Sudan University of Science and Technology

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Investigation of Optical and Electrical properties of Rock Samples from Darfur Using Spectroscopic Techniques

التحقق من الخواص البصرية والكهربية لعينات من الصخور الماخوذة من دارفور باستخدام التقنيات المطيافية

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيم

In The Name of Allah, the Beneficent the Merciful

مَرَجَ الْبَحْرَيْنِ يَلْتَقِيَانِ (19) بَيْنَهُمَا بَرْزَخٌ لَا يَبْغِيَانِ (20) فَبِأَيِّ
آلَاءِ رَبِّكُمَا تُكَذِّبَانِ (21) يَخْرُجُ مِنْهُمَا اللُّؤْلُؤُ وَالْمَرْجَانُ (22)

فِيهِنَّ قَاصِرَاتُ الطَّرْفِ لَمْ يَطْمِثْهُنَّ إِنْسٌ قَبْلَهُمْ وَلَا جَانٌّ (56) فَبِأَيِّ
آلَاءِ رَبِّكُمَا تُكَذِّبَانِ (57) كَأَنَّهُنَّ الْيَاقُوتُ وَالْمَرْجَانُ (58)

صدق الله العظيم

سورة الرحمن

DEDICATION

This thesis was dedicated to:

The sake of Allah, my Creator and my Master, My great teacher and messenger, Mohammed (May Allah bless and grant him), who taught us the purpose of life; my second magnificent home; My great parents, who never stop giving of themselves in countless ways , My wife ,My beloved brothers and sisters; particularly my dearest brother , Mohammed, who stands by me in all situations when things look bleak, To all my family, the symbol of love and giving, My friends who encourage and support me, All the people in my life who touch my heart.

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ABSTRACT

The main objectives of this research study were to know rock contents to classify their types through multi spectroscopic techniques and analyzing their electrical and optical properties. Energy Dispersive X-ray Fluorescence analysis showed that the major revealed composition as Al_2O_3, SiO_2, SO_3, Fe_2O_3, CaO and TiO_2. X-ray Diffraction scanning tests of the of rocks indicated the peaks corundum, quartz, rutile, albite, anorthite, orthopyroxene and feldspar composition the most the rock samples were quartz as main content except sample one was corundum as the basic compound, the comparison between x-ray fluorescence and x-ray diffraction results there is a similarity to determine the fundamental body of the rocks. for more investigation and delicacy Energy Dispersive X-ray Spectrometry coupling with Scanning Electron Microscope scan analyzing indicated that presence of the trace elements as Fe, Au, K ،and Ca, the weight percent wt.t of silicon has the great majority in the mast rock samples with the standard label of SiO_2. Laser-induced breakdown spectroscopy was used to detect rare earth elements in the rock samples. Elemental analysis has revealed trace and rare elements are present through spectral lines of low and high intensity and appropriate wavelength range between (420 and 720 nm). Rare earth elements such as Ce, Pr, Eu, and Gd were identified in spectra recorded from the samples and selected as the main targeted elements to study their properties. revealed that the number of average concentrations was 3919, 1153, 6823, and 2638ppm in all samples. Through the spectral lines, the most appearance elements were Aluminum, Silicon, Iron, Sulfur, Oxygen, and Lead. FTIR gives us information about the presence of many organic groups in the examined samples. The complexity of the FTIR spectrum is typical of most infrared spectra and illustrates their use of identifying materials through functional groups. the gap in the spectrum of between (1048 and 3618) cm-1. An unambiguous analysis of the IR spectra of rocks was difficult to clarify due to the presence of many ingredients. The bands in this region originate in interacting vibrational modes resulting in a complex absorption pattern. Usually, this region is quite complex and often difficult to interpret. Diffuse Reflectance Spectroscopy has been used as property prediction models to study the physical, optical and electrical properties. KM function, extinction, absorption, refractive index, optical band gap, electrical and optical conductivity, and many of properties have calculated and discussed in detail based on DRS provided background through related equations. overall, results have given different values two mineral categories of corundum and silica group with the preference of corundum specimen from silica group optical and electrical properties in most results obtained. The DRS results provide reliable information and new insights into the structural characteristics of the surface metal oxide species on different environmental conditions. Analyses and studies for selected rock samples were carried out to identify mineral type through physical and chemical characteristics and discrimination of basic contents as well as impurities the possibility to determine of chemical and concentration of specific mineral depends on the backbone of the basic body composition, available of chemical data always important to observe the behavior rock samples. In general, according to the analyzing outcome, optical and electrical the research can consider the rock samples as semi-conductors due to silicon contents were represented as greats of all rock samples until they were treated and extracted using the scientific methods which used for mineral treatment .The Sudanese corundum less quality than other countries corundum but quartz is nearly the same characteristics to the other countries due to SiO_2 content more than (98%)

المستخلص

الأهداف الرئيسية لهذه الدراسة البحثية هي معرفة محتويات الصخور لتصنيف أنواعها من خلال تقنيات التحليل الطيفي المتعددة وتحليل خواصها الكهربائية والبصرية. تم استخدام المطياف طاقه التشتت الاشعه السينية المتوجهة و بينت نتاتج ان المكونات الاساسية للصخور كانت اكسيد المونيوم ، اكسيد السيلكون ، ثلاثي اكسيدالكبريت ، اكسيد الحديد الثلاثي ،اكسيد كالسوم واكسيد تايتانيوم بنسب مختلفة .كما اظهرت نتاتج حيود الاشعة السينية من خلال القمم مكونات كالكوراندوم ، الكوارتز ، الروتيل ، الألبيت ، الأنورثيت ، الأورثوبوكسين ، والفلسبار . وكانت معظم عينات الصخور يمثل الكوارتز كمحتوى رئيسي باستثناء العينة الاولي يمثل أكسيد الألمونيوم كمركب أساسي و المقارنة بين نتاتج مطيافين هناك تشابة في تحديد المكون الاساسي لصخور وللمذيد من التحقيق والدقة تم التحليل بواسطة مطياف الطاقة المتشتتة مزدوج مع مجهر المسح اللاكتروني توصلت أن وجود العناصر النادرة مثل K , Au , Fe و Ca و نسبة الوزنية لسيليكون لديها الغالبية العظمى في معظم عينات الصخور .وتم استخدام التحليل الطيفي المستحث بواسطة الليزر لكشف العناصر الأرضية النادرة وتحليلها في العينات الصخور و اظهر التحليل عن وجود عدد من العناصر النادرة من خلال الخطوط الطيفية ذات الكثافة المنخفضة والعالية والاطوال الموجية المقابلة لشدة الطيف وكان مدى الاطول الموجية المستخدمة ما بين 420 و 720 نانومتر و تم التعرف على العناصر التالية : السيريوم و البراسيوديميوم ويوروبيوم وجادلينيوم من العينات الموخوذة واستهدف البحث معرفة خصائص العناصر المذكورة وتحليل بعض مميزاتها وتوصلت الدراسة بان متوسط التراكيز العناصر هي : 3919 ، 5763,2253 و2638 جزء في المليون علي التوالي. كما تم التعرف عناصر اخري أكثر ظهوراً في جميع العينات بناءً علي الاطوال الموجية كالمونيوم و السيليكون و الحديد و الكربون و الكبريت و الاكسجين و الرصاص. وباستخدام مطياف الأشعة تحت الحمراء تحويل فورييه اظهرت معلومات حول وجود عدد كبير من المجموعات العضوية في العينات التي تم فحصها. يعتبر الطيف الأشعة تحت الحمراء تحويل فورييه نموذجيًا لمعظم أطياف الأشعة تحت الحمراء ويوضح استخدامها في تحديد المواد من خلال المجموعة الوظيفية.بمدي الطيفي بين (1048 و 3618)سم-1. التحليلات من أطياف الأشعة تحت الحمراء من عينات الصخور صعب التفسير بسبب وجود العديد من المكونات. تنشأ النطاقات في هذه المنطقة في أوضاع اهتزازية متفاعلة مما يؤدي إلى نمط امتصاص معقد وعادة، هذه المنطقة معقدة جدا وغالبا ما يصعب تفسيرها. وقد استخدم التحليل الطيفي للانعكاس المنتشر كنموذج للتنبؤ المحتويات لدراسة الخصائص الفيزيائية والبصرية والكهربائية. دالة كوبولا- مونك ، و العوامل اخري كالمعامل الامتصاص، المعامل الانكسار، فجوة النطاق البصري، الموصلية الكهربائية والبصرية والعديد من الخصائص تمت حسابها ونوقشت بالتفصيل على أساس مطياف انعكاس من خلال المعادلات ذات الصلة .عموما، أعطت النتائج قيم مختلفة عينة الكوروندوم ومجموعة السيليكا مع تفضيل عينة الكوروندوم من خصائص مجموعة السيليكا في الخصائص البصرية والكهربائية في معظم النتائج التي تم الحصول عليها. . التحليلات والدراسات لعينات صخرية مختارة لتحديد نوع المعدن من خلال الخصائص الفيزيائية والكيميائية وتمييز المحتويات الأساسية وكذلك الشوائب ، وتعتمد إمكانية تحديد المواد الكيميائية و المكون الأساسي للمعدن ،و البيانات الكيميائية المتاحة مهمة دائمًا لمراقبة سلوك عينات الصخور بشكل عام ، وفقًا لنتائج التحليل والخصائص البصرية والكهربائية ، يمكن أن يعتبر البحث عينات الصخور على أنها أشباه موصلات نظرًا لمحتويات السيليكون التي تم تمثيلها على أنها العمود الفقري لجميع عينات الصخور المدروسة حتى تتم معالجتها واستخراجها بالطرق العلمية التي تستخدم لمعاجة المعادن . الكوروندوم السوداني اقل جودة من الكوروندوم في الدول الاخرى ولكن الكوارتز تقريبا بنفس مواصفات الدول الاخرى بسبب وجود المحتوى SiO_2 اكثر من (98٪).

Chapter One

Introduction

1.1 Background of Minerals

Rocks are generally made of two or more minerals. A main determining factor in the formation of minerals in a rock mass is the chemical composition of the mass, for a certain mineral can be formed only when the necessary elements are present in the rock. Calcite is most common in lime stones, as these consist essentially of calcium carbonate; quartz is common in sandstones and in certain igneous rocks like granite which contain a high percentage of silica. Two rock masses may have very much the same bulk composition and yet consist of entirely different assemblages of minerals.(1) Rocks are classified by their mineral and chemical composition, by the texture of the constituent particles and by the processes that formed them. These indicators separate rocks into igneous, sedimentary and metamorphic. Igneous rocks are formed when molten magma cools and are divided into two main categories: plutonic rock and volcanic. Sedimentary rocks are formed by deposition of either clastic sediments, organic matter, or chemical precipitates (evaporites), followed by compaction of the particulate matter and cementation during diagenesis. Metamorphic rocks are formed by subjecting any rock type (including previously-formed metamorphic rock) to different temperature and pressure conditions than those in which the original rock was formed. Minerals are naturally occurring solid materials mostly formed due to inorganic processes that have varied chemical composition within a specific limited range fixed or uniformly that provides clues to identify a mineral alongside with physical properties and there have been identified round 4000 different minerals, of which only about 50 are commonly used as gemstones.(2)Minerals have similarity in physical properties used a practical method for materials identification technically by specific tools.(3) Mineral identification in gemological circles is critical for determining the commercial value of a specimen. Factors like transparency and color of and inclusions in gemstone have to be taken into account when evaluating the value of a specimen.(4) .A gemstone is precious or semi-precious material that has a special value due to its fundamental quality, beauty durability and rarity highly used to make jewelry and adornments substances after underlined in some processes like polishing.(5).A gemstone can be described as a mineral with attractive visual appearance durable and high luster, making it suitable for jewelry and collecting purposes.(4) Natural gemstones have for long human desire beside its economic value.(6) .Corundum is chemically an aluminum oxide (Al_2O_3) has a hexagonal structure it is a relatively rare found igneous metamorphic and sedimentary mineral that requires unusual geochemical conditions of combined with high aluminum oxide contents of the host rock and deficit silica activity formation occurs deep extremely high pressures and temperatures.(7)Gemstones, especially the quality gemstones are most sought after minerals throughout ages due to their astrological and ornamental importance. The quality of gemstones is determined by its natural origin, beauty, durability, uniqueness, rarity, hardness, color, size, structural defects and chemical resistance.(8) silica is widely distributed mineral consisting of silicon dioxide (SiO_2) or silica when in its purest form.(9) It is one of the most common minerals and is found in many varieties and with very diverse mode of occurrence. The various forms of quartz have attracted attention from earliest times and the water-clear crystals were known to the Greeks as Crystallos “clear ice” being supposed by them to have been formed from water by the intense cold of the Alps; hence the name crystals or more commonly rock crystals applied to this variety.(10) .Quartz occurs as a primary and essential constituent of igneous rocks of acidic composition, such as Granite, quartz, Porphyry and Rhyolite. By the weathering of Silicates, Silica passes into solution and is deposited as quartz in cavities, crevices and long joints of rocks of all types.(11) Silica (SiO_2) and 0-1%impurities such as Fe_2O_3, Na_2O, CaO, MgO, Al_2O_3 and K2O (Vogel’s 1968).There are many fine-grained varieties of quartz; as Chalcedony, Agate ,Carnelian, Carnelian ,Basanite and Jasper . the percentage purity of the variety, mostly quartz contains 99-100%.This research intended to study rock mineral to determine thier origin by using multi specteroscpic techniques and study their same optical and electerical properties as well as investage of physical apperance of rock mineral with practical indentification with come from specteoscopic analyses in addition to compasion between rock from different counteries according to thier contents.

1.2 Problem Statement

Finding distinctive stones unknown and making sure of their nature are precious stones from the knowledge experiences and pictures previous studies looks like they are from gemstones and we want to make sure of that using scientific techniques as well previous data of same rock minerals.

1.3 General objective of The Study

Investigation of optical and electrical properties of rocks samples from Darfurusing spectroscopic techniques.

1.4 specific objectives

- to determine elemental contents using Energy Dispersive X-ray fluorescence(EDXRD) .

-to find crystal structure by using X-ray diffraction (XRD).

-to determine chemical composition and surface images through Energy Dispersive Spectroscopy (EDS) coupled with Scanning electron microscop(SEM).

- to find main fucntional groups by using Fourir Trnsform Infrared Spectroscopy (FTIR)

- Diffese Reflectance Spectroscpy (DRS)for studing elrctrical and optical properties of rocks.

- Laser Brackdown Induced Spectroscopy (LIBS) to finding Rare Earth Elements (REE) .

- To describe and compare different analytical methods used for mineral identification according to the physical appearance and given results with previous studies.

- To investigate the fact of corundum highly exists in environment of deficit silica activity

- To provide necessary information on minerals and increase researchers interest on natural minerals importance for future studies

- Contribution to research and development in natural mineral mining processes.

1.5 Methodology

The stones were searched with visible transportation from several areas. Mining people in Darfur, western Sudan, samples were collected manually using geographical positioning system(GPS), cleaning tools and water systems and after cleaning samples were sorted according to the physical appearance, luminosity, and hardness.

1.5 Organization of the Thesis

The skeleton of this thesis is divided into six chapters beginning with the introduction where the background, objectives of the study, specific objectives of the thesis, and key questions are covered in Chapter 1. The literature review in Chapter 2, focusing on the minerals setting; mineralogy, types, specific indications given through previous studies on minerals, and minerals beneficiation. Chapter three concentrated theoretical background and some physical concept that research may covered and find same values to interpreted. Chapter four provides a detailed description of the techniques and experimental methods used for ore characterization and batch flotation experiments. The results of this study are covered in Chapter five which concerned on discussion of experimental results and outcome analyses and finally the chapter six interested on conclusion and future work ..

Chapter Two

Literatuer review

2.1 Corundum properties and types

Corundum is a mineral commonly composed of aluminum oxide has chemical form (Al2O) a Pure corundum appears white or colorless Pure corundum (a-Al2O3) is a ceramic, physically tough, transparent material but presence of small amounts of trace impurities such as Cr, Ti, Fe, V, Cu, Mg produces color like red, pink, orange and several mixed shade. basically, corundum has two special familiar forms ruby and sapphire the are very hard, tough, and stable mineral. Characteristic features of the Highland complex are aluminous metasedimentary rocks with a chemical composition that allow formation of corundum and other gemminerals (Dissanayake et al., 2000).(4)Corundum (Al2O3) is a relatively rare metamorphic mineral that requires unusual geochemical conditions of low silica activity combined with high aluminum contents of the host rock. Corundum can grow in different rock types and is relatively common in metamorphic rocks formed at various pressure-temperature conditions. fluorescence in corundum is a useful method to confirm a natural origin, since the expected fluorescence colors of corundum are depending on the color in visible light.(4)Trace element analyses of corundum crystal sprovide investigative pathways into their source characteristics and crystallization conditions and are particularly useful indicators for detached gem corundum in secondary deposits.(12) no Fragments of gem-quality corundum were noted including clear blue sapphire, ruby and oriental emerald.(13) no Thosecorundums whose apparent colour is red are referred to as rubies. All other corundums are referred to as sapphires with the appropriate color prefix, viz. Pink sapphire, blue sapphire, yellow sapphire, purple sapphire, etc.(14)

2.1.1 Ruby

Ruby is a pink to blood-red colored gemstone of the mineral corundum the red distinguished color is caused by the existing of the chromium element contents is considered one the most desirable gem due to its hardness, durability, luster, and rarity . The only difference between a ruby and normal corundum is that ruby contains Cr-impurities that give themineral the typical red color. In this case, the Cr^{3+}-ion replaces an Al^{3+}-ion in the crystal structure. Other impurities are also possible, but only stones with the red color are called rubies while stones with other colors are called sapphires. Corundum and all its varieties are classified as oxides in the hematite group.(15)

2.1.2 Sapphire

Sapphire is a speardly used some industrial material for applications such as lasers, catalyst supports, and as substrate layers in photovoltaic devices.1–3. With the presence of iron and titanium chemical impurities, corundum crystals become vibrant blue sapphires. Isolated Fe(III) and Ti(III) incorporation results in yellow/green and pink crystals, respectively, so their chemical interaction is required to produce the blue response .(16) The most well-known type is blue sapphire, with intense colors and high luster.(4) Relatively common white gem corundum is referred to as white sapphire. Rare orange sapphire with a pinkish undertone is known as "padparadsha", meaning "lotus flower". All other sapphires are termed 'fancy' with a prefix to denote the color of the stone. The most desirable color for ruby is dark, purplish-red (pigeon blood red). The most attractive color for sapphire is velvety cornflower blue (Kashmir blue).(17)Natural crystalline aluminum oxide or alumina is named as corundum and its monocrystals are colorless and transparent. If they contain, microcrystals of magnetite (Fe_3O_4) or hematite (Fe_2O_3), they are called emery. If the corundum monocrystals contain some elements in isomorphic substitution for Al3+ in their structure, gemstones are formed, with specific names for their colors:(i) sapphire-blue (Fe, Ti);(ii)ruby-red(Cr);(iii)topaz-yellow(Fe^{2+},Fe^{3+});(iv)emerald-green(Fe^{2+})Chemical fluctuations between consecutive periods of crystal growth, as well as a preferential crystallographic orientation of the color-causing mechanisms of Cr^{3+} (ruby) or $Fe^{2+} \leftrightarrow Ti^{4+}$ (blue sapphire), are responsible for the color zoning observed in the samples.(18) Corundum (Al_2O_3) belongs to the trigonal crystallographic system. (Deer et al., 1992).

2.2 Quartz

Is a mineral occurs essentioally in all mineral enivrontment Quartz is widely distributed mineral consisting of silicon dioxide (SiO_2) or silica when in its purest form .(19)has a chemical composition of silicon dioxide (SiO_2)and it has different forms ,habit and colors. There are many varied of minerals represent quartz as basic constituent part of types of rock minerals like granite. Flalspar is a large group of rock-forming silicate minerals that make up over 50% of Earth's crust. They are found in igneous, metamorphic, and sedimentary rocks in all parts of the world. Feldspar minerals have very similar structures, chemical compositions, and physical properties. Common feldspars include orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$). All minerals in the feldspar group fit the generalized chemical composition below: $X(Al,Si)_4O_8$In this generalized composition, X can be any one of the following seven ions: K^+, Na^+, Ca^{++}, Ba^{++}, $Rb^{+,}$ Sr^{++}, and Fe^{++}. Feldspars that include potassium, sodium and calcium ions are very common. Barium, rubidium, strontium and iron feldspars are very rare.

2.3 Amethyst

Amethyst is a gemstone that has a main phase of SiO_2. Its refractive index is between 1544 -1553, with hardness about 7 mosh. They are available in four main purple colors i.e. lilac, mauve, and black and white. This gemstone is often given a symbol of sincerity, a sense of comfort and peace. Although amethyst is well known gemstone and has been used for centuries, but the scientific identification of amethyst is still not reported. Therefore, for maintaining the commercial value of natural gemstones, it is necessary to identify the gemstone. By identifying gemstones we can differ a hardness level of various amethyst.(20)

2.4 Topaz

Topaz is an aluminum silicate mineral with variable amounts of F and OH groups and its basic composition is $Al_2SiO_4(F,OH)_2$. It has trace impurities that vary from location to location. These impurities can affect color and activation products. The main gem topaz deposits are localized in Brazil and Russia. Other locations include Mexico, U.S.A (Texas and Colorado) Pakistan and Nigeria. Unfortunately, topaz is very rare in Egypt. Pure topaz is colorless or pale yellow. Blue topaz can occur naturally, Topaz has a hardness of 8, a specific gravity of 3.4–3.6, and a vitreous luster. Pure topaz is transparent but is usually tinted by impurities.

2.5 Rare Earth Elements

Rare- Earth Elements(REE) are a group seventeen chemical elements in periodic table, fifteen of them belonging lanthanides (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), promethium (Pm), scandium (Sc), terbium (Tb), thulium (Tm), and ytterbium (Yb) as well as elements(Sc) and (Y).Scandium(Sc)and Yttrium(Y) are considered as rare earth elements (REE)since tend to occur in similar physicochemical properties that exhibit in lanthanides REE have become important for both scientific and technological point of views.(21) Scientifically, Rare Earth Elements make the strongest permanent magnets that can in utilized in many electric motors to produce a high power and torque for specific engines besides of that Electric motors have become an important key component of hybrid modern vehicles as most spread use of REE products. The REEs are widely used in geochemistry due to their distribution in many different types of rocks and minerals in earth curst. mobilization of minerals and rocks needs environmental conditions can be verified to sort out important rare earth in geochemical and petro genetic processes. (22) the applications of REE and their alloys in several technology devices such as magnetic resonance ifpanels, fluorescent materials computer memory, DVDs, mobile phones, LED lighting, glass additives, phosphate binding agents, and. variety of applications.Consumption of REEs has been increasing dramatically through the modern technology items production spread round the global and china is dominated production and consumption .(23)

2.6 Previous studied

2.6.1-characteristics and chemical compounds ruby crystal

Than 450 natural sapphire samples (most of basaltic type) collected from 19 different areas were examined. They are from DakNong, Dak Lak, Quy Chau, two unknown sources from the north (Vietnam); Bo Ploi, KhaoPloiWaen (Thailand); Ban Huay Sai (Laos); Australia; Shandong (China); Andapa, Antsirabe, Nosibe (Madagascar); Ballapana (Sri Lanka); Brazil; Russia; Colombia; Tansania and Malawi.(17) The samples were studied on internal characteristics, chemical compositions, Raman-, luminescence-, Fourier transform infrared (FTIR)-, and ultraviolet-visible-near infrared (UV- Vis-NIR)- spectroscopy. The internal features of these sapphire samples were observed and identified by gemological microscope, con focal micro Raman and FTIR spectroscopy.(24) The major and minor elements of the samples were determined by electron probe microanalysis (EPMA) and the trace elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).(24)Natural sapphires contain many types of mineral inclusions. Typically, they are iron-containing inclusions like goethite, ilmenite, hematite, magnetite or silicate minerals commonly feldspar, and often observed in sapphires from Asia countries, like DakNong, Dak Lak in the south of Vietnam, Ban Huay Sai

(Laos), KhaoPloiWaen and Bo Ploi (Thailand) or Shandong (China). Meanwhile, CO2-diaspore inclusions are normally found in sapphires from Tansania, Colombia, or the north of Vietnam like QuyChau.Iron is the most dominant element in sapphire, up to 1.95 wt.% Fe_2O_3 measured by EPMA and it affects spectral characteristics of sapphire.. Furthermore these sapphires contain many silicate inclusions, typically feldspar. Sapphires from Andapa, Antsirabe and Nosibe in Madagascar show more feldspar inclusions. Zircon inclusions are observed in many areas in single crystals, and especially as clusters in sapphires from Colombia, Tanzania and Malawi. Sapphires from Tanzania, Malawi and northern Vietnam reveal a large number of diaspore inclusions.(25) Chemical analyses show that iron is a dominant trace element in sapphires, up to 1.947 wt.% Fe_2O_3. Sapphires from northern Vietnam show a low iron content, from "bdl" to 0.3 wt.% Fe_2O_3. Sapphires with high Fe_2O_3 content normally show the ratio of Cr_2O_3/Ga_2O_3 lower than 1, as a characteristic relative to basaltic origin, while Quy Chau sapphires show this ratio higher than 1. The iron content in Colombia sapphires is high, 0.4-1.0 wt.% Fe_2O_3but the Cr_2O_3/Ga_2O_3 typically higher than 1. (25)The trapiche like sapphires and unknown sapphires from northern Vietnam show this ratio from 0-2.The iron element influences the spectroscopic characteristics of sapphires. The strongest peak at around 418.3 cm-1 and the peak at around 577.7 cm-1 shift towards smaller wavenumber when the Fe_2O_3content increases. Furthermore, the FWHMs of the 418.3 cm-1 peak decreases when the Fe_2O_3 content increases. Two equations $y(418.3) = 418.29 - 0.53x$ and $y(577.7) = 577.96 - 0.75x$, in which x is the Fe_2O_3content in wt.% and y is the Raman peak position (cm-1) of the according peak can be used to determine the iron content in sapphire or corundum in general, and help to distinguish basaltic from metamorphic sapphires (25)

2.6.2-Characterization of Eluvial Corundum (Ruby) from India

Corundum and ruby occur sporadically in the soil horizons around Kermunda area, which is situated in Kalahandi district of Odisha. The area is constitutes a part of the Precambrian khondalite-charnockite-granite gneiss terrane of Eastern Ghats. Corundum is light pink while ruby is rose red, carmine or purple red in colour.(8) The corundum and ruby grains contain inclusions of rutile and zircon and are often surrounded by dark coloured spinel exhibiting corona texture. Sapphirine occurs as rim around spinel as well as corundum. Veinlets of hematite and diaspore traverse spinel and sapphirine aggregates. SEM-EDS analysis indicated that (i) corundum and ruby grains contains trace amounts of Fe and Cr, (ii) spinel is pleonaste and chromium pleonaste types and (iii) sapphirine is silica- poor and magnesian rich.(26) The corundum-spinel intergrowth showing corona texture suggests that under high P-T gradient in granulite facies metamorphism, corundum reacted with either phlogopite or garnet to form spinel by the reactions: (i) Corundum +Phlogopite= Spinel + K-feldspar + Water or (ii) Corundum+Garnet = Spinel. Sapphirine is possibly a reaction product of (i) Corundum+Spinel+Garnet= Sapphirine or (ii) Spinel+Silica= Sapphirine.(27)

2.6.3-Analysis of minerals in the lavender gemstone

Lavender gemstone is called for one kind of gemstone from Aceh province in Indonesia. This gemstone is well known in Aceh province in Indonesia. Its color is purple and it is so attractive.(28) Nonetheless, minerals contained in this gemstone are still unknown. It is alsounknown whether this gemstone can be classified as a jade or not until this study is presented. For this consideration, X-Ray Fluorescent (XRF) has been utilized to study the lavender gemstone from Aceh province in Indonesia. Our results showed that the lavender gemstonefrom Aceh Indonesia contains 90.80% of SiO_2, 4.69% of NiO, 3.54% of Fe_2O_3, and 0.78% of CaO. It was found that the percentage of oxide compounds contained in the lavender gemstone is significantly different than that in jadeite, nephrite-actinolite, nephrite-tremolite, serpentine clinochrysotile, serpentine-antigorite, and vesuvianite.(28)

2.6.4 Advances in Trace Element "Fingerprinting" of Gem Corundum, Ruby and Sapphire, Mogok Area, Myanmar

Mogok gem corundum samples from twelve localities were analyzed for trace element signatures (LA-ICP-MS method) and oxygen isotope values (δ18O, by laser fluorination). The study augmented earlier findings on Mogok gem suites that suggested the Mogok tract forms a high vanadium gem corundum area and also identified rare alluvial ruby and sapphire grains characterised by unusually high silicon, calcium and gallium, presence of noticeable boron, tin and niobium and very low iron, titanium and magnesium contents. Oxygen isotope values (δ18O) for the ruby and high Si-Ca-Ga corundum (20‰–25‰) and for sapphire (10‰–20‰) indicate typical crustal values, with values >20‰ being typical of carbonate genesis. The high Si-Ca-Ga ruby has high chromium (up to 3.2 wt % Cr) and gallium (up to 0. 08 wt % Ga) compared to most Mogok ruby (<2 wt % Cr; <0.02 wt % Ga). In trace element ratio plots the Si-Ca-Ga-rich corundum falls into separate fields from the typical Mogok metamorphic fields. The high Ga/Mg ratios (46–521) lie well within the magmatic range (>6), and with other features suggest a potential skarn-like, carbonate-related genesis with a high degree of magmatic fluid input The overall trace element results widen the range of different signatures identified within Mogok gem corundum suites and indicate complex genesis. The expanded geochemical platform, related to a variety of metamorphic, metasomatic and magmatic sources, now provides a wider base for geographic typing of Mogok gem corundum suites. It allows more detailed comparisons with suites from other deposits and will assist identification of Mogok gem corundum sources used in jewelry.(29)

2.6.5 Laser Induced Breakdown Spectroscopy application based on Local Thermodynamic Equilibrium assumption for the elemental analysis of alexandrite gemstone and copper-based alloys

Laser Induced Breakdown Spectroscopy (LIBS) is an appealing technique to study laser-induced plasmas (LIPs), both from the basic diagnostics point of view and for analytical applications. LIPs are complex dynamic systems, expanding at supersonic velocities and undergoing a transition between different plasma regimes. If the Local Thermodynamic Equilibrium (LTE) condition is valid for such plasmas, several analytical methods can be employed and fast quantitative analyses can be performed on a variety of samples. In the present paper, a discussion about LTE is carried out and an innovative application to the analysis of the alexandrite gemstone is presented. In addition, a study about the influence of plasma parameters on the performance of LTE-based methods is reported for bronze and brass targets.

2.6.6 Trace Element Analysis for Gemstones using Laser Ablation Inductively Coupled Plasma

The main driving force for trace element analysis of gemstones is the demand from the trade for laboratories to deliver a scientifically based opinion about the geographic origin of gemstones. This demand is essentially caused by the monetary impact such an origin “label” (e.g. Kashmir sapphire), but also by the growing need for traceability of gems due to political (trade bans) or ethical (fair trade) reasons.In this work, we first demonstrate analytical capabilities of trace element analysis using Laser Ablation Inductively Coupled Plasma Time Of Flight Mass Spectrometry (LA-ICP-TOF-MS). We take the benefit of simultaneous multi-element (from 7Li+ to 238U+) detection of the TOF-MS setup, so that users can measure gemstones with little or no knowledge about the matrix. This feature is desired when collecting unexpected/rarely appearing trace elements in gemstones or analyzing unknown inclusions. In addition, high mass resolving power and low limit of detection of nearly all elements in the periodic table allows improved precision and accuracy in elemental quantification. In a case study, we present how trace element analysis of gemstones may provide gemmologists complementary information in origin determination using machine learning (ML) based data visualization. This novel technique is compared with conventional statistical methods, such as principle component analysis (PCA). We illustrate that, by applying machine learning algorithm on multi-element chemical data, a more obvious and clearer separation can be seen among gemstones from different origins than that using PCA. Thus machine learning has great potential to be a highly versatile tool to visualize trace element data of gemstones and assist gemmologists in origin determination.

2.6.7The characterization of natural gemstones using non-invasive FT-IR spectroscopy

Fourteen samples of tourmaline from the Real Museo Mineralogico of Federico II University (Naples) have been characterized through multi-methodological investigations (EMPA-WDS, SEM-EDS, LA-ICP-MS, and FT-IR spectroscopy). The samples show different size, morphology and color, and are often associated with other minerals. Data on major and minor elements allowed to identify and classify tourmalines as follows: elbaites, tsilaisite, schorl, dravites, uvites and rossmanite. Non-invasive, non-destructive FT-IR and in-situ analyses were carried out on the same samples to validate this chemically-based identification and classification. The results of this research show that a complete characterization of this mineral species, usually time-consuming and expensive, can be successfully achieved through non-destructive FT-IR technique, thus representing a reliable tool for a fast classification extremely useful to plan further analytical strategies, as well as to support gemological appraisals.

