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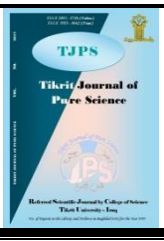

Characterization of Calcium Fluoride Prepared by Chemical Precipitation Method

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ABSTRACT
A solution composed of calcium fluoride (CaF_2) and methanol was precipitated using the chemical precipitation method for three samples in equal proportions. The samples were measured with X-ray diffraction with exposure times of (10, 15, and 20 sec). The peaks are displaced from each other towards the lower diffraction angles. This is attributed to the expansion of the crystal lattice due to the increase in the formation of atomic voids in the crystal structure of CaF_2. Using a UV-Vis device, the absorbance of CaF_2 suspended in methanol was measured and the energy gap was calculated, recording (3.7 eV) for direct transmission and (2.9 and 3.1 eV) for indirect transmission, resulting from crystalline defects. This represented another evidence of the presence of atomic voids in the crystal structure of CaF_2, as the energy gap of CaF_2 was (12.1 eV). The emission spectrum was taken at a wavelength of (300 nm) for the two samples with an exposure time of (10 and 20 sec) to X-rays, and (400 nm) for the sample with an exposure time of (15 sec). A shift was observed at the emission peaks, which confirmed a change in the intensity and displacement atomic voids.

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توصيف فلوريد الكالسيوم المحضر بطريقة الترسيب الكيميائي

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الملخص
تم ترسيب محلول مكون من فلوريد الكالسيوم (CaF_2) والميثانول باستخدام طريقة الترسيب الكيميائي لثلاث عينات بنسب متساوية. تم قياس حيود الأشعة السينية للعينات بزمن تعرض (10, 15, and 20 sec). حيث تم إزاحة القمم عن بعضها البعض نحو زوايا الحيود الاوطأ. ويرجع ذلك إلى توسع الشبكة البلورية بسبب الزيادة في تكوين الفراغات الذرية في التركيب البلوري لمركب CaF_2 . باستخدام جهاز UV-Vis تم قياس الامتصاصية لمركب CaF_2 المعلق في الميثانول وحساب فجوة الطاقة حيث كانت للانتقال المباشر (3.7 eV) وللانتقال غير المباشر (2.9 and 3.1 eV) الناتج عن عيوب بلورية وهذا دليل اخر على وجود فراغات ذرية في التركيب البلوري لـ CaF_2، حيث ان فجوة الطاقة لمادة CaF_2 هي (12.1 eV). تم أخذ طيف الانبعاث بطول موجي (300 nm) للعينتين بزمن تعرض (10 and 20 sec) للأشعة السينية، و(400 nm) للعينة بزمن تعرض (15 sec)، حيث لوحظ حدوث تحول عند قمم الانبعاث، مما يؤكد حدوث تغيير في شدة وإزاحة الفراغات الذرية.
الكلمات المفتاحية: فلوريد الكالسيوم، طريقة الترسيب الكيميائي، حيود الاشعة السينية، طيف التألق الضوئي، طيف الامتصاصية.

1- Introduction

Calcium fluoride (CaF_2) is a hemisphere with a face-centered cubic (FCC) structure with three sub-lattices. The single cell of matter is easily described, as a simple cubic lattice forms fluorine ion. The calcium ion is located in the second cube. The remaining empty cubes are very important for defect formation and diffusion and for containing undesirable impurities, such as the rare earth elements [1], as shown in Figure (1).

