INFRARED SPECTROSCOPY STUDY OF PURE OXIDES ZNO, SNO2 AND THEIR COMPARISON

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Abstract

Nanocrystals of semiconducting metal oxides have attracted great interest due to their interesting properties. Therefore, our study came to some physical properties of pure tin oxide and pure zinc oxide. Infrared spectral measurements of pure tin and zinc oxides showed that there are vibrational frequencies containing five frequencies for tin oxide and seven vibrational frequencies for zinc oxide . The permeability spectra for SnO2, ZnO compounds were measured and we calculated each of n , A α , optσ , and it was found through the comparison of those amounts for the two compounds that the conductivity for zinc oxide was the lowest possible, where $\sigma opt=0.0671$ $(\Omega cm)^{-1}$ corresponding to the vibration frequency of $\upsilon= 2500$ cm^{-1} . $A=0.422$, $\alpha=9.6$ cm^{-1} , $n=1.277$ corresponding to the same vibrational frequency of $\upsilon = 11900$ cm^{-1}.

Keywords: *tin oxide, zinc oxide, infrared spectrum, absorbance, absorption coefficient, refractive index, optical conductivity.*

INTRODUCTION

Transparent conducting oxides are technologically important materials with a wide range of applications in electronics, solar cells, flat panel displays, and more. Where these materials combine a unique property of being optically transparent and electrically conductive, and among these materials [1].

Where tin oxide (SnO_2) is one of the most important transparent conducting oxides (TCOs) due to its unique optical and electrical properties, in addition to being thermally and chemically stable, and is considered a material with high mechanical specifications as it has a low specific electrical resistance and optical transmittance. High in the visual field and stability when heat treatment.

It is among the n-type semiconductor materials with an energy interval of 3.6 eV. The electrical conductivity of the oxide comes from the unevenness in the structure of these materials due to the oxygen voids. The conductivity can be improved by adding impurities. The electrical conductivity is also affected by heat [1].

The primary cell of tin oxide contains six atoms, two tin atoms and four oxygen atoms, as shown in Figure (1). Whereas, the tin atom Sn4+ located in the center is surrounded by six oxygen atoms O^{2-} forming a regular octahedron, while it surrounds all three atoms located on the vertices of an isosceles triangle, and it crystallizes according to the structure of the tetragonal, where a, c are the network constants It is equal to (a=b=4.737 Å and c=3.185 Å) and belongs to the mnm/2P4 space group (the quadrupole class rhomboid according to the preferred orientation (200) [2].
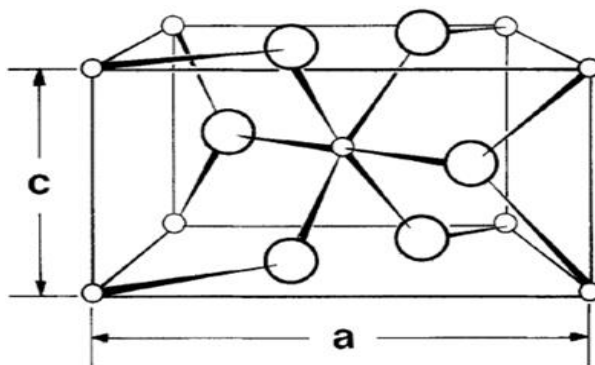

Figure 1: The crystal structure of tin oxide. The small circles indicate the locations of the tin atoms, the large circles indicate the locations of the oxygen atoms.[2]

This oxide is characterized by high electrical conductivity in the visible field and also reflective in the infrared field, where tin oxide has an electrical conductivity located in the range(10^3-10^8) (Ωcm)$^{-1}$ at room temperature. This conductivity is affected by many factors, including heat, light and magnetic field in the presence of Tiny amounts of impurity atoms, which makes it a very important material in electronic applications. Electrical conductivity is also considered one of the most important characteristics by which solids can be classified.

Because of the wide forbidden field, an absorption edge appears in the ultraviolet range, μ 0.36, which makes this compound transparent to visible and near infrared rays [3].

Zinc oxide is one of the inorganic compounds with the chemical formula (ZnO). It is a common compound of zinc. It forms when metal zinc is exposed to air, giving a protective layer that protects the rest of the minerals. It is also in the form of a white powder that is insoluble in water. ZnO is one of the most important transparent oxides (TCOs). Because it has a wide energy gap estimated at 3.3 eV.