2.6.8 Spectroscopic Studies of Natural Gem- Agate in Sedimentary and Volcanic host rocks from (Bellesa, Addis zemen and Bure), in Amhara National Regional State (Ethiopia)

The representative samples of gem-agate were collected from Bellesa (North Gondar), addis zemen (South Gondar) and Bure (West Gojam). The samples were identified and characterized by different physical property measuring devices and advanced spectroscopic techniques. In order to verify that the samples were indeed agate a refractometer, heavy liquid method and "MOHS HARDNESS PENCILS" were used. The performed physical analysis shows that the hardness value of Addis zemen and Bure are in the range of 6.5-7 and that of Bellesa is 7 while the refractive index and specific gravity of both agate samples are similar and in the range of 1.53-1.54 and 2.4-2.7 respectively. The XRD and FTIR spectral data of agate samples from three zones of the Amhara National Regional state have a significant contribution in their identification and characterization. The content of different trace elements (Ca, Mg, Fe, Cu, Cd and Mn) was analyzed by FAAS technique. Generally the investigated agate samples by using FT-IR show a broad band around 4000-2500 cm-1, for the O-H stretch of water molecule is around 3440 cm-1 , around 3585 cm-1 structural defect of silanol group and around 1084 cm-1 for Si-O stretch and at low frequency 694 cm-1 indicates the O-H stretch of silanol group. An agate yielded P-XRD pattern is characterized by four broad reflections, the sharp and most intense diffraction peak is pointed at 2θ = 26.65°, medium intense sharp peak at 2θ = 20.00o, 24.00o and 50.14o, broad peak at 20.83o and 68.85o and there is also weaker reflection band occur around 2θ = 55o and 64.00°. The results are in line with the literature data. The XRD pattern for the three samples from three localities (Bellesa, Addis zemen and Bure, Ethiopia) are almost similar and comparable with the results obtained from the previous studies of agate in other countries (Australia, Morocco, India and Turkey).

2.6.9 Classification of minerals on the electrical properties:

Conductors are minerals with high conductivity.,Semiconductors are minerals that have an average (low) conductivity.and Non-conductors (dielectrics) are minerals that don't conduct electricity.

Conductores: Anthracite,argentite,arsenopyrite,bornite,braunite, cassiterite(ferriferous), chalcocite, chalcopyrite,cobaltite,columbite,copper,covellite, chromite, enargite,galena, gold, graphite,hematite, ilmenite, magnetite,manganite,marcasite,molibdenite,pyrite,pyrolusite,pyrrhotite, rutile, silver,smaltite, titanomagnetite, wolframite.

Semiconductors: bauxite, cassiterite,cuprite,limonite, magnesite,siderite, sphalerite, vermiculite.

Non-conductors: Actinolite, albite, almandite, andesite, anglesite, anhydrite, apatite, azurite, barite, beryl,biotite,calcite,celestite,cerussite,chrome,chrisocolla,chlorite,corundum,crocidolite, crocoite, chromite, cryolite,diamond,diaspore,diopside,dolomite,enstatite, epidote, feldspar, fluorite,franklinite,gibbsite, quartz, halite, monazite, muscovite, phlogopite, scheelite, spinel, topaz, tourmaline, wollastonite, wulfenite, xenotime, zircon.(Natlia2016)

Chapter three

Basics of Spectroscopy

3.1 Introduction

The science of spectroscopy grew out of studies of the interaction of electromagnetic energy with matter. When light shines on an object, for example, we know that part of the light is scattered (reflected) and part is absorbed.(30) Spectroscopy is basically an experimental subject and is concerned with the absorption, emission or scattering of electromagnetic radiation by atoms or molecules. Electromagnetic radiation covers a wide wavelength range, from radio waves to g-rays, and the atoms or molecules may be in the gas, liquid or solid phase or, of great importance in surface chemistry, adsorbed on a solid surface.(31)

3.2 The Origins of Spectroscopy

The science known as spectroscopy is a branch of physics that deals with the study of the radiation absorbed, reflected, emitted, or scattered by a substance. Although, strictly speaking, the term 'radiation' only deals with photons (electromagnetic radiation), spectroscopy also involves the interactions of other types of particles, such as neutrons, electrons, and protons, which are used to investigate matter. It is easy to imagine a variety of spectroscopies, as many as the number of possible classifications according to the radiation used and/or the state of the matter (solid, liquid, or gas) interacting with this radiation. The tremendous development of new experimental techniques, as well as the sophistication of those that already exist, is giving rise to the continuous appearance of new spectroscopic techniques. Nevertheless, the different spectroscopies and spectroscopic techniques are rooted in a basic phenomenon: 'the absorption, reflection, emission, or scattering of radiation by matter in a selective range of frequencies and under certain conditions.(32)

3.3 The Electromagnetic Spectrum

Every day, different types of electromagnetic radiation are invading us; from the energy radiation of gamma rays (with frequencies up to 1022 Hz). These types of low-frequency radiation generated by an AC circuit (≈ 50 Hz) to the highest photon radiation are classified according to the electromagnetic spectrum (see Figure 1.1), which spans the above-mentioned wide range of

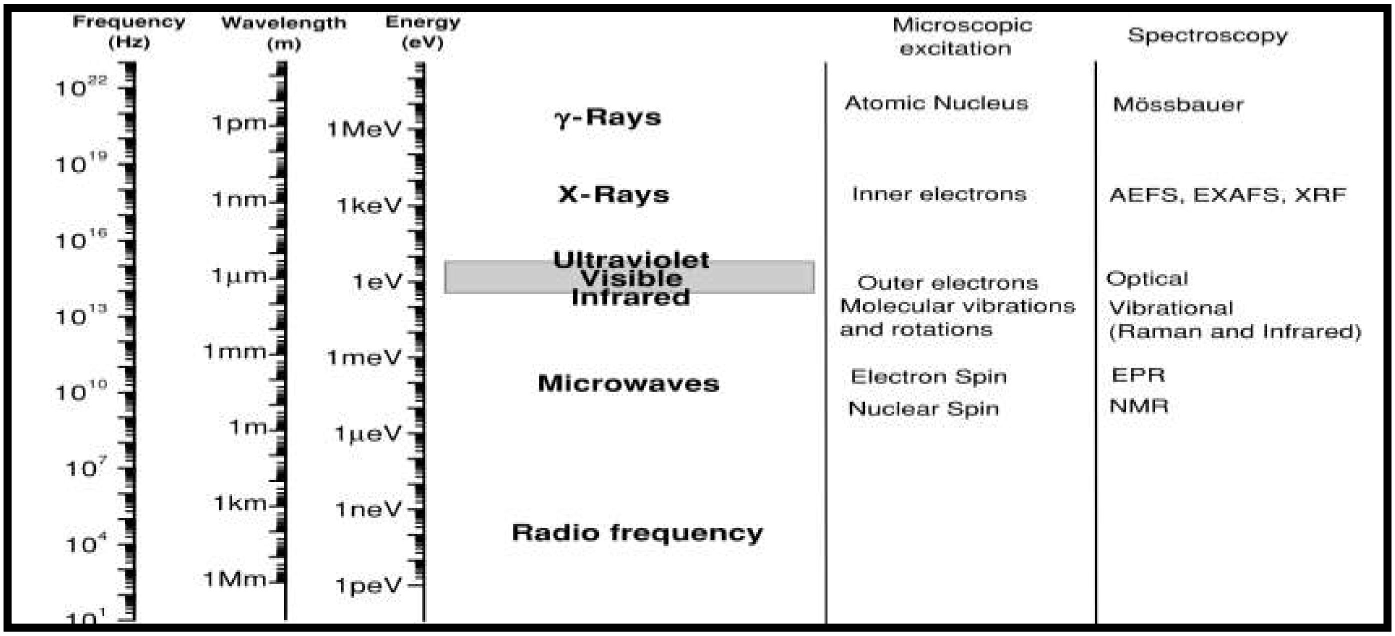


Figure (3.1) **The electromagnetic spectrum, showing the different microscopic excitation sources and the spectroscopies related to the different spectral regions**

frequencies. The electromagnetic spectrum is traditionally divided into seven well-known spectral regions; radio waves, microwaves, infrared, visible and ultraviolet light, X- (or Roentgen) rays, and γ-rays. All of these radiations have in common the fact that they propagate through the space as transverse electromagnetic waves and at the same speed, c ∼= 3 × 108 ms−1, in a vacuum. The various spectral regions of the electromagnetic spectrum differ in wavelength and frequency, which leads to substantial differences in their generation, detection, and interaction with matter. The limits between the different regions are fixed by convention rather than by sharp discontinuities of the physical phenomena involved. Each type of monochromatic elec- electromagnetic radiation is usually labeled by its frequency, ν, wavelength, λ, photon energy, E or wavenumber, ύ. These magnitudes are interrelated by the well-known quantization equation:

$$\mathbf{E = hv = \frac{\mathit{hc}}{\lambda} = hc\acute{\upsilon}} \qquad \textbf{(3.1)}$$

where h = 6.62 × 10−34 J s is Planck's constant. The different spectroscopic techniques operate over limited frequency ranges within the electromagnetic spectrum, depending on the processes that are involved and on the magnitudes of the energy changes associated with these processes.(33)

Figure 3.1 The electromagnetic spectrum, showing the different microscopic excitation sources and the spectroscopies related to the different spectral regions.

3.4 Brief History of the Development of X-ray

Fluorescence and Powder Diffraction Methods X-ray photons are a form of electromagnetic radiation produced following the ejection of an inner orbital electron and subsequent transition of atomic orbital electrons from states of high to low energy. When a monochromatic beam of X-ray photons falls onto a given specimen three basic phenomena may result, namely absorption, scatter or fluorescence. The coherently scattered photons may undergo subsequent interference leading in turn to the generation of diffraction maxima. These three basic phenomena form the bases of three important X-ray methods: the absorption technique, which is the basis of radiographic analysis; the scattering effect, which is then basis of X-ray diffraction; and the fluorescence effect, which is the basis of XRF spectrometry. X-rays were discovered by Wilhelm Roentgen in 1895.1/ and the property of the atomic number dependence of the absorption of X-ray photons was quickly established and applied for medical diagnostic purposes.(33)

3.5 X-ray interaction with matter

An X-ray (composed of photons) has a lot of intrinsic energy and when it passes through matter that comes on its path, it would interact with the matter and either by absorbed by the matter (energy gets transferred to the matter) or be redirected in other directions (scattered). Various substances depending on their inherent properties would absorb or scatter the X-ray photons and on this way produce an image on the X-ray. This process is known as ‘diffraction’. X-rays would interact with matter. There are five mechanism of interaction, namely: coherent (classical) scattering, Compton effect , photoelectric effect, pair production/annihilation and photodisintegration (Lundqvist, 2004). Usually, these five processes play a role in the production of X-rays to varying extents depending on the energy of the incident photons utilized. Crompton effect, coherent scattering and the photoelectric effect play a major role when lower energy levels are utilized (Lundqvist, 2004).

3.6 Emission and Absorption Spectra

As we have already mentioned, emission spectra for a substance occurs when the substance receives energy from an external source, absorbs the energy to raise its atoms to higher energy levels, then emits characteristic energy amounts as the excited atoms return to their previous energy levels.Absorption spectra are produced when white light, for example, is directed onto a particular substance and certain wavelengths in the spectrum of the white light are absorbed via internal energy excitations. This absorption leaves a dark line in the spectrum of the transmitted white light, at a wavelength characteristic of the energy levels in the substance which absorbed that part of the white light.(30)

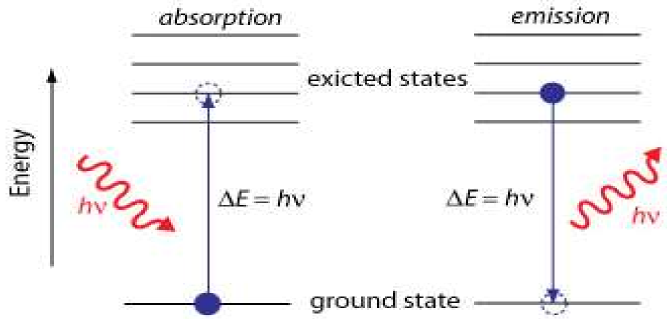


Figure (3.2) Absorption and emission

3.7 Energy Levels and Photons

The interaction of light with matter is best understood by treating light energy as if it were made up of photons more like localized wave packets of energy rather than like the waves described by Thomas Young and Christiaan Huygens. The details of the interaction including the absorption and emission of light involve atoms, energy levels, and photons. Let us review briefly how Niels Bohr’s model of the atom provides us with helpful insights to these interactions. All matter is made up of atoms. Recall that an atom is the smallest unit of matter that retains the characteristics of a chemical element. It consists of a positive nucleus surrounded by negative electrons arranged in distinct energy shells designated by the letters K through O, as shown in Figure The notation K(2) indicates that the K-shell is complete when it has 2 electrons. Similarly, L(8) indicates that the L-shell is complete with 8 electrons and M(18) indicates that the M-shell is complete with 18, and so on. Different chemical elements correspond to atoms with various numbers of electrons in the available shells. For example, hydrogen has one electron in the K-shell, helium has two electrons in the K-shell, lithium has two in the K-shell and one in the L-shell, beryllium has two in the K-shell and two in the L-shell, and so on until all chemical elements are accounted for. The drawing of shells in Figure 1-5 depicts an element with 11 electrons—2 in the K-shell, 8 in the L-shell, and 1 (another electron called a valence electron) in the M-shell. The chemical element with 11 electrons would have to be sodium, a very active chemical element. It is “active” because its lone outer electron can absorb energy easily and combine with other elements that need an electron to fill a shell or a subshell.

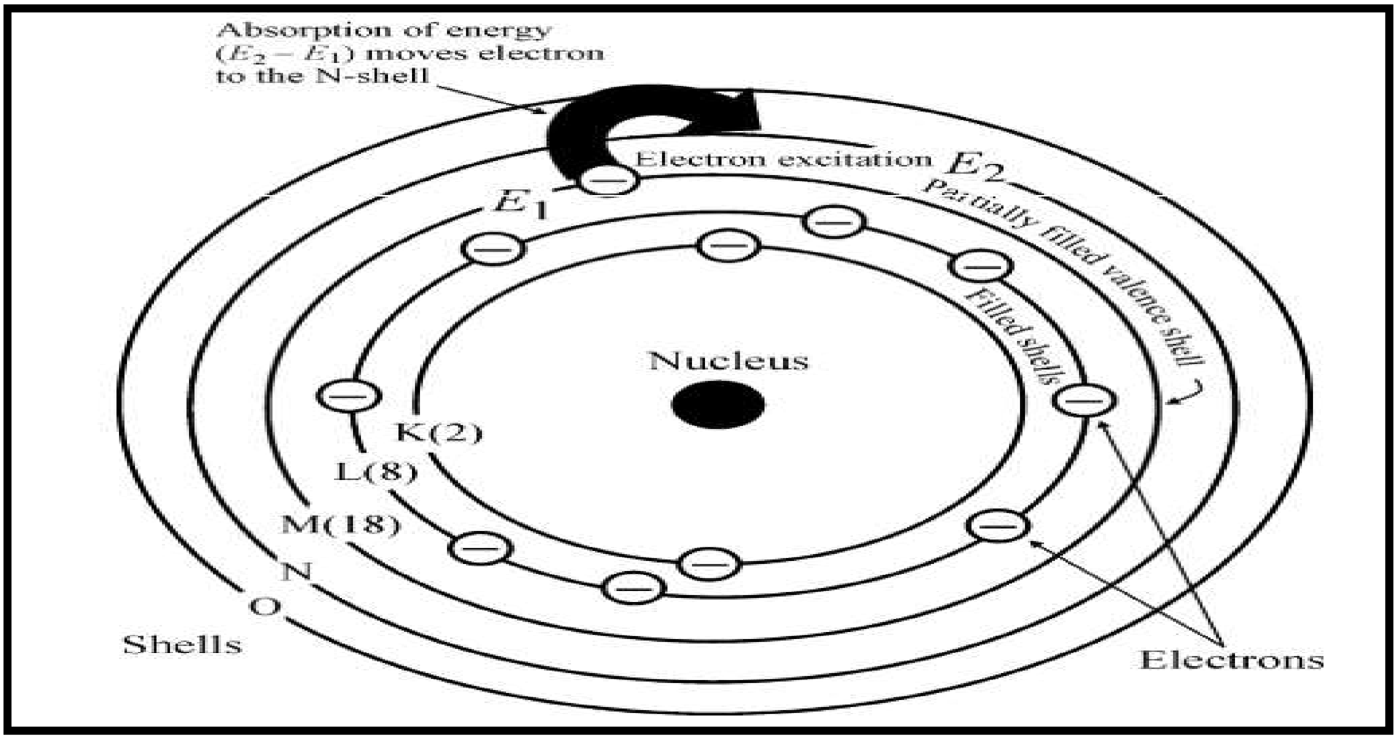


Figure (3.3) atomic model of energy shells

3.8 Fluorescence and Phosphorescence

Special materials are used to coat the interior walls of fluorescent light tubes and the dial faces of watches. These materials, when bombarded by photons of a given energy, cause the materials to glow and emit light in the visible regions. This emission is referred to as fluorescence and phosphorescence, each of which is important in spectroscopy. Materials fluoresce when photons of ultraviolet light first excite the atoms in the material to a higher energy level. Following this initial excitation, the atoms return via smaller energy jumps to their original energy level. The smaller jumps give off photons of lower energy with wavelengths in the visible region of the spectrum. We observe such fluorescence when special paint.(30).

3.9 Electromagnetic Wave Theory

The light propagation is described by two theories, considering the dual nature of light: particles and waves. In general, in tissue optics, both electromagnetic wave and flux of photons descriptions of light appear complementarily.(34) However, at the large wavelength (due to lower impulse and energy) the Maxwell's equations for the electromagnetic waves .The scattering process of electromagnetic waves is based on redistribution of the light with changing electric and magnetic fields, by re-emission of the energy of initial wave by a scattering particle into a solid angle. The brightness of initial and scattered light depends on the amplitudes of the waves. In this thesis we present only few main steps of mathematical description of the wave propagation into a medium(35). The universal Maxwell's equations are basic equations for electromagnetic field inside a continuous medium, expressing four vector functions:E - electric field intensity, B – magnetic induction, H - magnetic field intensity, and D electric induction, and are written as

$$\nabla . \mathbf{D} = \rho, \tag{3.2}$$

$$\nabla \times \mathbf{E} + \frac{\delta \mathbf{B}}{\delta t} = 0, \tag{3.3}$$

$$\nabla . \boldsymbol{B} = 0, \tag{3.4}$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\delta \mathbf{D}}{\delta t}, \tag{3.5}$$

where J is the current density, and ρ the volume charge density. In order to take into consideration the properties of the medium and their influence on electromagnetic waves, Maxwell's equations are completed by the expressions for D and H:

$$\boldsymbol{D} = \boldsymbol{\varepsilon_0 E} + \boldsymbol{P}, \tag{3.6}$$

$$\boldsymbol{H} = \frac{\boldsymbol{B}}{\mu_o} - \boldsymbol{M}, \tag{3.7}$$

where P is the electric polarization field, and M the magnetization field. The two universal constants (permittivity and permeability) of the free space are represented by ε0 and μ0, respectively. The constitutive relations are:

$$\boldsymbol{J} = \boldsymbol{\sigma} \boldsymbol{E}\,, \qquad (3.8)$$

$$\boldsymbol{B} = \boldsymbol{\mu} \boldsymbol{H}\,, \qquad (3.9)$$

$$\boldsymbol{P} = \boldsymbol{\varepsilon_0 \chi} \mathbf{E}\,, \qquad (3.10)$$

where σ is the conductivity, μ the permeability, and χ the electric susceptibility. It was found that a time-harmonic electromagnetic field (E, H) in a linear, isotropic, homogeneous medium must satisfy the following wave equations:

$$\boldsymbol{\nabla^2 E + k^2} \mathbf{E} = \mathbf{0}\,, \qquad (3.11)$$

$$\boldsymbol{\nabla^2 H + k^2} \mathbf{H} = \mathbf{0}\,, \qquad (3.12)$$

Where $k^2 = \omega^2 \varepsilon\mu$, ω is angular frequency ,and $\nabla . E = 0 , \nabla . H = 0$, E and H are interdependent $: \nabla \times E = i\omega\mu H , : \nabla \times H = i\omega\varepsilon E$.

3.10 **Optical properties**

The optical properties of a material define how it interacts with light. The optical properties of matter include many physical phenomena as absorption, refraction, reflection, polarization, diffraction, scattering and transmittance Optical properties are determined to a large extent by atomic structure and the band gap structure of crystalline grains, with optical transparency also being influenced strongly by the density and existing grain boundaries in polycrystalline bodies.

Conductors, semiconductors and insulators material can be distinguished on the ground of their conductivity and other properties. Conductors like metals show conductivity at room temperature, but as the temperature increases, their conductivity gets reduced. However, semiconductors act as the insulators at low temperature but as the temperature increases so their conducting properties also; however, insulators have no such effect of temperature variations as they do not have the conducting properties.

3.11 Electrical properties

The electrical conductivity of a metal (or its reciprocal, electrical resistivity) is determined by the ease of movement of electrons past the atoms under the influence of an electric field. This movement is particularly easy in copper, silver, gold, and aluminum—all of which are well-known conductors of electricity. The conductivity of a given metal is decreased by phenomena that deflect, or scatter, the moving electrons. These can be anything that destroys the local perfection of the atomic arrangement for example, impurity atoms, grain boundaries, or the random oscillation of atoms induced by thermal energy. This last example explains why the conductivity of a metal increases substantially with falling temperature: in a pure metal at room temperature, most resistance to the motion of free electrons comes from the thermal vibration of the atoms; if the temperature is reduced to almost absolute zero, where thermal motion essentially stops, conductivity can increase several thousand fold. Basically, semiconductors and conductors are mainly used in different types of electrical and electronic components. A semiconductor is one kind of material similar to Silicon, and it has some properties of both the insulators as well as conductors. The electric current behavior in the silicon is very poor. However, if we include some soils to Si like boron or phosphorus, then it conducts. But its behavior mainly depends on the added soils. When we add phosphorus soil to silicon, then it becomes an n-type semiconductor. Similarly, when we add Boron to Si, then it becomes a p-type semiconductor. The amount of electrons in a p-type semiconductor is few than a pure semiconductor whereas an n-type semiconductor has more electrons.

3.12 Classification of optical processes

The wide-ranging optical properties observed in solid state materials can be classified into a small number of general phenomena. The simplest group namely reflection, propagation and transmission This shows a light beam incident on an optical medium. Some of the light is reflected from the front surface, while the rest enters the medium and propagates through it. If any of this light reaches the back surface, it can be reflected again, or it can be transmitted through to the other side. The amount of light transmitted is therefore related to the reflectivity at the front and back surfaces and also to the way the light propagates through the medium The phenomena that can occur while light propagates through an optical medium are illustrated schematically in Fig

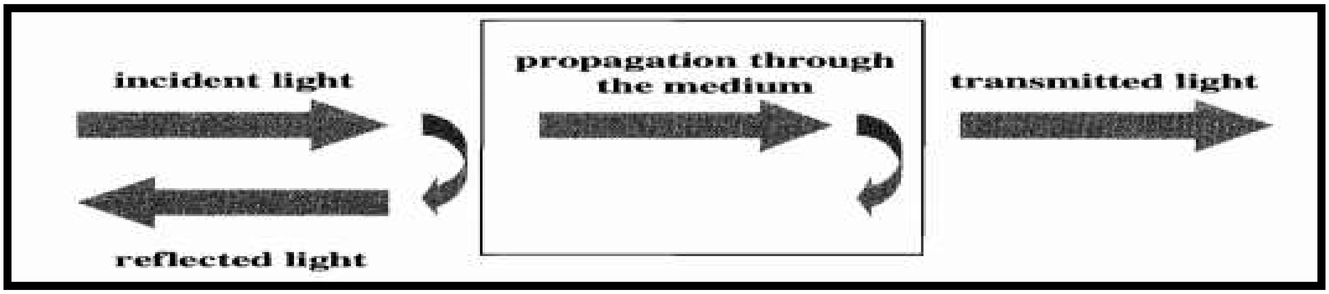


Figure (3.4) Reflection, propagation ,and transmission of a light beam on an optical medium.

Optical coefficients The optical phenomena described in the previous section can be quantified by a number of parameters that determine the properties of the medium at the macroscopic level.

The reflection (R)at the surfaces is described by the coefficient of reflection of the reflected power to the power incident on the surface. The coefficient of transmission or transmissivity (T) is defined likewise as the ratio of the transmitted power to the incident power. If there is no absorption or scattering, then by conservation of energy we must have that:

$$R + T = 1 \qquad (3.13)$$

The propagation of the beam through a transparent medium is described by the refractive index n. This is defined as the ratio of the velocity of light in free space c to the velocity of light in the medium v according to:

$$n = \frac{c}{V} \qquad (3.14)$$

The refractive index depends on the frequency of the light beam. This effect is called dispersion. The absorption of light by an optical medium is quantified by its absorption coefficient α.

This is defined as the fraction of the power absorbed in a unit length of the medium. If the beam is propagating in the z direction, and the intensity (optical power per unit area) at position z is 1(z), then the decrease of the intensity in an incremental slice of thickness dz is given by:

$$dI = -\alpha dz \times l(z). \qquad (3.15)$$

This can be integrated to obtain Beer's law:

$$I\,(z) = I_0 e^{-\propto z} \qquad (3.16)$$

where 10 is the optical intensity at z = O. The absorption coefficient is a strong function of frequency, so that optical materials may absorb one colour but not another.

3.13 The complex refractive index and dielectric constant

In the previous section we mentioned that the absorption and refraction of a medium can be described by a single quantity called the complex refractive index. This is usually given the symbol ň and is defined through the equation:

$$\check{n} = \mathbf{n} = \mathbf{ik} \qquad \mathbf{(3.17)}$$

The real part of ñ, namely n, is the same as the normal refractive index defined in eqn. 1.2. The imaginary part of ñ, namely K, is called the extinction coefficient. As we will sec below, K is directly related to the absorption coefficient α of the medium On comparing this to Beer's law given in eqn 1.4 we conclude that:

$$\boldsymbol{\alpha} = \frac{\mathbf{2}\boldsymbol{k\omega}}{\boldsymbol{c}} = \frac{\mathbf{4}\boldsymbol{\pi k}}{\boldsymbol{\lambda}} \qquad \mathbf{(3.18)}$$

where λ is the free space wavelength of the light and ω angular frequency . This shows us that K is directly proportional to the absorption coefficient. We can relate the refractive index of a medium to its relative dielectric constant $\varepsilon_r$by using the standard result derived from Maxwell's equations

$$\boldsymbol{n} = \sqrt{\boldsymbol{\varepsilon_r}} \qquad \mathbf{(3.19)}$$

This shows us that if n is complex, then Er must also be complex. We therefore define the complex relative dielectric constant Er according to:

$$\overline{\in} = \boldsymbol{\varepsilon_1} + \boldsymbol{\varepsilon_2} \qquad \mathbf{(3.20)}$$

real dielectric constant (ε_1) and imaginary dielectric constant (ε_2)

$$\boldsymbol{\varepsilon_1} = \boldsymbol{n}^{\mathbf{2}} - \boldsymbol{k}^{\mathbf{2}} \qquad \mathbf{(3.21)}$$

$$\boldsymbol{\varepsilon_2} = \mathbf{2}\boldsymbol{nk} \qquad \mathbf{(3.22)}$$

$$n = \frac{1}{\sqrt{2}}\ \left(\varepsilon_1 + \left(\varepsilon_1{}^2 + \varepsilon_2{}^2\right)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad (3.23)$$

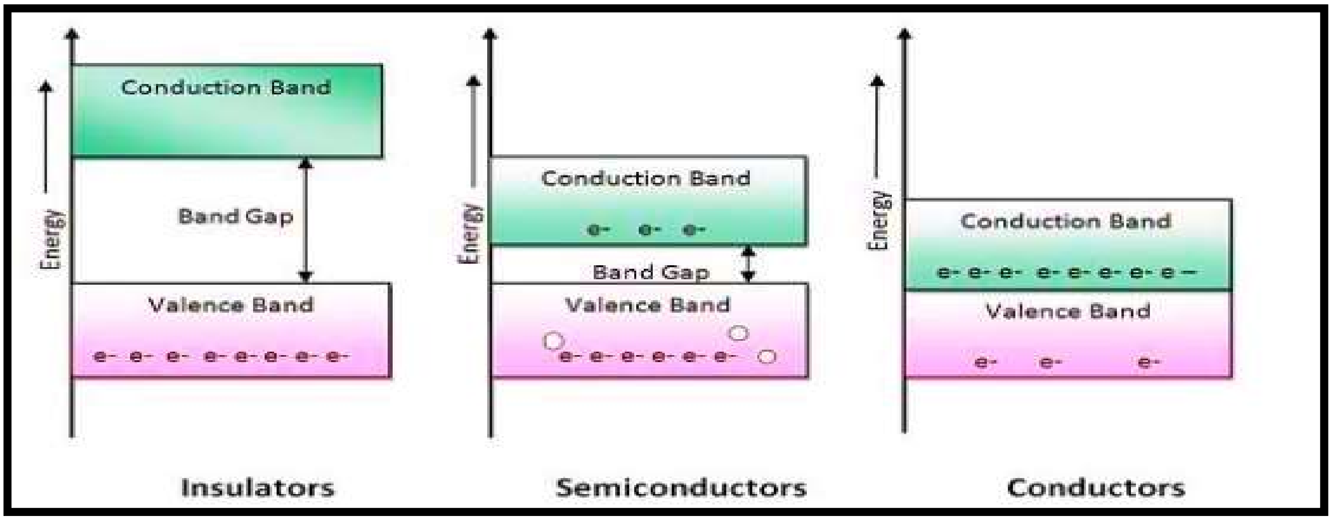
$$\boldsymbol{k} = \frac{\mathbf{1}}{\sqrt{2}}\ \left(\boldsymbol{\varepsilon_1} + \left(-\boldsymbol{\varepsilon_1}^{\mathbf{2}} + \boldsymbol{\varepsilon_2}^{\mathbf{2}}\right)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad \mathbf{(3.24)}$$

Table (3-1) Refractive index of same materials

Material	Refractive index	Material	Refractive index
Quartz(natural SiO2)	**1.45- 2.47**	**Al2O3**	**1.76**
CaCO3	**1.5- 1.7**	**Ca3 (PO4)2**	**1.60 – 1.66**
CaSO4	**1.57**	**TiO2**	**2.6 -2.9**
Formazine	**1.85**	**Bone Ash**	**1.60-1.66**
Amber	**1.55**	**Diamond**	**2.417**
ZnO	**2.00**	**PbO,Pb3O4,PbO2**	**2.3-2.7**

3.14 The Band Gap Energy

electronic band gaps including their importance for the optical absorption and emission properties of materials. .The application of quantum mechanics in solid-state physics has led to physical models which involve a continuum of states which can be occupied by electrons .In case of dielectrics (insulators) and semiconductors, the band gap energy is understood to be the width of the energy gap between conduction and valence band.



Figure(3.5) Calssication of material based of energy gap theory (e- =elections and o = holes)

The major difference between conductor, insulator and semiconductor is defined by the flow of charged particles under the influence of electric field. When any voltage is applied to the conductor, electric charged particles easily flow from valence band to conduction band. Thus conductor is a good conductor of electricity. A semiconductor allows very low charge particles to move from valence band to conduction band. In insulators, there is no flow of charge particles under the influence of electric field hence insulators are the bad conductor of electricity.

