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Cr-DOPED ZnO Prepared by Solid State Reaction Method

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Abstract
In this paper, the effect of doped concentrations of Cr at ZnO powder has been studied using structur, magnetic and electrical properties has been investigated by X-Ray Diffractometer (XRD), Vibrating Sample Magnetometer (VSM), I-V and C-V measurements. The preparation of doped ZnO was using solid state reaction method with high speedshaker mill and continued with sintering at 900^0C for 4 hours. Samples doped with Cr has polycrystalline hexagonal wurtzite structure with increasing Cr composition indicates the presence of impurity. From the results VSM of doping ZnO, Cr showed diamagnetic properties become paramagnetic. The results of the I-V and C-V meter Cr doped ZnO resistivity value increases ,decreases conductivity and dielectric constant decreases.
Keywords: Cr , ZnO, Structur, Magnetic, Electrical properties

1. INTRODUCTION

ZnO recently quite a lot of interest than GaN and is a promising material for ultraviolet (UV) LEDs and laser diodes, because it has a band gap (3:37 eV). ZnO has been predicted to maintain ferromagnetic properties at room temperature, ZnO doped with transition metals Mn, Fe, Co and Ni will become a ferromagnetic behavior. ZnO: TM is interesting not only in terms of room temperature ferromagnetic, Because the high energy gap, ZnO semiconductor very efficient in absorbing ultraviolet rays and emits blue light (Lojkowski et al., 2002). Because of these characteristics of semiconductor ZnO has potential there are many applications (Pivin J.C ., 2008). Previous studies (Prakash Chand et al., 2014, Yang Liu et al. 2010, Shubra Singh et al., 2008) suggests the addition of Cr doped affects the structure of the resulting crystals. Such changes result in magnetic and electrical properties.

Several methods have been used for the fabrication of Cr doped ZnO as: thin films (Fu Chang-feng ,et al., 2010, Xiaolu Pang., 2011), sol gel (Yang Liu et al., 2010), chemical vapor synthesis (CVS) (Wei Jin et al., 2007), co-precipitation (Vishwanath Dattu et al., 2012). ZnO: Cr has been widely studied, but little is using solid state methods rection. However, the method of solid state reaction is less expensive, simple in preparation and could be more easily to scaled-up compared to some of the earlier methods of doping such as ion implantation and thin film deposition (Owens, 2009). In this study solid state reaction method is used for fabrication ZnO: Cr. Effects composition variation of doped on the structure, the nature of electricity and magnetism was studied using XRD, I-V meter, C-V meter and VSM.

2. RESEARCH METHODS

The main material for this study was using source-based ceramic oxide (ZnO), while doping material (Fe and Cr) was used a pure metal. Doping concentrations were varied from 2.5 to 4.5% atom. The ZnO and Cr powders were mixed and milled in the cylindrical stainless steels with stainless steels ball, where the ratio of the powders and balls is 1: 10. That process is done by wet milling with the toluene as solvent for 3 hours. Afterwards, milled powders drayed on oven at 100°C for 3 hours. The result powders pressed in the bulk forms with diameter is 15 mm and thickness is 2mm. All samples synthesized by using aoutomatic axial hydrolic press with 1500 kgf/cm^2. This Bulk sintered in temperature 900°C for 4 hours in air. The Phase and crystal parameters of sintered ceramic are identified by XRD using Cukα radiation (λ = 1.5406 Å), diffractometer (40 kV, 30 mA), Smartlab-Rigaku. I-V using FLUKE 8842A Multimeter and C-V meter were used to analyze the electrical properties. And the magnetic properties is measured using Vibrating Sample Magnetometer Oxford types VSM 1.2H .

