STRUCTURAL PROPERTIES AND NON-LINEAR BEHAVIOR OF Mn DOPED ZnO VARISTORS

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Abstract

Mn doped ZnO ceramics are prepared in solid state reaction method and conventional funance annealing process. Mn (2 mol, 4 mol, 6 mol, 8mol & 10mol) are doped into ZnO, and heat treated at 500°C (melting point of Mn is 535°C) for 3 hrs. After pre heat treated at 500°C, samples are heat treated again at 1100°C for 2 hrs. XRD investigations are carried out to determine the structural properties, such as lattice parameters, crystalline size and micro strain of the samples. Mn doped ZnO ceramics are prepared as varistors and non-linear coefficients of varistors are studied. Optical band gaps of the ceramic samples are also determined.

Keywords : XRD, varistor& ceramics.

Introduction

Varistors are voltage dependent, nonlinear devices which have an electrical behavior similar to back - to - back zener diodes. The symmetrical sharp breakdown characteristics enable to the varistor to provide excellent transient suppression performance. When exposed to high voltage transients, the varistor impedance changes may orders of magnitudes from a near open circuit to a highly conductive level, thus clamping the transient voltage to a safe level. The potentially destructive energy of incoming transient pulse is absorbed by the varistor, there by protecting vulnerable circuit component.

Research activity in the area of ZnO based ceramics has been traditionally fuelled by the need for ideal candidate as intrinsic voltage regulator in the context of circuit protection. Consequently, a wide range of doped ZnO based systems have studied. Among the dopant materials, Mn is widely investigated as nonlinearity enhancer in ZnO varistor system.

In this research work, Mn doped ZnO ceramics with desired stoichiometric compositions are prepared by solid state reaction method and conventional annealing process. Structural properties of the prepared ceramics samples are investigated by using XRD. Band gaps of the ceramics samples are studied by using UV-V is spectrometer, (SHIMADZU UV-1800). Important parameters of the prepared ceramic varistors, such as, nonlinearity coefficient, threshold voltage and leakage current are also examined.

Experimental Procedure

Mn doped ZnO ceramics were prepared, using the solid state sintering method. Starting materialanalar grade ZnO and MnO_2 powders were mixed with (1 - x) ZnO + (x)MnO_2, where x = 0, 2 mol % , 4 mol % , 6 mol % , 8 mol % and 10 mol %respectively.The mixtures were mixed in agate mortarfor 2 hrs. After mixing the powders, the mixture was pre heated at 500°C (the melting point of MnO_2 is 535°C) for 3 hrs. After that, the mixture was grinded with ball

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milling for 6 hrs. Then, the mixture was heated at 500°C for 3 hrs. After heat treatment, the mixture was grounded again with ball milling for 6 hrs. Finally, the mixture was heated again at 1100°C for 3 hrs.

Structural characteristics of the ceramics were investigated from the XRD spectra, using Rigaku Multiflux. The diffraction patterns were recorded at room temperature from 10°to 70° of 2θ using Cu/K_α(λ = 1.5408Å) radiation at 0.01 degree/sec scanning speed. Structural properties of the ceramics were investigated from the XRD spectra. Optical characteristics of the ceramics samples were examined in the wavelength range from 190 nm to 700 nm, using UV Vis spectrometer, (SHIMADZU UV-1800). From the optical absorption spectra, band gaps of the ceramics were determined.

The mixture powder was uniaxially pressed into discs of 20 mm in diameter and 3.5 mm in thickness at a pressure of 19.5tons. Silver paste was coated on the both faces of the samples and the electrodes were formed by heating at 600°C for 10 min. The lnV - lnI characteristics of the ceramics were measured using, high voltage DC power supply. The threshold voltage (V_{1mA}) was measured at current 1mA and the leakage current was measured at 0.8 V_{1mA}.From the lnVvs lnI curve, nonlinear coefficient of the ceramics was studied.

