

# Studying the Infrared Spectroscopy of Compounds Fluoride That Blotched by in

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Submitted: 2023, Mar 28; Accepted: 2023, Apr 13; Published: 2023, Apr 29

**Citation:** Khoudro1, A., Zarouri, T., Alhasno, M. (2023). Studying the Infrared Spectroscopy of Compounds Fluoride That Blotched by in. *J App Mat Sci & Engg Res*, 7(1), 43-49.

### Abstract

The study of calcium fluoride is of great scientific importance due to its wide scientific applications. Therefore, our study came to some of the physical properties of the compounds of both pure Calcium fluoride and indium doped Calcium fluoride. By measuring the infrared spectrum of pure Calcium fluoride, it is found that there are six vibratory frequencies, namely:

$(3444.52 - 1517.59 - 1138.40 - 876.40 - 639.93 - 436.29) \text{ cm}^{-1}$  and six vibratory frequencies for indium doped calcium fluoride at 3wt%.

$(3441.94 - 1516.77 - 1138.44 - 876.55 - 642.09 - 436.44) \text{ cm}^{-1}$  The study showed that the absorbance values, the absorption coefficient, the refractive index and the optical length were in the indium doped sample by 3wt% greater than that of the pure Calcium fluoride compound and are respectively:  $\alpha=14.163 \text{ cm}^{-1}$ ,  $n=1.767$ .

**Keywords:** Powder, Calcium Fluoride, Solid State Reaction, Infrared Spectrum, Rare-Earth Ions, Optical Conductivity.

## 1. Introduction

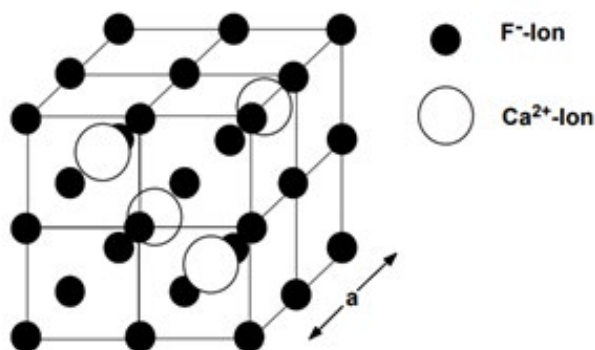
Calcium fluoride ( $\text{CaF}_2$ ) density is  $3.18 \text{ (g/cm}^3\text{)}$  melting at  $1633 \text{ (K)}$  and crystallize in cubic structure with lattice constants  $a = 5.432 \text{ \AA}$ .  $\text{CaF}_2$  is presently the fastest known scintillator. It has an emission component with sub nanosecond decay time [4,5].

$\text{CaF}_2$  has several scintillation emission bands. The fast scintillation light is emitted in the UV bands centered at  $220$  and  $200 \text{ nm}$ .

The decay time of the fast component varies between  $600$  and  $800 \text{ ps}$  [2].

$\text{CaF}_2$  has attracted much attention because of its wide range of potential applications in optoelectronic and microelectronic devices [3,6,7].

$\text{CaF}_2$  compounds doped with rare-earth ions have been reported to display unique luminescence properties and can thus be used as scintillators [1,8,9,10].



**Figure 1:** the crystalline structure of pure Calcium fluoride

## 2. Infrared Spectroscopy

Infrared is electromagnetic waves and it has all the basic properties of light, which are represented by the phenomena of diffusion, reflection, refraction, interference, diffraction and polarization. They are invisible thermal waves emitted by the sun or from artificial sources and have a high penetration ability as well as from our

bodies and their frequency is lower than the red ray frequency in the visible electromagnetic spectrum. The infrared spectrum is located between the visible spectrum and the microwave radiation spectrum. It is divided into three zones, as follows

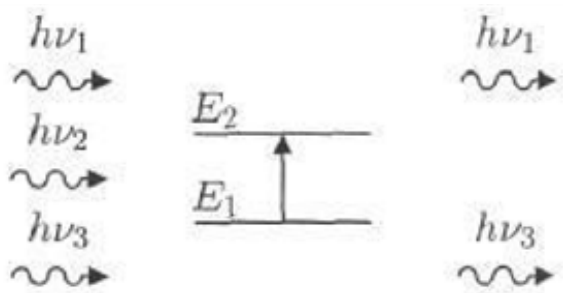
- Near infrared (NIR): It is the closest to the visible rays, namely the red color, and it lies within the range  $[4000 - 12000] \text{ Cm}^{-1}$
- Middle Infrared MIR: located between the two preceding zones within the range  $[200 - 4000] \text{ Cm}^{-1}$

