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Effect of Co-Dopant on the Structural and Optical Properties of Nanocrystalline Zro_2 Thin Films Prepared By Spray Pyrolysis Technique

Saleem Azara Hussain[1], Adel H. Omran A; lkhayatt[2], Eqbal Abduljalil Mahdi[1]
[1](University of Al-Qadisyah- College of Education- Department of Physics)
[2](University of Kufa – Faculty of Science – Physics Department)

Abstract: *In this work pure and Cobalt doped ZrO_2 thin films were prepared by chemical spray pyrolysis on glass substrate at 450°C .The structure properties have been investigated by using XRD, SEM and AFM. The XRD results show that the prepared films have polycrystalline structure in nature with tetragonal phase. The preferred orientation was along (011) plane, the intensity and the crystallite size nanostructured increased after doping process. The surface morphology SEM of ZrO_2 thin film seems relatively homogeneous and plated regularly integrate the granules after doping and the EDX spectra confirm the stoichiometry of the prepared films. The average roughness and root means square (RMS) values obtained from AFM measurements have been increased after the addition of Cobalt. The optical transmittance of the prepared films has been studied in the wavelength range (250–1100) nm, the results showed that the highest value of visual transmittance was (50%) and decreased with increasing doping concentration, because of the increase of impurity concentration resulted holds attenuation in the intensity of incident light. The optical band gap decreased from 4.31 to 3.7 eV with increase in Co doping concentration due to the introduce of impurity levels as a localized states in the band gap. By incorporation of the metal ions into the ZrO_2 lattice it was noted an increase in the optical conductivity with increasing the proportion of doping. The film surface morphology and structure depends on the precursor and doping solution and solvents used with their optimized parameters.*

Keywords: *Zirconia ZrO_2, Cobalt-doped zirconia, thin film, spray pyrolysis, Atomic force microscopy, Band gaps.*

I. Introduction

Spray pyrolysis has been widely used to produce thin films because it is simple and an inexpensive where this process is more economical than other processes (such as chemical vapor deposition and sol–gel) that involve multiple steps or that must be carried out under vacuum. Furthermore, spray pyrolysis offers numerous possibilities for controlled synthesis of advanced ceramic powders and films because of its chemical flexibility [1]. ZrO_2 has three polymorphs, cubic ZrO_2, tetragonal and monoclinic phases. At elevated temperatures the monoclinic phase of ZrO_2 to be more stable at low temperatures with the tetragonal phase and cubic becoming more favorable at high temperatures [2]. The nature of temperature induced phase transitions, as well as the effect of vacancies, dopants, and external strains on the transition temperature [2,3]. Zirconium oxide ZrO_2 is a very interesting material because of their applications that stand out stiff resistance of weather conditions as it combines excellent mechanical toughness and corrosion resistant [4]. Its applications span fuel cells, thermal barrier coating, and protection against the corrosion of nuclear fuel cladding in water cooled nuclear reactors. Furthermore, zirconia is used in biomedical hip implants, and dental restorations, and recently it was suggested as a gate dielectric for metal oxide semiconductor devices [5, 6]. ZrO_2 thin films have been prepared by different techniques such as DC magnetron sputtering [7], sol–gel dip coating [8,9], thermal annealing of zirconium thin films [10], spray pyrolysis [11] and electrostatic spray deposition[12]. In this study we report the deposition and structural, morphological , optical properties of Co doped ZrO_2 thin films by chemical spray pyrolysis method.

II. Experimental details

Pure and cobalt doped ZrO_2 thin films were prepared on glass substrates by chemical spray pyrolysis method at 450°C, inorganic precursor route was chosen for the fabrication of nanocrystalline transparent zirconia thin films. Zirconium oxy chloride octahydrate ($ZrOCl_2.8H_2O$) and Cobalt nitrite $Co(NO_3)_2$ were used for the preparation the precursor solutions as a source of Zr and Co ions respectively. Two solutions with 0.1 M concentration were prepared by dissolving (8.05gm) of $ZrOCl_2.8H_2O$ and 1.8294gm of $Co(NO_3)_2$ in 100 ml of distilled water for each one. The first and the second solutions was used to deposit pure and Cobalt doped ZrO_2 thin films with three different molar ratios (4, 8, 12) %. The solution is sprayed at 450°C onto glass substrates with dimensions of 2.5 × 2.5 cm^2 after it ultrasonic ally cleaned in acetone and Methyl ethyl ketone (C_4H_8O).

