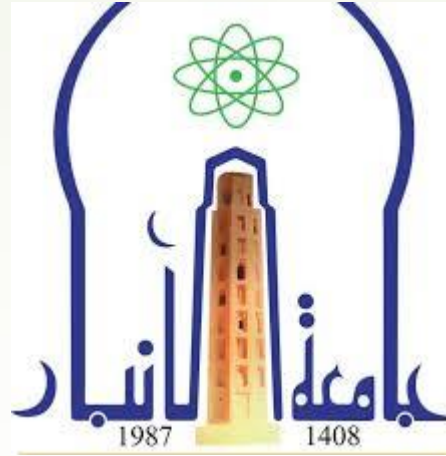


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Minerals / 1<sup>st</sup> stage.



# OXIDE, HALIDES AND SULFIDE MINERALS

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# OXIDE, HALIDES AND SULFIDE MINERALS



LECTURE SIX



# OXIDE MINERALS

The oxide mineral class includes those minerals in which the oxide anion ( $O^{2-}$ ) is bonded to one or more metal alloys. The **hydroxide**-bearing minerals are typically included in the oxide class. The minerals with complex anion groups such as the silicates, sulfates, carbonates and phosphates are classed separately.

Oxides contain one or two metal elements combined with oxygen. Many important metals are found as oxides. Hematite ( $Fe_2O_3$ ), with two iron atoms to three oxygen atoms, and magnetite ( $Fe_3O_4$ ) .with three iron atoms to four oxygen atoms, are both iron oxides.

The oxide minerals can be grouped as simple oxides and multiple oxides. Simple oxides are a combination of one metal or semimetal and oxygen, whereas multiple oxides have two nonequivalent metal sites. The oxide structures are usually based on cubic or hexagonal close-packing of oxygen atoms with the octahedral or tetrahedral sites (or both) occupied by metal ions; symmetry is typically isometric, hexagonal, tetragonal, or orthorhombic.

**Oxides:** Metals + oxygen

- **Hydroxides:** Brucite ( $\text{Mg}(\text{OH})_2$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ )
- $\text{OH}^-$ : arrange in planes
- Cation (Mg or Al): octahedral sites between the anion planes.
- **Oxides and hydroxides**
- These classes consist of oxygen-bearing minerals; the oxides combine oxygen with one or more metals, while the hydroxides are characterized by hydroxyl ( $\text{OH}^-$ ) groups.

- The oxides are further divided into two main types: **simple and multiple**. Simple oxides contain a single metal combined with oxygen in one of several possible metal: oxygen ratios (X:O): XO, X<sub>2</sub>O, X<sub>2</sub>O<sub>3</sub>, etc. Ice, H<sub>2</sub>O, is a simple oxide of the X<sub>2</sub>O type that incorporates hydrogen as the cation. Although SiO<sub>2</sub> (quartz and its polymorphs) is the most commonly occurring oxide, it is discussed below in the section on silicates because its structure more closely resembles that of other silicon–oxygen compounds. Two nonequivalent metal sites (X and Y) characterize multiple oxides, which have the form XY<sub>2</sub>O<sub>4</sub>.

### 1- **Simple oxides :-**

- X<sub>2</sub>O and XO group: Ice (H<sub>2</sub>O), Zincite, (ZnO)
- X<sub>2</sub>O<sub>3</sub> group: Hematite (Fe<sub>2</sub>O<sub>3</sub>), Ilmenite (FeTiO<sub>3</sub>), Corundum (Al<sub>2</sub>O<sub>3</sub>)
- XO<sub>2</sub> group: Rutile(TiO<sub>2</sub>)