Zinc oxide is a binary semiconductor present in group IV-II of n type. It has high transparency in the visible field and a large binding energy at room temperature. Its importance comes from its many applications. It is used in electronic devices such as blue light emitters and short-wavelength laser diodes [6,5].

Zinc oxide crystallizes in a hexagonal crystalline structure. Among these types, the hexagonal structure is the most stable structure and is found in nature more than others. This structure has lattice constants with values (Å = b = 3.249 Å and c = 5.207 Å) and angles (α = β= 90°) , (γ= 120°).
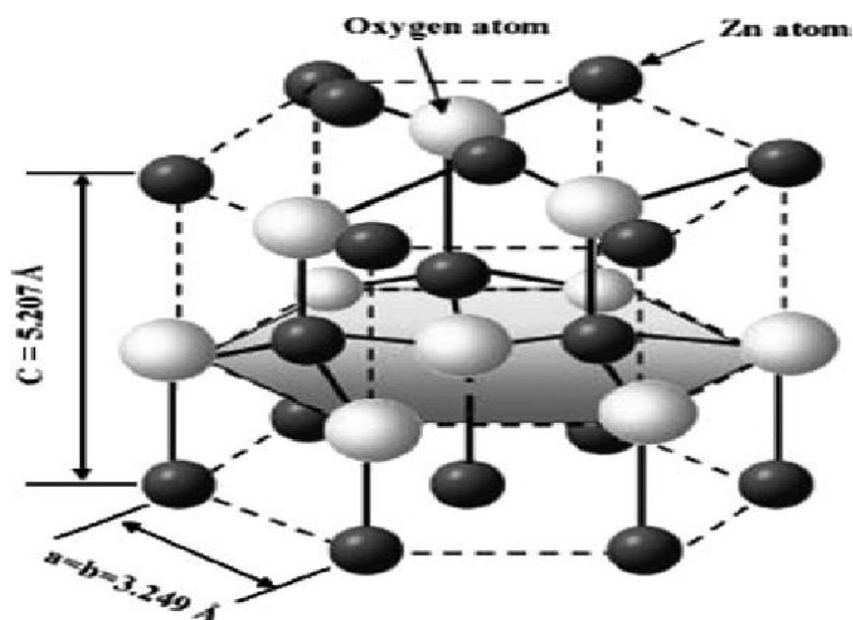

Figure 2: Hexagonal crystal structure of zinc oxide. The gray circles indicate the positions of the oxygen atoms, the red circles indicate the positions of the zinc atoms [6].

INFRARED SPECTROSCOPY

Infrared spectroscopy is one of the branches of spectroscopy that studies the infrared region of the electromagnetic spectrum and includes a set of implementations, the most famous of which is absorption spectroscopy, which is used to determine the active groups in the compounds under study. Infrared spectroscopy is one of the basic methods in the study of materials, as it enables us to identify the structure of the material without affecting its properties. It relies on studying the spectra absorbed by the sample in the energy range (14000-20)cm^{-1} . The energy of red radiation is not sufficient to cause electronic excitations in most materials, but it is sufficient to cause stretching and bending vibrations in the bonds. And all types of bonds respond to this amount of energy to cause vibrations of this kind, so they absorb in the infrared region, provided that the absorption leads to a change in the dipole moment of the molecule, and these vibrations are quantized, and their occurrence means that the compound absorbs infrared energy in a specific part of the spectrum Most of the spectral analyzes take place in the mid-infrared region (200-4000)cm^{-1} where most of the molecular vibrations occur, and the researcher finds enough information to determine the molecular structure of the studied compounds .

PRINCIPLE OF INFRARED SPECTROSCOPY:

