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Effect of KCl on the optical and structural properties of $CaZnO_3$ perovskite thin films

Wpływ KCl na właściwości optyczne i strukturalne cienkich warstw perowskitu $CaZnO_3$

The primary goal of this study is to determine whether the produced $CaZnO_3$ perovskite compound may be used in the production of solar cells and diodes. $CaZnO_3$ perovskite thin films have been prepared and examined using scanning electron microscopy (SEM), X-ray spectroscopy, and UV spectroscopy. The films were made using the chemical spray pyrolysis deposition (CSPD) method; they were prepared from a mixture of 0.6 g of $CaCl_2$ and $ZnCl_2$ with 1.2 g of KOH, and $CaZnO_3$ thin films were deposited on a glass substrate at a temperature of 150°C. Optical properties such as transmittance (T), absorbance (A), reflectance (R), the refractive index (n), and extinction coefficient (k) were studied. The energy gap varied from 3.19 eV for films without KCl to 3.22 eV for films with KCl, indicating that the presence of KCl had an impact on the energy gap; furthermore, the average particle's diameter for films with KCl was about 112.28 nm and decreased to 53.86 nm when KCl was removed from the solutions to obtain pure in $CaZnO_3$ perovskite thin films.

<u>Keywords</u>: $CaZnO_3$, perovskite, energy gap, diameter's grain, thin films

Głównym celem badania było określenie, czy wytworzony perowskitowy związek $CaZnO_3$ może zostać wykorzystany do produkcji ogniw fotowoltaicznych i diod. Przygotowano cienkie warstwy perowskitu $CaZnO_3$, które zostały zbadane za pomocą skaningowego mikroskopu elektronowego (SEM), spektrometru rentgenowskiego i spektrometru UV. Warstwy zostały wykonane przy użyciu metody chemicznego osadzania pirolitycznego (CSPD); przygotowano je z mieszaniny 0,6 g $CaCl_2$ i $ZnCl_2$ z 1,2 g KOH, cienkie warstwy $CaZnO_3$ osadzono na szklanym podłożu w temperaturze 150°C. Zbadano właściwości optyczne, takie jak transmitancja (T), absorbancja (A), współczynnik odbicia (R), współczynnik załamania światła (n) i współczynnik ekstynkcji (k). Przerwa energetyczna wynosiła od 3,19 eV w wypadku warstw bez KCl do 3,22 eV dla warstw z KCl, co świadczy o tym, że obecność KCl miała wpływ na przerwę energetyczną. Średnica cząstek w warstwach zawierających KCl wynosiła średnio 112,28 nm i zmniejszyła się do 53,86 nm, gdy z roztworów usunięto KCl w celu uzyskania czystych postaci cienkich warstw $CaZnO_3$.

<u>Słowa kluczowe</u>: $CaZnO_3$, perowskit, przerwa energetyczna, średnica ziarna, cienkie warstwy

1. Introduction

Perovskite materials are recognized as trustworthy alternatives to germanium and silicon in semiconductors. There are many configurations of perovskite, one of which is ABX_3, which includes five atoms [1], where A and B are two cations with radii that differ greatly from one another. Since many of the elements in the periodic table can take the place of the elements in positions A and B, many compounds have perovskite structures [2]. The B-site cation often occupies the core of the octahedron and is a transition-metal element with a small radius, such as Cr, Mn, or Sc. It works in tandem with six X anions [2]. The top corner of the cube is occupied by the A-site cation, which is usually an alkali metal, an alkaline earth metal, or a rare-earth element. It coordinates with 12 X anions and largely serves to support the perovskite structure. Six X anions and body-centered B-site ions create a BX_6 regular octahedron, and the BX_6 octahedral are regularly aligned (Fig. 1) [3].

