Non Linearity Coefficient Evaluation of Zinc Oxide Doped Modulated Red Sea Egyptian Clay as a Varistor

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Research Article

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Abstract

Doping ZnO with different ratios of clays can increase the value of nonlinear parameters. The natural clay has been precipitated in water column, as a result of the difference in the physical properties of the different phases, the clay will precipitate in layers lighter by lighter from the bottom of the water column, So SiO_2 concentrates in lower layers and decreases to the upper layers, whereas Albite, montomorillonite, and dolomite behaves in opposite.

ZnO has been doped with different layers up to 20 % clay and sintered at 1200 C for one hour. The obtained samples have been prepared for the different measurements XRD, J-E characteristics, and SEM. XRD showed different phases with different percentages along the whole divided layers of the precipitated column. The maximum value of SiO_2 concentrates at layer 3 while the other phases have their lowest values. The electrical measurements (J-E) declared that the maximum value of α obtained by dope ZnO with layer 7 or layer no.11. The peak in α obtained at doping levels 10% or 18% for all the studied layers, this indicates the proper concentration of Si and Al that stabilize the interface potential barrier.

Introduction

Varistors have a non-ohmic characteristics on the contrary with the completely ohmic behavior of potentiometers or rheostats [1]. ZnO is the base material for making Metal oxide varistors and some other additives as a filler between zinc oxide grains. Varistor is known as a voltage-dependent resistor and it is used to protect circuit from high voltage transients. Small current can pass through varistor under natural conditions but takes a large current if the voltage rises suddenly, consequently preventing high-voltage pulses from reaching the circuit [2]. The most known type of varistor is metal oxide varistor, which is called ZnO varistor. ZnO varistor consists of zinc oxide doped with little additives (2–10) % of other metal oxides such as Bi_2O_3, Al_2O_3, Pr_6O_{11}, CoO, MnO_2, SiO_2 and Sb_2O_3.The above additives condense the ceramic and improve nonlinear properties of the varistor. The doping of SiO_2 and Bi_2O_3 makes liquid phase during sintering process and the shrinkage of every sample is about 86%. Doping ZnO with SiO_2 and Bi_2O_3 which enhance other oxide to be propagated evenly in the ZnO grain boundaries. SiO_2 can relevantly upgrade the nonlinear characteristics of ZnO- based varistors [3] also AL_2O_3 additives promote the characteristics of ZnO varistors. It leads to reduce ZnO grain growth rate, and correspondingly increases the microstructural uniformity of ZnO varistor [4]. Clay consists roughly of about 50% SiO_2, 25% Al_2O_3 and some other oxides with low abundance ratio. Natural clays have various ratios of phases which is restricted in certain range, so adding natural clays to ZnO can gives nonlinear parameters restricted in certain range as well.

Experimental

The clay sample was combined from the phosphate mines in Hamrawein area on the Red Sea Egyptian coast. Clay was crushed manually by hammer and burned at 550 c for five hours to eliminate organic matters. After that 500 gm of burned clay is dissolved in 1.5 letters of distilled water and pour in a transparent plastic tube with 2.5 m long. After three days all of the clay is precipitated in the removable Aluminum part of the precipitation tube. During precipitation we observe different shapes of precipitated clay. Some layers visually rough and other layers smooth. The water is pulled out and the removable aluminum part filled of clay has been removed out from the main tube. A suitable piston has been inserted into the aluminum tube and pushed carefully in steps to give out a layer of nearly 2 cm thickness each step. The obtained layers were dried in an electrical furnace at 120 C for 24 hours. Fourteen layers are structurally modulated from the natural clay were obtained. Layers (1, 3, 5, 7, 9, 11, and 13) have been chosen to dope ZnO (99.5% purity) according to the chemical formula; (1-x) ZnO x (Sn), where Sn the precipitated layer starting from the bottom of the removable part, x is the Doping ratio and x takes the values (0.5, 1, 2, 4, 5, 7, 10, 13, 15, 18, and 20) %. This layers grinded for 10 hours and sent for X-ray analysis for check the separation of different phases. Electrical stirrer has been used to mix ZnO with the clay in alkohl for one hour. The mix was dried at 90 °C for 24 hours .The batches were grinded by ball Milling for 5 hours .The powder were isostatically pressed in a cylindrical Pellets (1 ± 0, 05 mm thickness and 130 ± 10 mm^2 area) using a pressure 6 tons /cm^2, and then sintered at 1200 C for 1 hour, silver paste was used for electroding the samples for electrical measurements. Current-voltage characteristics were investigated up to 5000 V/cm at room temperature by using Keithley electrometers 197 A and 179 TRMS. The microstructure of the highest α samples of the all layers was studied by SEM and EDAX.

Results And Discussion

The ratios of the crystalline phases found in each clay layer (2 cm thickness) after precipitation process obtained from X-Ray analysis.

Table 1
Phases found in the burned clay layers after precipitation process and their ratios used to dope ZnO.

Layers **Phases (%)**	**1**	**3**	**5**	**7**	**9**	**11**	**13**
1- Quartz	61.8	61.8	66.13	56.81	40.33	45.28	44.33
2- Albite	18.7	15.39	19.35	23.66	30.25	28.3	27.35
3- Montomorillionite	9.7	7.7	6.45	12.42	10.08	5.66	
4- Dolmite	9.7	7.7	8. 0 7	7.1	10.08	11.32	
5- Illite					9.24		5.66
6- Kaolinite 1A						9.44	
7- Microcline							22.64

1- SiO_2 2- $NaAlSi_3O_8$ 3- Na-Mg-Al-Si_4O_{11} 4- $CaMg(CO_3)_2$

5- $K(AlFe)_2AlSi_3O_{10}(Oh)_2H_2O$ 6- $(Al_2Si_2O_5(Oh)_4$ 7- $(KAlSi_3O_8$)

From the above ratios of the crystalline phases found in the all layers, we can drew the relation between the abundance of the phases (Quartz, Albite, Montomorillonite and Dolmite) in each clay layer and layer number as in Fig. 1.