3. RESULT AND DISCUSSION

From Figure 1-a, it can be seen that the XRD patterns of ZnO doped with Cr has similarities with the XRD pattern of ZnO doped with Fe. This result is also confirms that ZnO doped with Cr has a wurtzite hexagonal structure (Didik Aryanto. et al ,2016) with the dominant peaks intensity at planes (100), (002) and (101) (JCPDS No. 00-005-0664). The appearance of $ZnCr_2O_4$ secondary phase at ZnO doped with Cr is also found at angle 2θ of about 30.32°, 35.1° and 57.5° (JCPDS No. 01-087-0028). The increasing value of ion Cr dopant will affecting the number of Cr ion that insert themselves into the ZnO lattice. Which can be recognized by the increase of intensity peak (as shown in Figure 1-b). While details observation peak of ZnO at (002) plane, showed that there is also a shift to the greater value of 2θ (Figure 1-c). This can be indicated as the Cr ion is successfully substitutes ion Zn in ZnO lattice. The ionic radii value of Cr^{3+} (0.64 Å) that is smaller than Zn^{2+} ion (0.74 Å) is believed to be the cause that the peaks is shifted to a higher value of 2θ (12,6) also reported a similar results, with the increasing value of Cr dopant causes a shift in the diffraction peaks. Changes to the diffraction peaks may also indicate the change of crystal parameters (Richa Bhargava , et al., 2010).

Based on the data of FWHM of diffraction peak of (002) plane, the average size of the crystals (D) can be calculated using Debbey Scherrer formula as given in Equation (1) (S. M. Salaken . et al .,2013),

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where β is the FWHM of the diffraction peak (002). In this work, the crystal size of ZnO doped with Cr, in which the crystal size is directly proportional to the increase of dopant. (Sajid Ali Ansari , et al,2011) reported that the ZnO crystal size is reduced as the effect of the increase in the number of Cr dopant. This is because the ionic radius of Cr^{3+} smaller than the Zn^{2+} ions. The difference in the results of this work may be due to the effects of heat treatment that was performed to the sample, and the grain size will also be different due to the agglomeration (Didik Aryanto, et al 2016) .XRD patterns of pure ZnO and Cr doping ZnO were prepared by solid state reaction method shown Calculation of crystal parameters such as d-spacing, the average size of the crystals, the lattice parameter, of ZnO (002) for doping ZnO Cr shown in Table 1. *d-spacing* of the crystal planes (002) for the hexagonal structure is determined by using the equation

$$\frac{1}{d^2} = \frac{a\left(h^2 + hk + l^2\right)}{\left(3a^2\right)} + \left(\frac{l^2}{c^2}\right) \qquad (2)$$

Where *a* and *c* is a hexagonal crystal lattice parameter, *h k l* is the index miller. The value of the d-spacing is closely related to the presence of strain fields within the non-equilibrium grain boundaries inside of crystallite (Didik Aryanto ,et al., 2016).

In Figure 1 are: (a) shown XRD patterns of pure ZnO and ZnO doping Cr, (b) detail of the XRD pattern observation angle of 20 to 65°, and (c) detail observation of the peak of ZnO (002)

Table 1. Calculation of the lattice parameter and the average size of the crystals in the plane (002) for ZnO:Cr

Sampel	FWHM (deg)	*d*-spacing (Å)	D (*nm*)	*a* (Å)	*c* (Å)
ZnO	0,161	2.6035	46.06	3.2489	5.2049
Cr-25	0,159	2.5994	46.82	3.2450	5.1985
Cr-35	0,158	2.6000	47.16	3.2462	5.2000
Cr-45	0,159	2.5993	47.00	3.2451	5.1987

It is apparent in Table 1, the lattice parameters, distance changes with increasing Cr dopant. The crystal parameter value of ZnO doped with Cr in general is smaller than the value of pure ZnO. This indicates that the Cr^{3+}, which both have an ionic radi smaller than Zn^{2+} ions have been substituted into the ZnO lattice.Cr^{3+} ions that is filling the site of Zn^{2+} ion lattice is resulting crystal defects and charge imbalance in ZnO structure . These results are shown in the XRD patterns, where the peak intensity decreases and the FWHM become wider by increasing the number of dopants.