Natural particles vibrate according to all their vibration patterns, but with very weak amplitudes, just as the photon has a sinusoidal electric field if the frequency of the incoming photon corresponds to the frequency of vibration of the regular patterns of the molecule, then the molecule will enter into resonance and vibrate with very large amplitudes, or in other words it absorbs the photon whose energy is equal to the energy necessary for the molecule to move from a low energy state to an excited state, and its energy is transformed into vibration energy, as in Figure (4).
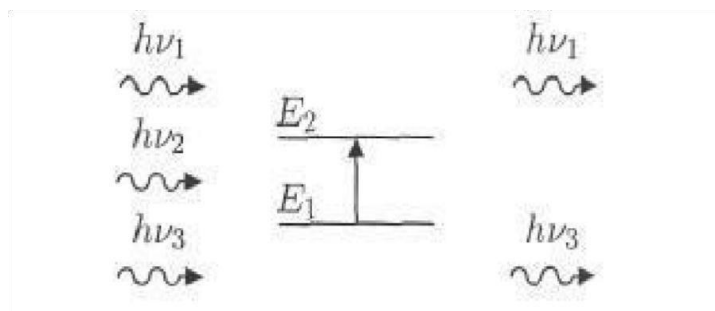

Figure 3: Infrared absorption

Only a photon whose energy is $2h\upsilon$ equal to the transition energy (E_2-E_1) is absorbed, thus creating an imbalance in the backscattered radiation. The absorption of some incoming photons leads to the appearance of harmonic lines of photons that have not been bounced and do not appear in the infrared spectrum curve of the molecule, this absorption characterizes the bonds between the atoms, and since each vibration pattern corresponds to a single movement of the molecule, this means that there is a direct correspondence between the frequency of the absorbed radiation and the structure of the molecule. When the infrared rays are returned to a medium, they suffer reflection, absorption and permeation from the medium.

The IR spectrum of the pure oxides ZnO and 2SnO was measured using the aforementioned spectrometer. Figure (5) shows the IR spectrum of those samples.

We measured:

1-Transmittance T: It is defined as the ratio between the intensity of the transmitted radiation to the intensity of the incoming radiation. It was taken from the device itself, and then using the appropriate mathematical relations, other optical coefficients were calculated.

2-Absorbance A: It is the ratio between the intensity of the absorbed radiation to the intensity of the incident radiation, and it is calculated from the equation: [7]

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

Where: T represents the Transmittance .

3-Reflectivity R: is the ratio between the intensity of the reflected radiation to the intensity of the incident radiation. According to the law of conservation of energy, R can be calculated from the equation: [8]

$$A + T + R = 1 \quad (2)$$

4-Absorption coefficient α: It is defined as the ratio between the decrease in the energy of the incoming radiation per unit distance in the direction of propagation of the incident light wave inside the medium, and it is calculated from the equation: [9]

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

Where: d=1 mm is the material thickness.

5-The damping factor K: is defined as the amount of energy absorbed by the atoms of the studied material from the energy of the incident radiation photons, and it is calculated from the equation: [10]

$$K = \frac{\alpha}{4\pi\upsilon} \qquad (4)$$

where α is the absorption coefficient .

-6-Refractive index n: It is the ratio between the speed of light in a vacuum to its speed in the medium, and it is calculated from the equation: [11]

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

Where R is the reflectivity .

] 7- Optical wavelength L: which is the reciprocal of the absorption coefficient:[9

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

8-Photoconductivity σ_{opt}: The optical conductivity is related to the refractive index and the damping factor k according to the following equation: [12]

$\sigma_{opt} = \frac{1}{30} nk\upsilon \quad (7)$

THE IMPORTANCE OF THE RESEARCH AND ITS OBJECTIVES

The importance of research lies in its broad applications in scientific applications through the study and determination of the range of frequencies and transmittance of the infrared spectra of pure tin and zinc oxides and finding the transmittance, absorbance, absorption coefficient, refractive index, optical wavelength, photoconductivity and damping factor (absorption index) .

RESEARCH METHODS AND MATERIALS

Materials used to prepare the samples:
Tin oxide (purity 99%, company TITAN BIOTECH LTD, originating in India .(
Zinc oxide (purity 99%, company TITAN BIOTECH LTD, originating in India .(

Devices and tools used:

1. A sensitive balance type (SARTORIUS) with an accuracy of gr (4-10) located in the Faculty of Science - Department of Physics - Tishreen University.
2. A high-temperature convection oven (co 1200) with a temperature regulator located in the Faculty of Science - Department of Chemistry - Tishreen University .
3. Small agate mortar, Gate Morator .
4. Jasco infrared spectrometer (Plus 460-IR -TF) - Central Laboratory of the College of Science .