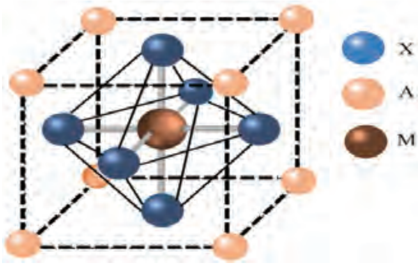

Fig. 1. A typical perovskite structure
Source: [4, p. 2].
Rys. 1. Typowa struktura perowskitu
Źródło: [4, s. 2].

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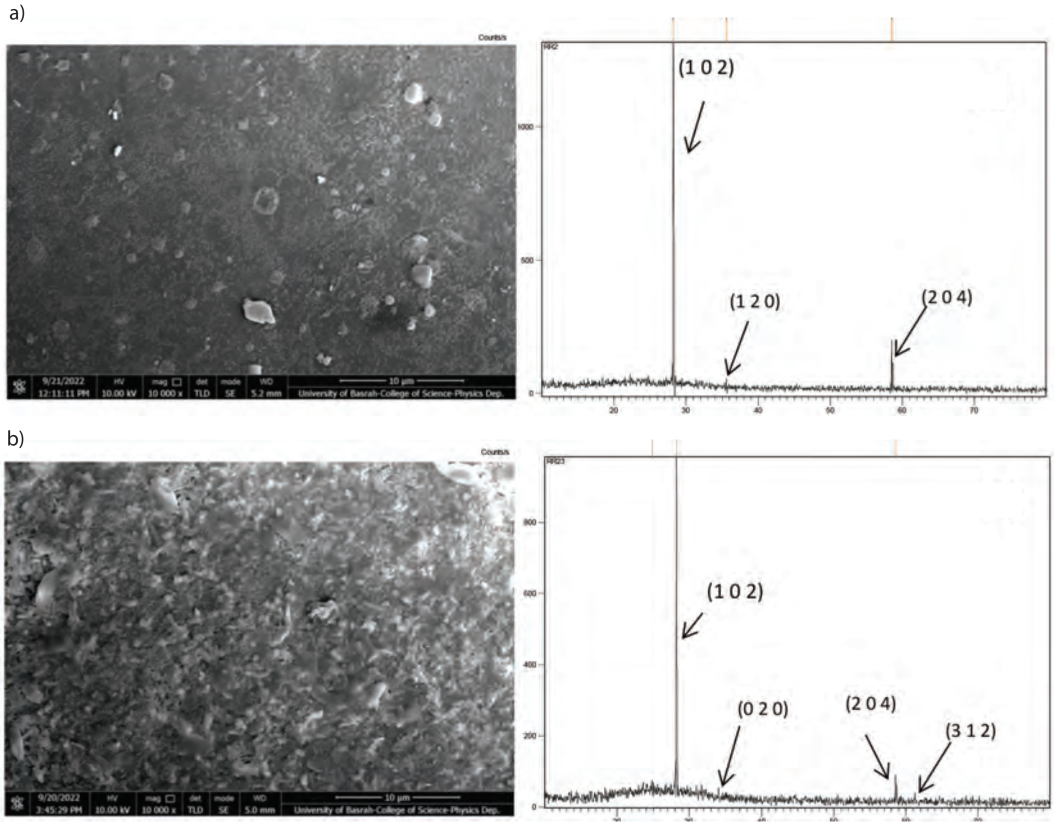

Fig. 2. XRD and SEM for $CaZnO_3$ thin films at $T = 150°C$: a) without KCl, b) with KCl

Rys. 2. XRD i SEM dla cienkich warstw $CaZnO_3$ w $T = 150°C$: a) bez KCl, b) z KCl

Perovskite can be produced quickly using a number of deposition techniques, such as chemical bath deposition (CBD) [5], chemical vapor deposition (CVD) [6], the SILAR method [7], the spin coating method (SCM) [8], and spray pyrolysis deposition (SPD) [9]. Transparent ceramics [10], photovoltaic cells [11], fuel cells [12], transistors [13], memory chips [14], capacitors [15], light-emitting diodes (LEDs) [16], radiotherapy dose measurement [17], photovoltaic cells and superconducting material synthesis at relatively high temperatures are the industrial applications for perovskite materials [18].

