Current Applied Science and Technology Vol. 18 No. 2 May-August 2018
DOI: 10.14456/cast.2018.7

A New Type of Dilute Magnetic Semiconductor: Saturation Magnetization Dependence on Level of Nonmagnetic Ion Doping

Prissana Robkhob[1], Sirikanjana Thongmee[1], I-Ming Tang[2*]

[1]Department of Physics, Faculty of Science, Kasetsart University, Bangkok, Thailand
[2]Computational & Applied Science for Innovation Clusters (CLASSIC)
Faculty of Science, King Mongkut's University of Technology, Thonburi, Thailand

Received:13 April 2018, Revised:18 July 2018, Accepted: 1 August 2018

Abstract

By definition, a dilute magnetic semiconductor is a II-IV or III-V semiconductor in which some of the nonmagnetic ions are replaced by magnetic ions. Defects due to Zn vacancies in ZnO nano particles (NP's) can induce virtual magnetic moments in this semiconduct or making it a room temperature ferro magnet. The systematic changes in the magnetic behaviors of ZnO NP's doped with non magnetic Al, Ag, Mg and Sb ions are observed. The changes are usually explained in terms of the increased stability of the zinc vacancies when the vacancies are a part of new impurity complexes formed when the impurity ions substitute for the zinc ions. In most cases, this explains the increases in the saturation magnetizations as more nonmagnetic impurities are substituted into the ZnO NP's.

Keywords: ZnO nanoparticles, Zn vacancies, Virtual magnetic moments, Hysteresis Loops, DFT calculations.

1. Introduction

Dilute magnetic semiconductors [1] or DMS's are semiconductors in which some of the nonmagnetic ions are replaced by magnetic ions. At the present time, the main examples are (Ga, M)As, (Ga, Mn)P and (Ga, Mn)N [2]. To be useful, the semiconductors must undergo a ferromagnetic transition above room temperature. The Curie temperature T_c of (Ga, Mn) As is $T_C \sim$ 170 K while (Ga, Mn) P and (Ga, Mn) N have T_C's of approximately 400 K and 940 K, respectively [3]. To help in the search for new DMS, Coey *et al.* [4] have calculated the T_C of possible new DMS created by the doping of the II-IV semiconductors with different magnetic TM impurities. The magnetic properties of the TM ions are due to the presence of unpaired electrons in the magnetic transition metal ions. The electron orbiting in one direction will create a magnetic moment in one direction, while the electron orbiting in the other direction will create a magnetic moment in the opposite direction. If the electrons are paired, the two magnetic moments will cancel out.

---

[*]Corresponding author: E-mail: fscimt@ku.ac.th

For T ≥ T_C a spontaneous magnetic field will arise in the DMS. This field will cause the electric current, which consists of both spin up and spin down electrons, to split into two currents, one consisting of a current of one spin and the other of the opposite spin. In other words, the magnetic field lowers the energies of the spin down electrons, and increased the energies of the spin up electrons; resulting in a current of spin down electrons and another of spin up electrons. The level of the energy gap of the semiconductor can be raised or lowered by adjusting a bias field. This could result in the filtering of one of the components of the current, allowing only currents of one spin direction to pass through. This phenomenon is needed in spintronics devices [5] where information is not only contained in the charges stored but also in the spins of the electrons stored.

The world of magnetism was turned upside down when Venkatesan *et al.* [6] observed magnetism in the dielectric oxide HfO_2 nanoparticles (NP's). Neither the Hf^{4-} nor the O^{2-} ions have unpaired electrons and according to Hund's rule, they should not have magnetic moments. Sundarssan *et al.,* [7] have stated that ferromagnetism is a universal feature of NP's of otherwise nonmagnetic oxides such as CeO_2, Al_2O_3, ZnO, TiO_2 and In_2O_3. All of these oxides are also the II-VI semiconductors. Anisotropic ferromagnetism has been observed in one of these oxide NP's, ZnO when doped with 5 atomic % Sc, Ti, V, Fe, Co or Ni by Venkatesan *et al.* [8]. Anghei *et al.* [9] have observed ferromagnetism in ZnO NP's doped with Cr and Mn. These reported behaviors of ZnO NP's doped with magnetic TM impurities makes them dilute magnetic semiconductors (DMS).