RESULTS AND DISCUSSION

FT-IR technology is used to obtain information about chemical bonds and functional groups in matter. Measuring the permeability in terms of vibrational frequency is useful in predicting the presence of some functional groups as they are absorbed at certain vibrational frequencies and so it reveals the structure of the material. Where the positions of the absorption bands and peaks depend on the crystal structure of the material and the chemical composition as well as on the morphology.

FT-IR analysis was performed for the samples at room temperature within the range of (400-4000 cm^{-1}), where some absorption bands appeared for the studied samples, and we found that each sample was characterized by vibrational frequencies within the range of (400-4000 cm^{-1}).

Tables (1, 2, and 3) contain the values of vibrational frequencies υ extracted from the IR spectra with the corresponding T values for each frequency.

And refractive index n, absorbance A, damping factor K, α (absorption coefficient or linear absorption coefficient), optical wavelength L, and photoconductivity σ_{opt} .

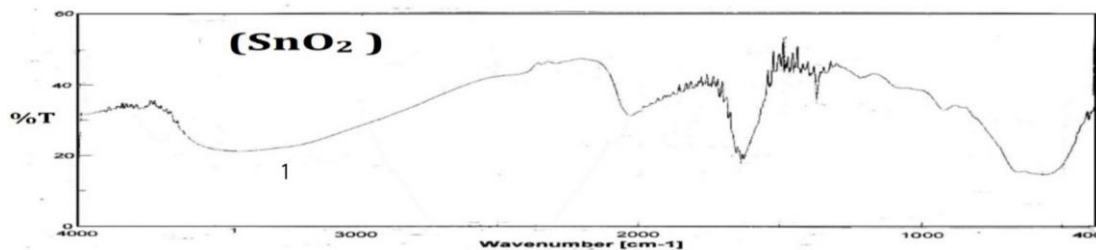https://www.gapinterdisciplinarities.org/
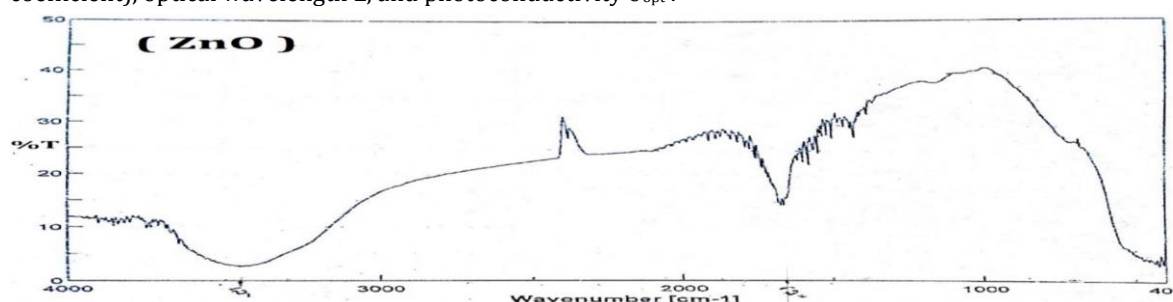
Figure (4): FTIR spectra for zinc oxide and tin oxide .

Table 1: The table shows pure zinc oxide with values of transmittance corresponding to each vibrational frequency, absorbance, reflectivity, absorption coefficient, damping factor, refractive index, optical wavelength and photoconductivity .

υ (cm^{-1})	T%	n^2	n	A	α (cm^{-1})	k*10^{-4}	L (cm)	$\sigma_{(opt)}$ (Ωcm)$^{-1}$	R
3890	11	8.09	2.844	0.958	22.034	4.5	0.045	0.1741	0.068-
3725	9	10	3.162	1.045	24.035	5.13	0.041	0.201	0.135-
3420	2.5	39	6.244	1.602	36.846	8.57	0.027	0.61	0.627-
2650	14	6.142	2.478	0.853	19.619	5.89	0.509	0.1289	0.007
2500	24	3.166	1.779	0.619	14.237	45.3	0.702	0.0671	0.141
2400	27.5	9.666	3.1	0.56	12.88	42.7	0.077	0.105	0.165
1190	38	1.631	1.277	0.422	9.6	19.4	0.104	0.0982	0.200

Table 1: The table shows pure tin oxide with values of transmittance corresponding to each vibrational frequency, absorbance, reflectivity, absorption coefficient, damping factor, refractive index, optical length and optical conductivity .