### 2-**Multiple oxide:**

Spinel group: XY<sub>2</sub>O<sub>4</sub>:

spinel series MgAl<sub>2</sub>O<sub>4</sub>

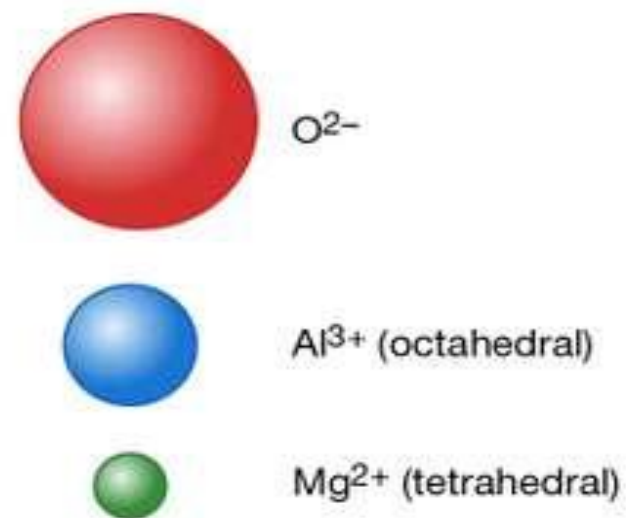
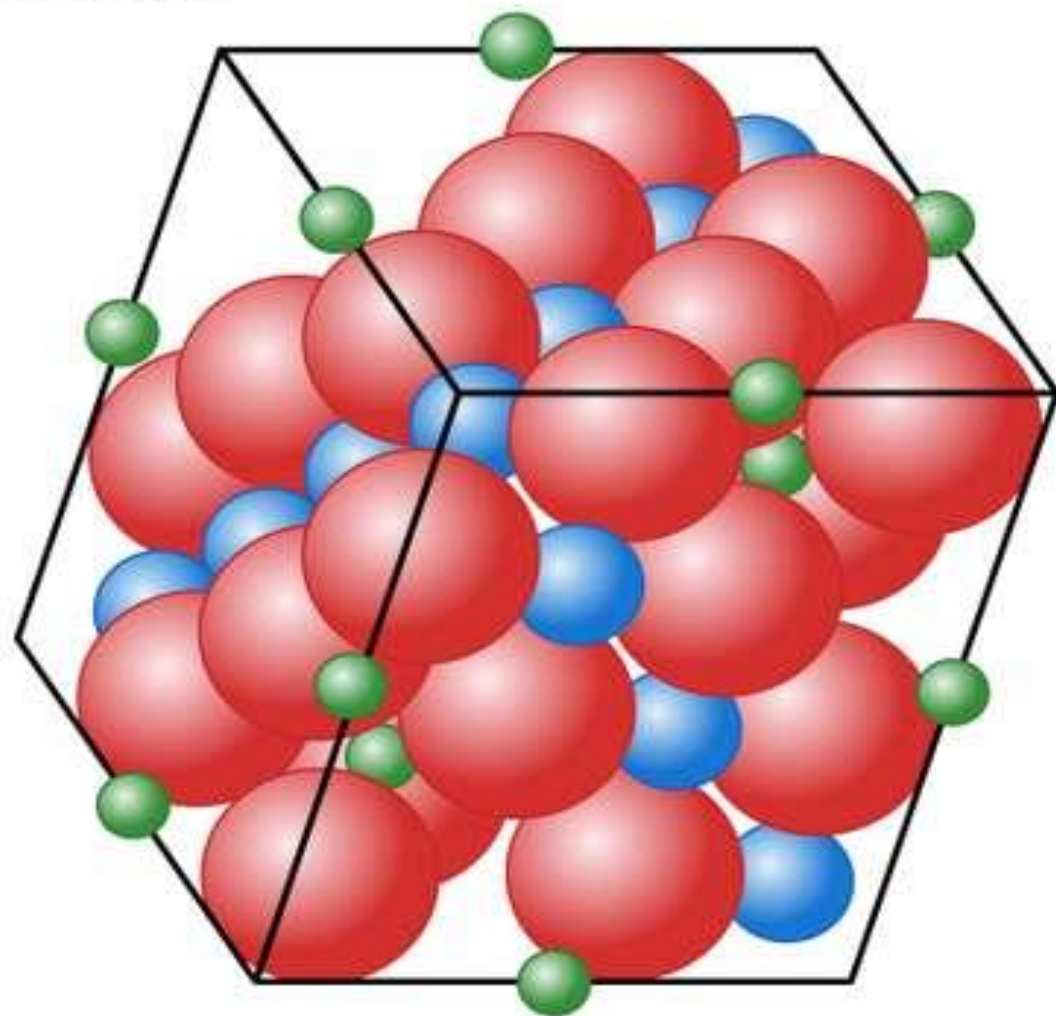
chromite series (Fe,Mg)Cr<sub>2</sub>O<sub>4</sub>

