a kind of limited solid solution of Ce<sub>6</sub> O<sub>11</sub> in the oxide. A maximum shift of 0.04 Å<sup>0</sup> was recorded in mix containing 0.4 mol % cerium oxide , XRD results showed that no binary compound was formed . Also, the shift in ZnO peaks did not exceed the recorded value .

#### 3.1. The electrical properties.

Figures (1-3) show the relation between dielectric constant ( $\epsilon'$ ) and temperature at a frequency ( 100 k Hz ) for different specimens. The observed dielectric constant of different mixtures was variably affected by increasing temperature from 313 to 520 K .Generally ( $\epsilon'$ ) appears to be constant with rise of temperature and slightly increases at the higher range .The increase of temperature raised the dielectric constant because it increases ionic response to the field again which is related to intergranular material at any particular frequency . Presumably these effects are associated with polarization currents arising from trapping states of various kinds and densities. In the ZnO - intergranular material interface, the states lying possibly in the transition region (interface) between ZnO and intergranular material[12]. Also the apparent dielectric constant in the measuring frequency range increased with increasing Ce<sub>6</sub>O<sub>11</sub> content. This is directly related to the average grain size, as can be seen in the following equation,  $\epsilon'_{app} = \epsilon_g(d / t)$ , where  $\epsilon_g$  is the dielectric constant of ZnO, d is the average grain size, and t is the depletion layer width. That is, this is because the increase of Ce<sub>6</sub>O<sub>11</sub> content causes the decrease of total depletion layer width within entire bulk due to the increase of average grain size.

The melting point of ZnO is about 1300<sup>0</sup>C. Therefore, the addition of cerium oxide to it probably lowered the temperature of liquid formation to 1150<sup>0</sup>C – 1200<sup>0</sup>C. As a result the liquid phase rich in ZnO is formed and partly dissolved the cerium first precipitate along the grain boundaries as small spots then accumulates intra – granularly . Part of cerium oxide entered the lattice of ZnO. This view coincides with that reported by Morris [15] in case of Bi<sub>2</sub>O<sub>3</sub> as it cannot form a solid solution with ZnO but undoubtedly it dissolves to some extent. Bi<sup>+3</sup> and Ce<sup>+3</sup> would not be expected to fit easily into the ZnO lattice either substituting or interstitially.

Figures (4-6) show the relation between conductivity and temperature at constant frequency (100 kHz). Mixes behave differently according to the percentage of dopant added. The variation of capacitance and resistance with temperature is thought to be associated with dielectric relaxation. Increasing the concentration of Ce<sub>6</sub>O<sub>11</sub> leads to a gradual decrease of  $\rho$  as a function of temperature, due to the fact that, the increase of temperature activates the mobility of ions and increases the carrier density and as a result the conductivity. This may be explained in the light of the microstructure developed formed at the semi- conductive ZnO grains surrounded by insulating glassy phase which is similar to that of grain boundary layer capacitors as a result the observed dielectric constant increased with increase in cerium oxide. Microstructure of ZnO varistors play an important role in the electric characteristic

displayed . there are two models postulated to describe the microstructure of ZnO depending on constitution. A three phase model comprising grains, intergranular material and particles. And two model comprising the first two only. The addition of  $Ce_6O_{11}$  leads to a two phase microstructure; well crystalline ZnO grains showing grain growth in preferred orientation, ZnO crystallizes in hexagonal system, it is characterized by perfect cleavage plane along (001) which was distinct in SEM of ZnO with different additives.

### 3.2. Microstructure analysis.

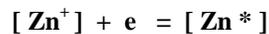
The SEM of mix B4 present in Fig .7., shows the inter-granular phase having an oval shape of various sizes ranging between 0.1 to 2  $\mu m$  situated at the triple points between the ZnO grains that proved by EDAX to be mainly Zn and cerium. Also examination of the ZnO grains indicate the presence of cerium too. The role played by cerium oxide in this case is during firing the valence state of cerium is changed into  $Ce_2O_3$  with the evolution of oxygen . This oxygen is responsible for the generation of electronic interface states out the grain boundaries.



The electrical conduction in ZnO is the interstitial  $Zn_i$  which can be ionized as follows :



These interstitial cations occupy a shallow donor level ( at  $\approx 0.05$  eV ) close the conduction band and are completely ionized to  $Zn^+$  ions and electrons .The interstitial  $Zn^+$  ions are thus produced in a concentration equal to that of electrons . The positively charged interstitial  $Zn^+$  in the depletion region migrates to the grain boundary and neutralizes the negative charge at the grain boundary interface ( recombination) forming a neutral interstitial zinc ion .



