دراسة مطيافية الأشعة تحت الحمراء لمركب أكسيد القصدير النقي والمشاب بالحديد (x=0.00,0.04)

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الملخص

تعتبر دراسة الأكاسيد الشفافة (TCO) ذات أهمية علمية كبيرة نظراً لتطبيقاتها العلمية الواسعة. لذلك ، توصلت دراستنا إلى بعض الخصائص الفيزيائية لمركبات كل من أكسيد القصدير النقي وأكسيد القصدير المشاب بالحديد. من خلال قياس طيف الأشعة تحت الحمراء لأكسيد القصدير النقي ، وجد أن هناك خمسة ترددات اهتزازية ، وهي: cm^{-1}(415.585 – 574.683 – 1641.13 – 2125.3 – 3432.67) ولأكسيد قصدير المشاب بالحديد cm^{-1}(580.49–1384.64 – 1640.16 – 3431.71) . أظهرت الدراسة أن أكبر قيمة للامتصاصية ولمعامل الامتصاص كانت في العينة النقية على التوالي   A = 0.725 cm^{-1} 16.687 = α المقابل للعدد الموجي $υ = 574.683 cm^{-1}$.

الكلمات المفتاحية: أكسيد القصدير – طيف الأشعة تحت الحمراء – الامتصاصية – قرينة الانكسار – الناقلية الضوئية

Studying the Infrared spectroscopy of the pure tin oxide and iron doped tin oxide compounds ;(x= 0.00,0.04)

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Abstract

The study of transparent oxides (TCO) 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 tin oxide and iron doped tin oxide. By measuring the infrared spectrum of pure tin oxide, it is found that there are five vibratory frequencies, namely:415.585 - 574.683 - 1641.13 – 2125.3- 3432.67) cm^{-1} and for iron doping tin oxide (580.49-1384.64-1640.16-3431.71) cm^{-1} . the study showed that the greatest value of the absorbance and absorption coefficient was in pure sample respectively A = 0.725, α = 16.687 cm^{-1} corresponding to the wavenumber v = 574.683cm^{-1}.

Keywords: Tin Oxide - infrared spectrum - absorbance - absorption coefficient - refractive index - optical conductivity.

1.Introduction:

The crystals of metal oxides semiconductor have attracted a great interest due to their intriguing properties, which are different from those of their corresponding bulk state.Tin Oxide (SnO_2) is one of the important metal oxides due to its many useful properties such as its wide band gap (E_g = 3.64 eV, 330 K), n-type conductivity, high transparency in the visible range (>80 %).

It crystallizes in the tetragonal rutile structure with space group P42/mnm , with lattice parameters $a = b = 4.738$ Å and $c = 3.187$ Å , and can be synthesized in variety of shapes and sizes using different low cost synthesis techniques relevant for a wide range of applications such as solid-state gas sensors, flat panel displays, solar energy cells [1-3] .

Its unit cell contains two tin and four oxygen atoms as is shown in figure (1) . The tin atom is at the center of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen molecule is surrounded by three tin atoms at the corners of an equilateral triangle [4].

Some properties can be drastically changed by the addition of adequate dopants. For instance, undoped stoichiometric SnO_2 is an insulator .
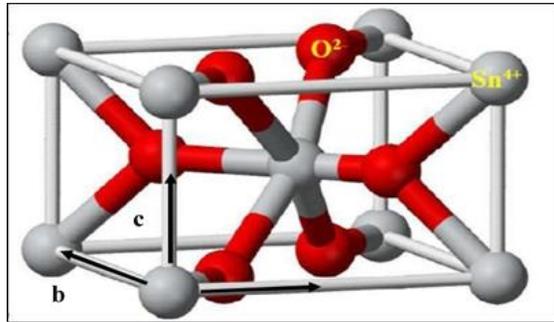

Fig (1) : Unit cell of the crystal structure of SnO_2 [5].

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:
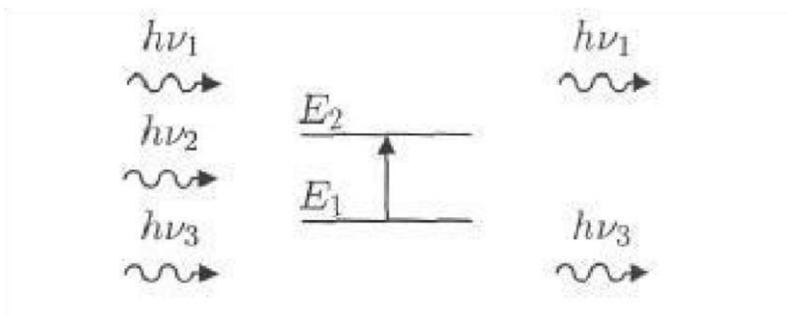
- Near infrared (NIR): It is the closest to the visible rays, namely the red colour, and it lies within the range [4000 -12000] cm^{-1} .