As clear from Fig. 1 Quartz phase is the major phase concentrated at layer 3 and decrease to reach plateau at layer 9 and higher layers. Albite phase decreases to layer 3 and increase to make plateau at layer 9 and higher layers. The other phases have the same behavior as Albite. This figure reflects our idea about the possibility of partial separation of the phases present in the natural clay by precipitation in water. At layer 3 quartz phase has its main effect while at layer 9 and higher layers quartz still high, 40%, but has its lowest effect, so it expected to participate with albite and other phases in any appeared phenomena.

After doping the all layers with ZnO, Electrical measurement was done and J-E characteristics for all layers doped with ZnO were obtained. Figure 2 and Fig. 3 declared J-E characteristics of ZnO doped with different ratios (up to 20%) from precipitated layer 5 sintered at 1200 ◌ C for 1 hour.

The all layers (1, 3, 7, 9, 11 and 13) have the same behavior as layer 5 and the values of nonlinearity Coefficients α for all layers are tabulated in table no. 2 and calculated as in [5]. We notice that there is a shift in most of the breakdown electric Field Eo to higher values with increasing the doping ratio especially at the higher doping.

Table 2

values of nonlinearity coefficient α for ZnO Doped clays from the mentioned layers(up to 20%).

Weight% Layer no.	1	2	4	5	7	10	13	15	18	20
1	2	3	2	2	4	3	6	15	20	10
3	2	2	2	2	3	4	3	3	6	3
5	2	2	3	3	4	5	3	5	4	5
7	3	3	3	3	4	18	3	4	9	18
9	2	2	4	5	7	13	5	6	10	5
11	2	4	2	4	4	27	11	19	27	18
13	2	4	3	3	3	4	6	14		6

From the above calculation of α, the relation between α and doping layer is given in Fig. 4 for low doping and Fig. 5 for high doping. As clear, before layer 7 or doping 7% α values are away from technical application while in Fig. 5 from 10% doping α decrease sharply to layer 3 then raised a small peak.

At layer 5, followed by two peaks at layers 7 and 11. Referring to Fig. 1 the small peak at layer 5 might be due to Quartz phase. The other two peaks at layer 7 and 11 can be attributed to mixed phases. This may be the reason of the equal height of the two peaks

The relation between α and the doping ratio from the different layers, some peaks are observed in Fig. 6 at 2%, 5%, 10% and 18%. This points that the proper concentration of Si and Al that stabilizes the interface potential barrier and enhances α achieved by doping ratio 10% and 18% from the layers (7, 9) and (1, 3, 11and 13) respectively. Pure Quartz phase has its maximum value at layer 3, but layer 3 is corresponding to the minimum α value, see Fig. 5. This points that pure quartz phase has little effect on the value of α, while mixed ratios of Albite and Quartz are much effective for α enhancement.

The microstructure of ZnO doped 15% clay from layer number 5 are given in Fig. 7. The photographs were taken in three different positions.

The elemental analysis was taken in three positions center of black grain, grain boundary and white grain as shown in Fig. 7 and tabulated in Table 3. A glance to SEM we can observe the presence of two phases black phase and white phase also there is two types of grains bare like grains and rounded edges grains. Elemental analysis declared that bare like grains are zinc silicates contaminated with Al ion as in Table 4.

Table 3
elemental analysis for 3 positions of ZnO doped clay layer no. 5

Positions	**O**	**Al**	**Si**	**Fe**	**Ca**	**Zn**
Center of black grain X5	4.6	1.5	3.6	0.8		85.2
Grain boundary X6	13.5	2.7	9.4	1.4	0.72	66.5
White grain X7	17.7	2	3.8			69.3
Positions	O	Al	Si	Fe	Ca	Zn
Center of black grain X5	4.6	1.5	3.6	0.8		85.2
Grain boundary X6	13.5	2.7	9.4	1.4	0.72	66.5
White grain X7	17.7	2	3.8			69.3

We notice from Table 3 that percentages of Si, Al, Fe and Ca at grain boundary are higher than other positions, this because silicon oxide has melting point lower than other oxides so it creates liquid phase during sintering process at low temperature, which promotes other oxides to be distributed evenly in the ZnO grain boundary [3]. Al, Si and Fe ions behave as donors that support the grain boundary barrier and increase nonlinearity coefficient.

Table 4
elemental analysis for bare like grain or rod phase.

Elements	**O**	**Al**	**Si**	**Zn**
Rod phase X4	13.75	1.03	11.06	64.23

Conclusion

Natural clay can be separated into layers enriched with certain phase by dissolving the clay in water. SiO_2 phase concentrates at lower layers, and decreases towards the upper layers, whereas Albite, Dolmite and montomorllonite behave in opposite. Doping ZnO by separated layers considerably effects on its microstructure and nonlinear properties. It seems that 18% doping gives the maximum value of α, regardless the layer number. Layer 11 doping 18% gives the maximum value of α in the studied samples.

Declarations

The work described has not been published before; it is not under consideration for publication anywhere; and publication has been approved by all co-authors and the responsible authorities at the Menoufia University and Bie.edu.eg.

