Determination of the band gap of a Semiconductor by Four Probe Set-Up

Experiment No:

Date:

1 Aim

To determine the bandgap of given semiconductor material using four probe method.

2 Apparatus Required

- Sample: Ge crystal
- Oven (heating range up to 200 °C)
- Four probe setup (measuring unit) includes oven controller
- Multi-range digital voltmeter and constant current generator

3 Procedure

- Put the sample on the base plate of the four probe arrangement. Unscrew the pipe holding the four probes, and let the four probes rest in the middle of the sample. Apply very gentle pressure on the probes and tighten the pipe in this position. Check the continuity between the probes for proper electrical contacts. Caution: The Ge crystal is very brittle. Therefore, use only the minimum pressure required for proper electrical contacts.
- Connect the outer pair of the probes (red/black) leads to the constant current power supply and the inner pair (yellow/green) to the probe's voltage terminals.

- Place the four-probe arrangement in the oven and connect the sensor lead to the resistance temperature detectors (RTD) connector on the panel.
- Switch on the mains supply of the four-probe set-up and put the digital panel meter in the current measuring inside. In this position, the LED facing mV will glow and the meter would read the voltage between the probes.
- Now, put the panel of the digital meter inside in voltage. In this position, the mV would glow and the meter would read the voltage between the probes.
- Switch on the temperature controller and adjust the set-temperature. The green LED would light up indicating that the oven is 'ON' and the temperature would start rising. Temperature of the oven in Kelvin is indicated by the digital panel meter (DPM).
- Now, take the voltage reading corresponding to the temperature and tabulate the data starting from 320K to 400K.

4 Formula Used

The resistivity can be determined using the relation

$$\rho = \frac{V \times 2\pi S}{I.G_7(w/s)} \qquad \text{(Ohm. m)}$$

Where,

S = Distance between the probes (meter)

V = Potential difference (volt)

I = Current (Ampere)

G_7(w/s) = Correction parameter (meter)

5 Observations – Table 1

Distance between the probes (S) = 2 mm, Thickness of the crystal (w) = 0.5 mm

Current (I) = mA, Correction parameter G_7 (w/s) = 5.89

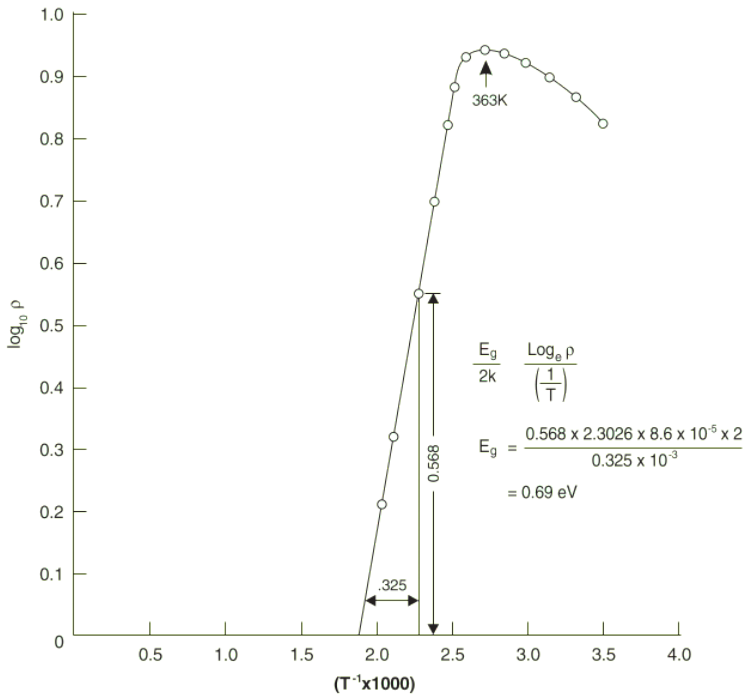


FIGURE 1

Model Graph: Resistivity of Ge crystal as a function of temperature

S. No	**Temperature (K)**	**Voltage (V)**	ρ **(ohm m)**	T^{-1} **($\times 10^{-3}$)**	**Log** ρ
1	310				
2	320				
3	330				
4	340				
5	350				
6	360				
7	370				
8	380				
9	390				
10	400				

