# Impedance Spectroscope (IS) and (I-V) Characterization of Organic Nanostructured Perovskite (CH3NH3PbCl3) Layer

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## Abstract

Organic nanostructured perovskite layer ($CH_3NH_3PbCl_3$) was prepared. Using XRD structural properties was studied, it showed that the crystalline structure of the perovskite is cubic. The crystalline constants were calculated ($a = b = c = 5.5874\ A^0$). From the absorption spectrum and by using Tauc relationship, energy band gap was calculated, it was found that ($E_g$ =2.985 eV), the absorption spectrum was fitting with theoretical spectrum relay on Mathcad program, and it had been analyses to seven individual spectrum beams depending on Gaussian subject, and it was noted that the most probable transitions are those corresponding to wavelengths(368.821, 325.416, 304.673) nm.

From (I-V) characterization determined at different temperatures, ideal factor is determined, that's mean that as prepared perovskite layer within a certain system behaves as semi-ideal diode. Barrier height was calculated ( $\psi = 7.228 \times 10^{-20}$ eV ), which was very small value, it's negligible, indicating

the absence of interface barriers; it has been found that the transport of charge carriers within the perovskite compound is (3D - VRH) depending on the determination of conductivity dimensions.

In order to know the mechanism of electrical transport and the equivalent electrical circuit of the studied system, impedance spectroscope (IS) was carried out, indicating that electrical model is followed model Cole-Cole, static and dynamic resistors was determined, the relaxation time ($\tau p$) ($7.66\times10^{-1}$, $1.18\times10^{-1}$, $1.62\times10^{-2}$) sec were calculated by extrapolation method at (30, 40, 50) $^0$C, activation energy was calculated ($E_a$ = 1.63 eV), then the dipole moment (D = 2.699 Debye) was determined.

*Keywords: perovskite, organic material, ideality factor, CH 3 NH 3 Pb Cl3 , IS, dipole moment*

## Introduction

Perovskite compounds were first discovered by the scientist Gustav Rose and the Russian metallurgist Lev Perovskite in 1839, where the active material within perovskite is an organic mineral hydrogen [1]. The crystalline structure of perovskite compounds takes the form of ABX3, A and B are cations, X represents the anion. The A and B cations can contain a variety

of charges according to the original minerals of the perovskite, so the A cations are divalent and are often of a family rare earths, B-cations

are quadrivalent, A can be methylamine ( CH3   NH 3 ( or cesium element (Cs), B can be (Pb), (Sn) or (Ge), and X should be one of the following halogens: (Cl, Br, I, F), Fig. 1 shows the crystalline structure of perovskite [2, 3].
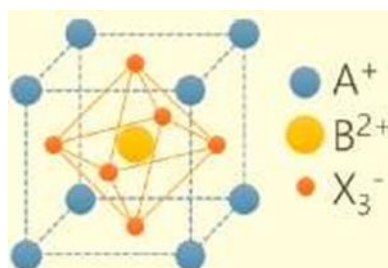


Fig. 1: **The crystalline structure of perovskite**

**Crystal structure of perovskite compounds**

Perovskite compounds can crystallize according to several phases depending on the change in temperature, when temperature is less than 100 K, perovskite compounds will crystallize according to stable orthorhombic structure, when temperature rises to 160 K, the crystalline structure will be tetragonal. As temperature rises to 330 $K^0$, the crystalline structure will be cubic, Fig. 2 shows comparison of all the crystal structures of perovskite compounds [4].
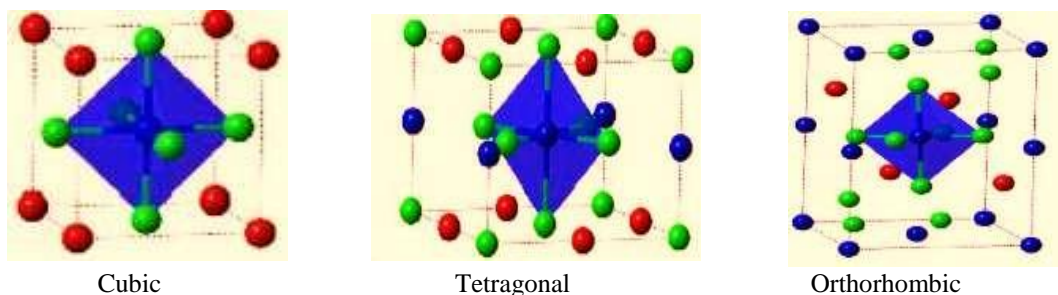


| Cubic | Tetragonal | Orthorhombic |

Fig. 2: **Comparison between the three crystal structures of perovskite compounds.**

The cubic crystalline structure which formed at room temperature can change according to the

change of the lattice coefficients of halides [2, 3].

