Digest Journal of Nanomaterials and Biostructures Vol. 18, No. 1, January - March 2023, p. 165 - 172

# Effect of substrate temperature on the optical and structural properties of $CaZnO_3$ perovskite thin films

R. H. AL-Saqa*, I. K. Jassim
*Department of Physics, College of Education for pure science, Tikrit University, Iraq*

In this study, thin films of $CaZnO_3$ perovskite were prepared using the spray pyrolysis deposition method (SPD) for different substrate temperatures (200, 250, 300, and 350 °C). In this study, we investigated the effect of the variation in substrate temperature on the crystal structure and optical properties of CaZnO3 thin films using a scanning electron microscope (SEM), an X-ray spectrum, and a UV spectrum. The absorbance and transmittance of the prepared films with wave length show a clear variation with substrate temperature. The band gap varied from 2.65 eV to 2.8 eV. The SEM images show that the grain size increases with substrate temperature, and this agrees with the grain size calculated from the X-ray spectrum. The grain size was within the range of 16.39–184.34 nm.

(Received May 12, 2022; Accepted February 1, 2023)

*Keywords:* Crystal structural, Pervoskite, Optical properties, Thin film

## 1. Introduction

Perovskite have provide very special class of materials with excellent optical and photoluminescence properties. Studying the optical properties of single domain crystals at various temperatures[1].

The Perovskite has been prepared in different forms "$A_2BO_4$ -Layered Perovskite, $ABO_3$ - Pervoskite, $A_2A`B_2B`O_9$"Triple Pervoskite" where B′ and B″ are two different elements in different oxidation states (Bhalla et al., 2000) and $A_2BB`O_6$ "Double Pervoskite"[2].

The Perovskite can be divided in general into two groups, the first is the oxide group, and the second is the halogen group, depending on the element X in the formula $ABX_3$. The two elements A and B are chosen so that the sum of their valence states is (+6) to equalize with the valiancy of the oxygen atoms (-6) [3][4]. There are several valence states in the oxide group, including $A^{+2}B^{+4}$ and $A^{+1}B^{+5}$ [5]. The sizes of the atoms of the elements A and B are different, but in order for the atoms to settle into the formula $ABX_3$, the ratio between the radii of the atoms A and B and the oxygen atom (X) must be taken into account. In the present work, Perovskite thin films were prepared using the spry pyrolysis deposition method "SPD". The layers have been examined using a scanning electron microscope (SEM) and an X-ray spectrum to investigate the grain size and surface topology or morphology, in addition to measurement the optical properties for all layers.

The ionic bonds and the tolerance factor are among the most important factors to be taken into account to achieve stability in the chemical formula $ABX_3$, where the tolerance factor is defined as a measure of the stability and distortion of the crystal structure [6], or it is a measure of the deformation in the cubic structure of the compound, and the tolerance factor is given by the following equation [7].

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (1)$$

$R_A$: the ionic radius of the cation A.
$R_B$: the ionic radius of the cation B.
$R_X$: the ionic radius of the anion X.

* Corresponding authors: raed.h.alsaqa@st.tu.edu.iq
https://doi.org/10.15251/DJNB.2023.181.165

This geometric factor describes the slope of the ideal of Perovskite, where the Perovskite structure is stable in the field, $0.7 < t < 1.06$, it is in the form of a perfect cubic lattice for $t = 1$. When you move away beyond this value, the structure can be subjected to various deformations, such as if the tolerance factor is present in the field of $0.99 < t < 1.06$ (and in the range of orthorhombique), the orthodontic deformation would be $0.75 < t < 0.96$, the structure will be cubic, so many positions can be distinguished according to the value of the tolerance factor as shown in table.1 [8,9].

*Table 1. Electronic structure according to the tolerance factor[8][10].*

| t<0.7 | 0.75<t<1.06 Perovskite | | | t >1.06 |
|---|---|---|---|---|
| Switching from Perovskite to fluorite | 0.75< t<0.96 orthorhombique | 0.96< t <0.99 rhombohedra | 0.99<t<1.06 Cubic | Hexagonal |

The binding ionic X* gives the ionic form of the formula $ABX_3$ or the difference in electronegativity as in the following equation[3]:

$$X^* = \frac{X_{A-X} + X_{B-X}}{2} \tag{2}$$

where $X_{A\text{-}X}$ and $X_{B\text{-}X}$ are the differences in electronegativity between the A and B cations and the adjacent anion X The Perovskite structure is most stable when the respective bonds have a strong ionic character [3]. The application of Perovskite can be observed in piezoelectric devices [11], sensors, capacitors [12] and solar cells [13]. Finally, changing the concentrations of the material constituting the perovskite compounds and changing the temperatures for preparing thin films of perovskite lead to a clear difference in the structural and optical properties [14]

## 2. Method of preparation

Several methods have been used to prepare Pervoskite components to be thin film, such as, co evaporation technique [15], sol-gel [16], chemical path deposition (CPD)[17], spin coting method[18][19] and pulsed laser deposition" PLD"[20].