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Figures

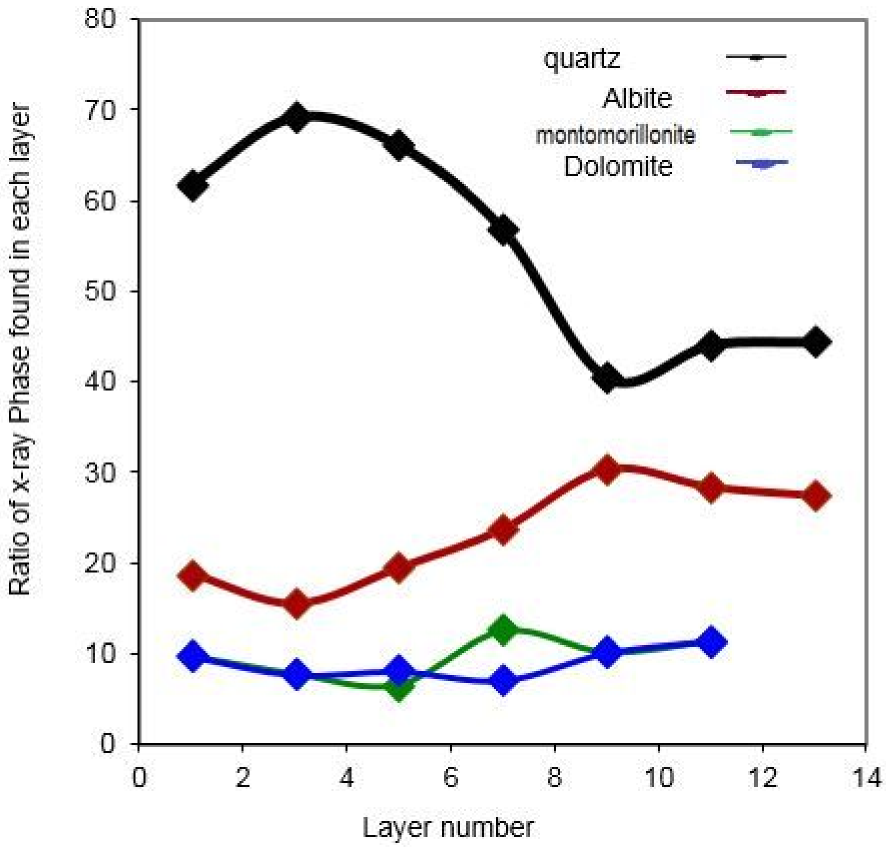
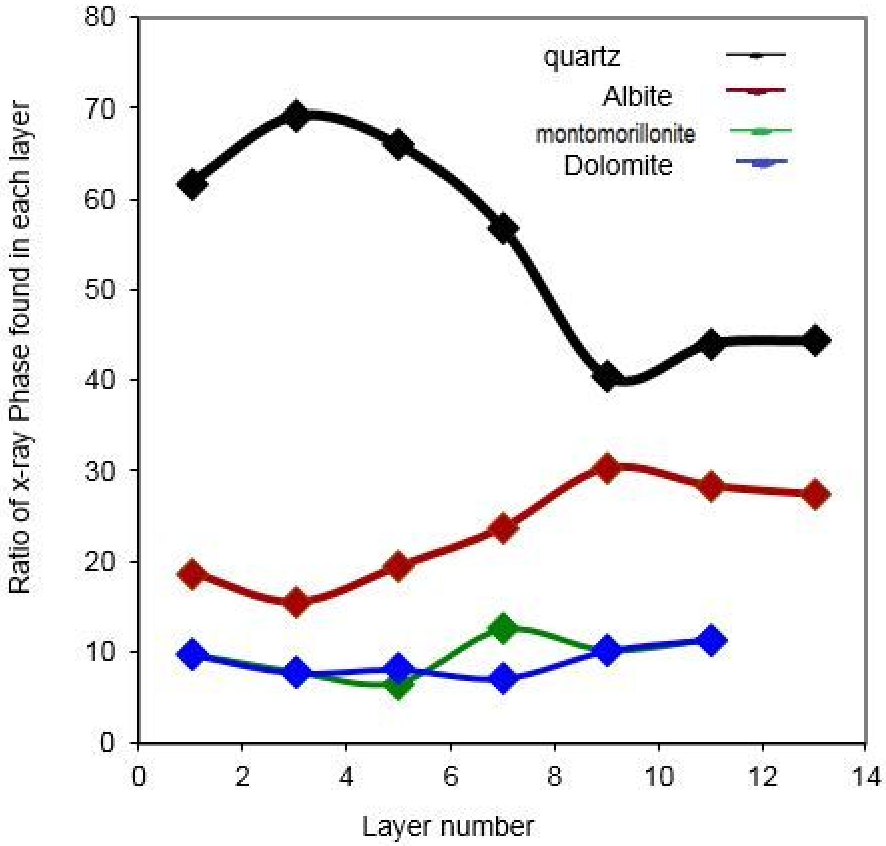