From Figure 2-a, can be observed magnetization of the magnetic field versus ZnO doped with Cr with variations in concentration (2.5, 3.5 and 4.5% atom), which indicates the nature of the diamagnetic become paramagnetic as shown in Figure 2-c, d and e. From Figure 2-b can be observed magnetization of the magnetic field versus pure ZnO without milling showed diamagnetic properties. In this case means ZnO powder used in this study before doped is diamagnetic. Similar results were also reported by previous researchers that the pure ZnO is diamagnetic (Singhal. A, 2012). ZnO doped with 2.5% Cr atoms showed minor effects diamagnetic phase up to 85 kOe (Figure 2-c). Whereas the addition of doping Cr 3.5 and 4.5% of atoms leads to minor effects diagmagnetik properties respectively to 31 kOe observed (Figure 2-d) and 84 kOe (Figure 2-e). In this case means ZnO powder used in this study before doped is diamagnetic. In this study, changes in magnetic properties due to formation of new phase indicated that $ZnCr_2O_4$ when ZnO doped with Cr (as shown in the results of characterization XRD). In this case the results of previous studies reported that $ZnCr_2O_4$ have antiferromagnetic properties on Neel temperature and are paramagnetic at room temperature (Nayak Rojali., 2013).

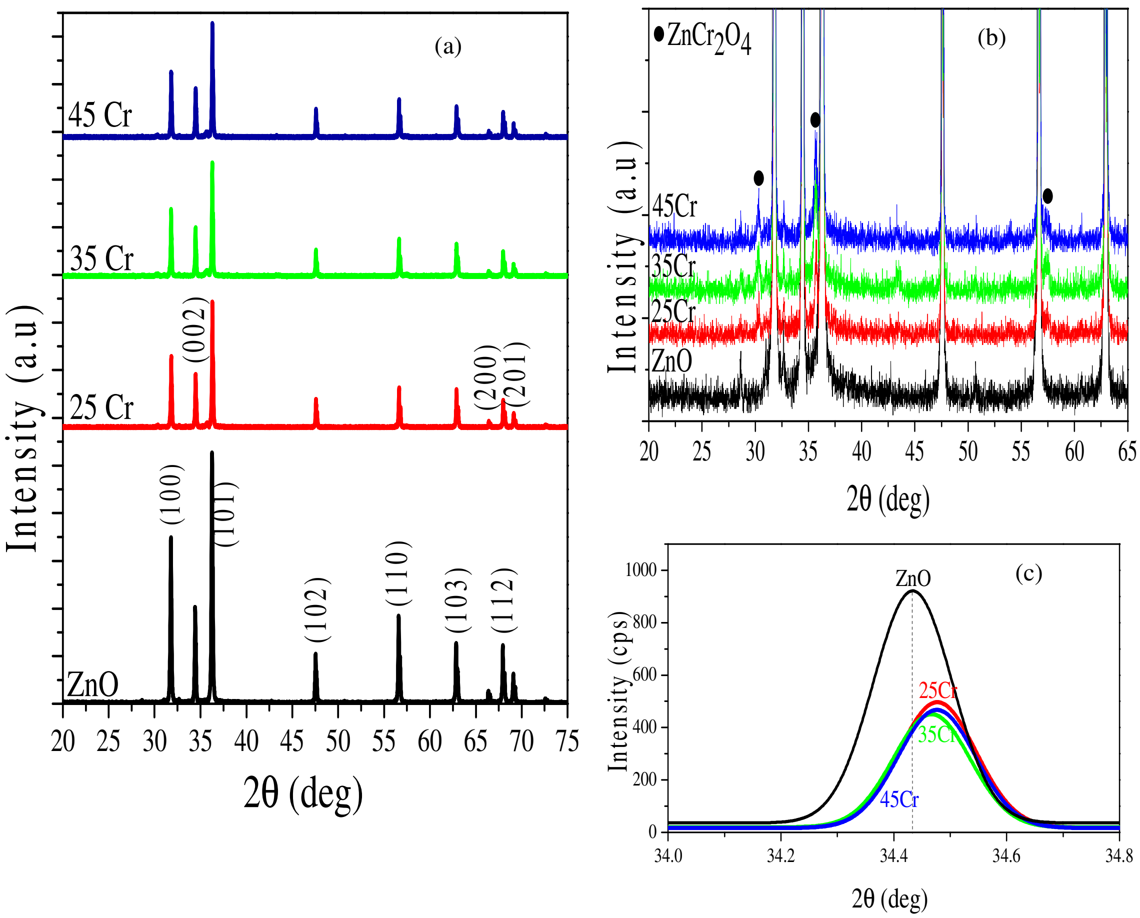
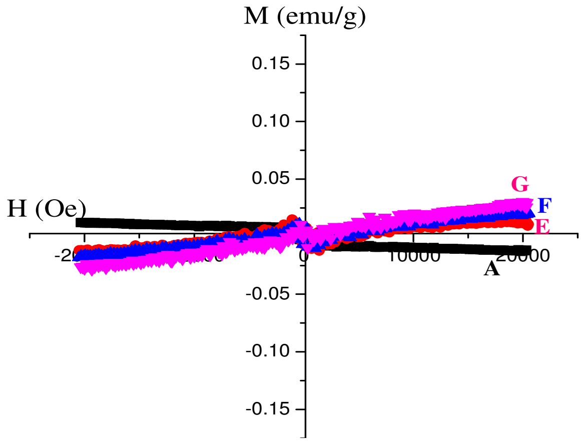
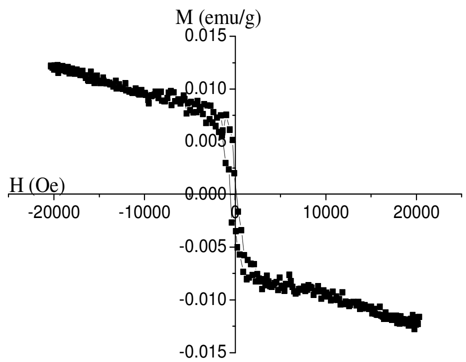


