Kingdom of Saudi Arabia
Imam Mohammad Ibn Saud Islamic University
College of Sciences
Department of Physics

Structural characterization and morphology of Bi_2O_3 nanoparticles

A graduation project submitted to the Department of Physics in partial fulfilment of the requirements for the degree of Bachelor of Science in Physics

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Contents

LIST OF ABBREVIATIONS

Bismuth oxide (Bi_2O_3)

Nanoparticles (NPs)

Energy Dispersive X-ray spectroscopy analysis (EDX)

Scanning Electron Microscopy (SEM)

X-ray diffraction (XRD)

Acknowledgment

I am deeply grateful to Allah, the Most Merciful, for granting me the strength and wisdom to complete this thesis. Any success achieved is solely by His grace, and any shortcomings are due to my own errors. I would like to express my sincere gratitude to my supervisor Dr. Nazir Mustapha, for his unwavering support, guidance, and valuable insights throughout this research. His expertise and encouragement have been instrumental in shaping this work. My heartfelt thanks go to my family for their endless love, patience, and belief in my abilities. Their sacrifices and continuous support have been my foundation. I am also indebted to my friends and colleagues who have aided, feedback, and companionship during this journey. Their presence has made this experience both enriching and memorable. Finally, I acknowledge the contributions of IMAMU Library for providing the resources, which have been vital to the completion of this thesis.

Abstract

In this study, nanopowders of Bismuth oxide was characterised by X-ray diffraction (XRD) technique; to confirm its structure and it was found to be cubic structure. The crystal structure is determined based on the Miller indices values, while the crystallite size was calculated by Scherrer method. Scanning electron microscopy SEM and energy dispersive X-ray analysis EDX were used to assess its morphology and Chemical composition, respectively. Based on our obtained results, the crystal size of Bi_2O_3 was observed to be well spherical with crystal size of 49.6 Angstrom. The EDX confirmed its atomic ratio of Bi and O to be 2:3 as Bi_2O_3.

الملخص

في هذه الدراسة، تم توصيف مساحيق نانوية من أكسيد البزموت بتقنية حيود الأشعة السينية (XRD) ، للتأكد من بنيتها، حيث وجد انها ذات بنية مكعبة. حددت البنية البلورية بناءً على قيم مؤشرات ميلر، بينما حُسب حجم البلورة بطريقة شيرر. استُخدم المجهر الالكتروني الماسح(SEM) وتحليل الأشعة السينية المشتتة للطاقة(EDX) لتقييم مورفولوجيا البلورة وتركيبها الكيميائي، على التوالي. بناءً على النتائج التي حصلنا عليها، لوحظ أن حجم بلورة(Bi_2O_3) كروي تماما، بحجم بلورة 49.6 انجستروم. أكد تحليل(EDX) أن النسبة الذرية للبيزو والأكسجين فيه هي 2:3 في صورة(Bi_2O_3).

Chapter 1

Introduction

Bismuth oxide Bi_2O_3 nano materials have a range of attractive properties including a high band gap (2-3.96eV), a high refractive index and photoluminescence and this oxide has attracted the attention of many researchers for many applications in specific diseases as well as optimized Bi_2O_3 nanostructures for electrical, medical, biological sensors, and other relevant applications. In addition to its structural and electronic properties, Bi_2O_3 exhibits strong stability under a variety of environmental conditions, making it suitable for long-term use in harsh environments. Recent studies have also explored its potential in *solar energy applications*, where Bi_2O_3-based composites are being developed for efficient *solar cells* and *photoelectrochemical water splitting* due to their ability to absorb visible light and facilitate charge separation. The catalytic behaviour of Bi_2O_3 is also influenced by the presence of an oxygen vacancy. Thus, small variation in the lattice structure due to the presence of inclusion impurities, substituted ions, surface defects in ppm concentration reveals successful degradation of photocatalytic properties. Several studies Bi_2O_3 have been carried out on reaction optimization and structural modification e.g. metal doping or material hybridization) in order to improve the photoactivity and energy conservation. The study also mentioned that while there are many ways to make Bi_2O_3, its properties depend on things like crystal size and shape. But making Bi_2O_3 nanoparticles that are all the same size is still difficult. This study was aimed to investigate the structural and morphological characteristics of Bismuth Oxide (Bi_2O_3) nanoparticles (NPs) to assess the possibility of its use as an anode in optoelectronic devices such as solar cells and light emitting diodes. The project will focus on assessing the structural properties by X-ray diffraction. Scherer method was used to determine the crystallite size. The morphology of the Bi_2O_3 NPs was examined using the Scanning Electron microscopy (SEM) at various magnifications. Furthermore, Energy Dispersive X-ray spectroscopy analysis (EDX) was performed to confirm the chemical composition of the Bi_2O_3 NPs.