Result & Discussion

Figure (1) shows the XRD spectra of Mn doped ZnO ceramics with different Mn contents. Peaks search algorithm, known as Jade software is used to identify the peaks in this study. Only the diffraction peaks corresponding to reference hexagonal wurtize ZnO(75 - 0576 > JCPDS library file) are observed. Mn has a solid solubility limit of about 13% in ZnO matrix . In this research, the Mn concentration of the samples are smaller than the solid solubility limit and Mn ions are possibly diluted in the ZnO host matrix. In addition, a shift of (101) peak maximum position is observed. This is probably due to substitution of the relatively large ionic radius Mn^{2+}(0.08 nm) at the smaller ionic radius Zn^{2+}(0.074 nm) sites.

No considerable changes in the lattice parameters are found for different Mn doping concentrations, as seen in figure (2).Figure (3) depicts the variation of lattice distortion with Mn concentration. These results can interpret as a unchanged of wuritize structure of ZnO, and the doping process is successful. Crystallite size and micro strain of ceramic samples, applying Debye-Sherrer formula is listed in table (1).

Table 1 Crystallite size and micro strain of Mn Doped ZnO Ceramics.

Mn concentration	crystallize size (nm)	micro strain
Pure ZnO	98.37	2.638×10^{-3}
Mn 2mol%	91.87	1.212×10^{-3}
Mn 4mol%	97.19	1.146×10^{-3}
Mn 6mol%	85.32	1.305×10^{-3}
Mn 8mol%	58.47	1.905×10^{-3}
Mn 10mol%	42.22	1.132×10^{-3}

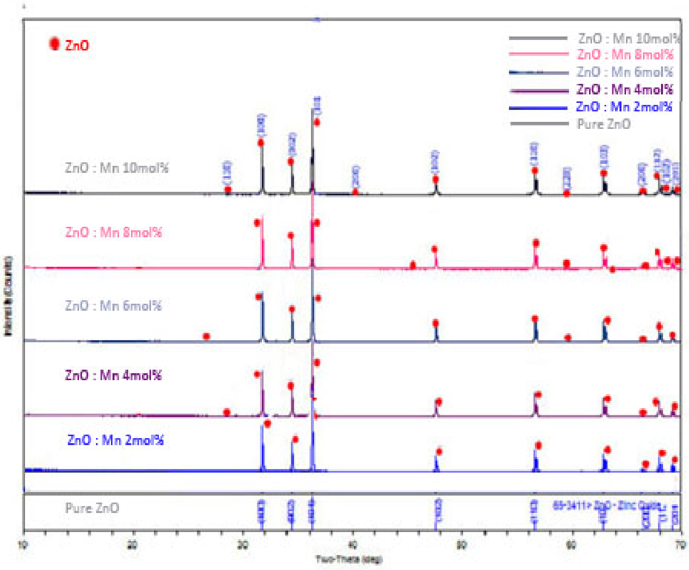

Figure 1 XRD spectra of Mn doped ZnO ceramics with different Mncontents.

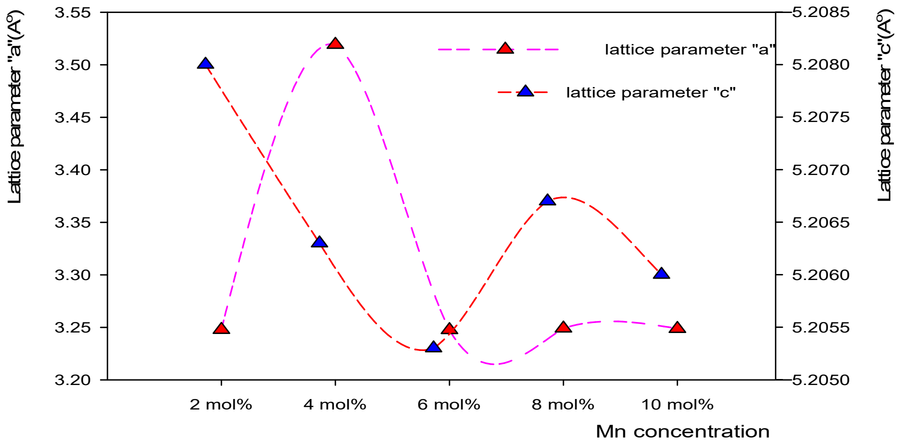

Figure 2 The variation of lattice parameters" a " and " c " with dopant Mnconcentration.

