Investigation of defect structures in metal oxides via spectroscopic techniques

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Abstract

Zinc oxide (ZnO) is an inorganic compound widely used in everyday applications. The advent of nanotechnology has led the development of materials with new properties for use as semiconductor material. First of all, we examined defects caused by properties such as semiconductors and electrical / optical. Second, ZnO has multiple crystal structures occurring in a variety of environments. Thus, ZnO has defects caused by crystal structure. Additionally, ZnO in nanoscale has shown physical properties and potential applications in various industries.Considering these informations above, it can be said that the aims were how to plot the defects data with detection technique and simulate these spectra by using EasySpin.

Keywords: Zinc Oxide, Crystal Structure and Lattice parameters, EPR and Raman, Defects

1. Introduction

Lately, zinc oxide (ZnO) has attracted much attention within the scientific community as a 'future material' instead of silicon; however ZnO is not a frequently discovered material. Research of ZnO has been extensively studied for many decades with our current industry. Growth technologies for the fabrication of high quality allowing for the realization of ZnO-based electronic and optoelectronic devices such as solar cells. ZnO is a direct and wide bandgap semiconductor. It is also an n-type semiconductor.

As fervent research into ZnO continues, difficulties such as the fabrication of p-type ZnO that have so far stalled the development of devices are being overcome.

Although it is asserted that ZnO is not useful in few ways, it should be main semiconductor material because it has a lot of advantages: large exciton binding energy, ability to grow single crystal substrates, wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility.All in all, it can safely be said that ZnO is a very suitable substance in the investigation of metal oxides.

2. Properties Of ZnO

In this section crystal structures, inclusive of lattice parameters, **s**emiconductor properties and Optical/Electrical properties

2.1 Crystal structure

Crystal structures are one of the most important properties of ZnO. The crystal structures shared by ZnO are wurtzite(B4), zinc blende (B3), and rocksalt (B1), as schematically shown in Figure 1. Özgür et al. stated that at ambient conditions, the thermodynamically stable phase is wurtzite. The rocksalt (NaCl) structure may be obtained at relatively high pressures. Zinc-blende is stable only by growth on cubic structures (2005, p.4).

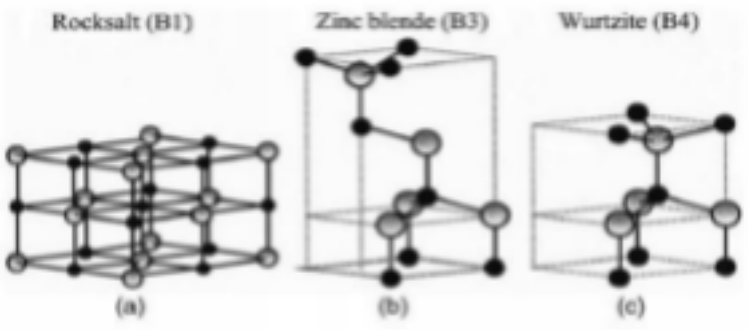

FIG. 1. Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt (*B1*), (b) cubic zinc blende (*B3*), and (c) hexagonal wurtzite (*B4*). The shaded gray and black spheres denote Zn and O atoms, respectively.

Wurtzite structure is a hexagonal lattice characterized by two interconnecting sublattices of Zn and O, such that each Zn ion is surrounded by a tetrahedra of O ions, and vice-versa. As Coleman and Jagadish stated that aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also a common indicator covalent bonding with an ionicity of fi 0.616 on the Phillips ionicity scale. However, the Zn–O bond also possesses very strong ionic character, and thus ZnO lies on the border line between covalent and ionic compound (2006, p.6).Therefore, atoms in densely areas have

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high interaction with ionic conditions due to polarity. These interactions increase the emergence of defect generations in wurtzite structure.