Table (3-2)Comparison of Conductors,Semiconductors and Insulators

S.No	Conductors	Semiconductors	Insulators
1	Easily conducts the electrical current.	Conducts the electric current less than conductor and greater than insulator.	Does not conduct any current.
2	Has only one valence electron in its outermost orbit.	Has four valence electron in its outermost orbit.	Has eight valence electron in its outermost orbit.
3	Conductor formed using metallic bonding.	Semiconductors are formed due to covalent bonding.	Insulators are formed due to ionic bonding.
4	Valence and conduction bands are overlapped.	Valence and conduction bands are separated by forbidden energy gap of 1.1eV.	Valence and conduction bands are separated by forbidden energy gap of 6 to 10eV.
5	Resistance is very small	Resistance is high	Resistance is very high
6	It has positive temperature coefficient	It has negative temperature coefficient	It has negative temperature coefficient
7	Ex: copper,aluminium,etc	Ex: silicon, germanium, etc	Ex: Mica, Paper, etc

3.15 - Minerals, Precious Metals and Gems Photos of some rocks

Asbestos

Halite

Quartz

Calcite

pearl

Hematite

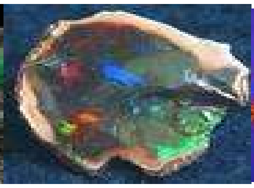
Gold

Amethyst

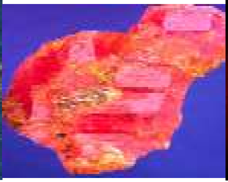
Diamond

Bicolor Beryl

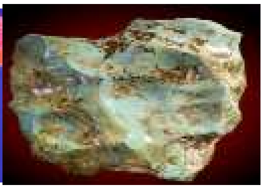
Emerald



Opal



Ruby



Turquoise

Fluorite

Rose Quartz

Spinel

Tourmaline

Garnet

Mosandrite

Garnet (tsavorite)

Sapphire

Green Diamond

Cabochon

Tremolite

Talc

Gypsum

Fluorite

pink and blue feldspar

Mica

Malachite

pyrite

Chalcedony

Citrine

Ametrine

Chapter Four

Materials and Methods

4.1 Samples collection

Rocks samples have been collected from natural minerals from different Darfur (western Sudan) and five representative samples have selected which resembling semi-preicous mineral samples due to their physical appearance which resembles precious metals as in precious stones whose presence is very rare only found in certain countries using geographical positioning system(GPS), cleaning tools and water . To find out the components of these stones and their proportions composition and impurities by the techniques of spectroscopy. Sample preparation methods As mentioned above, the accuracy of the investigation depends not only from a representative sampling but also from an adequate preparation of the sample for the analysis .(36)Taking advantage from previous studies that allowed to discriminate minerals through chemical physical analyzing .Each of the these samples have taken as representatives of different rock specimens due to their appearance resembling gemstone that in previous studies so this study concerns to investigate the reality these minerals contents in order to determine their origin. However, reprehensive samples have given codes to differentiate between them FDY for semi corundum sample and ODS for semi quartz samples as codes for sample A and B represented of studied minerals respectively.Cassification process have taken different methods which used to sort of minerals using perious studies indications ,long term experince of local miners as well as physical testing .

Figure (4.1) Parts of Studied Samples of rock Collected Form Darfur –Sudan

Figure (4.2) Two Representative Samples of Corundum Specimens and Silica Group Selected for Collected Samples of Semi Gemstone Natural Minerals Collected form Darfur –Sudan

4.2-Basic Principle, Working and Instrumentation of Experimental Techniques

In this chapter, a brief description of basic principle, working techniques and experimental set up of instrumentation used for studying structural, optical, electric and properties all these steps after samples preparation in appropriate requested methods for any device through the scientific ways that belong any analyzing technique listed below are show the characterization techniques:

1. Energy Dispersive X-ray Fluorescence (EDXRF)
2. X-ray Diffraction (XRD)

3-Energy Dispersive Spectroscopy (EDS)

4-Scanning Electron Microscopy (SEM)

5. Fourier Transform Infrared Spectroscopy (FTIR)

6-Laser Induced Breakdown Spectroscopy (LIBS)

7-Diffuse Reflectance Spectroscopy (DRS)

4.2.1 Energy Dispersive X-ray Fluorescence (EDXRF)

XRF and EDXRF spectrometers are the elemental analysis tool of choice, for many applications, in that they are smaller, simpler in design and cost less to operate than other technologies like inductively coupled plasma optical emission spectroscopy (ICP-OES) and atomic absorption (AA) or atomic fluorescence (AF) spectroscopy.(37) .XRF instrumentation is conventionally divided into Wavelength Dispersive (WDXRF) and Energy Dispersive (EDXRF) instruments, the distinguishing factor being the technologies used for the energy discrimination and detection of the X-ray photons.(14) WDXRF instrumentation typically has much higher power loading on the sample than EDXRF.(38)

4.2.2 Experimental Set Up of EDXRF and Working Principle :

The speciment is excited with the primary x-ray radiation in the process , electrons from inner shells are knocked out from the orbital ,the removal of an electron (hole)in this way makes electron in structure of the atom unstable ,and electron in higher orbitals fall into the lower orbital to fill the hole left behind .Either electron from the L shell or M shell will fill empty space .Electron falling to lower orbital ,energy released in the form of photon its energy equals energy diference between two orbitals involved .Thus ,the material emits radiation (K_{α},K_{β}),which has energy characteristic of the atom present. Fluorescence Phenomenon of absorbing energy (short λ) and subsequently emitting energy (longer λ) this fluorescence radaition is evaluated by detector ,and preamplifier next amplifier to manification analog signal then furture step lead to converter from analog to digital which generate spectrum using muti-chanal display elemenal peaks .fig shows work of EDXRF analyses process.

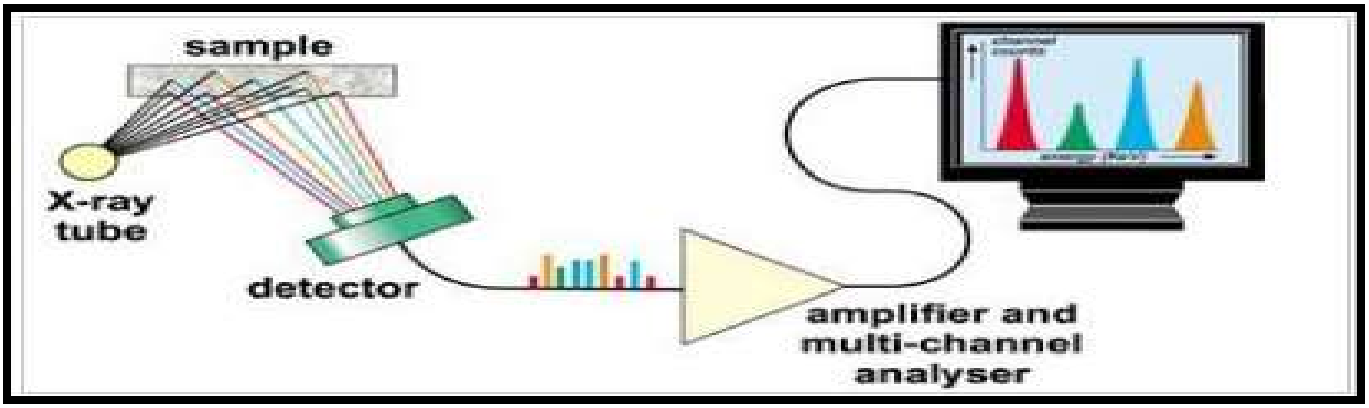


Figure (4-3) displays mechanism work of EDXRF Technique

4.2.3 X-ray Diffraction (XRD)

X-ray diffraction patterns, phase characterization and the estimation of crystalline sizes of materials identification fundamentally used to provide dimensions on unit cell information.

X –ray diffractometer has three main basic components a cathode ray tube - a sample holder – detector .When x-ray is bombarded on a material sample creates diffraction patterns the intensity of the diffracted X-rays is measured as a function of diffraction angle 2θ and orientation of the specimen through a constructive interference that satisfies Brag equation. The location of diffraction peaks is given by Bragg's law.(37).

$$2d \sin\theta = n\lambda \qquad \textbf{(3-1)}$$

Where n is diffraction series, θ is a diffraction angle, λ is the wavelength of X-ray, and d is an interplanar distance .figure displays XRD path principle of Brag's low .

X-ray diffraction patterns, phase characterization and the estimation of crystalline sizes of

synthesized powder samples were acquired by using Smart lab X-ray diffractometer (Rigaku) from the University of South Africa (UNISA). The XRD is a rapid non-destructive analytical technique primarily used for the identification of crystalline materials which is primarily used to provide information on unit cell dimensions.(39)

4.2.4 XRD Working Process

Typically, an X-ray diffractometer is comprised of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. A diffraction pattern is produced when a crystalline material is bombarded with a collimated beam of X-rays generated by a cathode ray tube. As the sample and detector are rotated, the intensity of the diffracted X-rays is measured as a function of diffraction angle 2θ and the specimen's orientation. A constructive interference occurs when the geometry of the incident X-rays bombarding the sample satisfies the Bragg equation.(40) XRD analyses determine grain size ,composition of solid , lattice constant and degree of crystallinity . fig displays XRD process work .XRD data, the results can be matched with existing join committee on powder diffraction standard (JCPDS) files so you find the crystal system of the material you have used for the experiment later JCPDS has changed into internatial center of diffraction data (ICDD)

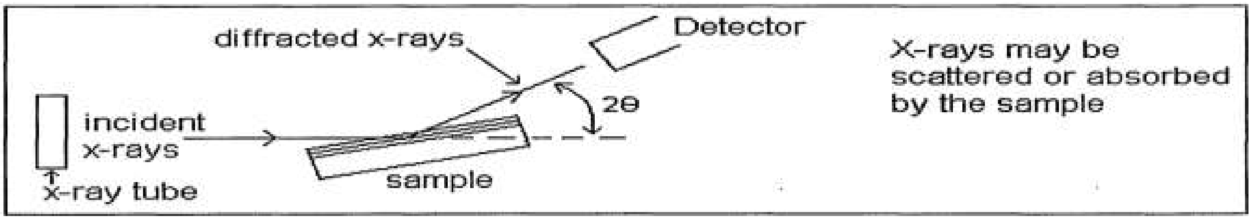


Figure (4-4) displays mechanism work of XRD Technique

4.2.5 Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy: analysis with a scanning electron microscope (SEM): ED's systems include a sensitive x-ray detector, liquid nitrogen for cooling, and software to collect and analyze energy spectra. study was to evaluate the potential of scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) for determination of mineral phases according to their stoichiometry and assessment of mineral composition.EDS /SEM analyzing of FDY sample in four division scans for more accuracy and better analyzing results.

4.2.6 EDS Work Mechanism:

EDS system Consists of four basics components: beam source, x-ray detector, pulse processor and analyzer Elemental composition or chemical characterization through interaction between electromagnetism radiation and matter its fundamental principle that each element has a unique atomic structure to allowing x-rays that are characteristic of an element's atomic structure to identified unique from each anther. To stimulate the emission of characteristic x-ray from specimen a high energy beam of charged particles such as electrons or a beam of x-ray is focused with the samples being studied .The EDS X-ray detector measures the relative abundance of emitted X-rays versus their energy The charge pulse is converted to a voltage pulse by a charge-sensitive preamplifier. The energy, as determined from the voltage measurement, for each incident X-ray is sent to a computer for display and further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample volume.EDS sysem mosly empolyed conjication with electron microscope (SEM)which measure charatrisicstic energies to dertermine composition.

4.2.7-Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a technique whereby highly focused beam of high-energy electrons interacts with a sample to produce various signals that contain information about topography, morphology and crystallography of the sample. Mostly data is collected over a selected area of the surface of the sample, and a 2-D image that displays spatial variations in these properties is generated

4.2.8 EDS and SEM Mechanism Work

The system can also provide qualitative chemical analysis if it is equipped with a dispersive X-ray spectrometer (EDS) [22]. In a typical SEM system, a beam of accelerated electrons with significant amounts of kinetic energy strikes the surface of the sample and generates a splash of electrons with kinetic energies much lower than primary incident electrons called secondary electrons (that produce SEM images). To create a SEM image, the secondary electron intensity is measured as a function of the primary beam position.[40] High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 – 30 kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sampleThe advantages of SEM (in contrast to traditional microscopes) include features such as higher magnification (> 100, 000X) and greater depth of field up to 100 times than that of traditional microscope [23]. In this study, SEM images of the specimen were obtained from the JEOL JSM-7500F field-emission scanning microscope (FE-SEM) equipped with energy dispersive X-ray spectrometer (EDX) from the CSIR-NCNSM.

4.2.9 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Analysis by infrared spectroscopy is based on the fact that molecules have specific frequencies of internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum: ~ 4000 cm-1 to ~ 200 cm-1.(41) When a sample is placed in a beam of infrared radiation; the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies. The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is called infrared spectrum of the material.(42) Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra. Furthermore, from the frequencies of the absorption it is possible to determine whether various chemical groups are present or absent in a chemical structure.(43) In addition to the characteristic nature of the absorption, the magnitude of the absorption due to a given species is related to the

concentration of that species. Fourier Transform Infrared (FTIR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process.(44) A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer.
Fourier transform infrared (FT-IR) spectroscopy is the study of interactions between matter and photons in the infrared region. In this region, electromagnetic waves usually excite molecules into the higher vibrational state .

4.2.10 The basic principle of FT-IR Testing Process

FTIR process can be summarized by the following steps, see Figure 3.6. Testing Process

- Step 1: Place sample in FTIR spectrometer. The spectrometer directs beams of IR at the sample and measures how much of the beam and at which frequencies the sample absorbs the infrared light. The sample needs to be thin enough for the infrared light to transmit through, or a thin slice of the material must be removed. Reflectance techniques can be used on some samples and no damage is done to the sample. Samples conducive to reflectance are residues, stains or films on a fairly flat reflective surface or somewhat pliable materials that are thin enough to fit under the microscope using the attenuated total reflectance attachment to the microscope.

- Step 2: The reference database houses thousands of spectra, so samples can be identified. The molecular identities can be determined through this process.(45)

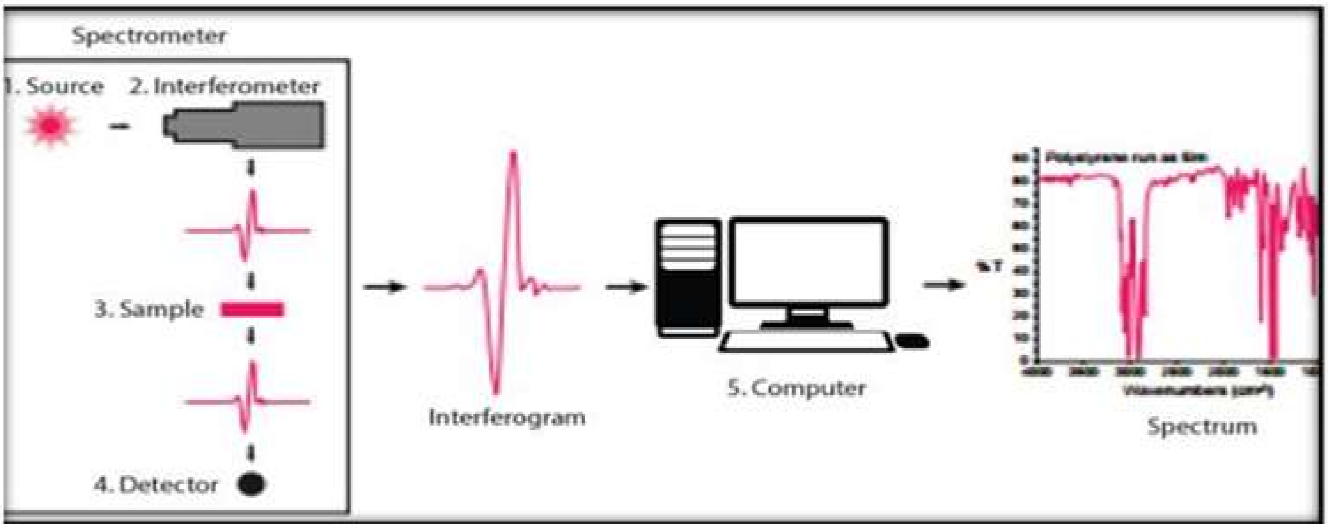


Figure (4-5) Schematic of a typical FTIR process analysis technique

4.2.11- Experimental Set-up of LIBS Processes

Laser- induced breakdown spectroscopy (LIBS) or laser induced plasma Spectroscopy (LIPS) is an emission spectroscopic technique using a laser generated plasma to ablate and excite the atoms in the sample, usually in solid form, although liquid samples can also be analyzed (Radziemski and Cremer's, 2013; Balaram, 2017). (46)Fundamentally, LIBS is performed by using a laser pulse to ablate a small amount of material from a sample surface. Nowadays, LIBS has developed rapidly as an analytical technique and considered as an attractive and effective technique when a fast and whole chemical analysis at the atomic level is required. The laser pulse heats the ablated material, fragmenting the sample molecules into individual atoms and ions and forming a plasma. certain operating environments or scenarios could be indicative of explosive material. Further technical information on the LIBS technique is available in several texts in different studies Figure 1 illustrated the experimental Set-up of LIBS analyzing means used were including a laser source(Nd: YAG), mirror, digital generator(DG535), focusing optics(lens), collection optics (optical fiber), DG535,adetectorand USB2000 spectrometer (reflective from 250-2200 nm).

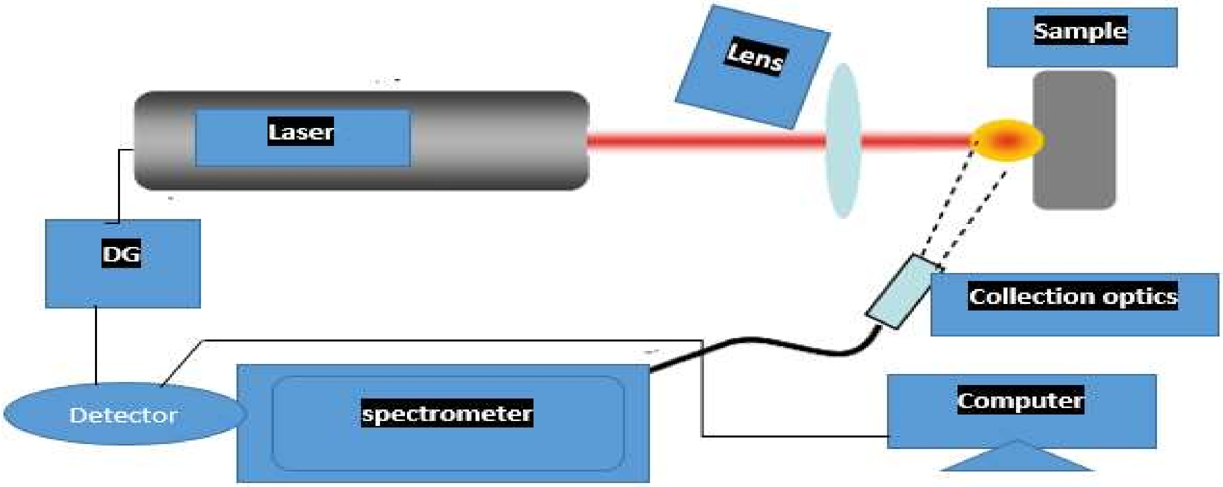


Figure (4-6). Schematic diagram of LIBS apparatus set-up

spectroscopic analysis technique of LIBS that uses of the light emitted from a laser-generated micro-plasma to determine the composition of a sample based on elemental and molecular emission intensities. (47)LIBS involves the vaporization of a small volume of sample material with sufficient energy for optical excitation of the elemental species in the resultant sample plume .The ability of LIBS to provide rapid ,multi-element microanalysis of bulk and residue samples (solid, liquid, gas, and aerosol) in the parts-per-million range with little or no sample preparation has been widely demonstrated and is the greatest advantage of LIBS compared with other analytical approaches.(48) Evaluation of analytical feasibility for detecting and identifying the sample should be decided by analyzing the LIBS spectra of specific components as well as matrix derived from the source of the samples.

4.2.12- Diffuse Reflectance Spectroscopy (DRS)

Difference reflectance is excellent sampling tool for powdered and crystalline material in the mid-IR and NIR spectral ranges difference reflectance relies upon the projected of the spectrometer beam into sample where it is reflected ,scattered and transmitted through the sample material figure shows two types of reflection specular reflection and diffuse reflection .(49) The specular reflectance component in difference reflectance spectra causes changes in band shapes their relative intensity and some cases for complete inversions difference reflectance can be also used to study the effects of temperature and catalysis by configuring the accessory with a heating chamber .The factors related to high spectral quality for difference reflectance like particle sizes ,refractive index ,homogeneity and packing these factors can effect quality of difference reflectance as reducing the size of the sample particles reduces the contribution of reflection from the surface sampling similarly lack of homogeneity will be difficult to quantify and less reproductively also the required sample is controlled by the amount of sample scattering the minimum necessary depth is about 1.5mm. When light strikes a large flat surface, like that of a crystal, most of it is reflected secularly, like a mirror. In contrast, when light strikes an uneven surface or a collection of randomly oriented small particles, it is reflected back at all angles, a phenomenon called diffuse reflectance.(50) Figure 1-16.

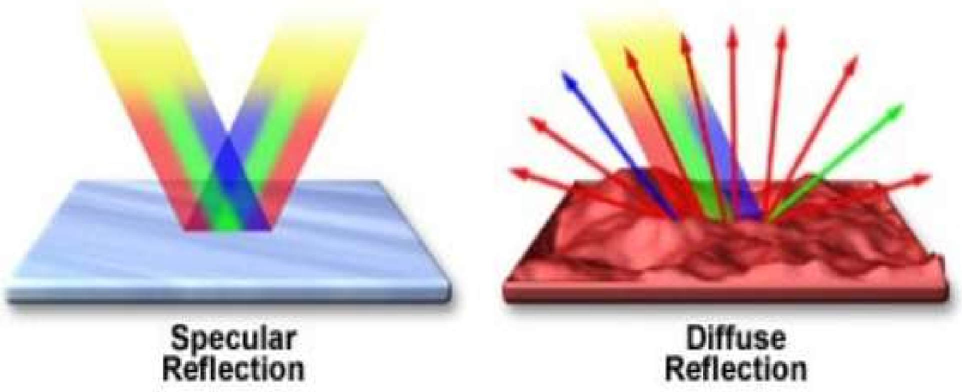


Figure 4-7. Difference in reflectance of light from smooth and rough surfaces.

Using of difference reflectance spectroscopy in various regions of electromagnetic spectrum involves different possibilities ,trade –off and experimental considerations in many different sample –handling techniques available to molecular spectroscopist including diffuse reflectance ,external reflectance ,internal reflectance and photoacoustic spectroscopy .

4.2.13 Defuse Reflectance Process Setup and Working:

diffuse reflectance work machinisim that consists of power source ,light , spectrometer , reflectance probe , sample and analyzing tool used to achieve process on an simple being studied

Diffuse reflectance relies upon the focused projection of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material The back reflected, diffusely scattered light (some of which is absorbed by the sample) is then collected by the accessory and directed to the detector optics figure (3.8) displays the mechanism of diffuse reflectance work that consists of power source ,light , spectrometer , reflectance probe , sample and analyzing tool .

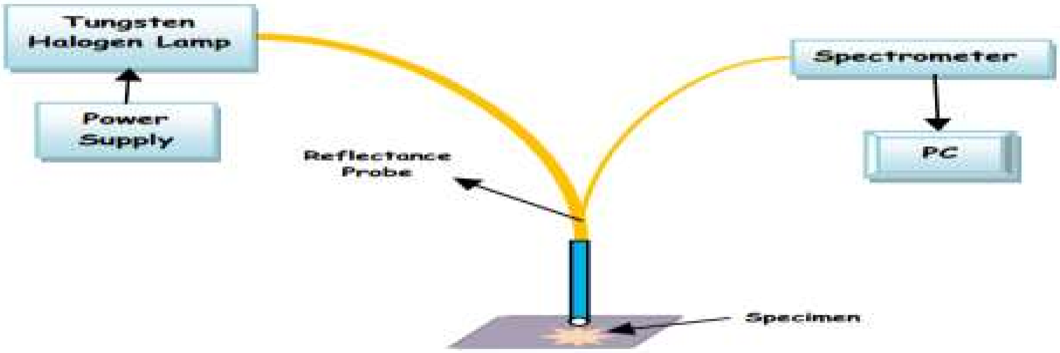


Figure (3-8): Schematic displays diffuse reflectance mechanism work set up

Chapter Five

Results and Discussion

5.1 Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) outcome:

EDXRF spectra of natural minerals exhibit strong X-ray peaks of aluminum and oxygen basic Al_2O_3(79.02%) composition besides some metal oxides in these details of FDY(semi corundum sample) $A1_2O_3$(79.02%)SiO_2(10.28%),SO_3(4.96%),Fe_2O_3(2.27%),TiO_2(1.08%),andCaO(1.06%) while in ODS(semi quartz sample) silicon and oxygen were detected in high peaks ,showed that the chemical composition SiO_2 (94.23%), has a great majority this indicated that silicon contents as basic in this samples as well as other contents in details besides of SiO_2 (94.23%), Al_2O_3(1.96%) ,SO_3(0.66%), Fe_2O_3 (2.10%), TiO_2 (0.03%)and CaO(0.59%).In order to determine whether these minerals can be categorized as gemstone or not , we need to compare the mineral contains in the sample .it's Clearly both samples have similar contains but their percentages were different $A1_2O_3$(79.02%),SiO_2(10.28%) and $A1_2O_3$(1.96%), SiO_2(94.23%) of two sample respectively, the majority dominant content which can be determine the rock type as well as both samples have nearly same percentage Fe_2O_3.The total difference between oxide compositions contained in the FDY sample is 166.4% with average 27.73% . Along with that there were a small fraction of same metal oxide such as K_2O, MnO and Cr_2O_3 in both samples. Furthermore, there have been shown some oxides including Ca_2O and MnO sample ODS did not appeared in other sample this can be clear difference between two samples in this contents. Minor, major and trace elements both have high level of specific elements like Al, Si, S, Fe, Ca and Ti at percentages (70.91, 12.33, 5.33, 5.22, 2.77and 1,96 %) respectively of sample majority elements but sample ODS Has 1.77% for Al, 89.78 % of Si ,0.63% of S, 5.35 of Fe and 1.38% of Ca. these analyses showed that the similarity in of Fe element percent. The total difference between oxide compositions contained in the ODS sample was 154.68% with average 14.06%. Table (4.1) gives details of composition percepts of the samples corundum and quartz obtained from EDXRF analyses (I) shows Comparison of oxide compound compositions of samples and (II)- Shows Major and Minor Elements with Spectral Analysis Data of the Study Samples from EDXRF results. Through the study, mineral samples with the EDXRF spectrometer showed the presence of a number of trace elements with a majority, such as silicon, aluminum, and iron and minority elements such as chromium, copper and manganese. Each sample was studied through three batches of the spectrum and the results revealed that the sample one represents aluminum with a majority of 94% and an average of 15.45 in all samples. As for the other samples, silicon is represented as the main component by 98.47 high -96.81 low, and average of 75.48% of all samples, while the sixth sample showed silicon with a compound base of less than 50%, and aluminum with an average of 13.96%. Sample six represents the properties of the sample one and The other five samples are in terms of basic components. Silicon and aluminum are represented as elements with a maximum amount of SiO2 and Al2O3, and trace elements with smaller quantities such as Ca, Ti, Mn, Fe, Cu, Pd, Cr, Na, and Mg with ratios of 2.25,0.19. 0.23,3.83,0.11,0.95,0.08,0.08, and 0.53 respectively represented by oxides such as CaO, TiO2, and Fe2O3 . Table (5.2) gives detail of EDXRF spectrum of seven rock samples majority contents and average of three batches of spectrum.

Table (5.1). Rock compositions and their differences in oxides, major and minor Elements from XRF results of two main representative samples

(I) -Comparison oxide compound compositions in the samples EDXRF results

Sample%\composition	**Al2O3**	**SiO2**	**SO3**	**CaO**	**Fe2O3**	**TiO2**	**Total difference**	**Average**
Corundum	**79.02675**	**10.88964**	**4.964388**	**1.064896**	**2.272726**	**1.089837**	**166.4**	**27.734**
Quartz	**1.96264**	**94.23852**	**0.66831**	**0.59283**	**2.10446**	**0.033531**		
Difference	**77.06435**	**83.34888**	**4.296078**	**0.472066**	**0.168266**	**1.056306**		

(II)- Major and Minor Elements with Spectral analysis data of the study- EDXRF results

Sample%\Element	**Al**	**Si**	**S**	**Cl**	**K**	**Ca**	**Ti**	**Cr**	**Mn**	**Fe**	**Zr**	**Total difference**	**Average**
Corundum	**70.91**	**12.60**	**5.33**	**0.33**	**0.53**	**2.17**	**1.96**	**0.29**	**0.06**	**5.22**	**0.11**	**154.68**	**14.06**
Quartz	**1.77**	**89.78**	**0.63**	**0.04**	**0.03**	**1.38**	**0.07**	**0.07**	**0.29**	**5.35**	**0.00**		
Difference	**69.14**	**77.18**	**4.7**	**0.29**	**0.5**	**0.79**	**1.89**	**0.22**	**0.23**	**0.13**	**0.11**		

Table (5-2) Rock majority contents of three EDXRF spectrum of each sample and their mean value of seven samples

Spectrum	Al	Si	Ca	Ti	Mn	Fe	Cu	Pd	Cr	Na	Mg
1 003	**94.19**	**2.28**	**0.22**	**0.19**	**0.02**	**1.02**	**0.01**	**1.06**	**0.42**	**0.00**	**0.00**
1 002	**91.98**	**3.42**	**0.71**	**0.26**	**0.00**	**1.12**	**0.00**	**1.19**	**0.45**	**0.00**	**0.00**
1 001	**94.03**	**2.07**	**0.29**	**0.17**	**0.00**	**1.01**	**0.01**	**1.00**	**0.51**	**0.00**	**0.00**
2 003	**0.10**	**97.45**	**0.07**	**0.00**	**0.00**	**0.74**	**0.00**	**1.10**	**0.14**	**0.00**	**0.00**
2 002	**0.10**	**98.47**	**0.00**	**0.00**	**0.01**	**0.15**	**0.00**	**0.78**	**0.02**	**0.00**	**0.00**
2 001	**0.09**	**97.77**	**0.02**	**0.13**	**0.00**	**0.43**	**0.00**	**1.10**	**0.00**	**0.14**	**0.00**
3 003	**0.14**	**97.93**	**0.01**	**0.01**	**0.02**	**0.27**	**0.00**	**1.01**	**0.00**	**0.00**	**0.00**
3 002	**0.12**	**98.20**	**0.00**	**0.00**	**0.19**	**0.10**	**0.01**	**0.76**	**0.00**	**0.00**	**0.00**
3 001	**0.13**	**97.97**	**0.02**	**0.04**	**0.08**	**0.42**	**0.00**	**0.93**	**0.00**	**0.00**	**0.00**
4 003	**0.18**	**98.10**	**0.07**	**0.02**	**0.06**	**0.17**	**0.00**	**1.01**	**0.02**	**0.00**	**0.00**
4 002	**0.11**	**97.42**	**0.04**	**0.00**	**0.05**	**0.20**	**0.01**	**1.48**	**0.03**	**0.28**	**0.00**
4 001	**0.19**	**98.19**	**0.00**	**0.41**	**0.00**	**0.07**	**0.00**	**0.73**	**0.00**	**0.00**	**0.00**
5 003	**0.09**	**97.82**	**0.01**	**0.01**	**0.39**	**0.12**	**0.02**	**1.11**	**0.04**	**0.00**	**0.00**
5 002	**0.16**	**96.81**	**0.10**	**0.00**	**0.12**	**0.94**	**0.00**	**1.11**	**0.00**	**0.42**	**0.00**
5 001	**0.16**	**97.12**	**0.03**	**0.02**	**0.17**	**0.41**	**0.00**	**1.18**	**0.00**	**0.55**	**0.00**
6 003	**12.59**	**33.77**	**17.98**	**0.99**	**1.42**	**27.39**	**0.80**	**0.81**	**0.02**	**0.00**	**3.45**
6 002	**13.96**	**41.07**	**16.97**	**0.86**	**1.07**	**20.30**	**0.79**	**0.54**	**0.01**	**0.00**	**3.91**
6 001	**14.07**	**39.25**	**16.77**	**0.82**	**1.05**	**22.27**	**0.65**	**0.70**	**0.01**	**0.00**	**3.79**
7 003	**0.11**	**97.96**	**0.00**	**0.00**	**0.00**	**0.68**	**0.00**	**0.77**	**0.00**	**0.00**	**0.00**
7 002	**1.77**	**94.53**	**0.36**	**0.05**	**0.04**	**1.96**	**0.00**	**0.65**	**0.07**	**0.13**	**0.00**
7 001	**0.16**	**97.48**	**0.05**	**0.00**	**0.18**	**0.65**	**0.00**	**0.99**	**0.00**	**0.06**	**0.00**
Mean value:	**15.45**	**75.48**	**2.56**	**0.19**	**0.23**	**3.83**	**0.11**	**0.95**	**0.08**	**0.08**	**0.53**

5.2 X-ray Diffraction (XRD) Results Analysis:

XRD with Cu-KĮ radiation (Bruker D4 Endeavor). The detector position is recorded as the angle 2theta (2θ). XRD was performed to detect and identify the phases in the powders to investigate and characterize the structure of the prepared samples (powders). XRD analysis detected aluminum oxides Al2O3 and Silica SiO_2 as predominant mineralogical phases can be seen in figure (2) the pattern indicated in corundum Al_2O_3 (93.2%) which has hexagonal structure trigonal crystal system and cell parameters[a = 4.75 Å, c = 12.982 Å; Z = 6], Quartz high SiO_2(2.8%) also named beta quartz which has cell parameters[a = 4.9133 Å, c = 5.4053 Å; Z=3] these two have high peaks beside of minor fraction of Rutile has chemical formula TiO_2 (0.7%) ,Muscovite2M which has sophisticated chemical formula of $KAl_2(Si_3Al)O_{10}(OH,F)_2$ (2.1%),Dolomite which has chemical formula of $CaMg(CO_3)$ and ,Biotite is phyllosilicate belongs to the mica group has very complicated of many existence of different element chemical formula of $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$(0.4%) the figure (2) showing XDS pattern of corundum sample indicated that the corundum (Al2O3) as main content the crystal , but quartz sample was showed a high majority of silicon which is a mineral composed of silicon and oxygen has chemical formula SiO_2(97.2%) and unit cell parameters [a = 4.9133 Å, c = 5.4053 Å; Z=3] with contrast of corundum sample here corundum is disappeared but shown fractions of some trace elements compound represented by some metal oxide and others such as Rutile TiO2(1.0%) , muscovite $KAl_2(Si_3Al)O_{10}(OH,F)_2$(1.6%)$CaCO_3$ (0.2%) .Figure

(3) displays XRD Patten of quartz sample indicated that obviously quartz as the principal component the crystal. Samples three, four ,five and seven were showed a very strong peaks quartz ,in addition to the presence of other weak peaks for the mineral compounds, but comparison of quartz peak strength can be considered small quantities and the rock type is classified as quartz according to the readings of the X-ray diffraction spectroscopy. Sample six has showed many of mineral compounds that include Albite($NaAlSi_3O_8$), Anorthite($CaAl_2Si_2O_8$), -Orthopyroxene $XY(Si,Al)_2O_6$,Feldspars ($KAlSi_3O_8 – NaAlSi_3O_8 – CaAl_2Si_2O_8$)and Quartz (SiO2) the most of mentioned minreals belong to the fledspar category ,therefore this rock type is considered to be fledspar , represents calcium, sodium, iron (II) or magnesium and more rarely zinc, manganese or lithium, and Y represents ions of smaller size, such as chromium, aluminium, iron (III), magnesium, cobalt, manganese, scandium, titanium, vanadium or even iron (II). Although aluminium substitutes extensively for silicon in silicates such as feldspars and amphiboles, the substitution occurs only to a limited extent in most pyroxenes.