Each spraying period lasts for about (12 s) following by about (3 min) waiting period to avoid excessive cooling of the hot substrates duo to the spraying. Appropriate thickness has been obtained for the films of about (155-250 nm). All samples, pure and Co-doped ZrO_2 thin films were prepared by incorporation of dopant is easy by this technique. Structural properties of ZrO_2 and ZrO_2:Co thin films was investigated by using the X-ray diffractometer (Model-XRD- 6000 Shimadzu) that have Cu K Alpha1 wavelength of 1.54056 ˚A radiation. The surface morphology of the films was examined by scanning electron microscopy SEM (INSPECT-550) and atomic force microscope (CSP model AA3000 AFM supply by Angstrom Company). A UV–Vis (Mega-2100) spectrophotometer was used to determine the optical properties of the prepared films in the wavelength range (250–1100) nm.

III. Results and discussion

3.1 Structural properties

The XRD patterns for as deposited (T_s = 450◦C) ZrO_2, and Cobalt doped ZrO_2:Co thin films on glass substrates are shown in Fig. 1. The figure shows that the prepared films had a polycrystalline structure with tetragonal phase. The characteristic peaks of all (ZrO_2, ZrO2: Co) thin films corresponding well with standard crystallographic data (JCPDS Card No 50-1089). The main diffraction peaks are (011), (110), (112),(121) with preferred orientation along the (011) plane and the doping process shows the presence of stabilized tetragonal ZrO_2 in the Co doped zirconia films. The crystallinity of the film was found to be enhanced, and the intensity of peaks improve dramatically with the increase of the cobalt concentration. The lattice parameter of the ZrO_2:Co thin films was found to be less than that of the pure ZrO_2 thin film as in **Table 1** this may due to the smaller size of ionic Co^{3+} (0.68Å), as compared to ionic Zr (ionic radius 0.86 Å for Zr^{4+}). Thus Co ions can be easily replace the Zr atoms at the lattice [8, 13]. the stabilization of tetragonal phase and decrease in c-parameters are the proof of the incorporation of Co ions inside the ZrO_2 crystal lattice .the crystallite size (D) of ZrO_2 thin films calculated from the full width at half maximum (FWHM) form XRD patterns by using Debye–Scherrer's equation[14]:

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \qquad (1)$$

Where λ is wavelength of X-ray,β is full width at half maximum in radian, and θ is Bragg angle. The crystallite size (grain size) was found to be increased from 17.6 to 30.8 nm with increase in Co dopant concentration 0-12% , which can be attribute to growth of particles in certain direction resulting in the decreases in the boundaries between grain, this behavior was in good agreement with the literatures A. H.Ataiwi and K. Šmits [15,16]. Therefore the $ZrO_2$and ZrO_2:Co thin films are nanocrystalline structure.

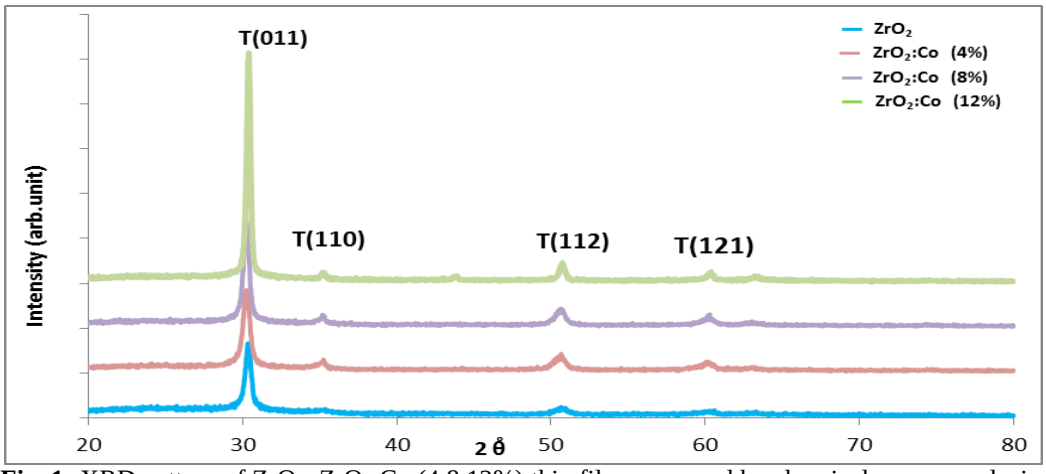

Fig. 1: XRD pattern of ZrO_2, ZrO_2:Co (4,8,12%) thin films prepared by chemical spray pyrolysis.