- Middle Infrared MIR: located between the two preceding zones within the range [200 -4000] 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] 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. [6]

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

3.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 amplitudes. 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 (hv) 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 [7].

Research objective:
This work aims to determine the field of absorption frequencies, that is the vibrations samples frequencies of the infrared spectra of pure tin oxide and iron doped tin oxide by (4wt%), and then finding the absorbance, reflectance , absorption coefficient, extinction coefficient, refractive index, optical length and optical conductivity to improve the physical properties of tin oxide.

Research materials and methods:
The following materials have been used in preparing the samples:
- Tin oxide SnO_2 (99% purity, TITAN BIOTECH LTD, origin India).
- Iron Fe (99% purity, TITAN BIOTECH LTD, origin India).

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 ($700^{°}$C) with a Temperature Regulator.

4- 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 $Sn_{1-x}Fe_xO_2$; (x=0.0- 0.04). Then grinding these materials in the agate mortar perfectly well to make the mixture homogeneous and sifting it with a sieve of 90 μm. 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 $100^{°}$ 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 $700^{°}$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° C for an hour and then we raise the temperature 50°C every 15min until we reach the

temperature of 700°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 - Tishreen University works at the range [400-4000] 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 tin oxide and iron doped tin oxide was measured using the spectrometer **asco** type **FT / IR-460 plus** available in the central laboratory of the Faculty of Science - Tishreen University, working in the range [400-4000] cm^{-1}. Where the transmittance T was measured by the frequency function υ , the absorbance A, the reflectance R, the absorption coefficient α, the extinction koefficient K, the refractive index n and optical conductivity σ_{opt} were calculated:

1- **Transmittance T**: It is defined as the ratio between the intensity of the penetrating radiation to the intensity of the

incident radiation, it has been taken from the device itself and then by using the appropriate mathematical equations, other optical parameters have been calculated.

2- **Absorbency A**: is the ratio between the intensity of the absorbed radiation and the intensity of the inciden radiation, calculated from the equation [8]:

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

T represents Permeability.

3- **Reflectance R** : is the ratio between the intensity of the reflected radiation and the intensity of the incident radiation , calculated from the equation [9] :

R+T+A=1 (2)

4- **Absorption coefficient α**: defined as the ratio between the decrease in the flow of the incident radiation energy to the unit of distance towards the spread of the incident light wave within the field, and is calculated from the equation [10] :

$$\alpha = 2.303\frac{A}{d} \quad (3)$$

A represents absorbency , d = 1mm the thickness of the material

5- **The extinction coefficient 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 [11]:

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

6- **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 [12] :

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - (K^2 + 1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \quad (5)$$

R represents reflectance .

7- **Optical length L**: the inversion of the absorption coefficient [10]:

$$L = \frac{1}{\alpha} \qquad (6)$$

8- **Optical conductivity σ_{opt}**: optical conductivity is related to the refractive index and the extinction coefficient according to the following equation [13]:

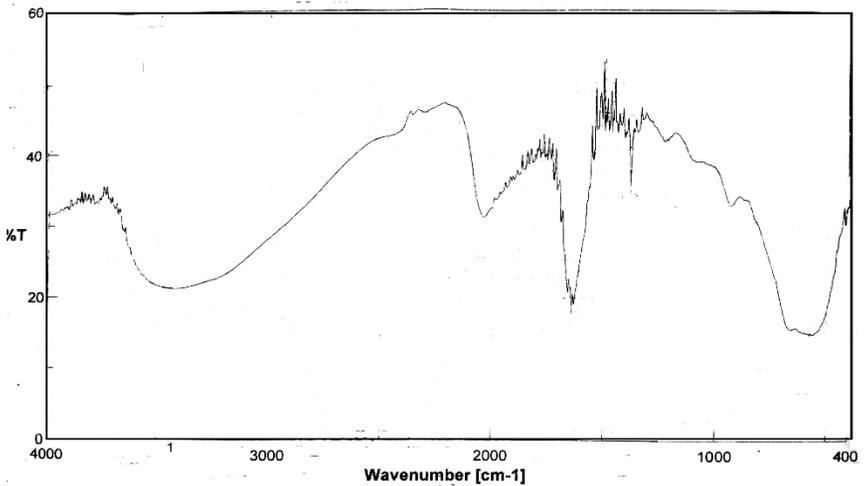$$\sigma_{opt} = \frac{1}{30} \, nk\nu \qquad (7)$$