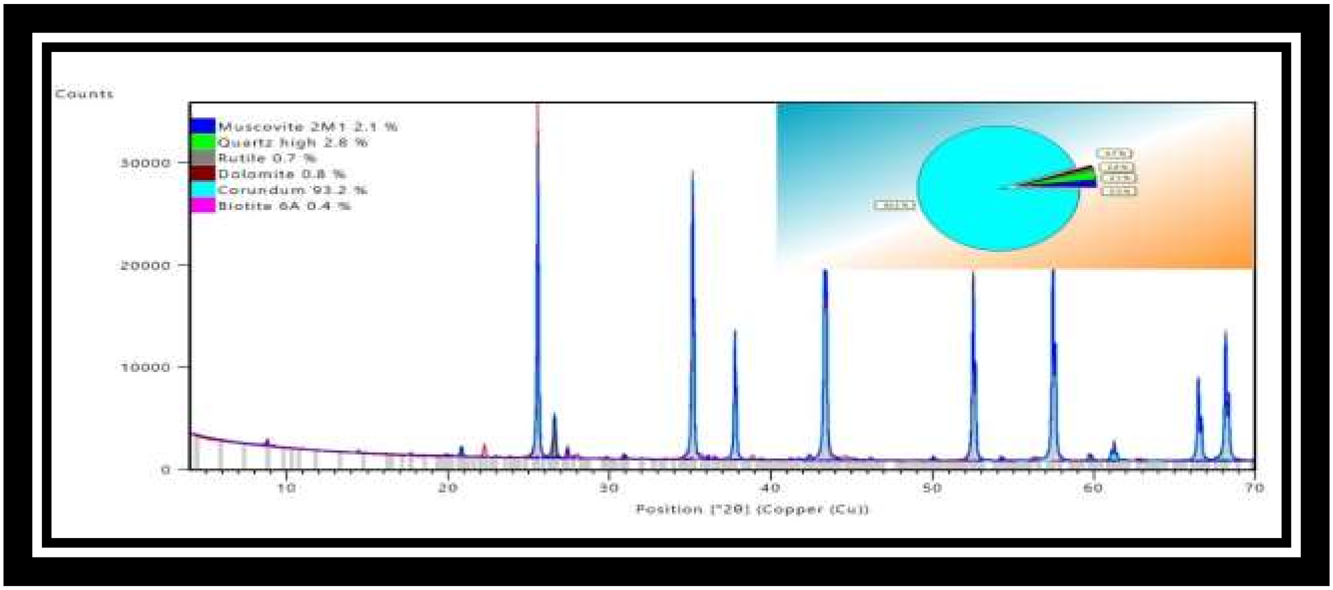


Figure (5-1). XRD Pattern from sample one of rock mineral

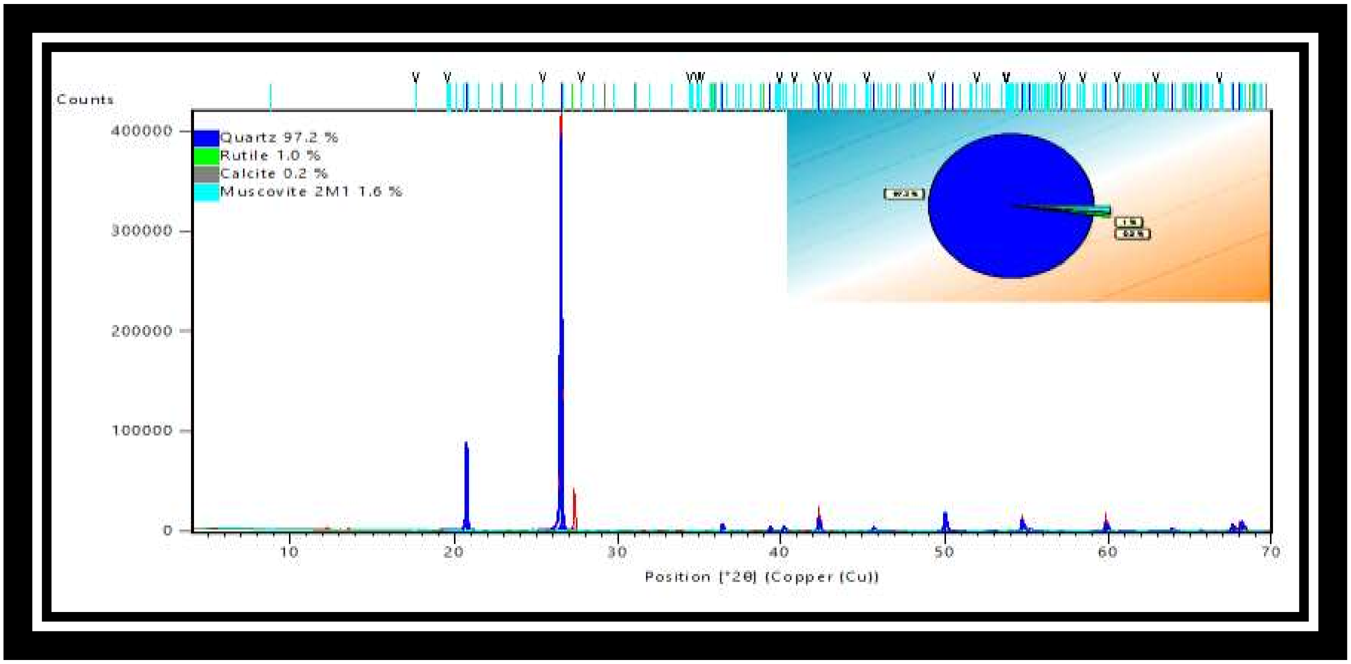


Figure (5-2) XRD Pattern from sample two of rock mineral

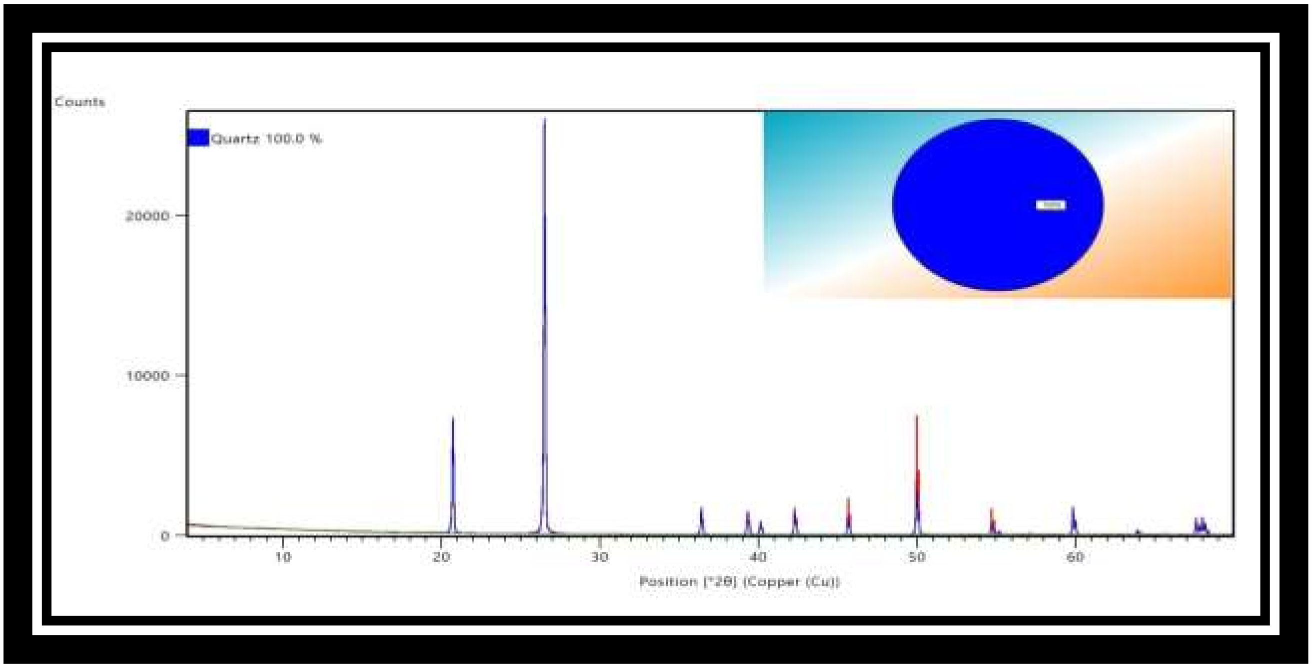


Figure (5-2) XRD Pattern from sample three of rock mineral

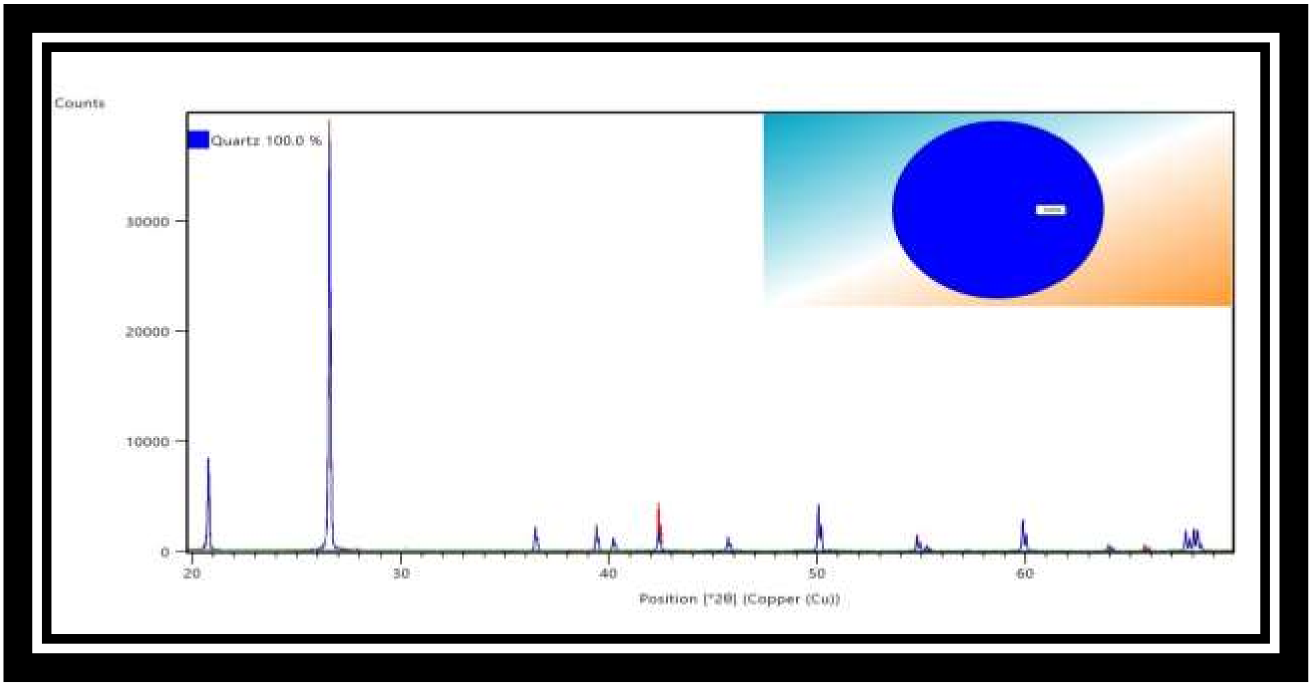


Figure (5-4) XRD Pattern from sample four of rock mineral

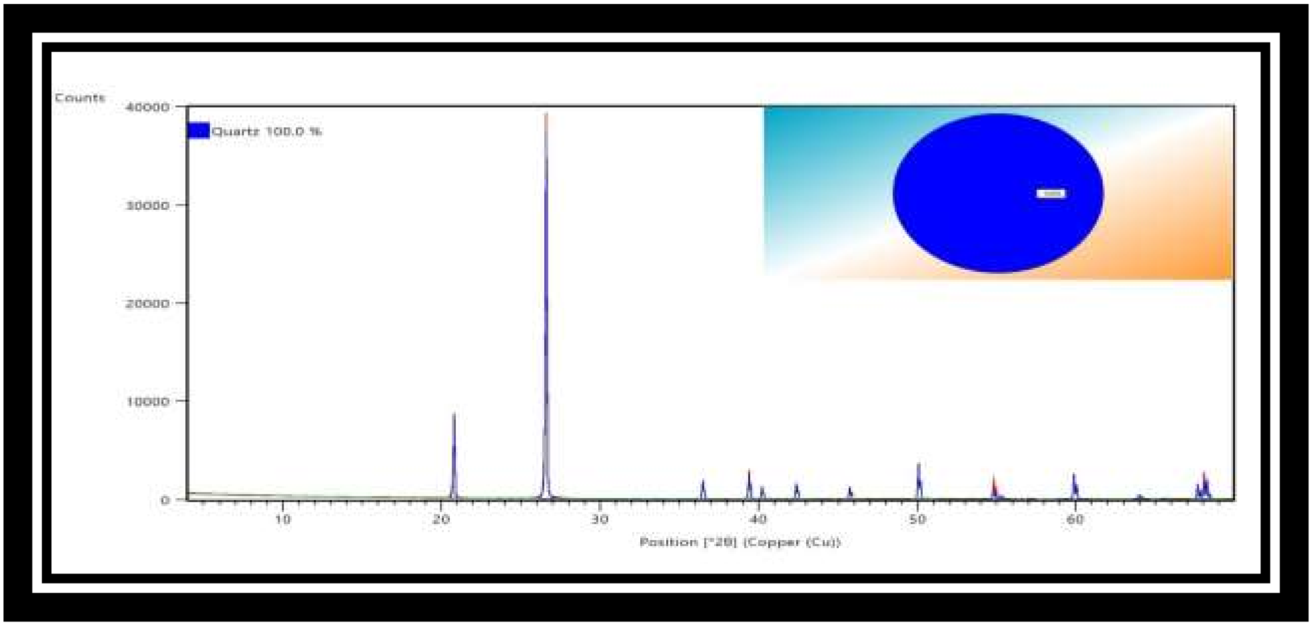


Figure (5-5) XRD Pattern from sample five of rock mineral

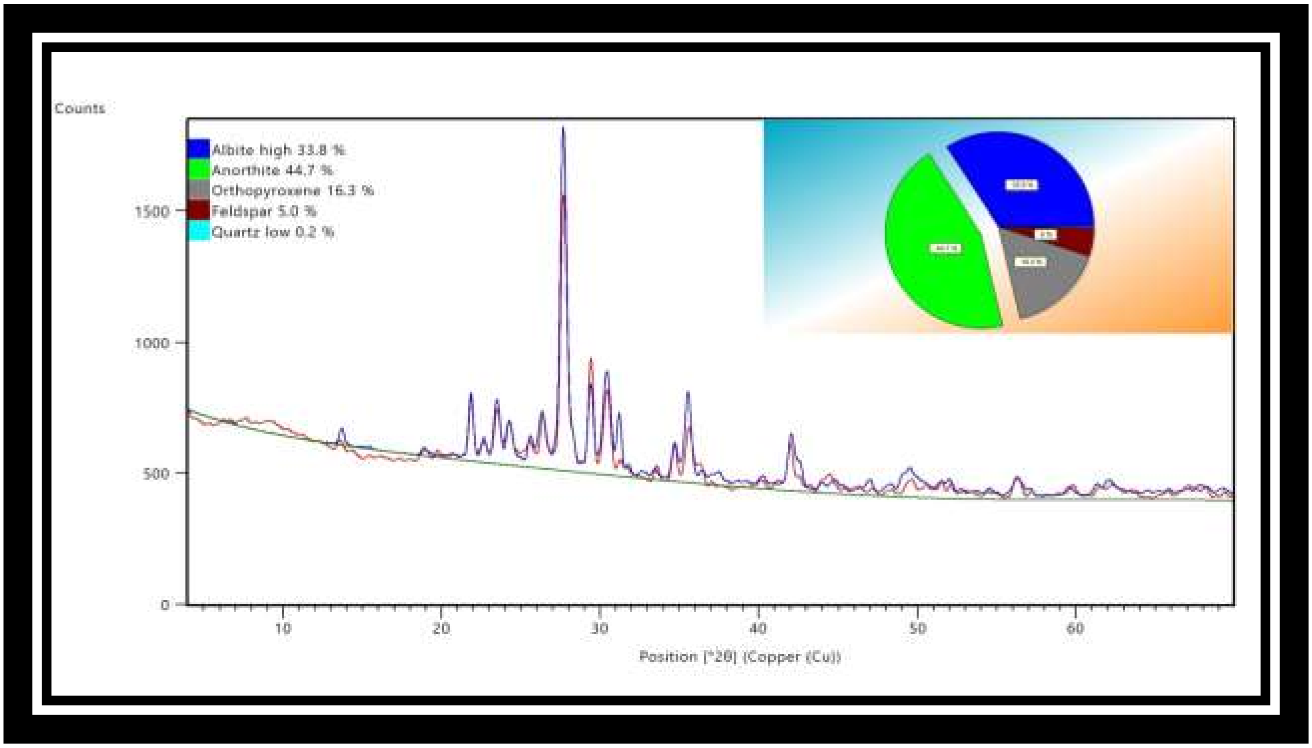


Figure (5-6) XRD Pattern from sample six of rock mineral

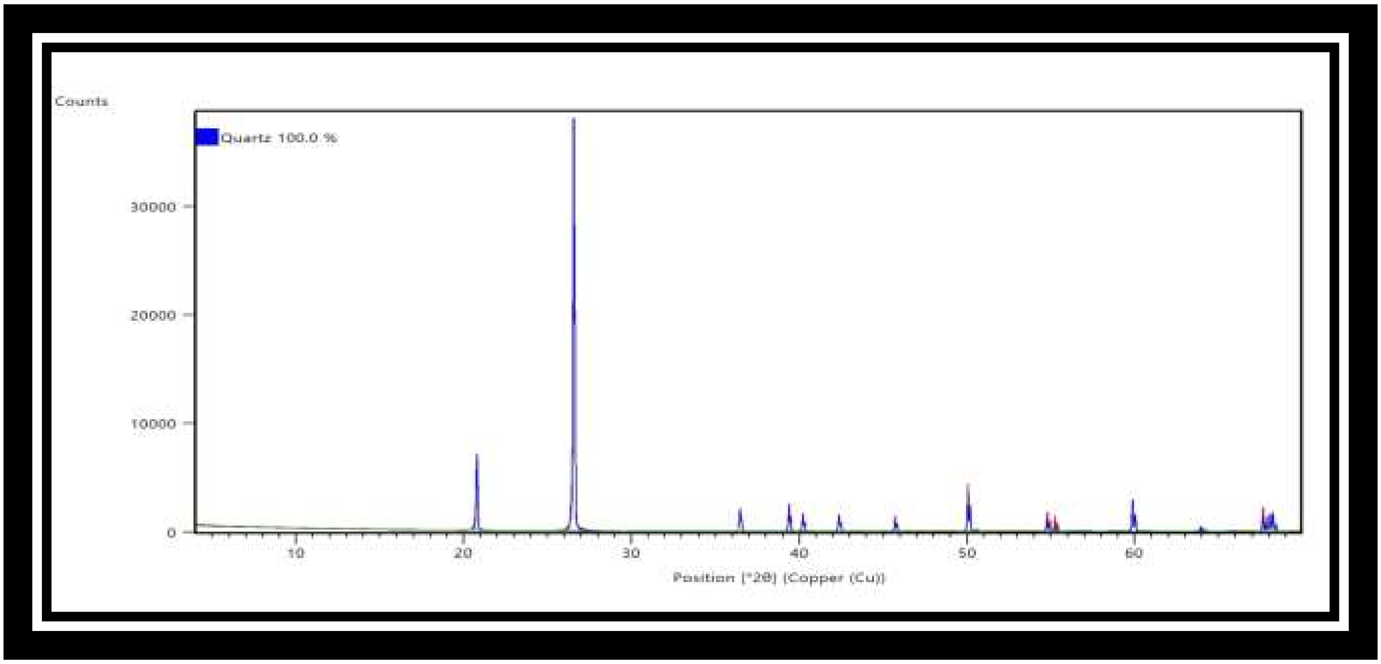


Figure (5-7). XRD Pattern of Natural Corundum Specimen Represented Sample

4.3 Energy Dispersive Spectroscopy (EDS) coupled with scanning electron microscope (SEM) analyses :

In order to confirm the information of the rocks samples on EDS analysis was performed during the EDX measurements at different surface areas of the sample were focused and corresponding peaks are shown in EDS elemental peaks with SEM image of selective spectrum element distribution. The elements which through the EDS /SEM conjugated process and each element has an appropriate standard label that indicated of element's composition in a rack-type all elements determined were(O, Al, Si, K, Ca, Fe, Mg, Au) with the standard label (SiO_2, Al_2O_3, KBr, $CaSiO_3$, Fe, MgO, Au) respectively.

In the sample, one scan showed the distribution of element(O, Al, Si, K,Ca and Fe) their appearance concentration which represents atomic percent (17.98 , 8.19 , 7.46 , 0.62 ,7.16 and 2.99) and their weight percent wt% (52.81 , 15.66 ,15.65, 1.01, 11.88, and 2.99)Subsequently.

All detected elements in K line series and the results showed the majority in the rock of sample one was represented into three standard labels were Aluminum oxide Al_2O_3 , silicon dioxide SiO_2 and Wollastonite ($CaSiO_3$) and the minority was represented by some trace elements as Potassium(K), Calcium (Ca) and Iron (Fe) in the whole compound this rock sample was SiO2 standard label with a 65.57 wt % of the total.

Samples two the scanned area exhibited the distribution of ((O ,Al, Si, K, Ca ,Fe) with their appearance concentration of (17.98 , 7.46 ,o.62 ,7.16 , 1.58) as well as their wt % (52.81,15.66,15.65,1.01,11.88,2.99)respectively .In this rock is predominated by SiO_2 standard labeled composition at 68.48 wt.% .

Sample three the scan displayed the peaks of Oxygen, Aluminum, and silicon with their atomic percent of 17.85 ,0.73 and 26.60 as well as their wt.% of 44.14 ,1.42 and 49.44 subsequently. according to the scanning results, this rock sample is dominated by SiO_2 standard labeled composition at 98.58 wt.% and nearly similar to the XRD result indication.

In sample four the spectrum of the elements of the selected area was (O ,Mg, Al, Si K, Au) with their atomic percent(46.03,0.43,14.78,18.7,0.56,9.19)in their specific proportion weight percent 47.52,0.50,15.40,21.90,0.61,14.08) respectively in this rock sample the results showed the Au as the single element without conjugating with other elements to make a chemical composition, however, the whole rock contents great majority is represented by silicon dioxide standard label.

Sample five sacaned area indicated distribution of (O, Mg ,Al, Si, K, Ca ,Fe ,Au) peaks in weight percent (wt.%)(46.68, 0.56, 13.89, 22.25, 0.65, 0.69, 1.04, 14.22) as well as their atomic percent of (38.15, 0.45,11.40,16.62,0.52, 0.56,0.78,8.07) respectively. According to the wt.% in this rocks analysis about 69 wt.% was silicon dioxide standard label compounds.

In sample six the taken spectrum indicated the presence of oxygen, aluminum, silicon and gold element peaks and their appropriate wt.% were 28.60, 0.79 ,46.08, and 24.88 as well as their appearance concentrations were 15.26, 0.68, 36.82 and 11.33 respectively. The great majority in this rock sample is SiO_2 contents.

Samples seven results showed about 81% of rock contents of SiO_2 and exhibits (O, Al, Si, Au) peaks in weight percent (wt.%) (36.60, 0.94, 44.33, 18.12) as well as their appearance concentration of (34.14 ,0.79 ,38.67 ,9.15) respectively. The spectrum of scanned of SEM image areas was 50 micrometers to 1mm, the accelerated maximum voltage was 20Kev and the spot size was 36 mm. Table (5.2) displays EDS results of the rocks and Fig [5.8-5.14] show EDS/SEM result in details of spectrum areas 50 μm- 1mm. The rocks samples SEM images show many layers , rough and porous surfaces .

Table (5.3) gives detail of EDS results

Sample one	Apparent Concentration	Wt%	Standard Label	Sample Five	Apparent Concentration	Wt%	Standard Label
Element/Line				Element/Line			
C K series	0.00	0.00	C Vit	O K series	38.15	46.68	SiO2
O K series	9.77	49.80	SiO_2	Mg K series	0.42	0.56	MgO
Al K series	6.23	20.12	Al2O3	Al K series	11.40	13.89	Al2O3
Si K series	4.87	18.74	SiO2	Si K series	16.62	22.25	SiO2
K K series	3.68	11.33	KBr	K K series	0.52	0.65	KBr
Total:		100.00		Ca K series	0.56	0.69	Wollastonite
Sample two	Apparent Concentration	Wt%	Standard Label	Fe K series	0.78	1.04	Fe
Element/Line				Au M seies	8.07	14.22	Au
O K series	17.98	52.81	C Vit	Total:		100.00	
Si K series	7.46	15.65	SiO2	Sample Six		Wt%	Standard Label

Al	**8.19**	**15.66**	**Al2O3**		**Apparent Concentration**		
K K series	**0.62**	**1.01**	**KBr**	**Element/Line**			
Ca K series	**7.16**	**11.88**	**Wollastonite**	**O K series**	**15.29**	**28.25**	**SiO2**
Fe K series	**1.58**	**2.99**	**Fe**	**Al K series**	**0.60**	**0.79**	**Al2O3**
Total:		**100.00**		**Si K series**	**36.82**	**46.08**	**SiO2**
Sample thee	**Apparent Concentration**	**Wt%**	**Standard Label**	**Au M series**	**11.33**	**24.88**	**Au**
Element/Line				**Total:**		**100.00**	
O K series	**17.85**	**49.14**	**SiO2**	**Sample Seven**	**Apparent Concentration**	**Wt%**	**Standard Label**
Al K series	**0.73**	**1.42**	**Al2O3**	**Element/line**			
Si K series	**26.66**	**49.44**	**SiO2**	**O K series**	**24.14**	**36.60**	**SiO2**
Total:		**100.00**		**Al K series**	**0.79**	**0.94**	**Al2O3**
Sample Four	**Apparent Concentration**	**Wt%**	**Standard Label**	**Si K series**	**38.67**	**44.33**	**SiO2**
Element/Line				**Au M series**	**9.15**	**18.12**	**Au**
O K series	**46.03**	**47.52**	**SiO2**	**Total:**		**100.00**	
Mg K series	**0.43**	**0.50**	**MgO**				
Al K series	**14.78**	**15.40**	**Al2O3**				
Si K series	**18.70**	**21.90**	**SiO2**				
K K series	**0.56**	**0.61**	**KBr**				
Au K series	**9.19**	**14.08**	**Au**				
Total:		100.00					

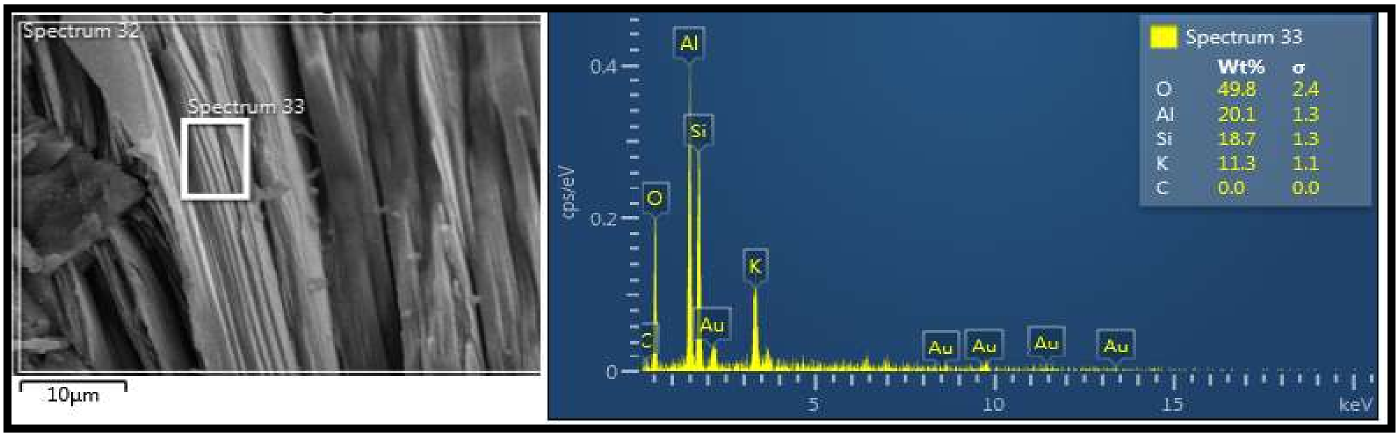


Fig (5.8)shows EDS\SEM samples one of rock samples 10micromerter spectrum scan area