Since there are two depletion regions , migration occurs on both sides of the grain boundary interface with alternation of field by polarity[6] . Charge neutralization thus occurs in both depletion layers resulting in a symmetrical lowering of the barrier height [16].

Fig.8. shows the AFM plane image for sample  $M_5$  scan range for a single scan is  $5\mu m \times 5\mu m$  which represent the higher  $Ce_6O_{11}$  concentration. Spinal,  $Ce_6O_{11}$  phases, and the ZnO matrix.  $Ce_6O_{11}$  is clearly present at grain boundaries with oval shaped particles. Fig. 9. shows the three dimensional image for  $M_5$ , AFM data can generate quantitative information from individual particles and between groups of particles as shown in Fig.10.

### Conclusion:

- Addition of  $Ce_6O_{11}$  alone to ZnO render it more conducting.
- The role played by cerium oxide in this case is during firing the valence state of cerium is changed into  $Ce_2O_3$  with the evolution of oxygen . This oxygen is responsible for the generation of electronic interface states out the grain boundaries.
- The addition of 0.5 mol%  $Bi_2O_3$  with the same mol%  $Ce_6O_{11}$  increased the electrical conductivity, this may explained by generation of carriers that cause an increase in the density charge carrier in the glassy phase developed by the  $Bi_2O_3$  added.

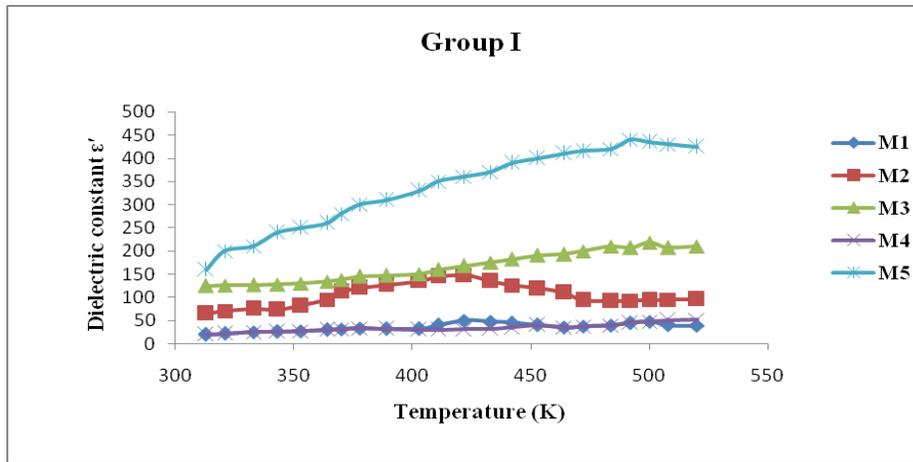


Fig .1. The relation between dielectric constant  $\epsilon'$  and temperature at 20 KHz for group I.

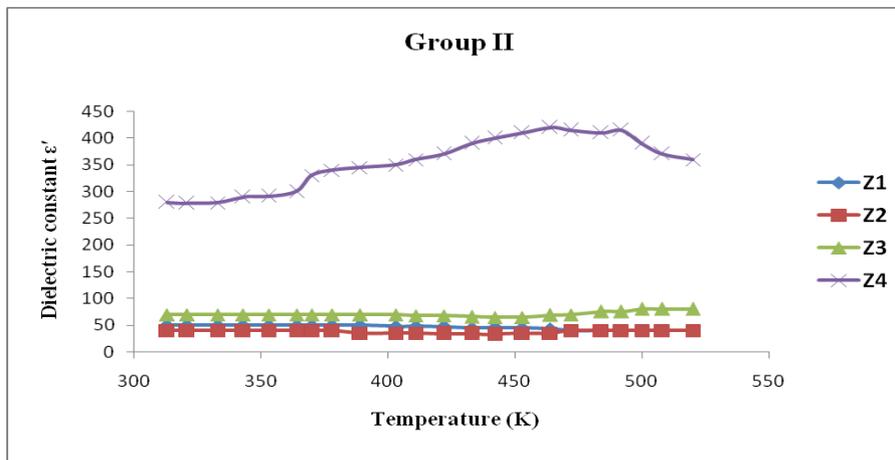


Fig .2. The relation between dielectric constant  $\epsilon'$  and temperature at 20 KHz for group II.