Our interests in this paper are the doping of ZnO NP's with nonmagnetic TM ions and other ions which do not possess unpaired electrons. We are interested in the ions Sb, Ag, Al and Mg. We begin by noting that ZnO NP's would be expected to be nonmagnetic since neither Zn^{2+} ions and O^{2-} ions (like the Hf^{4+} ions and O^{2-} ions in HfO_2 NP's) have unpaired electrons, but ferromagnetism has been observed in ZnO NP's. Hong *et al.,* [10] have observed ferromagnetism in the undoped semiconducting oxide TiO_2, $HfO_2$and In_2O_3nano films. Since the bulk form of these three oxides are diamagnetic, they proposed that the room temperature ferromagnetism observed are due to either defects caused by oxygen vacancies or zinc vacancies when the thin films were formed. Rainey *et al.* [11] proposed that these defects were also responsible for the room temperature ferromagnetism in ZnO. There was a large effort to determine which defect was responsible for the RTM. This was done experimentally by looking for correlations between the presence of RTM and whether there was oxygen or zinc defects present. Many of the early studies came to the conclusion that the oxygen vacancies were connected to the appearance of RTM [12, 13].

Using first principle density functional theory (DFT), Wang *et al.* [14] found that the introduction of vacancies at the Zn sites in the wurtzite structure of the ZnO crystal into the DFT calculations produced virtual energy levels located around the vacancy sites into which the 2*p* orbital electrons of the neighboring oxygen ions could occupy. The spin polarized configurations of these electrons had a lower energy than the nonspin polarized configuration. This meant that the formation of a virtual magnetic moment was favored. Peng *et al.* [15] developed the d^o model of magnetism in the DMS. Working against the formation of the virtual magnetic moment was the extreme instability of the zinc vacancy itself. DFT calculations have shown that the life time of V_{Zn} (designation of a zinc vacancy) can be stabilized by having the zinc vacancy be part of the impurity complex formed when impurities are doped into the ZnO NR's.

Wang *et al.* [14] studied the effects of doping LI, Mg or Al into ZnO NP's. Their DFT calculations found the magnetic moments on the zinc vacancies were 1.91, 1.5 or 0.92 μ_B when the zinc vacancies were part of the impurity complexes V_{Zn} + Li_{Zn}, V_{Zn} + Mg_{Zn}, or V_{Zn} + Al_{Zn}, respectively (X_{Zn} denoting a X ion replacing the Zinc ion at one of its sites). Lu *et al.* [16] studied the effects of substituting a group V element (N, Sb, As and P) into the ZnO NP's. They believed that the stability of the ferromagnetic phase arises from the *p-p* and the *p-d* and Zn-2*d* orbital and it would decrease with the increase in the dopant atomic number due to the lower electronegativity of the dopant ions. Thus the FM stability induced by the formation of the $X_{Zn} + nV_{Zm}$ complex decrease in the order N <Sb< As < P because of the delocalization of the O-2*p* orbital of the dopant ions. 'n' is the number which insure the charge neutrality of the substitution. Limpijumnong *et al.* [17] found that the formation energy of the As_{Zn}+ $2V_{Zn}$complex (1.59 eV) is lower than that of the Sb_{Zn} + $2V_{Zn}$ complex (2.00 eV). Tian *et al*. [18] obtained direct experimental evidences for the importance of the Sb_{Zn} + $2V_{Zn}$ complex to the properties of the Sb-doped ZnO NP's.

Thus the physics behind the increase in the magnetizations of the doped ZnO NP's with magnetic or nonmagnetic impurities are different. The changes in the magnetic properties of ZnO NP's when doped with magnetic ions are due to the increases in the number of magnetic ions while the changes due to the doping with nonmagnetic ions are due to the increases in the stability of the zinc vacancies when they are part of a impurity complex. To gain more insights into this facet, we have looked at the changes in the magnetic properties of ZnO NP's when the number of nonmagnetic ions replacing the Zn ions in the NP's are systematically changed. As pointed out by Ventekasen *et al.* [6] and by Peng *et al.* [15] the observation of ferromagnetism in a series of materials which do not contain ions with partially filled *d* or *f* bands is a challenge to the theory of magnetism. Peng *et al.,* further asked "*whether the observed magnetismis an intrinsic property of the host material or an extrinsic property depending sensitively on the type of dopant used to induce the magnetization.*" We have performed some magnetization studies to help gain more insights into these new types of DMS.