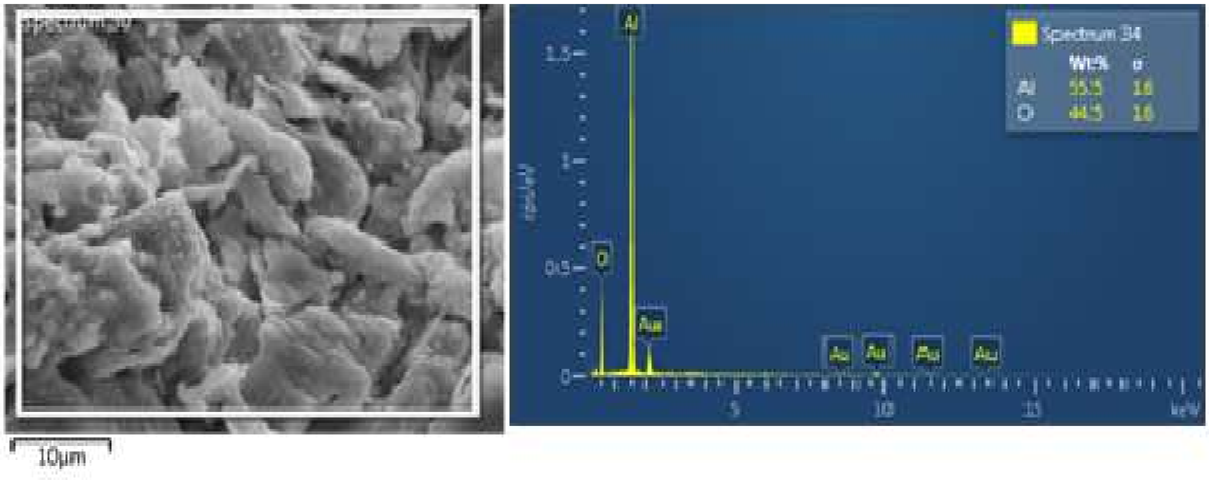


Fig (5.9) shows EDS\SEM samples two of rock samples

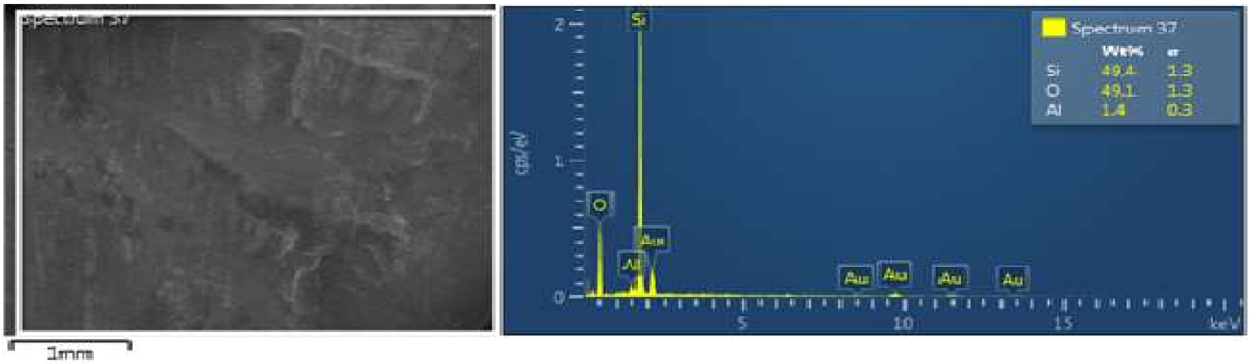


Fig (5.10)shows EDS\SEM samples three of rock samples

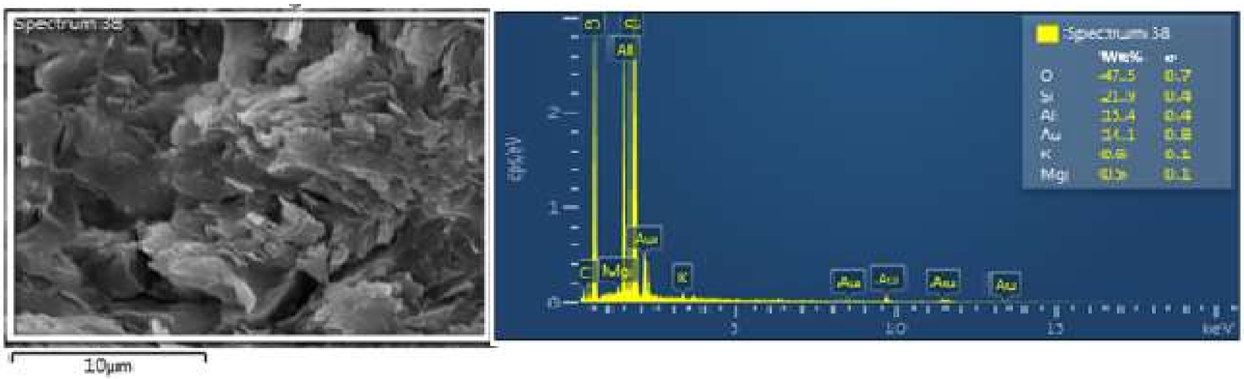
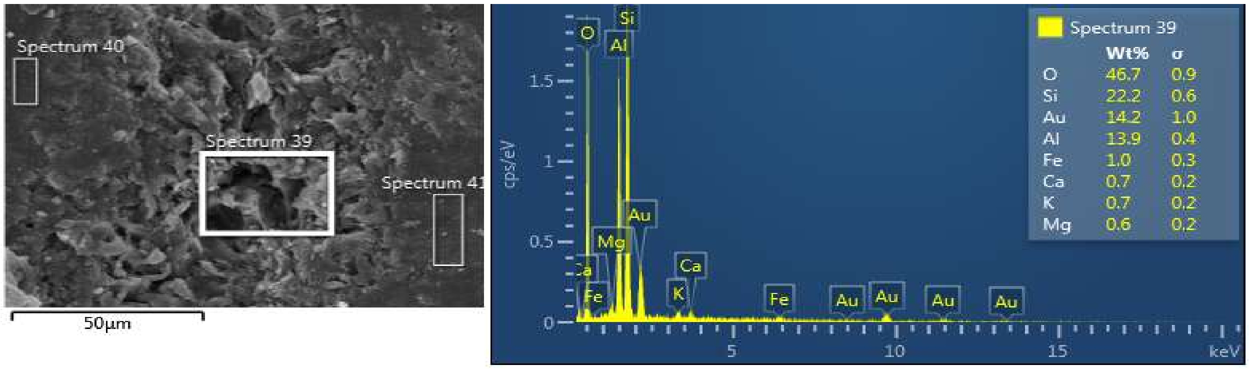
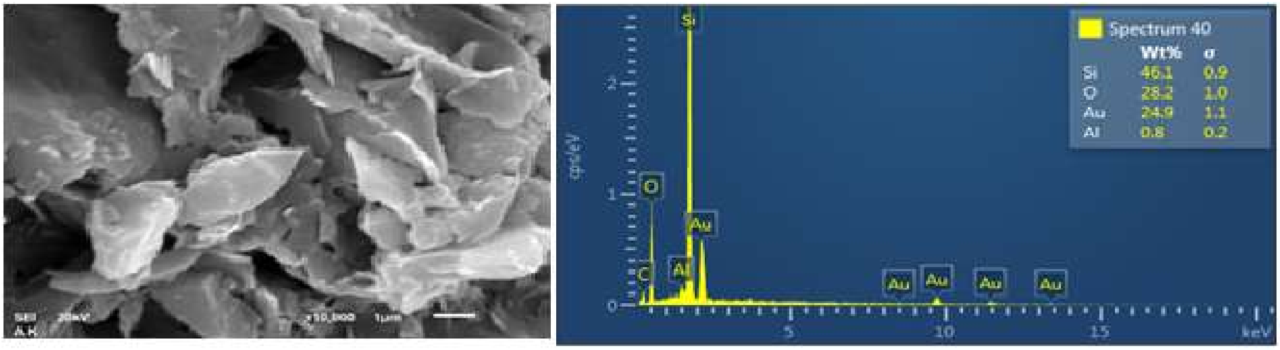


Fig (5.11) shows EDS\SEM samples four of rock samples



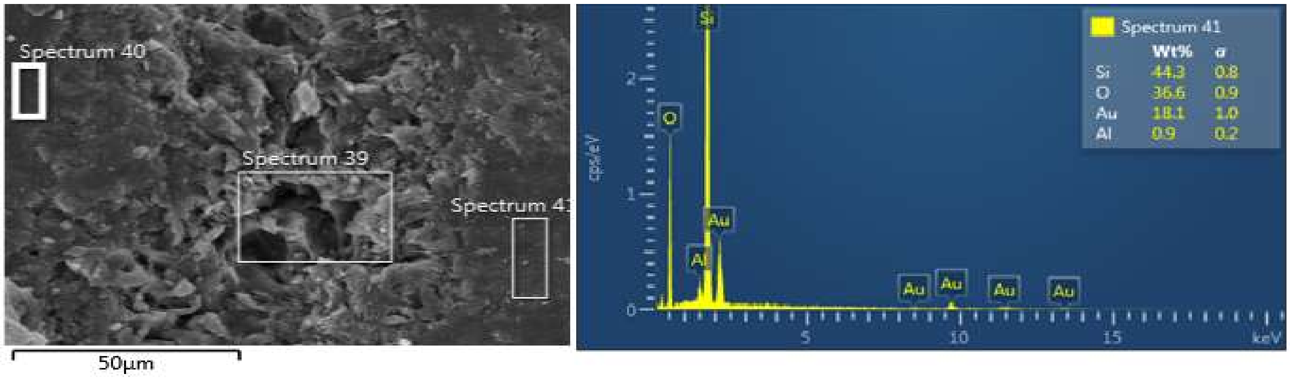
	Wt%	σ
O	46.7	0.9
Si	22.2	0.6
Au	14.2	1.0
Al	13.9	0.4
Fe	1.0	0.3
Ca	0.7	0.2
K	0.7	0.2
Mg	0.6	0.2

Fig (5.12) shows EDS\SEM samples five of rock samples



	Wt%	σ
Si	46.1	0.9
O	28.2	1.0
Au	24.9	1.1
Al	0.8	0.2

Fig (5.13) shows EDS\SEM samples six of rock samples



	Wt%	σ
Si	44.3	0.8
O	36.6	0.9
Au	18.1	1.0
Al	0.9	0.2

Fig (5.14) shows EDS\SEM samples seven of rock samples

5.4 Laser Induced Breakdown Spectroscopy(LIBS) investigated materials:

In this study used to investigate different mineral samples have been collected from mine sides randomly by miners due to their shining and brightness besides general physical appearance resembling precious minerals as sapphire and quartz figure 1 displays studied samples. In order to determine the basic compounds of specific minerals needs different techniques to accomplish that here, basically used laser induced breakdown spectroscopy(LIBS) as one of the spectra analyzing technique which uses an intense laser pulse irradiated on material to determine the elemental composition and constituent parts of target. LIBS is highly a great alternative technique due to simple preparation of samples, rapid and multi-elemental detection. Rare earth elements(REE) are found in many minerals and rocks and they have become essential because of wide spread use in manmade items and modern technology devices parts. Peculiarity of REE analysis plays an important role in determining the value of mineral or rocks precisely. In this study highly concentrated to detection of four of most important within rare earth element were cerium (Ce) , Praseodymium(Pr) ,europium (Eu) and gadolinium (Gd) by libs spectral lines analysis to reach some facts about the mineral and some physical properties using adapted LIBS database, national institute of standard and technology (NIST)spectral database as well as associated previous studies facts. Laser produced plasma plume has high irradiative ,high electro density and high temperature from emitted spectrum gives information about the specimen.

5.4.1 LIBS Spectral Analysis

quantitative and semi –quantitative analysis by using technique of LIBS for elemental analysis depends on some basic assumptions that can be verified on samples. NIST data and LIBS database are widely used in all the conditions of plasma causes and Local Thermodynamic Equilibrium (LTE) highly underlying laser induced plasma studies through processes emission spectroscopy for fundamental studies and for analytical applications. With respect to the round state

$$\frac{N_j}{N_o} = \frac{g_i}{Z\exp(-E_j/KT)} \qquad \textbf{(4-1)}$$

For relative population

$$\frac{N_j}{N_i} = \left(\frac{g_j}{g_i}\right)\exp\left[\frac{(E_j - E_i)}{KT)}\right] \qquad \textbf{(4-2)}$$

where i and j stand for lower and higher levels, No is the total species population, Ni and Nj are the populations of levels Ei,j , gi,j are the statistical weights of the levels 2J + 1, J is the total angular momentum quantum number of the term, and Z is the partition function usually taken as the statistical weight of the ground state. The spectral line radiant intensity is given by:

$$\mathbf{I = \frac{hvgAN}{4\pi} \quad = (\frac{hcNogA}{4\pi\lambda Z})exp(-\frac{E}{KT})} \qquad \textbf{(4-3)}$$

I is in units of W/sr, h is the Planck constant v is the line frequency.c is speed of light, and A is the transition probability (Einstein coefficient). N may be the absolute number or the number density. The radiant intensity per unit volume of source the case of equation (3) gives the ratio of the interties of two lines is:

$$\mathbf{\frac{I'}{I} = \left(\frac{\lambda g' A'}{\lambda' gA}\right) ex\,p[-\frac{E' - E}{KT}]} \qquad \textbf{(4-4)}$$

Choosing lines for which the g, A and E values and the wavelengths are known, and measuring the relative intensities, enables one to calculate T by the two-line method. Basic parameters for Saha-Boltzmann to determine element concentration were wavelength(nm), intensity (a.u),Einstein coefficient (A_{ij} S^{-1}), lower and upper energies (Ei,j Cm-1), g factor (2J+1) temperature(K) electron density(cm3) and atomic number(z) to reach specific concentration under LTE assumption the integrated line intensity(I) proportional with concentration(C). Distribution of atoms and ions can evaluate by Saha equation rules assuming a simplified model that considers observing lines radiant intensity that identical elemental amount calculated by Equations (3) and (4) produced concentration under LTE assumptions.

5.4.2 Elemental Analysis of Selected Elements in The Samples

As shown in table 1, the intensity for identification of elements were found between (420–720 nm) region using NIST database and LIBS references. According to the intensity of spectrum measurement the cerium shown all samples in two isotopes Ce (I,II) .In sample one and sample four have been shown four spectra lines each one spectrum between(425.77 nm and 625.573 nm)with contrast with sample three and five similarly showed three at range [420.296- 629.573nm] but sample only two peaks spectra were detected (425.77 and 456.698 nm) respectively .The most noticeable thing in cerium spectrum that(425.77 nm)wavelength has been appeared in three samples except sample two and five .Pr spectrum represented by two isotopes Pr(I,II)have been detected in all five samples 6 spectra peaks were shown in three samples (1,2,5) with wavelengths between (426.953-501.815 nm) for sample three and four there seven spectra peaks have seen between 426.90and 532.269 nm three peaks detected in sample three while there 4 spectra lines measured in sample 4 . Eu (I,II) spectra a total of thirteen peaks were measured at wavelength range 426.953-719.181nm that three peaks of each of samples (1,4,5) and likewise for sample (2.3) have two spectra lines in each between 459.403 and 592.716 nm .Gd (I,II) spectrum has less appearance with compare to other samples only eight peaks have been detected from four samples and sample three has a great portion of peaks represented in three wavelengths 4232.71,465.352and 525.118nm and 4 peaks for sample two and five two peach each other but only one peak in sample one at 447.608 nm the most different thing in this part of the study Gd has never been detected in sample 5.to look at generals spectra detected the sample one highly dominated by aluminum and silicon as well as promethium (Pm), and yttrium (Y) REE but the sample two showed yttrium (Y) , ytterbium (Yb) samarium (Sm), lanthanum (La), thulium (Tm), REE and silicon gallium spectra were overpowered the sample for sample three were detected many of REE spectrum such as ytterbium (Yb) , erbium (Er), yttrium (Y),samarium (Sm), and lutetium (Lu), besides of same trace elements were overcame the sample .As general the sample four have seen wide ranges of REE as holmium (Ho), samarium (Sm), promethium (Pm), lanthanum (La)and yttrium (Y)in addition to Nickel(Ni), Carbon (C) and Calcium(Ca) the most frequent appearance trace element in the sample. Finally, sample five similar to sample four showed promethium (Pm), lanthanum (La), samarium (Sm), erbium (Er), neodymium (Nd), and terbium (Tb) REE and Carbon and lead are outnumbered other elements in compare with other samples so all samples wire rich with REEs except sample one has showed only two rare earth elements in general unselected rare elements used to analyzing in this work.

Table 5.4. The Spectrum of Recorded from LIBS Analysis of Selected Elements

Sample 1		**Sample 2**		**Sample 3**		**Sample 4**		**Sample 5**		**Sample 6**		**Sample7**	
Wavelength (nm)	**Element**	**Wavelength (nm)**	**Element**	**Wavelength (nm)**	**Element**	**Wavelength (nm)**	**Element**	**Wavelength (nm)**	**Element**	**Wavelength (nm)**	**Element**	**Wavelength (nm)**	**Element**
425.77	**Ce II**	**420.296**	**Ce I**	**425.77**	**Ce II**	**425.771**	**Ce II**	**409.707**	**Gd I**			**497,75**	**Pr I**
447.608	**Gd II**	**426.953**	**Pr II**	**432.712**	**Gd I**	**426.902**	**Pr I**	**428.05**	**Gd I**			**499.84**	**Ce I**
463.228	**Pr I**	**434.28**	**Gd II**	**456.608**	**Ce II**	**459.403**	**Eu I**	**439.164**	**Ce II**			**511.07**	**Pr II**
522.79	**Ce I**	**465.355**	**Gd I**	**465.352**	**Gd II**	**463.24**	**Ce I**	**470.978**	**Pr I**			**629.516**	**Ce I**
629.554	**Ce II**	**499.46**	**Ce II**	**497.594**	**Pr I**	**492.363**	**Pr I**	**491.133**	**Eu I**			**629.92**	**Eu II**
630.341	**Eu II**	**596.71**	**Eu1**	**504.383**	**Pr I**	**499.467**	**Ce I**	**497.567**	**Pr I**				
707.71	**Eu I**	**629.554**	**Ce I**	**516.67**	**Eu I**	**508.765**	**Pr I**	**511.976**	**Ce I**				
708.635	**Ce II**	**635.986**	**Pr I**	**525.118**	**Gd I**	**517.369**	**Pr II**	**627.274**	**Ce I**				
719.181	**Eu II**	**719.481**	**Eu II**	**532.269**	**Pr I**	**529.368**	**Eu I**	**707.48**	**Eu I**				
501.815	**Pr I**	**--**				**596.716**	**Eu I**	**601.815**	**Eu I**				

The spectral data of the elements we obtain trough relevant wavelength of detected peaks and analyzed all elected peaks as figures of samples from one to five of showing the spectrum of several elements have seen in each sample separately and chose spectrum of Ce ,Pr ,Eu and Gd rare earth elements as in figures (3-7)showing Ce and Pr pecks as highest in most samples in contrast with Eu peaks have seen slightly low whereas the Gd peaks have seen in the middle between two high and low peaks in figure (8) has investigated probability of most repeated wavelength within five samples that found in range between(418.97 and 541.635 nm). With an increase in laser irradiance, both electron temperature and density increase and saturate at higher irradiance levels.

4.4.3 Spectra of Selected Elements and Probability of Wavelength Percentiles

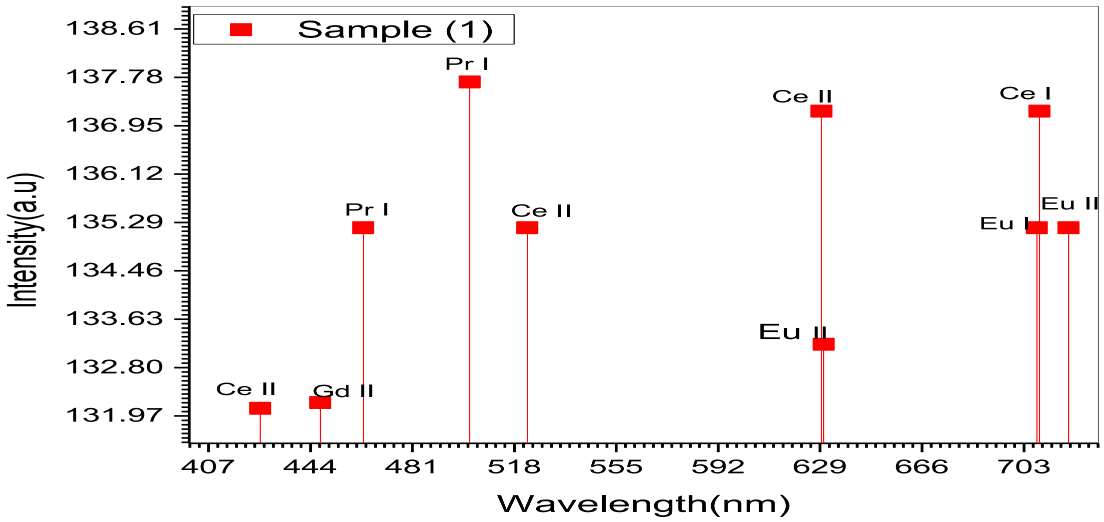


Figure 5-15 LIBS spectrum of rare earth element showed form sample one

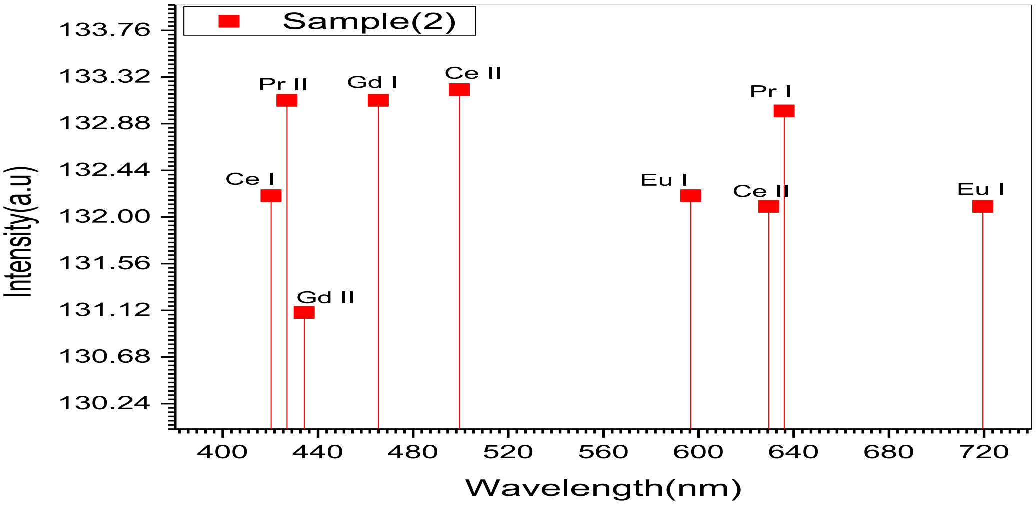


Figure 5-16 LIBS spectrum of rare earth element showed form sample tow

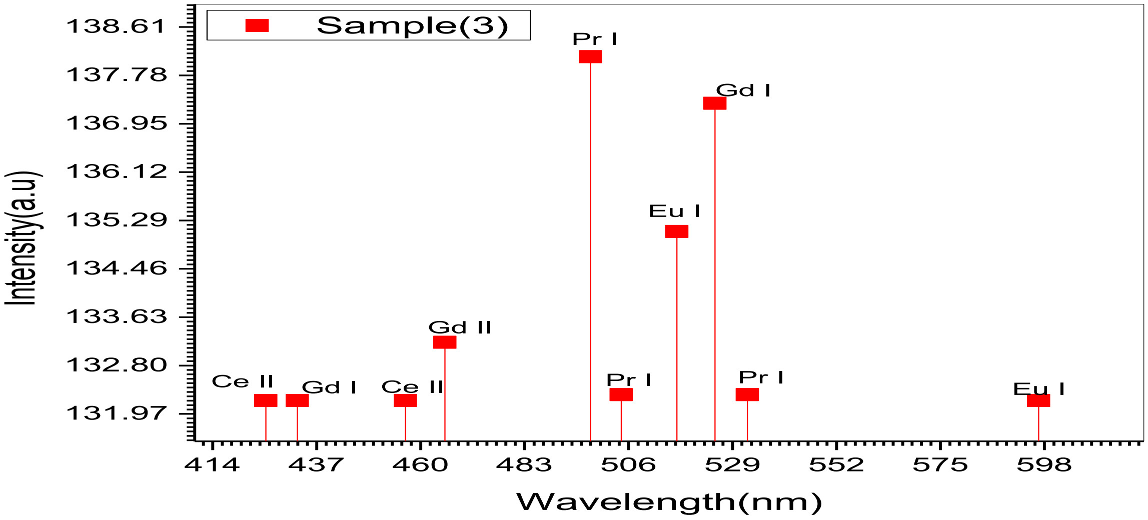


Figure 5-17 LIBS spectrum of rare earth element showed form sample three

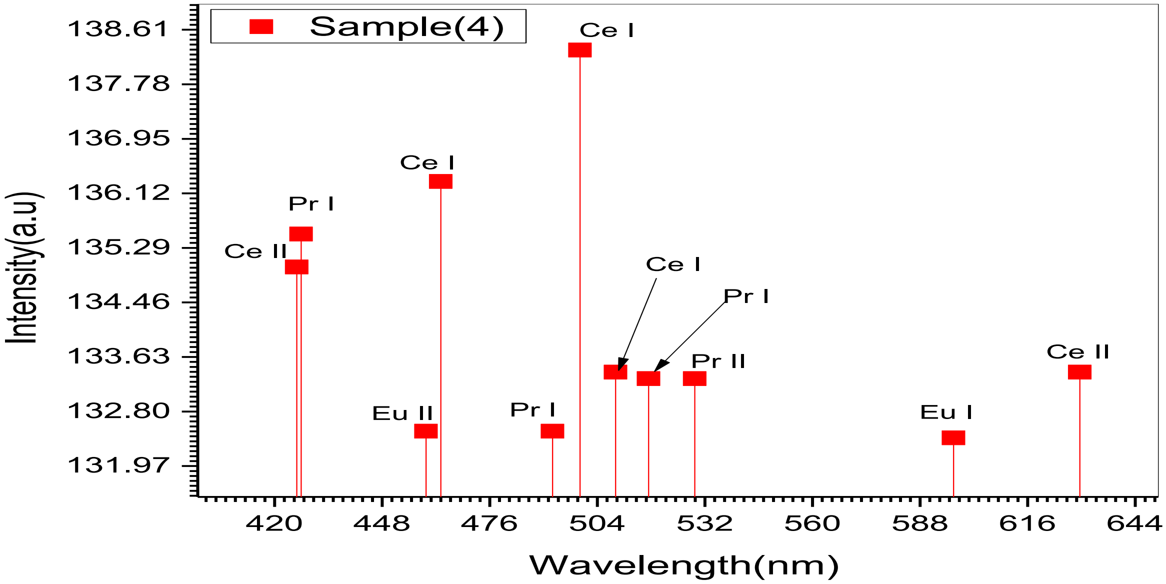


Figure 5-18 LIBS spectrum of rare earth element showed form sample four

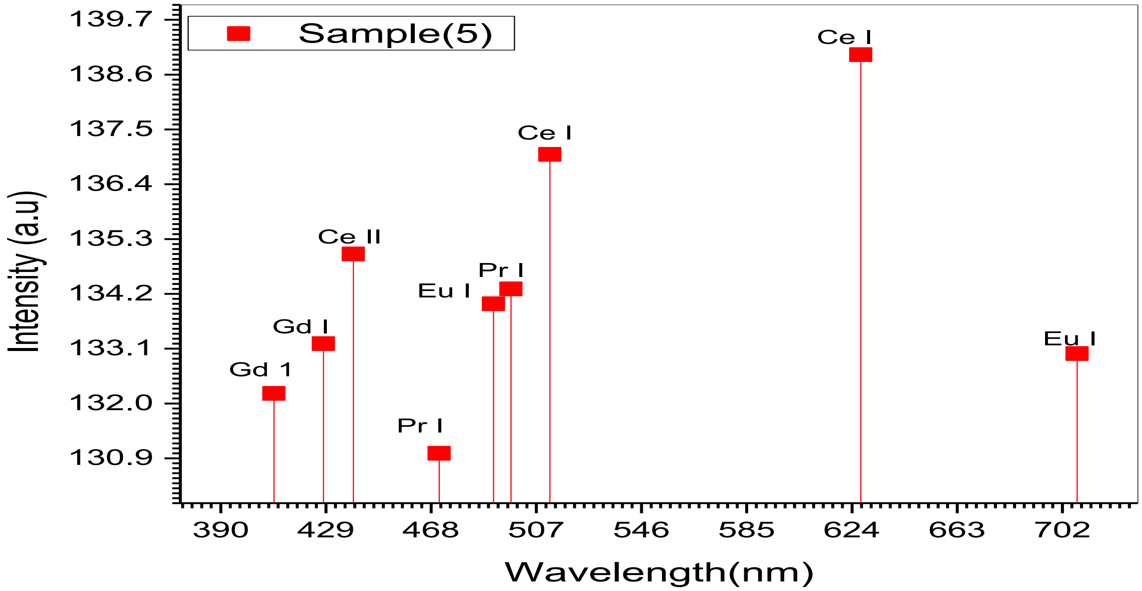


Figure 5-19 LIBS spectrum of rare earth element showed form sample five

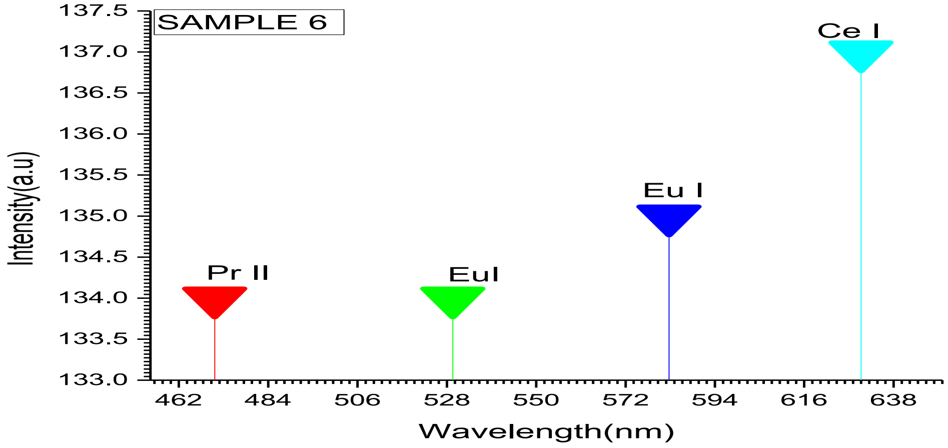


Figure 5-20 LIBS spectrum of rare earth element showed form sample Six

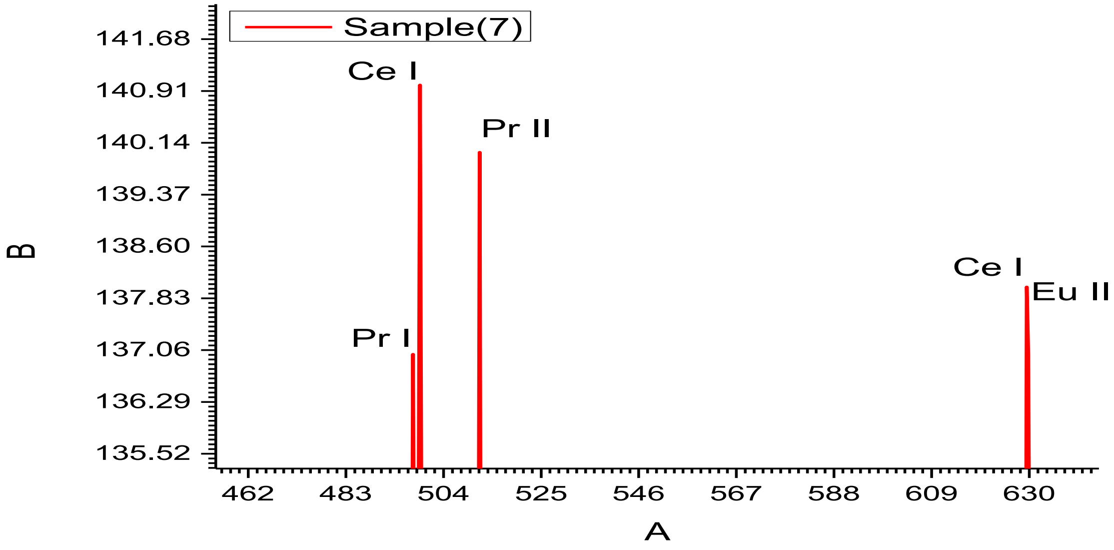


Figure 5-21 LIBS spectrum of rare earth element showed form sample Seven

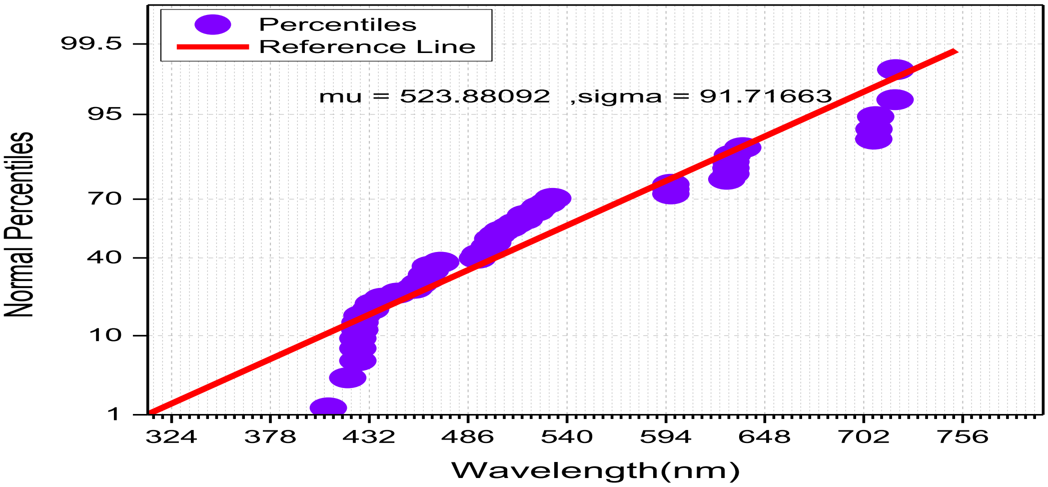


Figure 5-22 shows the probability plot of most frequent wavelengths in all samples given from LIBS spectrum of rare earth element

5.4.4: Selected Rare Earth in Samples spectra

Cerium (Ce)

Cerium is the most abundant of the rare earth elements. It makes up about. basically, Cerium has an atomic number (58), atomic mass (140.12)gmol-3, melting point(799)°C, poling point (3426)°C ,9 isotopes and Electronic shell [Xe] 4f1 5d1 6s2. Ductility, softness, malleability as well as irony -grey metal are characteristics of cerium also it is slightly hard than lead it oxides rapidly in hat water and slowly in cold water slowly. Cerium is used in many applications such as arc lamps electrodes, aluminum alloys and some house equipment like fluorescent lamps. Biologically cerium has no health ramifications.

Praseodymium (Pr)

Praseodymium is a soft malleable, silvery-yellow metal and has Atomic number 59, Atomic mass(140.91) g.mol-1,Melting point(931)°C Boiling point(3512)°C, Five isotopes and Electronic shell [Xe] 4f3 6s2. In chemical properties it oxides when exposes to air and slowly reacts. Praseodymium can be used as resistant to corrosion and it reacts with water rapidly. Praseodymium Compounds are used in energy-saving lamps and glass , magnesium alloying agent to create strength metal of aircraft engines and alloys with some metals .Praseodymium in earth about four times than tin's abundance .it can be found in monazite rocks and some bastnasite ores .Health effects of Praseodymium it has low to moderate toxicity in soluble Praseodymium salts by ingestion but insoluble Praseodymium salts is not toxic except fewer skin and eye irritant for long term exposure also can cause embolism of lung and infuctionous on reproduction and nervous system damage when it gradually increased in soil and water.

