The Structural and Optical Properties of Perovskite Thin Films

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Abstract

Perovskite materials have many interesting properties such as modulation of the optical band gap and the properties of quantum wells. In addition, they have a stable structure. For these reasons, perovskites have attractive properties for optoelectronic devices. Additionally, the structural and optical properties can be changed by means of different halide atoms doped into materials. In this study, the effect of iodine on the structural, and optical properties of perovskite thin films was investigated. $KCaCl_2$ I and $KCaCl_3$ perovskite were prepared by chemical bath deposition on a glass substrate. The crystal structures of the films were determined by X-ray diffraction. X-Ray Diffraction (XRD) analysis revealed that the films had a crystalline structure. In addition, $KCaCl_2$ I perovskite thin film has better crystalline than $KCaCl_3$ perovskite thin films. Linear optical parameters were determined using transmittance and absorbance measurements. And then, the optical band gap values, extinction coefficient, refractive index, and dielectric constants were determined as linear optical properties. It was understood that these properties were affected by iodine.

Keywords: perovskite, thin films, chemical bath deposition, optical properties, structural properties.

Introduction

A perovskite structure has the form ABX_3, where A, and B are cations, and X is the anion (Wiley, et al. 2019; Korkmaz and Ozpozan-Kalaycioglu, 2012). Perovskites can have interesting a lot of properties because of the molecules in their structure (Kangning, et al. 1998). Therefore, studies on perovskite structures, in other words, perovskite thin films have increased in the last few years to improve the performance of devices such as optoelectronic devices. At end of the 19th century, perovskite structures were formed in an aqueous solution by researchers (Mitzi, 1999; Soto-Montero, et al. 2020). However, these structures contained lead which is so dangerous for the environment (Katsanoulas, 1999). Hence, the research groups have tried to find materials that can be not dangerous to environmental and human health (Daskeviciute-Geguziene, et al. 2022).

Different deposition techniques such as ink-jet printing (Xie, 2018), co-evaporation (Park, 2019), and spin coating (Fong, 2021) have been used to form perovskite thin films.

In this work, the chemical bath deposition technique was used to obtain the perovskite thin films. The technique involves controlled precipitation of a solution of the compound on the substrate. With this technique, the structural and optical properties of the film can be changed by variables, such as solution temperature and precursor concentration. In the CBD method, a film can be formed on any substrate (Güneri, 2019). The aim of this study is to obtain $KCaCl_2I$ and $KCaCl_3$ perovskite thin films using the CBD technique. Additionally, it is to show how iodine affects the structural and optical properties of perovskite thin films.

Experimental Details

The chemicals calcium chloride ($CaCl_2$, Sigma Aldrich 99%), potassium iodide (KI, Sigma Aldrich 99%), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were used in this study. The deposition of perovskite films was carried out using chemical bath deposition (CBD). Prior to the deposition of the thin films by CBD, the glass substrates were cleaned with detergent, deionized water, acetone, ethanol, isopropyl alcohol, and deionized water, respectively. To obtain $KCaClI_2$ perovskite thin films, $CaCl_2$, KI, DMSO, and DMF were used in the bath. First of all, the stoichiometric ratio with $CaCl_2$ and KI was separately mixed in DMSO: DMF (3:7). The solvent mixture DMSO: DMF was used to boost the morphology control. To obtain a clear and homogenous solution, these mixes were continuously blended at room temperature for 24 hours. After obtaining homogenous solutions, the solutions were poured into the beaker, where the substrate cleaned was put. The deposition temperature and time were fixed at room temperature and 48h, respectively, to fabricate the film. The chemical reaction of the composition is given as follows:

$$CaCl_2 + Kl \quad KCaCl_2l \quad \longrightarrow$$

To obtain $KCaCl_3$ perovskite thin films, $KCaCl_2$, KCl, DMSO, and DMF, were used in the bath. The aforementioned process was repeated for $KCaCl_2I$ perovskite thin film as well. The chemical reaction of the composition is given as follows:

$$KCl + KCaCl_2 \longrightarrow KCaCl_3$$

The phase and orientation of the films were determined by XRD using a Panalytical Empyrean Model diffractometer. SHİMADZU & UV-2700 spectrophotometer were used to determine the optical properties of films. All measurements were made at room temperature.

Results and Discussion

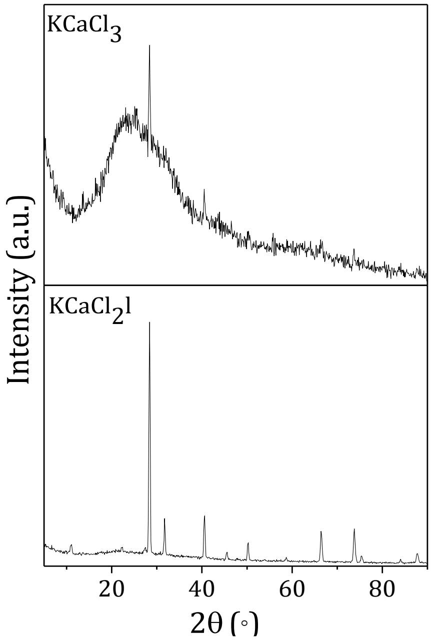


Fig. 1. XRD diffractograms pattern of $KCaCI_2I$ perovskite thin film and $KCaCI_3$ perovskite thin film.