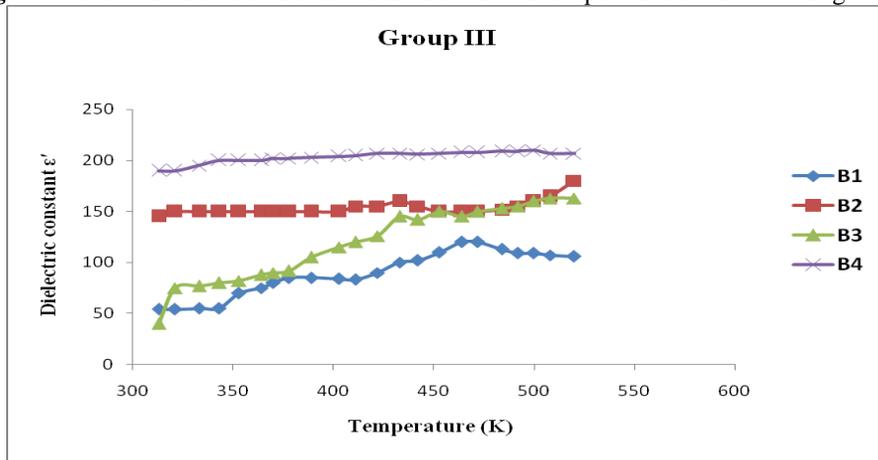
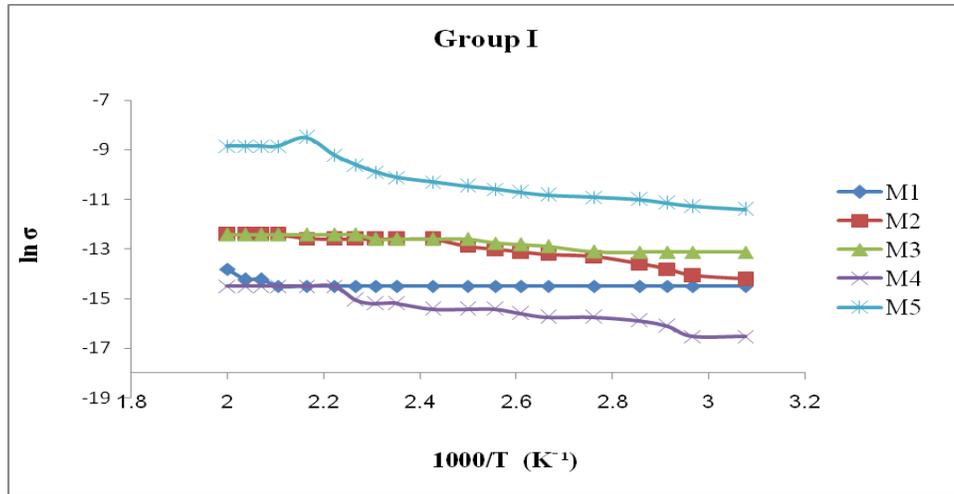
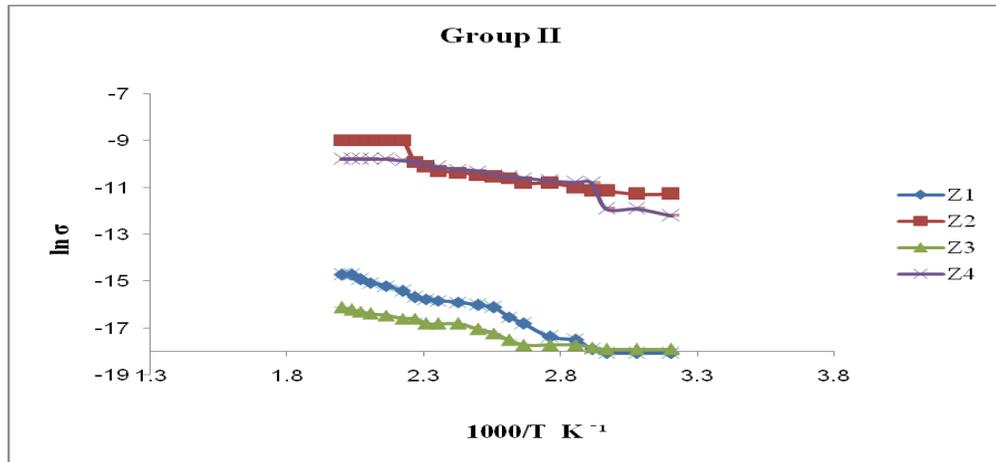