The lattice parameters of $CaZnO_3$ inorganic perovskite are: $a = 5.95393$ Å, $b = 5.80739$ Å, $c = 7.17103$ Å, $\alpha = \beta = \gamma = 90°$ [19–20]. These values are similar to the dimensions of the silicon atom referred to in [21], which has a good energy gap, which stimulates the possibility of using the perovskite compound as a semiconductor.

2. Materials and methods

The spray pyrolysis method has been used to prepare $CaZnO_3$ thin films on glass slides as a substrates. They were cleaned with methanol, ultrasound, distilled water, and a variety of other cleaners, then were left to dry. $CaCl_2$, $ZnCl_2$, and KOH were used as sources for Ca, Zn and O_2, respectively. The concentrations of the compounds are listed in Table 1. Each compound was dissolved separately in 25 ml of distilled water, then the three solutions were mixed together to prepare a solution of $CaZnO_3$. The latter solution was divided into two solutions. One of them was used to prepare $CaZnO_3$ thin films with KCl, while the other part was filtered to remove KCl. Afterwards, 50 ml of distilled water was added, and the resulting solution was precipitated to prepare thin films of $CaZnO_3$ without KCl.

Table 1. Concentration of $CaCl_2$, $ZnCl_2$ and KOH
Tabela 1. Stężenie $CaCl_2$, $ZnCl_2$ i KOH

Chemical compounds	Concentrations [g]
$CaCl_2$	0.6
$ZnCl_2$	0.6
KOH	1.2

3. Chemical reaction mechanism

The compound was prepared in the laboratory by dissolving 0.6 g each of $CaCl_2$ and $ZnCl_2$ with 1.2 g of KOH, both separately in 50 ml of distilled water, then mixing the solutions with a magnetic stirrer at a constant temperature of 80°C for one hour to form a single solution consisting of the compound $CaZnO_3$ with KCl and water. Such a solution was used to deposit thin films in the presence of KCl at 150°C on glass slides by chemical spray pyrolysis deposition according to the interaction equation shown below. The solution was prepared again and washed with distilled water to remove the KCl, after which it was used for the second time to deposit thin films.

$$CaCl_2 + 2KOH \xrightarrow{H_2O} Ca(OH)_2 + 2KCl, \quad (1)$$

$$ZnCl_2 + 2KOH \xrightarrow{H_2O} Zn(OH)_2 + 2KCl, \quad (2)$$

$$Ca(OH)_2 + KCl + Zn(OH)_2 \xrightarrow{\triangle} CaZnO_3 + KCl + H_2O\uparrow + H_2\uparrow. \quad (3)$$

Thin films of $CaZnO_3$ were produced on the glass slides using the latter solution doped with KCl at 150°C. For the other samples, the solution was washed three times with distilled water to make thin films of $CaZnO_3$ without KCl doping. The substrate temperature