Fig.1 shows the XRD diffractograms of $KCaCI_2I$/glass and $KCaCI_3$/glass, which have crystalline structures. The XRD diffractogram of $KCaCI_2I$ perovskite thin film has four strong diffraction peaks, which are located at the angles 2θ: 28.39°, 40.56°, 66.4639°, and 73.7692°. These peaks didn't index the other materials. In this context, the new perovskite structure was fabricated in this work. The XRD diffractogram of $KCaCI_3$ perovskite thin film has a background due to dirtiness on the glass. Furthermore, there are just two peaks in its spectrum at the angles 2θ: 28.29°, and 40.29°

Fig. 2 shows the transmission, reflection, and absorption spectra of the $KCaCI_2I$ and $KCaCI_3$ perovskite thin films. The transmission ratio of the $KCaCI_2I$ perovskite thin film was lower than that of the $KCaCI_3$ perovskite thin film despite depositing time the same. There can be a lot of reasons. One of them is deposition velocity. The deposition velocity of the $KCaCl_2I$ perovskite thin film can be faster than that of the $KCaCI_3$ perovskite thin film. When the refractive spectrum of both films was investigated, the refractive spectrum of $KCaCl_2I$ perovskite thin films is higher than that of the $KCaCI_3$ perovskite thin film (Fig. 2). The origin of this difference can be iodine. The $KCaCl_2I$ perovskite thin films have two maximum absorption peaks at 307 nm and 362 nm. These values show that there are two transmissions in the films. One of them can be connected from the lower valence band (VB2) to the minimum conduction band (CB), and the other can be fatigued to the transition from the higher valence band (VB1) to the CB (Al-Asbahi, et al. 2020). The $KCaCI_3$ perovskite thin film absorbed most light below 350 nm.

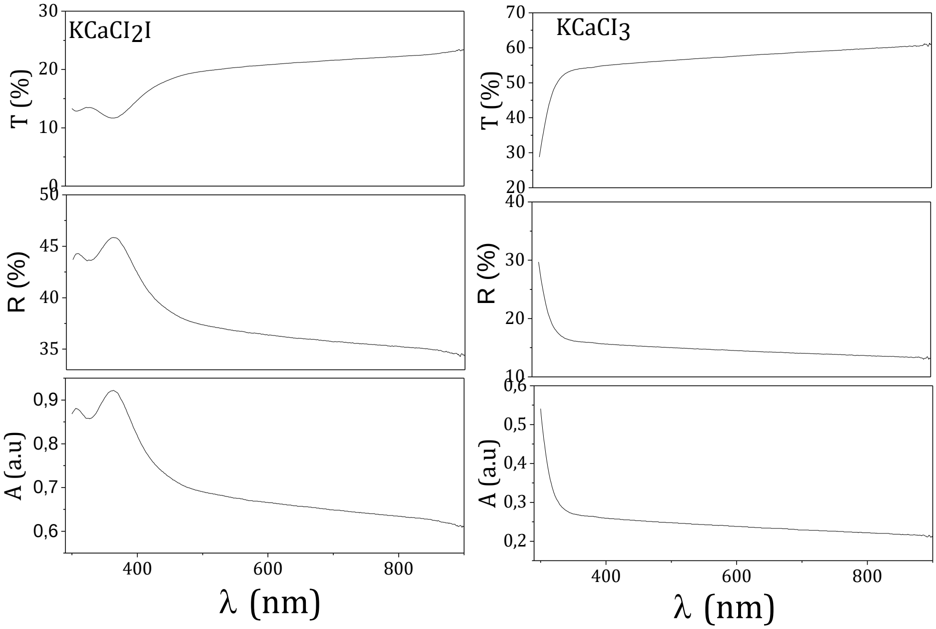


Fig. 2 The transmission, reflection, and absorption spectra of the $KCaCI_2I$ and $KCaCI_3$ perovskite thin films.

The values of the direct energy band gaps of perovskite thin films were estimated from the Tauc plot of the absorption spectrum (Tauc, 1974). As seen in Fig. 3, the band gap values of the $KCaCI_2I$ perovskite thin film are 2.45 eV (VB1 →CB) and 2.65 eV (VB2 →CB) while that of the $KCaCI_3$ perovskite thin film is 3.85 eV. These band gap values show that these films can be used as a window layer of a solar cell (Sharmin, et al. 2019).