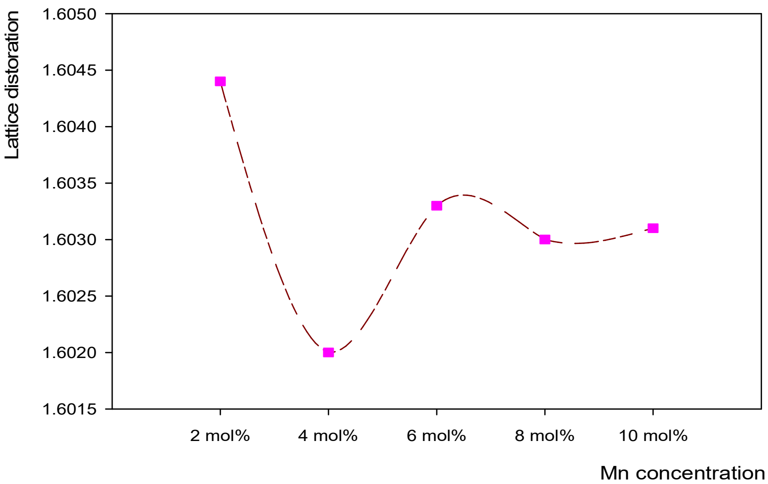

Figure 3 The variation of lattice distortion with dopant Mn concentration.

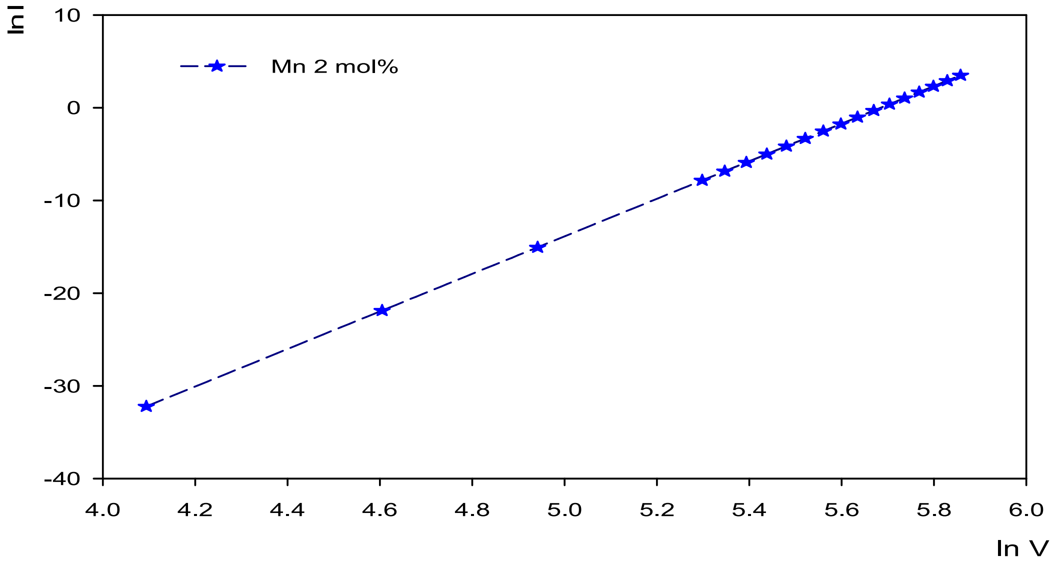

Figure 4 (a) Non- linear behavior of Mn 2mol% doped ZnO ceramics.