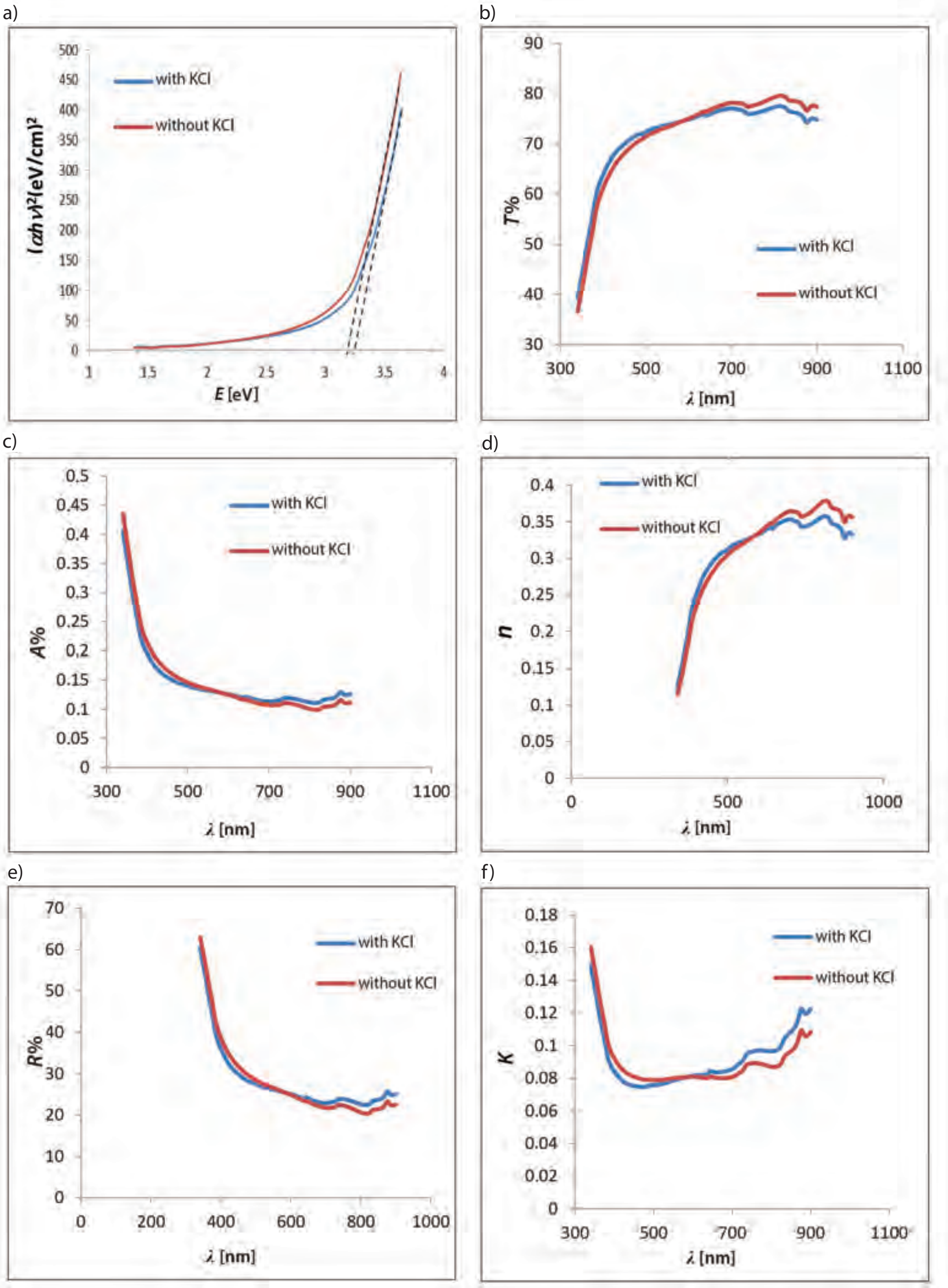

Fig. 3. Effect of KCl on the energy gap and the optical properties of perovskite thin films $CaZnO_3$

Rys. 3. Wpływ KCl na przerwę energetyczną oraz właściwości optyczne cienkich warstw perowskitu $CaZnO_3$

during the deposition process was 150°C, with an atmospheric pressure of 7.5 bars and 10 spray steps lasting 5 seconds each.

According to images of the layers obtained via scanning electron microscopy, the size of the grains is correlated with the amount of KCl present in their precursors. The SEM and XRD images show the crystalline structure (Fig. 2a), while the second image shows the formation of grains with random growth (Fig. 2b).