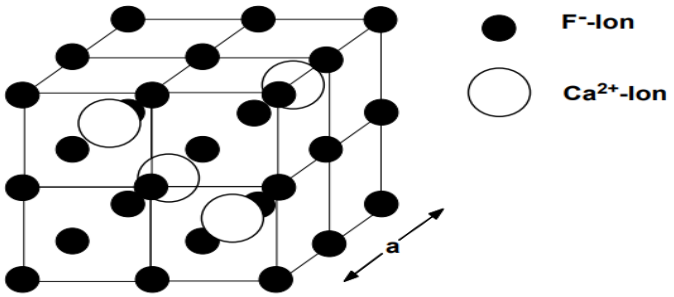

Fig (1): the cubic structure of Calcium fluoride [1]

Figure (1) shows one cell of calcium fluoride. The crystal lattice constant is (5.45 Å). The position of fluorine ions is limited to black corpuscles, while the position of calcium ions is limited to white corpuscles. The calcium ion is surrounded by (8) fluorine ions, whereas the fluorine ion is surrounded by (4) calcium ions. The ionic radius of calcium is (0.99 Å), while the ionic radius of fluorine is (1.36 Å) [2,3]. Calcium fluoride is used in the manufacture of optical crystals and microscopic mirrors [4]. Microspheres are spheres with a dielectric structure and have dimensions from (1-1000 μm). The light is confined inside the dielectric sphere by continuous total internal reflections at the curved borders of the surface. The response patterns (resonance) are obtained at distinct frequencies that depend on the refractive index of the sphere and its radius [5-13]. It is characterized by low spectral dispersion according to the API number, which is a measure of the dispersion of the material and is used to describe the dispersion phenomenon. Whenever the API number is high, the spectral dispersion is low, as its value in calcium fluoride reaches (95.23). It is considered a chemical element that is stable to the changes in pressure and temperature. Calcium fluoride particles possess high technology in the field of advanced optical photons, display screens, imaging, and optical amplification. It can be obtained in the liquid phase by several methods, including co-precipitation, hydrolysis at high temperatures, gel structures, and radiochemical generation [4]. The chemical precipitation method (CPM) is used, as it has many advantages. It is a simple, economical, low-cost, widely used, and applicable technique. It is employed by adding chemicals, such as

methanol, to a compound (CaF_2). This will change the physical state of the dissolved and suspended solids as the percentage of dissolved and suspended materials increases in the resulting solution, and is then treated by centrifugation method. In this study, CaF_2 was prepared by employing the chemical precipitation method and characterized using XRD and optical fluorescence spectroscopy in order to study its optical properties in the future as an optical material for microspheres.

2- Experimental Part

In this respect, (5g) of calcium fluoride was dissolved in (30 ml) of methanol using a magnetic stirrer. This solution was expelled once during (5 min) at a rate of (4000 cycles), and washed with distilled water to get rid of impurities. Then, it was expelled four times for (3 min) at a rate of (3000 cycles) and washed after that. It was treated in a convection oven at a temperature of (70 °C). Three samples of equal proportions were taken to measure the X-ray diffraction of the samples with an exposure time of (10, 15, and 20 sec), and also to study their photoluminescence.

3- Results and Discussion

3-1 Structural properties

The spectrum of the calcium fluoride compound was studied for the three samples using an X-ray diffraction device with an exposure time (10,15,20 Sec), respectively. The results showed that the structure of CaF_2 was cubic of (FCC) type, as shown in figure (2). This result agrees with that found in [14]. In addition, there was a shift in the peaks of the X-ray spectrum characteristic of crystalline planes.