Result

The bandgap of the semiconductor material (Ge) calculated using Four-Probe method is E_g = eV

Preparation of CuO Nanoparticles by Sol-Gel Method

Experiment No:

Date:

1 Aim

To synthesize copper oxide nanoparticles by sol-gel method and assess the crystalline characteristics with powder XRD pattern.

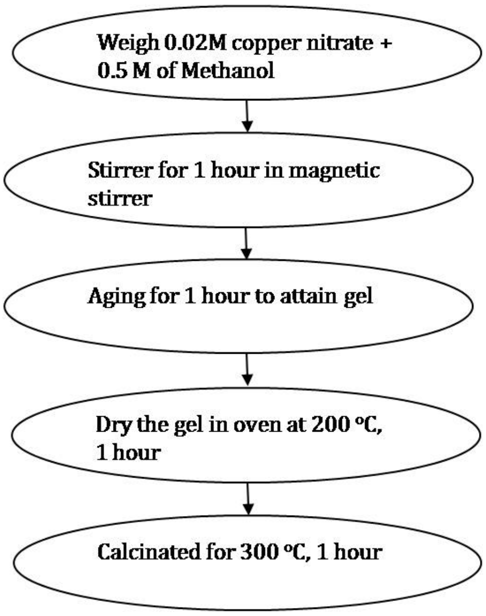
2 Required materials

Copper nitrate ($Cu(NO_3)_2.3H_2O$), methanol (CH_3OH), Beakers, Stirrer, Double distilled water (DD).

3 Procedure

1. 0.02 M of copper nitrate ($Cu(No_3)_2.\ 3H_2O$) is taken and made to dissolve in 0.5 M of methanol.
2. To obtain homogeneity the solution is stirred in a magnetic stirrer for 1 hour.
3. The prepared solution is kept for aging for about 1 hour.
4. After aging the gel is made to dry at 200 °C for 1 hour in an oven to remove the absorbed water molecules.
5. Dried powder is then kept at furnace at 300 °C, 1 hour for calcinations.
6. Powder XRD of the synthesized powder is analysed by comparing with JCPDS data to make preliminary identification.
7. Crystalline size for various peaks is estimated by Scherrer formula

Flowchart for synthesis of copper oxide



4 Formula Used

The average crystallite size (D) was estimated using Scherrer formula is

$$D = \frac{k\lambda}{\beta Cos\theta}$$

where k is Scherrer constant; λ is wavelength of X-ray used (nm); β is Full-width Half Maximum and θ is diffraction angle.

Table 1: Preliminary Identification by Powder XRD

2θ	(hkl)	Name of the Compound	JCPDS Card No.

Table 2: Estimation of Crystallite Size

Major Peaks	**Crystallite Size (nm)**
Average Crystallite Size (nm)	

5 Results

Copper oxide nanoparticles were successfully prepared by sol-gel method and the preliminary confirmation was made through powder XRD analysis. Also the average crystallite size was estimated to be __________ nm.

Preparation of Magnesium Ferrite by Single-Step Combustion Method

Experiment No:

Date:

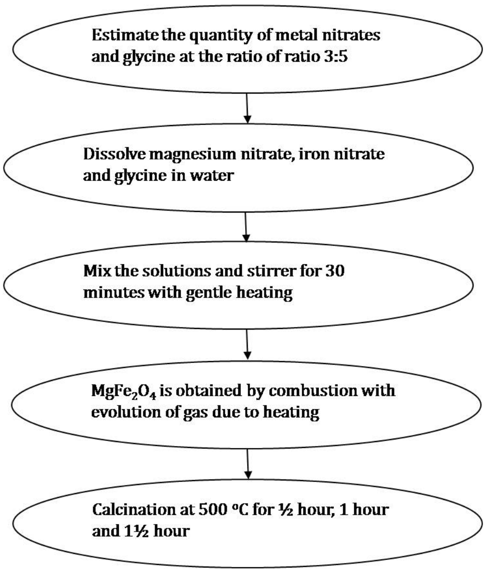
1 Aim

To prepare magnesium ferrite ($MgFe_2O_4$) spinel structure by combustion method and study its morphological arrangement by SEM analysis.