Table1: The XRD data of undoped and Co doped ZrO_2 thin films.

No	Sample	2θ degree	d (Å) Observed	d (Å) Standard	(hkl)	Grain Size nm	a (Å)	C (Å)	FWHM (degree)
1	ZrO_2 Undoped	30.378	2.940	2.950	011	17.6	3.60	5.12	0.466
2	Co 4%	30.264	2.950	-	011	16.6	3.59	5.13	0.525
3	Co 8%	30.261	2.951	-	011	18.8	3.60	5.09	0.461
4	Co 12%	30.403	2.940	-	011	30.8	3.57	5.07	0.285

Fig. 2 shows the surface morphology of ZrO_2, ZrO2:Co thin films. The SEM images include large and small grain size and the films were homogeneous and dense with no detectable microcracks. The average grain

size has an effect on the distribution of material density of the films, therefore the addition of cobalt dopant increases the film density and crystallite size of the material with less porosity as shown in Fig. (2 a-d). At the proportion (4%), and with increasing the proportion of cobalt impurity ratios (8, 12) % the growth in spherical granules and docking gradually as in formats [11]. The EDX analysis confirms the stoichiometry of the films and the presence of the correct atomic ratios of components of film elements (zirconium, cobalt, and oxygen) as shown in Fig.2.

Fig. (3a-d) shows the AFM images of ZrO_2, ZrO2: Co thin films deposited at 450◦C . The measured root means square (RMS) and the average roughness values obtained from AFM measurements have been increases with the increase of dopant ratio from 0 -12% (0.39 to 3.01 nm) and from (0.33 to 2.57 nm), these result was in good agreement with M. Muthana [17].