2. Materials and Methods

The various doped ZnO nanorods (NR's) were fabricated using the standard hydrothermal method. To fabricate the Sb dopedNC's, stoichiometric amounts of (Zn $(NO_3)_2{\cdot}6H_2O$) and $SbCl_3$ were weight out to yield $Zn_{1-x}Sb_xO$ NP's (x = 0.05 0.15, 0.25 and 0.30) and mixed together in an aqueous solution. The pH was adjusted to 10 by the addition of NaOH. Each solution was then placed separately into a Teflon-lined auto cave and heated to 150° C for 20 hrs. To fabricate the Ag doped NR's, stoichiometric amounts of $(Zn(NO_3)_2{\cdot}6H_2O)$ and $Ag(NO_3)_2$ were weight out to yield $Zn_{1-x}Ag_xO$ NP's (x = 0.03, 0.04 and 0.05) and the same procedure was repeated except that the temperature of the auto cave was set at 180º C. For the Al doped NR's, stoichiometric amounts of $(Zn(NO_3)_2{\cdot}6H_2O)$ and $Al(NO_3)_2$ were weight out to yield $Zn_{1-x}Al_xO$ NP's (x = 0.01, 0.02 →0.01) and the last process was repeated. For the Mg doped NC's, stoichiometric amounts of (Zn $(NO_3)_2{\cdot}6H_2O$) and Mg $(NO_3)_2$ were weight out to yield $Zn_{1-x}Mgb_xO$ NP's (x = 0.01, 0.02, 0.03, 0.04 and 0.05) and the previous process was repeated. When the concentration of Zn^{2+} and $(OH)^-$ ions in the each of the solution placed in the auto cave reached the critical super saturation value of ZnO, ZnO nanoparticles began to form. During the rest of the time in the auto cave, the remaining Zn^{2+}, (OH) and the various impurity ions would be deposited on the (001) face of wurtzite structure of the initial ZnO nanocrystals resulting in the formation of nanorod shaving a hexagonal structure.

3. Results and Discussion

The magnetizations of the various nonmagnetic doped ZnO NR's were measured at room temperature using either a vibrating sample magnetometer or a SQUID magnetometer located in the Department of Material Science, Faculty of Engineering, National University of Singapore. From the hysteresis loops of $Zn_{1-x}Sb_xO$ (x = 0.0, 0.05, 0.15, 0.25 and 0.30) we extracted the values of the saturation magnetizations. This was done by subtracting the diamagnetic contribution to the magnetization. The results taken from Nakarungsee *et al.* [19] are plotted in Figure 1. In Figure 2, we have plotted the values of the saturation magnetization of Zn1-xAgxO (x = 0.0, 0.1, 0.2, 0.3, 0.4

and 0.5) taken from Robkhob *et al.* [20]. The dependences of the saturation magnetizations of the two are quite different. For the Sb doped ZnO NR's, the saturation magnetization decreases as more nonmagnetic Sb ions are substituted in, while the saturation magnetization increases as more nonmagnetic Ag ions are substituted in. This latter behavior is keeping with the assumption that the magnetizationis due to the increased stability of the Zn vacancies when it becomes part of an impurity complex $Ag_{Zn} + 2V_{Zn}$.

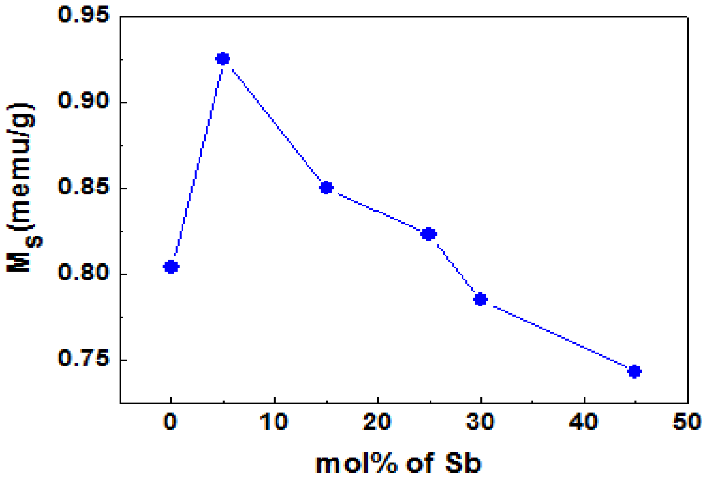

Figure 1. Dependence of the saturation magnetization of $Zn_{1-x}Sb_xO$ NR's on the level of Sb doping. The replacement of the Zn ions by the non-magnetic Sb ions leads to increase in M_S. The increase is not a systematic one, i.e., the increase in M_S is not a systematic one.