### 2.1. Experimental section

Experimental work was carried out in the laboratories of the University of Mosul, Iraq, where glass slides were prepared for the purpose of depositing the thin film on them after they were completely cleaned using methanol and then washed with distilled water, as for the preparation of the Perovskite $CaZnO_3$ compound. 0.6gm of each of $CaCl_2$ and $ZnCl_2$ was used, while 0.8gm of KOH was used to obtain the required Perovskite compound $CaZnO_3$. Each of the above-mentioned substances was dissolved in 50mL of distilled water, then $CaCl_2$, $ZnCl_2$ were added at the same time to the KOH solution, and then the resulting solution was placed The Perovskite compound $CaZnO_3$ is formed in a magnetic stirrer device at a temperature of 60 °C.

The prepared compound was placed in a "Spry pyrolysis deposition (SPD)" system. Where the deposition base was placed on a thermal radiator, whose temperature can be easily changed. The thin film was deposited using the "SPD" system at different temperatures (200, 250, 300, 350 ℃), in a clean room that contains an electric vacuum to withdraw the resulting vapors and gases. It was deposited for a period of 5 seconds and 10 times of precipitation. Pump the material to be settled at a constant pressure of 7.5 Pa.

## 3. Results and discussion

Thin films of $CaZnO_3$ were prepared from a constant concentration of precursors and different substrate temperatures within the range of 200, 250, 300, and 350 °C. The layers was examined using Scanning electron microscope and X-ray spectrum, in addition to the measurements of their optical properties.

The Scanning electron microscope images show a clear variation in the structure of the films with substrate temperature. The grain size increases with temperature due to the growth and aggregation of the grains (figure 1).

The X-ray spectrum also showed that the film structure changed with temperature. At 200 °C, the structure of the film was amorphous with a clear presence of the crystalline phase. The film at 250 °C was fully crystalline with orientation (200), while the amorphous phase appears again at 300 °C and 350 °C as shown in figure (1). The X-ray spectrum shows that the grain size was extremely small, between 16.39 and 184.34 nm with temperature, and this agree with SEM images as shown in table (1).