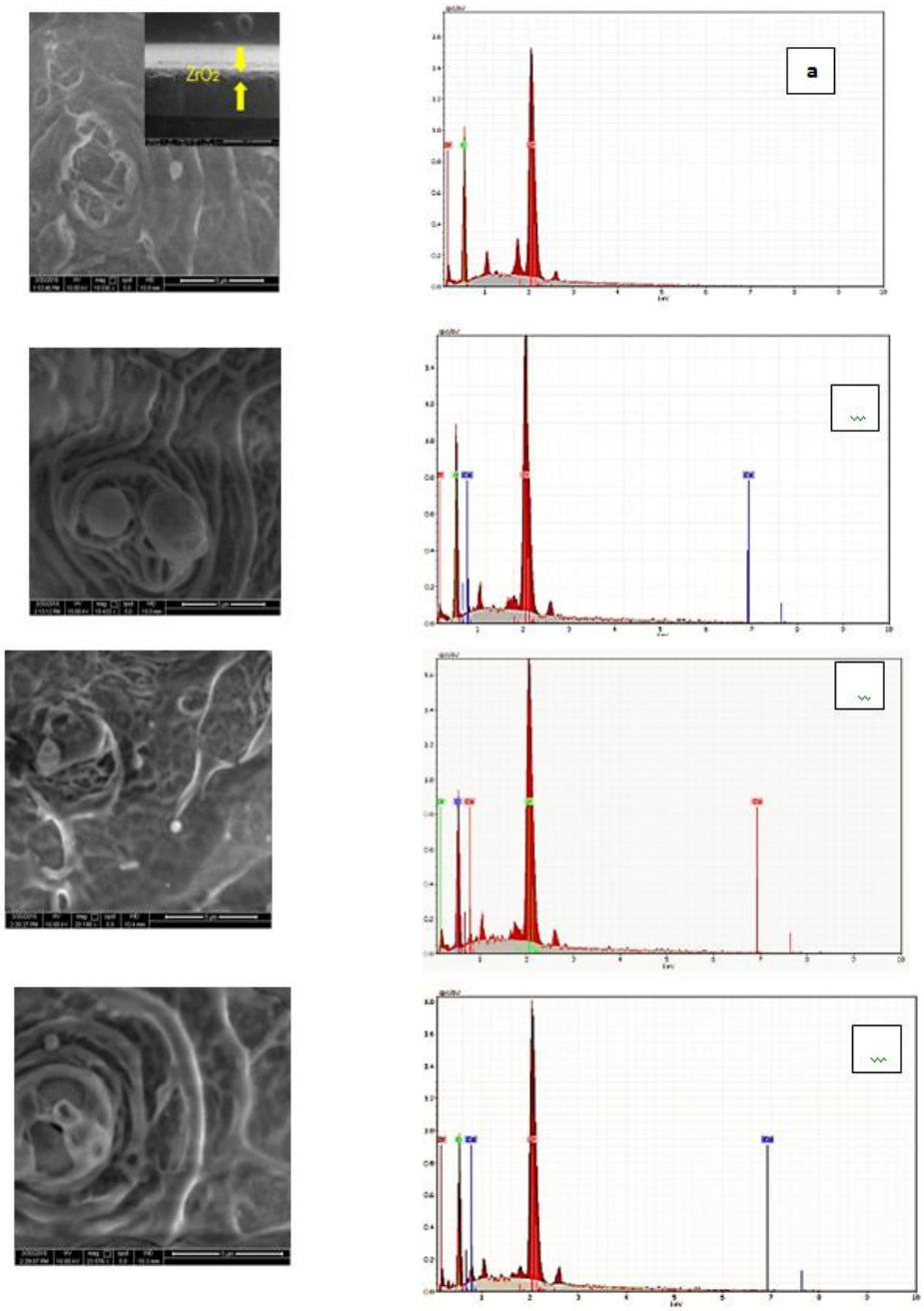

Fig.2. SEM, EDX image of (a) pure ZrO_2 ,(b) 4% (c) 8% (d) 12% Co doped ZrO_2 thin films.

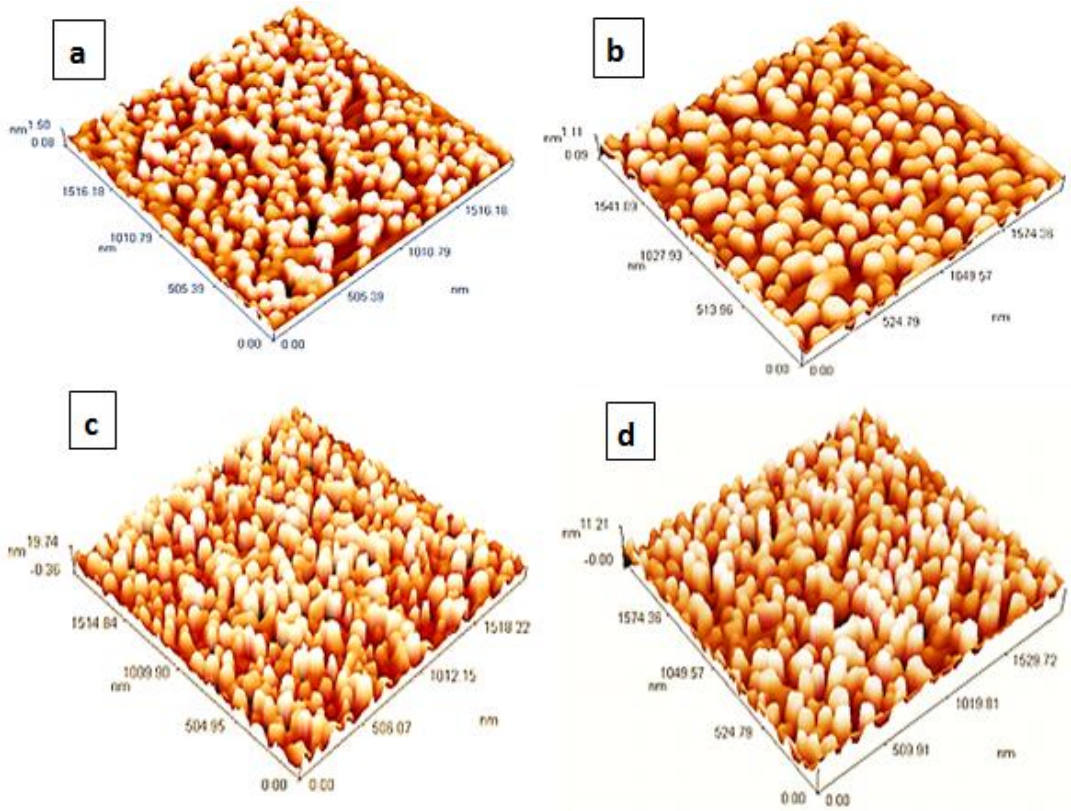

Fig.3. AFM image of (a) pureZrO2, (b) 4% (c) 8% (d) 12% Co doped ZrO_2 thin films.