Chapter 2

Theoretical background

2. X-Ray Diffraction

2.1. Definition

X-rays are electromagnetic radiation of wavelength about 1A (10^{-10} nm), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. X-ray powder diffraction (XRD) is a rapid analytical technique and it the most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. There are several parameters that can be determined by X-ray diffraction such as lattice parameters, crystallites size and residual strain (macrostrain).

2.2. Fundamental Principles

X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law:

$$n\lambda = 2d\sin(\theta) \qquad (1)$$

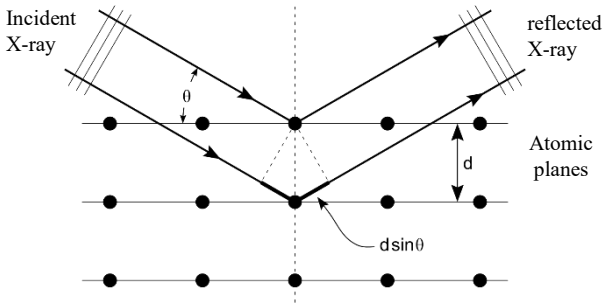

Figure 1: X-ray diffraction principle.

These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 20angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the elements because each element has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder diffraction data can be collected using either transmission or reflection geometry, as shown below.

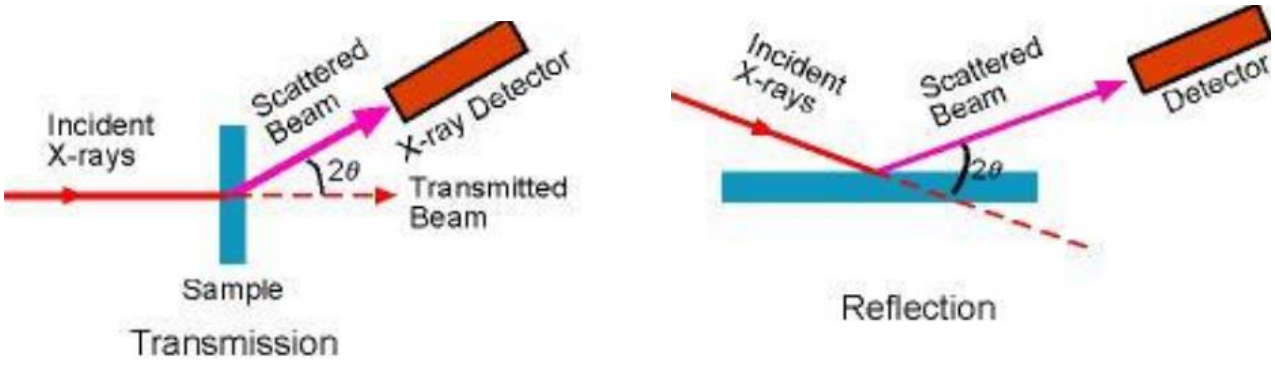

Figure 2: Reflection and transmission scattering rays in materials

2.3 XRD Instrumentation

2.3.1 Source:

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. Copper is the most common target material for single-crystal diffraction (And the one we will use in Part 2), with CuKa radiation = 1.5406 **Å**. These X-rays are collimated and directed onto the sample.

2.3.2. Detector:

An x-ray detector generates a pulse of current when it absorbs an x-ray, the ideal detector should produce an output pulse for every incident x-ray. The fraction of photons that produce pulses is the "quantum efficiency" of the detector.

2.3.1. Source:

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2.4 Structure factor

Structure factor of a lattice with basis:

- x , y and z are the position of the atoms.
- h,k and l are the miller indices.
- F is the atomic factor.

Chapter 3

Experimental

This analysis is often combined with other characterization techniques such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), to provide a comprehensive understanding of the structural, optical, and photocatalytic properties of the nanoparticles. Studies show that EDX effectively confirms the presence and concentration of elements within the nanoparticles, which is essential for evaluating their performance in various applications including optoelectronic devices and photocatalysis.