Magnetite series (FeFe<sub>2</sub>O<sub>4</sub>)

- Unlike the minerals of the sulfide class, which exhibit ionic, covalent, and metallic bonding, oxide minerals generally display strong ionic bonding. They are relatively hard, dense, and refractory.
- Oxides generally occur in small amounts in **igneous** and **metamorphic** rocks and also as preexisting grains in **sedimentary** rocks. **Several oxides have great economic value, including the principal ores of iron (hematite and magnetite), chromium (chromite), manganese (pyrolusite, as well as the hydroxides, manganite and romanechite), tin (cassiterite), and uranium (uraninite).**
- Members of the hematite group are of the **X<sub>2</sub>O<sub>3</sub> type** and have structures based on hexagonal closest packing of the oxygen atoms with octahedrally coordinated (surrounded by and bonded to six atoms) cations between them. Corundum and hematite share a common hexagonal architecture. In the ilmenite structure, iron and titanium occupy alternate Fe-O and Ti-O layers.

- **The  $XO_2$ -type** oxides are divided into two groups. The first structure type, exemplified by rutile, contains cations in octahedral coordination with oxygen. The second resembles fluorite ( $CaF_2$ ); each oxygen is bonded to four cations located at the corners of a fairly regular tetrahedron, and each cation lies within a cube at whose corners are eight oxygen atoms. This latter structure is exhibited by uranium, thorium, and cerium oxides, whose considerable importance arises from their roles in nuclear chemistry.
- The spinel-group minerals have **type  $XY_2O_4$**  and contain oxygen atoms in approximate cubic closest packing. The cations located within the oxygen framework are octahedrally (sixfold) and tetrahedrally (fourfold) coordinated with oxygen.

## Spinel structure



Cubic packing of a spinel mineral composed of magnesium aluminum oxide (MgAl<sub>2</sub>O<sub>4</sub>)



- The (OH)<sup>-</sup> group of the hydroxides generally results in structures with lower bond strengths than in the oxide minerals. The hydroxide minerals tend to be less dense than the oxides and also are not as hard. All hydroxides form at low temperatures and are found predominantly as weathering products, as, for example, from alteration in hydrothermal veins. Some common hydroxides are brucite [Mg(OH)<sub>2</sub>], manganite [MnO · OH],

# Magnetite

*Chemical classification:-*

*Oxide Mineral*

*Formula :-  $Fe_3O_4$*

- **Color** is black.
- **Luster** is metallic to dull.
- **Transparency:** Crystals are opaque.
- **Crystal System** is isometric;  $4/m\bar{3}2/m$
- **Crystal Habits** are typically octahedrons
- **Cleavage** is absent although octahedral parting can be seen on some specimens.
- **Fracture** is conchoidal.
- **Hardness** is 5.5 - 6.5
- **Specific Gravity** is 5.1+ (average for metallic minerals)
- **Streak** is black.



# Hematite

*Chemical classification:-*

*Oxide Mineral*

*Formula :-  $Fe_3O_4$*

- **Color** is steel or silver gray to black in some forms and red to brown in earthy forms.
- **Luster** is metallic or dull in earthy. **Transparency:** Crystals are opaque.
- **Crystal System** is trigonal; bar  $3 2/m$ .
- **Cleavage** is absent.
- **Fracture** is uneven.
- **Hardness** is 5 - 6
- **Specific Gravity** is 5.3
- **Streak** is blood red to brownish red for earthy forms



# • HALIDE MINERAL

The **Halides** are a group of minerals whose principle anions are halogens. Halogens are a special group of elements that usually have a charge of negative one when chemically combined.

