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RESEARCH ARTICLE / ARAŞTIRMA MAKALESİ

Investigation of Ferromagnetism and Growth Correlation of Transition Metal Doped ZnO

Geçiş Metali Katkılı ZnO'in Ferromanyetizma ve Büyüme Korelasyonunun İncelenmesi

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Abstract
In this study, a series of 3d transition metal (TM) (Co, Ni and Fe) doped ZnO particles synthesized by simple co-precipitation method. Structural, morphological and magnetic properties were investigated to determine correlation between growth process and ferromagnetism of metal doped ZnO samples. All samples had ZnO hexzagonal würtzite structure and slightly shift of ZnO indexed peaks was observed by TM incorporation in ZnO. Although ZnO samples had granular forms, agglomerative forms had emerged in TM:ZnO samples due to the fast growth process. The pure ZnO sample transformed paramagnetic to ferromagnetic by TM incorporation due to carrier mediated exchange interaction between TM ions. The results demonstated that doping with Fe^{3+} ions in ZnO structure had enhanced ferromagnetism although fast growth and high particle agglomeration.
Keywords: ZnO, transition metal, co-precipitation, structural, ferromagnetic

Öz
Bu çalışmada, bir dizi 3d geçiş metali (TM) (Co, Ni ve Fe) katkılı ZnO parçacıkları basit çöktürme yöntemi ile sentezlenmiştir. GM katkılı ZnO örneklerinin manyetik özelliklerini incelemek için yapısal, morfolojik ve manyetik çalışmalar yapılmıştır. Kimyasal bileşimde Zn, O ve katkı elementlerin yüzdesi elementel analiz tarafından doğrulandı. Katkılı iyonlar Zn2+ iyonları ile ikame edilirken, ZnO yapısındaki dramatik değişim GM katkısı ile saptandı. Yüzey morfolojilerinden nanokümelerin oluşumu gösterildi. FTIR spektrumu, saf ve GM katkılı ZnO oluştuğunun bir kanıtıdır. GM iyonları arasındaki değişim etkileşimi nedeniyle Fe, Ni ve Co katkısı ile paramanyetik durumdan ferromanyetikliğe saf ZnO örneği geçmiştir. Fe: ZnO örnekleri ZnO kristal kalitesini düşürmüş ve yığılma yüzey görüntüleri tespit edilmiş olsa da, ferromanyetizmanın ZnO'ya Fe katkısıı ile artması ilginçtir.
Anahtar Kelimeler: ZnO, geçiş metali, çöktürme, yapısal, ferromanyetik

I. INTRODUCTION

As a metal oxide, ZnO is an attractive material that used in the opto-electronic devices [1], gas- and bio-sensors [2,3], photocatalysis devices [4] and magnetic devices [5] with unique properties such as high chemical and physical stabilization, wide optical band gap (~3.7 eV) and abundant in nature. Microstructures and nanostructures have been preferred more than their bulk counterparts because of their finite size effect and high surface to volume ratio. Doping of ZnO structure is effective way with metals, non-metals and vacancy-defect atoms to arrangement electron transport and tailor Fermi energy levels [6]. Among them as a diluted magnetic semiconductor, ZnO is so important due to its electronic controlled spin properties in order to develop spintronic devices [7], magnetically targeted drug delivery systems [8] and nonvolatile magnetic memory devices [9].

In the practical applications, the long-term magnetization of ZnO structures can be enhanced appropriately by using single cationic/anionic atoms so new electron trap levels can arise [10]. Theoretical studies have been proven that doping with partially filled 3d transition metal (TM) ions with unpaired electrons to obtain residual room temperature ferromagnetism of ZnO [11]. Permanent ferromagnetism can be obtained by method and method parameter arrangement however un-control growth process and depending on this unpredictable impurities and surface defects are crucial problems. Particle growth is difficult to control, including optimization of particle sizes and their shapes and agglomerative formations reduce in the co-precipitation. This procedure is similar with graphene oxide nanoparticle synthesis [12].

Recently, TM doped ZnO structures and their ferromagnetism have been investigated extensively. Wang et.al. reported that Zn1-xNixO nanorod arrays exhibited room temperature ferromagnetism with a strong coercive field [13]. Zong et. al. synthesized that different concentrated Co doped ZnO nanoparticles showed that magnetization

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saturation curves, indicating formation of oxygen defect induced bound magnetic polarons [14]. Beltran et.al. investigated that Fe was not effective directly in room temperature ZnO ferromagnetism although additional single charged oxygen vacancies, zinc vacancies, and more oxygen-ended polar termination influenced magnetization with Fe doping [15].

