HALITE: A REVIEW ARTICLE

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Halite, mostly known as "salt rock", or simply sodium chloride (NaCl), is an abundant mineral existing in a wide variety of regions on Earth. It is especially important for its chemical, industrial, and agricultural use. Due to its being edible and food preserving utilization, it has been an indispensable part of the human history. In this article, general properties and crystallographic information of Halite, experimental analysis methods to analyze it, and its historical importance are provided, along with the geographical regions where Halite mineral is found and extracted. The current situation of Halite deposits in Turkey are discussed further. X-Ray Diffraction, Raman and Infrared (Reflectance) Spectroscopy methods and their resulting spectograms are analyzed in detail by introducing both the working principles of the methods and interpreting their spectogram results for Halite. Overall, due to its wide use of areas and abundance, Halite turned out to maintain its importance for the people, while inheriting the potential for further use.

INTRODUCTION

Halite is a mineral that is consisted of sodium (Na) and chloride (Cl) ions. It is more generally known as rock salt, due to its being a type of salt. The main difference between rock salt and table salt is table salt's including iodine (I), although they both are edible and widely produced. [1].

Halite is an isometric -cubic- crystal whose unit cell is cube-shaped (See FIG 1 below). Sodium and chloride atoms are equidistant from each other. Some general properties of Halite are listed as follows. Its formula mass is 58.433 g/mol. It has a melting point of 800.8°C and boiling point of 1465°C. An important optical property of it is its being isotropic, meaning that its physical properties are the same regardless of direction. It is easily soluble in water (e.g.: Sea water), and is edible [2] It is the only edible mineral known today [1].

Halite crystal is fundamentally colorless. However, it is possible to observe it in a variety of colors, discussed in

the next section . Etymologically, there exists two main views on the word "Halite". The first view [4] is that the word "*Halite*" is a combination of "*Halos*" (meaning salt), and "*Lithos*" (meaning rock), which in return forms salt rock, or rock salt in reverse. Since both words generating the word "Halite" is of Ancient Greek language, this view traces the roots of the word back to the Ancient Greece. The second view [5], on the other hand, goes back to an earlier period of the history. It asserts "**sals*" is the original etymological root of the word. "**sals*" means salt, and is of Proto-Indian-European language. According to the same source, this word "**sals*" is then became "*hals*" in the Ancient Greek language, and added the suffix "*-ite*" (which is a chemical noun suffix) in the end when it came to the English language. Although both are considered to be plausible, the eponymist of the word "Halite" in crystallography is clear: Ernst Friedrich Glocker. He was a German mineralogist who coined the term in 1847 from its Greek version "*hals*" [4]

The purpose of this articleis to provide a holistic review about Halite. For this purpose pieces of its historical, cultural, and economical background along with its crystallographic properties and experimental analysis methods-results are incorporated.

COLOR

Halite crystal is fundamentally colorless. However, its color changes depending on the materials, impurities, structural abnormalities in the crystal. In his article [6], Sonnenfeld explains how rock salt's color changes depending on the type of impurities, admixtures, defect structures, etc. for a wide range of rock salt colors. Some of them are presented in the FIG 2 below.

Some examples of rock salt crystals of different colors are presented in FIG 3. The upper left crystal is an example of milky-white colored Halite. Its color is due
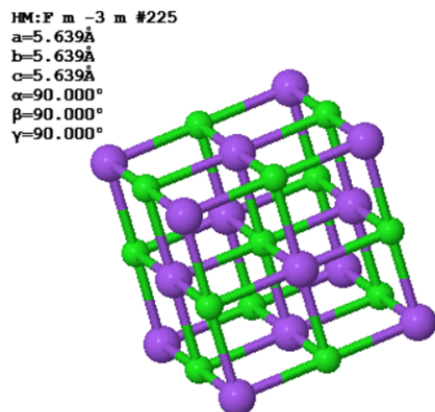

HM:F m −3 m #225
a=5.639Å
b=5.639Å
c=5.639Å
α=90.000°
β=90.000°
γ=90.000°

FIG. 1: *Unit Cell of Halite* [3]

Table 1
Common colors in rock salt (for references see text)

Color	Impurity
milky white	entrained air bubbles or fluid inclusions
grayish black	clay admixtures
brownish black	organic matter
blue	lattice defects/colour centers admixture of KBr + Au in sylvinite zone particles 90–110 nm Pb, Cu, Ag, Au as pigments by adding metallic Na in Na-vapor Cl⁻ removal by ionization rapid growth
violet	slow growth particles 80–90 nm + 0.5% KCl or RbCl exposure to radioactivity

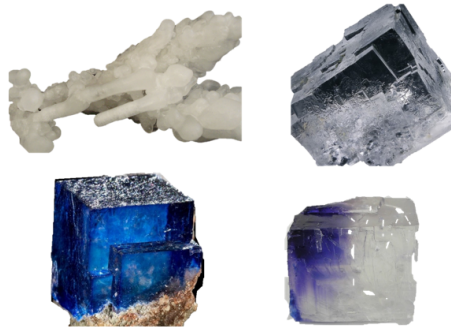FIG. 2: *Some of the Colors of Rock Salt and Impurity causing it* [6].