3.2 Optical Properties

Fig. 4shows the optical transmittance (T%) spectra of ZrO_2,ZrO_2:Co thin films in the wave length range of 250–1100 nm. The maximum value of transmittance T % was ~0.51%.in the near IR region for the pure ZrO_2 film then it decreases with the increase of cobalt dopant proportion and the absorption edge of the transmittance spectra shift towards higher wave length (red shift). The increase of Co concentration in ZrO_2 films lead to increases the oxidation of Co^{+3} .Doping Zr^{4+} with cations Co^{3+} can suppress the oxygen vacancies in the crystal lattice due to the charge balance, these results agree with S. López-Romero [18].

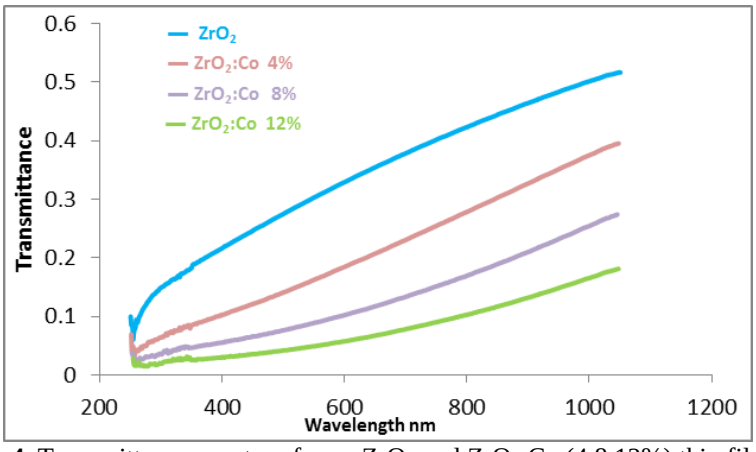

Fig.4. Transmittance spectra of pure ZrO_2 and ZrO_2:Co (4,8,12%) thin films.

The optical energy band gap $\mathbf{E_g}$ for direct allowed electronic transition of pure ZrO_2 and ZrO_2:Co (4,8,12%) thin films have been determined using Tauc relation [19] :

$$\alpha h\upsilon = B(h\upsilon - Eg)^{1/2} \qquad (2)$$

Where α is the absorption coefficient, B is constant and $h\upsilon$ is the photon energy. The direct allowed energy band gaps were calculated from the plots $(\alpha h\upsilon)^2$ vs. $h\upsilon$ Fig. 5.. This was made by extrapolating the linear portion of the curves until they intercept the photon energy axis, i.e., at $(\alpha h\upsilon)^2 = 0$. The optical direct band gap

was estimated to be 4.31 eV for pure ZrO_2 and it decreased to 3.05 eV with increase in Co doping concentration to 12%. The reduced of band gap value is due to the impurity levels that are introduced into the band gap by the incorporation of the metal ions into the ZrO_2 lattice [20].

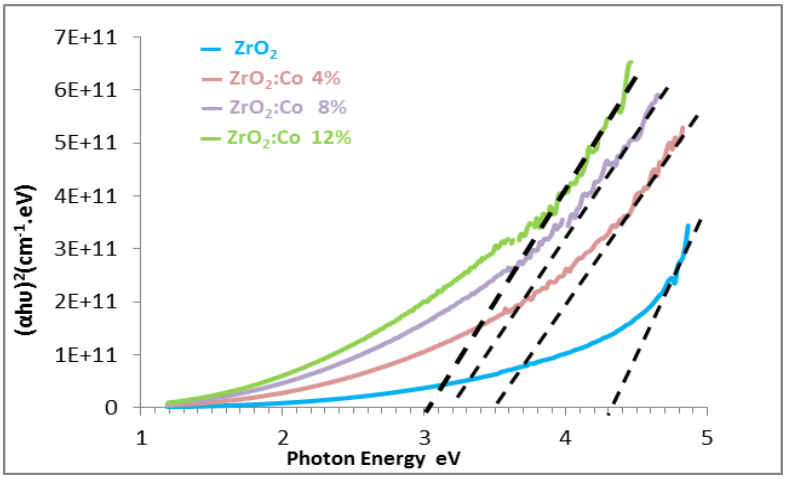

Fig. 5. The direct allowed optical energy band gap of ZrO_2, ZrO_2:Co (4,8,12%) thin films.

