LECTURE 3

OPTICAL PROPERTIES AND MINERALOGICAL DETERMINATIONS

3.1 LECTURE OUTLINE
Welcome to lecture 3. In this lecture you will learn some optical properties of minerals and mineralogical determinations using both the transmitted light (petrological) and reflecting microscope. You are going to learn about reflection and refraction of light and about Snell’s Law of Refraction. You are going to learn the characteristic optical properties of isotropic and anisotropic substances and how their refractive indices vary with their crystallographic vibration directions. You will learn how to derive the optical indicatrix and how you can use it to distinguish between isotropic, uniaxial and biaxial crystals. You are going to learn how to determine characteristic optical interference figures that are used to distinguish between isotropic and anisotropic minerals. You will learn how to determine the refractive index of isotropic (or non-opaque) substances using the immersion method. Finally you will be introduced to the scientific analytical technique and identification of minerals using the X-ray diffraction method.

At the end of this lecture you will be able to:

- State the Law of Reflection and Refraction and define Snell’s Law of Refraction.
- Explain the differences between isotropic and anisotropic minerals using the optical indicatrix.
- Distinguish isotropic and anisotropic minerals using the petrological microscope.
- Determine whether an anisotropic mineral is uniaxial or biaxial using characteristic interference figures.
- Determine the refractive index of isotropic or non-opaque substances using the immersion method.
- Explain the use of the X-ray diffraction method for mineral analysis and identification.
3.2. REFLECTION AND REFRACTION

When a ray of light in air impinges obliquely on the surface of a non opaque solid, part of the light is reflected back into air (the reflected ray) and part enters the solid (the refracted ray) as indicated in Figure 3.1.

![Figure 3.1 Refraction and Reflection of a light ray at an interface; i = angle of incidence, r = angle of refraction, r' = angle of reflection.](image)

The direction of the reflected ray is governed by the **Law of Reflection**, which states that the angle of reflection $r$ is equal to the angle of incidence $i$ and that the reflected and incident rays lie in the same plane. The light that passes into the solid is known as the refracted ray since its path is bent or refracted from the path of the incident ray. The relationship between the paths of the incident and refracted rays is known as the **Law of Refraction**, or **Snell's Law**, having been discovered in about 1621 by Willebrod Snellius (1591-1626), professor of mathematics at Leyden in Holland. It states that for any given substance, the index of refraction $n$ can be defined as follows:

**Index of refraction $n$:** the ratio of the sine of the angle of incidence $i$ to the sine of the angle of refraction $r$:

$$n = \frac{\sin i}{\sin r}$$
It was later proved that the index of refraction is also the ratio of the velocity of light in air to the velocity of light in the solid, so that if $V$ is the velocity of light in air, and $v$ the velocity in the solid, then

$$n = \frac{V}{v}$$

The velocity of light in air is 300,000 km sec$^{-1}$. Hence, if the velocity of light in a particular substance is 200,000 km sec$^{-1}$, then the refractive index $n$ of that substance is $= 300,000/200,000$ or 1.5. Note that most solids have refractive indices that range between 1.4 and 2.0.

### 3.3 Optical Properties and Crystal Structure

#### 3.3.1 Isotropic and Anisotropic Minerals

There is a close connection between optical properties and the crystal structure of a solid. In isometric and non-crystalline (or amorphous) substances, the velocity of light is the same in all directions, and hence the refractive index is the same for all directions. Such substances are said to be optically isotropic. In other substances, the velocity of light varies according to its direction of vibration. Such substances are said to be optically anisotropic.

A ray of light entering an anisotropic substance is split into two rays vibrating at right angles to each other, generally traveling with different velocities and thus having different refraction indices. The difference in refractive indices, known as birefringence, is typically quite small (e.g. quartz it is 0.009) and essentially unobservable except for instruments. In some minerals, however, the difference is relatively large (e.g. for calcite is 0.172).

#### 3.3.2 Optical Indicatrix

The relationship between refractive indices and crystallography can be best visualized by extending lines in all directions from the center of a crystal or a crystalline grain with the
length of each line proportional to the refractive index for that vibration direction. The resulting figure is known as the indicatrix (see Figure 3.2). For non-crystalline and isometric substances, the form of the indicatrix is a sphere since the refractive index is the same in all directions (Figure 3.2 (a)).