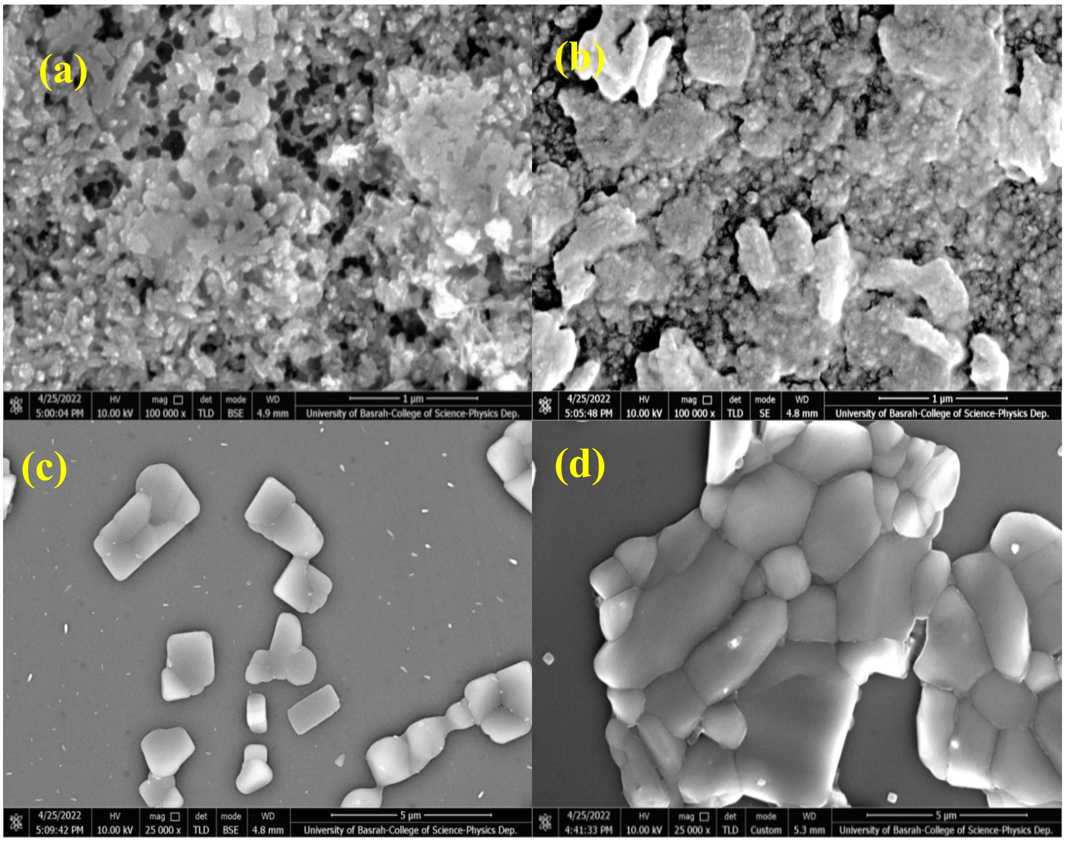


*Fig. 1. Shows SEM images of $CaZnO_3$ Perovskite thin films prepared at different temperatures a-200°C, b-250°C , c-300°C , d-350°C.*

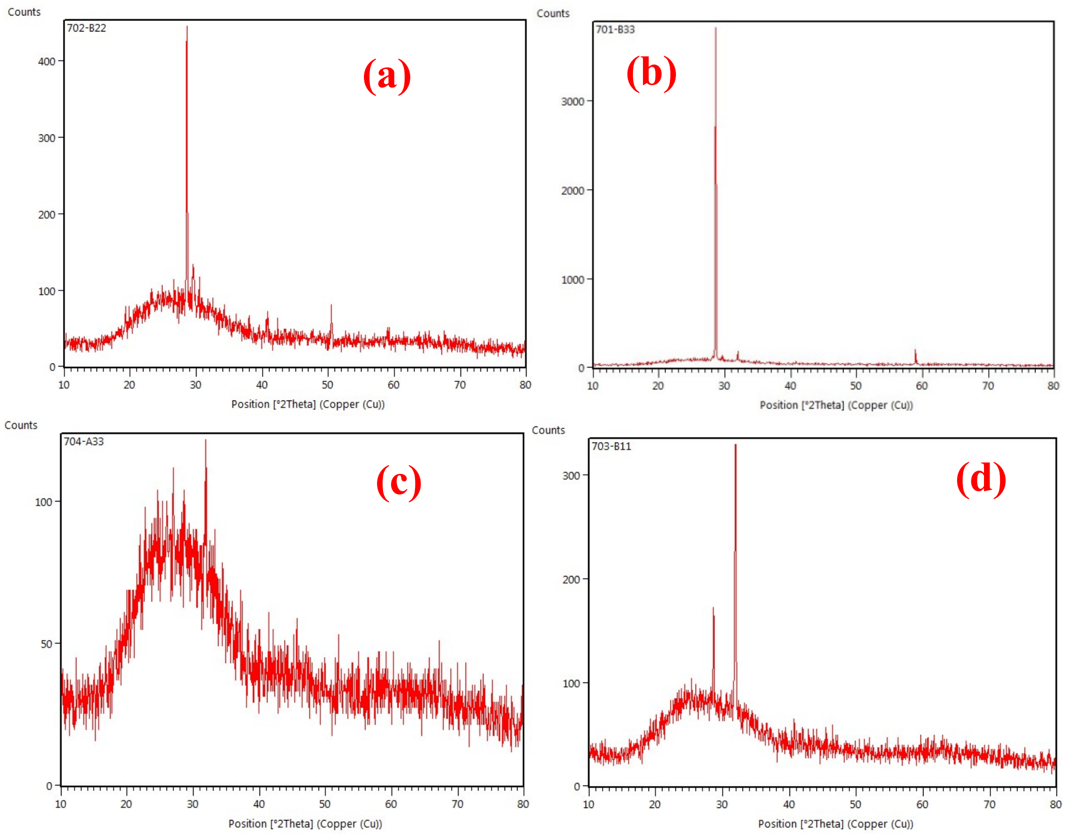


*Fig. 2. X-ray spectrum of $CaZnO_3$ Perovskite thin films prepared at different temperatures a-200°C, b-250°C, c-300°C, d-350°C.*