The halogens that are found commonly in nature include **Fluorine, Chlorine, Iodine and Bromine**. ( $F^-$ ,  $Cl^-$ ,  $I^-$  and  $Br^-$ ). Halides tend to have rather simply ordered structures and therefore a high degree of symmetry. The most famous halide mineral, halite ( $NaCl$ ) or rock salt has the highest symmetry  $4/m \bar{3} 2/m$ . The colorful mineral fluorite ( $CaF_2$ ) also has  $4/m \bar{3} 2/m$  symmetry and its cubic crystals are very popular mineral specimens. There are only a few common halide minerals. The typical halide mineral is soft, can be transparent, is generally not very dense, has good cleavage, and often has bright colors.

- Halide minerals are salts that form when salt water evaporates. Halite is a halide mineral, but table salt is not the only halide. The chemical elements known as the halogens (fluorine, chlorine, bromine, or iodine) bond with various metallic atoms to make halide minerals



- **Halides**

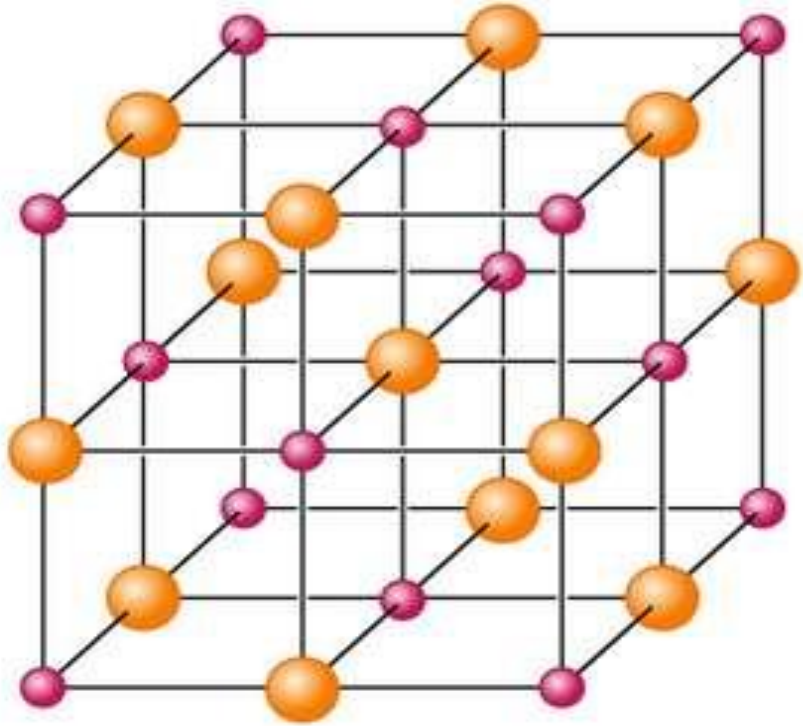
- Pure ionic bonding is exemplified best in the isometric halides, for each spherical ion distributes its weak electrostatic charge over its entire surface. These halides manifest relatively low hardness and moderate-to-high melting points. In the solid state they are poor thermal and electric conductors, but when molten they conduct electricity well.
- Halogen ions may also combine with smaller, more strongly polarizing cations than the alkali metal ions. Lower symmetry and a higher degree of covalent bonding prevail in these structures. Water and hydroxyl ions may enter the structure, as in atacamite  $[\text{Cu}_2\text{Cl}(\text{OH})_3]$ .

- The halides consist of about 80 chemically related minerals with diverse structures and widely varied origins. The most common are halite (NaCl), sylvite (KCl), chlorargyrite (AgCl), cryolite (Na<sub>3</sub>AlF<sub>6</sub>), fluorite (CaF<sub>2</sub>), and atacamite. No molecules are present among the arrangement of the ions in halite, a naturally occurring form of sodium chloride. Each cation and anion is in octahedral coordination with its six closest neighbours. The NaCl structure is found in the crystals of many XZ-type halides, including sylvite (KCl) and chlorargyrite (AgCl). Some sulfides and oxides of XZ type crystallize in this structure type as well—for example, galena (PbS), alabandite (MnS), and periclase (MgO).