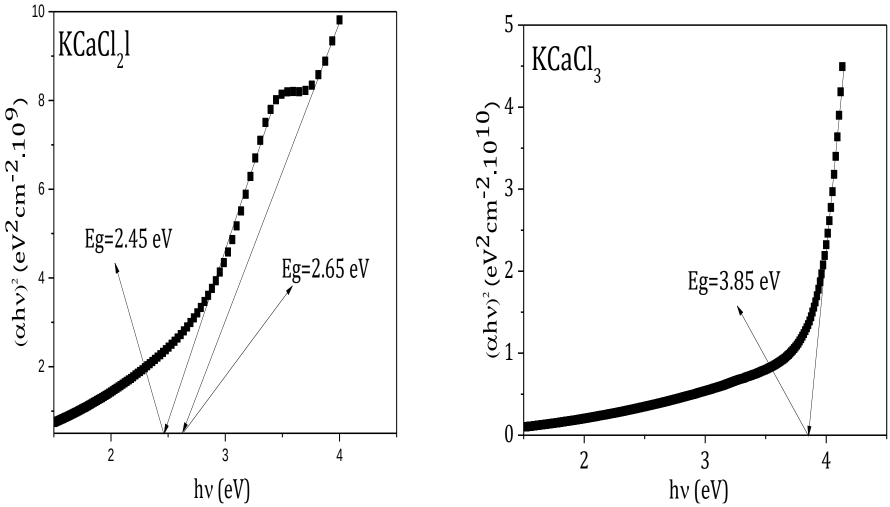
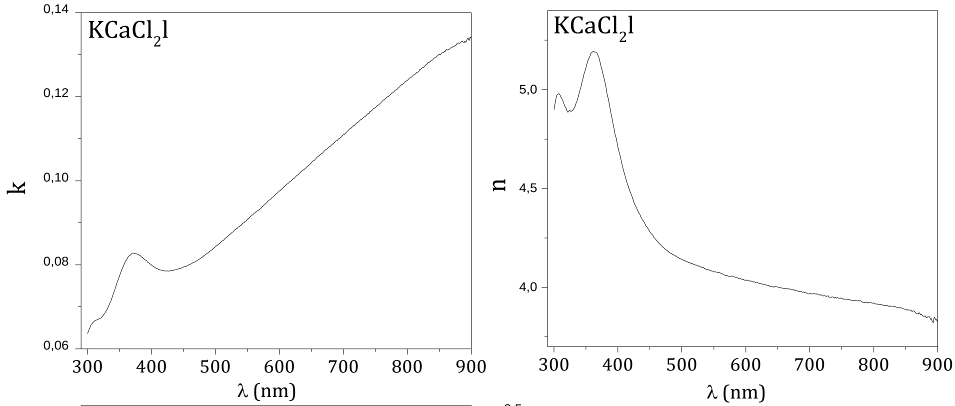


Fig. 3 $(\alpha h\nu)^2$ versus photon energy for the KCaCI$_2$I and KCaCI$_3$ perovskite thin films.

The refractive index and extinction coefficient of the films were determined using equations (Benramdane, et al. 1997). The non-linear dependence of the refractive index (n) and extinction coefficient (k) on the wavelength at room temperature can be seen in Fig. 4. Fig. 4 shows that KCaCI$_2$I and KCaCI$_3$ have different behavior for both parameters. The extinction coefficient of KCaCI$_2$I perovskite thin film increased from 425 nm. The refractive index of this film has also a reverse situation after 362 nm. The extinction coefficient of KCaCl$_3$ perovskite thin films increased from 325 nm. Additionally, the refractive index of KCaCl$_3$ perovskite thin films is almost constant and approximately 2.24–2.18. These values show that this film can be used for antireflection coating (Al-Asbahi, 2020).