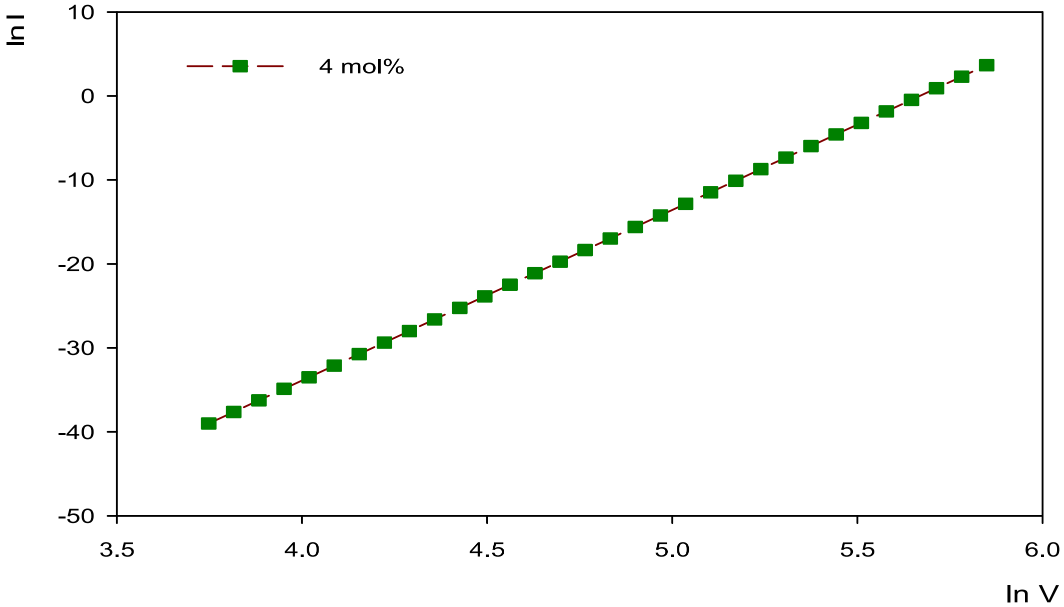

Figure 4 (b) Non- linear behavior of Mn4 mol% doped ZnO ceramics.

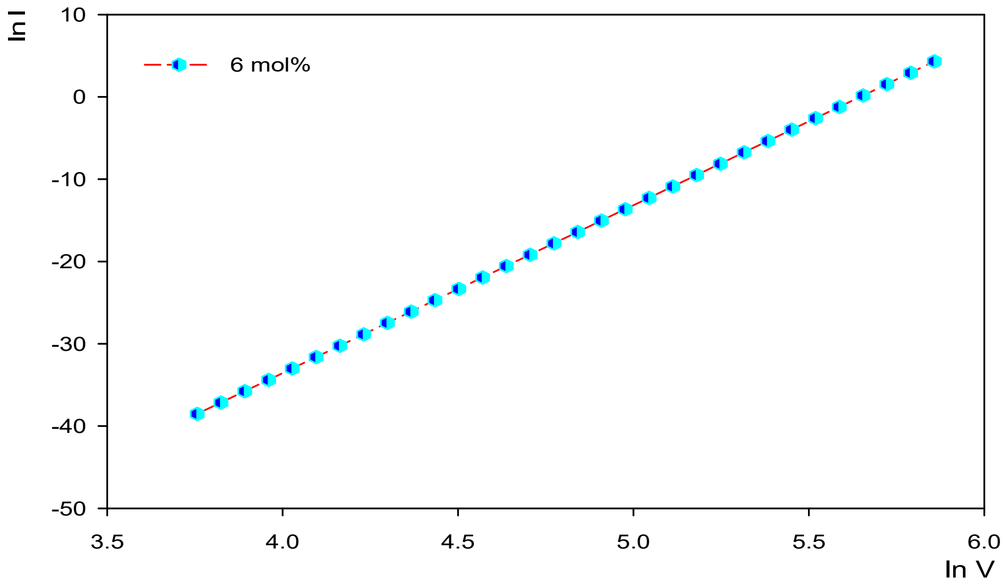

Figure 4 (c)Non- linear behavior of Mn 6 mol% doped ZnO ceramics.