2.2 Lattice parameters

There are 4 lattice parameters, they are: a,c,u,c/a ratio As Özgür et al. stated that the lattice parameters of a semiconductor usually depend on the following factors: (i)free-electron concentration ii) concentration of foreign atoms,–(iii) external strains (for example, those induced by substrate), and (iv) temperature. The lattice parameters of any crystalline material are commonly and most accurately measured by high resolution x-ray diffraction (HRXRD) for symmetrical and asymmetrical reflections(2005,p.6-7). According to the wurtzite ZnO, lattice constants at room temperature determined by various experimental measurements and theoretical calculations are in good agreement.These two slightly different bond lengths (a and b) will be equal if the following relation holds Figure 2.

$$u = \left(\frac{1}{3}\right)\left(\frac{a^2}{c^2}\right) + \frac{1}{4}.$$

Figure 2: u parameter is the bond length in wurtzite ZnO

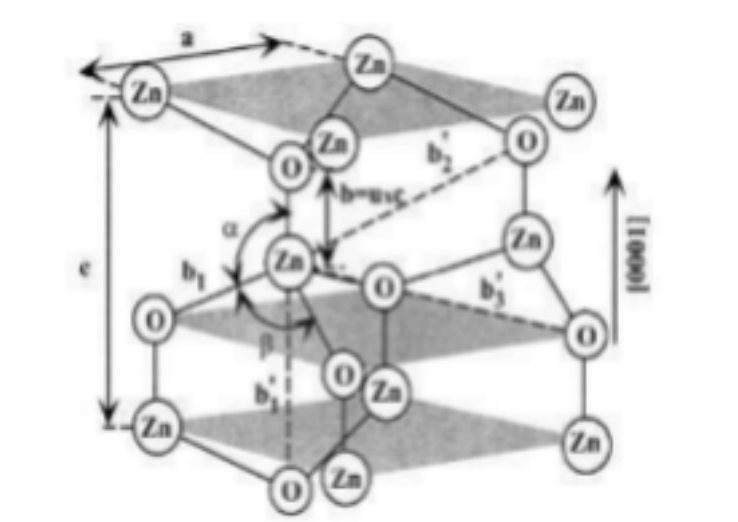

Figure 3:Schematic representation of a wurtzite ZnO structure having lattice constants a in the basal plane and c in the basal direction; u parameter is expressed as the bond length or the nearest-neighbor distance b divided by c (0.375 in ideal crystal), and α and β (109.47° in ideal crystal) are the bond angles

2.3 Semiconductor Properties and Optical/Electrical Properties

In recent decades the metal oxides have become attractive issues due to their optical and electrical properties. In particular ZnO which is semiconductor material has attracted much attention within the scientific community. Furthermore many studies are made on this subject. In this part, semiconductor properties of zinc oxide will be discussed.

It must be known the meaning of band-gap before passing to the zinc oxide's electrical properties. Electrons settle into the atom's orbit and each of the orbits corresponds to the energy level such as1s, 2s, 2p … The distribution of energy levels creates what are called energy bands. The highest band filled with electrons is called the valence band and the lowest band that contains few or no electrons is called the conductivity band. Electrical conductivity of metal is determined with band-gap. The band- gap is the gap between the maximum of the valence band and the minimum of the conduction band. (Kuş O., 2019)