While there are a lot of TM doped ZnO studies in the literature the phenomenon between ferromagnetism and the growth process has been still controversial. Therefore, structural and magnetic properties of TM:ZnO were investigated in detail.

II. EXPERIMENTAL

Zinc chloride, sodium hydroxide (99%) and cobalt (II) chloride hexahydrate (99%) were purchased from Merck Company and ethylene glycol (99%), iron (II) sulfate heptahydrate (99%) and Ni (II) chloride hexahydrate (99%) were supplied by Sigma Aldrich Company. Zinc chloride, ethylene glycol and sodium hydroxide were used as zinc source, polymerization agent and complex agent, respectively. To prepare the particles, 0.5 M zinc chloride was added in 100 ml distilled water and mixed on the magnetic stirrer. Then 0.1 M metal source added into solution to obtain TM:ZnO solution. After 0.4 M sodium hydroxide and 10 ml ethylene glycol added and homogeneous solution was obtained. Aqueous solution was mixed at 80 °C along 1 hour. After one day waiting, they were washed with distilled water, ethanol and acetone. Dried powders were annealed at 500 °C along 2 hours in the furnace to remove surface impurities.

III. ANALYTICAL INVESTIGATION

The crystal structures and structural parameters of the microparticles were determined by Rigaku SmartLab X-ray diffractometer, employing λCuKα =1.5406 Å radiation with 0.0130 step size which was operated under 40 mA and 45 kV, using powder method. The surface morphology and elemental analysis (wt %) of the microparticles were detected by JEOL JSM-7100F-SEM (scanning electron microscope) and OXFORD Instruments X- Max EDX (energy-dispersive x-ray spectrometer), which had been attached to each other. To detect chemical bonding of samples, FTIR (Fourier Transform Infrared Spectrum) were monitored by VERTEX 70 model spectrophotometer with an attenuated total reflectance (ATR) Bruker, Germany. Magnetization properties of samples were investigated Lake Shore 7407 model vibrating sample magnetometer (VSM) device was used. The magnetic field was applied as 1 T in parallel to the sample surface. All measurements were performed at room temperature.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Elemental Analysis Results

Homogeneous regions from SEM images were selected and these regions were used to determine elemental analysis of the samples as showed in Fig.1. All samples different percentages (w%) of zinc, oxygen species while doped samples also had their own metal elemental percentage (w%). While doping ratio was kept the same, elemental Zn and metal dopant percentage (w%) changed, indicating solubility limit of TM in ZnO were different from each other.

4.2. Structural Properties

In the range of 2θ=20º-80°, XRD patterns of the samples were shown in Fig.2. All of the samples were polycrystalline hexagonal würtzite ZnO structure which corresponding to JCPDS Card No: 36-1451 and they had (101) preferential orientation [16]. As seen in Fig. 2, no secondary phase or cluster of Co, Ni or Fe was observed, indicating that high quality material formed [17]. It could be concluded that required structural stability for magnetic applications had been achieved. Structural parameters of the samples were showed in Table 1. As seen in Table 1, XRD patterns of TM doped samples slightly shifted which indicated that imperfections were formed [18]. Ni- and Co-doping had an improving effect on the crystal quality compared to pure ZnO due to larger radius of Fe^{2+} ion (77 pm) than Zn^{2+} (72 pm) [19]. Due to the zinc and TM (Ni- and Co-) solutions were of the same chlorine origin, growth process thereby crystallization had also been improved [20].

4.3. Surface Morphologies

Surface morphology of the samples were showed in Fig.3 (a-e) at high magnification ratio (x30000). While pure ZnO surface had granular forms, relatively different non-uniform granular shaped forms were observed with TM ion type. It was known that surface morphology was affected by the reactant initial concentration sogrowth process could be different [21]. According to this, growth of Fe:ZnO faster than Co:ZnO and Ni:ZnO due to high agglomerative forms on the ZnO surface. Granular ZnO forms had between 0.68 μm and 0.92 μm and their dimension decreased with Co- and Ni- doping which was indicated that it was consistent with increasing crystallinity of ZnO from obtained XRD patterns.