υ (cm^{-1})	T%	n^2	n	A	α (cm^{-1})	k*10^{-4}	L (cm)	$\sigma_{(opt)}$ (Ωcm)$^{-1}$	R
3432.67	21.092	4.056	2.014	0.675	15.545	3.61	0.064	0.083093	0.113
2125.3	27.692	5.621	2.371	0.557	12.825	4.8	0.077	0.080712	0.165
1641.13	18.841	3.363	1.834	0.724	16.672	8.09	0.0599	0.081178	0.0866
574.683	18.813	3.356	1.832	0.725	16.687	23.12	0.0599	0.08114	0.0863
415.585	20.188	3.786	1.946	0.694	15.982	30.62	0.062	0.082572	0.1032

Figure (5-a) shows the changes of the absorption coefficient in terms of the vibrational frequency of ZnO, where the value of the absorption coefficient increases with the increase in the frequency of the vibrational sites until it reaches a maximum value α = 36.846 cm^{-1} for the absorption coefficient at a vibrational frequency υ = 3420 cm^{-1}, and begins to decrease until It reaches a value for the absorption coefficient α = 22.034 cm^{-1} at a vibration frequency υ = 3890 cm^{-1}, and we note that the lowest value for the absorption coefficient α = 9.6 cm^{-1} corresponding to a vibrational frequency of υ = 1190 cm^{-1}.

Figure (b-5) shows the changes of the absorption coefficient in terms of the vibrational frequency of SnO$_2$, where the absorption coefficient increases with the increase of the vibrational sites until it reaches the highest value α = 16.687 cm^{-1}. The value of α = 12.825 cm^{-1} at vibrational frequency υ = 2125.30 cm^{-1} .

(a)   (b) .

Figure (5): represents changes of absorption coefficient as a function of vibrational frequency SnO$_2$ (b) ZnO (a).

Table (4) shows the average values of the absorption coefficient and the highest and lowest values of the absorption coefficient for the pure oxides, ZnO, SnO$_2$:

Sample	The average value of the absorption coefficient	The highest value of the absorption coefficient	The lowest value of the absorption coefficient
ZnO	19.893	36.864	9.6
SnO$_2$	15.542	16.687	12.825

Figure (a-6) shows the changes in the absorbance in terms of the vibrational frequency of ZnO, where the absorbance increases with the increase in the frequency of the vibrational sites until it reaches the highest value of A = 1.602 of the absorbance at a vibrational frequency υ = 3420 cm^{-1}, and begins to decrease until it reaches the value of A = 0.958 at a frequency of Vibrational υ = 3890 cm^{-1}, and we note that the lowest value of absorbance A = 0.422 corresponding to a vibrational frequency of υ = 1190 cm^{-1} .

Figure (b-6) shows the changes in the absorbance in terms of the vibrational frequency of SnO2, where the absorbance increases with the increase in the vibrational sites until it reaches the highest value of A = 0.725 of the absorbance at a vibrational frequency υ = 574.683 cm^{-1}, then decreases again until it reaches the lowest value of A = 0.558 at Vibration frequency υ = 2125.3 cm^{-1} .

(a)   (b)   .
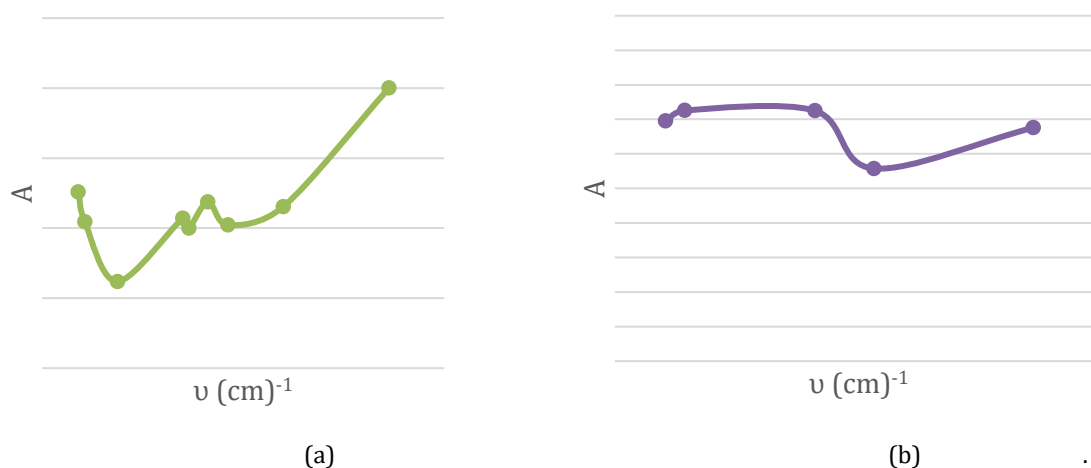
Figure (6): represents the absorbance changes as a consequence of the vibrational frequency SnO$_2$ (b) ZnO (a).