Figure 1

Ratio of crystalline phases found in each layer (2cm thickness) vs layer number



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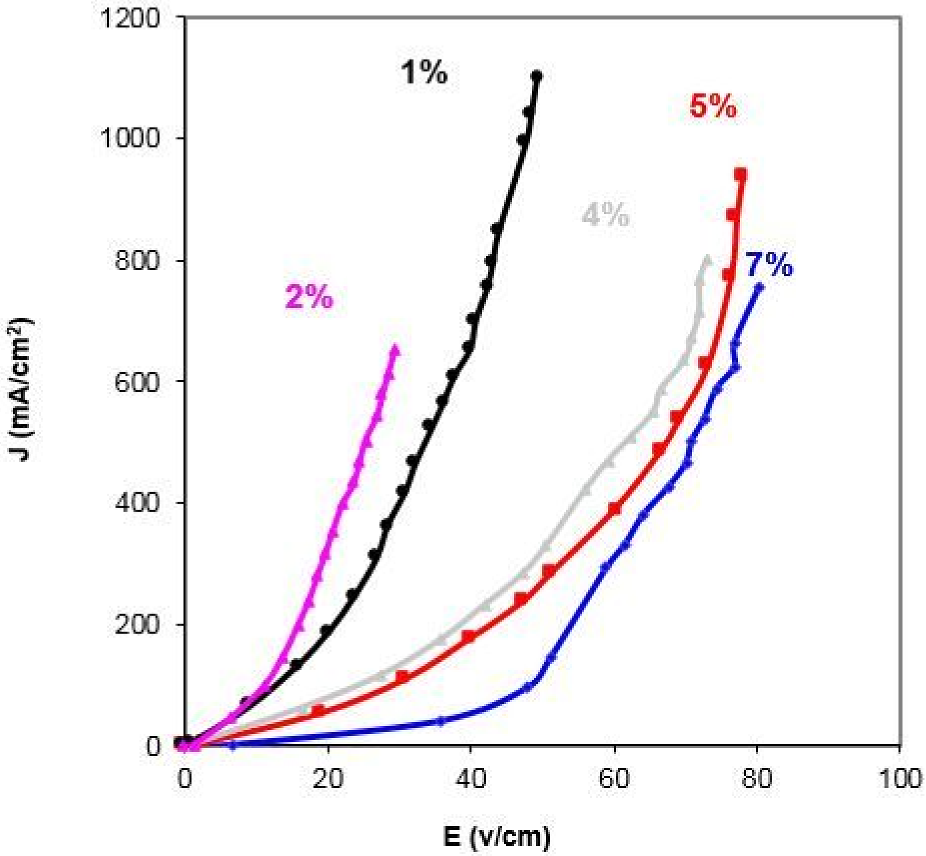
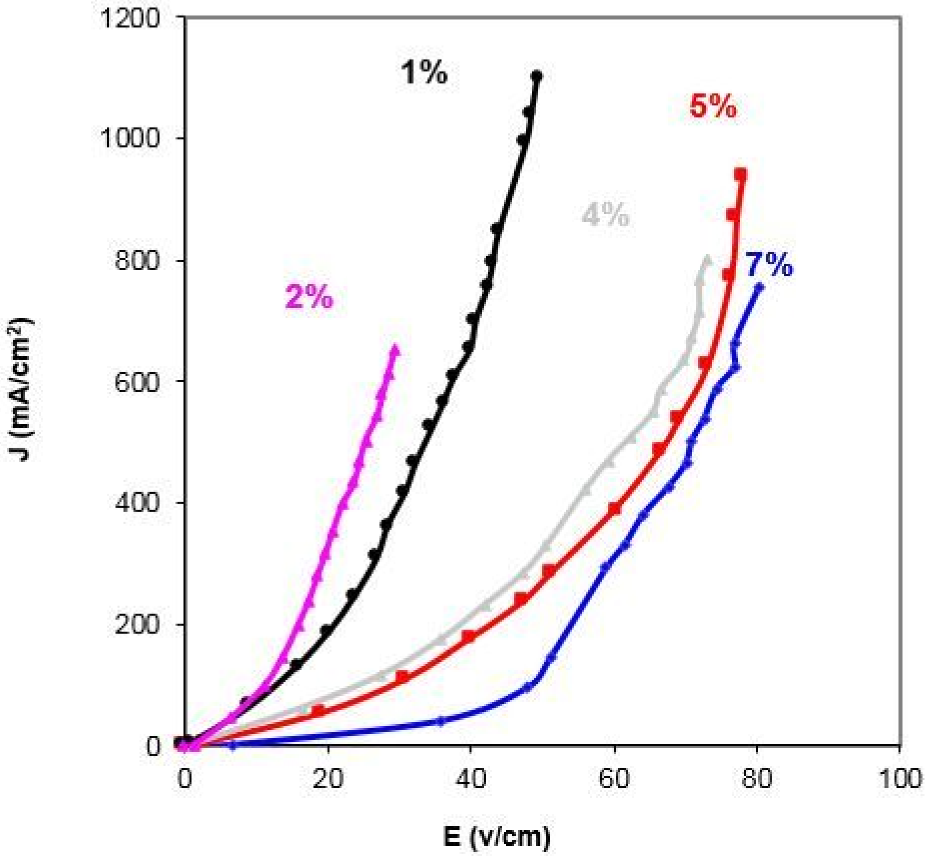


Figure 2

J-E characteristics results from doping Layer no. 5 with ZnO for low doping



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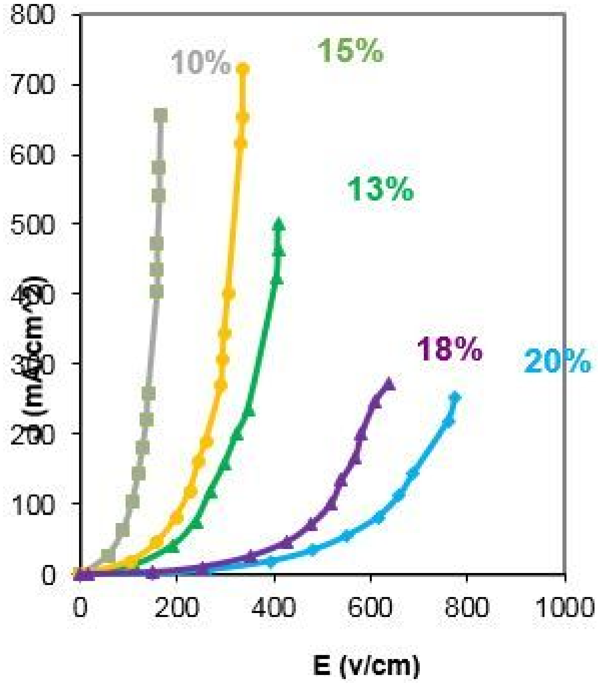
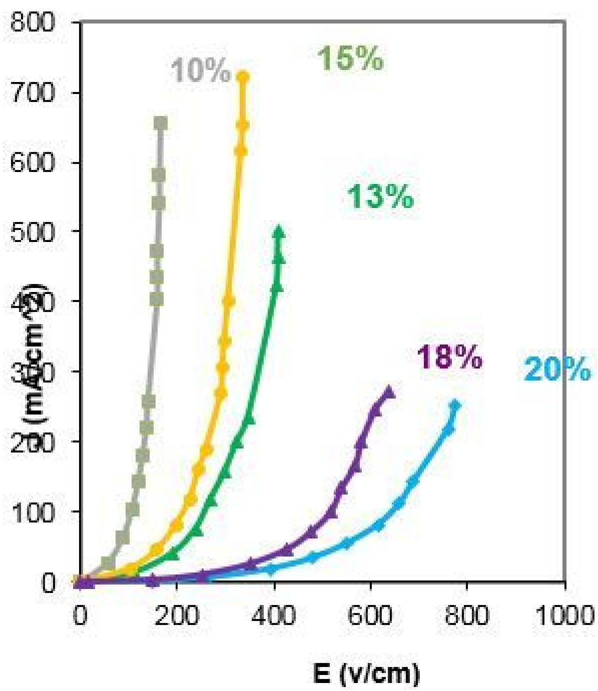