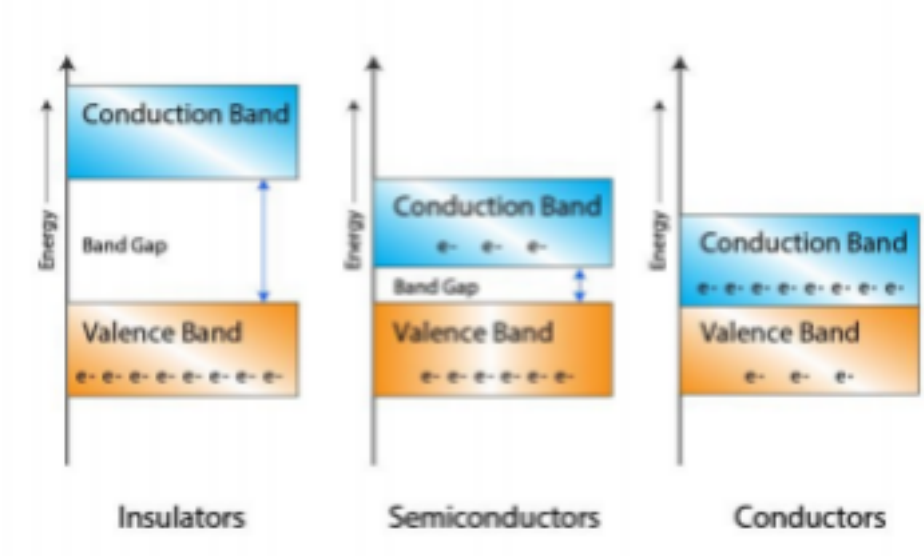

Figure 4 : Possible energy band diagrams of a crystal

ZnO is a semiconductor material with direct wide-band gap approximately 3,437 eV at 300 K. This band gap property of ZnO nanoparticles, encouraged their usage in the field of photonics and chemical sensors.

Electron hall mobility is the second important electrical property of ZnO nanoparticles. Defects and impurities of ZnO affect the electrical conductivity. Electrical conductivity is created by electron mobility. Electron mobility of ZnO strongly depends on temperature and corresponding electron hall mobility at 300 K for n-type conductivity is 200 cm^2/(v.s).

Third ZnO's electrical property is about it's hole mobility. If there is a hole which is moved through a metal or semiconductor in electrical field, it is defined as hole mobility. Data on hole mobility are scarce with values in the range 5-50 cm^2/(v.s). Furthermore dielectric constant of ZnO is 8.66 F/m. (Büyük G. İ. at al, 2019)

Last but not least of the electrical properties are the large exciton binding energy of EB=60 meV at room temperature makes ZnO a prominent candidate for device application. (Erdem E.,2012) Investigation of defect structures in metal oxides via spectroscopic techniques

Another important point of concern is optical properties ZnO is of great interest as it is a transparent

semiconductor material. ZnO is transparent to visible light. (0.4-2 μm). It strongly absorbs ultraviolet light below 375.75 A.

In light of this information we can clearly say that ZnO is suitable for optoelectronic applications such as Light Emitting Diode (LED's), solar cells, photo deters thanks to it's electrical and optical properties.

3. Methods

In this section,type of defects and detection techniques

3.1 Type of Defects

ZnO has a crystal structure. At a crystal structure, there are 2 possible defects. One of them is the vacancy and the other one is interstitial. Due to the fact that ZnO has 2 types of atoms. We can have 4 types of defects.

One of these defects is zinc interstitial whose electron configuration ends with 4s2. When the electron configuration of an atom ends with 4s2, it means that this atom has diamagnetic properties. Its g factor is 1.96.

The other defect is oxygen interstitial which may end up with 2p4, 2p5, and 2p6. When electron configuration ends with different orbitals, it gives different isotopes and that's why all of them have different properties. For example, if it ends up with 2p4, it gives Oi or if it ends up with 2p5, it is Oi-. These two isotopes are paramagnetic. However, there is a possibility that we can get a diamagnetic atom. For example, if our atom ends up with 2p6, then we get Oi-2.

Another defect is oxygen vacancy which means that we are missing one oxygen. The g value of O vacancy is 1.995.

The last defect is zinc vacancy which is a double acceptor.

3.2 Detection Techniques

There are two ways to detect these defects.

One of them is ERP. ERP is a method for the determination of the geometric and electronic structure. ERP focuses to find the unpaired electron and nuclei. Therefore, if an atom is diamagnetic, ERP cannot find that defect. That's why it is hard to detect zinc interstitial, Oİ-2 via ERP. However, we can detect other defects.

From the ERP graph, we can calculate the g factor. G factor helps us to determine what kind of defect we have. As we see from the graph, if we get g as 2.00, it means it is a shell defect. If we get g as 1.96, then it means that it is a core defect.