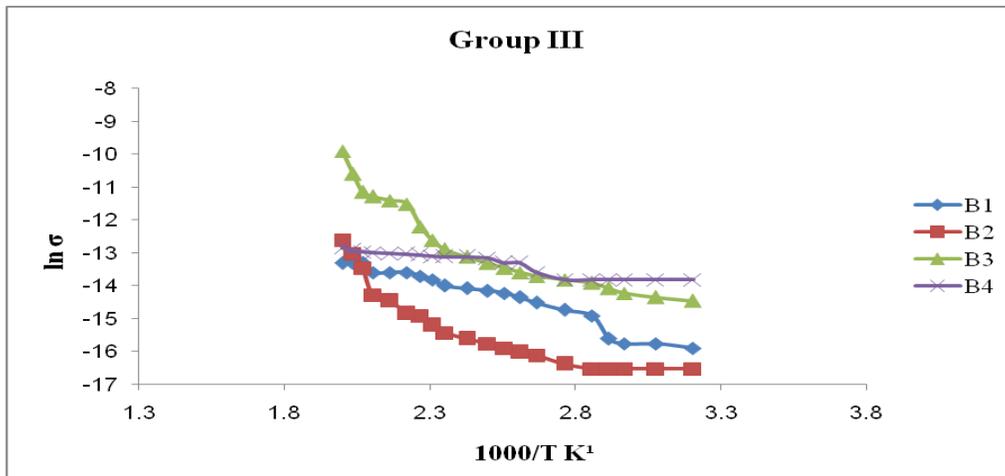
Fig .3. The relation between dielectric constant  $\epsilon'$  and temperature at 20 KHz for group III.



**Fig .4.** The relation between  $\ln \sigma$  and  $1000/T$  at constant frequency 20 KHz for group I.



**Fig .5.** The relation between  $\ln \sigma$  and  $1000/T$  at constant frequency 20 KHz for group II.



**Fig .6.** The relation between  $\ln \sigma$  and  $1000/T$  at constant frequency 20 KHz for group III.

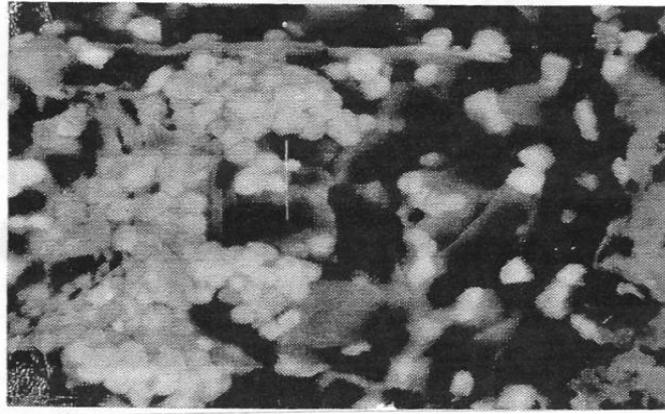


Fig .7.SEM of mix ( B4 ).

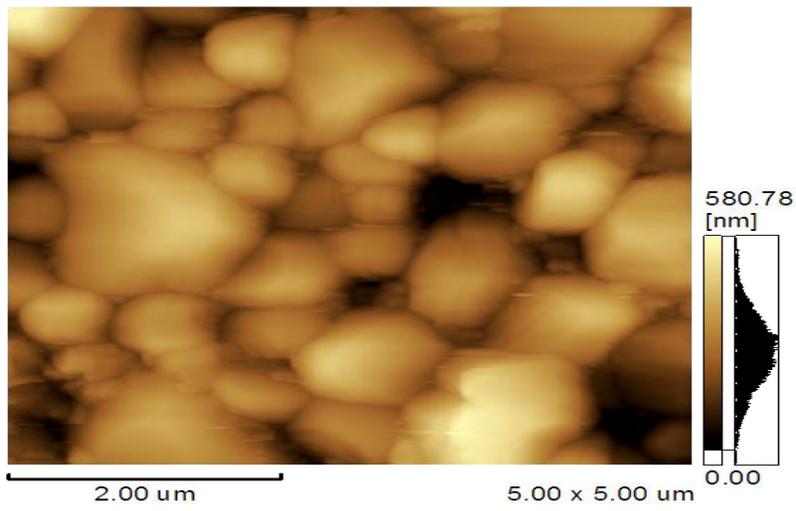


Fig.8.AFM plane image for sample M<sub>5</sub>.