The optical conductivity σ of pure and Cobalt doped ZrO_2 films with (4,8,12%)were determined according to the relationship [21]:

$$\sigma = \frac{n\alpha c}{4\pi} \qquad (3)$$

Where n is the refractive index and c is the velocity of light . Fig.6 show the variation of the optical conductivity with photon energy, the increase in the optical conductivity values with the increase of photon energy and Cobalt dopant concentration ratios, and tend to gradually decline at higher near the energy gap values of energy level[22].

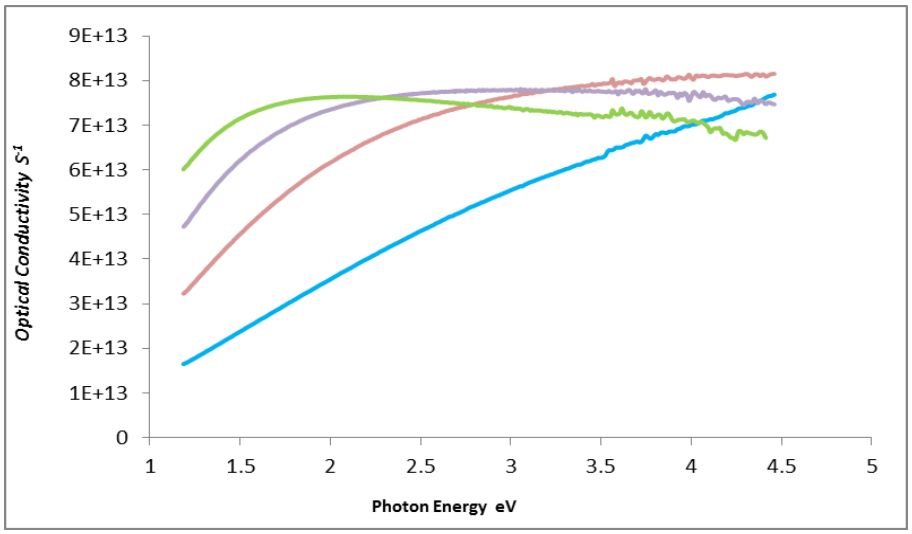

Fig.6: The optical conductivity as a function of photon energy.

IV. Conclusion

ZrO2 and ZrO2:Co thin films were deposited on to glass substrates by spray pyrolysis technique at 450◦C. X-ray diffraction spectra shows that ZrO2,ZrO2:Co films were polycrystalline with an tetragonal structure and preferred orientation(011) plane. The tetragonal phase has been achieved stabilize the ZrO2 into with the increasing Cobalt dopant concentration. SEM image shows the morphology of ZrO2 and ZrO2:Co thin films seems relatively homogeneous and plated regularly and the stoichiometric ratio was confirmed with EDX spectra. The RMS values were increased with the increasing dopant Co (4 ,8,12)% concentration from 0.39 to 3.01 nm, it may be due to the different kinetics of the dopant atoms and the host atoms Zr and also increasing grain size of the films. The optical band gap decreased from 4.31 to 3.05 eV with increase in Co doping concentration. The reduced band gap is due to the impurity levels that are introduced into the band gap by the

incorporation of the Co ions into the ZrO2 lattice. The transmittance was decreased after doping process and it was noted an increase in the optical conductivity values when increasing the concentration of Co impurities.