One of the most important methods of characterizing the electrical properties of materials and electrodes is Impedance Spectroscope (IS). This technique has been widely used to obtain information about the dynamics of charge carriers in material, both in polar solutions and solids materials, where most researches has focused on using this technique to study and characterize membranes in electrolyte solutions, biosensors, composite nanofibers, double- layer capacitors, organic optical detectors and the analysis of PV devices based on different techniques using IS such as silicon, dye sensitized solar cell (DSCs), organic solar cell (OSCs), and finally third-generation solar cells (perovskite) [5].

**Preparation method**

 1.Preparation of methyl amine:

The first stage: Weighed 12.5 gr of acetamide which placed in an ice bath, and then added 3.7 ml of bromine to it, the color of the solution orange, thus we got the solution (A).

-10.9 gr of hydride sodium was dissolved in 100 ml of distilled water in an ice bath, then added to solution (A) in small batches, after that, it was observed that the color shifted from orange to transparent yellow, thus we got the N-Bromo Asset Amide.

The second stage: 30 gr of hydride sodium was dissolved in 75 ml of distilled water in a three neck bottle while maintaining the reaction temperature at (60 - 70) 0C with presence of a temperature regulator, then, N-Bromo Asset Amide was added to contain three neck bottle in the form of drops while maintaining the temperature at (60 - 70) 0C.

## 2. Preparation of methylamine hydrochloride ($CH_3$ $NH_3$ $Cl_3$ ):

The third stage: 50 ml of concentrated water chloric acid was mixed with 50 ml of distilled water within erlenmeyer flask is placed in a ice bath.

-The process of clucking between the content of the previous erlenmeyer flask and the content of the final three neck bottle in the second phase.

-When it has observed the emergence of boiling bubbles, begin to set a period of time of 50 min while maintaining the three neck bottle within the hot air bath.

-After the clucking process, put the content of erlenmeyer flask on the surface of the heater at a temperature of 100 0C while maintaining the presence of a temperature regulator, wait until the solution evaporates so that only 25 ml of it remains.

-The solution is poured into a porcelain vessel with a small depth, and placed in the desiccator at 80 0C until the whole solution has evaporated and a dry powder (yellow color precipitate) is obtained.

The fourth stage (recrystallization): The goal of this stage is obtain a pure methylamine hydrochloride without any other products, and for that the following steps have been followed:

-60 ml of ethanol is poured on the former precipitant within the erlenmeyer flask to dissolve the whole precipitate, and place on the surface of a heater to boil in order to dissolve the whole precipitate, and then filter this solution.

The filtrate part represents the pure methylamine hydrochloride, and the nonfiltrate part represents ammonium chloride, which is known to be dissolved in ethanol.

-The filtrate part is dried until all ethanol has evaporated, thus obtaining yellow powder.

In order to ensure that the output is pure methylamine hydrochloride, its melting point was measured and found to be 190 0C.

## 3. Preparation of perovskite (CH 3 NH 3 Cl3 ):

0.118 gr of methylamine hydrochloride and 0.287 gr of lead chloride were dissolved in a mixture of
0.8 ml of methyl formamide (DMF) and 0.2 ml of methyl sulfoxide (DMSO) by a magnetic stirring mixer at room temperature produces a white opaque solution which is the wanted perovskite compound.

## Results and Discussion
### 1. X-ray diffraction (XRD) Study

Fig. 3 shows XRD spectrum of prepared sample perovskite compound (CH3NH3PbCl3) within 2 θ: (20˚- 60˚).

Fig. 3. X-ray diffraction spectrum of the perovskite compound which formed at room temperature.

It is noted from Fig. 3 that the crystalline structure is a cubic [6, 7].

The distance between the crystal planes can be determined according to the dominated directions using the Brag relationship (1) [8]:

$$2d_{hkl} \sin \theta_{hkl} = n/\lambda$$

Where: dhkl: distance between parallel crystalline planes according to the direction hkl,

θhkl: diffraction angle, n: diffraction grade, λ : X-ray wavelength which equals to 1.5401 0A

The following equations give the relationship between the constants of the cell unit and the distance between the parallel crystalline planes as well as the size of the cell unit for the cubic structure [8].