FIG. 3: *Some Rock Salt Crystal of the color white* [2], *colorless* [7], *blue* [7], *and violet* [2].

to tiny air bubbles inside it or any fluid inclusions inside. The upper right one is colorless (partly grayish color is due to the background), which indicated that the crystal is pure. The colors -blue and violet- of the bottom crystals are almost always due to the emplacement of various colloidal (gel like substance) metals into defects in crystal lattices. This metal can be gold, silver, copper, etc. The most common one is excess sodium, which results with blue color as in the bottom left crystal in FIG 3.

CRYSTALLOGRAPHY

The unit cell structure of Halite is provided in FIG 1, which is a cubic (isometric) unit cell composed of sodium and chloride ions. Since it is of the shape of a cube, each side has an equal length of $a = 5.6402$ Å. Due to the same reason, the volume of the unit cell is $V = a^3 = 179.43$ Å^3. As it is visible in FIG 1, the distance between the Na$^+$ and Cl$^-$ ions are equal. As a result, interatomic distance is the same as the half of the length of a side of the cube: 2.8 Å.
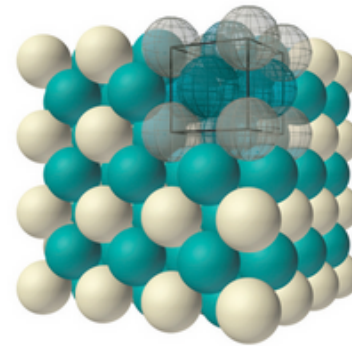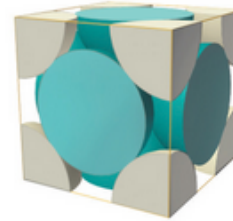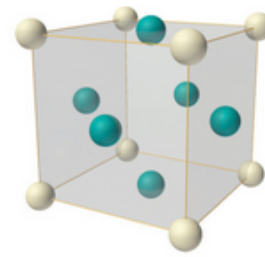

FIG. 4: *FCC unit cell structure* [8]

Both Na$^+$ and Cl$^-$ form a separate face centered cubic (FCC) lattice. See FIG 4 above. It is straightforward to observe that this unit cell describes the Cl atoms (purple dots in FIG 1). Also, since crystal has repetitive unit cells, the other type of atom in the same figure (Na, green atoms) also constitute an FCC lattice.

The space group of Halite is $Fm\bar{3}m$, also known as 225, out of 230 space groups in 3D. Its refractive index n is 1.544, which is very close to the n_{glass}. The cleavage of Halite crystal is {001}, {010}, {100}. It means that the crystal has the tendency to split along those planes. This is because the crystal has repeating surfaces along these directions.

The number of ions is calculated as follows:

$$Na^+ : 1_{center} + 12_{edge} \times \frac{1}{4} = 4 \qquad (1)$$

$$Cl^- : 6_{face} \times \frac{1}{2} + 8_{corner} \times \frac{1}{8} = 4 \qquad (2)$$

Once the number of ions is calculated, the density of the unit cell is calculated as follows:

$$\rho = \frac{4 \times (m_{Na} + m_{Cl})}{a^3} = 2.16 \frac{g}{cm^3} \qquad (3)$$

METHOD

There exists many characterization techniques for crystals. Some of these techniques are X-ray diffraction, Raman spectroscopy, microscopy observation, solid-state nuclear magnetic resonance spectroscopy, nuclear quadrupole resonance spectroscopy, etc [9]. Although it may be beneficial to know all of them, only the most common ones and the ones with the results are available for halite are of interest here. Therefore, X-ray diffraction (XRD), Raman Spectroscopy (RS), and Infrared (Reflectance) Spectroscopy (IR) are explained here, along with their spectograms for Halite.