Infrared spectroscopy is one of the basic methods of studying materials. It enables us to identify the structure of the material without affecting its properties. It depends on the study of the spectra absorbed by the sample, and its field is limited to  $[20 - 1400] \text{ Cm}^{-1}$ . Red radiation energy is not enough to cause electronic excitation in most materials, but it is sufficient to cause elasticity vibrations and flexion in the bonds. All types of these bonds respond to this amount of energy in which vibrations of this type occur. Therefore, they are absorbed in the zone beneath the red under the condition that absorption leads to a change in the polar moment, and these vibrations are quantized, and their occurrence means that the compound absorbs infrared energy in a specific part of the spectrum [11].

Most spectroscopic analysis occur in the central infrared zone  $[20 - 1400] \text{ Cm}^{-1}$  where the most molecular vibrations occur to determine the molecular structure of the studied compounds.

### 2.1 Infrared Spectroscopy Principle

Natural molecules vibrate according to all their vibrating patterns, but with very weak amplitudes. However, the photon has a sinusoidal electric component. If the frequency of the photon corresponds to the frequency of the vibrations of the normal patterns of the molecule, the molecule will enter the resonance and vibrate at very large capacities. In other words the photon whose energy is Equal to the energy necessary for the molecule to pass from a low energy state to an excited state is absorbed and its energy is transformed into a vibration energy as in Figure (2).



**Figure 2:** Infrared absorption

Only the photon whose energy ( $h\nu$ ) equals to the transmission energy ( $E_2 - E_1$ ) is absorbed and thus the emission of the emitted radiation is impaired. As the absorption of some of the incoming photons leads to the appearance of the lines of compatibility of the photons that were not emitted in the curve of the infrared spectrum

of the molecule. This absorption distinguishes the bonds between the atoms, since each vibration pattern corresponds to the single movement of the molecule, so there is a direct correspondence between the frequency of the absorbed radiation and the structure of the molecule (10)

### 3. Research Objective

This work aims to determine the field of absorption frequencies, that is, the vibrations samples frequencies of the infrared spectra of pure calcium fluoride and indium doped calcium fluoride by 3wt%. And then finding the absorbance, absorption coefficient, damping factor, refractive index, optical length and optical conductivity to improve the physical properties of calcium fluoride.

### 4. Research Materials and Methods

The following materials have been used in preparing the samp Calcium fluoride  $\text{CaF}_2$  (99% purity, TITAN BIOTECH LTD, origin India).

Indium In (purity 99%, TITAN BIOTECH LTD, origin India).

#### 4.1 Devices and Tools Used

1. Sensitive scale type (SARTORIUS) with an accuracy of  $(10^{-4})$  gr is available in the Faculty of Science - Physics Department.
2. Small agate mortar.
3. High temperature thermal Oven ( $1200^\circ\text{C}$ ) with a Temperature Regulator.

#### 4.2 Preparing the Samples

The samples are prepared by the solid-state reaction method. Accordingly the weights of the powders required for each sample are mixed and calculated using the molecular weight method in order to obtain the compounds required for the study where  $\text{CaF}_{2-1-x}\text{In}_x$ ; ( $x=0.0-0.03$ ). Then grinding these materials in the agate mortar perfectly well to make the mixture homogeneous and sifting it with a sieve of  $90 \mu\text{m}$ . Then it is put it in a container and we add distilled water to increase the mixing process and homogeneity of the powder. Then we put it on a heater for 3 hours at a temperature of  $100^\circ\text{C}$  and the mixing and homogeneity process of the powder occurs by stirring.

After that, the powder is placed on a heater with direct contact with the air, then the water evaporates and then we perform a preliminary roasting process inside the oven (pre-sinter) to increase the degree of homogeneity of the mixture. We fix the oven temperature at  $700^\circ\text{C}$  for three hours, then we turn off the oven, which means to stop the roasting process and leave the sample inside the oven until it cools and reaches room temperature, thus we get rid of impurities that evaporate at high temperatures.