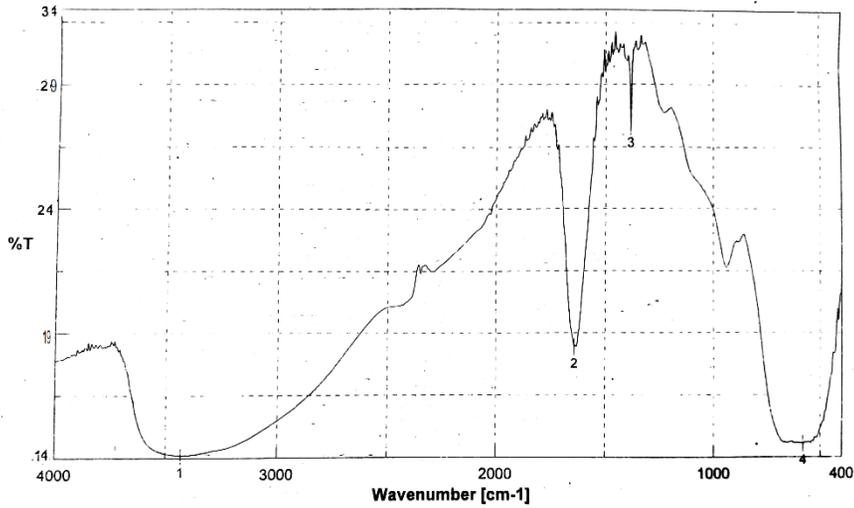Figure (3): Represents the FTIR spectrum for pure tin oxide.

Figure (4): represents FTIR spectrum of iron doped tin oxide by (4wt%).

FTIR is a technique used to obtain information regarding chemical bonding and functional groups in a material. In the transmission mode, it is quite useful to predict the presence of certain functional groups which are adsorbed at certain frequencies; thus, it reveals the structure of the material. The band positions and numbers of absorption peaks depend on the crystalline structure, chemical composition, and also on morphology [6]. To investigate chemical groups on the surface of sintered samples, an FTIR analysis was carried out at room temperature over the wave number range of 400– 4000 cm^{-1}. There are several bands appearing in the wave number range 400–4000 cm^{-1}. The broad absorption band at 3423 cm^{-1}, the peaks at 2977 cm^{-1}, and 1630 cm^{-1} are assigned to the vibration of hydroxyl group due to the absorbed/adsorbed water and show a stretching vibrational mode of O–H group [7]. Absorption peaks observed around 2380 cm^{-1} belong to the stretching vibrations of C–H bonds that could be due to the adsorption and interaction of atmospheric carbon dioxide with water during the firing process [8]. The bands observed in the range of 970–700 cm^{-1} are due to the vibration of Sn=O and Sn–O surface cation oxygen bonds [7]. The very strong absorption bands observed in the range of 420–700 cm^{-1} are attributed to the Sn–O antisymmetric

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vibrations. In that region, the peak at 686 cm^{-1} are assigned to Sn–O–Sn vibrations, respectively . The bands exhibited in the low wave number region 430–620 cm^{-1} are attributed to the Sn–O stretching vibrations [10]. The Fe doping shifts the positions of the absorption bands. It has been previously reported that changes observed in the shape, width, and positions of FTIR peaks are attributed to the variation in the local defects, grain size and shape of the samples [11]. In all samples, the vibrations associated to C–H and O–H bonds are seen. This implies that the surface is highly active and adsorbed these molecules.

Table: (1) shows the vibrations frequency of pure tin oxide with corresponding permeability values for each frequency, absorbance, reflectance , absorption coefficient, extinction coefficient, refractive index, optical length and optical conductivity.