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References

[1]. L. Vergnieres, P. Odier, F. Weiss, C.-E. Bruzek, J. M. Saugrain," Epitaxial thick films by spray pyrolysis for coated conductors", J. Eur. Ceram. Soc.25 (12) ,2951–2954, (2005).
[2]. A. Kuwabara, T. Tohei, T. Yamamoto, and I.Tanaka, "Ab initio lattice dynamics and phase transformations of ZrO2", Phys. Rev. B 71,064301 (2005).
[3]. S. Dankesreiter," Advanced Synthesis of Gold and Zirconia Nanoparticles and their Characterization", Diplomica, Hamburg Verlag Gmb, (2011).
[4]. G. Fadda, L. Colombo, and G. Zanzotto," First-principles study of the structural and elastic properties of zirconia", Physical Review B 79, 214102 ,(2009).
[5]. Uuganbayar Otgonbaatar, Wen Ma, Mostafa Youssef, and Bilge Yildiz," Effect of Niobium on the Defect Chemistry and Oxidation Kinetics of Tetragonal ZrO_2", J. Phys. Chem. C, 118, 20122−20131, (2014).
[6]. P. Pittayachawan ," Comparative study of physical properties of zirconia based dental ceramics" ,M.Sc. Thesis, University College London,(2008)
[7]. M. Santamaria , F. Di Quarto and H. Habazaki ," Influences of structure and composition on the photoelectrochemical behaviour of anodic films on Zr and Zr–20 at.%Ti", Electrochimica Acta, 53 (2008) 2272–2280.
[8]. K. JOY," OPTICAL AND PHOTOLUMINESCENCE PROPERTIES OF NANOSTRUCTURED ZrO_2:TB THIN FILMS", THIN SOLID FILMS, 556 , 2014. 99–104.
[9]. I. John Berlin, S. Sujatha lekshmy , V.Ganesan , P.V. Thomas and K. Joy," Effect of Mn doping on the structural and optical properties of ZrO2 thin films prepared by sol–gel method", Thin Solid Films 550 (2014) 199–205.
[10]. Alireza Hojabri ," Structural and optical characterization of ZrO2 thin films grown on silicon and quartz substrates", J Theor Appl Phys., 10, 3,2016, 219–224.
[11]. P. Peshev , I. Stambolova , S. Vassilev , P. Stefanov , V. Blaskov , K. Starbova and N. Starbov," Spray pyrolysis deposition of nanostructured zirconia thin films" Materials Science and Engineering, B97, 106-/110, (2003).
[12]. Roberto Neagu, Dainius Perednis, Agnès Princivalle and Elisabeth Djurado," Zirconia coatings deposited by electrostatic spray deposition A chemical approach", Solid State Ionics 177 (2006) 1451–1460.
[13]. ARUP K. ATTA, PRASANTA K. BISWAS, DIBYENDU GANGULI "PREPARATION AND PROPERTIES OF ZIRCONIA COATINGS FROM AQUO-ORGANIC SOLUTIONS OF ZIRCONYL CHLORIDE OCTAHYDRATE",VOLUME 197, ISSUES 1–2, 10 MARCH 1991, PAGES 187-193.
[14]. S.R. Elliott, Physics of Amorphous Materials, Long Man Group Limited, 1983.
[15]. A. H.Ataiwi and A. A. Abdul-Hamead," Study Some of the Structure Properties of ZrO_2 Ceramic Coats Prepared by Spray Pyrolysis Method", Eng. &Tech.juronal,V.27,N_O.16,(2009).
[16]. K. Šmits," Luminescence of Zirconia Nano crystals" Ph.D.Thesis, Solid State Physics, University of Latvia,(2010).
[17]. M. Muthana Abd-Alkadum," Structural , Electrical and Optical Properties of ZrO_2:CuO Thin Films Prepared by Pulsed Laser Deposition", M.Sc. Thesis, University of Babylon, (2014).
[18]. S. López-Romero, M. García-Hipólito and A. Aguilar-Castillo," Bright Green Luminescence from Zirconium Oxide Stabilized with Tb^{3+} Ions Synthesized by Solution Combustion Technique", World Journal of Condensed Matter Physics , Vol. 3, 173-179,(2013).
[19]. J. Tauce, Amorphous & Liquid Semiconductors, Plenum, London & New York,1974.
[20]. J.A. NAVIO, M.C. HIDALGO, G. COLÓN, S.G. BOTTA, M.I. LITTER, "PREPARATION AND PHYSICOCHEMICAL PROPERTIES OF ZrO_2 AND FE/ZrO_2PREPARED BY A SOL–GEL TE", LANGMUIR 17, (2001), 202–210.
[21]. L. TOMAR, P. BHATT, R. DESAI AND B. CHAKRABARTY," EFFECT OF PREPARATION METHOD ON OPTICAL AND STRUCTURAL PROPERTIES OF TiO_2/ZrO_2 NANOCOMPOSITE", J. NANO. ADV. MAT. 2, NO. 1, 27-33 (2014) .
[22]. R.H.French, S.J.Glass and F.S.Ohuchi, "Experimental and Theoretical Determination of The Electronic Structure and Optical Properties of Three Phases of ZrO_2",Physical Review B Condensed Matter ,vol.49,No.8,5133-5142,(1994).