

## **Preparation and characterization of SnO<sub>2</sub> nanoparticles using pulsed laser ablation in liquid**

**Assist.Prof.Dr.Wisam J. Aziz**

**Dr.Raad S. Sabry**

**Ahmed Sadek Ottman Ali**

**Al-Mustansiriyah-University, College of Science, Physics Department,  
Baghdad, Iraq**

### **Abstract**

In this work, colloidal SnO<sub>2</sub> nanoparticles were prepared by laser ablation of tin target immersed in solvent (deionized water) without the use of any chemical/surfactant. The effects of solvents, laser energy and number of pulses on the morphology, optical, chemical and electrical properties, of the synthesized nanoparticles were studied on glass substrate using different pulses at (1000 - 1500 - 2000) pulses. then  $E_g = (3.57 - 3.8 - 3.85)$  and the average grain size found to be about (218 nm) while the RMS value about (0.859 nm).

**Keywords:** SnO<sub>2</sub> nanoparticles, X-ray diffraction, Morphology, AFM, SEM, Optical Properties.

**تحضير ودراسة خصائص ثنائي اوكسيد القصدير النانوي باستخدام  
تقنية القشط بالليزر في السائل**

### **المستخلص**

في هذا البحث تم تحضير ثنائي اوكسيد القصدير النانوي باستخدام تقنية القشط بالليزر لقطعة معدنية نقية بنسبة (99,99%) من القصدير مغمورة في مذيب (ماء اللايوني) من دون استخدام اضافات كيميائية عند التحضير. حيث ان هذه الطريقة تسمح لتحضير مواد نانوية مختلفة لأنها تقنية بسيطة ويمكن بسهولة السيطرة على معالم الليزر. كما تمت دراسة تأثير المذيبات وطاقة الليزر وعدد نبضات الليزر على خصائص التركيبية والبصرية للجسيمات النانوية المحضرة.

## **1. Introduction**

The metastable stages as far as oxides could be created when a strong target is inundated in a liquid medium and the laser shaft is engaged through the fluid onto the objective surface [1]. A beat ruby laser was connected to remove a high immaculateness iron inundated in water to plan iron oxide. This system is called Pulsed Laser Ablation in liquid (PLAL). From that point forward, PLA in liquids has been demonstrated as a promising method to deliver nanomaterials. Among every one of the techniques that were connected to plan nanostructure materials, PLA in liquids has one of a kind component of being a spotless and basic what's more, it doesn't oblige unique and complex setup, for example, vacuum chamber and sputtering unit. Likewise, chemicals such as surfactants can be included into liquid media in PLA technique to control the size and accumulation condition of nanoparticles. Points of interest of the instrument of PLA in liquid and the creation of the nanostructure materials have been accounted for in an audit by Yang [2]. SnO<sub>2</sub> is sort semiconductor precious stone with direct band crevice (3.7 eV at 300 K) having high excitonic tying vitality (130 eV). SnO<sub>2</sub> has been connected in numerous applications, for example, straightforward directing covering of glass, gas sensors, sunlight based cell, and warmth mirror [3–5]. SnO<sub>2</sub> nanostructure can be manufactured utilizing methods, for example, particle sputtering [6], sol–gel [7], converse cell [8], warm vanishing [9] and surfactants intervene [10,11]. The present work is continuation of Tin Oxide center toward union of metal oxides like nano-ZnO and nano-ZnO<sub>2</sub>.using PLAL method [11-12].