4.4. FTIR Spectrum of the Samples

The FTIR spectra is useful method to determine chemical composition of the samples. FTIR spectra of pure and TM doped ZnO particles were depicted between in 500 cm^{-1} and 4000 cm^{-1} at room temperature in Fig.4. The broad peak at ~3450-3500 range was assigned to O-H stretching mode of hydroxyl group which showed that emerging water absorbed on the surface of ZnO, causing agglomerative formations [22]. The weak peak at ~2365 cm^{-1} was related atmospheric carbon dioxide which formed in the synthesis process [23]. A weak peak was observed at ~1635 was due to asymmetric stretching of the zinc carboxylate. All samples had different impurity-based

peaks in the range between 600-1200cm^{-1}, indicating TM clusters on the ZnO surface [24]. The bond between 500–550 cm^{-1} was associated with stretching vibration mode of ZnO samples [25].

4.5. Magnetic Properties

Vibrating sample magnetometer (VSM) was used to determine the magnetization properties of the samples. Fig.5(a) illustrated the dependence of magnetic field (H, between the field -2 T and +2 T) on the magnetization (M) at room temperature for ZnO and Fe, Ni, Co doped ZnO samples. The M values changed depending on the doped transition metals. It was understood from Fig. 5a. that ZnO was diamagnetic in nature at room temperature that can be associated with the uncompensated Zn^{2+} surface spin [26]. For the Fe, Ni and Co doped samples, the hysteresis loops display a straight line, indicating the ferromagnetic contribution without saturation, which is commonly observed in magnetic systems [27-29]. The ferromagnetic contribution for these samples can be observed with more detail in the Fig.5b. The coercivity values for the Fe-ZnO, Co-ZnO and Ni-ZnO samples are 8.4017 Oe, 49.33 Oe and 40.42 Oe respectively. Coercivity is a complicated parameter for magnetic materials and is related to the reversal mechanism, anisotropy energy, and the magnetic microstructure, i.e., shape and dimensions of the crystallites, nature of the boundaries, and also the surface and initial layer properties, etc.. The observed increase in coercivity of Co-doped zinc oxide could be due to the presence of large anisotropy energy for Co [30].

V. CONCLUSION

In summary, Co, Ni and Fe doped ZnO particles were produced by the co-precipitation and annealed at 500 °C along 2 hours. According to the x-ray diffraction patterns Co^{2+}, Ni^{2+} and Fe^{3+} ions were occupied Zn^{2+} tetrahedral sites substantially. SEM images exhibited that agglomerative formations were observed by TM doping due to fast growth in calcination although sedimentation was not observed in graphene based nano-fluids [32]. M-H measurements revealed that ZnO was transformed from paramagnetic to ferromagnetic state by Fe, Ni and Co doping. The stable ferromagnetizm was observed in Fe:ZnO sample which indicated that fast growth process caused increase of Fe clusters on the ZnO surface so surface impurities increased. Ferromagnetism weakened with Ni and Co doping although improved ZnO crystallinity. It could be concluded that Fe:ZnO particles were relative proper for spintronic applications.

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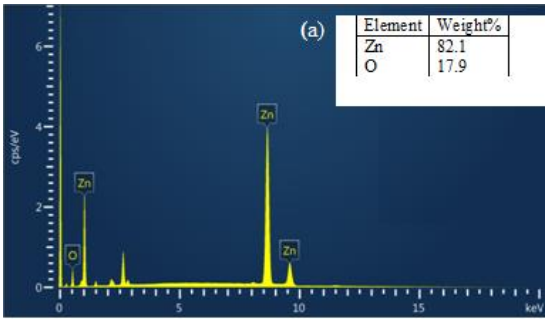
Fig. 5 – Magnetization curves of (a) the ZnO and TM-doped ZnO samples, (b) enlarged region.

Table 1. Structural parameters of ZnO and TM doped ZnO samples

	2θ (°)	**FWHM (rad)**	**d (Å)**	**Lattice parameters (Å) (a and c)**	**Strain (ε)**
ZnO	36.92	0.0021	2.4362	3.24, 5.13	-0.013
Ni:ZnO	36.63	0.0022	2.4511	3.21, 5.14	-.0.011
Fe:ZnO	36.71	0.0026	2.4477	3.20, 5.13	-0.013
Co:ZnO	36.80	0.0033	2.4419	3.20, 5.12	-0.015