Table (5) shows the average values of absorbance, the highest and the lowest value of absorbance for pure oxides, ZnO, SnO$_2$:

Sample	The average absorbance value	The lowest absorbance value	The lowest absorbance value
ZnO	0.865	1.602	0.422
SnO$_2$	0.675	0.725	0.558

Figure (7-a) shows the changes of the photoconductivity in terms of the vibrational frequency of ZnO where the largest value of the photoconductivity σ_{opt} = 0.61 (Ωcm)$^{-1}$ at a vibrational frequency υ = 3420 cm-1, while we note that the smallest value of the photoconductivity σ_{opt} = 0.067 (Ωcm)$^{-1}$ at an estimated vibrational frequency υ=2500

Figure (7-b) shows the changes of the photoconductivity in terms of the vibrational frequency of 2SnO, where we can see from the curve the value of the optical conductivity decreases with the increase of the vibrational sites until it reaches the lowest value σ_{opt} = 0.0807 (Ωcm)$^{-1}$ for the photoconductivity at a vibrational frequency υ = 750 cm^{-1}, and it starts to increase until it reaches a value of photoconductivity σ_{opt} =0.214406 (Ωcm)$^{-1}$ at a vibrational frequency υ=2125.300 cm^{-1}, and then the value of the optical conductivity increases with increasing vibrational frequency to reach the greatest value of photoconductivity σ_{opt}=0.0831 (Ωcm)$^{-1}$ Corresponding to a vibrational frequency of υ = 3432.67 cm^{-1}, due to the spatial voids between the atoms .
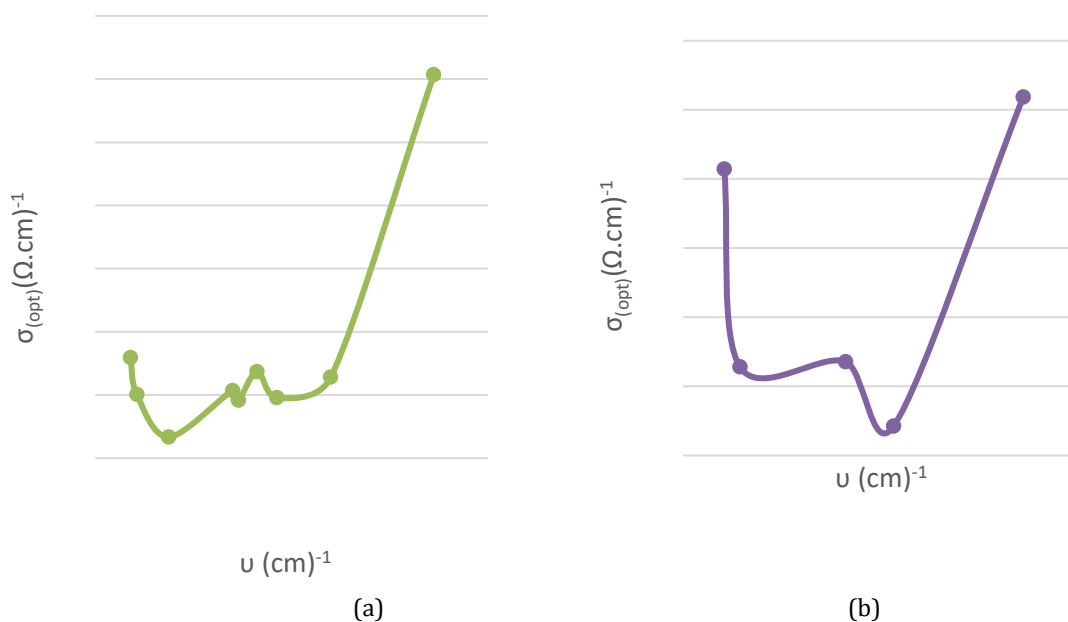
(a)   (b)

Figure (7): Represents the changes in photoconductivity as a consequence of the vibrational frequency SnO_2 (b) ZnO (a) .