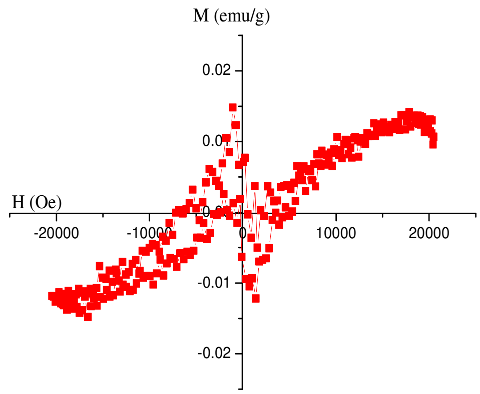
Figure 1. (a) XRD patterns of pure ZnO and ZnO doped with Cr, (b) detail of the XRD pattern observation angle of 20 to 65° and (c) detail observation of the peak of ZnO (002).



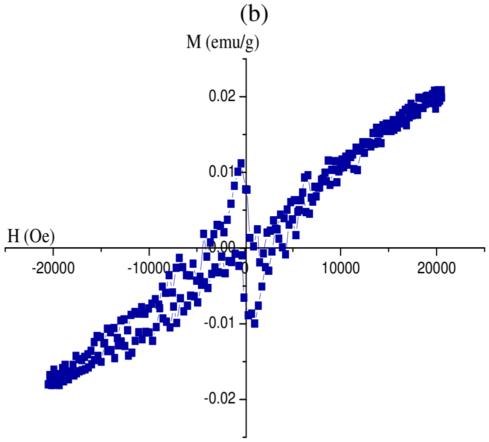
(a)



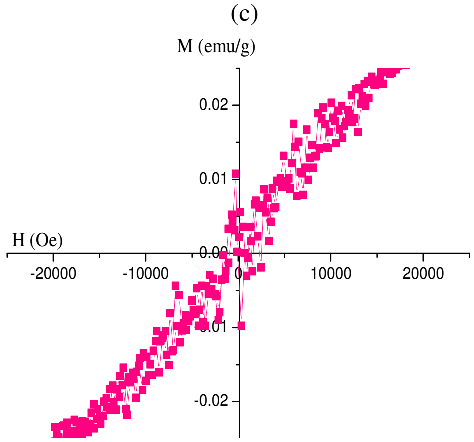
(b)