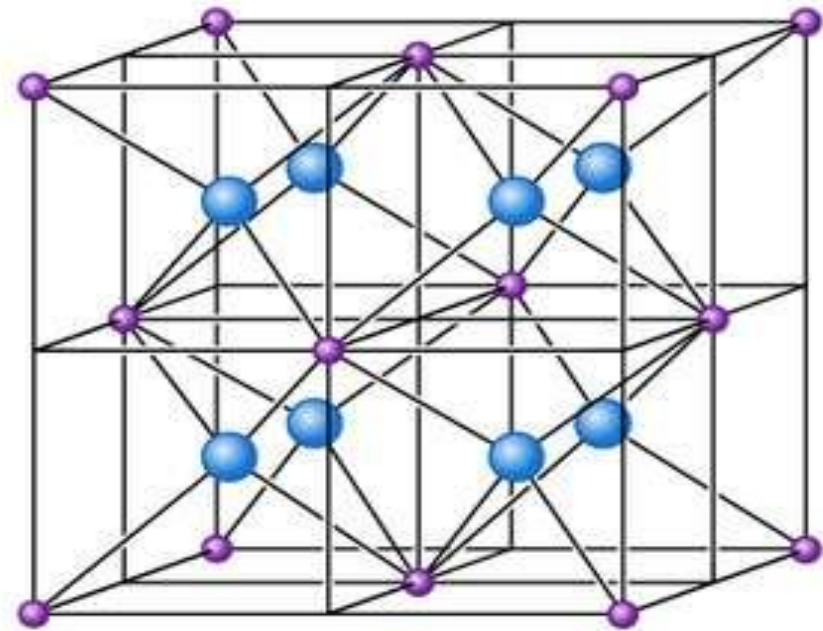
- Several  $XZ_2$  halides have the same structure as fluorite ( $CaF_2$ ). In fluorite, calcium cations are positioned at the corners and face centers of cubic unit cells. (A unit cell is the smallest group of atoms, ions, or molecules from which the entire crystal structure can be generated by its repetition.) Each fluorine anion is in tetrahedral coordination with four calcium ions, while each calcium cation is in eightfold coordination with eight fluorine ions that form the corners of a cube around it. Uraninite ( $UO_2$ ) and thorianite ( $ThO_2$ ) are two examples of the several oxides that have a fluorite-type structure.

## Mineral structures: halite and fluorite

halite  
(NaCl)



fluorite  
(CaF<sub>2</sub>)





- Many of the halide minerals occur in marine evaporite deposits. Other geologic occurrences include arid environments such as deserts. The Atacama Desert has large quantities of halide minerals as well as chlorates, iodates, oxyhalides, nitrates, borates and other water-soluble minerals. Not only do those minerals occur in subsurface geologic deposits, they also form crusts on the Earth's surface due to the low rainfall (the Atacama is the world's driest desert as well as one of the oldest at 25 million years of age)

## *Physical Properties of Halite*

<i>Chemical Classification</i>	<i>Halide</i>
<i>Color</i>	<i>Colorless or white when pure; impurities produce any color but usually yellow, gray, black, brown, red</i>
<i>Streak</i>	<i>White</i>
<i>Luster</i>	<i>Vitreous</i>
<i>Diaphaneity</i>	<i>Transparent to translucent</i>
<i>Cleavage</i>	<i>Perfect, cubic, three directions at right angles</i>
<i>Mohs Hardness</i>	<i>2.5</i>
<i>Specific Gravity</i>	<i>2</i>
<i>Diagnostic Properties</i>	<i>Cleavage, solubility, salty taste (The taste test is discouraged. Some minerals are toxic or contaminated by other people tasting them.)</i>
<i>Chemical Composition</i>	<i>NaCl</i>
<i>Crystal System</i>	<i>Isometric</i>
<i>Uses</i>	<i>Winter road treatment, a source of sodium and chlorine for chemical processes, food preservation, seasoning</i>