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$V_{Cubic} = a \times b \times c$$

Depending on the relationships (1), (2) and (3), the distance between the crystalline planes, the cell unit constants and the cell size can be calculated for the prepared sample as shown in table 1.

**Table 1**. Distance between crystalline planes and cell unit constants and cell unit size for perovskite compound

| Sample | d(111) (A) | a = b = c ( ) | V Cubic (A)3 |
|---|---|---|---|
| CH 3 NH 3 Pb Cl3 | 2.79371 | 5.5874 | 174.4345 |

The size of crystallization D is determined based on the Williamson-Hall method, which takes into account all exposures for X-ray curves [9]:

$$\beta_{hkl} = \beta_D + \beta_{strain} + \beta_{instrumental}$$

Where

D : Debay exposure which given in relationship (5):

$$\beta_{hkl} = \frac{k\ \lambda}{D \cos \theta_{hkl}}$$

$$\beta_{strain} = 4\ \varepsilon\ \tan \theta$$

$$\beta_{hkl} = \beta_D + \beta_{strain}$$

$$\beta_{hkl} = \frac{\lambda}{D \cos \theta_{hkl}} + 4\varepsilon \tan \theta_{hkl}$$

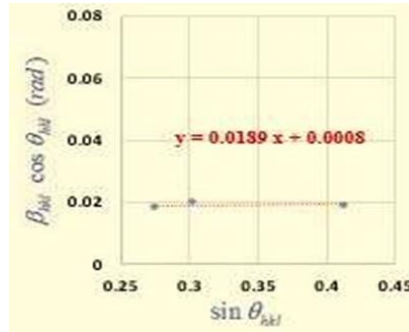$$\beta_{hkl} \cos \theta_{hkl} = \frac{\lambda}{D} + 4\varepsilon \sin \theta_{hkl}$$



Fig. 4: **Williamson - Hall relationship of CH3NH3PbCl3.**

The dislocations density can be defined as the length of the lines of per crystal size, and can be obtained by using the crystallization size D, according to relationship (10) [10]:

$$\delta = \frac{n}{D^2}$$

Where n is a constant equal to one.

Table 2. shows the crystallization size, stress and crystalline dislocations density:

Table 2. Measurement of the size of crystallization, stress and density of dislocations in the crystalline net for compound CH3NH3PbCl3.

| D (nm) | $\varepsilon$ (Line-2 . m-4 ) | $\delta$ (Line . m -2 ) |
|---|---|---|
| 7.5174 | 0.004725 | $1.7695 \times 10{16}$ |

Absorption spectrum the sample had been taken within the wavelength range (200-1100) nm as shown in Fig. 5:
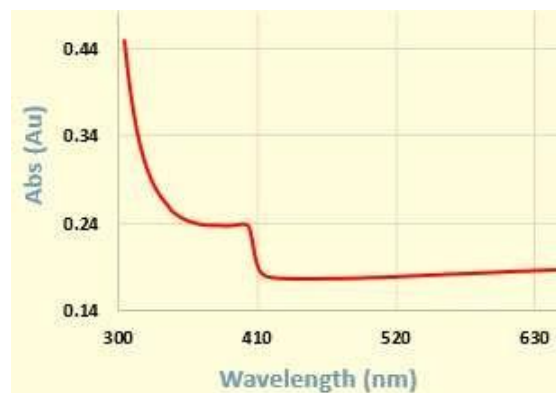


Fig. 5: **The absorption spectrum of the CH3NH3PbCl3 compound**

It is observed from Fig. 5 that there is an absorption peak at (400 nm) wavelength, then the band energy gap calculated using the Tauc relationship (11)
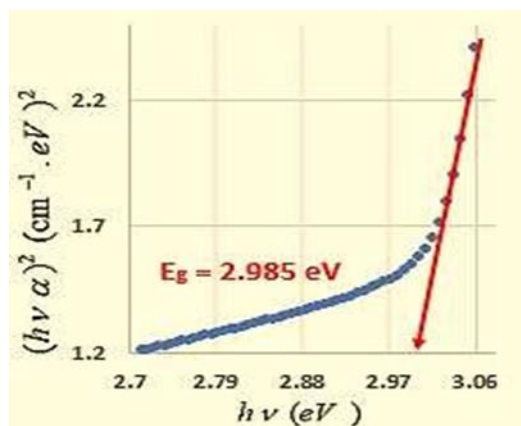
$$\alpha h\upsilon = A(h\upsilon - E_g)^n$$



