

## Effect of Sprayed Solution Volume on Structural and Optical Properties of Nickel Oxide Thin Films

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Undoped Nickel oxide (NiO) thin films were deposited on 500 °C heated glass using spray pyrolysis technique. Effect of volume sprayed solution on structural and optical properties of NiO thin films was studied. Volume amount was ranged in 5 – 30 ml and stepped by 5ml. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and UV-visible spectrophotometer were used to investigate elaborated thin films. XRD results show that the deposited films with volume lower than 10 ml is amorphous and with increasing volume up to 10 ml NiO thin films structure become polycrystalline with cubic structure and (111) as preferential orientation. An increase in diffraction intensity of preferred peak and narrowing in full width at half maximum were observed with sprayed volume increasing, which leads to better crystallinity of NiO thin films. Also it was observed that the grain size increased with increasing volume solution and were averaged in 10 – 28 nm. FT-IR analysis of product confirms the NiO bond formation and the results were compared with previous studies. All films exhibit an average optical transparency between 50 % and 80 % in the visible range and their band gap values are ranged in 3.38 – 3.62 eV.

**Keywords:** Nickel oxide, Thin films, Spray pyrolysis, XRD diffraction, FT-IR technique.

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### 1. INTRODUCTION

Transparent conducting oxides (TCOs) are a unique class of materials that exhibit both transparency and electronic conductivity simultaneously; as important fields in semiconducting transparent films materials science are their fundamental studies and applications aspects. The common TCOs are binary compounds [1]. TCOs are wide band gap semiconductors that have a large area of applications in transparent electronics such as transparent diodes, transparent transistors, sensors, displays, touch screens and solar cells. Most of them are n-type semiconductors, such as tin dioxide (SnO<sub>2</sub>), zinc oxide (ZnO), cadmium oxide (CdO), etc. [2]. However the current research is focused on preparing p-type transparent semiconductors materials [3]. Among these materials, nickel oxide (NiO) is one of the few known p-type semiconductor; which is stable and transparent transition metal oxides. Its band gap energy ranges in 3.6 – 4.0 eV. NiO thin films have attracted special attention due to its interesting optical, electrical and magnetic properties [4]. Also due to their technological applications, NiO thin films draw considerable attention, such as anti-ferromagnetic materials, electrode material for Li-ion batteries, hydrogen gas sensing and anode of organic light-emitting diodes [5 – 7].

According to the literature, NiO films can be grown using various techniques including electron beam evaporation, pulsed laser deposition, RF magnetron sputtering, chemical vapor deposition (CVD) and bath deposition (CBD) and spray pyrolysis (SP) [8, 9]. All these methods offer different advantages depending on its application of interest. Many efforts have been conducted to obtain films with the desirable physical and/or chemical properties. Among those methods, (SP)

is considered as promising technique, which holds several key advantages, such as low cost, simplicity of the apparatus, homogeneity over large areas of deposited thin films and good control of the composition and structure [10, 11]. With SP method, the growth of films can easily be controlled by one or more deposition parameters such as spray rate, substrate temperature, doping concentration, nozzle distance and carrier gas flow-rate. We focused in this study on the effect of sprayed solution volume on structural and optical properties of NiO thin films deposited by the predicted method (SP) with fixed temperature. For this X-ray diffraction, Fourier transformed infrared spectroscopy FT-IR measurements and UV-visible spectrophotometer were used to study the envisage properties.

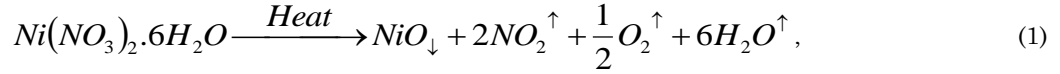
### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Synthesis of Thin Films

NiO films were prepared by spray pyrolysis process with different amount of volume. Range of spraying solution volume was varied from 5 ml to 30 ml with step of 5ml. As source of nickel a starting solution was prepared by dissolving 0.5 M (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) in 40 ml double distilled water. The solution was stirred thoroughly using a magnetic stirrer at 50 °C for half an hour to yield a clear and transparent solution; then it was sprayed on 500 °C heated glass substrate. Other deposition conditions such as distance nozzle-substrate was fixed at 45 cm, whereas sprayed flow rate of the solution was taken 2ml/min, each spray time took 10 s and time interval between successive sprays was 10 s to maintain constant the heat of substrate. The later was (R217102) microscopic glass slide in size of