Europium (Eu)

Europium is a soft silvery metal, it easily tarnishes in air at room temperature, burns at temperature about(150 C to 180 C) and reacts easily with water. in physical properties it has an Atomic number 63, Atomic mass (167.26)g.mol-1 ,Density (9.2)g.cm-3 at temperature (20)°C ,Boiling point(1510) °C Melting ,point(1522) °C, nine isotopes and electro shell [Xe] 4f12 6s2 .Europium can be used as nuclear control rods ,a neutron absorber, activation yttrium –based phosphorous and phosphorescent powder and paints .it is less abundance REE and it never been found as free element in nature .biologically has no known health effect of Europium and it toxicity also no yet been fully investigated .

Gadolinium (Gd)

Gadolinium is a shiny, soft, ductile silvery meatal belonging lanthanide group in periodic table it reacts with dissolves acids and water slowly and it is a strong magnet at room temperature and at 108k becomes superconductor. Gadolinium Atomic number (64), Atomic mass (157.25)g.mol-1, Density (7.9) g.cm-3 at temperature(20)°C, boiling point(93266)°C, melting point (1313)°C, 13 isotopes and electro shell [Xe] 4f7 5d1 6s2 Gadolinium is used in nuclear reactor plants, magnetic and electric compounds, computer memory and compact desk. the abundance of Gadolinium in earth is more within rare earth elements although it never been found as a free element but containing in some minerals. the world production of pure Gadolinium is about (400)tons per year. Gadolinium has moderate toxicity excepts of Gadolinium salt irritate skin eyes can be developed to be tumor-genesis for wide range gadolinium toxicity cannot fully investigated in details. Environmentally, gadolinium has no impacts on animals and plants. The facts reached through this study represented by predicted concentration of the sample and some essential physical properties using NIST atomic database, LIBS database and Solid state references as well as previous studies associated with work this study. Table 2 demonstrates concentrations of studied rare earth elements and some physical properties. cerium concentrations commonly seen as having different highs and lows .Generally, hold a high concentration nearly similar in sample one and sample four with(6400 and 6800 ppm) respectively in contrast with sample two and five have least concentration found at(680 and 74 ppm) per capita whereas the sample three has moderate concentration of (5640 ppm) .however ,total concentration of cerium were calculated at(19593 ppm) with average of (3919ppm).Praseodymium overall concentration measured at 5763 ppm and average 1153 ppm for maximum and maximum values have been determined in sample one(1170ppm)and sample four(1810ppm) there has seen a similarity in sample two and four with 1020 and 1017ppm individually . Europium elements showed a Variety of concentrations (3330,324,733,779 ,1020 ppm) independently form sample one to five beside of total concentration of (6823ppm and 1137 ppm) average concentration. Gadolinium has been a substantial concentration of (8510 ppm) in sample two it is significantly different with all concentrations among five samples and as all Gd separately single concentrations but Gd spectrum never been showed in sample four. In general, Gd has seen average concentration of(2638 ppm) and total of (13 ppm) and minimum of (311 ppm) as well as (2570 ppm) as medium concentration in sample three.

Table(5.5) Shows Rare Earth Elements Concentrations and Physical Properties

Sample	Ce concentration (ppm)	Pr concentration (ppm)	Eu concentration (ppm)	Gd concentration (ppm)
1	6400	1170	3330	311
2	680	1020	324	8510
3	5640	1810	733	2570
4	6800	1017	779	0
5	74	746	1020	1800
6	365	5763	1137	13191
7	653	1153	6823	2638
Total	19593			
Average	3919			
Physical Properties of REE				

Property	Ce	Pr	Eu	Gd
Crystal structure	FCC	HEX	BCC	HCP
Density in (g cm-1)	6.77	6.78	5.25	7.87
Thermal conductivity at 300 k (Wcm-1 K-1)	0.11	0.12	0.1	0.11

Electrical conductivity*I0^5 (ohm cm)-1	**0.12**	**0.25**	**0.11**	**0.07**
Resistivity*10^-6 (ohm cm)	**81**	**67**	**89**	**134**
Vickers's hardness	**24**	**37**	**17**	**67**
Category	**Light REE**	**Light REE**	**Heavy REE**	**Heavy REE**

5.4.5 Mapping of elements

In order to deeply understand of the Detection elements and Comparisons between the measured results were used to build the relationships between the experimental conditions and detected elements by comparison between the intensity(irradiance) and the simulated spectra to measure a slope that represented concentration of elements and converted into ppm concentration.

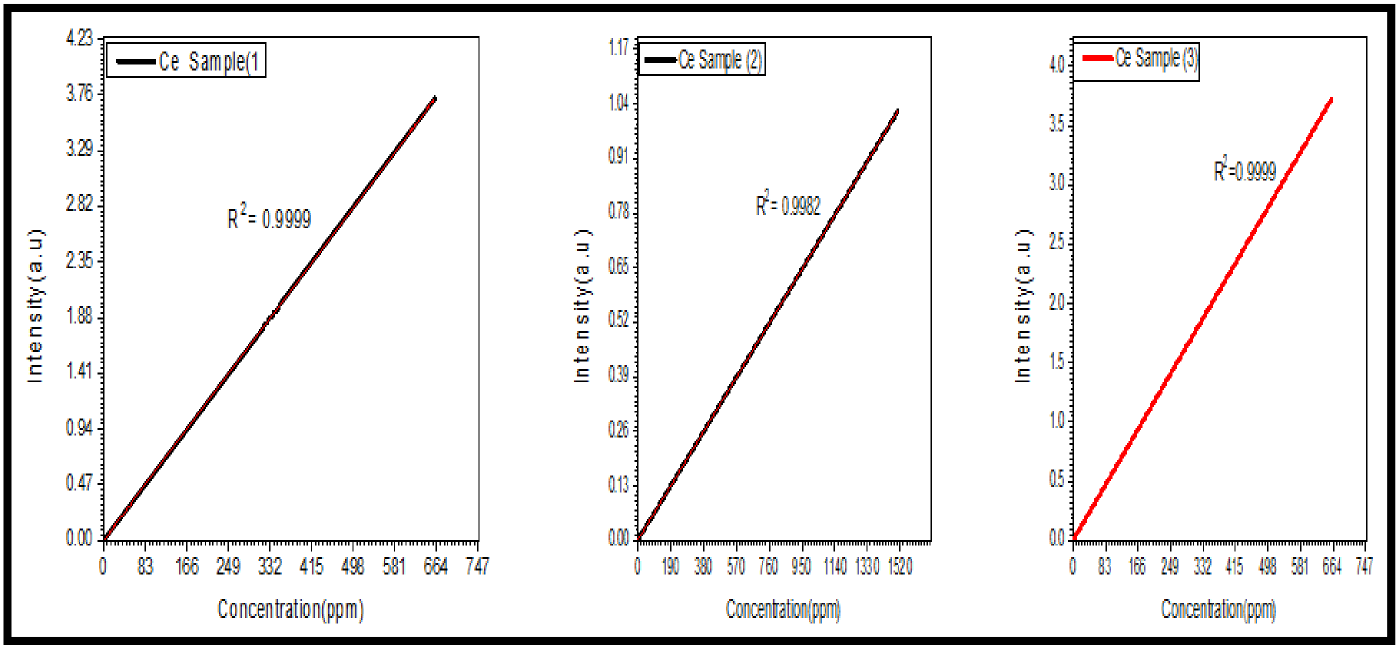
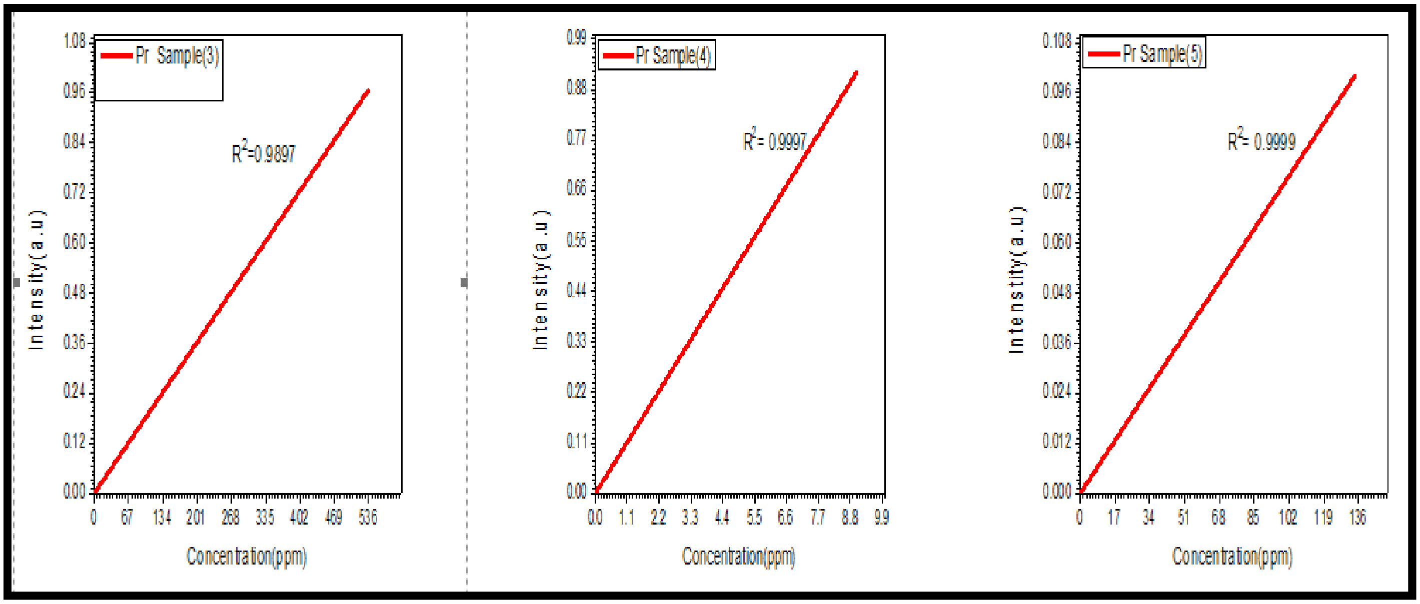


Fig (5-23): parts CeConcentration mapping from the LIBS measurements



Fig(5-24): parts Pr Concentration mapping from the LIBS measurements

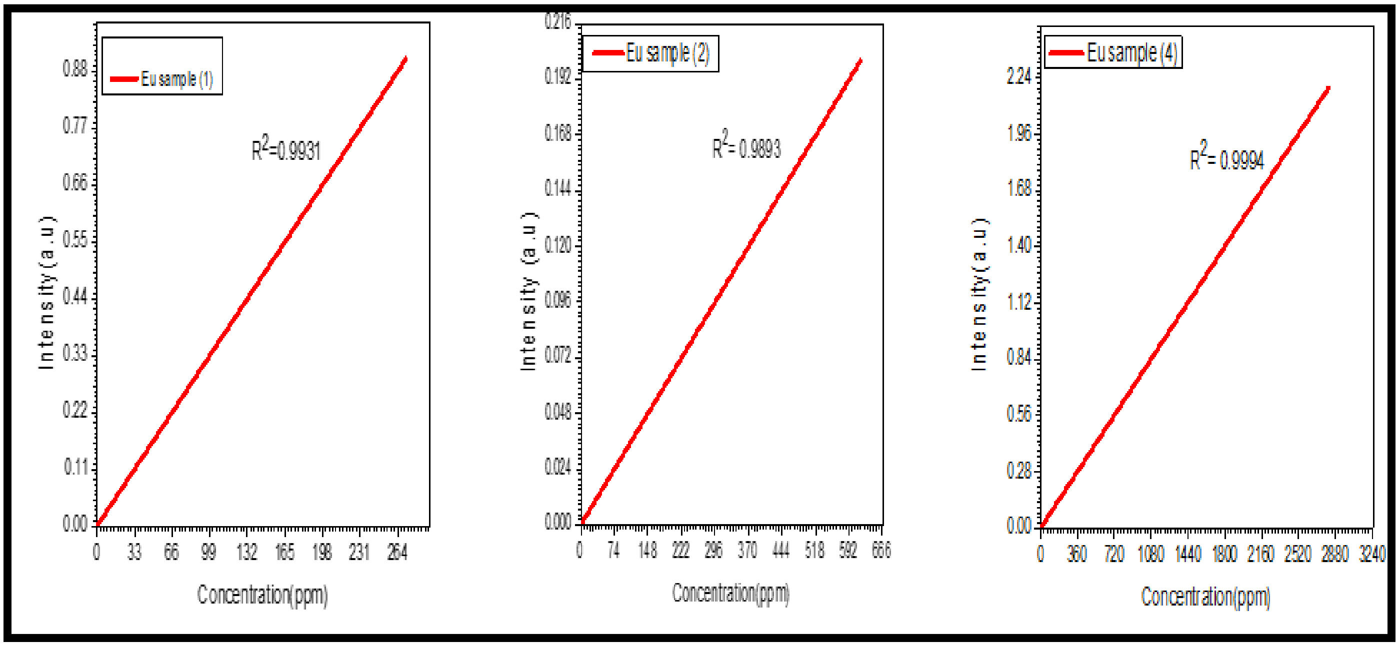


Fig (5-25): parts Eu Concentration mapping from the LIBS measurements

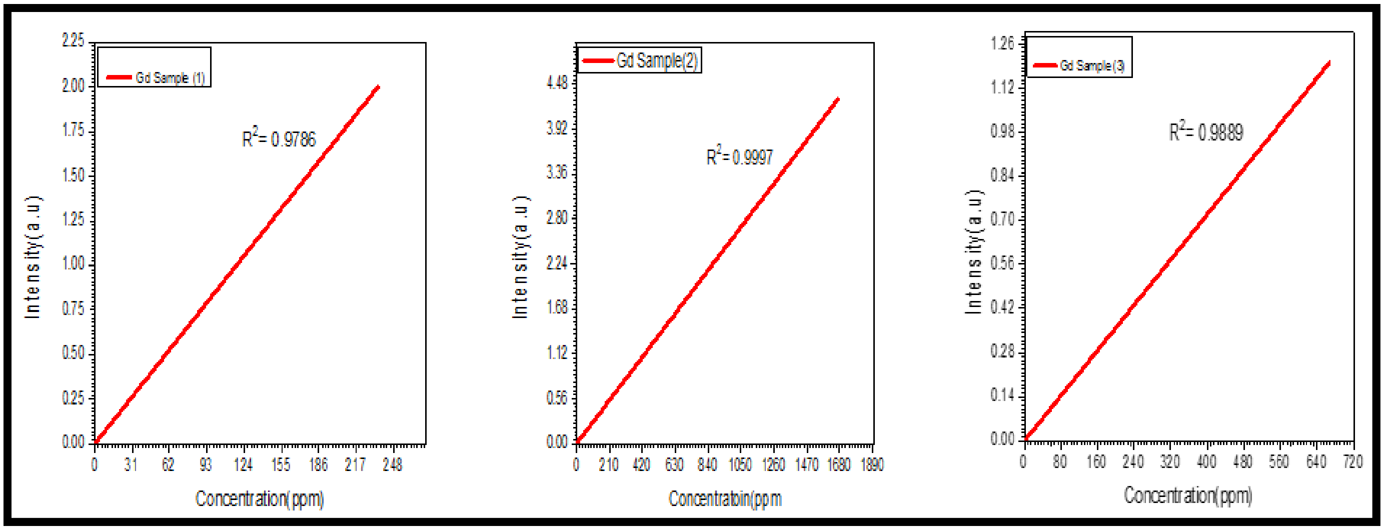
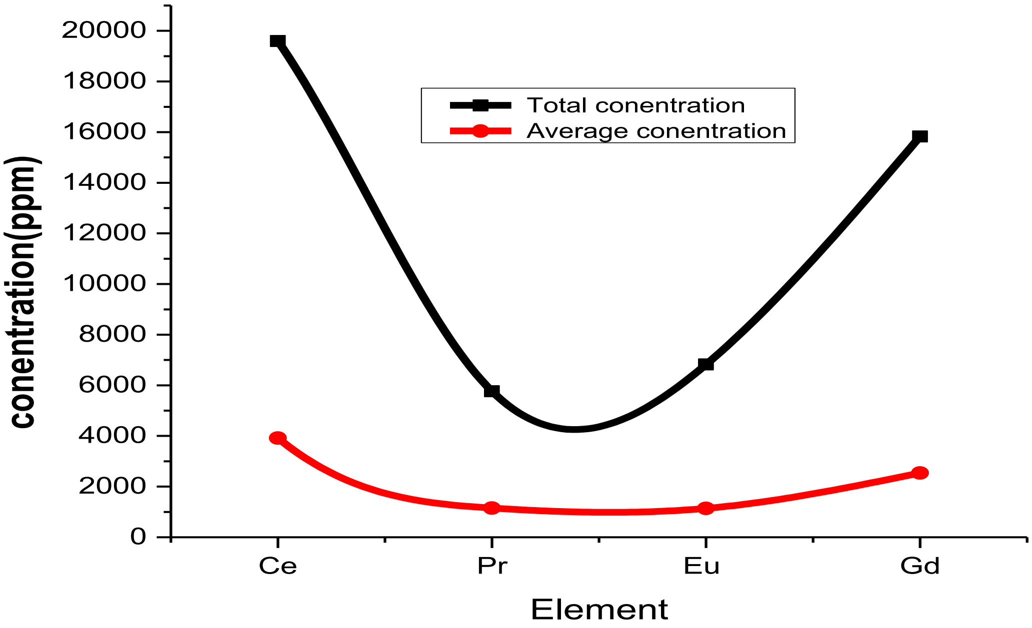


Fig (5-26): parts Eu Concentration mapping from the LIBS measurements



Fig(5-27) shows total concentration vs a part concentration of selected rare earth elements

5.5 FTIR Data Analysis

The absorption band of sample one showed specific peaks in the FTIR SPECTRUM were 1132,1414,1632,3495and 3595cm-1in the peaks of 1132 cm-1 had the strong appearance of C-O stretching group attributed aliphatic ether class and at 1133cm-3 can be identified butane at 1130-1150 contributed C-C rocking vibration and 1100-1140 contribute C-H symmetric deformation vibration. In silica studies considered the band of 1175 for Si-O-Si stretching vibration . the peak of 1414 cm-1 had strong S=O stretching sulfate compound, at 1415 had Boric acid compound at 1400-1450 cm had C-H asymmetric deformation vibration, at 1415-1425 had C-H symmetric deformation vibration, at 1445 -1430 contributed CH2 deformation vibration that metal like Cd, Hg Zn and Sn direct conjugated -CH2- as (R-CH2-metal). The peak of 1632 is due to vibration of C=C stretching had conjugated alkene compound class, at 1630 cm-1 contributed 1,3 butadiene, at 1130- 1100 – 1140 had C-H symmetric deformation vibration. However, these peak assignments are based on molecular interaction and the environment within the cell wall. Also at the peak of 1632 cm-1 for H-O-H stretching vibration. The peak at 3495cm-1 is assigned to all stretching alcohol group compound, at absorption peak of 3494cm-1 attributed nitric acid compound, at 3400 – 35000cm-1 involved the contribution of –N.H stretching vibration (free pyrrole) and at 3475 – 337 contributed N2H stretching vibration of SiNH2, at 3480 -350 contributed asymmetric stretching vibration of amides. The peat at 3395cm1 is due to stretching vibration of O.H(alcohol), at 3580 – 3670 had free O.H.

In the sample two had fixed 1123, 1414,1650 and 3450cm1 peaks, at the peak of 1123cm is due to stretching vibration of C-O stretching which is a secondary alcohol, at that peak can be Ethane,1,2 dichloro compounds, also 1100-1180cm1 gives information of(-N=S=O), and 1125-1145cm1 stretching vibration of(C-O-C-OC). At 1650 peak is due to a strong stretching vibration of C=O can be δ-lactam compound at the near wave number of 1660cm-1 found out of phene1,2,3,4-trifluoro- compounds, at 1680-1680cm-1 absorption peaks, are assigned to(C=C)stretching vibration (CH2=CH2 isolated) and 1600-1680 peaks are assigned to C-H vibration. An absorption peak at 3430cm-1 is due to vibration of O-H stretching which is an alcohol compound and the peak at 3445cm-1 in attributed ammonia class compound.

In the sample, three showed the absorption peaks of 11,23,1414,1641,2968 and 2859cm-1. At the 1641cm-1 peak is contained information of C=C stretching vibration which is conjugated alkene group was also given information of 1,4- Dioxane compound at that peak, at 1565-1650 had C=C stretching vibration and heavy element directly attached to C=C vibration. description of the 2468cm-1 absorption band of N-H stretching vibration which is found out information of amine salt and butane, propandinitrite and 1,4 Dioxane compound vibration and 1455-2450 had asymmetrically CH3 stretching vibration of CH3-C-S compound. The signal at 2859cm-1is attributed to the C-H stretching vibration of alkene and given a near functional group 1,4 Dioxane Compound 2050 cm-1 . at a range of 2890 -2870 cm-1 found out the info of Symmetric C-H stretching vibration.

Sample four hat fixed 1142,1414 ,1641 ,2913, and 3404 The wideband in 1142 cm-1 can be attributed to the stretching vibration (C-O) which is classed as aliphatic either also at that peak found out information of ethylene oxide. At the wavelength range of 1140-1150 cm-1 had C-C rocking vibration Compounds.

The absorption band spectra of untreated mineral compound at2900-3200 cm-1had N-H 2050 cm-1 of (P-NH) compound and 2862-2930 cm-1 had Symmetrically CH stretching vibration (CH-S). major absorption spectra at 3404cm-1Assigned a strong, O-H stretching vibration of an alcohol O –H compound AND ranged were the number of 3200-3400 cm-1 given info of N-H stretching vibration of free pyrroles two bonds, NH2 stretching vibration amino acid, at 3390-3410 cm-1 had si-NH2 of NH2 stretching vibration compound.

Major observation peaks showed at sample five were 1142, 1423, 1650, and 3586 cm-1at 1423 cm-1peaks attribute a medium O-H bending vibration which is appeared as carboxylic acid compound and at that peaks also found information of pyrone ,3- iodo compound. The observed peak at 1650 cm-1can is attributing to a strong stretching vibration of C=O which is given the name of δ-lactam also at the same peak found out of C=C stretching vibration of an aromatic compound. The spectrum peak at 3586 cm-1 is due to stretching vibration of OH alcohol also given found out info of hydrogen peroxide compound of the same peak.

Sample six had 1048,1398,1622 and 3618 cm-1in . the peak spectrum at 1048 cm-1 peak is assigned a strong, broad of (CO-O-CO) stretching vibration and fount out the information given a name of anhydride class compound and also involved in the contribution of glyoxal and acetic acid compound at same wavenumber, at 1100 cm-1 had C-H symmetric deformation of (AI-CH) class and at 1000-1050 cm-1had C-C starching vibration. The absorption peak at 1398 cm-1 is due to medium O-H bending vibration of carboxylic acid and at 1388 cm-1 just given information of ether compound furthermore, at 1390-1440cm-1had C-H symmetric deformation vibration likewise at the wavenumber of 1385-1425 had a weak deformation vibrating as in (CH2=CH-NCH). the wideband in 1622 cm-1can be contributed a medium C=C stretching vibration of conjugated alkene, at 1123 cm-1 is marketed as 1623 cm-1 Ethylene and methylamine compound of 1620 -1680 cm-1had C=C stretching vibration as H2C=CH2 compound in addition to C=CH stretching attached with heavy metal (metal-CH=CH2) at 1565-1650 cm-1 wavenumber.At 3618 cm-1 absorption peak is assigned to O- H stretching vibration of alcohol class compound and also found out info Hydrogen peroxide in the same wavenumber.

Sample seven Had fixed peak of 1587 ,1408,1642 and 3550at 1087 cm-1 absorption peak is due to a strong C-O stretching vibration of aliphatic ether class can pound and at same wavenumber found out ether, 1,2 dibromo –compound information and in the peak at 1408 cm-1is contributed due to a strong, bread vibration CO-O-CO stretching vibration of anhydride also at 1409 cm-1had thiophene compound class. At 1642 cm-1 1642 cm -1 is due to stretching of the carbon-carbon double bond At 3550 cm-1abserption peak involved various strang, broad O-H stretching vibration and nitric acid from figured out information of FTIR database.

For a better visibility, FT-IR spectra presented further in this work were divided into two ranges: 4000–2000 cm–1 (where mainly –OH and –CH groups vibrations are visible) and 2000–600 cm–1 (fingerprint region).The sharp band of -OH at 3676 cm–1 and broadband of SiO in the range of 1270-850 cm–1 indicates the presence of silica. An unambiguous analysis of the IR spectra of rock samples is difficult due to the presence of many ingredients.

The region from about 1300-900 cm-1 is called the fingerprint region. The bands in this region originate in interacting vibrational modes resulting in a complex absorption pattern. Usually, this region is quite complex and often difficult to interpret; however, each organic compound has its own unique absorption pattern (or fingerprint) in this region and thus an IR spectrum be used to identify a compound by matching it with a sample of a known compound. Alkynes are compounds that have a carbon-carbon triple bond (–C≡C–). The –C≡C– stretch appears as a weak band from 2260-2100 cm-1. The –C≡C– stretch from 2260-2100 cm-1 ,–C≡C–H: C–H stretch from 3330-3270 cm-1 and –C≡C–H: C–H bend from 700-610 cm-1 .Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorine, or iodine (usually Br or Cl in the organic chemistry teaching labs). In general, C–X vibration frequencies appear in the region 850-515 cm-1.The =C–H stretch in aromatics is observed at 3100-3000 cm-1. n. the distinctive bands of the common functional bands shows in table (4-6):

Table (5-6) demonstrates the distinctive bands of the common functional bands

Wavenumber range	Functional band	Group
3500-3300 cm^{-1}	**N–H stretch**	**amines**
3500-3200 cm^{-1}	**O–H stretch**	**alcohols, a broad, strong band**
3100-3000 cm^{-1}	**C–H stretch**	**alkenes**
3000-2850 cm^{-1}	**C–H stretch**	**Alkanes**
1760-1665 cm^{-1}	**C=O stretch**	**ketones, aldehydes, esters**
1680-1640 cm^{-1}	**C=C stretch**	**Alkenes**

Table (5.7) FTIR results and FTIR database information

Sample wavenumber (cm-1)	Appearance	Group	Compound Class	Exact or Near Compound Name
Sample one				
1132	Strong	C-O stretching	aliphatic ether	1133 cm-1 Butane
1414	Strong	S=O stretching	sulfate	1415 cm-1 Boric acid
1632	medium	C=C stretching	conjugated alkene	1630 cm-1 1,3-Butadiene
3495	strong, broad	O-H stretching	alcohol	3492 cm-1 Nitric acid
3595	medium, sharp	O-H stretching	alcohol	
Sample two				
1123	strong	C-O stretching	secondary alcohol	1123 cm-1 Ethane, 1,2-dichloro-
1414	Strong	S=O stretching	sulfate	1415 cm-1 Boric acid
1650	strong	C=O stretching	δ-lactam	1660 cm-1 Phenol,2,3,4-trifluoro-
3450	medium, sharp	O-H stretching	alcohol	3444 cm-1 Ammonia
Sample three				
1123	strong	C-O stretching	secondary alcohol	1123 cm-1 Ethane, 1,2-dichloro-
1414	Strong	S=O stretching	sulfate	1415 cm-1 Boric acid
1641	medium	C=C stretching	conjugated alkene	1641 CM-1 cyclic alkenes
2859	medium alkane	C-H stretching	alkane	2856 cm-1 1,4-Dioxane
2968	strong, broad	N-H stretching	amine salt	2968 cm-1 Butane , 2968 cm-1 Propanedinitrile
Sample 4				
1142	Strong	C-O stretching	aliphatic ether	1142 cm-1 Ethylene oxide
1414	Strong	S=O stretching	sulfate	1415 cm-1 Boric acid
1641	medium	C=C stretching	conjugated alkene	1641 CM-1 cyclic alkenes
2913	strong, broad	N-H stretching	amine salt	2912 cm-1 Butane
3404	strong, broad	O-H stretching	alcohol	alcohol O-H

Sample5				
1142	Strong	C-O stretching	aliphatic ether	1142 cm-1 Ethylene oxide
1423	medium	O-H bending	carboxylic acid	1423 cm-1 1-Propyne, 3-iodo-
1650	strong	C=O stretching	δ-lactam	C=C stretching aromatic
3586	medium, sharp	O-H stretching	alcohol	Hydrogen peroxide3586
Sample6				
1048	strong, broad	CO-O-CO stretching	anhydride	1048 cm-1 Glyoxal 1048 cm-1 Acetic acid
1398	medium	O-H bending	carboxylic acid	1388 cm-1 Ethane
1622	medium conjugated alkene	C=C stretching	conjugated alken	1623 cm-1 Ethylene 1623 cm-1 Methylamine
3618	medium, sharp	O-H stretching	alcohol	3618 cm-1 Hydrogen peroxide
Sample7				
1087	Strong	C-O stretching	aliphatic ether	1087 cm-1 Ethane, 1,2-dibromo-
1408	strong, broad	CO-O-CO stretching	anhydride	1409 cm-1 Thiophene
1642	medium conjugated alkene	C=C stretching	conjugated alkene	1442 cm-1 Butane
3550	strong, broad	O-H stretching	alcohol	3550 cm-1 Nitric acid