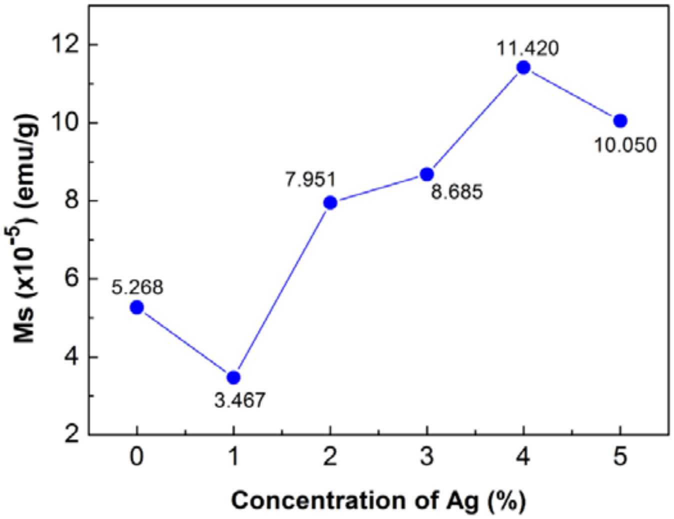

Figure 2. Dependence of the saturation magnetization of $Zn_{1-x}Ag_xO$ NR's on the level of Ag doping. The increase in the M_S is explained as being the result of the increase stability of the Zn vacancies when they are part of an impurity complex made up of Zn vacancy defect the defect arising from the replacement of Zn ion by an Ag ion.

To clarify this, we measured the saturation magnetization of Al doped ZnO NR's, $Zn_{1-x}Al_xO$ (x = 0.0 → 0.1 in steps of 0.01) and plotted the results [21] in Figure 3. Ignoring the saturation value of $Zn_{0.95}Al_{0.05}O$ NR's, the saturation magnetizations of $Zn_{1-x}Al_xO$ NR's tend to increase as more Al isdoped in until concentration of the Al ions reaches x = 0.07. This behavior is consistent with the explanation used to explain the behavior of the saturation magnetization of $Zn_{1-x}Ag_x0$ $Zn_{1-x}Ag_x0$, the substitution of the nonmagnetic ions stabilized the Zn vacancies. To gain more insight in these new types of DMS, we have fabricated Mg doped $Zn_{1-x}Mg_xO$ (x = 0.02. 0.046, 0.054 and 0.07). The hysteresis loops of the $Zn_{1-x}Mg_xO$ were taken with a VSM at room temperature. From these loops, we obtained the saturation magnetization of each of the Mg doped ZnO NR's. The saturation magnetization are plotted on Figure 4. As is seen, as x increases from 0.046 to 0.07, the saturation magnetizations increase in line with the behaviors seen in Figures 2 and 3. The behavior of M_S for the Sb doping and the magnetization values which do not follow the general increase in the magnetization of the other (Al, Ag and Mg) doped ZnO NR's, may reflect the point raised by Peng *et al.* [15] that the observed properties may be an extrinsic property which depends on the type of dopant used to induce magnetization and whose nature is not understood.

