Structural, Optical and Electrical Properties of KCsI$_2$ Film Deposited by Spray Pyrolysis

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Abstract. A KCsI$_2$ film has been deposited on the glass by chemical spray pyrolysis (CSP) technique using an equal mixture of solvent solutions of KI and CsI at substrate temperature in the range of (150-300) $^\circ$C. X-ray diffraction (XRD) results show that potassium cesium iodide films were polycrystalline in nature with centred cubic structure with sharp peaks along (200), (210), (003) and (110) planes. The electrical resistivity of the film increases with increasing the deposition temperatures reaching 3.59x10$^8$ $\Omega$cm, while the mobility of films decreases from $1.47x10^4$ to the value of $1.18x10^2$ cm$^2$/Vs after increasing the substrate temperature from 150 to 300 $^\circ$C. The energy gap of the film increased from 3.25 to 4.15 eV as the substrate temperature increases from 150 to 300 $^\circ$C.

Keyword: KCsI$_2$; Spray pyrolysis; X-Ray diffraction; mobility; Resistivity

1. Introduction
Great attention has been paid to organic-inorganic compounds due to their properties enable them to be used for many applications. These semiconducting materials were promising for photovoltaic devices which are simple and cost-effective devices [1–5]. Due to the reality that lead is toxic, harmful and not co-friendly. For this reason, it possible to replace it by several ions such as Sn, Ge, Cu, Bi and Sb that produce a new environmental free lead perovskite [6–7]. The infrared absorption of small molecules enhances by Organic–inorganic hybrid Perovskite efficiently, because the quantum wells of perovskites enable the electrons of the Perovskite to be excited by infrared light [2]

Hybrid perovskites is a fascinating material in this field with a high energy conversion efficiency of up to 20% science first use of the three-dimensional (3D) hybrid Perovskite material (CH$_3$NH$_3$PbI$_3$) in 1990 [8-12]. These triggered researchers in the field of hybrid Perovskite application involving light-emitting diode (LED) and laser [13-18]. In this work, we proposed new material KCsI instead of PbI$_2$ in order to to prepare black- Perovskite solar cells which friendly to the environment and human body. We have used the spray technique to prepare the film. The optical and structural properties of the film were studied as a function of substrate temperature.

2. Experimental Work
2.1. Substrate preparation
KCsI$_2$ was deposited on borosilicate glass slides with dimensions of 1.5 x 1.5 cm. These substrates pass through several conventional stages of cleaning. The first cleaning process is carried out by washing with double distilled water DDW to remove the impurities, and then transfer to the second cleaning stage by immersed them in chromic acid for two days. The third phase samples were washed repeatedly in DDW, and finally were placed them in an ultrasonic bath with distilled water for 15 minutes and then dried.

2.2. Deposition of the films of KCsI$_2$

KCsI$_2$ films were deposited by the spray pyrolysis technique. Powder of CI s of 0.3g weight (DEHANE radial deform) with a purity of 99% was dissolved in 25 ml of ionized water DI at 30°C using the magnetic stirrer for 30min and 0.3g of KI powder with 99% purity was dissolved separately in 25 ml in ionized water at 30°C using the magnetic stirrer for 30min. These two aqueous solutions are mixed in a beaker containing of 75 ml of DI using a magnetic stirrer for 30min. The substrate temperature was varied from 150 to 300 °C with a step of 50 °C and the distance between the nozzle to the substrate was 20 cm. The deposition time was taken to be 60 min and the spraying is carried out at pulses with a time of 4 s for each pulse with a stopping period with each spraying pulse of 26 s. The photograph of the experimental set-up of home-made spraying system is shown in Fig.1

2.3. Structural properties

The structural properties of KCsI$_2$ film were determined using an X-ray diffractometer (XRD-6000/ Shimadzu) with a wavelength of $\lambda$=0.154 nm from Cu-Kα with a scanning speed of 8 degrees/min and the incident angle was taken to be in the range of 10-60°. The crystallite size ($D$) of the KCsI$_2$ was found by using Scherrer relation [19],

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

The dislocation density ($\sigma$) of KCsI$_2$ was calculated using the following formula [20],

$$\sigma = \frac{1}{D^2}$$

The thickness of the films ($d$) was measured using weight technique as the thickness of the deposited film is more than 1 µm. The difference in weight is calculated by calculating the substrate weight before and after the process of deposition by using sensitive four-digit Balance type SartOrions TE214S. The film thickness was estimated according to the following relation

$$\text{Thickness (d)} = \frac{\Delta M}{\rho \times A}$$

2.4. Optical properties

The optical transmission (T) of the films was investigated at a wavelength in the range of (300-900) nm using Shimadzu UV- Visible double beam spectrophotometer (UV-1650PC). The absorption coefficient ($\alpha$) was calculated by using the following equation [21],

$$\alpha = \frac{1}{d} \ln \frac{1}{T}$$

The optical energy gap ($E_g$) was determined using Tauc law

$$\alpha h \nu = A(h \nu - E_g)^n$$

2.5. Electrical properties
Four aluminum ohmic contacts were made on the films using a thermal evaporation system through a specially designed mask made from a thin metal sheet. Hall measurements were conducted using the Hall system type (ECOPIA – HMS-300). The measurements were occurred at room temperature.