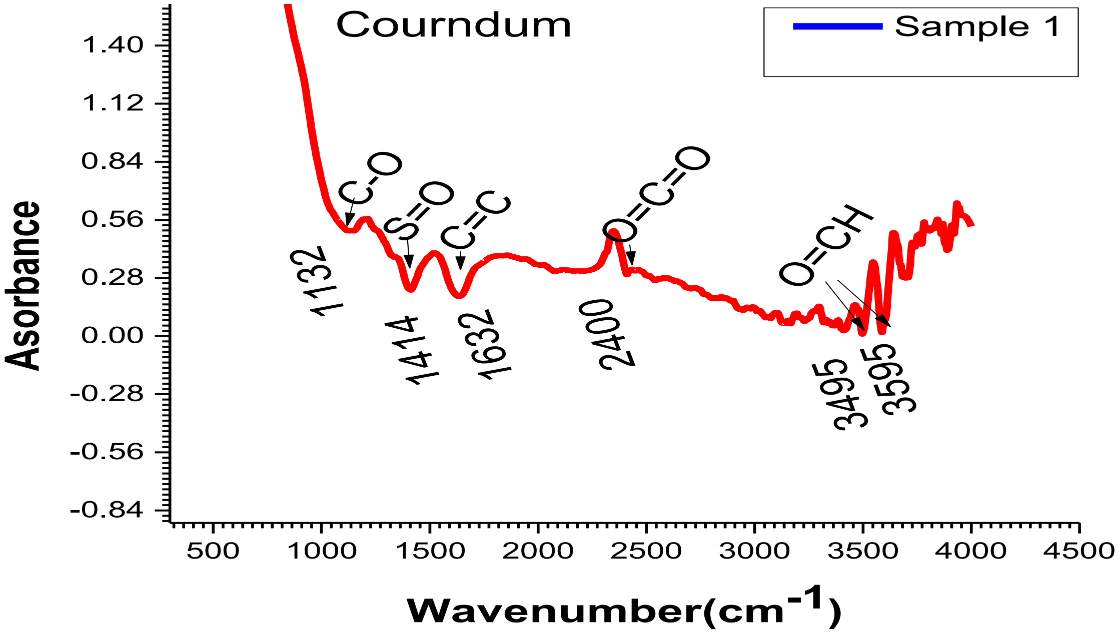


Figure (5-28) Sample one FTIR spectrum of rocks samples

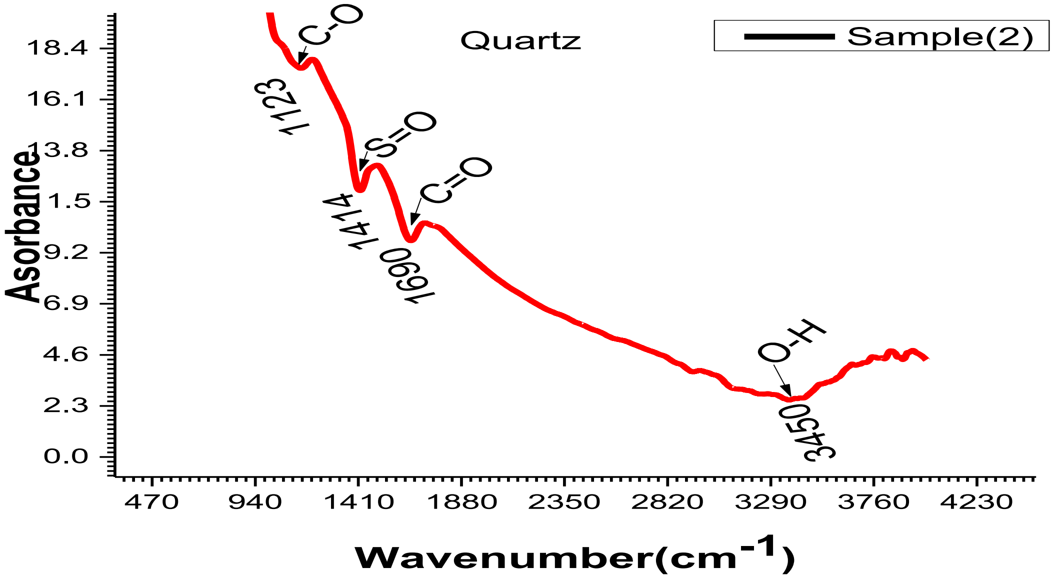


Figure (5-29) Sample two FTIR spectrum of rocks samples

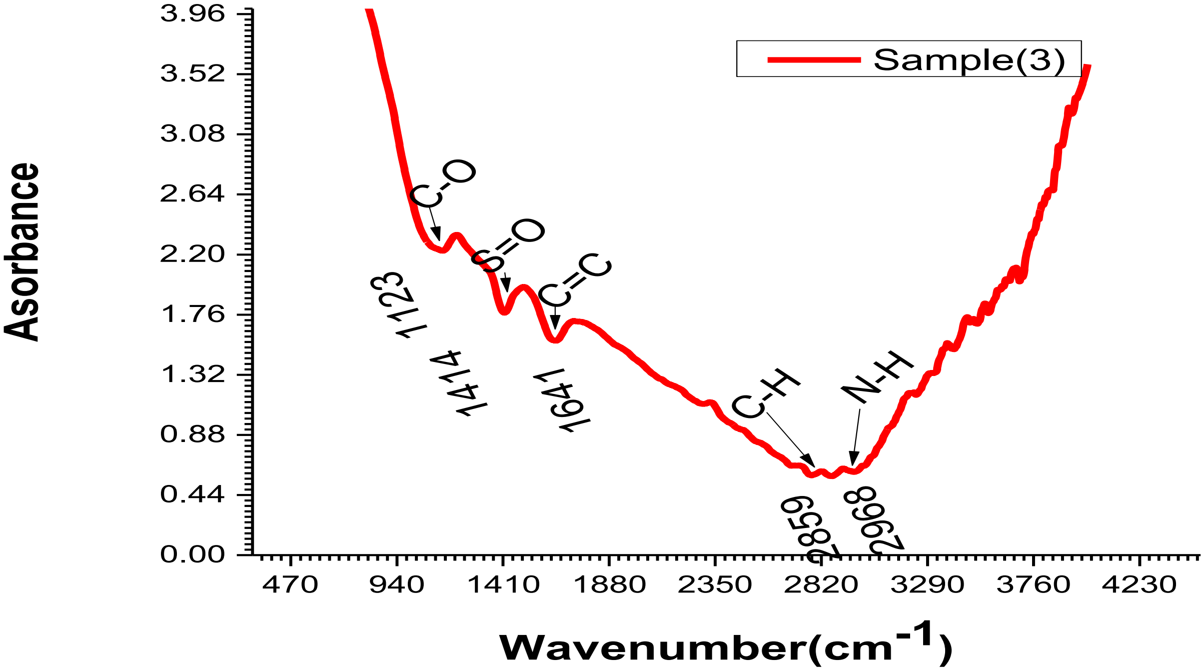


Figure (5-30) Sample three FTIR spectrum of rocks samples

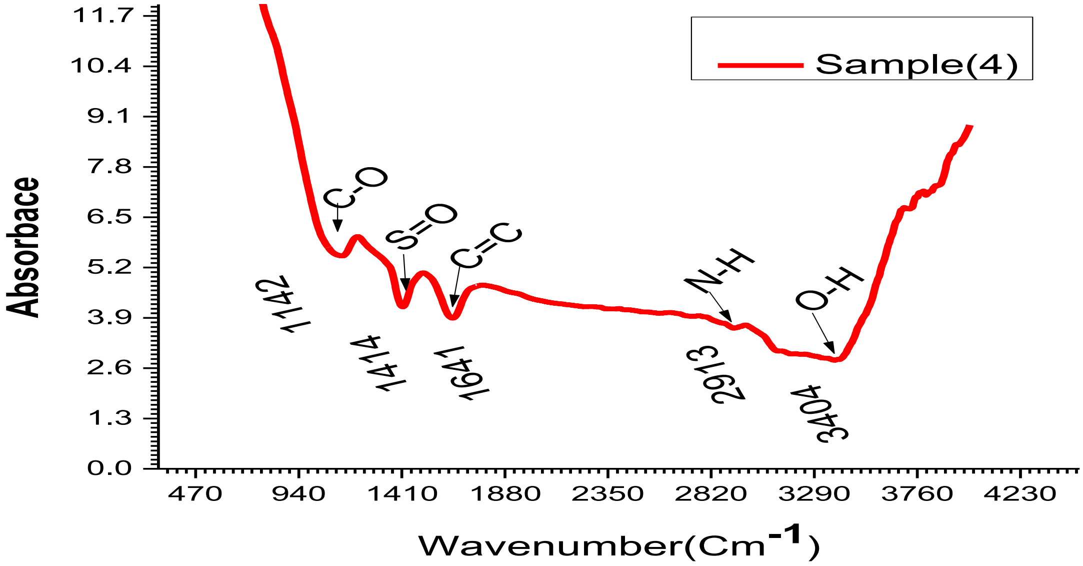


Figure (5-31) Sample four FTIR spectrum of rocks samples

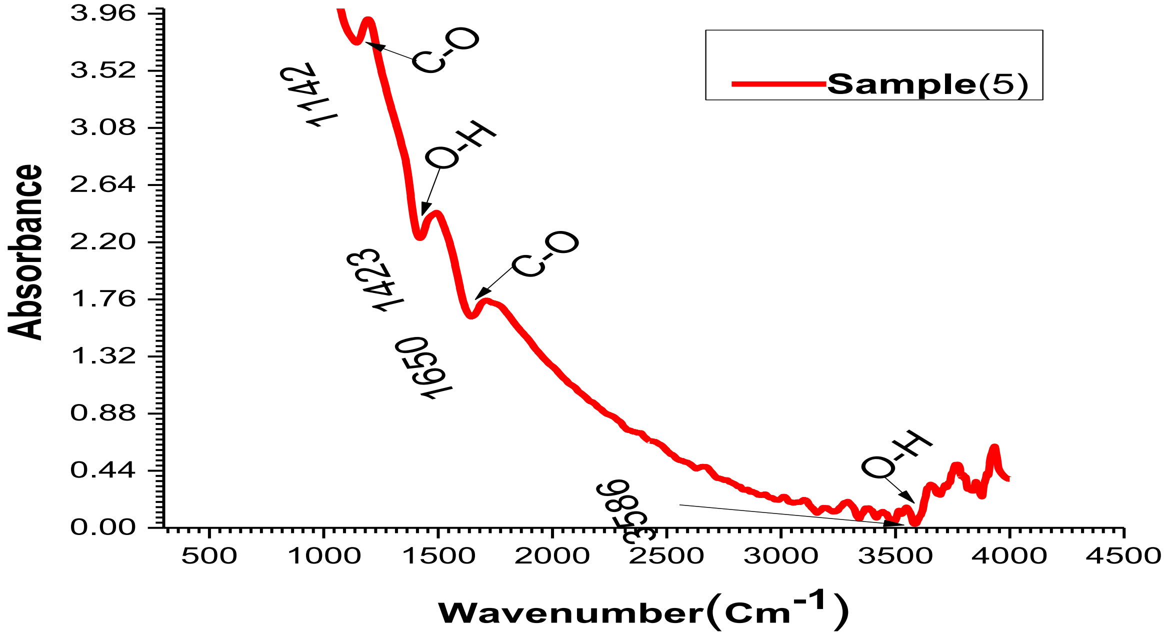


Figure (5-32) Sample five FTIR spectrum of rocks samples

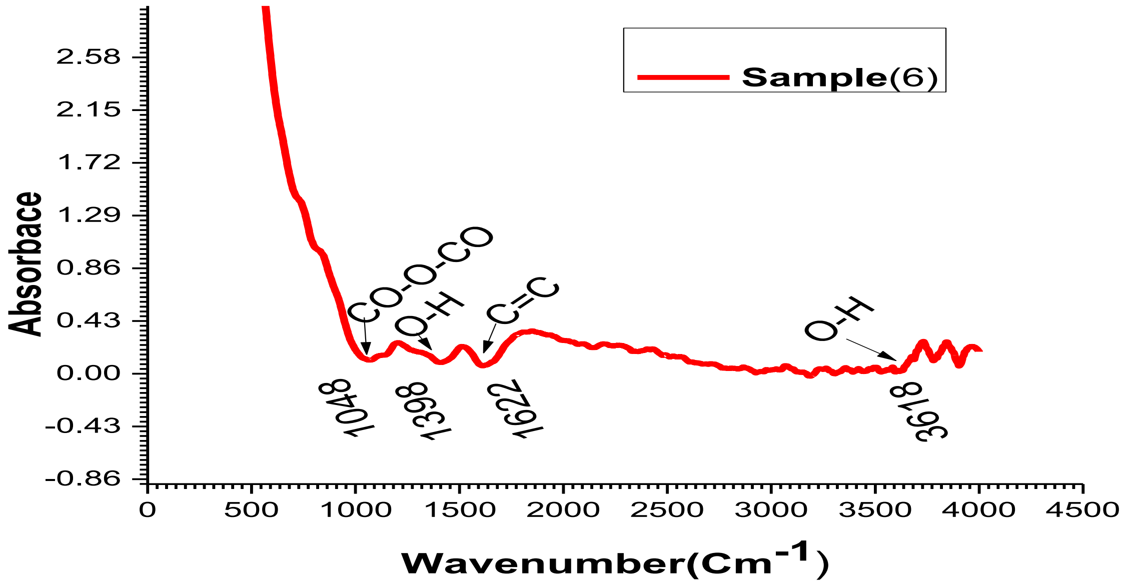


Figure (5-33) Sample six FTIR spectrum of rocks samples

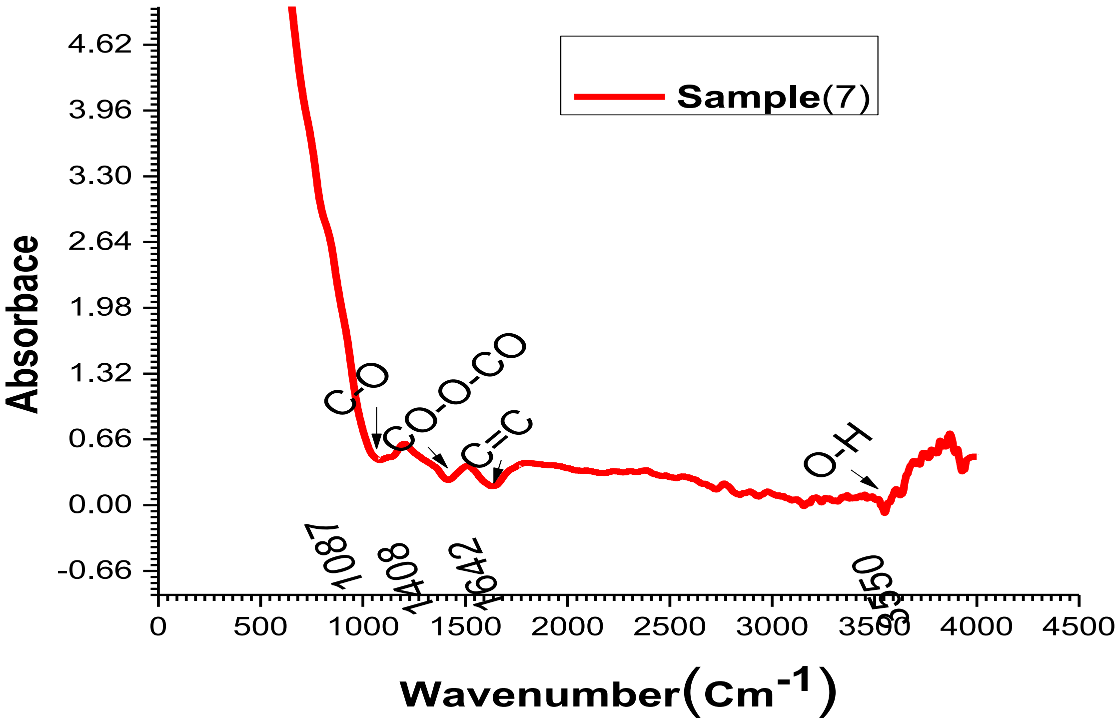


Figure (5-34) Sample seven FTIR spectrum of rocks samples

5.6 Diffuse reflectance Data Analysis:

Spectral analysis to approach in the same facts of the rock samples and study of same optical and electrical properties. The former was based on the variability of the shape of measured spectra and evaluated by calculating with specific relations and correlation coefficient for measurement .optical and electrical properties were performed by fitting each spectrum using a software program. The results of measurement of DR over the wavelength range 200<λ<2500nm are used to study natural semi-precious stone minerals properties of some special assignment, have been made. Reflectance spectra are obtained by setting up a simple diffuse reflectance spectroscopic system based on fiber optic.

Optical properties are related to the absorption spectrum through the mineral's composition and structure in a rotational way. The original spectra in the form of a plot of DR against photon energy, are given by wood (1971). They have converted to the plot of Kubela –Munk Function F(R) against wavelength (λ in nm) and photon energy (hν in eV), F(R)being defined as of well known equation that has a form fo $\mathbf{F(R)} = \frac{\mathbf{(1-R)^2}}{\mathbf{2R}}$ or $F(R)= \frac{\mathbf{K}}{\mathbf{S}}$ .Hence R is reflectance of the material ,$(1-R)^2$ is absorbance coefficient(K) and 2R is scattering coefficient (S).Kubela –Munk Function F(R) versus wavelength showed a significant different spectrum exhibits in the sample one which belongs to corundum type mineral its curves were dramatically increased from 496nm and peaked and sharply declined at 520 nm whereas the six silica origin samples have given the similarity in their curves besides of weak peaks comparatively clearly. However after transformation the intensity of peaks decreases and the relative intensity between peaks analogs to the absorption spectrum. Figure (4-29) displays the DR spectrum of natural minerals of corundum and silica. in general KM theory is applied to describe diffuse reflectance spectra.

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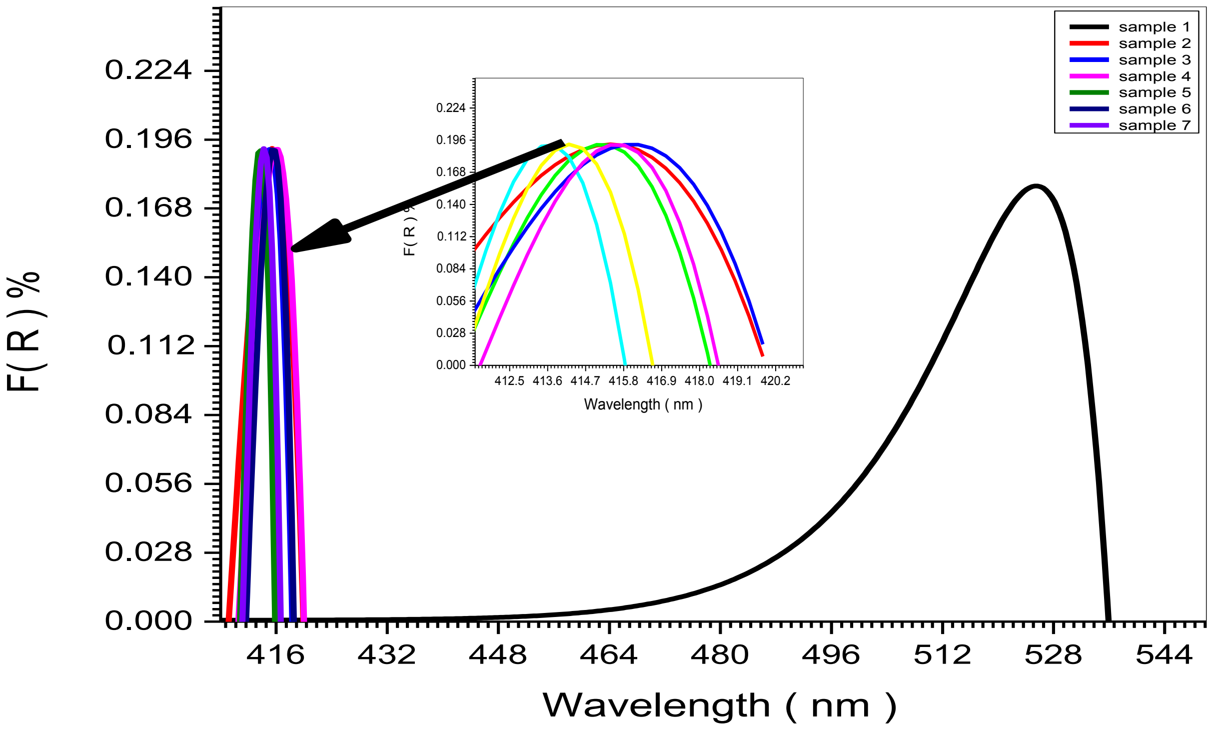

Figure (4-35) Diffuse Reflectance spectroscopy of K-M Function F(R)

The Reflectance: found the behavior of curves is the same for six samples of untreated natural mostly belong to the silica which is dominated by silicon dioxide (Si2) studied using diffuse reflectance spectrophotometer. Figure (4-30)Shows the results of Reflectance(%) relation between absorbance and wavelengths for the natural semi-gemstone samples, the rapid increase of the Reflectance(%) at wavelengths ranged (570 -680 nm). maximal value of Reflectance (the maximum value equal (0.204) a,u) in six silica origin samples have near the same value approximately at 375 nm wavelength while the sample one which belongs to the corundum (ruby) origin the Reflectance(%) showed to two different peaks at 660 nm and 755nm and clearly showed different curve from the six samples of silica. (the maximum value equal (0.204) a,u).In general, reflectance had a nearly similar value in all samples but they have a different wavelength in addition to the huge wavelength value to the corundum's samples.

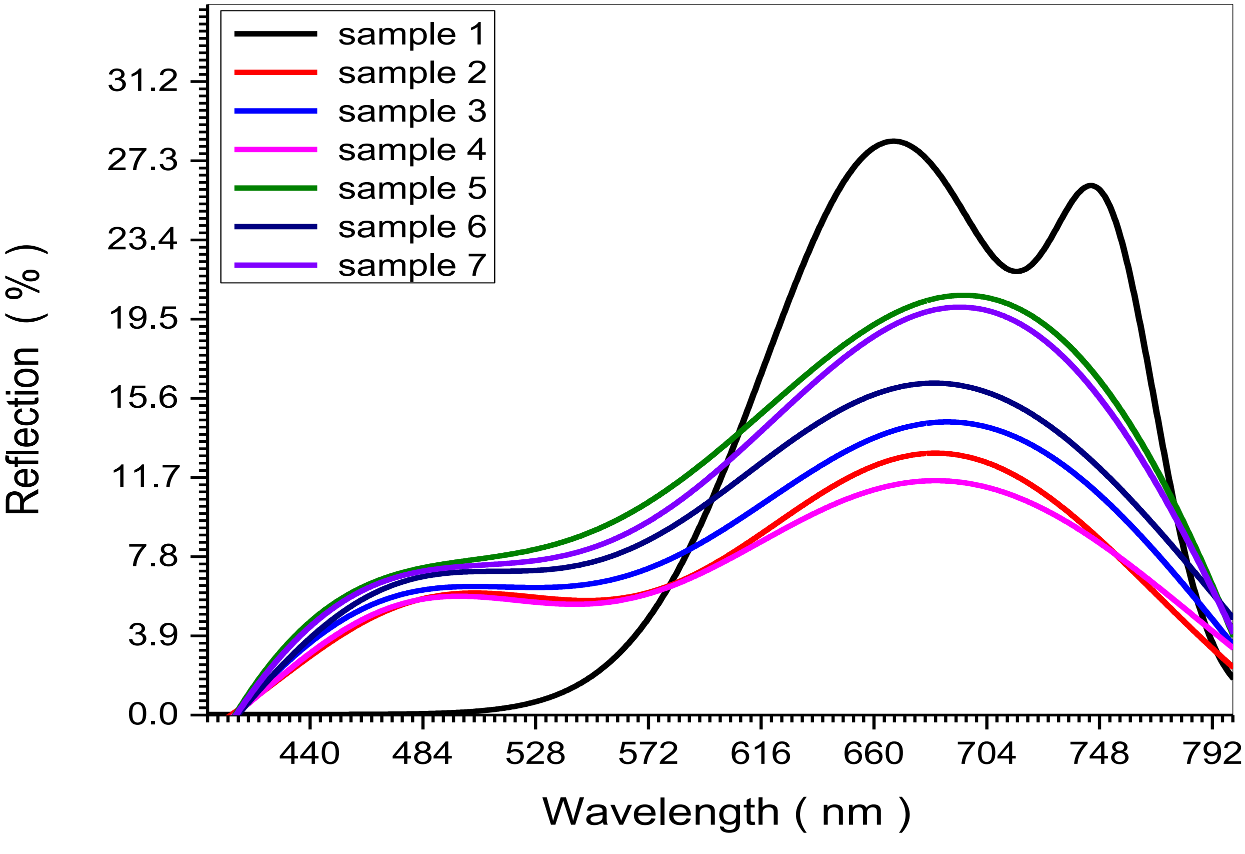

Figure (4-36) Diffuse reflectance reflectance of **rocks samples**

Absorption coefficient (α): The absorption coefficient (α)of prepared samples was given by using Eg of $\alpha = \frac{2.303xA}{t}$ where (A) is the absorbance and (t) is the optical legth on the samples obtained that the maximal value of(α) equal 56.98 cm-1,57,37 cm-1 and 57.45cm-1 for six silica origin samples (413.41 nm,415.41nm and 416.22) respectively for every two samples of six samples group, UV. while corundum origin sample had considerably different curves and had the maximal value of(α) equal 53.65 cm-1 at 525.73nm, this means that the transition must be corresponding to a direct electronic transition, and the properties of this state are important since they are responsible for electrical conduction. Also in Figure (4-31) shows that the value of (α) for the samples of decrease intel reached maximal value and leveled off. Measurement of the absorption of light is one of the most important techniques for optical measurements in solids. the frequency dependence of the absorption coefficient is quite different for the various physical processes which occur in the optical properties of solids. The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. The more light a material absorbs, the higher its absorption coefficient will be.

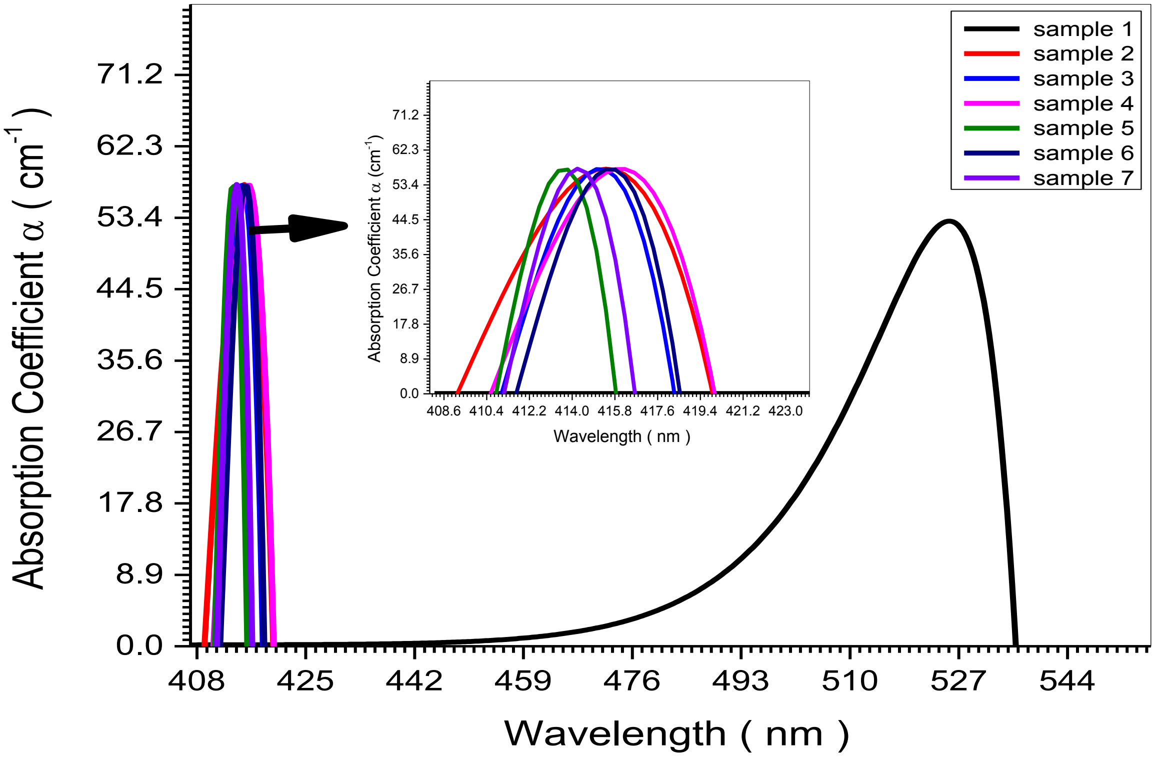

Figure (4-37) displays the absorption coefficient spectrum of natural rocks samples

Extinction coefficient (K):

The extinction coefficient (K) was calculated using relation of $k = \frac{\alpha\lambda}{4\pi}$. The variations at the (K) values as a function of (λ) are shown in fig. (5 the observed curves in the spectrum shape of (K) as the same shape of (α). The Extinction coefficient (K) for six samples of (silica) in Figure (4-32) obtained the value were nearly every three samples had same and had the same value of 1.88 x10-6 at the (413.82 nm) region and other three of six groups had a value of 2.6 x10-6 at 447.2m nm was depended on the samples prepared method, where the value of (K) at 375 nm while the sample corundum(ruby) had unique curve compared with six silica and had a maximal value of 2.3 x10-6. The complex interaction of light with matter involves reflection and refraction from the index of refraction boundaries, a process we call scattering, and absorption by the medium as light passes through the medium. The amount of scattering versus absorption controls the number of photons we receive from a surface. In general silica, samples have higher than corundum samples.

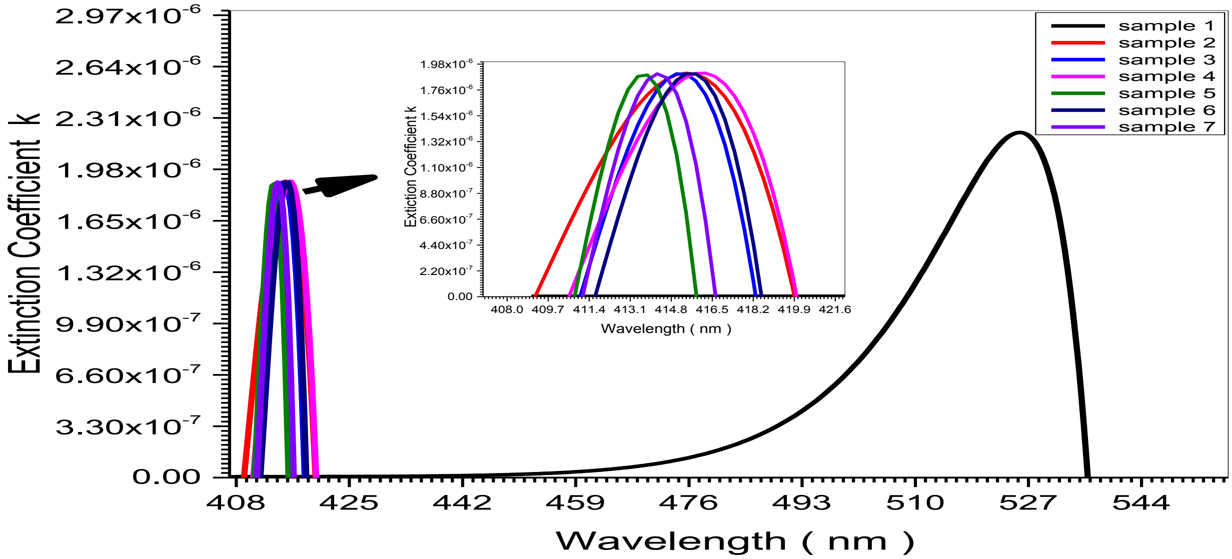

Figure (4-38) displays the extinction coefficient spectrum of natural rocks samples

The optical energy gap (Eg): The optical energy gap (Eg) has been calculated by using Eg of $(\alpha h\upsilon)^2 = C(h\upsilon - Eg)$ where (C) is constant.) Achieving extrapolating the straight thin portion of the curve to intercept the energy axis, the value of the energy gap has been calculated. In Figure (4-33) the values of (Eg) obtained the optical energy gap of seven studied were

(1.590,1.663,1.6131, 1.652,1.592,1.6323and 1.598 eV) respectively . It was observed that the differences and similarities in the values confirmed the reason for the bandgap shifts. the energy gap is an energy range in a solid where no electronic states can exist. the band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. It is the energy required to promote a valence electron bound to an atom to become a conduction electron, which is free to move within the crystal lattice and serve as a charge carrier to conduct electric current.in general, given energy gab values similar to silicon and CdSe compounds which have approximately 1.14eV and 1.7 ev subsequently.Broadening and narrowing of band gap in metal oxides semiconductors are extensively influenced by doping or impurity presence . The energy of band gap depends on the interactions of the guest(dopant) and host material(metal oxide). Doping formed a new energy levels which causes a decreasing in band gap energy value. Doping with donor impurities create energy levels in the band gap near the conduction band edge while doping with acceptor impurities create energy levels near the valence band edge. As the percentage of doped material increases the energy of band gap continues to decrease.

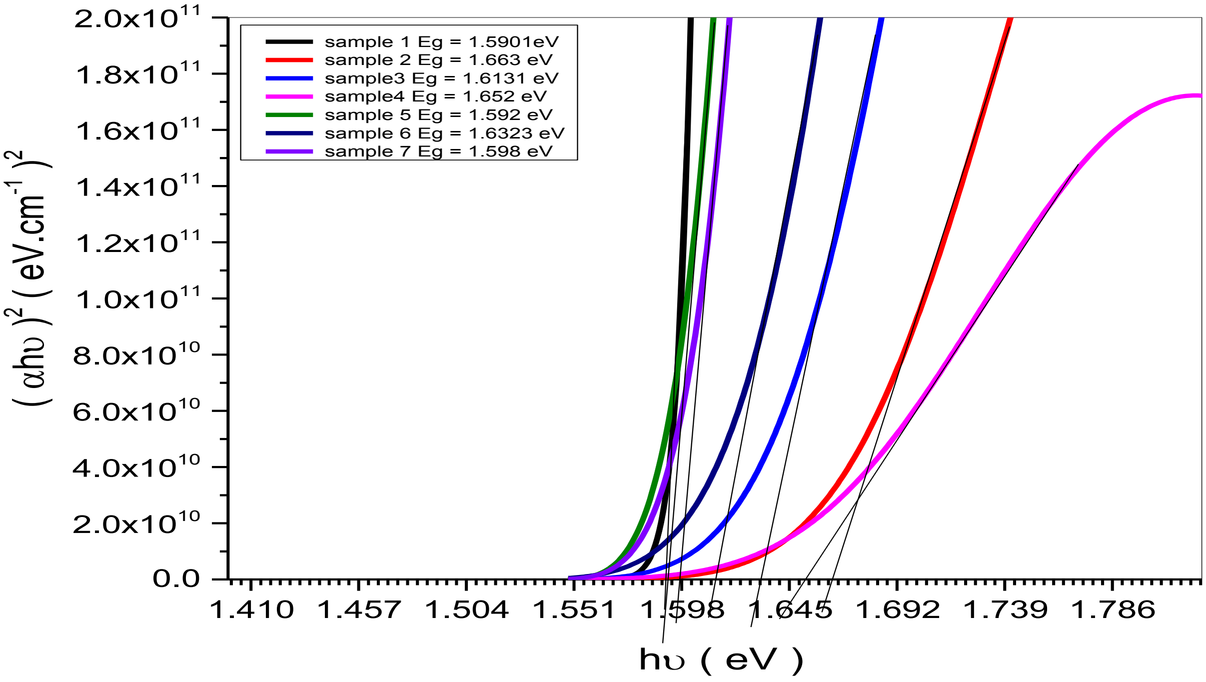

Figure (4-39) displays the optical energy band of natural semi-gemstone minerals

The refractive index (n) : The refractive index (n) is the relative between the speed of light in a vacuum to its speed in a material that does not absorb this light. The value of n was calculated using mathematical statement on $n = [\left(\frac{(1+R)}{(1-R)}\right)^2 - (1 + k^2)]^{\frac{1}{2}} + \frac{(1+R)}{(1-R)}$. The variation of (n) vs (λ) for seven untreated samples was shown in Figure (4-33). Figure (4-33) Show the relationship of refractive index (n) spectra, which shows that the maximum value of (n) is (2.9) for samples one at(666.92) nm, the minimum value of 1.01 at region ranged (400 -512.40) nm and medium value of (6.69)at 74413nm wavelength while six samples had similarity in all values of refractive index (n) and their maximum values were (2.19-2.10 -1.88,1.73 -1.64 -1.53) respectively for six samples from two to seven these values of refractive index (n) of the different sample have lied at the wavelength range (686.39 -694.95)nm. Many materials have a well-characterized refractive index, but these indexes depend strongly upon the frequency of light. Hence most of the refractive indexes have been values resembling liquid at 2Co some have refractive indies similar to solid refractive indexes.