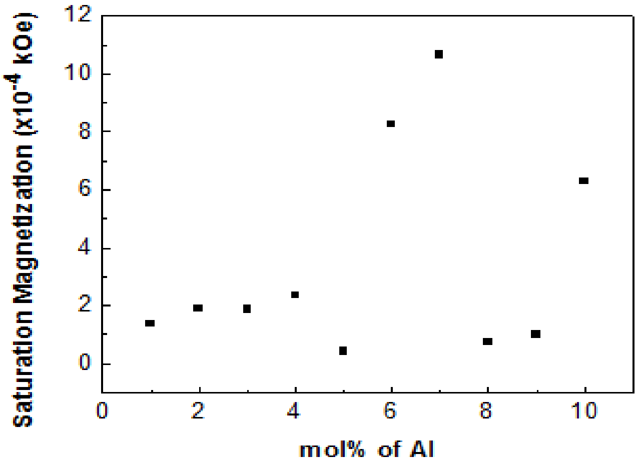

Figure 3. Dependence of the saturation magnetization of $Zn_{1-x}Al_xO$ NR's on the level of Al doping. Since the dependences of M_S on the level of substitution of one nonmagnetic ion (Zn) by another nonmagnetic Ag ions are quite defferent, the change in M_S due to the replacement of a Zn ion by a third nonmagnetic ions (Al) was done to see which behavior is the typical behavior and which is atypical. Except for the x = 0.05 NP, the saturation magnetization is seen to increase as x is increased from x = 0.01 to 0.07, meaning that the behavior due to Ag doping is the typical one, i.e., the increase in M_S in the increase stability of the Zn vacancies when other nonmagnetic ions are substituted for the Zn ions.

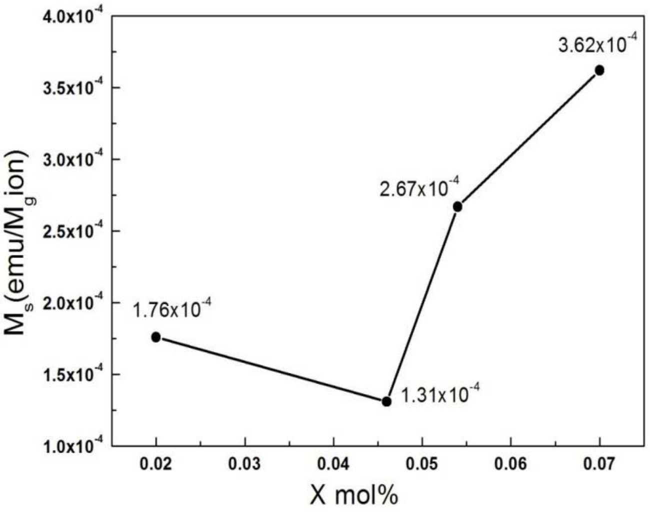

Figure 4. Dependence of the saturation magnetization of $Zn_{1-x}Mg_xO$ NR's on the level of Mg doping. If the increase in the M_S as additional nonmagnetic ions replaces the nonmagnetic Zn ions is a general feature of the new class of dilute magnetic semiconductors, the same behavior would be ex-pected if another nonmagnetic ion is used. The Mg ions are another nonmagnetic ions. As we see, the saturation magnetization increases as more Mg ions replace the Zn ions.

4. Conclusions

According to the definition of Dilute Magnetic Semiconductors (DMS), the doped ZnO NR's which we are studying are not dilute magnetic semiconductors since the impurities being substituted for the nonmagnetic Zn ions are not magnetic ions. They are nonmagnetic ions, so that the systems we are studying do not fit the definition of DMS. Complicating matters the magnetism observed in ZnO NP's are due to defects, missing Zn ions, i.e., vacancies. The magnetic moments are virtual moments which arise when virtual energy levels of the virtual electronic statesformed about the missing Zn ions are occurred by a pair of electrons from the neighboring oxygen ions in the wurtzite structure ZnO NP's. This virtual magnetic moment are magnetic since theoreticalbcalculations show that the spin polarized configuration of the electrons in the virtual atom have a lower energy than that of the non spin polarized configuration. This makes them real leading to real consequences so virtual reality becomes real. Thus, our virtual DMS become real DMS and should be further studied to see if they have real applications.

5. Acknowledgements

IMT would like to acknowledge the financial support provide to him by the King Mongkut's University of Technology, Thonburi through the 55thAnniversary Commemorative Fund. PR wouldlike to thank the Thailand Research Fund (TRF) for a Royal Golden Jubilee PhD Fellowship.

ST would like to acknowledge financial support from the Faculty of Science, Kasetsart University and Kasetsart University Research and Development Institute.

References

[1] Furdyne, J.J., 2010. Dilute magnetic semiconductors. *J. Appl. Phys*., 64, R29.

[2] Dietl, T., Ohno, H., Matsukura, F., Cibert, J. and Ferrand, D., 2000. Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors. *Science,* 287, 1019.

[3] Dietl, T. and Ohno, H., 2014. Dilute Ferromagnetic Semiconductors Physics and Spintronics Structures. *Rev. Mod. Phys.,* 86, 187.

[4] Coey, J.M.D., Venkatesan, M. and Fitzgerald, C.B., 2005. Donor impurity exchange in dilute ferromagnetic oxides, *Nature Materials,* 41, 173-179.