Then we grind the powder resulting from the roasting process in its first stage. Then we perform the second roasting process where we fix the oven temperature at  $100^\circ\text{C}$  for an hour and then we raise the temperature  $50^\circ\text{C}$  every 15min until we reach the temperature of  $700^\circ\text{C}$  where we fix the oven temperature at it for 3 hours in order to get the crystal structure in its correct form.

To study the infrared spectra, we use an infrared spectroscopy device, which is a simple device whose main components are an infrared source, a sample holder and a detector. This device is considered one of the best spectroscopic devices used to identify the chemical composition of the compounds. It is available in the Faculty of Science - Aleppo University works at the range [400-4000]  $\text{Cm}^{-1}$ .

The spectrometer is characterized by a computer memory that analyzes the waves gathered on the detector, computerizes them, and draws the spectrum resulting from absorption. Or a vibratory transmission of the atoms occurs relative to each other in the molecule, which leads to a periodic change in the length of chemical bonds or a change in the angles between the chemical bonds in the molecule. Each vibrational motion results from the movement of two atoms, or it may include a group of its constituent atoms. The wavelength or frequency at which this absorption occurs depends on several factors, including the mass of the atom, the strength of the bonds that make up the molecule, and the geometry of the atoms in the molecule.

## 5. Results and Discussion

The IR spectrum of pure calcium fluoride and indium doped calcium fluoride was measured using the spectrometer asco type FT / IR-460 plus available in the central laboratory of the Faculty of Science - Aleppo University, working in the range [400-4000]  $\text{Cm}^{-1}$ . Where the permeability  $T$  was measured by the frequency function  $\nu$ , the absorbance  $A$ , the absorption coefficient  $\alpha$ , the damping factor  $K$ , the refractive index  $n$  and optical conductivity  $\sigma_{opt}$  were calculated

**5.1 Permeability  $T$**  It is defined as the ratio between the intensity of the penetrating radiation to the intensity of the fallen radiation, it has been taken from the device itself and then by using the appropriate Mathematical equations, other optical parameters have been calculated.

**5.2 Absorbency  $A$**  is the ratio between the intensity of the absorbed radiation and the intensity of the fallen radiation, calculated from the equation [15]:

$$A = \log\left(\frac{100}{T\%}\right) = \log\left(\frac{1}{T}\right) \quad (1)$$

$T$  represents Permeability.

**5.3 Absorption Coefficient**  $\alpha$  defined as the ratio between the decrease in the flow of the fallen radiation energy to the unit of distance towards the spread of the fallen light wave within the field, and is calculated from the equation:

$$\alpha = 2.303 \frac{A}{d} \quad (2)$$

$A$  represents absorbency,  $d = 1\text{mm}$  the thickness of the material

**5.4 The Damping Factor  $K$**  is defined as the amount of energy

absorbed by the electrons of the studied material from the energy of the radiation photons that fall on it, and is calculated from the equation [17]:

$$k = \frac{\alpha}{4\pi\nu} \quad (3)$$

**5.5 Refractive Index  $N$**  which is the ratio between the speed of light in the vacuum to its speed in the field, and it is calculated from the equation [18]:

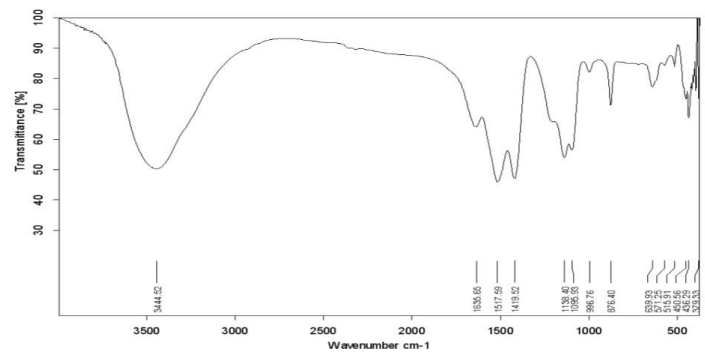
$$n = \left(\frac{100 - T\%}{T\%}\right)^{1/2} \quad (4)$$