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( $75 \times 25 \times 1.1 \text{ mm}^3$ ). Before deposition process, glass substrates were treated in standard cleaning procedure as follow: rinsing in acetone and distilled water respectively for 10min, and then blowing dry with a compressed air. The reaction process can be expressed as



## 2.2 Thin Films Characterization

The structural properties of prepared thin films were investigated using X-ray diffraction (BRUKER - AXS type D8) equipped with X'Pert High Score under  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The scanning range of ( $2\theta$ ) was taken between  $20^\circ$  and  $90^\circ$ . Survey of NiO bonding formation was obtained by Fourier transformed infrared spectroscopy (Shimadzu IR-Infinity1); for all prepared samples the scan of the FT-IR measurements was performed in ( $400 - 4000 \text{ cm}^{-1}$ ) range. The optical transmission spectra were obtained using an UV-visible spectrophotometer (Shimadzu, Model 1800); the scanning measurements were ranged in  $300 - 900 \text{ nm}$ . Film thickness ( $t$ ) was measured by the well-known weight difference method considering the density of the bulk nickel oxide taken in this work ( $6.67 \text{ g/cm}^3$ ). All measurements were carried out at room temperature (rt).

## 3. RESULT AND DISCUSSIONS

### 3.1 Structural Properties

At various sprayed solution volume, X-ray diffraction patterns of the sprayed NiO thin films, on  $500^\circ \text{C}$  heated substrates, were scanned in  $20 - 90^\circ$  range and shown in Fig. 1. It has been observed from this figure that the film prepared with 5ml spraying solution volume is amorphous in nature, indicating a poor crystallinity of the film. This may be due to the dispersed starting nucleation of NiO formation. With increasing the volume to 10ml, only one peak at ( $111$ ) was observed whereas for the others (15, 20, 25 and 30 ml) sprayed solution volume, one can observe that two peaks are present at  $2\theta = 37.2^\circ$  and  $43.3^\circ$  assigned to the ( $111$ ) and ( $200$ ) crystal planes respectively, these diffraction peaks were indexed to the face-centered cubic (FCC) crystalline structure of NiO and matched well with the standard spectrum (JCPDS, No. 47 - 1049) under the space group  $\text{Fm}\bar{3}\text{m}$  (225). The presence of such peaks indicates that the films are polycrystalline in nature. From the XRD analysis it was found that the ( $111$ ) peak has the highest intensity indicating the preferred orientation. It can also be seen from Fig. 1 that the intensity of the peaks gradually increases with spraying solution volume. The increase in the intensity of the peaks may be attributed to the increase in the degree of crystallinity caused by increasing of the sprayed quantity in conjunction with heat stay at  $500^\circ \text{C}$  of samples due to time deposition of solution. Similar results are also reported in literature [9, 13].

The lattice parameter  $a$  of the deposited films has been calculated from the values of  $2\theta$  and inter-planar

heat decomposition of nickel nitrates to clusters of nickel oxide in the presence of water, temperature and air. Sprayed solution leading to NiO formation the following reaction defined as follow [12]:

spacing relation for the cubic structure of NiO. The mean strain  $\varepsilon$  developed in the prepared NiO thin films was calculated using  $a$  and  $a_0$  which are the lattice constant of the prepared NiO thin films and  $a_0$  the standard lattice constant of bulk material ( $a_0 = 4.1769 \text{ \AA}$ ) according to standard card (JCPDS, No. 47-1049).

The average grain size was calculated from Debye-Scherrer formula [2]:

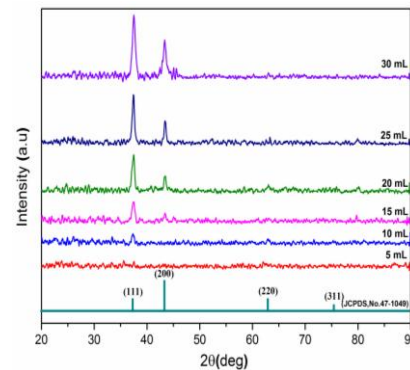
$$G = \frac{0.9\lambda}{\beta \cos \theta}, \quad (2)$$

where  $G$  is the grain size,  $\beta$  is the full width at half-maximum (FWHM) of the most intense diffraction peak,  $\lambda$  is the X-ray wavelength ( $1.54056 \text{ \AA}$ ) and  $\theta$  is the Bragg angle at ( $111$ ) peak.