3.1. X-ray diffraction

X-ray powder diffraction (XRD) measurements were performed using Bruker D8 Discover diffractometer (0-2 θ) equipped with Cu-Kα radiation (λ=1.5406 **Å**) located at the physics department as shown in figure 3.

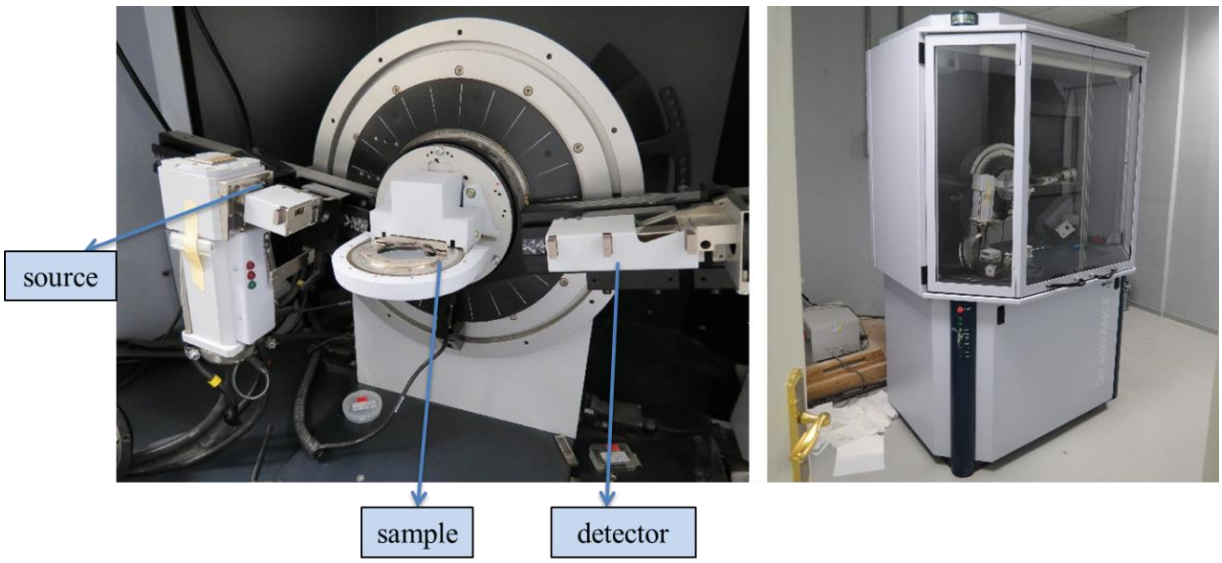


Figure 3: Bruker D8 Discover diffractometer

The X-ray diffraction (XRD) analysis confirmed the presence of the expected crystalline phases. Scanning Electron Microscopy (SEM) images showed uniform particle size and distribution. Energy Dispersive X-ray (EDX) analysis verified the presence of the main elements without significant impurities. These results indicate good sample preparation and reliable experimental data.

By using Bargg's Law we can find the interplanar distance (d):

$$2d \sin \theta = n\lambda \qquad (2)$$

The normal equation for cubic Structure is:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

It will know that for cubic structure a=b=c so we get:

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2 + l^2}{a^2}\right)$$

Where:

d: is the inter-planar distance.

a is the interatomic distance.

h, k. l are Miller indices.

From equation (2) and using the peak (220), the value of inter-planar distance is:

d = (1.54) ÷ 2sin $(\frac{30}{2})$

d = 2.97 **Å**

Lattice parameter (a) is determined by using equation:

a = (2.97) x$\sqrt{2^2 + 2^2}$

a = 8.40 **Å**

3.1.2. Lattice parameters

- Bismuth oxide Bi_2O_3

Bismuth oxide is a cubic structure with the following properties:

a = b = c

a = β = y = 90º

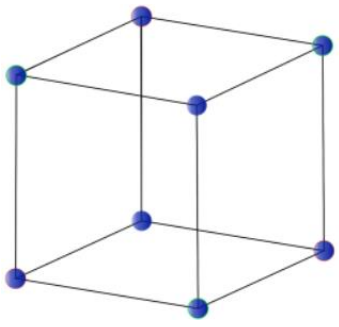


Figure 4: cubic structure

3.2 Scanning Electron Microscopy SEM

is a powerful imaging technique used to analyze the surface structure and composition of materials at high magnifications. SEM works by scanning a focused beam of electrons over the sample's surface, causing the emission of secondary electrons, which are then detected to create detailed, high-resolution images. This technique provides information on surface morphology, texture, and topography at the micro to nanoscale, and can also be coupled with energy-dispersive X-ray spectroscopy (EDX) for elemental analysis. SEM is widely used in materials science, biology, and semiconductor industries to study the surface of samples.