**5.6 Optical Length  $L$**  the inversion of the absorption coefficient [16]:

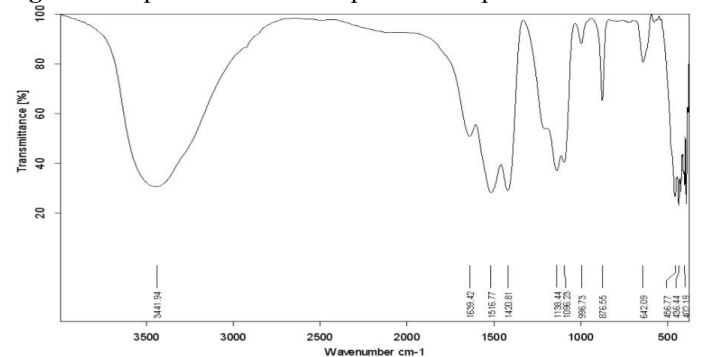
$$L = \frac{1}{\alpha} \quad (5)$$

**5.7 Optical Conductivity  $\sigma_{opt}$**  optical conductivity is related to the refractive index and the damping factor according to the following equation [18]:

$$\sigma_{opt} = \frac{1}{30} nk\nu \quad (6)$$



**Figure 3:** Represents the FTIR spectrum for pure calcium fluoride



**Figure 4:** shows the FTIR spectrum of In doped  $\text{CaF}_2$  samples (3wt%).

FTIR analysis of samples has been performed at room temperature within the range [400-4000]  $\text{Cm}^{-1}$ . Some bundles appeared within

this range, including the absorption bundle at the top corresponding to the number of vibratory frequency 1516.77 cm<sup>-1</sup>, 3441.94 cm<sup>-1</sup> which belongs to the vibratory pattern of the hydroxyl group (vibration of hydroxyl group). This is due to the absorption of water vibration, the vibratory pattern also shows stretching and retraction (stretching vibrational mode) belonging to the O-H group [12]. The location of the absorbent bundles and peaks also depends on the crystalline structure of the material and its chemical composition, as well as on the morphology of the material [13]. Pure calcium fluoride is characterized by a set of vibrational frequencies within the range [400-4000] Cm-1 which is: (3444.52 – 1517.59 – 1138.40 – 876.40 – 639.93– 436.29) cm<sup>-1</sup>. Indium doped calcium fluoride by 3wt% is characterized by a set

of vibrational frequencies within the range [400-4000] Cm<sup>-1</sup> which is: (3441.94 – 1516.77 – 1138.44 – 876.55 – 642.09– 436.44) cm- 1

An absorbent value has been observed at about the frequency 1138.44 cm-1 belonging to the C-H group, and this could be due to adsorption and interaction between carbon dioxide atoms with water during the sintering process [14].

From the permeability spectrum by the frequency function indicated in Figure (3), the physical quantities of pure calcium fluoride have been calculated, which are the absorbance, the absorption coefficient, the damping coefficient, the refractive index, the wavelength, the optical conductivity, which are shown in Table (1).

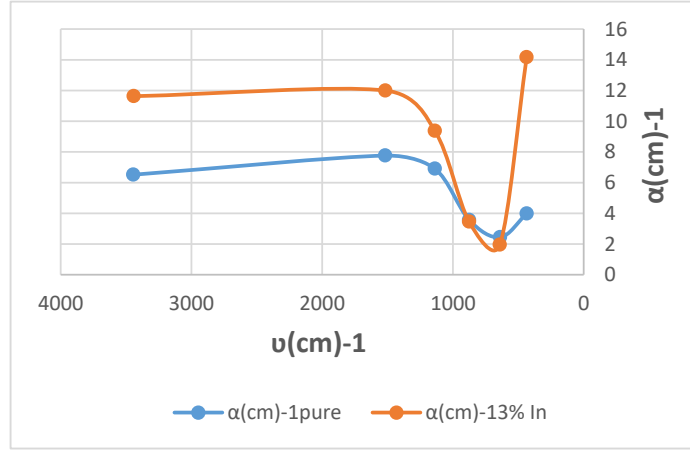
$\nu(\text{cm})^{-1}$	T%	A	$\alpha(\text{cm})^{-1}$	N	$k \times 10^{-4}$	L(cm)	$\sigma_{\text{opt}}(\Omega\text{cm})^{-1}$
3444.52	50.006	0.283	6.517	0.999	1.506	0.153	0.017
1517.59	46.022	0.337	7.761	1.082	4.071	0.128	0.022
1138.40	50.082	0.300	6.909	0.998	4.832	0.144	0.018
876.40	69.825	0.155	3.569	0.657	3.242	0.280	0.006
639.93	78.265	0.106	2.441	0.526	3.037	0.409	0.003
436.29	67.128	0.173	3.984	0.699	7.271	0.251	0.007