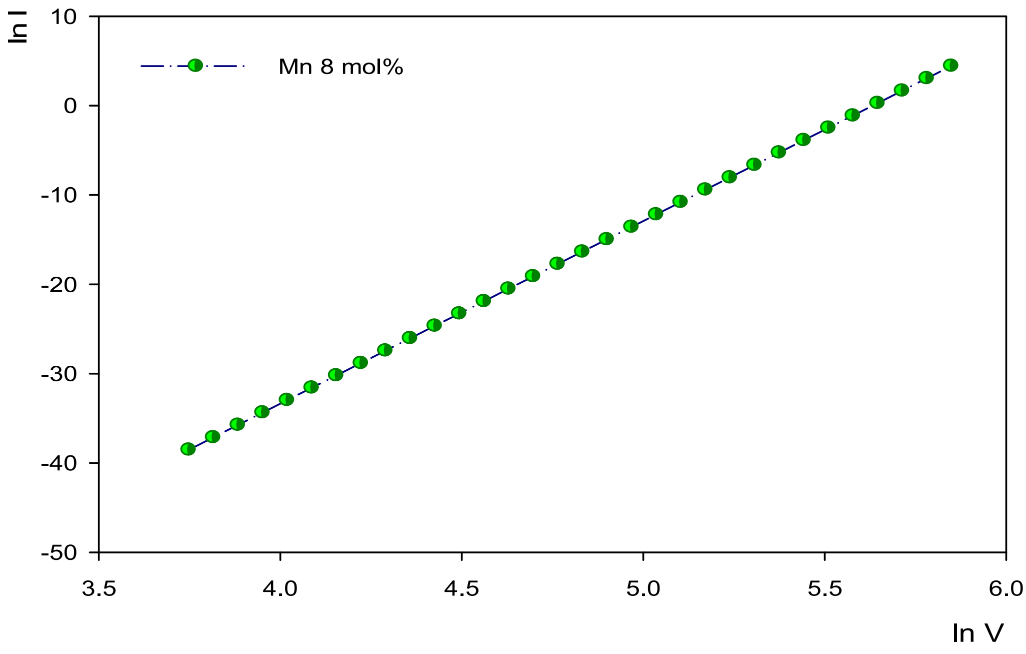

Figure 4 (d)Non- linear behavior of Mn 8mol% doped ZnO ceramics.

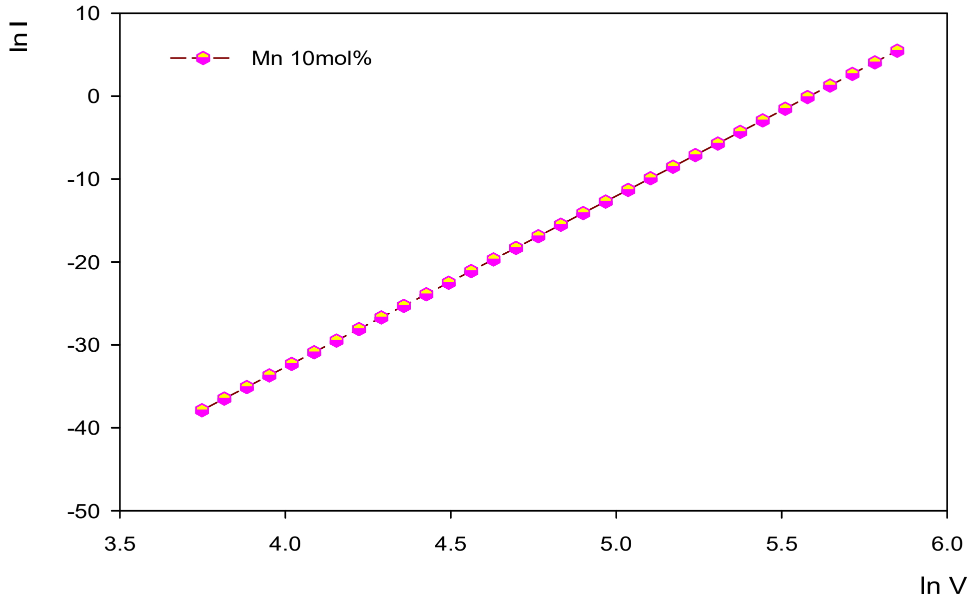

Figure 4 (e) Non- linear behavior of Mn10mol%doped ZnO ceramics.

Varistor behavior of the ceramic samples are investigated from the current - voltage characteristics of the samples (lnV vs lnI curves), as depicted in figure (4).From the

lnV vs lnI curves, nonlinear coefficients of the samples are obtained by the following relation.

$$\propto = \frac{\log\left({}^{I_2}/_{I_1}\right)}{\log\left({}^{V_2}/_{V_1}\right)}$$

where, I_1= 1 mA and I_2 = 10 mA and, V_1 and V_2 are the voltages corresponding to I_1 and I_2.Threshold voltages ($V_{1\ mA}$), which are measured at current 1 mA and leakage currents are studied at 0.8 $V_{1\ mA}$. Data are collected and listed in table (2).