Fig. 6: **Determination of energy band gap based on the reflection spectrum of CH3NH3PbCl3**

**Study of electronic transitions:**

To determine the possible electronic transitions in the material, the experimental UV absorption spectrum was fitted with the theoretical spectrum using the Mathcad for perovskite compound, after the spectral lines of the theoretical spectrum were deconvolution, the wavelengths corresponding to the absorption peaks were precisely determined, Fig. 7 shows the conformance spectrum for the experimental absorption spectrum with the theoretical spectrum.
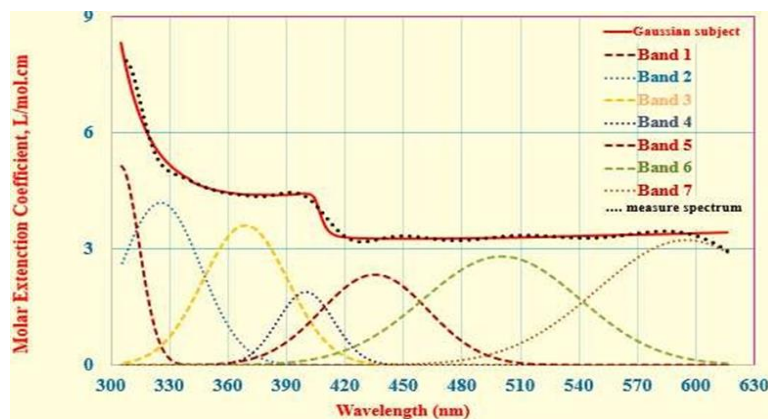


Fig. 7: **Fitting between the experimental absorption spectrum and the theoretical spectrum of CH3NH3PbCl3**

From Fig. 7, there are seven electronic transitions, the following table. 3 shows the parameters related to each absorption peak of a specific electronic transition

| $\varepsilon$ (L / mol . cm) | lmax (nm ) | FWHM (nm) | f )oscillator strength( |
|---|---|---|---|
| 5.154 | 304.673 | 13.48 | 4.436 ´10-7 |
| 4.197 | 325.416 | 29.013 | 8.789 ´10-7 |
| 3.611 | 368.821 | 30.837 | 7.627 ´10-7 |

| 1.893 | 399.736 | 20.334 | $5.523 \times 10^{-7}$ |
|-------|---------|--------|------------------------|
| 2.34  | 435.211 | 38.78  | $1.62 \times 10^{-7}$  |
| 2.811 | 500.275 | 56.87  | $9.19 \times 10^{-8}$  |
| 3.233 | 595.015 | 64.448 | $9.181 \times 10^{-9}$ |

Table 3: **Parameters related to each absorption peak of a specific electronic transition**.
Where molar absorption coefficient (molar extension coefficient), max wavelength corresponding to the greatest peak absorption, FWHM represents the full width half maximum, f oscillator strength.

The table. 3 shows that, the most likely transitions are those corresponding to wavelengths (368.821, 325.416, 304.673) nm, which were clearly appear within the spectrum shown in Fig. 7, the rest of the transitions did not appear on the spectrum because their probability of transmission is low. The corresponding energy per wavelength as shown in table. 4 is calculated based on Planck's relationship

## Conclusions and Outlook

-Organic nanostructured perovskite material was prepared; it has cubic crystalline structure.

-From UV-VIS, it was showed that absorption range of prepared perovskite layer was at the visible range, and that the corresponding energy band gap (Eg = 2.985 eV), by fitting the experimental absorption spectrum with theoretical one based on the Gaussian function, seven electronic transitions were observed, three of them had a high transmission probability.

-From DC current measurements at different temperatures, it was found that this material within a certain system behaves semi- ideal diode due to (n >> 2), in addition the prepared system can be considered p-n heterojunction, and from the calculation of the height barrier value, it was found that this material has a high conductivity due to the absence of interface barriers.

-From Determination of conductivity dimensions, it was found that the transport of charge carriers within the perovskite compound is (3D - VRH).

-From AC current measurements at constant potential (3 Volt) and different temperatures, it was observed that perovskite followed the Cole-Cloe model, and it was noted that loss factor increase with increasing applied frequency at low frequencies to reach a maximum value at (424 Hz) and after this value begins to decrease slightly.

-Finally, it can said that, the (perovskite compounds: CH3NH3PbX3) have promising electrical properties to improve the performance of third generation solar cells.

**Conflicts of Interest**: The authors declare no conflict of interest.

## Data Availability Statements

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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