[5] Zutic, I., Fabian, J. and Das Sarma, S., 2004. Spintronics: Fundamentals and Applications, *Rev. Mod. Phys*.,76, 323.

[6] Venkatesan, M., Fitzgerald, C.B. and Coey, J.M.D., 2004. Unexpected magnetism in a dielectric oxide. *Nature,* 430, 630.

[7] Sundaresan, A., Bhargavi, R., Rangarajan, N., Siddesh, U. and Rao, C.N.R., 2006. Ferromagnetism as a universal feature of nanoparticles of otherwise nonmagnetic oxides. *Phys. Rev., B*, 74, 161306.

[8] M. Venkatesan, M., C.B. Fitzgerald, C.B., J.G. Lunney, J.G., J.M.D. Coey, J.M.D., 2004. Anisotropic ferromagnetism in substituted zinc oxide. *Phys. Rev. Lett.,* 93, 177206.

[9] Anghei, J., Thurber, A., Tenne, D.A., Hanna, C.B. and Punnoose, A., 2010. Correlation between saturation magnetization, bandgap and lattice volume of transition metal (M =Cr, Mn, Fe, Co or Ni) doped Zn1-xMxO nanoparticles. *J. Appl. Phys.,* 107, 09E314.

[10] Hong, N.H., Sakai, J., Poirot, N. and Brize, V., 2006. Room-temperature ferromagnetism observed in undoped semiconducting and insulating oxide thin films. *Phys. Rev., B*, 73, 132404.

[11] Rainey, K., Chess, J., Eixenberger, J., Tenne, D.A., Hanna, C.B. and Punnoose, A., 2014. Defect induced ferromagnetism in undopedZnO nanoparticles. *J. Appl. Phys.,* 115, 17D727.

[12] Liu, W., Li, W., Hu, Z., Tang, Z. and Tang, X., 2011. Effect of oxygen defects on ferromagnetic of undoped ZnO. *J. Appl. Phys.,* 110, 013901

[13] Gao, D., Zhang, Z., Fu, J., Xu, Y., Qi, J. and Xue, D., 2009. Room temperature ferromagnetism in pure ZnO nanoparticles. *J. Appl. Phys.,*105, 113928.

[14] Wang, Q.J., Wang, J.B., Zhong, X.L., Tan, Q.H., Hu, Z. and Zho, Y.C., 2012. Magnetism mechanism in ZnO and ZnO doped with nonmagnetic elements X (X = Li, Mg, and Al): A first-principles study. *Appl. Phys. Lett*. 100, 132407.

[15] Peng, H.W., Xiang, H.J., Wei, S.H., Li, S.S., Xia, J.B. and Li, J.B., 2009. Origin and enhancement of hole-induced ferromagnetism in first-row d0 semiconductors. *Phys. Rev. Lett.,* 102, 017201.

[16] Lu, Y.B., Dai, Y., Guo, M., Yu, L. and Huang, B.B., 2013. Investigation of magnetic properties induced by Group V elements in doped AnO. *Phys. Chem. Chem. Phys*., 15, 5208.

[17] Limpijumnong, S., Zhang, S.B., Wei, S.H. and Park, C.H., 2004. Doping by large size mismatched impurities: The microscopic origin of arsenic or antimony doped zinc oxide. *Phys. Rev. Lett.,* 15, 155504.

[18] Tian, S., Zeng, D., Xie, C. and Zhao, X., 2014. Direct experimental evidence for SbZn + 2VZn complex as the important defect in the Sb-doped ZnOnanocrystals, *Material Letters,* 116, 363.

[19] Nakarungsee, P., Chen, G.S., Herng, T.S., Ding, J., Tang, I.M. and Talabthong, Thongmee, S., 2016. Sb substitution into ZnO nano-compoisite: Ferromangetic behavior. *JMMM,* 397, 79.

[20] Robkhob, P., Herng, T.S., Dingm J., Tang, I.M. and Thongmee, S., 2017. Magnetic behavior of ZnO nanorods doped with silver (Ag^{3+}) ions. *J. Nanosci. & Nanotech,* 17, 5631.

[21] Yingsamphancharoen, T., Nakarungsee, P., Herng, T.S., Ding, J. and Tang. I.M., 2016. Ferromagnetic behavior due to Al^{3+} doping into ZnO nanorods. *JMMM,* 419, 274.