2 Materials Required

Magnesium nitrate ($Mg(NO_3)_2.6H_2O$), Iron nitrate ($Fe(No_3)_2.9H_2O$), Glycine ($C_2H_5NO_2$), Beakers, Stirrer, Acetone, Double distilled water (DD), Furnace.

Flowchart for synthesis of magnesium ferrite



3 Procedure

- Metal nitrates and glycine is taken in the molar ratio of 3:5.
- Weigh appropriate quantity of magnesium nitrate ($Mg(NO_3)_2.6H_2O$), iron nitrate ($Fe(No_3)_2.9H_2O$) and glycine ($C_2H_5NO_2$).
- The precursors are dissolved in double distilled water and made us solution with continuous stirring on magnetic stirrer for half an hour.
- The solutions are mixed together and heated gently on the hot plate until the solution turns into a gel.
- Raw magnesium ferrite ($MgFe_2O_4$) is obtained by single step combustion process with evolution of gas due to heating.
- To remove the excess fuel and nitrates the obtained sample is heated at 500 °C
- Calcination is carried out at various time (½ hour, 1 hour and 1½ hour).
- Recorded SEM pattern is analysed and the change in textural arrangement as a function of calcination time is studied.

Table 1: Morphological Texture Analysis of Magnesium ferrite.

Reaction Condition	Shape	Size	Comments

4 Results

Magnesium ferrite ($MgFe_2O_4$) with spinel structure was prepared by single-step combustion technique. Also the change in textural arrangements with calcinations time is analysed.

Cell refinement using computer programs

Experiment No:

Date:

1 Aim

To refine and calculate the cell parameters of given crystallographic data file.

2 Motivation

Crystals are the important arena of condensed matter physics and materials science. The properties of the materials are often described based on their crystalline structure. Ideally, crystals are formed by the repeating basic units called ‘unit cells’, over the three dimensional space. Which means, if you look into a crystal from any direction, it resembles same over the space. This is only in the case of ideal crystals. But practically, due to the experimental limitations, crystals have some defects in their structure. Analysing such a defects are important, especially when we consider the crystal for applications. There are many methods and programs are available to estimate the defects and to refine the crystal structure in literature. Here we use two of such programs to demonstrate the cell refinement process.

3 Basics

3.1 X-ray diffraction

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg's Law, $n(\lambda) = 2d.sin(\theta)$. The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure.

3.2 Single crystal XRD

Single-crystal X-ray diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.

3.3 Powder XRD

PXRD is primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

3.4 Crystal structure refinement

The electron density map generated by solution of the phase problem from the single crystal XRD can be seen as a basic structure map. However, the assignment of atoms to different intensity centers is key to understanding the structure. The step of atom assignment is referred to as solving the crystal structure and these resolved structures are given in a 'crystal information file' (cif) for further reference.

4 Method

Eventhough the cif files carries good quality data, they may have slight deviation from the ideal crystals. To analyse such a deviations, crytal refinement programs are used. Here we use two programs for the analysis the single crystal data. The data file can be downloaded from the crystallographic open database (COD) with information card number. To analyse this structure we need ‘Mercury program’ - to visualize the crytal structure and to simulate the PXRD data, and ‘checkcell package’ - for cell refinement.