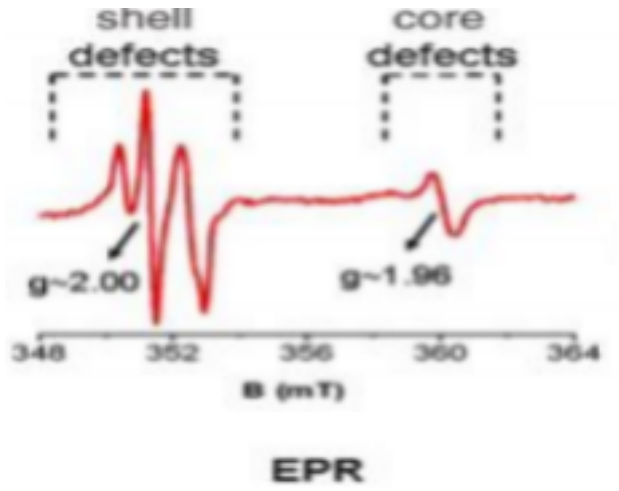

Fig 5. ERP Graph of ZnO

The other way to detect these defects is photoluminescence (PL). The PL consists of 2 emission bands. One of them is located at the absorption edge, the other one is in the visible region. From the data we get from PL, we can find the type of defect we have. For example, if we get red emission in the range from 620 to 690 nm, it shows us that we have oxygen interstitials. If our range is between 690 to 750, then we have oxygen vacancies.

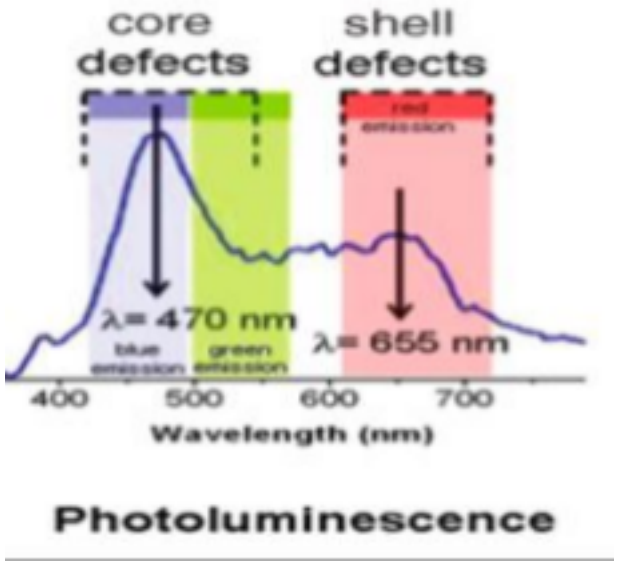

Fig 6. PL Graph of ZnO

4.1 Applications

At the first half of the twentieth century Zinc Oxide has been noticed for its luminescent properties along with low - toxicity, high catalytic efficiency, strong adsorption capability and biocompatibility; therefore, also turned ZnO into one of the central nanomaterials for manufacturing. Likewise, Zinc Oxide with Investigation of defect structures in metal oxides via spectroscopic techniques

mentioned uniqueness leads the role of nanoparticle with therapeutic activity against cancer, microbial infection and diabetes. Additionally, ZnO nanoparticles have also shown the potential to aid in wound healing. (Martínez-Carmona M., 2018, p.1-2)

ZnO is an enormous world production material with the capacity around 10^5 tons per year. Thus, the majority of percentage is consumed by the rubber production industrie. Hence, ZnO is in the group of thermal conductivity fillers along with Al2O3 and SiO2, it can improve pure silicone rubbers' low thermal conductivity without dispersing its high electrical resistance. Moreover, the nanomaterial has most efficient for manufacturing crystal structures, such as: wurtzite which is thermodynamically stable form and cubic rock-salt form - stable under extreme pressures, about 2 GPa. (Moezzi A. et al., 2012, p. 10) Currently ZnO is used in the rubbery industry as a major application as a vulcanizing activator. Therefore, the nanpparticle's small amount could accelerate the vulcanization process. (2012, p.13)
Fig.7. Chart showing the various uses of zinc metal. Zinc oxide is the main chemical produced from zinc metal. Compiled using data from diverse sources. (Moezzi A. et al., 2012, p.2)