*Table 1. Shows the of temperature variation substance.*

| **Temp.°C** | **Size particle nm** |
|---|---|
| 200 | 16.39023 -25.0808 |
| 250 | 16.39023 |
| 300 | 13.76526 - 27.32009 |
| 350 | 8.83044 - 184.3462 |

The tolerance factor was calculated of about 0.93, where $R_{Ca}$=197 Pm, $R_{Zn}$=134 Pm, $R_O$=66 Pm[21,22], and this prove that the $CaZnO_3$ is a Pervoskite with orthorhombique structure. The transmittance, absorbance, and reflectance have been measured for the layers prepared from the same concentration and different substrate temperatures.

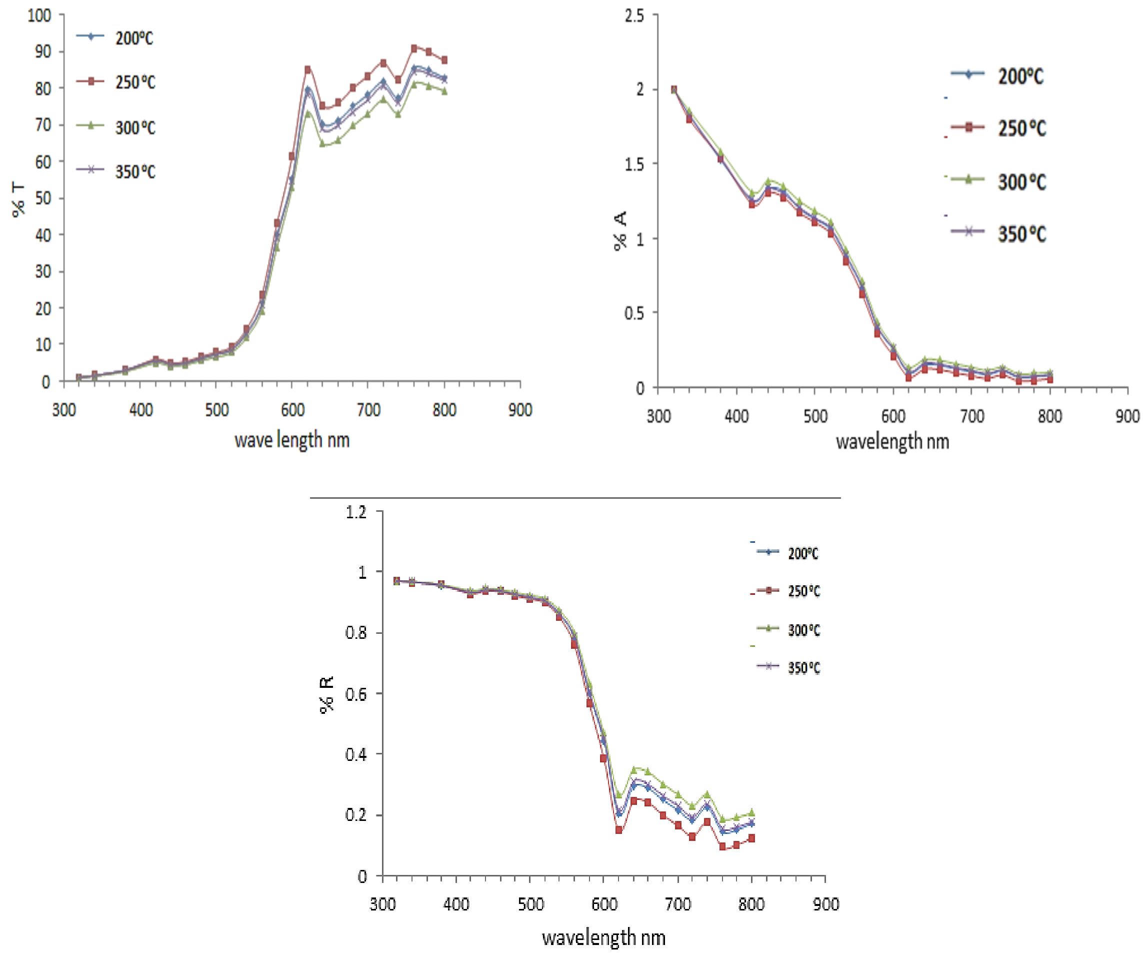


*Fig. 3. The transmittance (T), absorbance(A) and reflectance(R) of $CaZnO_3$ thin films prepared at different temperatures.*