3.3 Energy Dispersive X-ray EDX

Energy Dispersive X-ray Spectroscopy (EDX) is an analytical technique used in conjunction with Scanning Electron Microscopy (SEM) to determine the elemental composition of a sample. When the sample is irradiated with an electron beam, it emits characteristic X-rays specific to the elements present. EDX detects these X-rays and provides information about the types and amounts of elements in the sample. It is useful for elemental mapping, microanalysis, and identifying the presence of specific elements at high spatial resolution. EDX can analyze a wide range of elements, from light elements to heavier metals.

Figure 5: Electron Microscopy | SEM-EDX

3.4 Samples

The commercially processed powder of Bi_2O_3 are characterized by XRD, SEM and EDX without further annealing and as received.

Chapter 4

Results and Discussion

4.1 XRD results

Fig.7 shows the XRD pattern of Bi_2O_3 nanopowder. Scherrer's method is used to calculate the average crystallite size by using the following formula:

$$D = \frac{K\lambda}{\beta exp\ csc(\theta)}$$

where **k** is the shape factor (~0.8-1.39), **D** is the mean size of the crystallite thickness, λ is the wavelength of the X-rays, θ is the Bragg angle, and β is the full-width at half-maximum (FWHM) of the peak (radians).

XRD pattern of Bi_2O_3 nanopowder:

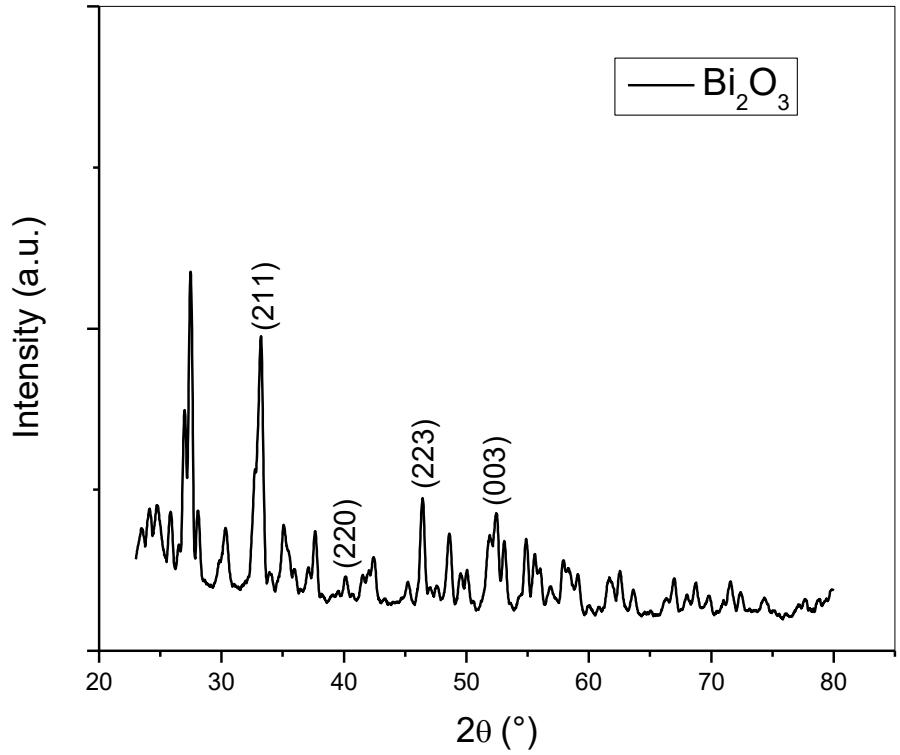


Figure 6: XRD pattern of Bi_2O_3 powder

To determine the average crystallite size, the main peak (211) is used to study the phase and crystalline structure of the synthesized Bi_2O_3 material, X-ray diffraction was performed as depicted in **Fig7**. The pattern showed that the material was polycrystalline. The diffraction peaks located at 2θ = 33.3, 40.1, 46.6 and 52.6 ° corresponding to (211), (220), (223) and (003), respectively, indicated the formation of monoclinic Bi_2O_3 phase according to JCPDS card N° 01-072-0398. In addition to the existence of other peaks, probably corresponding to the $Bi(OH)_3$ phase since the sample was characterized without a heat treatment.