ν (cm)$^{-1}$	T%	A	R	α (cm)$^{-1}$	k	n	L(cm)	$\sigma_{(opt)}(\Omega.cm)^{-1}$
3432.670	21.092	0.6758	0.1131	15.54529	0.000361	2.014	0.06430	0.083093
2125.300	27.692	0.5576	0.1654	12.82585	0.000480	2.371	0.07790	0.080712
1641.130	18.841	0.7248	0.0866	16.67261	0.000809	1.834	0.05997	0.081178
574.683	18.813	0.7255	0.0863	16.68746	0.002312	1.832	0.05992	0.081140
415.585	20.188	0.6949	0.1032	15.98285	0.003062	1.946	0.06250	0.082572

Table: (2) shows the vibrations frequency of the iron doped tin oxide by (4 wt%) with corresponding permeability values for each frequency, absorbance , reflectance, absorption coefficient,

ν (cm)$^{-1}$	T%	A	R	α (cm)$^{-1}$	k	n	L(cm)	$\sigma_{(opt)}(\Omega.cm)^{-1}$
3431.71	14.1154	0.8503	0.0085	19.5570	0.00045	1.2036	0.0511	0.0624
1640.16	19.4074	0.7120	0.0938	16.3767	0.00079	1.8835	0.0610	0.0818
1384.64	27.3105	0.5636	0.1632	12.9644	0.00074	2.3557	0.0771	0.0810
580.49	14.5440	0.8373	0.0172	19.2582	0.00264	1.3023	0.0519	0.0665

extinction coefficient, refractive index, optical length and optical conductivity.

Figure (5) shows the change in the absorbance of pure and iron doped tin oxide , we note that the largest absorbance value corresponds to the pure tin oxide at the value 0.7255 corresponding to the wavenumber (574.683) cm $^{-1}$, and the smallest value of absorbance corresponds to the Fe doped tin oxide at the value 0.5636 corresponding to the wavenumber (1384.64) cm^{-1}.

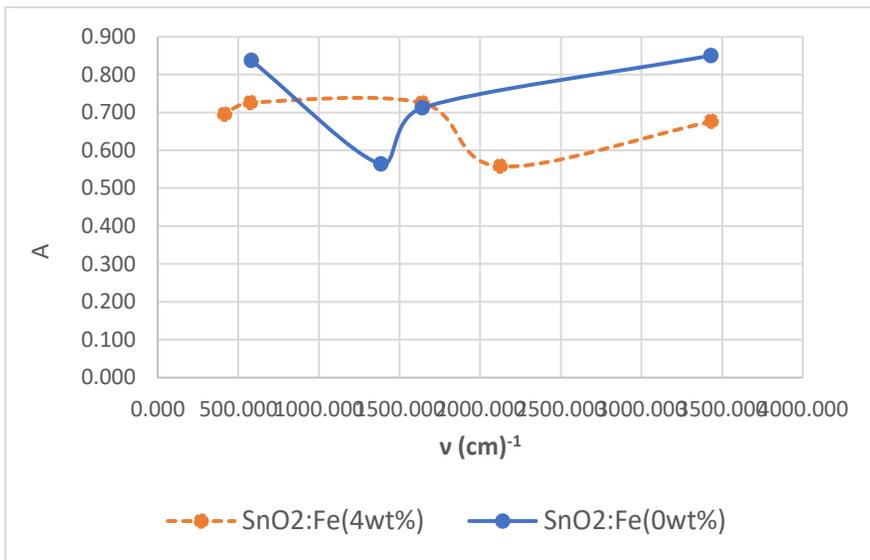Figure (5): the absorbance by the wavenumber function of pure SnO$_2$ and Fe doped SnO$_2$ powder by (4wt%) .

The absorption coefficient variations have been studied by the frequency function as in Figure (6), and that the largest value absorption coefficient corresponds to the pure tin oxide at the value 16.6874 cm^{-1} corresponding to the wavenumber 574.683cm $^{-1}$, and the smallest value of absorption coefficient corresponds to the Fe doped tin oxide at the value 12.9644 cm^{-1} corresponding to the wavenumber 1384.64 cm^{-1}.
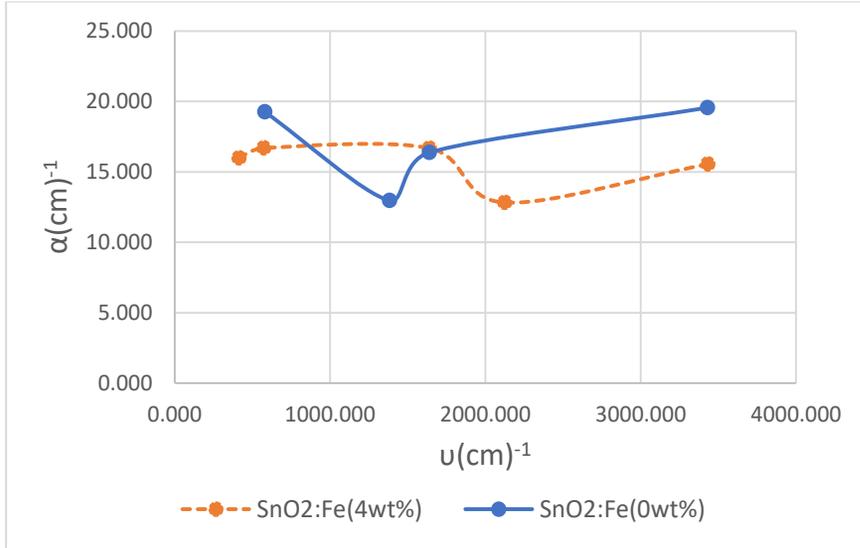
Figure (6): the absorption coefficient by the wavenumber function of pure SnO_2 and Fe doped SnO_2 powder by (4 wt%) .