![Figure 3.2. The optical indicatrix for (a) isotropic, (b) uniaxial, (c) biaxial substances.](image)

With reference to Figure 3.2, (a) is the indicatrix represented by a sphere whose radius is proportional to $n$, the refractive index of the substance. In (b) the indicatrix is a rotation ellipsoid, the horizontal equatorial section being a circle with radius proportional to $\omega$, one of the principle refractive indices, and with the vertical axis proportional to $\epsilon$, the other principle refractive index; $\epsilon$ may be greater or less than $\omega$, and its vibration direction is always parallel to the $c$ crystallographic axis. In (c), the indicatrix is a triaxial ellipsoid, the lengths of the principal axes being proportional to $\alpha$, the smallest index of refraction in the substance, $\gamma$, the greatest index, and $\beta$, the intermediate index. In (d) is represented the $\alpha\gamma$-section of the ellipsoid; AA and BB are the optic axes, at right angles to the two circular sections of radius $\beta$.

### 3.3.3 Indicatrix for Tetragonal and Hexagonal systems

For substances crystallizing in the tetragonal and hexagonal systems, the indicatrix has the form of a rotation ellipsoid in which all sections perpendicular to one axis are circular, this
axis coinciding with the c-axis of the crystal. This form results from the fact that all rays traveling in the direction of the c-axis have the same velocity since their vibrations are in the plane of the horizontal axes, which are equivalent in these systems. For this reason, substances crystallizing in the tetragonal and hexagonal are said to be uniaxial (see Figure 3.2 (b)).

### 3.3.4 Indicatrix for Orthorhombic, Monoclinic and Triclinic systems

For substances crystallizing in the orthorhombic, monoclinic and triclinic systems, the indicatrix has lower symmetry, in agreement with the lower crystallographic symmetry. It gives a **triaxial ellipsoid**. A property of such an ellipsoid is that it has only two circular sections, all the others being ellipses. Rays traveling at right angles to the circular sections have the same velocity no matter what the direction of vibration in these sections. The two directions at right angles to the circular sections are known as the **optic axes**. For this reason, orthorhombic, monoclinic, and triclinic substances are said to be optically biaxial (see Figure 3.2 (c)).

Because the optical properties of a substance are so closely related to its crystallographic symmetry, optical studies have been used widely to determine the crystal system of minerals that do not occur in well-formed crystals.

Explain the use of the optical indicatrix to differentiate isotropic and anisotropic minerals.
3.4 OPTICAL MINERALOGICAL DETERMINATIONS

The general relationship between crystal structure and optical properties is summarized in Table 3.1. As indicated by the table, the most useful optical properties for identifying most minerals are optical class and refractive index.

Table 3.1. Correlation of crystal systems and optical classes.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Optical Class</th>
<th>Refraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isometric</td>
<td>Isotropic</td>
<td>Single refractive index</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>Anisotropic</td>
<td>Uniaxial (+ or -)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Anisotropic</td>
<td>Uniaxial (+ or -)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Anisotropic</td>
<td>Biaxial (+ or -)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Anisotropic</td>
<td>Biaxial (+ or -)</td>
</tr>
<tr>
<td>Triclinic</td>
<td>Anisotropic</td>
<td>Biaxial (+ or -)</td>
</tr>
</tbody>
</table>

Given the importance of these two optical parameters (i.e., optical class and refractive index) in the identification of minerals, it is imperative for us to learn the techniques or methods of their determination as outlined in section 3.4.1 and 3.4.2.

3.4.1 Determination of Optical Class

Anisotropic substances are easily distinguished from isotropic substances when grain mounts are observed in the polarizing microscope with the analyzer inserted. Liquids and isotropic substances are dark and remain so upon rotation of the microscope stage, whereas most anisotropic grains show interference colors and become dark (extinguish) four times at intervals of 90° in a complete rotation of the stage.

To determine whether an anisotropic mineral (or other material) is uniaxial or biaxial, the usual procedure is to find a grain that will give a definitive interference figure. Differently oriented grains exhibit different interference figures, most of which can be used once you become a competent optical mineralogist. However, as a beginning student, you are strongly
recommended to first familiarize yourself with the group of figures referred to as **optic figures** before you go on to other types of figures.

The **optic figures** are usually given by grains that show very weak interference colors (i.e., they appear dark grey) even at 45° from their extinction positions. To obtain an interference figure we must observe the grain *between crossed polarizers, in strongly convergent light, and with a high-power objective lens*. This means that the analyzer is inserted, the substage convergent lens is moved into place, and a 40X to 50X objective lens is used. The interference figure is then seen when the ocular lens is removed or the accessory Bertrand lens is inserted. For a uniaxial substance, the figure is a black cross (Figure 3.3(a)). For a biaxial substance, the figure may have any of several diverse appearances, such as those illustrated in Figures 3.3 b, c, and d.