4.1 Procedure

1. Download the cif file from this page:
   `http://www.crystallography.net/cod`
2. Open the structure in Mercury program and note down its crystall cell parameters.
3. Now from the calculation options, simulate the PXRD data of the given file and save it into a desired folder.
4. Open checkcell program, assign source wavelength and fix 2theta values and enter your simulated data in the given space.
5. Then in the parameter selection page choose the parameters corresponding to your data and proceed to calculation area.
6. Here match your simulated data with theoretical data and calculate the refinement parameters.

5 Observations

5.1 Crystallographic parameters

Identifier		
Formula		
Compound name		
Space group		
Cell lengths	**a**	
	b	
	c	
Cell angles	α	
	β	
	γ	
Cell volume		

5.2 Simulated PXRD data

2θ	**Intensity**

5.3 Refinement Data

Cell Parameters	**Intial**	**Refined**	**Sigma**
a			
b			
c			
α			
β			
γ			
Volume			

Mean square deviation of cell parameters = ____________________

6 Results

The given crystallagraphic data file is refined and the mean square deviation of cell parameters is about ___________________

Simulation of Vibrational Spectrum by Density Functional Theory Analysis

Experiment No:

Date:

1 Aim

To simulate the vibrational spectrum of carbon dioxide (CO_2), water (H_2O) and methane (CH_4) by density functional theory and to assign its vibrational components.

2 Motivation

Computational materials science involves computational tools for solving materials related problems. There exist different mathematical models for investigating problems at multiple length and time scales which help in understanding evolution of material structures (at different length scales) and how these structures effectively control material properties. With this understanding we can select materials for specific applications and also design advanced materials for new applications. At electronic level, Density Functional Theory (DFT) is a popular computational tool while Molecular Dynamics (MD) and Monte Carlo (MC) methods are considered as preferred tools for atomistic simulations. This experiment is intent to perform some basic steps in computational materials science such as geometry optimization and the simulation of vibratioanl spectrum.

3 Basics

3.1 Density Functional Theory

Quantum chemical wavefunctions can be used derive the complete information about a system. But it is hard to solve the quantum equations as it is. DFT is one of the available methods, in a simplified form, to solve those equations. In DFT, molecular properties of a many electron system is determined by fucntionals, which is nothing but the spatial distribution electron density. These functionals are pre-implemented in many packages and for the present analysis, DFT implemented in Dalton 2016 is used.

3.2 Basis sets

In DFT, in order to perform the desired calculations, basis sets have to be specified. Basis sets are nothing but mathematical functions that represents electronic wave functions. Present case, 6-31G** basis set, which has the support for the atoms H through Zn is used for the analysis. 6-31G** is a valence double-zeta polarized basis set and it is one of the widely used basis set in DFT calculations.

3.3 Vibrational spectrum

Absorption of energy by specific bonds of the molecule can induce a specific pattern corresponds to particular bonds. These finger prints can be used to confirm the molecular structure.

3.4 Simulation of vibrational spectrum

Vibrations that result in change of dipole moment give rise to IR absorptions. So, the computer program simulates an oscillating electric field of the radiation that couples with the molecular vibration to cause an alternating electric field produced by the changing dipole.

3.5 Types of molecular vibrations

1. *Stretching* (ν) vibrations that alter the bond lengths
2. *Bending or deformation* vibrations that alter the bond angles, (the bond lengths remain unchanged). They can be subdivided into in-plane (δ) and out-of-plane modes (γ). These modes are often referred to as twisting, wagging, and rocking vibration of a fragment.

3. *Torsional vibrations* involve an alternation of the torsion angle. A further division into symmetric (s), antisymmetric (as), and degenerated (e) vibrations are possible.

4 Procedure

1. Login into the system with your credentials.
2. Open Avogadro package and draw the corresponding molecular structure and save it in .mol format
3. Open the saved .mol file (in Avogadro package) and optimize it with UFF algorithm.
4. After optimization, export the structure as Dalton input file.
5. Open .dal file and include commands for geometry optimization.
6. Run the .dal file through command line (> dalton filename.dal).
7. Open the output and copy the last (optimized geometry). Create a new file with commands for vibrational analysis.
8. Run the file and view the output in Gabedit.
9. Note down the frequencies, their intensities and the corresponding vibrations.