**Table 1:** shows the vibrations frequency of pure calcium fluoride with corresponding permeability values for each frequency, absorbance and absorption coefficient, damping factor, refractive index, optical length and optical conductivity.

$\nu(\text{cm})^{-1}$	T%	A	$\alpha(\text{cm})^{-1}$	N	$k \times 10^{-4}$	L(cm)	$\sigma^{(\text{opt})}(\Omega\text{cm})^{-1}$
3441.94	31.248	0.505	11.630	1.483	2.690	0.085	0.045
1516.77	30.0885	0.521	11.998	1.524	6.298	0.083	0.048
1138.44	39.128	0.407	9.373	1.247	6.555	0.106	0.031
876.55	70.645	0.150	3.454	0.644	3.137	0.289	0.005
642.09	82.080	0.086	1.957	0.467	2.426	0.510	0.002
436.44	24.246	0.615	14.163	1.767	25.840	0.070	0.066

**Table 2:** shows the vibrations frequency of the indium doped calcium fluoride by (3wt%) with corresponding permeability values for each frequency, absorbance and absorption coefficient, damping factor, refractive index, optical length and optical conductivity.

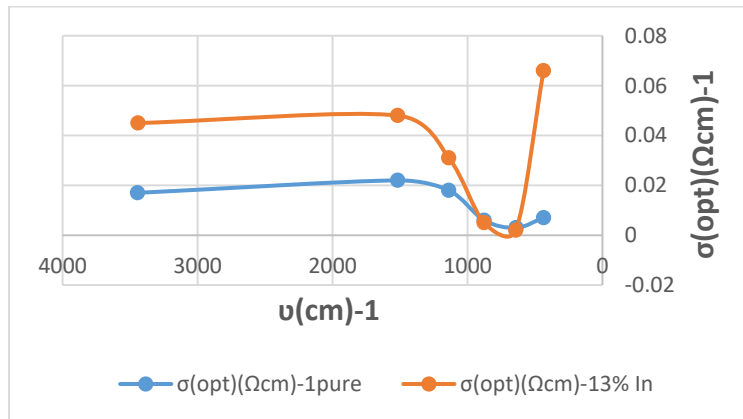
The absorption coefficients variations are drawn by the function of the vibrational frequency of pure calcium fluoride and the indium doped calcium fluoride as shown in Figure (5).



**Figure 5:** shows the absorption coefficient variations by the function of the vibrational frequency of pure calcium fluoride and the indium doped calcium fluoride by (3wt%).

Figure (5) shows the change in the absorption coefficient of pure and indium doped calcium fluoride, we note that the largest absorption coefficient value was (7.761cm<sup>-1</sup>) corresponding to the frequency (1517.59 cm<sup>-1</sup>) cm<sup>-1</sup> and the smallest absorption coefficient value was (2.441cm<sup>-1</sup>) corresponding to the frequency (639.9 cm<sup>-1</sup>), and the largest value of absorption coefficient to the In doped