The textile industries also demand Zinc Oxide nanomaterial for their usagt as a textile product. ZnO has a high resistance level towards UV lights, thus, scientists worked on discovering the UV light blocking and water repellent textile. As further detected, ZnO not only has UV light resistant properties, but also nanomaterial coating is biologically compatible and its coating structure is air-permeable which allows the body to breath underneath the clothes. (Kołodziejczak-Radzimska A. & Jesionowski T., 2014, p.31) the self cleaning property of ZnO was examined and has shown that methylene blue degrades under UV. Thus, researches suggest that ZnO is multifunctional and beneficial material as a cloth textile. (2014, p. 32)

Zno also has been studied as a drug delivery nanomaterial for the medical application due to its biocompatibility. Zinc is a fundamental element that cultivates homeostasis by regulating activity of enzymes and thus zinc oxide nanoparticles have capability to execute the cancer cells through the reactive oxygen species (ROS). (Jin S. & Jin H., 2019, p.13) Besides cancer treatment, with the antibacterial, descenfecting and drying capabilities ZnO is largely demanded in the production of plethora medicines and cosmetic creams. The ability of accelerating wound healing is applied towards itching and inflammation; hence, it is recommended by dermatologists to use products that contain ZnO in it. (Kołodziejczak-Radzimska A. & Jesionowski T., 2014, p. 31) Similarly, with the ability of absorbing UVB and UVA radiation lights, ZnO recently became the main ingredient for the sun screen cream production. Thus, it is cosmetically admirable since it rubs easily into the skin and occurs to be more transparent. (2014, p.31)
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Furthermore, in recent years the importance of ZnO as a semiconductor is largely emphasized due to the wide energy bond (3.37 eV) and high bond energy - 60 meV. aslo, with the phenomenon of luminescent property it is widely used in field emission display) equipment, for instance, as a television. As mentioned before, zinc oxide's resistance to UV radiation and high electrical conductivity emphasize the material as an irreplaceable tool, additionally with those properties it is remarkable to the phosphorus and sulfur, which in fact are exhibiting phosphorescence compounds. (2014, p.32)

4.2 Simulations

Electron Paramagnetic Resonance (EPR) means the same as Electron Spin Resonance. It is a spectroscopic technique that detects unpaired electrons. It is a very useful and powerful sensitive technique used for the characterization of the nature of magnetic impurities/defects and spin dynamics in materials that have paramagnetic defects in nanocrystalline zinc oxide. (Zargar at al., 2015) Microwave energy was used in the experiment. As known, the resonance condition arises when the microwave energy equals the Zeeman energy.

$$E = g \beta B$$

$E = h \times \nu$ (Microwave Energy)

$E = g \times \beta \times B$ (Zeeman Energy)

$h \times \nu = g \times \beta \times B$ (Resonance Condition)

h= Planck Constant, ν= microwave energy frequency s-1 , g= g factor, β= Bohr magneton constant, B: external Magnetic Field

ZnO places in a magnetic field and the microwave beam sends to the magnetic field. The resonance condition appears as an EPR signal. EPR spectra were simulated by using the toolbox called EasySpin in MATLAB program to understand this signal. The aims were how to plot the EPR data and simulate these spectra by using EasySpin. EPR data was given by supervisor Emre ERDEM in advance. This EPR data was plotted and then simulated.