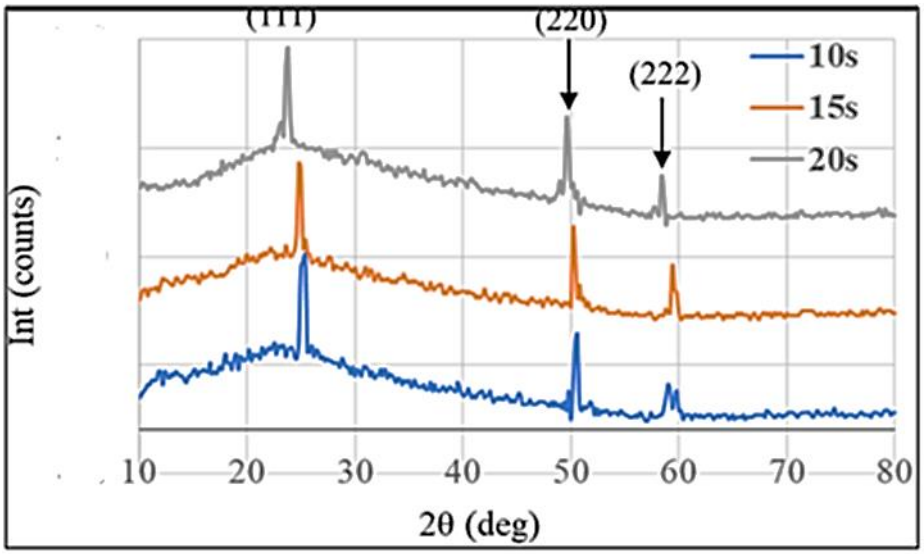

Fig (2): XRD of the CaF_2 samples with exposure times (10, 15, 20 sec)

Crystal plane (111) appeared at ($2\Theta = 28^{o}$) and crystal plane (220) appeared at ($2\Theta = 50.6^{o}$), the crystal plane (222) appeared from ($2\Theta = 59.1^{o}$). Figure (2) illustrates that plane (111) had a high intensity and displacement was clear. The longer exposure time of the material to X-ray, a shift occurs in peaks of X-ray spectrum (2Θ). This means that the crystal lattice has expanded due to the increase in calcium voids and the movement of calcium atoms towards the new levels. Thus, there is repulsion between the fluorine ions as a result of the

repulsive electrical forces. Based on the X-ray spectrum and Bragg's law, the distance between the crystalline planes was calculated using this relationship: $n\lambda = 2dsin\theta$ ……..…… (1) [15]

Where (λ) represents the wavelength of X-ray (1.5418 Å). From relation (2), the crystal lattice constant was calculated [16].

$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$ ……..… (2)

Where (d) represents the lattice planes, (a) represents the lattice constant, and (hkl) represents miller indices.

The average crystallite size (D) for samples was estimated by the standard Scherrer formula [17].

$D = \frac{k\,\lambda}{\beta \cos\theta}$ ……..(3)

Where (k) is constant (0.9), (β) is the full width at half maximum (FWHM) of the diffraction peak, and (Θ) is the diffraction angle. The strain of the crystal lattice (ε) and dislocations density (δ) were estimated, which were extracted from the diffraction spectrum of the three prepared samples, as per the following relationships [15]:

$\varepsilon = \frac{\beta \cos\theta}{4}$ ……..(4)

$\delta = \frac{n}{D^2}$ ……(5)

Where (n) is a factor that gives minimum dislocations when (n =1), as shown in table (1).

Table (1): The values of crystallite size (D), the distance between the crystalline planes (d), strain of the crystal lattice (ε), dislocations density (δ), and crystal lattice constant (a) of the three CaF_2 samples

Sample CaF_2	D (Å)	d(Å)	ε	δ $(Å)^{-2}$	a(Å)
10 s	44.6	3.22	0.004	0.16	5.41
15 s	48.9	3.26	0.006	0.37	5.47
20 s	51.2	3.29	0.008	0.61	5.57

Table (1) clarifies that when the exposure time to X-ray increases, the crystallite size increases, and the crystal lattice constant and the strain of the crystal lattice also increase. This indicates an expansion of the crystals, so the number of calcium atom voids increases, which increases the dislocation density and creates trap levels located in the energy gap of the sample.

3-2 Optical properties

Using a UV-Vis spectrometer to measure the absorption spectrum of CaF_2 suspended in methanol, figure (3) shows the presence of two absorption peaks for wavelengths (λCaF_2 = 285 nm, λCaF_2 = 335 nm).