Table (6) shows the average values of the photoconductivity and the highest and lowest values of the photoconductivity for the pure oxides, ZnO, SnO_2 :

Sample	The average value of the light transmittance	The highest value of the light transmittance	The lowest value of the light transmittance
ZnO	0.197	0.61	0.067
SnO_2	0.081	0.0831	0.0807

Figure (8-a) shows changes in the index of refraction in terms of the vibrational frequency of ZnO, where the value of the index of refraction increases with the increase in the frequency of the vibrational sites until it reaches a maximum value of n = 6.244 for the index of refraction at a vibrational frequency υ = 3420 cm^{-1}, and it begins to decrease until it reaches the value of the index of refraction. Refraction n = 2.844 at a vibrational frequency of υ = 3890 cm^{-1}, and we note that the lowest value of the refractive index is n = 1.277 corresponding to a vibrational frequency of υ = 1190 cm^{-1} .

Figure (b-8) shows the changes of the index of refraction in terms of the vibrational frequency of SnO_2, where the index of refraction decreases with the increase in the vibrational sites until it reaches a minimum value of n =1.832 the index of refraction at a vibrational frequency υ = 574.683 cm^{-1}, then it increases again until it reaches the highest value n=2.371
. at vibrational frequency υ = 2125.30cm^{-1}

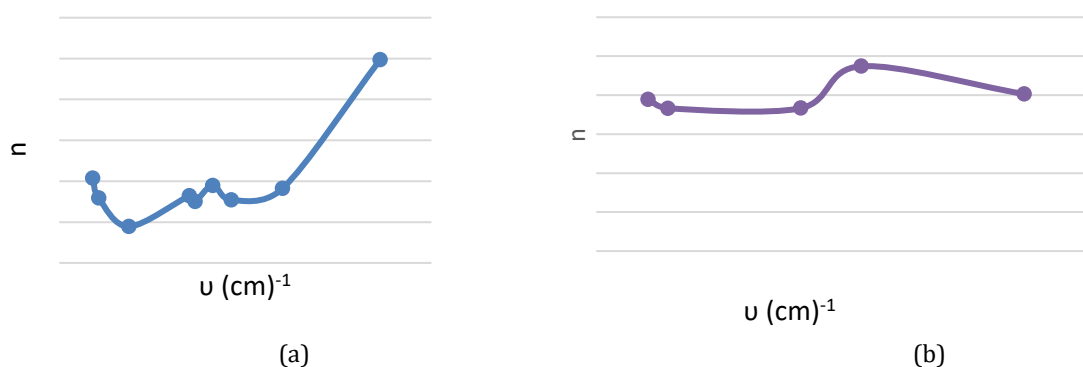(a)   (b)

Figure 8: Representing the changes of the refractive index as a function of the vibrational frequency SnO_2 (b) ZnO (a) .

Table (7) shows the average values of the index of refraction and the highest and lowest values of the index of refraction for the pure oxides ZnO and SnO_2 :

Sample	The average refractive index value	The highest refractive index value	The lowest refractive index value
ZnO	2.983	6.244	1.277
SnO_2	1.999	2.371	1.832

CONCLUSIONS AND RECOMMENDATIONS

1. The RI spectrum of zinc oxide is characterized by seven vibrational frequencies, and tin oxide is characterized by five vibrational frequencies within the range (400-4000) cm^{-1}

2. The value of absorbance A for each of the studied oxides ranges within the range for zinc oxide, [0.725-0.558] for tin . [0.420-1.602] oxide

3. he value of the refractive index n ranges within the for zinc oxide range [2.371-1.832], for tin oxide.-6.244] [1.277

4. The value of the optical wavelength, L, ranges within the range [0.027-0.702] -For zinc oxide, [0.078-0.060] for tin oxide 4

5. The value of the absorption coefficient α ranges within the for zinc oxide range [16.687-12.826], for tin oxide range [9.60-36.846]

6. The value of the photoconductivity σ ranges within the for zinc oxide range [0.0831-0.0807], for tin oxide for zinc oxide, [0.0831-0.0807].

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