Plotting EPR spectra by MATLAB

```
cd C:\c

clear all

load znopure.txt

I = znopure(:,3)'; % the sign ' symbolize the transpose of the coloumn I=intensity (y-axis) I = I - I(1);

%normalization


I = I / max(I); %normalization

B = znopure(:,2)'; % B=magnetic field (x-axis)

B = B / 10; %note that x-axis is magnetic field in mT unit, 10 Gauss=1 mT

figure(1)
```

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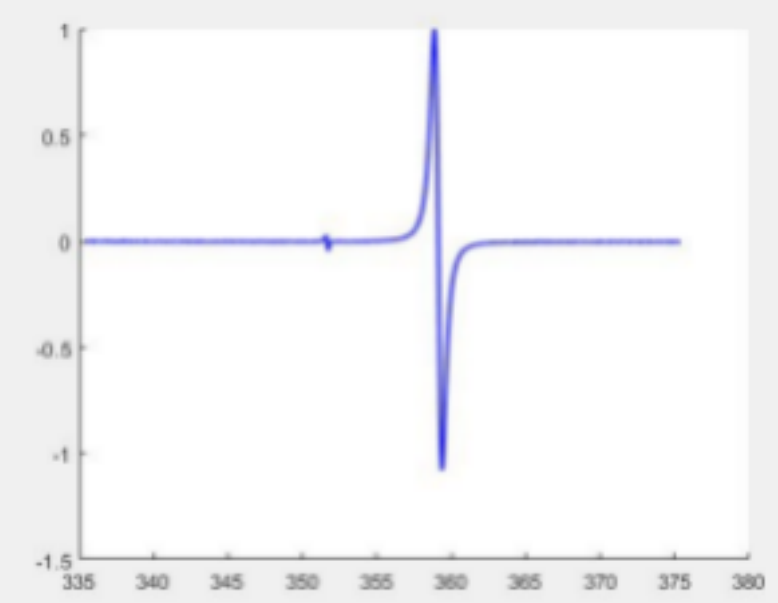
```


clf %clear figure

hold on %keep all figures in one plot

plot(B,I,'b','LineWidth',1.5); %Linewidth:is the thickness of the line

plot(Bsim,Isim,'r','LineWidth',1.5);
axis([min(B) max(B) min(I) max(I)])

title('ZnO - PURE-test for project')
xlabel('B_0 [mT]'); %labeling of the x-axis

ylabel('EPR Int. [a.u.]'); %labeling of the y-axis
```



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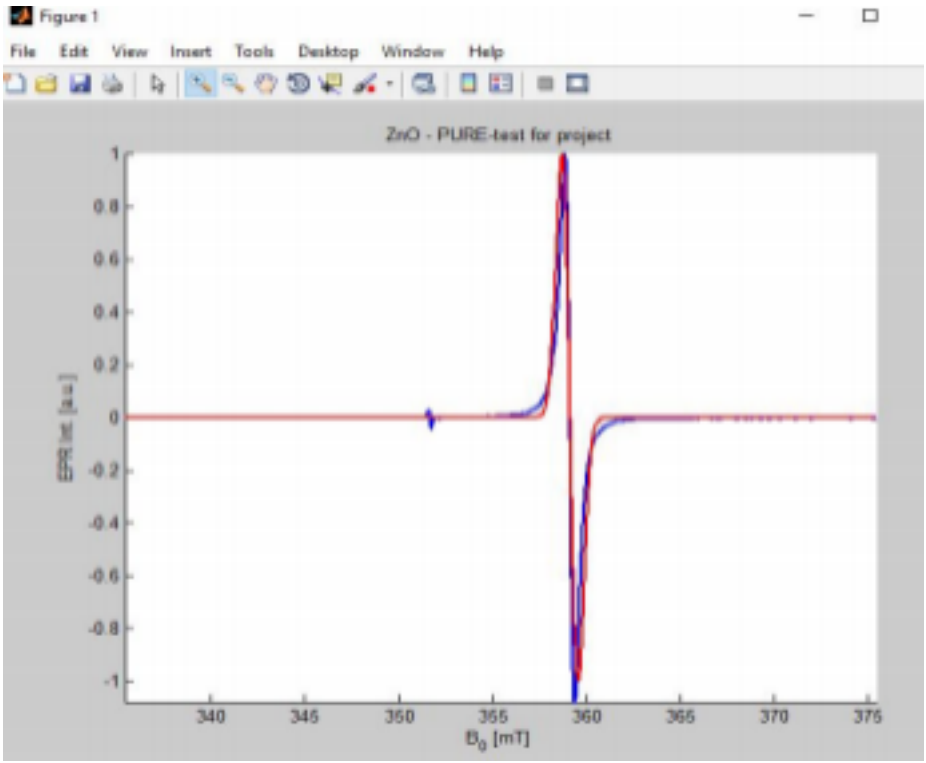
Following Matlab code was used for simulating the EPR spectra

```
%***********here is the parameters for SIMULATION******

g   = [1.962 1.962 1.962]; %play little bit...g-factor from the resonance (matrix so it
lw   = 1; %(in mT giving the peak to peak linewidth)

%useful commands for Easyspin to describe our ZnO crystal system
Sys = struct('S',1/2,'g',g,'lw',lw); %constructing my sample system in physical variabl
Exp = struct('Range',[335.4 375.4],'mwfreq',9.86228,'Temperature',300); %defining exper
Opt  = struct('nKnots',40,'Verbosity',1,'Intensity','on'); %in new versions some of the

%Calculation of the spectra
[Bsim,Isim] = pepper(Sys,Exp,Opt); %Bsim (simulated magnetic field), Isim: (simulated i
Isim    = Isim / max(Isim);


%*****************************************************
```