The dislocation density  $\delta$  was calculated from Williamson and Smallman's formula [11]:

$$\delta = \frac{n}{G^2}, \quad (3)$$

where,  $n$  is a factor taken equal to unity,  $\delta$  gives the minimum dislocation density and  $G$  is the grain size. Average grain size  $G$ , dislocation density  $\delta$ , lattice constant  $a$  and mean strain  $\varepsilon$ , of the NiO thin films are presented in Table 1 with different sprayed volume.



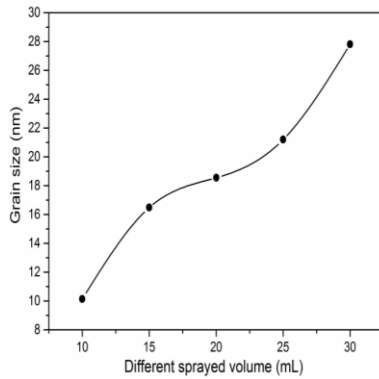
**Fig. 1** – X-ray patterns of NiO thin films prepared at  $500^\circ \text{C}$  with different sprayed volume

As can be seen, the calculated lattice parameter values are lower than standard  $a_0$  given by the cards (JCPDS, No. 47 - 1049). The deviation in the values of the lattice constant of the as-prepared NiO films from the bulk value indicates the presence of strain in the films. The origin of internal strain is related to the grain size of the film, which depends upon to deposition condition of the films [14].

Fig. 2 shows the variation of grain size, calculated using Scherrer's formula of the NiO samples versus sprayed solution volume. As can be seen the value of

**Table 1** – Values of Bragg angle  $2\theta$ , lattice constants  $a$ , grain size  $G$ , mean strain  $\varepsilon$  and dislocation density  $\delta$  for the (111) plane of NiO thin films prepared at 500°C with different sprayed volume

Sprayed solution volume (ml)	$2\theta$ (deg)	Lattice constants (Å)		Grain size (nm)	$\varepsilon$ (%)	$\delta \times 10^{15}$ (lines /m <sup>2</sup> )
		$a$	$\Delta a = a - a_0$			
5	-	-	-	-	-	-
10	37.292	4.1728	-0.0040	10.0	-0.096	9.734
15	37.431	4.1610	-0.0158	16.0	-0.378	3.679
20	37.438	4.1614	-0.0154	18.5	-0.370	2.906
25	37.457	4.1586	-0.0182	21.0	-0.436	2.225
30	37.318	4.1735	-0.0033	27.8	-0.080	1.292

**Fig. 2** – Variation of grain size of NiO thin films prepared at 500 °C with different sprayed volume

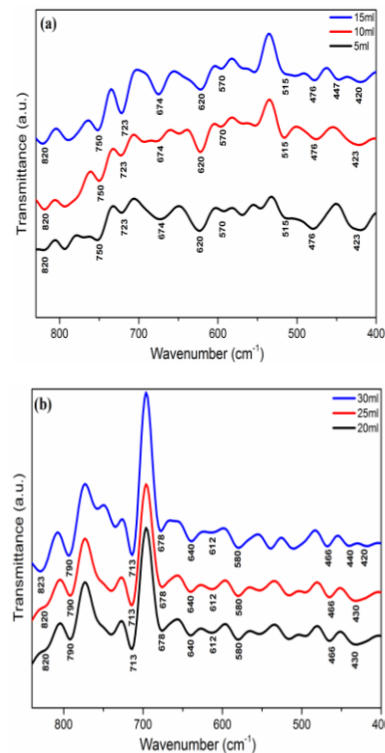
grain size was found to increase from 10 nm to 28 nm with increasing of sprayed solution volume from 10 ml to 30 ml respectively. These results confirm the enhancement in the crystallinity of the films. Furthermore, the increase in the grain size indicates a decrease in the lattice defects, which in turn reduces dislocation density as seen in Table 1. and carried out in literature [15].