![Figure 3.3. Optic axis figures. (a) Uniaxial figure; (b) biaxial figure exhibiting a small 2V; (c) biaxial figure, moderate 2V; (d) biaxial figure, large 2V.](image-url)
The darkened areas – the uniaxial cross and the biaxial bars – are both referred to as isogyres. The curvature of the biaxial isogyres is an expression of the angle between the optic axes, generally designated as 2V (see Figure 3.4).

The optical character – that is, whether the mineral is positive or negative – can be determined from these interference figures by using an accessory plate. For example, if a gypsum plate is inserted, the isogyre (black cross) of a uniaxial figure becomes purplish red, and opposite pairs of quadrants are colored blue and yellow directly adjacent to the area of the isogyres. The relative positions of the blue and yellow spots indicate the optic sign (see Figures 3.5 (a) and (b). As the diagrams in Figures 3.5 (c) and (d) indicate, interpretations of the effects of a gypsum plate on biaxial interference figures, no matter what their axial angles, also follow a similar logical pattern.

The gypsum plate (or the sensitive tint plate) is an accessory plate used to aid observations between closed polars in a microscope. The plate is used for determining (i) optic sign and (ii) the fast and slow directions for elongated minerals.

You will learn more about the usage of the sensitive plate in lecture 4.
Figure 3.5. Optic sign determination. Accessory plate (gypsum) has its slow ray vibration direction NE-SW. Lined pattern indicates yellow; light stippling indicates blue; dark stippling indicates position of isogyres. (a) uniaxial negative; (b) uniaxial positive; (c) biaxial negative; (d) biaxial positive.

### 3.4.2 Determination of Refractive Index

Each mineral has a characteristic index (or indices) of refraction. Consequently, the determination of refractive index values constitutes a frequently used procedure in mineral identification.

Of the several techniques available for such determinations, the immersion method has found the most general application and the widest use. This method is a comparative procedure whereby the mineral (or other non-opaque crystalline solid) is immersed in liquids of known refractive index until a match is found. It is an extremely powerful method because it can be applied to minute grains, and it is available to anyone who has access to a microscope and a set of liquids of known refractive indices.

Sets of specially prepared index oils can be procured from many scientific supply houses. Indices for several liquids are listed in the *Handbook of Chemistry and Physics.*
The technique of measuring the refractive index of a non-opaque, isotropic mineral is extremely simple. All you need to do is to find a liquid of known refractive index as the mineral. When mineral grains are immersed in a liquid with the same refractive index, the grains become practically invisible; that is, light, in passing from the liquid into the solid and from the solid into the liquid, is not refracted, so the edges of the solid grains cannot be seen. The whole liquid-solid mixture acts as a homogeneous medium in its effect on light.

The procedure is to immerse the mineral particles in a drop or so of a liquid of known refractive index on a glass slide, and to observe the grains under low or moderate magnification (e.g., 7.5X ocular and 10X objective lenses) with transmitted light. If the grains are invisible, or nearly so, the mineral has the same, or nearly the same, index of refraction as the liquid; if the grains show up plainly, their refractive index differs considerably from that of the liquid. Hence, in the latter case, other liquids of different refractive indices are tried until a liquid is found in which the grains are invisible or very nearly so, and hence the index of refraction of the grains becomes known.

The search for the matching liquid is not as laborious and time-consuming as one might suppose because it is possible, by observing the Becke line effect (see Figure 3.6), to tell whether the refractive index of the liquid is higher or lower than that of the mineral.

![Becke Line](image)

Figure 3.6. The Becke Line. After careful focusing, upon raising the tube of the microscope (or lowering the stage), the Becke line moves into the medium with the higher index (a), (b), (c).

A more detailed discussion on the Becke test is provided in the next lecture, Lecture 4, section 4.3.1.5
3.5 X-RAY DIFFRACTION ANALYSIS

The effects of X-ray diffraction by mineral structures constitute the basis of a generally applicable method for identifying minerals and other crystalline substances. X-ray diffraction method plays a vital analytical role in scientific research institutions. This technique is currently being used by various research institutions and even more by industry for the purpose of process and quality control. Through X-ray diffractometry, the constituent compounds in almost any solid material can be identified quickly and accurately.