(c)



(d)



(e)

Figure 2. (a) hysteresis curve of ZnO doped with Cr, (b), (c), (d), (e) doping ZnO Cr (x = 0, 2.5, 3.5 and 4.5% atom)

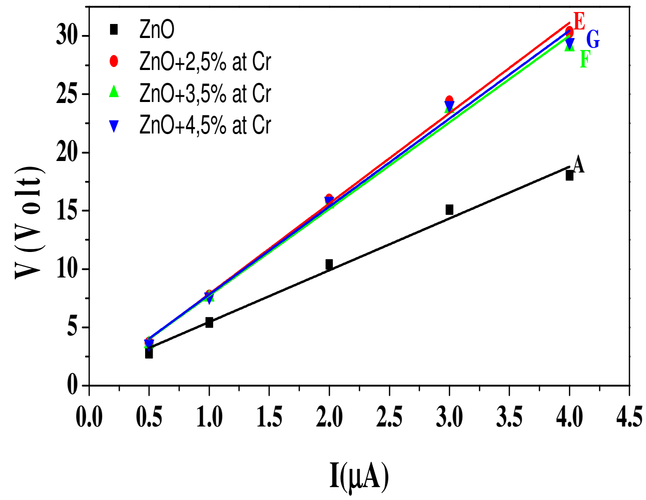


Figure 3. I-V curve of ZnO doped Cr

Figure 3 shows the characteristics of the current (I) - voltage (V) of ZnO: Cr (x = 2.5, 3.5 and 4.5 at%) with atmospheric environment at room temperature. The measurement results show a linear relationship between current and voltage on all samples.

Table 4. Results of Measurement and Calculation of Electrical Properties Of ZnO Doping Cr

Sample	ρ (10^7Ωcm)	σ (10^8S/cm)	C (10-12F)	εr
ZnO	3.31	3.02	3.82	12.5
Cr-25	5.72	1.75	2.09	3.2
Cr-35	5.79	1.72	2.06	3.0
Cr-45	5.87	1.70	2.21	3.2

From the calculation, the value resisitivitas pure ZnO sample is 3.31 x 10^7 Ωcm this result is greater when compared with the results of the research reported by (Barker Anthony, et al., 1997) the value of the electric resisitivitas of ZnO are deposited by the method of r.f. magnetron sputtering consistently for 3 x 10^7 Ωcm, whereas in the study of (Chundong Li, et al., 2012) reported without doping pure ZnO has a high resistivity value of 2.3 x 10^8 Ωcm, while the results of the study (Didik.Aryanto, et al., 2014) reported a thin film of pure ZnO have resisitivitas of 0.697 x 10^7 Ωcm, This research Cr doped ZnO resisitivitas generate value increases ranged from 5.72 x 10^7 Ωcm to 5.87 x 10^7 Ωcm with increasing doping (conductivity decreases), indicated resources happen scattering at grain boundaries related to her present Cr in the lattice of ZnO affecting grain growth and decrease the carrier mobility according to the results of the study (Shubra Singh et al., 2008) and indicated resources the occurrence of agglomeration ion Cr^{3+} at the grain boundaries (Renitta. K, 2016). The different results conducted by previous researchers using magnetron sputtering method that returns a value resisitivitas decreased with increasing concentration of this happened because of the increasing concentration of Cr in the presence of increasing the charge carrier transitions between the grains (Gurbuz Osman et al., 2016).

4. CONCLUSION

Characterization XRD, VSM, I-V and C-V meter has been used to study the structure, magnetic and electric properties of ZnO doping Cr were prepared by solid state reaction method. XRD patterns of ZnO doping Cr showed the main phase structure of ZnO with hexagonalwurzite and secondary phases is $ZnCr_2O_4$, which has a crystal size in the range of 51.7 nm to 51.9 nm. From the results of doping ZnO VSM Cr showed diamagnetic nature becomes paramagnetic. The results of the I-V and C-V meter Cr doped ZnO resistivity value increases ,decreases conductivity and dileketrik constant decreases.

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