### 3.2 Fourier Transform Infrared (FT-IR) Analysis

To further support the XRD results, the quality and composition of NiO thin films were investigated by FT-IR spectroscopy. FT-IR is known as one of the very useful method to find out information about chemical bonding and identification of material elemental constituents. Metal oxides generally give absorption bands below 1000  $\text{cm}^{-1}$  arising from inter-atomic vibrations [16]. FT-IR spectra in of the NiO thin films prepared with spraying solution volume ranged in 5 – 30 ml are represented in Fig. 3. From 5 to 15 ml sprayed solution volume, as seen in Fig. 3 (a) which shows absorption wave number bands located at 420, 423, 447, 476, 515, 570, 620, 674, 723, 750 and 820  $\text{cm}^{-1}$  which were assigned to Ni-O stretching vibrations modes [17 – 25]. Fig. 3 (b) represents the FT-IR spectra obtained from the NiO films prepared at sprayed solution volume varied from 20 to 30 ml, one can observe that absorption bands at 420, 430, 440, 466, 580, 612, 640, 678, 713, 790 and 820  $\text{cm}^{-1}$  corresponding to a stretching vibration of the Ni-O bond and also authenticates the presence of NiO material [17 – 19, 22 – 25], whereas bond at around 466  $\text{cm}^{-1}$  is resulting from the NiO lattice vibration [25]. It worth noting that absorption band at 820  $\text{cm}^{-1}$  appears in all spectra; this bond is evaluated using Hook's law giving by the following formula [26]:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}, \quad (4)$$

where  $c$  is the light velocity,  $k$  is the bond force constant and  $\mu$  is the reduced mass of nickel and oxygen atoms. Thus the position of specific band absorption of nickel oxide powders is determined on the basis of the bond force constant  $k = 5.105$  dyne/cm and the reduced mass  $\mu = 1/m_{\text{Ni}} + 1/m_{\text{O}}$  which leads to an absorption band at 821  $\text{cm}^{-1}$  closely to the observed one in all spectra of Fig. 3(a-b).

**Fig. 3** – FT-IR spectra of NiO thin films prepared at 500 °C with sprayed volume (a) from 5 ml to 15 ml, (b) from 20 ml to 30 ml

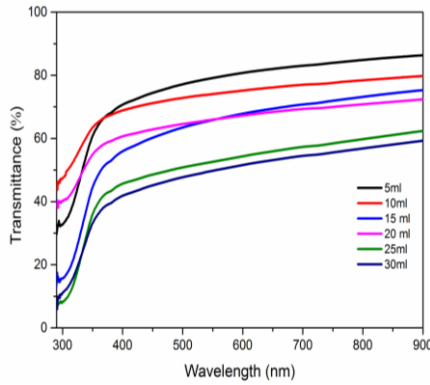
### 3.3 Optical Properties

Fig. 4 shows the optical transmission as a function of the wavelength in 300 – 900 nm range of undoped NiO thin films for different sprayed solution volume. It is clear that the obtained films exhibit high transparency in the visible region. The average transmission value is over than 80 % for the 5 ml deposited sample and decrease to reach the value of 50 % for the 30 ml deposited one revealing the effect of the thickness given

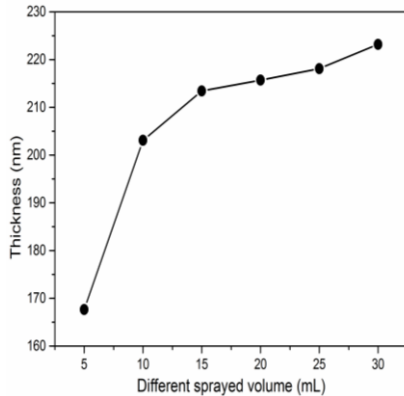
by Lambert's law.

A drastic decrease in transmission is located between 300 – 360 nm revealing the region of the absorption edge in the layers due to the transition between valence and conduction bands due to onset fundamental absorption.

The thickness ( $t$ ) of the films was calculated by using weight difference method. Thickness values are reported in Table 2. As can be seen from Fig. 5, film thickness increases from 168 to 223 nm when sprayed volume increases from 5 to 30 ml. This reveals the amount of sprayed quantities of material hence precursor concentration was kept constant during the deposition process.



**Fig. 4** – Spectral transmittance plots of NiO thin films prepared at 500 °C with different sprayed volume



**Fig. 5** – Variation of NiO thin films thickness prepared at 500 °C with different sprayed volume

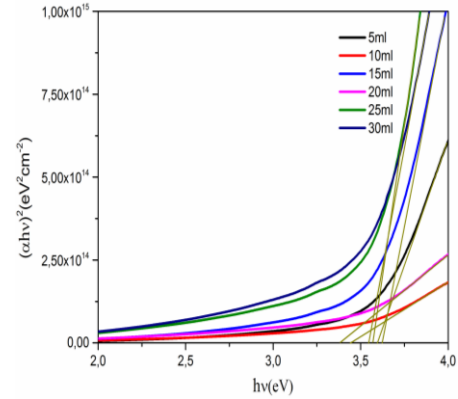
The absorption coefficient has been calculated from Lambert's formula [9]:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right), \quad (5)$$