3.5.1 The Technique

The x-ray diffractometry works on the principle that, when a sample is irradiated, the x-rays are diffracted in a way that is characteristic of the compounds present in the sample under analysis. By measuring the angles at which diffraction peaks occurs and their intensities, the type and amount respectively of the samples constituent compounds can be determined. In any crystalline compound (most solids are crystalline), the atoms are arranged in a regular, three-dimensional pattern unique to that compound. X-rays striking a crystal interact with the atoms creating waves of scattered x-rays that reinforce each other in certain directions. It has been shown (by Bragg) that reinforcement occurs when the rays diffracted from parallel atomic planes are in phase (i.e., when the path difference is an integral number of wavelengths).

3.5.2 Diffraction by planes of Atoms and The Bragg Law

In crystals, the planes of atoms are arranged parallel to one another at a regular repeat spacing, thus forming a crystal lattice.

Figure 3.7 depicts a vertical section through a crystal lattice. Each pointrow PP’ QQ’, RR’ is equally spaced, so the points form a lattice plane. For a regular stacking of such planes to produce a diffracted beam, the rays diffracted from each plane must reinforce one another. Thus, a diffracted beam results when the path difference between reflections from adjacent identical planes is equal to a whole number of wavelengths of the X-rays in use.
Figure 3.7. Diffraction of X-rays by equally spaced, identical planes of atoms governed by the Bragg Law, $n\lambda = 2d \sin \theta$.

For example, on Figure 3.7, the path difference between AXD and BYE is GYH. $GY + YH = 2d \sin \theta$, where $d$ is the inter-planar spacing between regularly spaced identical planes and $\theta$ is the glancing angle. Thus, a diffracted beam will follow the direction XD or YE if

$$n\lambda = 2d \sin \theta$$

Where $n$ is a whole number (integer) and $\lambda$ is the wavelength of the X-rays used. This relationship is called the **Bragg’s Law**.

### 3.5.3 The X-Ray Powder Method of Identification.

One application of the X-ray diffraction in mineralogy is the identification of an unknown by its powder diffraction pattern. A useful and diagnostic pattern can be obtained from any substance that posses an ordered internal structure (e.g. see the characteristic diffraction pattern for the mineral dolomite in Figure 3.8). The powder pattern can be used for identification by comparing it with tabulated data.
Figure 3.8. An X-ray pattern of the mineral dolomite, as obtained from a powder diffractometers. $2\theta$ values are indicated below the record (e.g. 31.01 for the highest peak); d values (e.g. 2.883) and Miller indices (e.g. 104) for the crystal planes that yield the peaks are given above the record.

3.5.4 Interpretation of X-ray Powder Patterns

The powder pattern yields the relative intensities of the diffractions from a crystalline material. Measurement of the pattern plus appropriate calculations gives the absolute values for the inter-planar spacings of the crystal structure. The powder pattern also provides indirect information about the symmetry of the structure. The dimensions of a unit cell of the structure can be deduced from the spacings, and the indicated geometry of the unit cell will then suggest its probable symmetry. The descriptions of all the procedures used for these determinations are beyond the scope of this unit. However if you are interested to learn more details of analysis of the X-ray diffraction method you can refer to the relevant literature cited at the end of this Lecture.

Explain how the Braggs equation, $n\lambda = 2d \sin \theta$, is derived using the diffraction of X-rays by equally spaced identical atomic planes in a crystalline material.
3.5.5 Application areas

The X-ray diffractometry system has all the basic essentials for high precision qualitative and quantitative phase analysis of powdered or solid specimens. It is a universal instrument, which finds application both in the industry and virtually in every field of research. In industry, the system is used in a variety of fields, e.g., mining, aluminum and steel production, the food and pharmaceutical industries and in the manufacture of pigments and ceramics.

3.6 SUMMARY

In crystals belonging to the tetragonal and hexagonal systems there is one preferred direction, called the optic axis, along which light propagates without splitting into two rays. These crystals are called uniaxial. In the orthorhombic, monoclinic, and triclinic systems there are two such directions. These crystals are called biaxial.

To determine whether an anisotropic mineral is uniaxial or biaxial, the usual procedure is to find a grain that will give a definitive interference figure. To obtain an interference figure we must observe the grain between crossed polarizers, in strongly convergent light, and with a high-power objective lens. This means that the analyzer is inserted, the substage convergent lens is moved into place, and a 40X to 50X objective lens is used.

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The X-ray diffraction method works on the principle that, when a sample is irradiated, the x-rays are diffracted in a way that is characteristic of the compounds present in the sample under analysis. By measuring the angles at which diffraction peaks occur and their intensities, the type and amount respectively of the samples constituent compounds can be determined.

REFERENCES