The transmittance of all $CaZnO_3$ thin films increases rapidly over the wavelength range of 400-600nm regardless of the temperature, but the maximum transmittance decreases with temperature as shown in figure(3-a). Inversely, the absorbance was decreased within the range of 400-600nm and was proportional to the substrate temperature over a 600nm wavelength. The reflectance remains extremely constant over the wavelength range of 320-550 nm and then decreases rapidly within the wavelength range of 550-630 nm while being proportional to temperature over the wavelength of 630 nm.

The extinction coefficient is inversely proportional to temperature within the wavelengths 320–500nm, decreases rapidly over the wavelengths 500–610nm, and finally is directly proportional to substrate temperature for wavelengths above 610nm.

The refractive index showed no effect on temperature for the 320-610nm wavelength range then proportional with wave length for the wavelengths above 610nm.

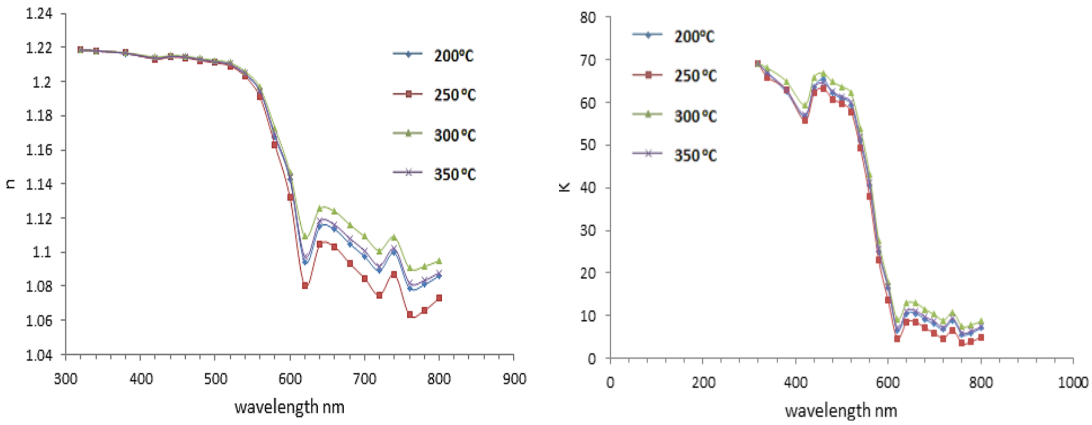


*Fig. 4. Shows the refractive index (c) and extinction coefficient (k) of $CaZnO_3$ thin films prepared at different temperatures.*

The energy gap $CaZnO_3$ thin film prepared at substrate temperature 200°C was about 2.8eV then it decrease to 2.65eV for films prepared at 250°C due to the change in the films structures while the energy gap of the films that prepared at 300°C increases to 2.75eV and finally become 2.8eV again at 350°C , This can be explained by the fact that the increase in temperature will produce a change in the structure as a result of grew and aggregation of grains as shown in SEM image in figure (1).