where  $T$  and  $t$  are the transmittance and thickness of the films respectively. The dependence of absorption coefficient on photon energy in the high absorption regions is carried out to obtain the detailed information about the energy band gaps. The optical energy gap values depend in general on the structure of the films. The band gap values are obtained from the Tauc's relation [5]:

$$(\alpha h\nu)^2 = B(h\nu - E_g), \quad (6)$$

where  $\alpha$  is the absorption coefficient,  $(h\nu)$  is the photon energy,  $B$  is a constant which does not depend on photon energy,  $E_g$  is the optical band gap, and  $n$  is an index characterizing optical absorption process and it is theoretically equal to 1/2 or 2 for indirect or direct allowed transitions respectively (in our case it was taken  $n = 2$ ). Direct band gap was determined by extrapolating the straight-line portion  $(\alpha h\nu)^2$  vs  $(h\nu)$  to the energy axis at  $(\alpha h\nu)^2 = 0$ , as shown in Fig. 6.



**Fig. 6** – Estimation of band gap energy ( $E_g$ ) from Tauc's relation of NiO thin films prepared at 500 °C with different sprayed volume

Obtained  $E_g$  values are given in Table 2. As clearly seen from this table, optical band gap variation of NiO thin films is ranged in 3.59 – 3.55 eV when solution volume changed from 5 to 30 ml. Those obtained  $E_g$  values are in good agreement with earlier reports [27]. Fluctuation in optical gap energy which is directly related to presence of energy levels in the gap of material. This suggests modifications in its electronic structure. The width of the localized states, what so called Urbach tail, is available in the optical band gap of the NiO films and affects both optical band gap structure and transitions. Urbach tail is related directly to a similar exponential tail for the density of states near band edges as can be expressed by the following relation [11]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right), \quad (7)$$

where  $\alpha_0$  is a constant,  $(h\nu)$  is the photon energy and  $E_u$  is the Urbach energy which refers to the width of the exponential absorption edge.  $E_u$  can be estimated from the inverse slope of the linear plot between  $\ln(\alpha)$  versus photon energy  $(h\nu)$  for the NiO films with various sprayed solution volume.  $E_u$  values were calculated as the reciprocal of the straight line slopes and presented in Table 2. The estimated  $E_u$  values are found to be averaged between lowest value 342.46 meV (for 5 ml

**Table 2** – Values of thickness  $t$ , band gap energy  $E_g$  and Urbach energy  $E_u$  of NiO thin films prepared at 500 °C with different sprayed volume

Sprayed solution volume (ml)	Thickness $T$ (nm)	Band gap energy $E_g$ (eV)	Urbach energy $E_u$ (meV)
5	168	3.59	342.47
10	203	3.44	370.37
15	213	3.62	355.87
20	216	3.38	413.22
25	218	3.56	363.64
30	223	3.55	401.61

sprayed solution) and highest value 413.22 meV (for 20 ml sprayed solution) for the undoped NiO thin films.

Also we found that the  $E_u$  values change inversely with the optical band gap of the films, as discussed earlier and expressed in the literatures [11].

We can easily observe from Table 2 that Urbach energy is inverted to gap energy. Such decrease in the optical band gap with increasing Urbach energy can be attributed to the presence of unstructured defects that increase the density of localized states in the band gap and consequently decrease the energy gap and vis-versa [28].

#### 4. CONCLUSION

Nickel oxide (NiO) thin films have been successfully deposited on 500 °C heated glass substrates by spray pyrolysis technique. Effect of volume sprayed solution, ranged in 5 – 30 ml, on structural and optical properties of NiO thin films was studied. XRD, (FT-IR) and UV-visible spectrophotometer were used in investigating elaborated thin films properties. From XRD results it was shown that the deposited thin film with volume lower than 10 ml was amorphous and with increasing volume up to 10 ml NiO thin films structure become polycrystalline with cubic structure and (111) as preferential orientation. An increase and narrowing in