$$\beta = 36.68 - 35 = 1.68\, deg$$

By using $\frac{\beta\text{Ⅲ}}{180}$ convert to radian

$$\frac{(1.68)(3.14)}{(180)} = 0.029\,, take{:}\, 2\theta = 36\,, \theta = 18deg$$

$$D = \frac{(0.89)(1.54)}{(0.029)\mathrm{coc}(18)} = 49.6\text{Å}$$

Similar results were reported by (Mohammadi et al [6] who examined the possibility of using Bi_2O_3 as a nanoparticle Contrast agent. They reported a crystallite size of 40 nm.

4.2 Scanning Electron microscopy (SEM)

(a) SEM image of Bi_2O_3 sample at 10,000× magnification.

The image displays fine microstructures with flower-like or layered morphologies, indicating possible crystal growth patterns. Captured at 13.0 kV, WD = 9.4 mm, scale bar = 5 µm.

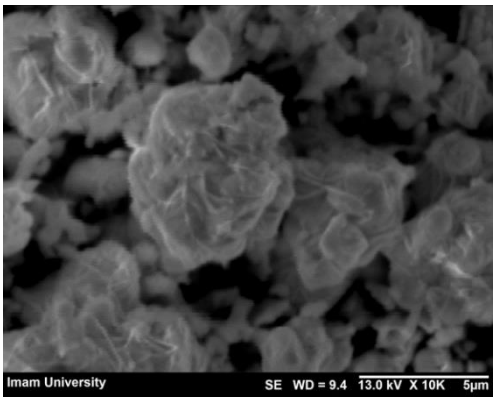


Figure 7: (a) shows the Bi_2O_3 images at various magnifications 10000x

(b) SEM image of Bi_2O_3 sample at 3000× magnification.

The image reveals an agglomerated structure with porous morphology, indicating potential surface reactivity. Taken at 20.0 kV, WD = 8.5 mm, scale bar = 10µm.

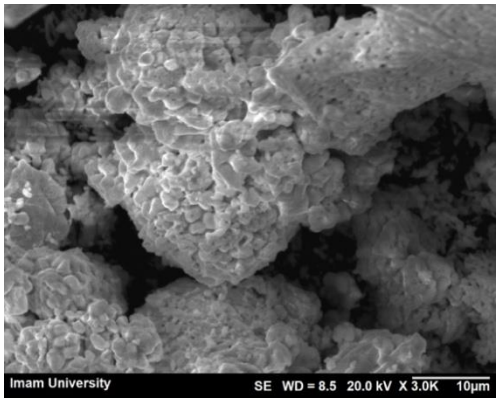


Figure 7: (b) shows the Bi_2O_3 images at various magnifications 3000X

(c) SEM image of Bi_2O_3 sample at 550× magnification.

The image shows a heterogeneous distribution of particles with varying sizes and rough surfaces. Some plate-like structures are also visible, indicating possible morphological diversity. Captured at 13.0 kV, WD = 9.4 mm, scale bar = 100 µm