Table 2 Threshold voltage, leakage current and non-linear coefficient of Mn Doped ZnO Ceramics.

Mn concentration	Threshold Voltage V_{th}(V)	Leakage Current I_L(mA)	Non-linear coefficient
Mn 2mol%	167.20	0.01675	19.57
Mn 4mol%	163.60	0.01636	20.18
Mn 6mol%	160.24	0.0160220.28	
Mn 8mol%	158.24	0.01582	21.17
Mn 10mol%	151.04	0.01510	21.23

An attractive properties of the metal oxide varistor, fabricates from ZnO, is that the electrical characteristics are related to the bulk of the device. Each ZnO grain of the ceramics acts as if it has a semiconductor junction at the grain boundary. Since the non electrical behavior occurs at the boundary of each semiconducting ZnO grain, the varistor can be considered as multi - junction device composed of many series and parallel connections of grain boundaries.

The nonlinear coefficient is enhanced when Mn content increases from 2 mol % up to 10mol %,as listed in table (2)This suggests that the segregation of Mn in grain boundary has promoted the development of essential potential barrier at interface. It is also believed that the transition metal oxides, like Mn, are involved in the formation of interfacial states and deep bulk traps, both of which contribute to highly nonohmic behavior. Threshold voltage and leakage current decrease with increasing Mn content, as listed in table (2).In general, the threshold voltage is affected by the number of grain boundaries across a series between the electrodes, which is inversely proportional to the average grain size. It is probably due to the increase of grain size which leads to lower threshold voltage in this study. The nonlinearity is required for the suppression of leakage current during the clamping of transient voltage. The higher the value of alpha, the lower the leakage current, the better the varistor ceramics.