(111) diffraction intensity and FWHM respectively were observed with sprayed volume increasing, which leads to better crystallinity of NiO thin films. Also XRD results reveal that the deposited thin films have a good polycrystalline with 30 ml sprayed solution. Moreover the grain size increased with increasing volume solution and were averaged in 10 – 28 nm. The film thickness increases from 168 to 223 nm with increasing sprayed volume of solution. FT-IR analysis of product confirms the NiO bond formation and the results were in agreement with previous studies. All films exhibit an average optical transparency between 50% and 80% in the visible range and their band gap values were ranged in 3.38 – 3.62 eV. Elaborated NiO thin films leads to highly optical transparency are promising for optoelectronic devices in technological applications.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- K.H.L. Zhang, K. Xi, M.G. Blamire, R.G. Egdell, *J. Phys. Condens. Matter.* **28**, 383002 (2016).
- H. Wanga, D. Mishra, P. Chen, J. Ting, *J. Alloy. Compd.* **584**, 142 (2014).
- H. Kim, J. Lee. *J. Sens. Actuat. B* **192**, 607 (2014).
- X. Chen, J. Jennings, M. Hossain, K. Zhen Yua, Q. Wang, *J. Electrochem. Soc.* **158**, H733 (2011).
- B. Subramaanian, M. Mohamed Ibrahim, V. Senthilkumar, K. Murali, V. Vidhya, C. Sanjeeviraja, M. Jayachandran, *J. Physica B* **403**, 4104 (2008).
- Y-H. Lin, B. Zhan, C-W. Nan, R. Zhao, X. Xu, M. Kobayashi, *J. Appl. Phys.* **110**, 089902 (2011).
- A. Soleimanpour, Y. Hou, A. Jayatissa, *Sens. Actuat B* **182**, 125 (2013).
- I. Faaski, A. Koutoulaki, M. Kompitsas, C. Charitidis, *Appl. Surf. Sci.* **257**, 429 (2010).
- R. Sharma, A.D. Acharyaa, S.B. Shrivastavaa, T. Shripathi, V. Ganesan, *Optik* **125**, 6751 (2014).
- M. Jlassi, I. Sta, M. Hajji, H. Ezzaouia, *Appl. Surf. Sci.* **308**, 199 (2014).
- C. Mrabet, M. Ben Amor, A. Boukhachem, M. Amlouk, T. Manoubi, *Ceram. Int.* **42**, 5963 (2016).
- W. Chia-Ching, Y. Cheng-Fu, *Nanoscale Res. Lett.* **8**, 33 (2013).
- P.S. Patil, L.D. Kadam, *Appl. Surf. Sci.* **199**, 211 (2002).
- M.A. Islam, M.S. Hossain, M.M. Aliya, M.M. Aliyu, J. Husna, M.R. Karim, K. Sopian, N. Amin, *IEEE Phot. Spec. Conf.* **38**, 000151 (2012).
- N. Khedmi, M. Ben Rabeh, M. Kanzari, *J. Mater. Sci. Tech.* **30**, 1006 (2014).
- I.G. Morozov, C.V. Belousova, D. Ortega, M.-K. Mafinac, M.V. Kuznetsov, *J. Alloy. Compd.* **633**, 237 (2015).
- A.S. Adekunle, J.A.O. Oyekunle, O.S. Oluwfemi, A.O. Joshua, Wasuu. O. Makinde, A.O. Ogunfowokan, M.A. Eleruja, E.E. Ebenso, *Int. J. Electrochem. Sci.* **9**, 3008 (2014).
- X. Song, L. Gao, *J. Am. Ceram. Soc.* **91**, 3465 (2008).
- V. Biju, M. Abdul Khadar, *Spectrochim. Acta A* **59**, 121 (2003).
- N. Dharmajar, P. Prabu, S. Nagarajan, C.H. Kim, J.H. Park, H.Y. Kim, *Mat. Sci. Eng. B* **128**, 111 (2006).
- A. Rahdar, M. Aliahmad, Y. Azizi, *JNS.* **5**, 145 (2015).
- K. Sajilal, A.M.E. Raj, *Optik* **27**, 1442 (2016).
- R.A. Ismail, S. Ghafari, G.A. Kadhim, *Appl. Nanosci.* **3**, 509 (2013).
- A. Mhamdi, R. Dridi, A. Arfaoui, C. Awada, M. Karyaoui, I.A. Velasco-Davalos, A. Ruediger, M. Amlouk, *Opt. Mater.* **47**, 386 (2015).
- M. Aghazadeh, A.N. Golikand, M. Ghaemi, *Int. J. Hyd. Energy.* **36**, 8674 (2011).
- A. Franco Jr, H.V.S. Pessoni, *Physica B Condens. Mater.* **476**, 12 (2015).
- N.S. Das, B. Saha, R. Thapa, G.C. Das, K.K. Chattopadhyay, *Physica E* **42**, 1377 (2010).
- M.R. Islam, J. Podder, *Cryst. Res. Tech.* **44**, 286 (2009).