The Experimental and Simulated EPR Spectra of ZnO in MATLAB



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5. Discussion and Conclusion

ZnO is a promising material with a range of different properties that emphasizes its uniqueness in the era of nanotechnology. Also, ZnO is an encouraging semiconductor material due to the activity that is commonly used for decades in a wide range of applications which has a high resistance to the severe processing condition. Crystal structures are one of the most important properties of ZnO. The crystal structures shared by ZnO are wurtzite - the thermodynamically stable phase, zinc blende - stable only by growth on cubic structures, and rocksalt rare structure, but might be obtained at relatively high pressures. Additionally, there are 4 lattice parameters, they are a,c,u,c/a ratio; As Özgür et al. stated that the lattice parameters of a semiconductor usually depend on the following factors: free-electron concentration of foreign atoms, external strains (for example, those induced by substrate), and temperature. (2005,p.6-7)

ZnO is a semiconductor material with direct wide-bandgap approximately 3,437 eV at 300 K. ZnO's Defects and impurities affect the electrical conductivity. Thus, Electrical conductivity is created by electron mobility. (Büyük G. İ. at al, 2019) The electrical properties are the large exciton binding energy of EB=60 meV at room temperature makes ZnO a prominent candidate for device application. (Erdem E.,2012)

However, there are 4 types of defects. ZnO has a crystal structure; therefore, there are 2 possible defects for such a structure - vacancy and interstitial. Due to the fact that ZnO has 2 types of atoms. It is possible to have 4 types of defects. Hence, 2 methods are in use to find those imperfect structures. First one, ERP
is a method for the determination of the geometric and electronic structure and it focuses on finding the unpaired electron and nuclei. The second one is the photoluminescence method - PL. The PL consists of 2

emission bands. One of them is located at the absorption edge, the other one is in the visible region. From the data received from PL, it is efficient to find defects by this data.
Zinc Oxide has been noticed for its luminescent properties along with low - toxicity, high catalytic efficiency, strong adsorption capability and biocompatibility. Hence, those properties turned ZnO into one of the central nanomaterials for manufacturing. It is widely used in the rubber industry, in pharmaceutical and cosmetic purposes, textile factories for its air - permeability and UV lights resistance and takes essential part as a semiconductor the electronics and electrotechnology industries.

Also, simulations detecting EPR spectra were simulated by using the toolbox called EasySpin in MATLAB program to understand this signal. The aims were how to plot the EPR data and simulate these spectra by using EasySpin. EPR data was given by supervisor Emre ERDEM in advance. This EPR data was plotted and then simulated.

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