Figure 3

J-E characteristics results from doping layer no. 5 with ZnO for high doping



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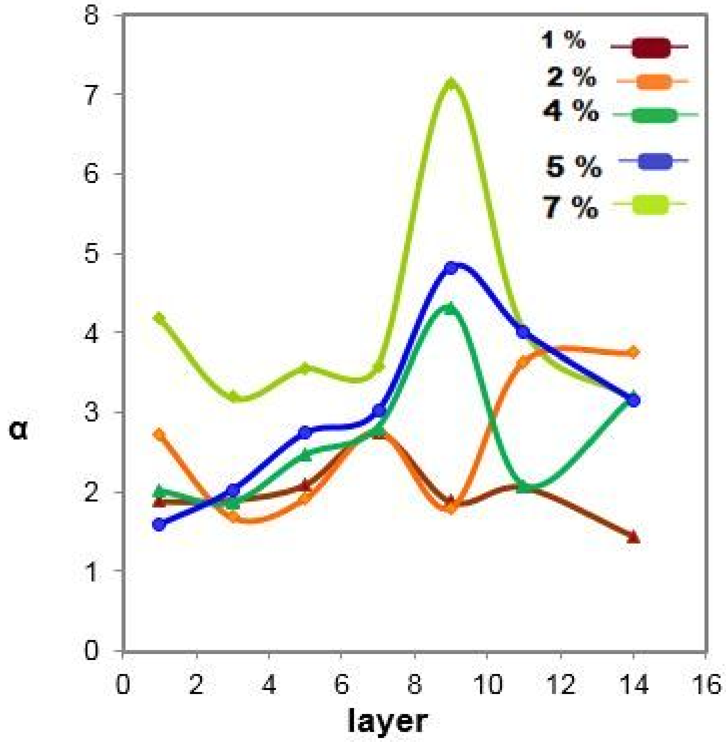
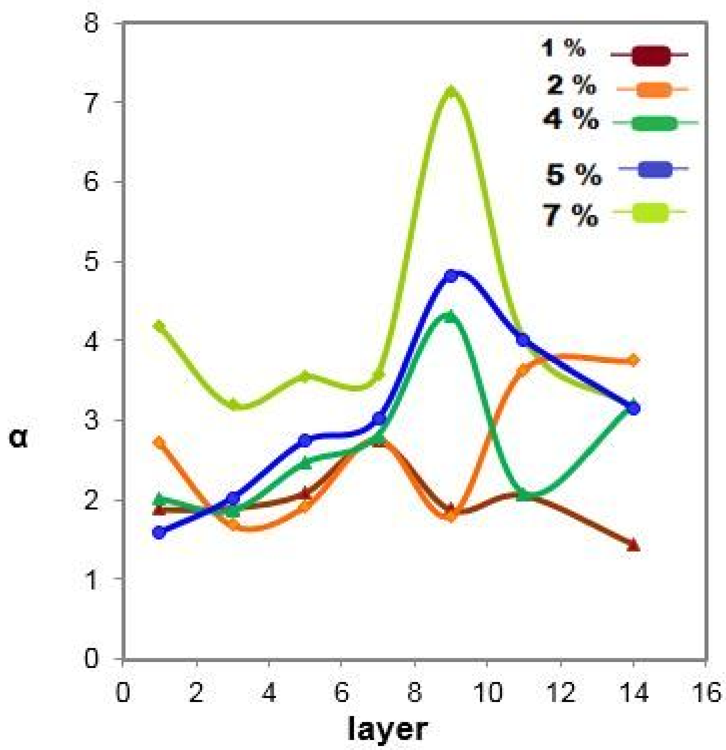


Figure 4

α versus layer number at different doping ratio in the range (1% - 7%).



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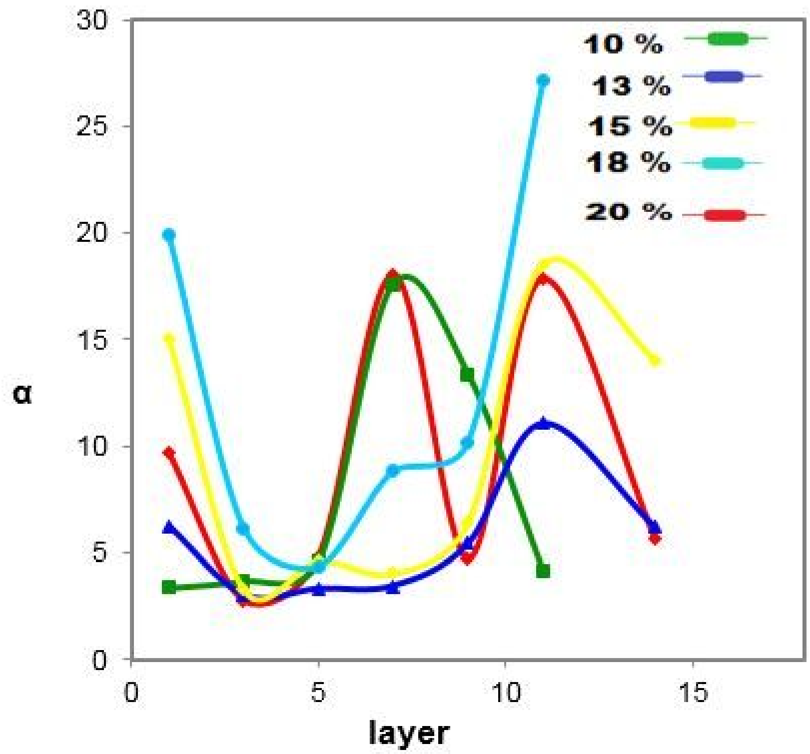
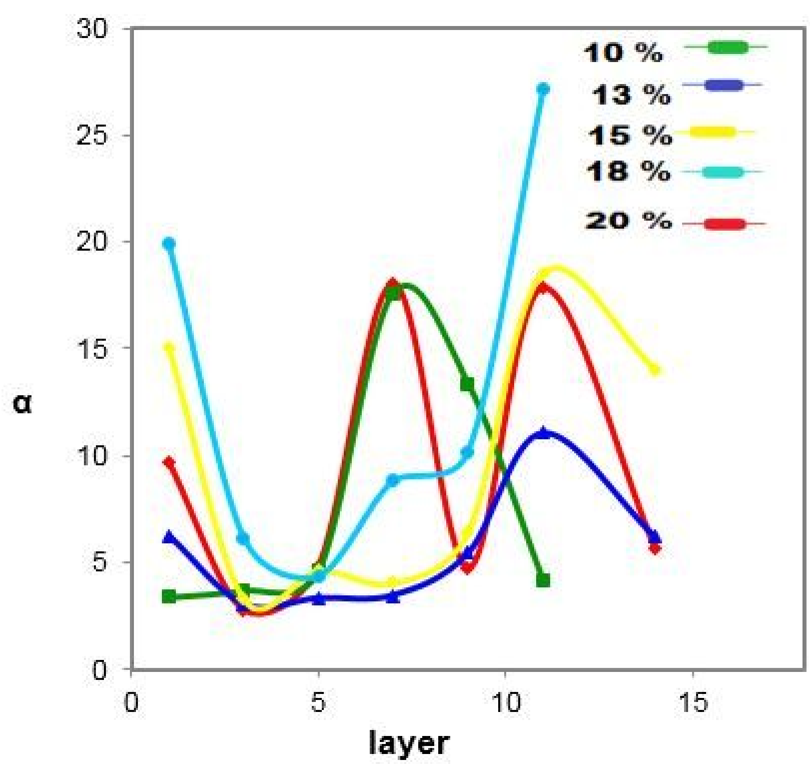