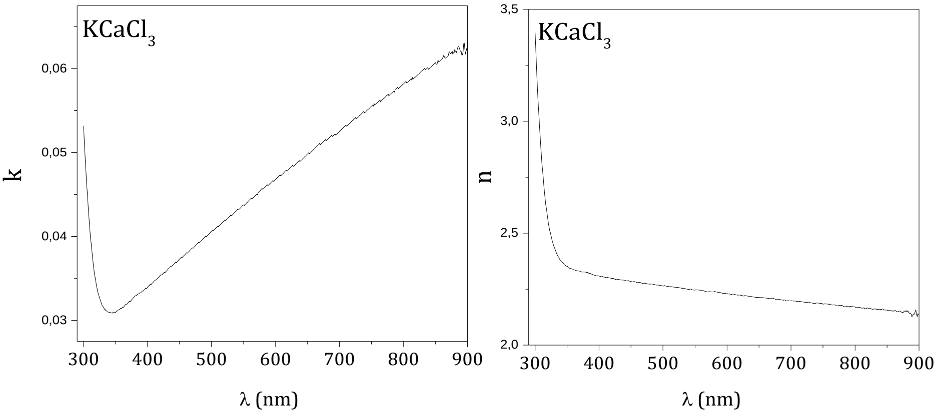
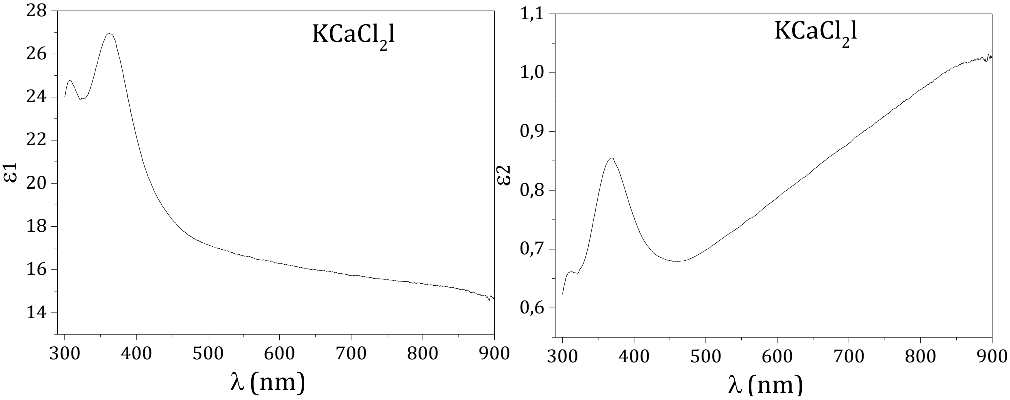
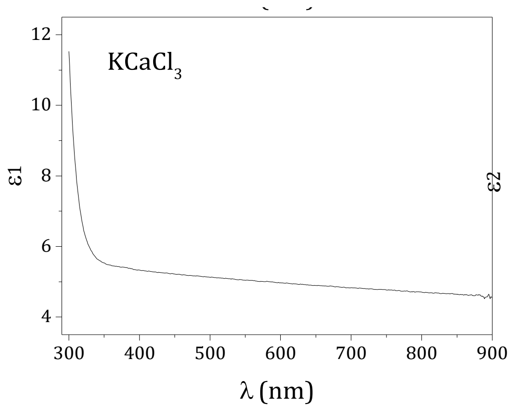


Fig. 4 The refractive index and extinction coefficient on wavelength in $KCaCI_2I$ and $KCaCI_3$ perovskite films.

The real and imaginary parts of the dielectric constant of the films were calculated using the equations (Hodgson, 1970). According to Fig. 5, while the real and imaginary parts of the dielectric constant for $KCaCI_2I$ perovskite films were found to be 16.23 and 0.78 at 600 nm, respectively, the real and imaginary parts of the dielectric constant for $KCaCI_3$ perovskite films were determined to be 4.99 and 20.21 at 600 nm, respectively.





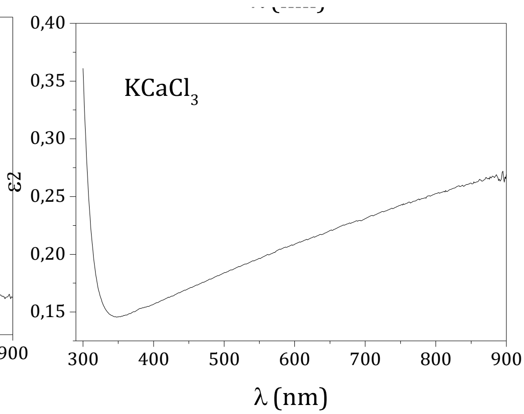


Fig. 5 The dependence of dielectric constants on wavelength in $KCaCI_2I$ and $KCaCI_3$ perovskite films.

Conclusions

In this study, we successfully obtained $KCaCI_2I$ and $KCaCI_3$ perovskite films via the CBD technique and compared the effect of iodine on the structural and optical properties of films by using characterization methods. According to XRD patterns, $KCaCI_2I$ perovskite films have better crystalline structures than $KCaCI_3$ perovskite films. The band gap values of the $KCaCI_2I$ perovskite thin film are 2.45 eV and 2.65 eV. The band gap value of the $KCaCI_3$ perovskite thin film is 3.85 eV. These band gap values show that both films can be used as a window layer of a solar cell. However, the $KCaCI_3$ perovskite thin film can be a better performance than the $KCaCI_2I$ perovskite thin film as a window layer. To understand the effect of iodine on the properties of thin films, we plan to fabricate new films which will include different perovskite. Additionally, we will try using water instead of DMF: DMFO for green chemistry. In addition to all these, obtaining new perovskites using the solid state method and their differences can be investigated.

Acknowledgments

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