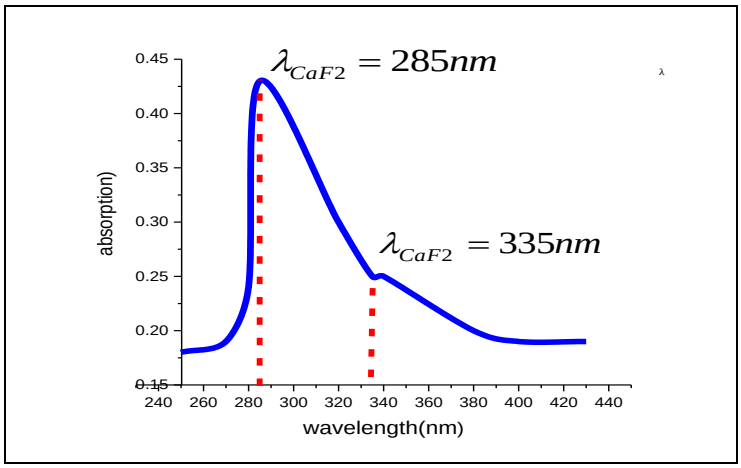

Fig.(3): The absorption spectrum of CaF_2 suspended in methanol

The absorption coefficient is given by the following relationship [8]:

$$\alpha h\nu = A(h\nu - Eg)^n \quad \ldots\ldots(6)$$

where (Eg) is the energy gap, (hν) is the photon energy, (A) is constant, and (n) is the amount that indicates the nature of electronic transition. In CaF_2, the electronic transition is direct if (n = 1/2), as shown in figure (4-a), while the value of (Eg = 3.7eV) will be an indirect electronic transition, occurring at (n = 3/2), as shown in figure (4-b). Then, there will be two energy levels resulting from crystalline defects (Eg = 2.9 eV) and (Eg = 3.1 eV).

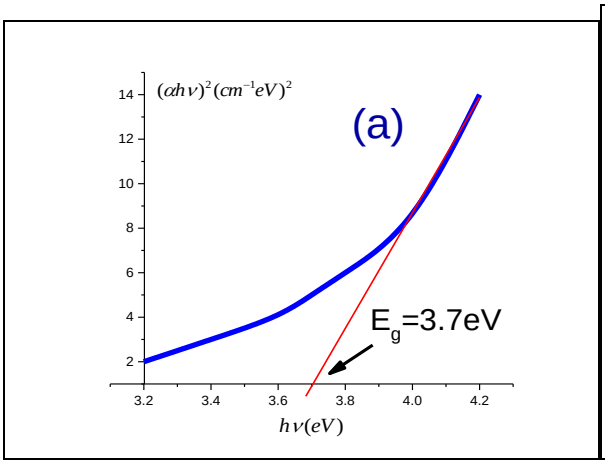

Fig.(4-a): The direct energy gap of CaF_2

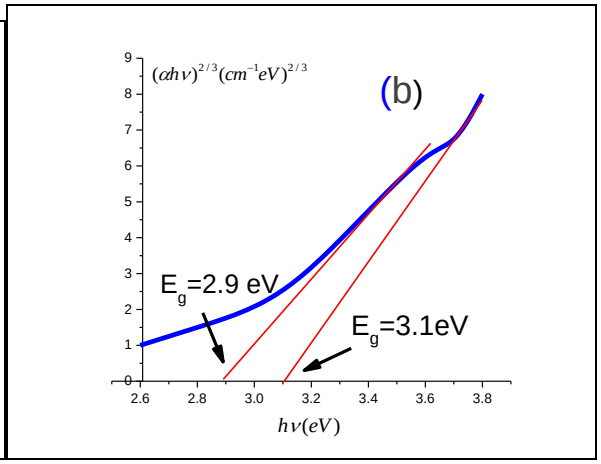

Fig.(4-b): Indirect energy gap of CaF_2

CaF_2 has a wide energy gap (12.1 eV) whose value in references ranges from (11.6 – 12.1 eV) [19], but due to the exposure of calcium fluoride to X-ray, defects are produced in the crystal lattice. These defects are limited to the negative sub-lattice, while the charge is much less than the energy needed to excite the positive charge [20]. The structural defects and voids of calcium atoms are from the traps levels in the energy gap and when the material is excited, it leads to the formation of pair (electron-hole). In the presence of electrons and holes, the self-trapped excitons (STE) process occurs with a time of (10^{-12} sec) and has an efficiency of approximately (1). One of the fluoride ions releases an electron and moves to one of the trap levels.