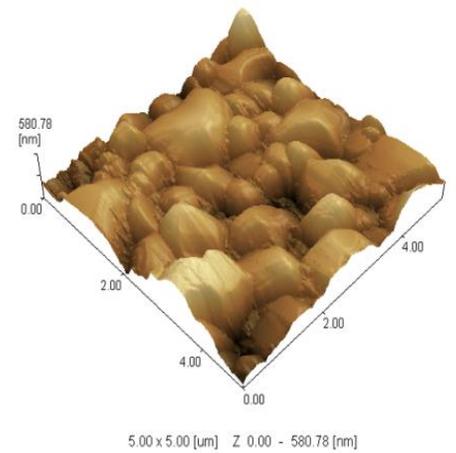
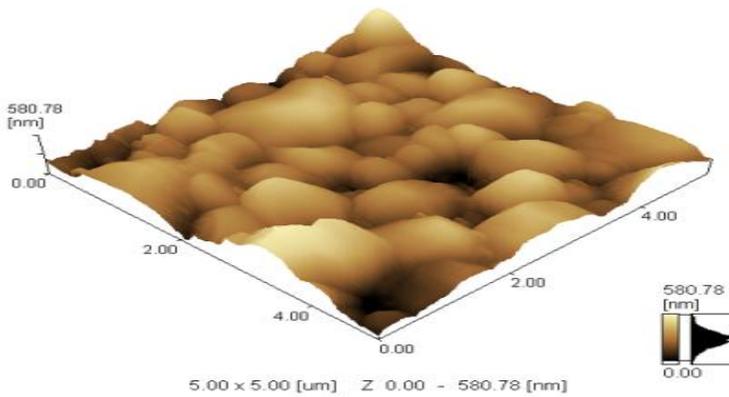


Fig.9.AFM 3D image for sample M<sub>5</sub>.

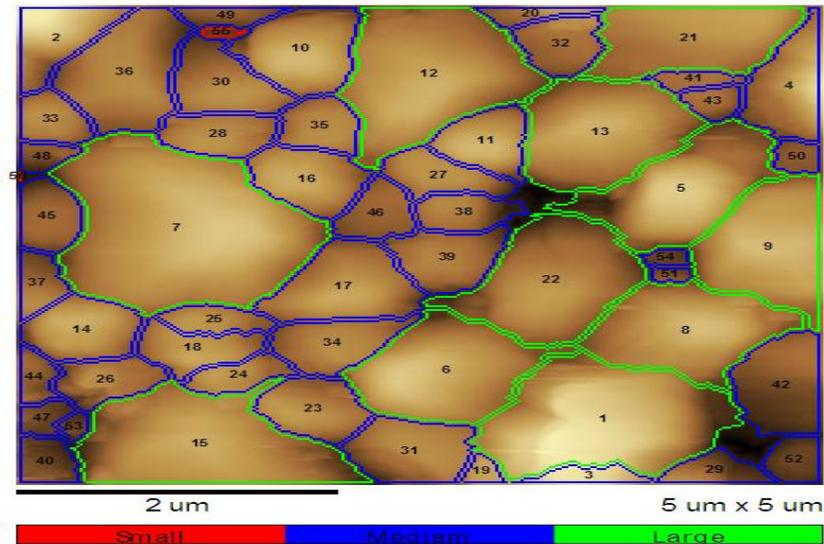


Fig.(10):AFM particle analyses image for sample M<sub>5</sub>.

Table .1. Composition of different mixes in mol %

Oxides		ZnO	Ce <sub>6</sub> O <sub>11</sub>	CoO	Cr <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>
<b>Group I</b>	M1	99.95	0.05			
	M2	99.92	0.08			
	M3	99.9	0.1			
	M4	99.8	0.2			
	M5	99.6	0.4			
<b>Group II</b>	Z1	99.45	0.05	0.25	0.25	
	Z2	99.4	0.1	0.25	0.25	
	Z3	99.3	0.2	0.25	0.25	
	Z4	99.1	0.4	0.25	0.25	
<b>Group III</b>	B1		0.05			0.5
	B2		0.1			0.5
	B3		0.2			0.5
	B4		0.4			0.5

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