## *Physical Properties of Fluorite*

<i>Chemical Classification</i>	<i>Halide</i>
<i>Color</i>	<i>Typically purple, green, and yellow. Also colorless, blue, red, and black.</i>
<i>Streak</i>	<i>White</i>
<i>Luster</i>	<i>Vitreous</i>
<i>Diaphaneity</i>	<i>Transparent to translucent</i>
<i>Cleavage</i>	<i>Four directions of perfect cleavage</i>
<i>Mohs Hardness</i>	<i>4</i>
<i>Specific Gravity</i>	<i>3.2</i>
<i>Diagnostic Properties</i>	<i>Cleavage, hardness, specific gravity, color</i>
<i>Chemical Composition</i>	<i>CaF<sub>2</sub></i>
<i>Crystal System</i>	<i>Isometric(Cubic)</i>
<i>Uses</i>	<i>Numerous uses in the metallurgical, ceramics, and chemical industries. A source of fluorine, hydrofluoric acid, metallurgical flux. High-clarity pieces are used to make lenses for microscopes, telescopes, and cameras.</i>



# SULFIDE MINERALS

- Sulfides are formed when metallic elements combine with sulfur. Unlike sulfates, sulfides do not contain oxygen. Pyrite, or iron sulfide, is a common sulfide mineral known as *fool's gold*. People may mistake pyrite for gold because the two minerals are shiny, metallic, and yellow in color.
- The **sulfide minerals** are a class of minerals containing sulfide ( $S^{2-}$ ) or persulfide ( $S_2^{2-}$ ) as the major anion . Some sulfide minerals are economically important as metal ores. **The sulfide class also includes the selenides, the tellurides , the arsenides , the antimonides, the bismuthinides,** the sulfarsenides and the sulfosalts. Sulfide minerals are inorganic compounds.



- **This important class includes most of the ore minerals.** The similar but rarer sulfarsenides are grouped here as well. Sulfide minerals consist of one or more metals combined with sulfur; **sulfarsenides contain arsenic replacing some of the sulfur.**
- Sulfides are generally opaque and exhibit distinguishing colors and streaks. (Streak is the color of a mineral's powder.) The non opaque varieties (e.g., cinnabar, realgar, and orpiment) possess high refractive indices, transmitting light only on the thin edges of a specimen.

- Few broad generalizations can be made about the structures of sulfides, although these minerals can be classified into smaller groups according to similarities in structure. Ionic and covalent bonding are found in many sulfides, while metallic bonding is apparent in others as evidenced by their metal properties. The simplest and most symmetric sulfide structure is based on the architecture of the sodium chloride structure. A common sulfide mineral that crystallizes in this manner is the ore mineral of lead, galena. Its highly symmetric form consists of cubes modified by octahedral faces at their corners. The structure of the common sulfide pyrite ( $\text{FeS}_2$ ) also is modeled after the sodium chloride type; a disulfide grouping is located in a position of coordination with six surrounding ferrous iron atoms. The high symmetry of this structure is reflected in the external morphology of pyrite. In another sulfide structure, sphalerite ( $\text{ZnS}$ ), each zinc atom is surrounded by four sulfur atoms in a tetrahedral coordinating arrangement.

- Sulfides occur in all rock types. Except for dissemination in certain sedimentary rocks, these minerals tend to occur in isolated concentrations which make up mineral bodies such as veins and fracture fillings or which comprise replacements of preexisting rocks in the shape of blankets. Sulfide mineral deposits originate in two principal processes, both of which have reducing conditions: (1) separation of an immiscible sulfide melt during the early stages of crystallization of basic magmas; and (2) deposition from aqueous brine solutions at temperatures in the 300–600° C (572–1,112° F) range and at relatively high pressure, such as at the seafloor or several kilometres beneath Earth's surface