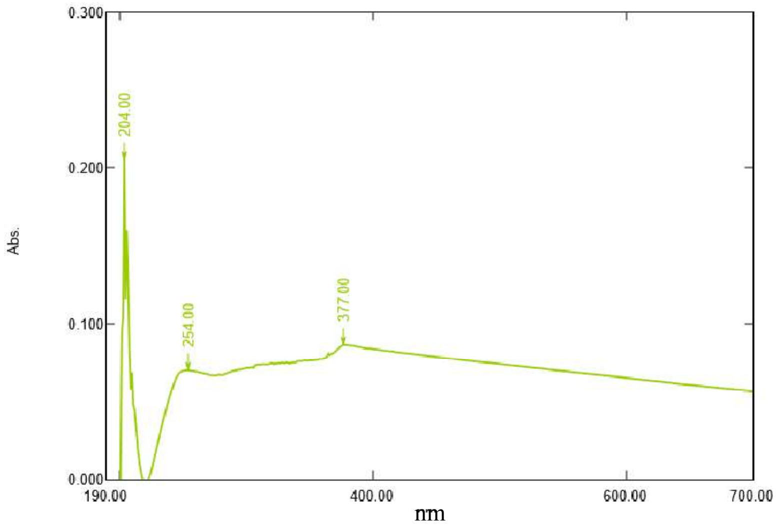

Figure 5 (a) Absorbance spectrum of pure ZnO ceramics

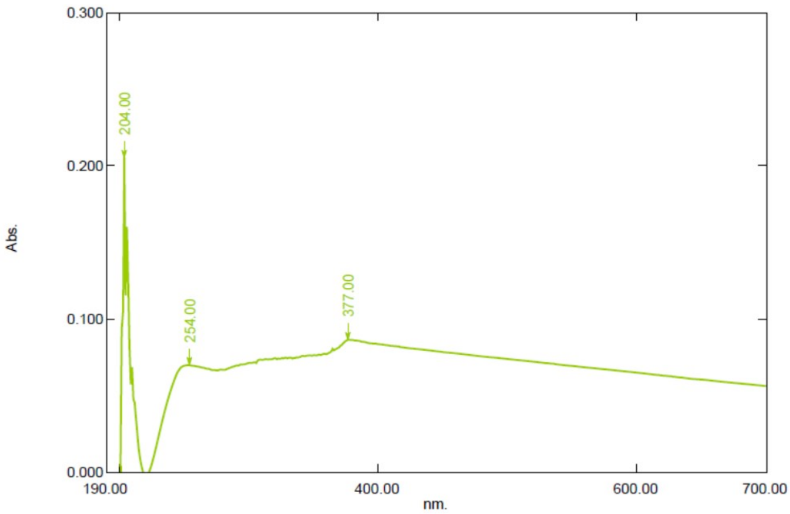

Figure 5 (b) Absorbance spectrum of Mn-2 mol % doped ZnO ceramics

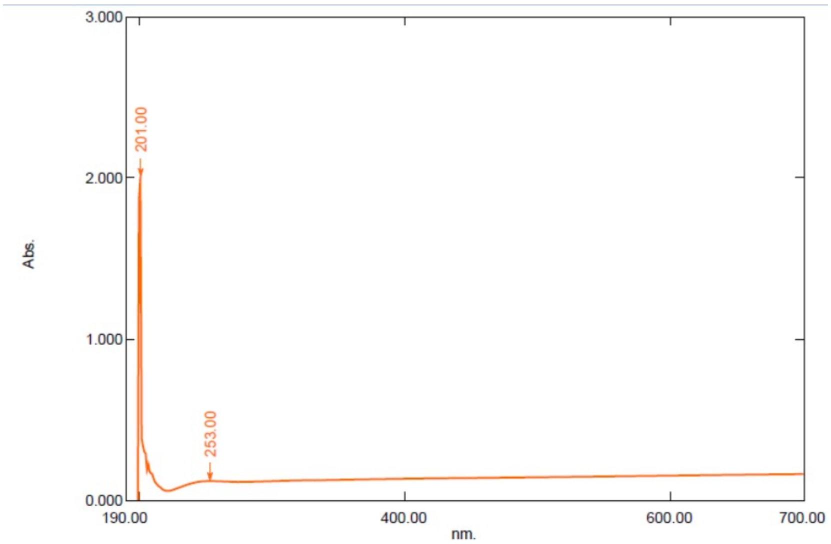

Figure 5 (c) Absorbance rum n-4 mol % doped ZnO ceramics.

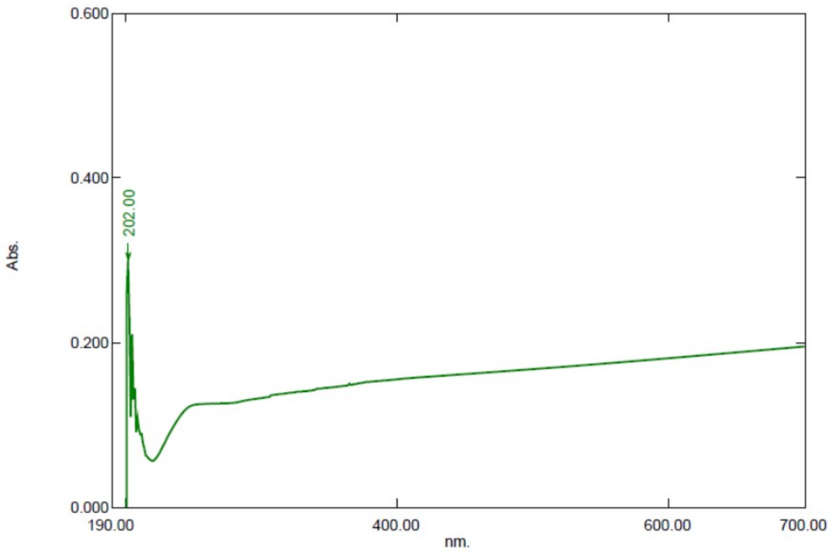

Figure 5 (d) Absorbance spectrum of Mn-6mol % doped ZnO ceramics.