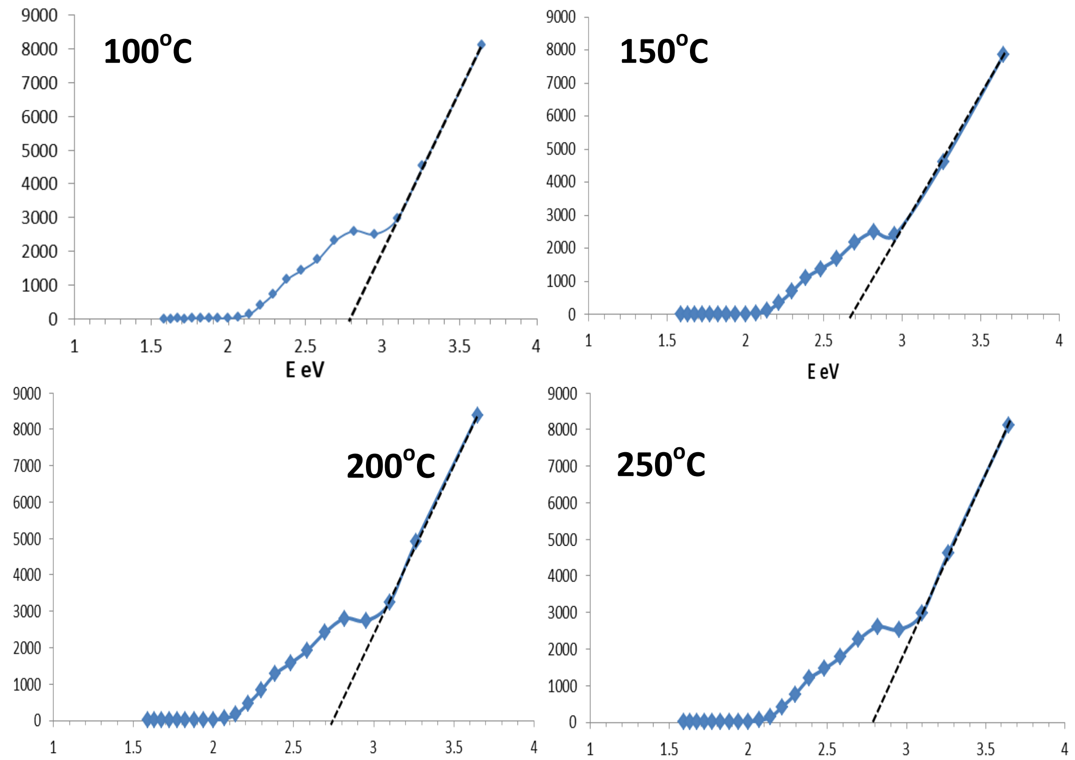


*Fig. 4. Shows the refractive index and extinction coefficient of $CaZnO_3$ thin films prepared at different temperatures.*

## 4. Conclusion

The scanning electron microscope images show an increase in grain size with temperature. The X-ray spectrum shows that at 200 $^oC$, the structure of the film was amorphous with a clear presence of the crystalline phase, and the films prepared at 250 $^oC$ were fully crystalline with orientation [200], while the amorphous phase appeared again at 300 $^oC$ and 350 $^oC$ . The X-ray spectrum also shows that the grain size was extremely small, between 16.39 and 184.34 nm with temperature.

$CaZnO_3$ is a perovskite with an orthorhombique structure and a tolerance factor of about 0.93. The transmittance of all $CaZnO_3$ thin films increases rapidly over the wavelength range of 400–600 nm, regardless of temperature. Inversely, the absorbance decreased within the range of 400–600nm and was proportional to the substrate temperature over a 600 nm wavelength. The reflectance remains extremely constant over the wavelength range of 320–550 nm and then decreases rapidly within the wavelength range of 550–630 nm. The extinction coefficient is inversely proportional to temperature within the wavelengths 320–500nm, decreases rapidly over the wavelengths 500–610nm, and finally , the energy gap of $CaZnO_3$ thin films prepared at substrate temperature 200$^oC$ was about 2.8eV then it decrease to 2.65eV for films prepared at 250$^oC$ while the energy gap of the films that prepared at 300$^oC$ increases to 2.75eV and finally become 2.8eV again at 350$^oC$ .

## 5. Acknowledgements

We particularly wish to acknowledge the important contributions of Dr. Mohammad M. Unise at the University of Mosul, Dr. Sattar Jabbar Kasim and Mazin Anuy Mahdi at Basra University for their assistance in performing XRD and SEM tests.