Figure (7) shows the optical conductivity of the pure tin oxide and Fe doped tin oxide by (4 wt%) powder , where the values of the optical conductivity in the pure sample ranges between [0.0807-0.0830] $(\Omega cm)^{-1}$. where the highest value was corresponds to the Fe doped tin oxide at 0.0818 $(\Omega cm)^{-1}$ corresponding to the wave number (1640.16) cm^{-1} for Fe doped SnO_2 , and the smallest value corresponds to the Fe doped tin oxide at the value 0.0624 $(\Omega cm)^{-1}$ corresponding to the wavenumber (3431.71) cm^{-1}.
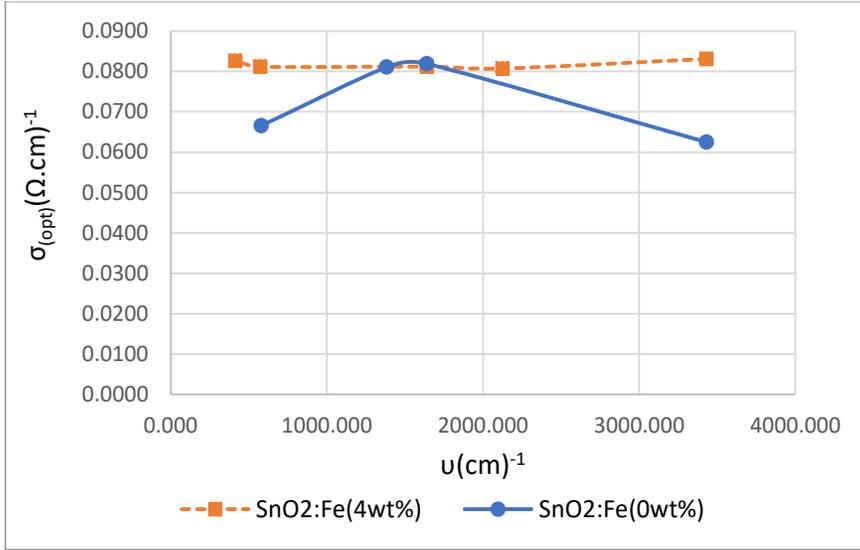
Figure (7): the optical conductivity by the wavenumber function of pure SnO_2 and Fe doped SnO_2 powder by (4wt%) .

Conclusions:

1. The pure tin oxide FTIR spectrum has shown some vibrational frequencies within the range [400-4000] cm^{-1} which are (415.585 - 574.683 - 1641.13 – 2125.3- 3432.67) cm^{-1}

2. The FTIR spectrum of the iron doped tin oxide by 4wt% showed vibrational frequencies within the range [400-4000] Cm-1, the most notably are: (3431.71-1640.16-1384.64-580.49) cm^{-1}

3. The absorbance value for the pure sample varies within the range [0.557 – 0.725], and for the doped sample, the absorbance value varies within the range [0.5630 – 0.8503].

4. The absorption coefficient value varies within the range of the pure sample [12.825 – 16.687] cm^{-1} , and for the doped sample, the absorption coefficient value varies within the range [12.9644 – 19.5570]cm^{-1}.

5. The optical conductivity value σ_{opt} for the pure sample varies within the range [0.0807 – 0.0830](Ωcm)$^{-1}$, for the doped sample, the value of the optical conductivity varies in the range [0.0624 – 0.0818] (Ωcm)$^{-1}$.

8. The Fourier transformed infrared (FTIR) spectrum showed a band O – Sn – O and Sn – O stretching vibration

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