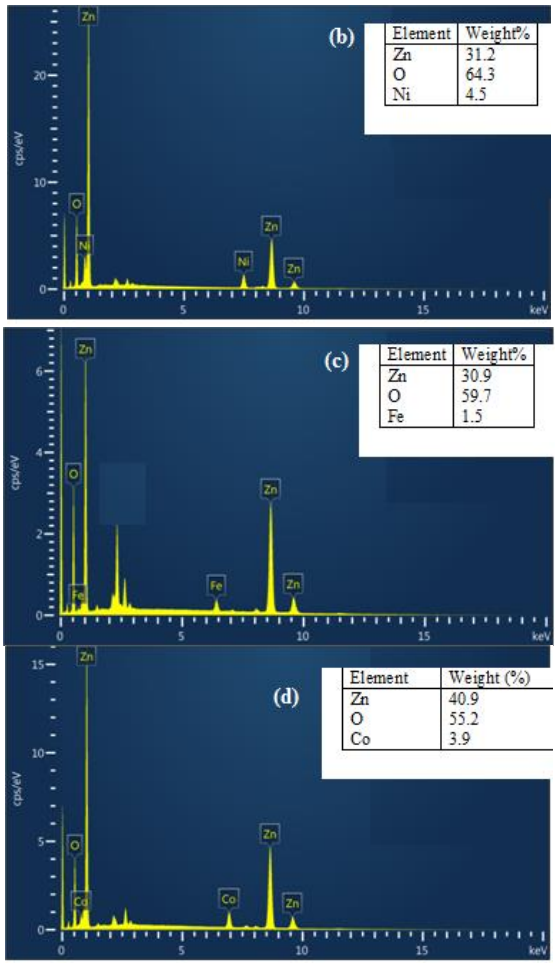


Fig. 1. EDX results of the samples a) un-doped ZnO, b) Ni-doped ZnO, c) Fe-doped ZnO and d) Co-doped ZnO

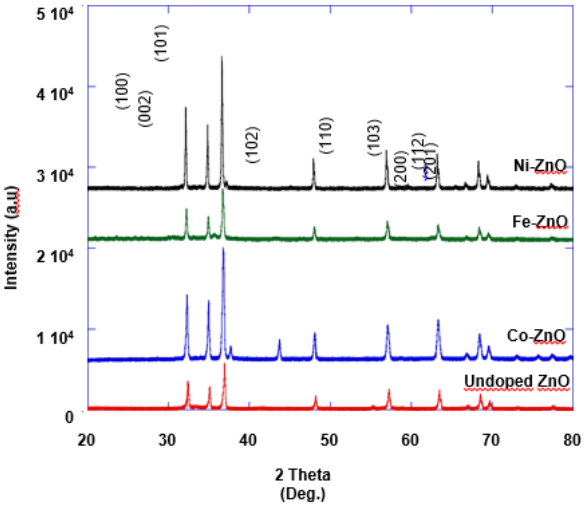
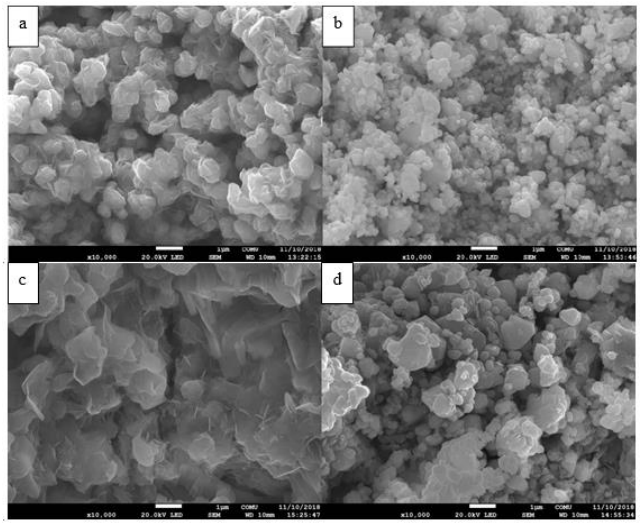