X-ray Diffraction

XRD is one of the spectroscopy techniques that is used to identify a material by looking at its diffraction pattern, based on the angle difference between the incident and diffracted beam of X-rays. The crystal is placed inside the XRD machine, and an incident beam -produced by an X-ray source- is sent through it. Because the incident beam is controlled, its wavelength is known. See FIG 5, a schematic of XRD and FIG 6, a schematic of Bragg's Law for reflection.
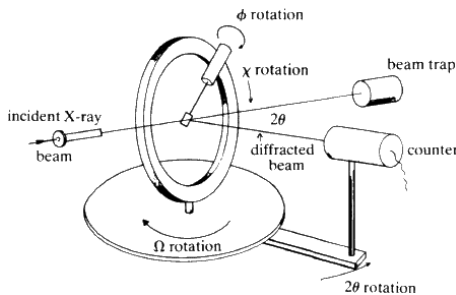

FIG. 5: *XRD Schematic* [10]

When the incident beam hits the crystal, the interaction between the crystal and beam causes either destructive or constructive interference. Consider constructive interference, that is when diffracted rays are amplified, making them observable by the photo detector. Ray is reflected from the material to reach the photon detector (see FIG 6). This clearly occurs only at specific angles, at which the inner structure of the crystal allows this constructive interference to happen. The constructive interference condition is formulated by Bragg's Law, as provided below.

$$n\lambda = 2d\sin\theta \qquad (4)$$

where λ is the wavelength of the beam, d is the inter-atomic distance between the atomic planes of the crystal,
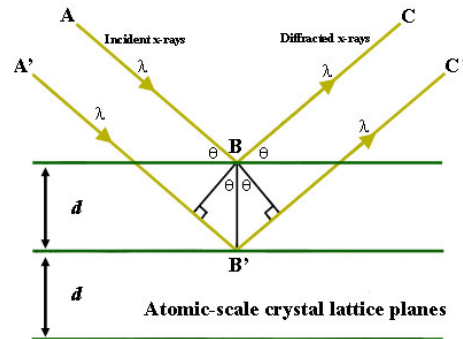

FIG. 6: *Bragg's Law Reflection* [11]

and θ is the diffraction angle. The important part of this equation is that it allows us to calculate d, so that the spectogram gives information about the atomic structure of the crystal.

Raman Spectroscopy

Raman spectroscopy is another characterization technique, which is based on the vibrational modes of the material. In Raman spectroscopy, a high intensity monochromatic light (mostly laser) is shone onto the material. This laser light interacts with molecular vibrations -phonons- of the material. After hitting the material, the light scatters either elastically (Rayleigh Scattering) or inelastically (Raman Scattering). Most of the light is scattered elastically, so that its wavelength is unchanged. However, a portion of light scatters inelastically, meaning an interaction with the crystal, resulting in a change of its energy (thus wavelength). The difference between this new wavelength and the original wavelength of the laser is called *Raman shift*.

At some Raman shifts, the intensity of the scattered light is higher than for other Raman shifts. These peaks give information about the crystal. This is because at which Raman shift crystal causes the highest intensity peaks is directly related to its phononic inner structure.
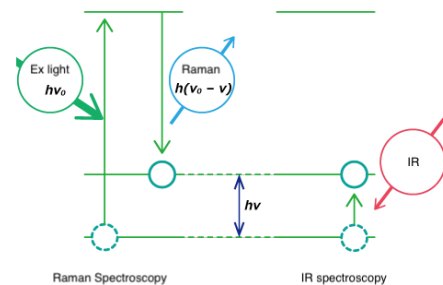

FIG. 7: *Raman and IR Spectroscopy with scattered / absorbed light schematics* [12]

Infrared (IR) Spectroscopy

Like Raman Spectroscopy, IR Spectroscopy is also based on the molecular vibrations of the material. While Raman Spectroscopy is based on the **scattering** of the incident light, IR Spectroscopy is based on the **absorption** of the light energy, corresponding to the vibrations of the material. The reader can refer to the FIG 7 to see the essential difference between the Raman and IR Spectroscopy methods.

Infrared spectrometer produces infrared spectrum electromagnetic waves, and these waves are shone onto the material. At some characteristic frequencies (related to the vibrational excitation of atoms by the light), the material absorbs the most (at which intensity drops). Due to the same reasoning in Raman Spectroscopy, IR Spectroscopy gives information about the vibrational modes of the crystal. Like in Raman Spectroscopy, the typical units is cm^{-1} for IR Spectroscopy.

RESULTS

XRD, Raman, and IR spectroscopy results for Halite crystal are provided in the subsections of this part. At last, electronic band structure of Halite -theoretically calculated and experimentally measured- are also provided.