Figure 5

α versus layer number at different doping Ratio (10% - 20%).



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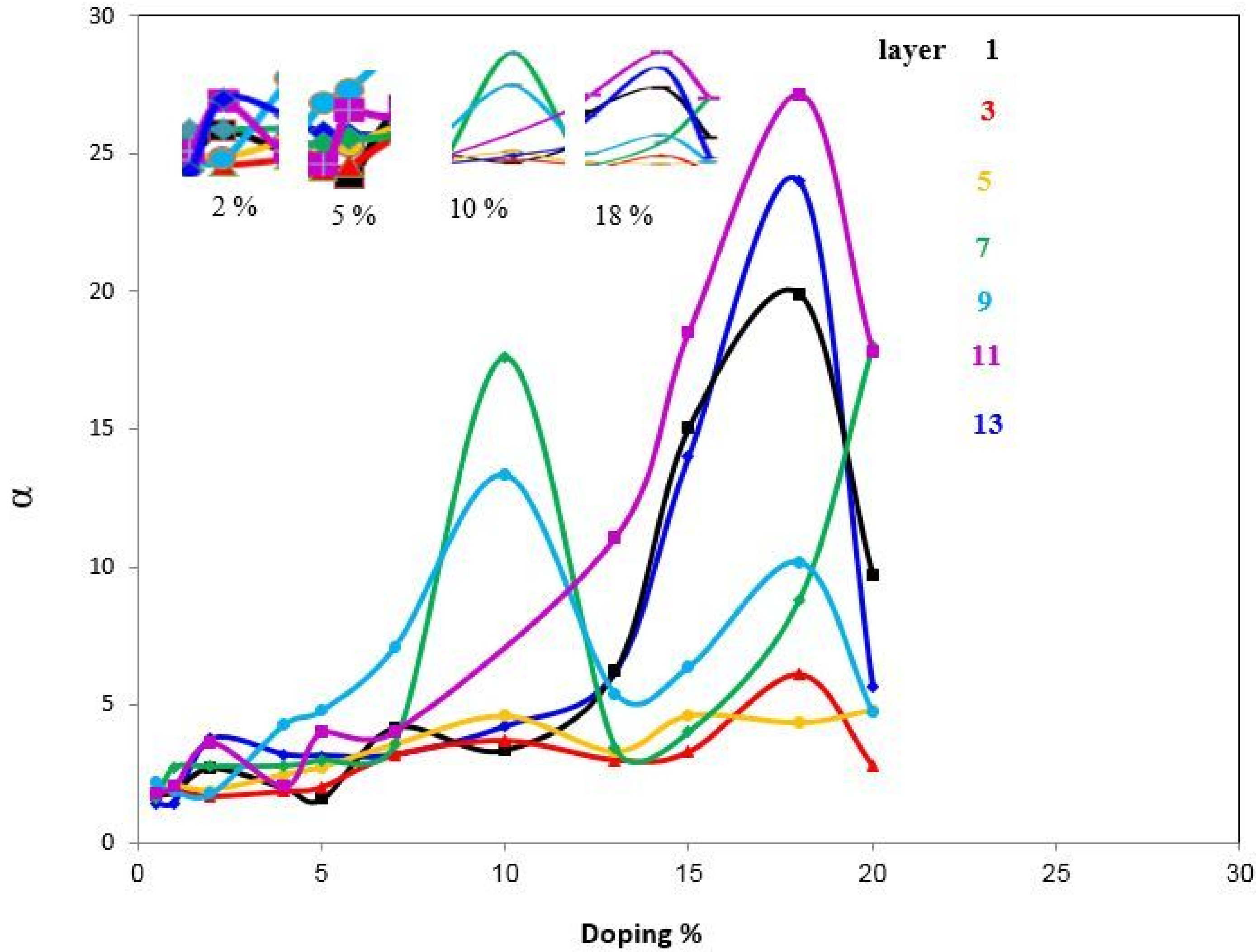
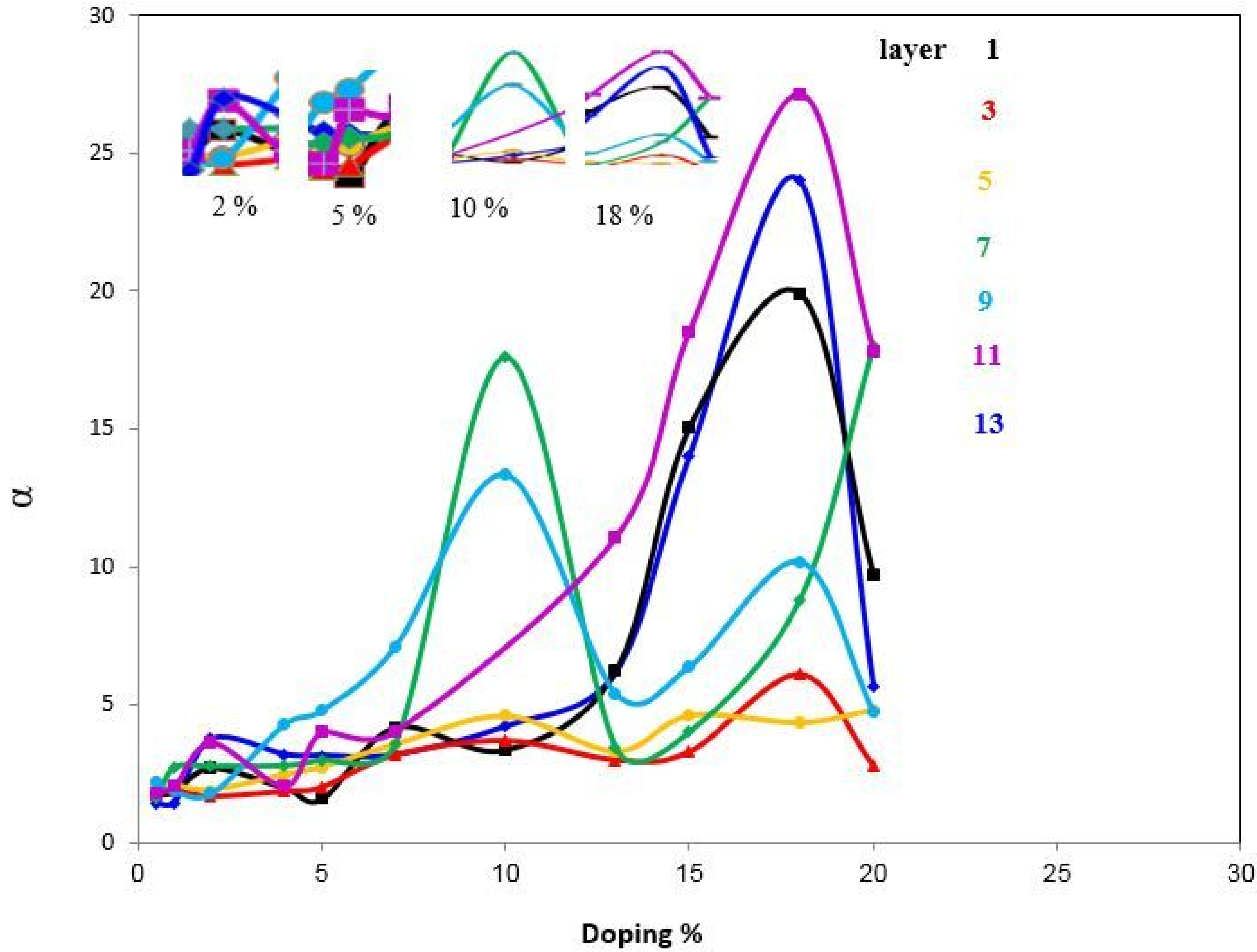