## References

[1] Hiromichi Ohta, Hidenori Hiramatsu, 2018, "Fabrication, characterization, and modulation of functional nanolayers. Part III Nanoinformatics. pp. 207-235; https://doi.org/10.1007/978-981-10-7617-6_10
[2] E. A. R. Assirey, 2019, Saudi Pharmaceutical Journal, V. 27, Issue 6, pp.817-829; https://doi.org/10.1016/j.jsps.2019.05.003
[3] L. Djoudi, 2016. Synthesis and properties of mixed oxides based on Lanthanum, Aluminum and and Nickel, doctoral thesis, Mohamed Khider University. Biskra; https://doi.org/10.1016/j.jsps.2019.05.003
[4] Lu, T. Y.; Huang, B. R.; Wen, Z. Q.; Huang, L. T.; Wei, X. P.; Zou, Z. G. 2022. Influence of structural, electronic and optical properties of boron and nitrogen doping in tetragonal PbTiO3: insight from first-principles.Digest Journal of Nanomaterials & Biostructures. Jul-Sep 2022, Vol. 17 Issue 3, p715-730, https://doi.org/10.15251/DJNB.2022.173.715
[5] D. Chenine, 2019. Ab-Initio study of the structural, electronic, magnetic and thermodynamic properties of antiperovskite materials. doctoral thesis, Abdelhamid Ibnbadis University. Abdelhamid Ibnbadis. Mostaganem,
[6] S. Amel, 2017. Study of the Spintronic Properties of Double Perovskite Type ABCO6, thesis of PhD, Abdelhamid Ibnbadis University. Mostaganem.
[7] Bartel CJ, Sutton C, Goldsmith BR, Ouyang R, Musgrave CB, Ghiringhelli LM, Scheffler M., 2019. New tolerance factor to predict the stability of perovskite oxides and halides. Sci Adv. Feb 8;5(2):eaav0693; https://doi.org/10.1126/sciadv.aav0693

[8] A. Benaicha, 2018.synthesis and properties of lafe1-xcuxo3 oxides, doctoral thesis, Universite Mohammad Khider. Biskra,
[9] J. B. Philipp, P. Majewski, L. Alff, A. Erb and R. Gross, 2003. Phys. Rev. B, 68 144431.
[10] Atta, N. F. , Galal, A., El-Ads, E. H. , 2016, Perovskite Nanomaterials - Synthesis, Characterization, and Applications', in L. Pan, G. Zhu (eds.), Perovskite Materials - Synthesis, Characterisation, Properties, and Applications, IntechOpen, London.10.5772/61280; https://doi.org/10.5772/61280
[11] Raghavan, V., 2015. Material Sciences and Engineering. PHL Learnt private Limited, Delhi, India, p. 463.
[12] Kawamura, Y., Mashiyama, H., Hasebe, K., 2002, J. Phys. Soc. Jpn 71, 1694-1697; https://doi.org/10.1143/JPSJ.71.1694
[13] Moiz, S.A., 2022. Photonics 9, 23; https://doi.org/10.3390/photonics9010023
[14] Raed H. AL-saqa, I. K. Jassim, "Effect of KOH Concentration on the Optical and Structural Properties of Perovskite CaZnO3 Thin films", International Journal of Scientific Research in Science and Technology (IJSRST), Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 10 Issue 1, pp. 33-37, J.F 2023. doi : https://doi.org/10.32628/IJSRST229692
[15] Bayrammurad Saparov, Feng Hong, Jon-Paul Sun, Hsin-Sheng Duan, Weiwei Meng, Samuel Cameron, Ian G. Hill, Yanfa Yan, and David B. Mitzi, 2015. Chemistry of Materials, 27 (16), 5622-5632; https://doi.org/10.1021/acs.chemmater.5b01989
[16] Gatea, Hamed & Nahi, Iqbal, (2020), Muthanna Journal of Pure Science. 7. 1-11; https://doi.org/10.52113/2/07.02.2020/1-11
[17] Iman Ahmed Younus, Anwar M. Ezzat & Mohammad M. Uonis, 2020. Preparation of ZnTe thin films using chemical bath deposition technique, Nanocomposites,6:4,165-172; https://doi.org/10.1080/20550324.2020.1865712
[18] Yaxian Pei, Xiaoping Zou, Xiaolei Qi, Gongqing Teng, Qi Li, Dongdong Guo and Shuangxiong Zeng, 2016, Journal of Chemistry, vol. Article ID 1975763, 10 pages,2016; https://doi.org/10.1155/2016/1975763
[19] S. Laalioui, K. B. Alaoui, W. Ayadh, B. Ikken, K. E. Assali and A. Outzourhit, 2019. 2019 7th International Renewable and Sustainable Energy Conference (IRSEC),pp.1-4; https://doi.org/10.1109/IRSEC48032.2019.9078231
[20] AIP Advances 6, 015001 (2016); https://doi.org/10.1063/1.4939621
[21] VFI Atomic Radii: Vainshtein BK, Fridkin VM, Indenbom VL, 1995. Structure of Crystals (3rd Edition). Springer Verlag, Berlin; https://doi.org/10.1007/978-3-642-97512-7
[22] CPK Atomic Radii: Clementi E, Raimondi DL, Reinhardt WP, 1963. Journal of Chemical Physics, 38:2686; https://doi.org/10.1063/1.1733573