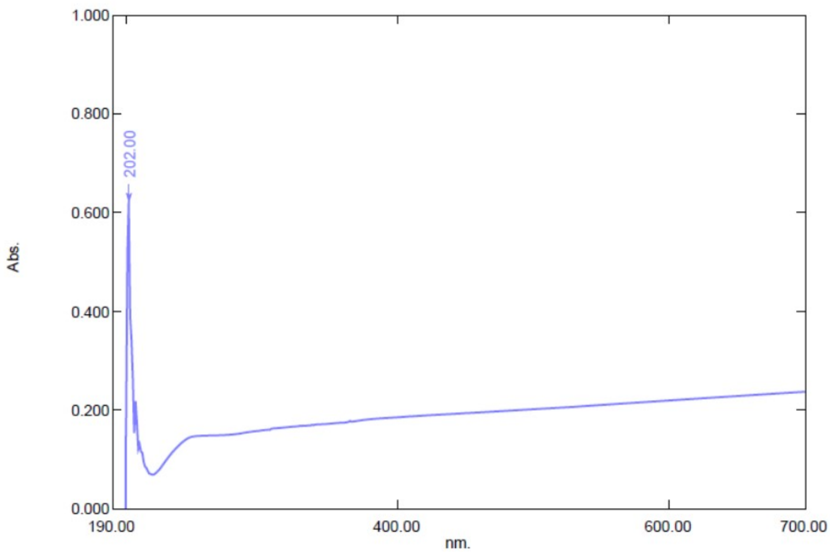

Figure 5 (e) Absorbance spectrum of Mn-8 mol % ZnO doped ceramics.

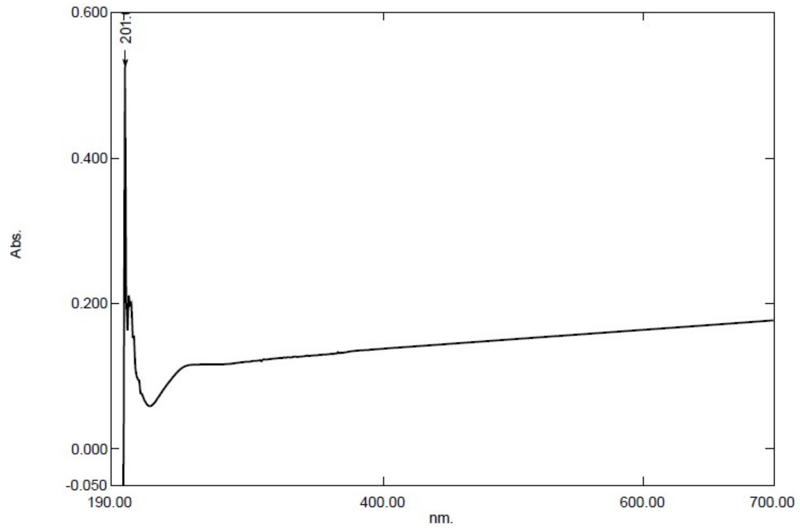

Figure 5 (f) Absorbance spectrum of Mn-10 mol % doped ZnO ceramics.

Figure (5) shows the optical absorption spectra of ZnO:Mn ceramic samples in the wavelength range 190 nm to 700 nm. It is observed that absorbance increases with Mn doping concentration. The optical bandgaps of the samples were determined by applying Tauc - Mott relation. Optical bandgaps of the samples at different Mn contents are listed in table(3). It is noted that, optical bandgap varies with Mn content. It is possible due to the quantum confinement effect. In semiconducting materials, when particle/crystallite size (in nano scale) decreases,the increases or widen up the band gap and ultimately band gap energy also increases, known as quantum confinement effect.

Table 3 Energy gaps of ZnO cermanics at different Mn Contents

Mn concentration	Energy gap (eV)
Pure ZnO	3.274
Mn 2mol%	3.315
Mn 4mol%	3.377
Mn 6mol%	3.417
Mn 8mol%	3.446
Mn 10mol%	3.523

Conclusion

Transition metal oxide, Mn ions were successfully doped into ZnO host matrix via solid state sintering method in this study. XRD technique was used to analyze the structural properties of ceramic samples. Influence of dopant materials Mn on lattice parameters, latttice distortion, crystallite size and micro strain were examined. Ceramic samples were prepared with standard varistor preparation process and non- ohmic properties of the samples were determined. Variation of dopant materials Mn with varistor parameter, such as, threshold voltage, leakage current and nonlinearity factor were determined. Furthermore, optical bandgaps of the samples were evaluated.

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