Figure 6

α versus doping percent for all the studied Layers. The insertion is the isolation of the Appeared peaks in the figure.



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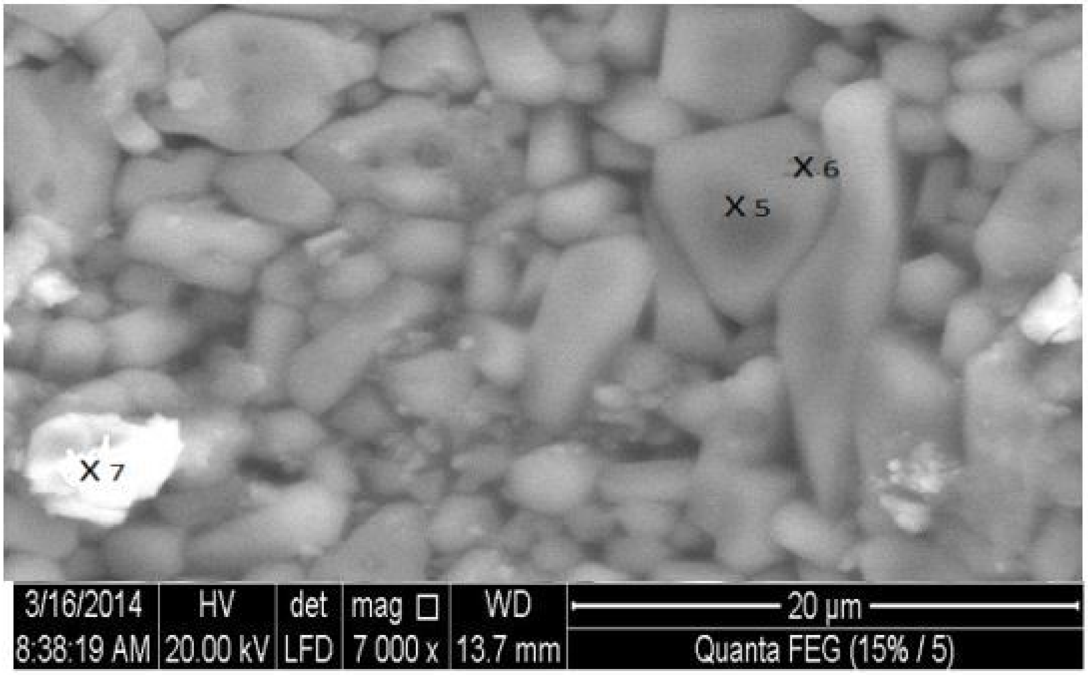