The photoluminescence device was used to measure the fluorescence spectrum of samples prepared for CaF_2, as well as the time of exposure to X-rays. Figure (5-a) shows the sample prepared with a time of (10 sec), figure (5-b) clarifies the sample with a time of (15 sec), and figure (5-c) presents sample with time (20 sec). The E_g values for the energy levels are calculated from the following relationship [8]:

$$E_g = \frac{1240}{\lambda} \quad \ldots\ldots\ldots(7)$$

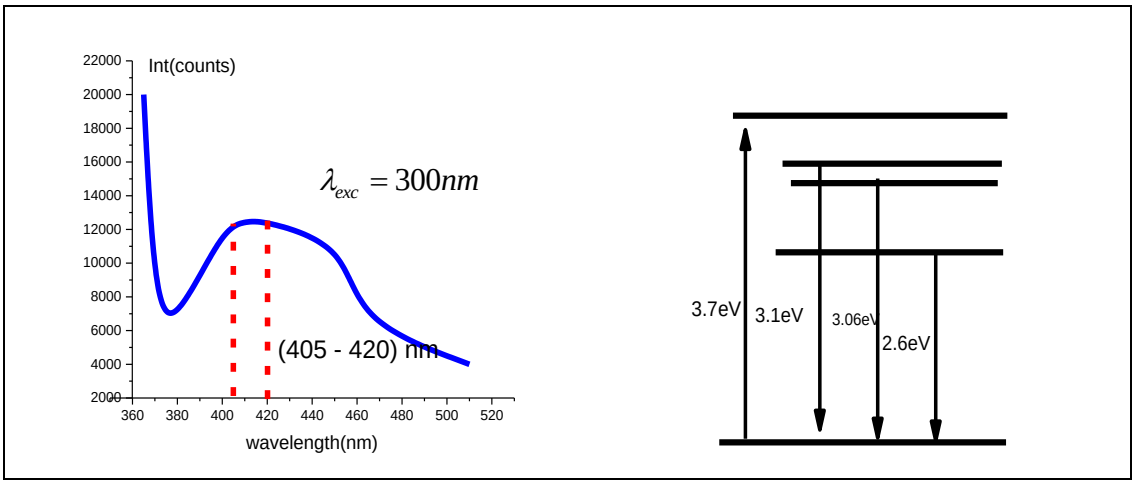

Fig.(5-a): The energy levels and photoluminescence spectra for sample prepared (CaF_2) with (10 sec) for X-ray