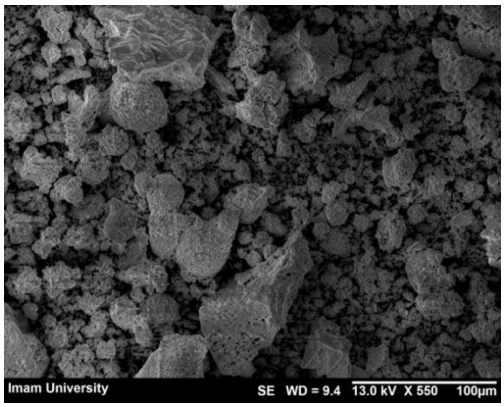


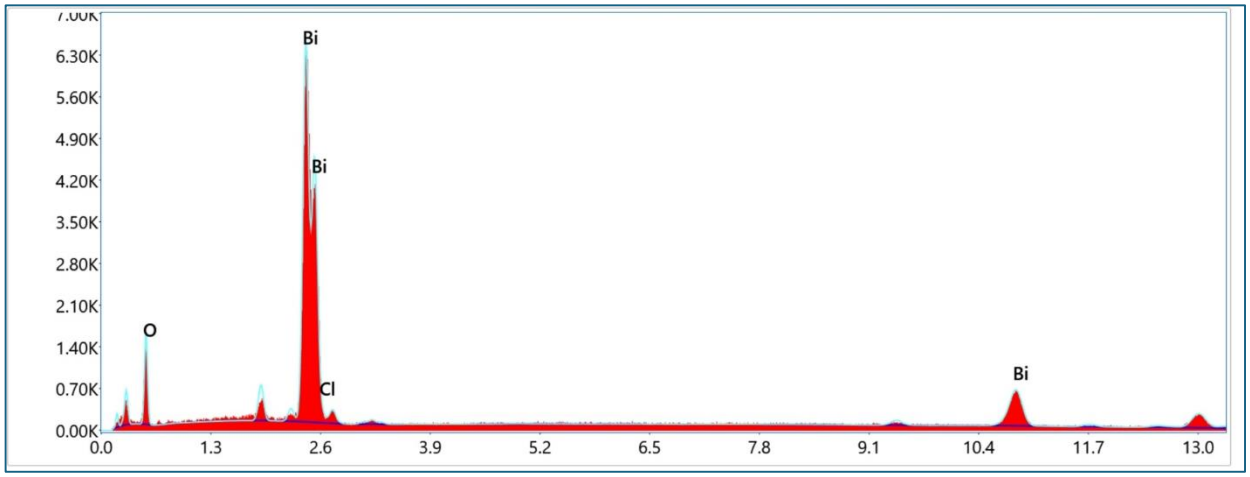
Figure 7: (c) shows the Bi_2O_3 images at various magnifications 550X.

Figure 8: shows the SEM images of Bi_2O_3 nanoparticles with various magnifications of 3000, 550, and 10000 times, indicating the morphology of the Bi_2O_3 nanoparticles is agglomerated.

4.2. Energy Dispersive X-ray Spectroscopy (EDX)

Energy Dispersive X-ray Spectroscopy (EDX) is widely used in the study of bismuth oxide (Bi_2O_3) nanoparticles to accurately determine their chemical composition. According to the EDX spectrum as shown in figure (9), the quantitative EDX analysis indicates that the atomic ratios of Bi and O are 2:3 which is confirmed as Bi_2O_3.

Figure 8: EDX pattern is displayed Below:



eZAF Quant Result - Analysis Uncertainty: 10.16 %

Element	Weight %	MDL	Atomic %	Net Int.	Error %	R	A	F
O K	16.2	2.67	70.1	116.4	12.1	0.6784	0.0408	1.0000
Cl K	1.4	2.75	2.6	20.3	21.5	0.7306	0.2899	1.0160
Bi M	82.4	3.59	27.3	912.9	7.0	0.7284	0.4710	1.0087

4.3 Crystal Structure Comparison with Previous Studies

The presence of cubic and related crystal structures in previous studies has been demonstrated through various characterization techniques. For instance, Police et al. (2018) reported the synthesis of a $Cu_2O/TiO_2/Bi_2O_3$ ternary photocatalyst, where Cu_2O exhibited a cubic crystal structure as confirmed by X-ray diffraction (XRD) analysis. In another study, Vinoth et al. (2017) synthesized BiOI incorporated with reduced graphene oxide (rGO), and the XRD results revealed a tetragonal crystal structure, which shares some geometric characteristics with cubic and hexagonal systems in specific crystallographic planes. These findings highlight the relevance of cubic and related phases in photocatalytic materials.

The formation of the monoclinic phase of bismuth oxide (Bi_2O_3), which is thermodynamically stable at room temperature, requires specific processing conditions. In this study, the material was calcined at temperatures between 400°C and 600°C for a duration of 2 to 4 hours in ambient air. Slow cooling after calcination was essential to stabilize the monoclinic structure and prevent transformation to the high-temperature cubic phase (Bi_2O_3), which typically forms above 730°C. These conditions ensured the successful formation of α-Bi_2O_3 with the desired crystalline structure.

Conclusion

The lattice parameters and crystallite size were determined by XRD diffraction for different crystal structures. The lattice parameters (b,c) of Bismuth oxide, which is hexagonal are 3.244 **Å** and 5.2 **Å**, respectively. The Bi_2O_3 oxide has cubic crystal structure (a=b=c) and the lattice parameter is 8.4 **Å**. Scherrer method was used to calculate the average crystallite size of Bismuth oxide by using the most intense peak (211). The value is around 49.6 **Å**. SEM images showed an agglomerated morphology. EDX showed the atomic ratio 2:3 of the chemical composition.

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