Figure 7

SEM of ZnO doped 15% clay layer no 5

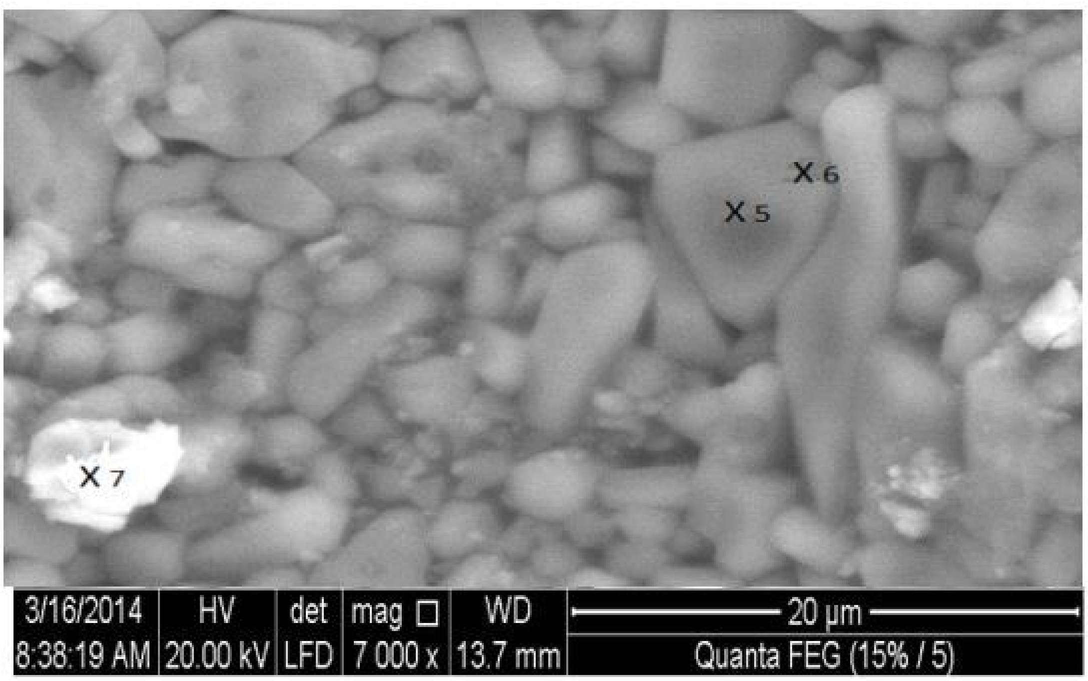

Figure 7

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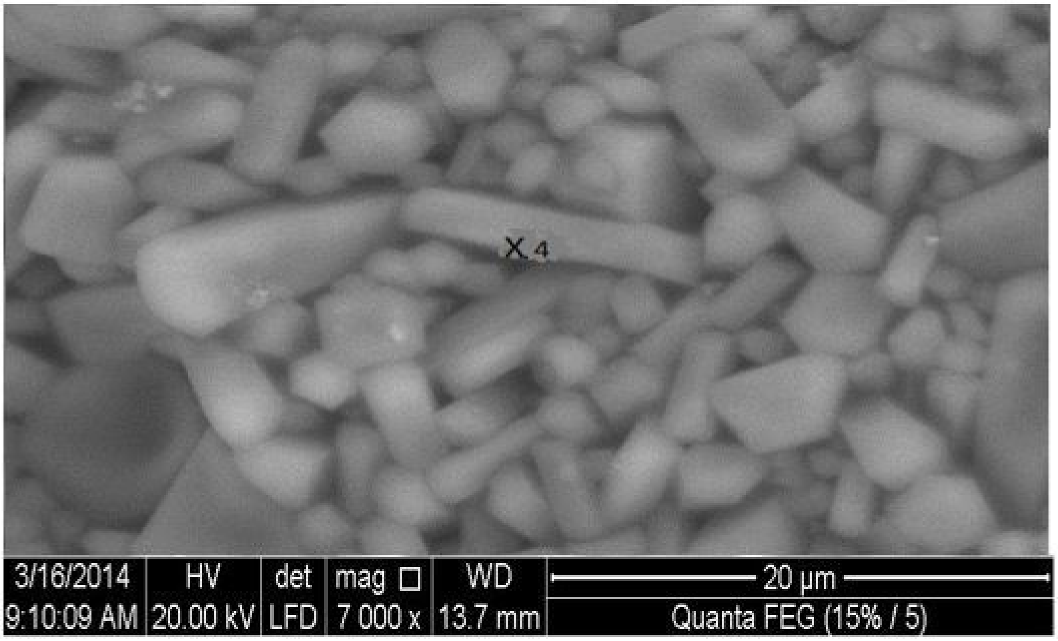
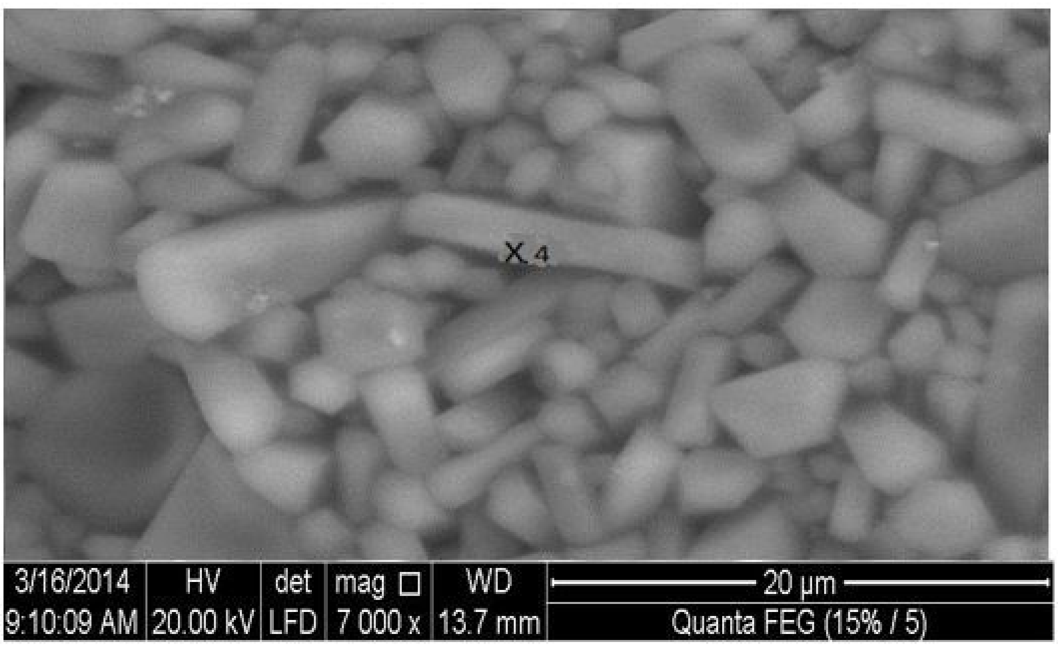


Figure 8

SEM photograph of bare like grain



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