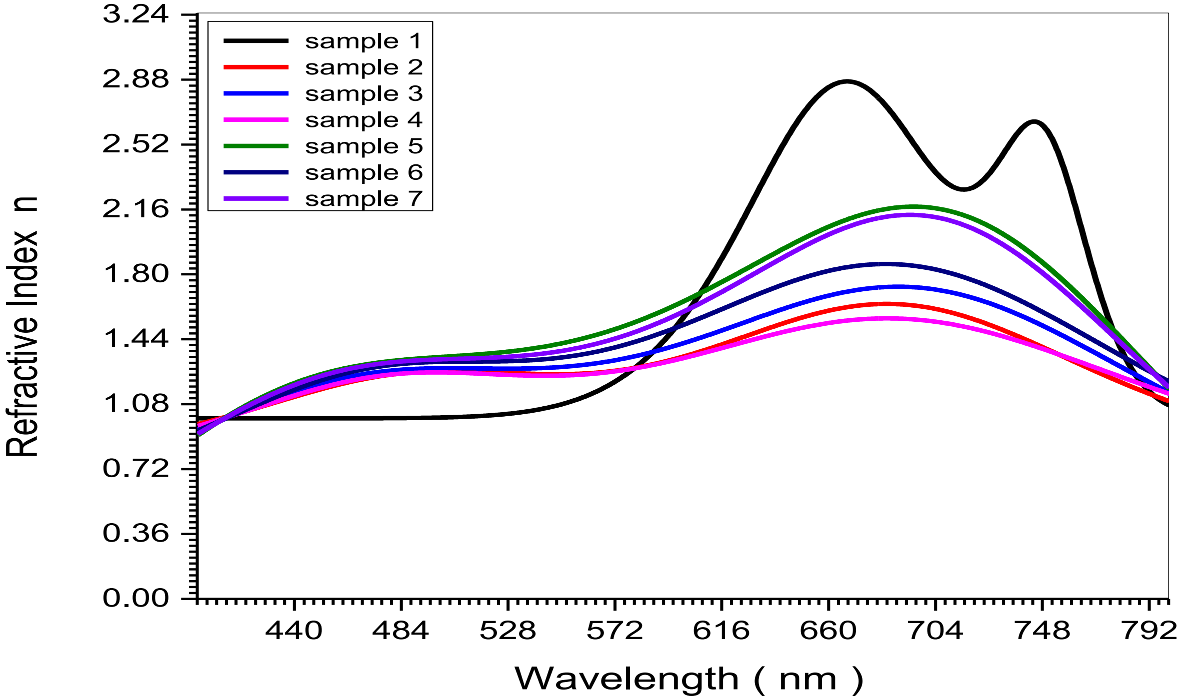

Figure (4-40) displays the refractive index of natural rocks samples.

Optical Conductivity :

The optical conductivity is a material property, which links the current density to the electric field for general frequencies. Optical conductivity was measured using equation of $\boldsymbol{\delta}_{\mathbf{opt}} = \frac{\alpha nc}{4\pi}$ .of the observed value of the minerals had semi-conductor like optical conductivity. the calculations reveal many similarities between silica cluster minerals samples from two to six optical conductivity values were found in a range between 416.03 and413.48nm besides of a high value of 1.43 × 109s-1 and a low value of 1.40× 109 s-1 as well as three samples had the same value of optical conductivity in two different wavelengths whereas the sample one which is identified as corundum had a value of 1.3× 109 s-1 at 525.26nm wavelength this given a specific characteristic from silica group untreated minerals. Figure (4-34) shows the optical conductivity features of studied minerals.in general, the silica group had higher than corundum samples.

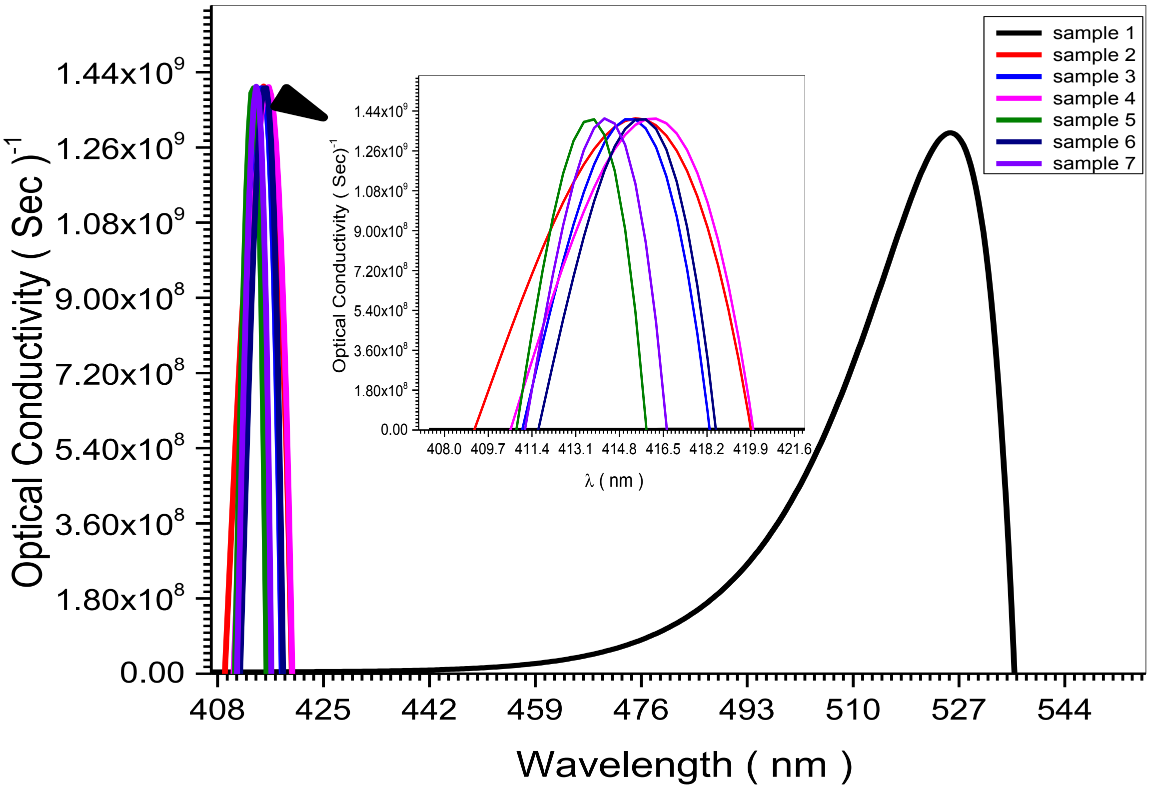

Figure (4-41) displays the Optical conductivity spectrum of natural rocks samples minerals

Electrical conductivity **(δopt)**: is a property of materials that determines how well a given material will conduct electricity and measures a material's ability to allow the transport of an electric charge. A conductor such as a metal has high conductivity, and an insulator like glass or a vacuum has low conductivity. A semiconductor has a conductivity that varies widely under different conditions. The electrical conductivity of the samples was obtained by using mathematical relation of $\delta_e = \frac{2\lambda\delta_{opt}}{\alpha}$. Conductors, semiconductors, and insulators can be distinguished on the ground of their conductivity and other properties. Conductors like metals show conductivity at room temperature, but as the temperature increases, their conductivity gets reduced. However, semiconductors act as insulators at low temperatures but as the temperature increases so their conducting properties also; however, insulators have no such effect of temperature variations as they do not have the conducting properties. The observed values are given in the following Table (4- 7) .the corundum sample has higher than silica group samples.

Table (4- 8) Electrical conductivity of studied minerals

Sample	**One**	**Tow**	**Three**	**Four**	**Five**	**Six**	**Seven**
Wavelength nm	**670.86**	**697.01**	**699.61**	**704.90**	**707.50**	**645.76**	**706.15**
Electrical conductivity (Ω m)$^{-1}$	**91.79**	**54.07**	**57.85**	**51.14**	**73.77**	**62.04**	**72.08**

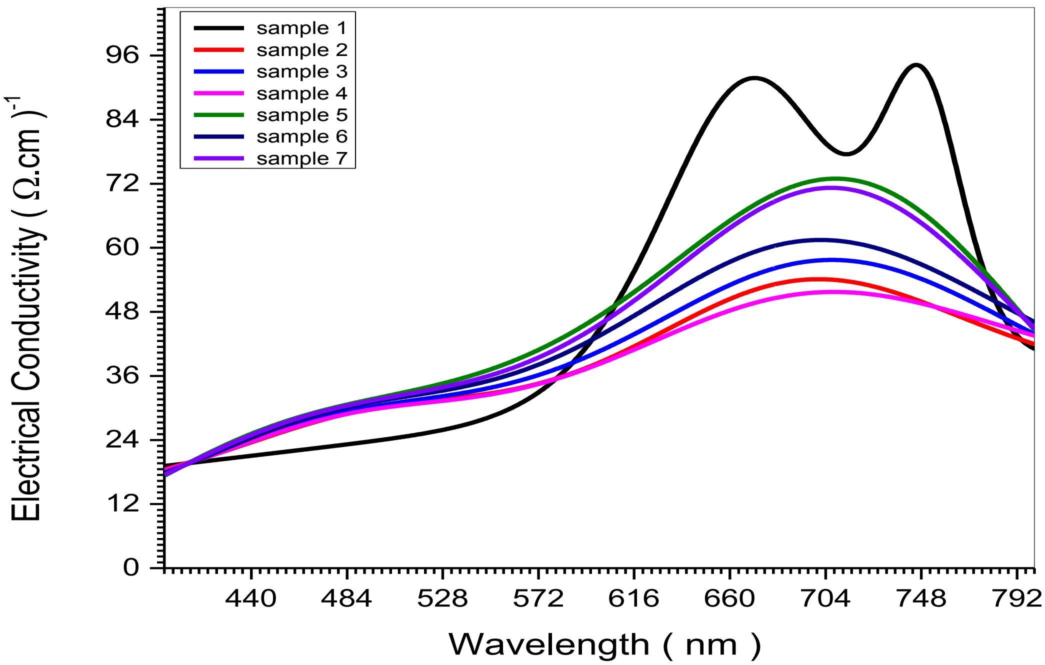

Figure (4-42) displays the Electrical conductivity of natural **rocks samples**

Real Dielectric constant (ϵ1) imaginary Dielectric constant (ϵ2) :

The dielectric constant is associated with specific materials such as those used in cable insulation, capacitors, and printed circuit board substrates. It is a complex number with the imaginary part associated with dielectric losses and the real part (Ɛr) an indication of the degree to which a material can be polarized. Our focus will be on the real portion of the dielectric constant and what it means for cable applications. the real component describes the phase lag between the driving and response frequency (slowing down of light in a material, described by the refractive index) and the imaginary component is the damping factor (loss of energy or absorption of light, described by the absorption coefficient. Here ε1 = n2-k2and ε2= 2nk form of equation were used to calculate.

The diectric costant is the efficiency of dielectric material to store the electrical energy and the dielectric loss indicates to loss of electrical enenergy as heat energy.The absorbed values shown the highest of Real dielectric constant for same in two values 8.19 and 7.09 at wavelength 668.26 nm and 744.13 nm respectively in contrast with the samples two, three, and four small values nearly their values and wavelengths have similarity but sample five, six and seven have medium values at average of 3.09. Imaginary dielectric constant results were exhibited nearly constant value at average of 3.89 and also their wavelength convergent in all sample except sample one has a high value of 4.57×10-6 , but very inconsistent with the values of other samples at 525.73 which corresponding 2.35832 eV photon energy .

Table (4.9)displays real and imaginary dielectric constant of studied minerals

Sample	Real dielectric constant(ε1)	Wavelength	Imaginary dielectric constant(ε2)×10-^{6}	Wavelength
One	8,19 7,04	668.26 744.13	4.57	525.73
Tow	2.66	681.34	3.89	415.33
Three	2.98	683.94	3.89	415.25
Four	2.40	682.59	3.91	416.05
Five	4.74	694.42	3.93	413.67
Six	3.44	682.59	3.93	415.63
Seven	4.50	693.07	3.87	414.22

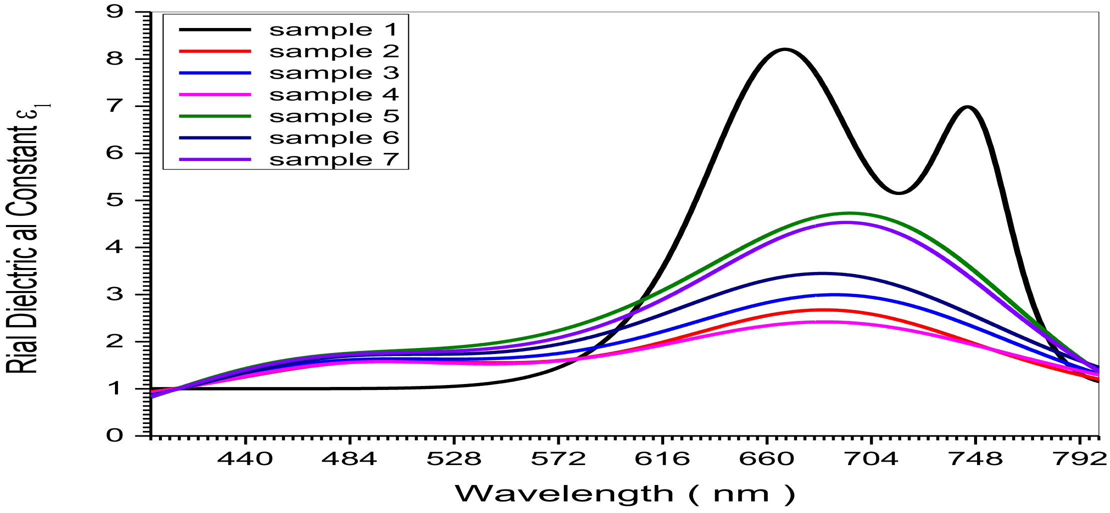

Figure (4-43) displays real dielectric constant of natural rocks samples

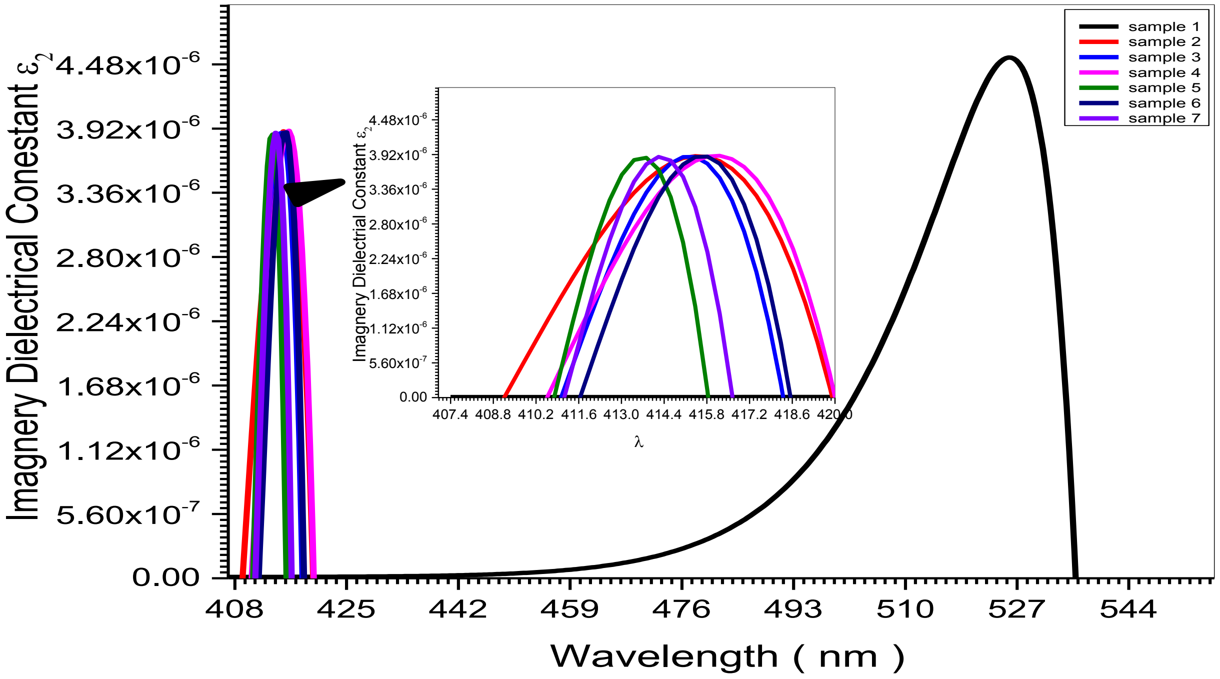

Figure (4-44) displays imaginary dielectric constant of rocks samples

5.7 Comparison Between Different Spectroscopic Techniques And Previous studies Data

Tables of comparisaon of this research and perivious studies to determine a rock as well as optical and optical properties of studied samples using different spectroscopic techniques, XRD was given better cyrtal composition and their samples pencents , futhermare the XRD rsults supperted by EDXRF analeysis which given elemental and oxides percents ,these two techinques were highly determined the origin of rock due main compostion of rock as well as specific element impurites in rock content .EDS/SEM conjacated was gave existance of many trance elements at spectrum scan areas and most EDS elecmental composition was oxygen and silicon with the standard label of SiO2 here given a slightly better match to the colesly of XRD results ,but in sample there was different due to Al2O2 has dominated ,alsa there EDS Scan showed in sample one Al (20.12wt%) and Si (18.74 wt%),Silicon and oxygen each have one the same composite symbol SiO2 in the EDS analyzes, so their combination exceeds the amount of aluminum by symbol Al2O3.LIBS was indicated existance many of elements ,the selected REE was given 20612ppm , 12679ppm, 14146 ppm and 2920ppm for Ce , Pr , Eu and Gd respectively with a total of 76457 ppm and average 19114ppm for seven rock samples this cosidered to significalty different from previeous of REE conxenteration in rock samples.FITR analyese shown many functional groups but a few absortion pesks were in fingerprint rigion probobly due to various igredaints or/and hyroxide related moleclues as well as likely due to untreated process can give difficulty of interpertation until the reak samles undergoge to the treatment processes and So that the samples are subjected to processing operations and stripping some components and impurities by scientific methods to be pure or close to the ideal sample, so that the infrared analyzes and other metallurgical analyzes are repeated to find out the functional links and the impurities associated with the metal that change some properties of the mineral after scientific treatment .Table (5.9) datail of spectroscopic data of seven rock samples

Table (5.10) Comparison of **Seven rock samples studied by spectroscopic techniques and indicted all rack samples were Quartz expect sample was exhibited as corundum mineral**

sample	EDXRF- Elemenal composition%	XRD- compound %	EDS-SEM- Element weight percent wt%	LIBS- Rare Earcth Element	FTIR- Functional group	Charactrization according to the main contents
1	A12O3(79.02%) SiO2(10.28%),SO3(4.96%) ,Fe2O3(2.27%),TiO2(1.08%) ,and CaO (1.06%)	corundum (93.2%) , Quartz (2.8%) , Muscovite(2.1%),and Biotite	O(52.81%), Al(15.66 % Si (15.65 %), K(1.01 %), Ca(11%) and Fe(2.99%)	Ce II, Gd II, Pr I, Ce I ,Eu I and Eu II	C-Ostretching S=O stretching C=C stretching O-H stretching	Cornuduom (ruby) High of Al2O3 and Red colour
2	89.78 % of Si ,0.63% of S, 5.35 of Fe and 1.38% of Ca.	Quartz (97.2%), Rutile (1.0%), Muscovite (1.6%) ,and calcite(0.2%)	O((36.60%) , Al(0.94%), Si(44.33%), and Au (18.12%)	CeI,Pr,II, Gd I , Gd II,Pr I and EuII	C-O stretching S=O stretching C=O stretching O-H stretching	Quartz –high of SiO2 Transparnce
3	Si (98.20%) ,Al(0.13%)Ca(0.02%) ,Ti(0.04%) and Fe(0.27%)	Quartz (100%)	O(44.14 %) ,Al(1.42 %)and Si(49.44%)	CeI,Pr,II, Gd I , Gd II,Pr I and EuII	C-O stretching S=O stretching C-H stretching N-H stretching	Quartz –high of SiO2 Transparnce
4	Si (98.20%) ,Al (0.19%)Ca(0.04%) ,Ti(0.41 %) , Fe(0.20%), and Cr(0.03%)	Quartz (100%)	O(46.68%) ,Mg,(0.56%),Al(13.89 %), Si (22.25%) K(0.65%),Au(14.22%)	CeI,Pr,II, Gd I , Gd II,Pr I and EuII	C-O stretching C-O stretching S=O stretching C=C stretching N-H stretching O-H stretching	Quartz –high of SiO2 Transparnce
5	Si (97.82%) ,Al (0.16%)Ca(0.03 %) ,Ti(0.02%) ,Mn(%),Fe(0.94%),Cu(%),Pd(1.11%),Cr(0.04%) , and Na(0.55%)	Quartz (100%)	(O, Mg ,Al, Si, K, Ca ,Fe ,Au) (wt.%)(46.68, 0.56, 13.89, 22.25, 0.65, 0.69, 1.04, 14.22)	CeI,Pr,II, Gd I , Gd II,Pr I and EuII	C-O stretching C=C stretching O-H stretching	Quartz – Amrthesr high of SiO2 Transparnce+barble
6	Si (41.07 %) ,Al (13.96 %)Ca(17.98%) ,Ti(0.99 %) ,Mn(1.42%),Fe(27.39 %),Cu(0.80%),Pd(0.54%),Cr(0.02 %)and Mg(3.45%)	Albite (33.8%), Anorthite (44.7), Orthopyroxene (16.3%),feldspar (5%)and Quartz (0.2%)	O(28.60%), Al(0.79%),Si(46.08 %)Au (24.88%)	CeI,Pr,II, Gd I , Gd II,Pr I and EuII	C=O stretching CO-O-CO stretching O-H stretching	Fledspar –High SiO2 and presence of anorthite and albite
7	Si (97.96 %) ,Al (1.77%)Ca(0.36 %) ,Ti(0.03 %) ,Mn(0.18 %),Fe(	Quartz (100%)	(O, Al, Si, Au) (wt.%) (36.60, 0.94, 44.33, 18.12)	Ce I,PrII, Pr I and EuII	C-O stretching CO-O-CO	Quartz –high of SiO2 Transparnce

	%),Pd(0.99%),Cr(0.07%) , and Na(0.13%)				**Stretching C=C str O-H Str**	

diffuse reflectance spectroscopy was applied to study the surface structures of rock samples the results showed samples one has better electrical and optical properties with 1.59ev energy gap and 2.9 refractive index, nearly the same of TiO2 refractive index which had 2.6 -2.9 at room temperature the most properties indicated as semiconductors characteristics range and due to existence of silicon and silicon dioxide dominated all rock ,except sample one was controlled by aluminum and Aluminium oxide . in previous sudies quartz has refractive index 1.45 and group refractive index 1.75 .in general all rock samples as transparent have a great value refractive index can govern both refraction and reflection that occur when a light passes thought into or out of material and using of optical system design and lens . Table (5.10) gives detail of optical and electrical properties of seven rock samples

Table (5 .11)Comparison of rock minerals optical and electrical properties

Sample	Physical property	High Value	Wavelength	sample	Physical property	High Value	Wavelength
1	**absorption coefficient**	53.65	525.73	5	**absorption coefficient**	56.84	413.9
	extinction coefficient	$2.88*10^{-6}$	525.73		**extinction coefficient**	$2.6*10^{-6}$	414.1
	optical energy gap	1.590	797		**optical energy gap**	1.592	776
	refractive index	2.9	666.92		**refractive index**	1.73	685.57
	optical conductivity	$1.3*10^{9}$	525.26		**optical conductivity**	$1.43*10^{9}$	707.50
	Electrical conductivity	91.79	670.86		**Electrical conductivity**	73.77	707.50
	ϵ1 ϵ2	8.19 $4.57*10-^{6}$	668.26 525.73		**ϵ1 ϵ2**	2.73 $3.93*10-^{6}$	694.42 414.22
2	**absorption coefficient**	56.9	415	6	**absorption coefficient**	56.33	415.3
	extinction coefficient	$2.8*10^{-6}$	415.1		**extinction coefficient**	$1.88*10^{-6}$	415.4
	optical energy gap	1.663	745.5		**optical energy gap**	1.598	773
	refractive index	2.19	691.92		**refractive index**	1.64	681.63
	optical conductivity	$1.43*10^{9}$	697.01		**optical conductivity**	$1.43*10^{9}$	681.6
	Electrical conductivity	54.07	697.01		**Electrical conductivity**	62.04	645.76
	ϵ1 ϵ2	2.66 $3.89*10-^{6}$	681.34 415.25		**ϵ1 ϵ2**	3.44 $3.93*10-^{6}$	682.59 415.63
3	**absorption coefficient**	57.45	414.2	7	**absorption coefficient**	57.47	413.6
	extinction coefficient	$1.88*10^{-6}$	414.22		**extinction coefficient**	$2.6*10^{-6}$	413.5
	optical energy gap	1.613	768.6		**optical energy gap**	1.632	757
	refractive index	2.10	685.57		**refractive index**	1.53	691.92
	optical conductivity	$1.43*10^{9}$	685.57		**optical conductivity**	$1.43*10^{9}$	691.90
	Electrical conductivity	57.85	699.61		**Electrical conductivity**	72.08	706.15

	ϵ1 **ϵ2**	**2.98** **$4.57*10^{-6}$**	**683.94** **416.05**		**ϵ1** **ϵ2**	**4.50** **$3.87*10^{-6}$**	**693.07** **414.22**

	Physical property	**High value**	**wavelength**
4	**absorption coefficient**	**56.13**	**414.2**
	extinction coefficient	**$2.8*10^{-6}$**	**414.2**
	optical energy gap	**1.652**	**748**
	refractive index	**1.88**	**680.09**
	optical conductivity	**$1.43*10^{9}$**	**788**
	Electrical conductivity	**51.14**	**704.90**
	ϵ1 **ϵ2**	**57.46** **2.40 $3.91*10^{-6}$**	**415.9** **416.1**

The rock samples showed different results through spectroscopic techniques, but they have similarities in determining the basic compound of any rock in a controlled quantity that determines some characteristics of the mineral in a way, and also the samples agree in the presence of certain metal oxides in certain quantities which play an important role in physical properties and depend on environmental factors. Sudanese quartz showed more purity than other countries' rocks by more than 90 percent in all the quartz samples examined similar the Nigerian quartz which had SiO2(99. o1%), while the Sudanese ruby was of less purity compared to samples from Sapphire and Ruby from Myanmar, which showed a percentage of aluminum oxide above 90 percent, while the Sudanese ruby showed less than 80 percent of aluminum oxide. Table (5.11) gives detail of different counters rocks contents and composition.

Table (5 .12) comparison between rock of different countries and studied rock samples (Sudan)

Mineral	**Country**	**Main composition**	**Techinque**
Quartz	**Nigiria**	**SiO2(99.o1%),Al2O3(0.170%),Fe2O3(0.020%),NaO(0.242%)and K2O(o.020%)**	**XRF**
Ruby	**Myanmar**	**Al2O3(91.62%) ,Fe2O3(1.221 %), Cr2O30.819%), (SO3(5.559%) ,and CaO 0.790(%)**	**XRD**
Sapphire	**Myanmar**	**Al2O3(91.43%) ,Fe2O3(4.682%) ,SO3(3.489%) and TiO2 (0.401%)**	**XRD**
Jade	**Indonesia**	**SiO2 (90.80%),Fe2O3(3.54 %), NaO (4.69%),SO3(5.559%) ,and CaO(0.780%)**	**XRF**
Quartz	**Sudan**	**Al2O3(1.19%) ,SiO2 (94.23%),Fe2O3(2.10 %), TiO2(0.039%),SO3(0.66%) ,and CaO (0.59%)**	**EDXRF**
Corundum	**Sudan**	**Al2O3(79.025%) ,SiO2 (10.28%),Fe2O3(2.27 %), TiO2(1.08 %),SO3(4.96%) ,and CaO (1.o6%)**	**EDXRF**
Corundum	**Sudan**	**Corundum 93.2 % , quartz 2.8 % muscovite 2.1% , dolomite 0.8%,and biotite 0.4%**	**XRD**
Quartz	**Sudan**	**quartz 97.2 % muscovite 1.6% , calcute 0.2%,and rutie 1.0%**	**XRD**
Hematite	**Brazil**	**O 3.78wt% , Al 4.01 wt% , P 0.54 wt% and Fe 64 wt%.**	**EDS**
Pollucite	**Vietnam**	**SiO2 (50.73%), Al2O3(29.63%) , NaO (1.89%),,Fe2O3(0.06%), SO3(0.19%), MgO(0.23%) Rb2O (0.67%)and Cs2O (16.45%)**	**EDXRF**

Chapter Six

Conclusion and future work

6.1 Conclusion

In summary, this dissertation provides an overview of electron microscopy, solid-state, and plasmatic materials. The principle, background, and associated techniques of electron microscopy are discussed in detail in the early chapters. Different case studies in later chapters have demonstrated how powerful electro-microscopy methods are to analyze the relationships between rocks samples and their advanced properties. The study primarily concentrated on characterization of Sudanese natural minerals to classify their types and sort out the most beneficial group of mineral be the source of national economic same to the gold which become the first top of public and governmental concerns so the current research highly concentrated to find out other option of economic sources besides of gold mining and provide data for current and future of natural traditional and modern mining processes. An important calculation to be drawn frames the results of studied minerals. Any spectroscopic technique has been developed to study specific characteristics in a mineral.

EDXRF analytical technique used for the elemental analysis or chemical characterization of a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum.EDXRF analysis provided the elemental composition of minerals in percent which gave the main existence content that dominated a mineral is represented the basic compound to complete form body of a mineral through the abundance of impurities and physical factors. XRD is used as a laboratory-based technique commonly used for the identification of crystalline materials, analysis of unit cell dimensions, and quantitative determination of modal amounts of minerals in a sample. The XRD given crystallography and unit cell information of the rocks samples and given of main composition names as corndum and quartz in percents EDS\SEM gave information of mineral composition as weight percent, apperance concentration standard labels and provided a microscopic image of existence impurities and main contents thrugh spectrum taken of range 50**µm** – 1mm SEMimage and given information of presence of trance element as Al ,Si ,Ca,K,Fe ,and Au . The Functional groups studied by the FTIR technique (FTIR) provide crucial information on the molecular structure of organic and inorganic components via The Functional groups. The wavenumber of each IR absorbance peak is determined by the intrinsic physicochemical properties of the corresponding molecule, and is thus diagnostic, like a fingerprint of that particular functional group like (C–H, O–H, C=O). The absorbance of molecular vibrations under IR radiation is proportional to the abundance of the functional groups. The absorbance of each vibrational band is often measured by the maximum height or the integrated area between the peak and a baseline. Diffuse Reflectance Spectroscopy (RDS) has been used as property prediction models to study physical, optical, and electrical properties have been calculated and discussed in detail based on DRS provided background through related equations. Diffuse reflectance accessories analyze a wide range of solid samples easier, faster, and more efficiently. Advanced options for diffuse reflectance provide the ability to greatly increase sample throughput

LIBS well an established technique for qualitative and quantitative analysis of different materials many kinds of physical status. LIBS has been used to study specific rare earth elements their concentration in selected minerals using LIBS spectra.

6.2 Future work and recommendations

For better mineral studying must be more plans to ensure the mining activities of precious and semi-precious gemstones path in Sudan are adequately utilized in steps to promote this sector. The study recommends the establishment of implementable policies that will help to ensure activities carried out in the field mining of rare minerals. The policies should give a comprehensive plan for more training centers, mineral identification laboratories and regulatory frameworks for the miner to avid random and illegal artisanal mining activities risks as well as engorge the miners to take confidence in government efforts to achieve intended targeted economic benefits and preservation of the environment.

The term semi-precious applies to the material of the natural origin including minerals and rock in complex crystalline aggregates or amorphous forms resembling gemstone or precious minerals. The word gem or gemstone uses for economic and aesthetic value purposes of jewelry grade stones like diamonds, emeralds, sapphires, and rubies based on their quality and beauty. These concepts may need the effort to know more about the minerals and their background and the government should support the existing gemological institutions in the training of artisanal and small-scale miners, cutters, and jewelers to improve the quality of the products and encourage the participants to establish the local market for the gem or precious business to increase country's economic resources.

End .

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