3. Result and discussion

3.1. Structural analysis
As reported, the XRD peaks of KCsI$_2$ are much closer to the CsI than of KI. Fig. 2 shows the typical X-ray patterns of KCsI$_2$ film prepared at various deposition temperatures. All films are polycrystalline in nature and the film crystallinity is depended on deposition temperature. Four XRD peaks located at 20 $= 23^\circ, 27^\circ, 30^\circ$ and 50$^\circ$ corresponding to (200), (210), (003), and (211), respectively, were observed for film prepared at $T_s = 150$ °C. Increasing the deposition temperature to 250 °C resulted in increasing the intensity of (210) plane and further increasing in deposition temperature leads to appear new XRD peaks. This could be due to variation of the film stoichiometry with deposition temperature. Most of the observed XRD peaks are indexed to stoichiometric CsI according to JCPDs # 00-001-0722 [22] and other peaks can be attributed to KCsI$_2$ phase.

![Figure 2](image.png)

**Figure 2.** Typical XRD patterns of KCsI$_2$ film deposited at different deposition temperatures.

Fig.3 shows the variation of average crystallite size of the film with deposition temperature for (110) plane. The crystallite size decreased sharply when the deposition temperature increased from 150 to 200 °C and then increased slightly with increasing temperature. We have observed that the film crystallinity along (110) plane decreased with increasing the deposition temperature. This could be attributed to the preferential substitution incorporation of dopant atoms [23]. The relationship of between the dislocation density of the deposited film is plotted and given in Fig.4. The dislocation density of KCsI$_2$ films increased with deposition temperature which agrees with XRD results because increasing the deposition temperature plays a vital role in increasing the structural defects in the film due to dis uniformity of films as shown in X-Ray analysis, which leads to an increase of the grain boundaries and this will be discussed in details later on.
Figure 3. Average crystallite size dependence on the deposition temperature.

Figure 4. Variation of dislocation density of KCsI$_2$ films with deposition temperature.

The plot of the FWHM as a function of 2θ of doped KCsI$_2$ films is presented in Fig.5. As shown, the value of FWHM of KCsI$_2$ films influenced by deposition temperatures and diffraction angles. The FWHM decreases as 2θ increase, this trend is more pronounced in (110) reflection plane. Increasing the FWHM at fixed deposition temperature may be due to the increase of structural defects of the deposited film.
Figure 5: dependence of FWHM on the 2θ for doped films

Fig. 6 displays the inter planner spacing (d) as a function of 2θ which shows that the d – spacing is strongly dependent on the reflection plane. Deposition temperatures of KCsI₂ films do not lead to a change in the inter planner spacing (d). The constancy in the d-values suggests that the lattice of the host is not shrinking and expanding, thus, the cell symmetry is not distributed by temperatures.

The optical energy gap of the film is determined from (αhν)² versus (hν) plot since the extrapolation of the straight line to the axis of photon energy gives the band gap [23,25]. The band gap of the films varied from 3.25 to 4.15eV depending on deposition temperature which are in good agreement with that of potassium-doped CsI films [26]. Increasing the band gap with deposition temperature is due to decreasing the grain size with Ts as supported by XRD investigation.
Fig. 7. \((\alpha h \alpha)^2\) versus \((h\nu)\) plot of \(\text{KCsI}_2\) films deposited at various temperatures.

Fig. 8 shows the dependence of the electrical resistivity on the deposition temperature. Increasing the electrical resistivity of \(\text{KCsI}_2\) films with deposition can be ascribed to increasing the structural defects and it can be explained this by the disoriented of crystal growth at higher deposition temperature as clearly seen from the XRD patterns which arising from the increase in the carriers scattering at the boundaries of grain and defects of crystal, which lead to decrease the ability of carrier for movement [27].

The mobility of the film versus deposition temperature is shown in Fig. 10. It decreases from \(1.47 \times 10^4\) to \(1.18 \times 10^2\ \text{cm}^2/(\text{V.s})\) as the temperature of deposition increased from 150 to 300 °C. This could be ascribed to the reduction of grain sizes and increasing grain boundaries [28,29].
4. Conclusions
In this work, we have films of KCsI$_2$ successfully deposited using a spray pyrolysis technique on a glass substrate. The effect of the deposition temperature on the structural, optical and electrical properties of the film was studied. The deposited films are crystalline and the major XRD peaks are indexed to the CsI phase. The crystallite size decreases for deposition temperature $\leq 200 ^\circ$C and then increased with increasing the deposition temperature. The energy gap of the KCsI$_2$ film was increased from 3.25 to 4.1 eV as temperature increased from 150 to 300 $^\circ$C. The electrical resistivity of the film increased with deposition temperature and the mobility of films decrease with increasing deposition temperature. By selecting the optimum deposition conditions, the KCsI$_2$ film can candidate as good materials for UV detection and organic-inorganic solar cells.

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