X-ray Diffraction of Halite

Consider FIG 8, which is the X-ray diffraction pattern of Halite. The most dominant peak is around $2\theta = 32°$. According to the figure, this occurred at when beam went through $\{200\}$ plane of the Halite crystal. In other words, a very strong constructive interference is observed in the diffraction diagram at around $2\theta = 32°$, which corresponded to the $\{200\}$ direction of the material.
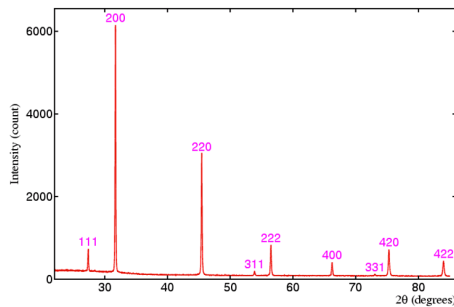

FIG. 8: *XRD Spectogram of Halite* [13]

Since crystal kept rotating, this peak did not last much and extinguished in the next degree. There are some other peaks in the figure, which also correspond to other different crystal orientations. It is clear that none of crystal orientations give rise to more dominant peaks than

the crystal orientation $\{200\}$ for Halite and the $\{200\}$ and $\{220\}$ peaks are the most dominant characteristic peaks of it.

Raman Spectroscopy of Halite

Consider FIG 9, which is a Raman spectogram of NaCl (Halite). It is observed that there is a peak in intensity around the wavenumber 3500 cm^{-1}. It means the following: When the difference between the incident beam wavelength and the Raman scattered light wavelength difference is 3500 cm^{-1}, NaCl phononic modes cause the largest intensity scattering. Therefore, one can characterize a Halite crystal by observing its peaks in the Raman spectrum and comparing with the ones in the literature, that is, FIG 9.
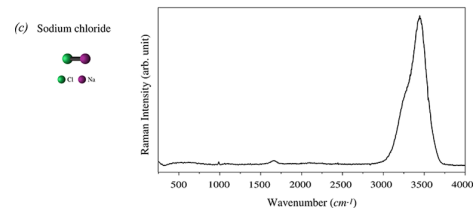

FIG. 9: *Halite Raman spectrum* [14]

Infrared Spectroscopy of Halite

Comparing 10 with 9 can be instructive, and useful for checking the results. Up until here, Raman and IR Spectroscopy methods are presented in a way that their working principles are similar but in the reverse manner. Therefore, a reciprocal relation between their results is also expected.
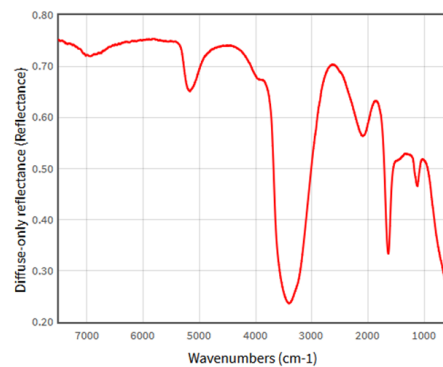

FIG. 10: *Halite IR Spectrum,* [15]

Observe that in the Raman Spectrum, the maximum intensity is around $3500 cm^{-1}$, while the minimum intensity is around $3500 cm^{-1}$ in the IR Spectrum for Halite.

In conclusion, it is observed that wavenumber $3500cm^{-1}$ is a special characteristic of the vibrational modes of Halite. Therefore, it is important to observe a peak (valley) in Raman (IR) Spectroscopy to conclude that it is a Halite crystal.

Electronic Band Structure

The electronic band structure of Halite is briefly introduced here. The upper figure in FIG 11 is the theoretical calculation of the band structure of Halite and the lower figure is the experimental result.
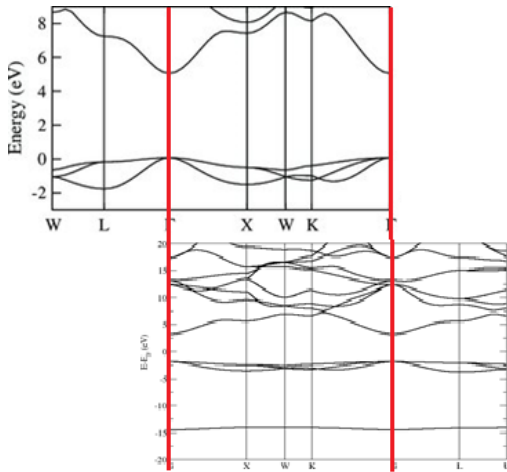

FIG. 11: *Electronic Band Structure of Halite. Upper* [16]*figure is theoretical calculation while the lower* [17] *figure is experimental measurement*

First, one observes that the conduction band minima and valence band maxima occur at the same symmetry point (also known as "k-vector"). Therefore, the gap (which is 5.145 eV [17]) is a *direct gap*. Second, the theoretical and experimental data fits (Red lines are drawn to emphasize the match of the band gap symmetry points). In general, direct gap means that an electron can directly emit photon when moving from conduction band to valence band, whereas indirect gap requires for it to pass an intermediate state first, which results with momentum transfer with the lattice.