From Scherer's equation:

$$(D = K\lambda / \beta.\cos\theta). \quad (4)$$

The Bragg angle, the K factor, also known as Scherer's constant, which is close to = 0.9 [22], and the β crest width at mean height (FWHM) at any 2θ were used to compute the diameter of the crystallite (D) using XRD at wavelength (nm). The grain size ranges from 53.86 nm without KCl (Table 3) to 112.28 nm with KCl (Table 4), as the grains assemble and grow.

Table 2. The effect of KCl on the energy gap for $CaZnO_3$
Tabela 2. Wpływ KCl na przerwę energetyczną w wypadku $CaZnO_3$

Thin film	Energy gap [eV]
Without KCl	3.19
With KCl	3.22

Table 3. Grain diameter and peak position (XRD) for $CaZnO_3$ without KCl
Tabela 3. Średnica ziarna oraz pik (XRD) dla $CaZnO_3$ bez KCl

2θ°	θ°	FWHM	D [nm]	Average D [nm]
35.556	12.42825	2.2042	3.689208	–
28.223	14.1117	0.0787	104.0445	53.8668
58.544	29.2723	0.072	126.44	–

Table 4. Grain diameter and peak position (XRD) for $CaZnO_3$ with KCl
Tabela 4. Średnica ziarna oraz pik (XRD) dla $CaZnO_3$ z KCl

2*θ*°	*θ*°	FWHM	*D* [nm]	Average *D* [nm]
28.2284	14.1142	0.0984	83.21534	–
35.5838	17.7919	0.059	141.3573	112.2863
58.5258	29.2629	0.072	126.4284	–
58.6944	29.3472	0.096	94.89965	–

According to the XRD images, the structures of the films in Fig. 2a are signs that the films are all crystalline. In addition to the formation of minor peaks in Fig. 2b due to the varied orientation in the structure, there are a few peaks from the single crystal phase present at the same angle (2θ), which may be connected to the KCl in the produced films.

4. Results and discussion

SEM and XRD were used to study the structural properties of the obtained layers, while UV spectrophotometers were used to study the optical properties of transmittance, absorbance, refractive index, and extinction coefficient, where the extinction coefficient represents the characteristic which determines how strongly a species absorbs or reflects light at a particular wavelength. Thin films were produced from $CaCl_{2(0.6\ g)}$, $ZnCl_{2(0.6\ g)}$ and $KOH_{(1.2\ g)}$ to form thin films of the $CaZnO_3$ structure. The layers' optical and structural characteristics were assessed.

Fig. 3 illustrates how the optical properties of the two types of $CaZnO_3$ thin films clearly differ, with the transmittance dropping with KCl and the absorbance increasing spatially from wave lengths 300 nm to 550 nm, which affected on energy gap.

The energy gap was 3.19 eV for thin films without KCl and increased to 3.22 eV when KCl was in the solution (Fig. 3a). This means the band gap increases with doping (KCl). The energy gap varies as a result of the produced films' ongoing changes in structure and grain size (Fig. 3a).

5. Conclusions

The main aim of this study was to determine the possibility of using the prepared perovskite $CaZnO_3$ compound in the manufacture of solar cells and diodes. Absorbance and transmittance differ depending on $CaZnO_3$ purity. The optical and structural characteristics of perovskite thin films are affected by KCl. The *A* and *T* index spectrum exhibits steady values for two types of thin films along the range of 320–570 nm before decreasing over the range of 550–600 nm. The band gap is 3.19 eV for pure thin films, i.e., without KCl, and increase to 3.22 eV for the second type of layer (with KCl). The layers are entirely crystalline, the structure of the films varies significantly, and certain peaks of the second type of films (with KCl) emerge at the same 2θ with varying strengths. These peaks are the result of KCl presence. Additionally, doping the layers with KCl increased the predicted grain size (Tables 2 and 3).

The results also show that $CaZnO_3$ perovskite has the potential to be converted into a thin film with an acceptable energy gap, which makes it suitable for use in the manufacture of solar cells and diodes when KCl is removed from the solution.

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