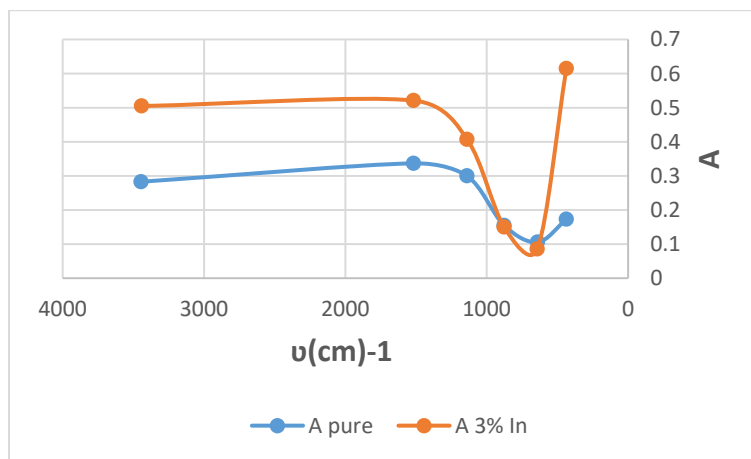
calcium fluoride was (14.163 cm<sup>-1</sup>) corresponding to the frequency (436.44 cm<sup>-1</sup>) and the smallest value of absorption coefficient was 1.957cm<sup>-1</sup> corresponding to the frequency (642.09 cm<sup>-1</sup>). The optical conductivity variations are also drawn by the frequency function of pure calcium fluoride and the indium doped calcium fluoride, as shown in Figure (6).



**Figure 6:** shows the studying of the conductivity variations by the frequency function of pure calcium fluoride and the indium doped calcium fluoride by (3wt%).

Figure (6) shows the change in the conductivity of pure and indium doped calcium fluoride, we note that the largest value of the conductivity was (0.022 Ωcm<sup>-1</sup>) corresponding to the frequency (1517.59 cm<sup>-1</sup>) cm<sup>-1</sup> and the smallest value of conductivity was (0.003 Ω cm<sup>-1</sup>) corresponding to the frequency (639.93 cm<sup>-1</sup>), and

the largest value of the conductivity to the In doped calcium fluoride was (0.066 (Ωcm<sup>-1</sup>) corresponding to the frequency (436.44 cm<sup>-1</sup>) and the smallest value of conductivity was (0.002 Ωcm<sup>-1</sup>) corresponding to the frequency (642.09 cm<sup>-1</sup>).



**Figure 7:** Absorbance variations by the frequency function of pure calcium fluoride powder and the indium doped calcium fluoride by (3wt%).

Figure (7) shows the change in the absorbance of pure and indium doped calcium fluoride, we note that the largest absorbance value was (0.337) corresponding to the frequency (1517.59cm<sup>-1</sup>) and the smallest value of absorption was (0.106) corresponding to the frequency (639.93cm<sup>-1</sup>), and the largest value of absorbance corresponds to the In doped calcium fluoride was (0.615) corresponding to the frequency (436.44cm<sup>-1</sup>) and the smallest value of absorbance was (0.086) corresponding to the frequency (642.09cm<sup>-1</sup>).

## 6. Conclusions

1. The pure calcium fluoride FTIR spectrum has shown some vibrational frequencies within the range [400-4000] Cm<sup>-1</sup> which are:
2. (3444.52 – 1517.59 – 1138.40 – 876.40 – 639.93– 436.29) cm<sup>-1</sup>
3. The FTIR spectrum of the indium doped calcium fluoride by 3wt% showed vibrational frequencies within the range [400-4000] Cm<sup>-1</sup>, the most notably are:
4. (3441.94 – 1516.77 – 1138.44 – 876.55 – 642.09– 436.44) cm<sup>-1</sup>.
5. The absorbance value for the pure sample varies within the range [0.106 – 0.337], and for the doped sample, the absorbance value varies within the range [0.086 -0.615].
6. The absorption coefficient value varies within the range of the pure sample [2.441-7.761] Cm<sup>-1</sup>
7. The value of the refractive index for the pure sample varies within the range [0.526-1.082].
8. The value of the optical length L concerning the pure sample varies in the range [0.128–0,409] cm, and for the doped sample the value of the optical length varies within the range [0.070 - 0.510] cm.
9. The optical conductivity value  $\sigma_{opt}$  for the pure sample varies within the range [0.003 – 0.022] ( $\Omega\text{cm}$ )<sup>-1</sup>, for the doped sample, the value of the optical conductivity varies in the range [0.002 – 0.066] ( $\Omega\text{cm}$ )<sup>-1</sup>.
10. The largest values of absorbance, absorption coefficient, re-

fractive index and optical length were greater in the indium doped sample by 3wt% for the vibrational frequency 436.44 cm<sup>-1</sup>.

11. The largest values of the absorbance, the refractive index, and the absorption coefficient were in the pure sample for the frequency 1517.59cm<sup>-1</sup>.

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