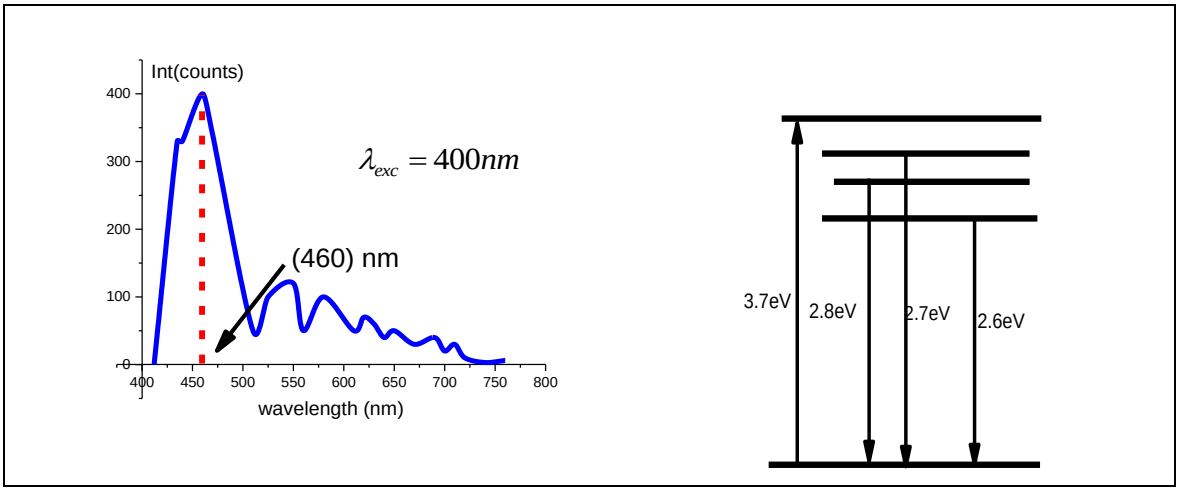

Fig.(5-b): The energy levels and photoluminescence spectra for sample prepared (CaF_2) with (15 sec) for X-ray

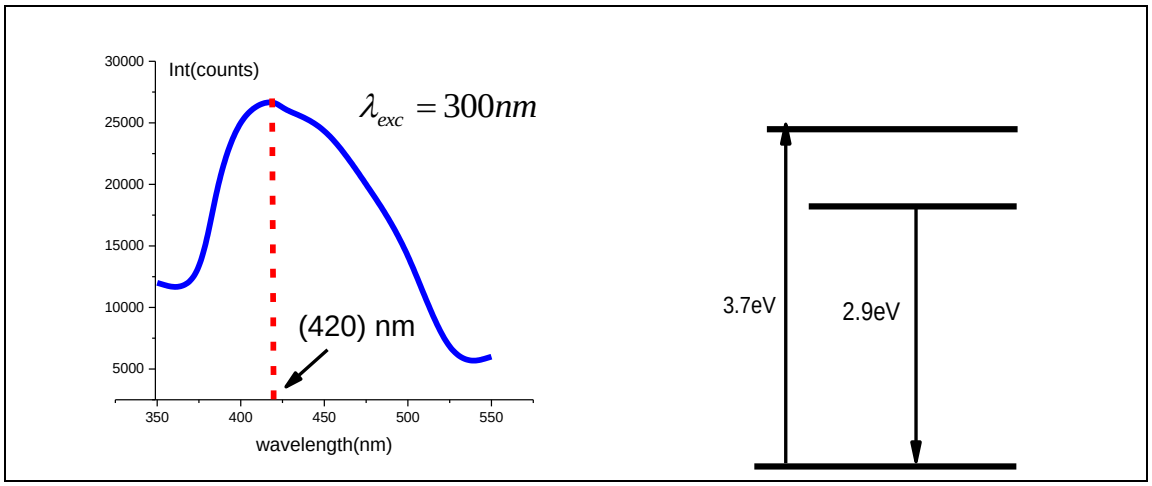

Fig.(5-c): The energy levels and photoluminescence spectra for sample prepared (CaF_2) with (20 sec) for X-ray

Figures (5-a,b,c) show the energy levels and fluorescence. It is noticed that the peaks shifted towards the longer wavelengths with increasing exposure time of the samples to X-rays. The sample with an exposure time (10 sec) had peaks at (405 - 420 nm), the sample with an exposure time (15 sec) had the highest peak at (460 nm), and the sample with an exposure time (20 sec) had peaks at (420 nm). This occurs due to the increased formation of voids in calcium atoms [21,22].

Conclusion

The method of Chemical precipitation is easy and inexpensive to obtain a compound of calcium fluoride. It is observed that the crystal lattice expands as a result of an increase in atom voids, and these voids increase with the increase in exposure time to X-ray. It is found that the energy gap is (3.7 eV) for direct transitions and (2.9 and 3.1 eV) for indirect transitions, due to the crystal defects of CaF_2, where the energy gap of CaF_2 is (12.1 eV). The fluorescence spectrum also shifts towards longer wavelengths with increasing exposure to X-rays. In the future, it is preferable to study the properties of CaF_2 as optical material for microspheres.

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