Fig. 2. XRD patterns of the ZnO and TM-doped ZnO samples



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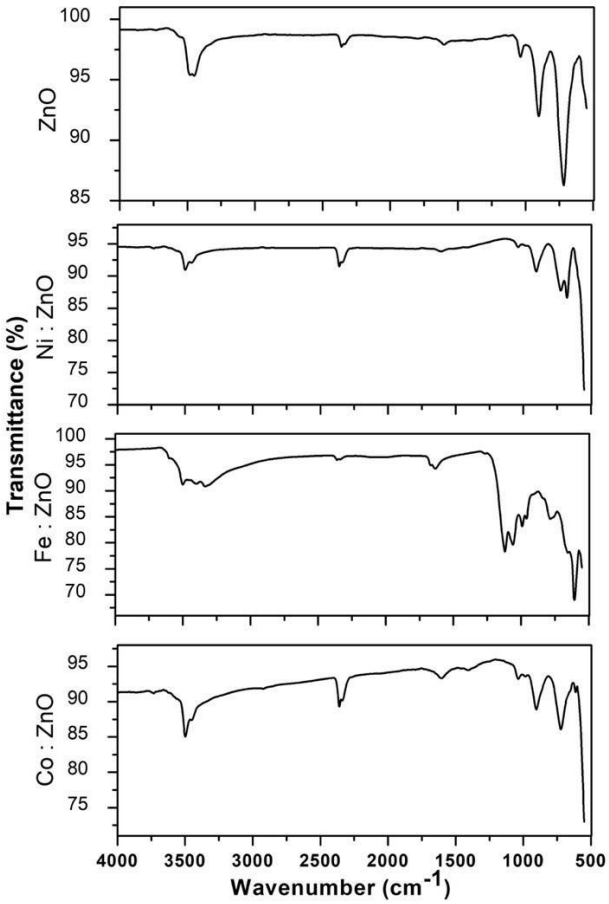

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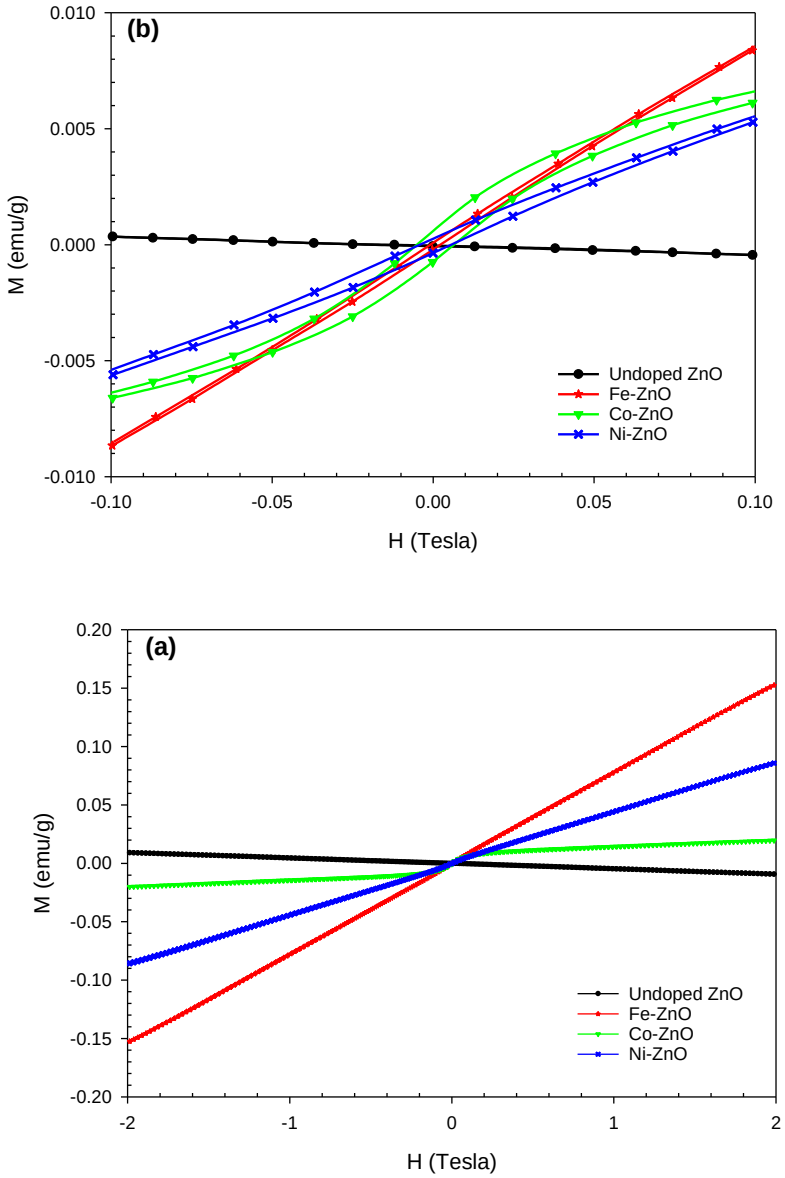

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