5 Input files

5.1 Water

5.1.1 *Geometry optimization*

```
BASIS
6-31G**
Water
----------
Atomtypes=2 Angstrom
Charge=8.0 Atoms=1
O       -0.01310   -0.01860    0.00000
Charge=1.0 Atoms=2
H       -0.29940    0.91860    0.00000
H        0.96590    0.02390    0.00000

**DALTON INPUT
.OPTIMIZE
**WAVE FUNCTION
.DFT
 B3LYP
**END OF INPUT
```

5.1.2 *Vibrational analysis*

```
BASIS
6-31G**
Water
----------
Atomtypes=2 Angstrom Nosymmetry
Charge=8.0 Atoms=1
O
Charge=1.0 Atoms=2
H
H

**DALTON INPUT
.RUN PROPERTIES
**WAVE FUNCTION
.DFT
 B3LYP
**PROPERTIES
.VIBANA
**END OF INPUT
```

5.2 Carbon dioxide

5.2.1 *Geometry optimization*

```
BASIS
6-31G**
Carbon dioxide
----------
Atomtypes=2 Angstrom
Charge=6.0 Atoms=1
C        0.00000    0.00000    0.00000
Charge=8.0 Atoms=2
O       -1.19700    0.00000    0.00000
O        1.19700    0.00000    0.00000

**DALTON INPUT
.OPTIMIZE
**WAVE FUNCTION
.DFT
 B3LYP
**END OF INPUT
```

5.2.2 *Vibrational analysis*

```
BASIS
6-31G**
Carbon dioxide
----------
Atomtypes=2 Angstrom Nosymmetry
Charge=6.0 Atoms=1
C
Charge=8.0 Atoms=2
O
O

**DALTON INPUT
.RUN PROPERTIES
**WAVE FUNCTION
.DFT
 B3LYP
**PROPERTIES
.VIBANA
**END OF INPUT
```

5.3 Methane

5.3.1 *Geometry optimization*

```
BASIS
6-31G**
Methane
----------
Atomtypes=2 Angstrom
Charge=6.0 Atoms=1
C        0.00002     0.00002    -0.00000
Charge=1.0 Atoms=4
H       -0.36405    -0.51484     0.89178
H        1.09222     0.00001     0.00000
H       -0.36403     1.02976     0.00000
H       -0.36405    -0.51484    -0.89178

**DALTON INPUT
.OPTIMIZE
**WAVE FUNCTION
.DFT
 B3LYP
**END OF INPUT
```

5.3.2 *Vibrational analysis*

```
BASIS
6-31G**
Methane
----------
Atomtypes=2 Angstrom Nosymmetry
Charge=6.0 Atoms=1
C
Charge=1.0 Atoms=4
H
H
H
H

**DALTON INPUT
.RUN PROPERTIES
**WAVE FUNCTION
.DFT
 B3LYP
**PROPERTIES
.VIBANA
**END OF INPUT
```

6 Observations

6.1 Water

6.1.1 *Optimized geometry*

Atom	x	y	z
O			
H			
H			

6.1.2 *Vibrations*

S. No	Frequency	Intensity	Assignment
1.			
2.			
3.			

6.2 Carbon dioxide

6.2.1 *Optimized geometry*

Atom	x	y	z
C			
O			
O			

6.2.2 *Vibrations*

S. No	Frequency	Intensity	Assignment
1.			
2.			
3.			

6.3 Methane

6.3.1 *Optimized geometry*

Atom	x	y	z
C			
H			
H			
H			
H			

6.3.2 *Vibrations*

S. No	Frequency	Intensity	Assignment
1.			
2.			
3.			
4.			

7 Results

Vibrational spectra of the given molecules are simulated and their molecular vibrational components are assigned.