HISTORY & CULTURE

Since Halite is essentially a salt, the history of Halite involves the history of salt. Therefore, it is relevant to consider salt and Halite as the same in this context. Moreover, due to salt's role in the history of humanity and the civilization, this section both deals with the history of Halite (salt) and salt (Halite) in the history.

Being the only edible mineral is one of the distinguished properties of Halite. Clearly, there had been other minerals in the history of humanity that are used for some other purposes. For example, iron is an important part of human nutrition, graphite has been used for writing (pencils) since the 17th century, phosphorus is essential for its role in energy generation in the animal body (Adenosine tri**phosphate**)[18]. Halite's role in the history, on the other hand, is based on its ability to preserve food other than its being an important spice. Preserved food with salt had been able to resist for seasons, and transported to other places [19].

Humans extracted salt since thousands years ago. Early Neolithic salt production dates back to -approximately- 6,000 BCE in Romania [20]. Some civilizations are based near Halite deposits. Solnitsata, located in Bulgaria now, is an example of such a town. Being the earliest town in Europe, it was built near a salt production facility [21].

Last, but not the least, is the use of salt in military, which is known as "salting the earth". More than an idiom, it is a ritual in old times that involves pouring salt on the conquered lands of the people. By doing so, nothing grows on those lands anymore, in other words, it is *cursed* [22].

FIG. 12: *Romans salting the Carthaginian soil* [23]

IN THE WORLD

Halite is an evaporative mineral. When sea water, or any other salty water, is evaporated, halite is deposited. As this water evaporates, layers of halite is left behind in layers [1]. Due to its being easy to form, there exists many very old and very young halite deposits in the world. Finger Lakes region of New York State is an example of Halite deposits around 300 million years old [1]. There exists 4 operation mines there, none open to public. Those mines in Finger Lakes are run by 4 big companies, one of which is Cargill Salt, world's largest marketer of salt products [24]. On the other hand, not

all Halite deposits are that old, as mentioned previously. Great Salt Lake in Utah, or Dead Sea between Israel and Jordan are examples of newly forming Halite deposits at the present time [1].

Other than these, there exists many Halite deposits in all continents of the world [25]. Some important rock salt deposits in the world are Wieliczka (Poland) , New York and New Mexico (USA), Sicily (Italy), Stassfurt (Germany), France, Bex (Switzerland), and Austria [7]. Clearly, these are not all the deposits, but it is a fact that the USA and Europe holds the majority of Halite mines [25]. Some sources [26] also account for Canada and China, by verifying that the United States is undeniably the largest salt producer in the world.

IN TURKEY

Turkey is not among the countries that produce the most amount of Halite. However, it is noteworthy that Turkey has large salt deposits because of its geological structure. Turkey has millions of tons of rock salt deposits. Besides, it also has lake salt deposits along with sea salt deposits. Extraction of sea and lake salts are different than rock salt mining due to the former one depending on evaporation. Due to rock salt production (per ton) is 2-3 times of sea salt production cost and is 4-5 times of lake salt production cost, rock salt production is 4 to 16 times less than other methods [26].

The salt extracted is used in many areas in Turkey. Major areas of use are chemical industry (chloralkali sector), food processing (packaging), general industry, agricultural industry , water treatment (water-softening), and ice control and road stabilization. Although its wide use of areas, Turkey produces around 1% of total world salt production. This rate is not small, but can be increased mainly by increasing exports, decreasing costs (especially in rock salt mines), and increasing the number of production facilities. [26]

CONCLUSIONS

In this paper, a holistic approach is followed to describe Halite. Etymologically tracing its roots provided a better understanding of the word itself with its changes in time; investigating its color showed how purity and defects are important on the physical appearance of the crystal; crystallographic investigation provided atomic-level understanding of the mineral; characterization methods (XRD, Raman, IR) provided ways to determine the type and the purity of Halite; history of Halite helped us to develop a historical perspective to understand the current situation of Halite, and local investigations (World and Turkey) revealed which countries are the major producers and what can be done to be a major player in Halite

production sector. Sources used in this paper for Turkey was 20 years old. Further research on the current situation of the Halite in Turkey, and a comparative analysis of the production and technological development in the production (especially in rock salt) in the past and today in Turkey are strongly suggested.

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