# *Physical Properties of **Pyrite***

<i>Chemical Classification</i>	<i>Sulfide</i>
<i>Color</i>	<i>Brass yellow - often tarnished to dull brass</i>
<i>Streak</i>	<i>Greenish black to brownish black</i>
<i>Luster</i>	<i>Metallic</i>
<i>Diaphaneity</i>	<i>Opaque</i>
<i>Cleavage</i>	<i>Breaks with a conchoidal fracture</i>
<i>Mohs Hardness</i>	<i>6 to 6.5</i>
<i>Specific Gravity</i>	<i>4.9 to 5.2</i>
<i>Diagnostic Properties</i>	<i>Color, hardness, brittle, greenish black streak, specific gravity</i>
<i>Chemical Composition</i>	<i>Iron sulfide, <math>FeS_2</math></i>
<i>Crystal System</i>	<i>Isometric (Cubic)</i>
<i>Uses</i>	<i>Ore of gold</i>



# *Physical Properties of Galena*

<i>Chemical Classification</i>	<i>Sulfide</i>
<i>Color</i>	<i>Fresh surfaces are bright silver in color with a bright metallic luster, tarnishes to a dull lead gray</i>
<i>Streak</i>	<i>Lead gray to black</i>
<i>Luster</i>	<i>Metallic on fresh surfaces, tarnishes dull</i>
<i>Diaphaneity</i>	<i>Opaque</i>
<i>Cleavage</i>	<i>Perfect, cubic, three directions at right angles</i>
<i>Mohs Hardness</i>	<i>2.5+</i>
<i>Specific Gravity</i>	<i>7.4 to 7.6</i>
<i>Diagnostic Properties</i>	<i>Color, luster, specific gravity, streak, cleavage, cubic or octahedral crystals.</i>
<i>Chemical Composition</i>	<i>Lead sulfide, PbS</i>
<i>Crystal System</i>	<i>Isometric</i>
<i>Uses</i>	<i>An ore of lead</i>





# Native minerals

Minerals that are composed of atoms from a single element are referred to as **native elements**

## Graphite

Chemical classification:-

Native elements

Formula :- C



<b>Color</b>	<b>Steel gray to black</b>
<b>Streak</b>	<b>Black</b>
<b>Luster</b>	<b>Metallic, sometimes earthy</b>
<b>Cleavage</b>	<b>Perfect in one direction</b>
<b>Diaphaneity</b> (transparency)	<b>Opaque</b>
<b>Mohs Hardness</b>	<b>1 to 2</b>
<b>Crystal System</b>	<b>Hexagonal</b>
<b>Tenacity</b>	<b>Flexible</b>
<b>Density</b>	<b>2.09 – 2.23 g/cm<sup>3</sup></b> <b>(Measured) 2.26 g/cm<sup>3</sup></b> <b>(Calculated)</b>
<b>Fracture</b>	<b>Micaceous</b>

# Copper

Chemical classification:-

*Native elements*

Formula :- *Cu*



<i>Color</i>	<i>Copper red on a fresh surface, dull brown on a tarnished surface</i>
<i>Streak</i>	<i>Metallic copper red</i>
<i>Luster</i>	<i>Metallic</i>
<i>Cleavage</i>	<i>None</i>
<i>Diaphaneity(transparency)</i>	<i>Opaque</i>
<i>Mohs Hardness</i>	<i>2.5 to 3</i>
<i>Specific Gravity</i>	<i>8.9</i>
<i>Crystal System</i>	<i>Isometric</i>
<i>Tenacity</i>	<i>Malleable</i>
<i>Fracture</i>	<i>Hackly</i>
<i>Density</i>	<i>8.94 – 8.95 g/cm<sup>3</sup> (Measured) 8.93 g/cm<sup>3</sup> (Calculated)</i>

# REFERENCES

S. K. HALDAR & JOSIP TISLJAR 2013, INTRODUCTION TO MINERALOGY AND PETROLOGY - Elsevier 225 Wyman Street, Waltham, MA 02451, USA Publishers . 341 p. ➤

Blackburn, W.H. and Dennen, W.H., 1988, Principles of Mineralogy: Iowa, WCB Publishers . 413 p. ➤

ابراهيم مضوي بابكر. ٢٠٠٤. علم المعادن، جامعة النيلين، كتاب منشور. ٢٣٢ ص ➤