## **2. Experimental processers**

SnO<sub>2</sub> utilizing PLAL system as a part of water and laser based setup was outlined and manufactured by regional standards as portrayed in Figure (1) .A high-immaculateness metallic Tin (0.5mm thick, and virtue 99.999% secured from Sigma–Aldrich) was settled on the base of glass cell as an objective, and was pivoted by a natively constructed attractive stirrer to maintain a strategic distance from profound covering and to accomplish consistency in removal procedure.Commonplace laser heartbeat vitality for PLAL procedure was 180 factory joules per beat. The laser pillar was collected by a lens with a optical length of 250mm keeping in mind the end goal to get adequate laser removal. After 40min laser

illumination, a yellow colloidal arrangement of SnO<sub>2</sub> based nanomaterials was acquired. The colloidal suspension was isolated from water after laser light utilizing rotator process. A mixed bag of systems were connected for the portrayal of orchestrated SnO<sub>2</sub>. X-ray diffraction (XRD) (Shimadzu XRD Model)

was utilized to focus crystalline stages and normal crystalline size. Photoluminescence spectra were considered utilizing a Spectrofluorometer (Shimadzu RF-5301 PC) outfitted with (150 w) Xe light as the excitation source. The optical absorbance of the deionized water solution containing SnO<sub>2</sub> nanoparticles was measured in the wavelength between 200 and 532nm at room temperature using a JASCOV-570 spectrophotometer. UV-visible spectrometer was utilized to record the UV-visible retention spectra.

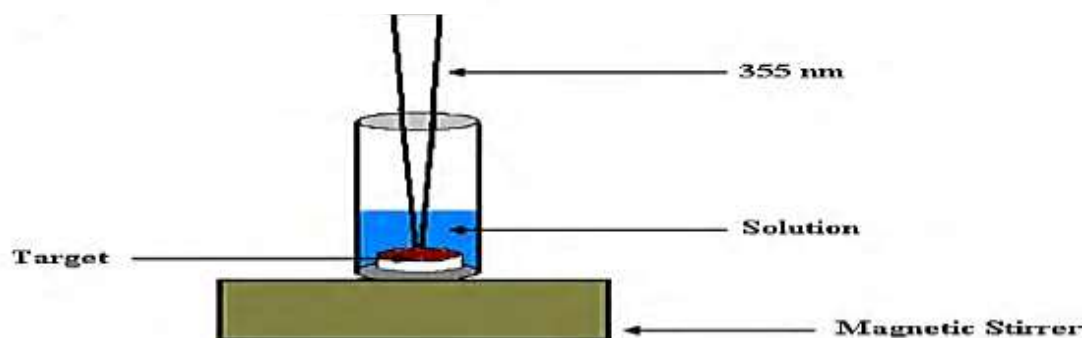


Figure 1: Typical setup for synthesis of nano-SnO<sub>2</sub> using pulsed laser ablation in liquid.

### **3. Results and discussions**

The X-ray diffraction investigation of SnO<sub>2</sub>-NP arranged by PLAL strategy in water was done on a dry film got by drop covering nanoparticles suspension on glass substrate and vanishing the water. Figure (2) delineates the XRD range of combined SnO<sub>2</sub>-NP utilizing PLAL as a part of deionized water. The diffraction range furthermore, entomb plane dividing of the items were in concurrence with the standard diffraction example of SnO<sub>2</sub>, affirming the arrangement of SnO<sub>2</sub> nanocrystals suggesting that removed Sn species were by one means or another oxidized in the vicinity of water. The primary overwhelming crests of SnO<sub>2</sub> were recognized at  $2\theta = 26.66^\circ, 34.18^\circ, 52.3^\circ, 61.34^\circ, 64.4^\circ$  and  $65.54^\circ$  which relating to (1 1 0), (1 0 1), (2 1 1), (1 1 2), (3 0 1) and (3 0 2) and the three solid crests are allocated to the (1 1 0), (1 0 1) and (2 1 1). The cross

section parameters of SnO<sub>2</sub> which speak to the tetragonal rutile were assessed by the mathematica [9]:

$$\sin\theta = \frac{\lambda}{2} \sqrt{\left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right)}$$

Where  $\lambda$  is the wavelength of the occurrence X-beam, h, k, l are mill operator lists,  $\theta$  is the diffraction edge and an and c are the cross section parameters. In this manner, the grid parameter  $a = 4.741\text{\AA}$  and  $c = 3.187$ .

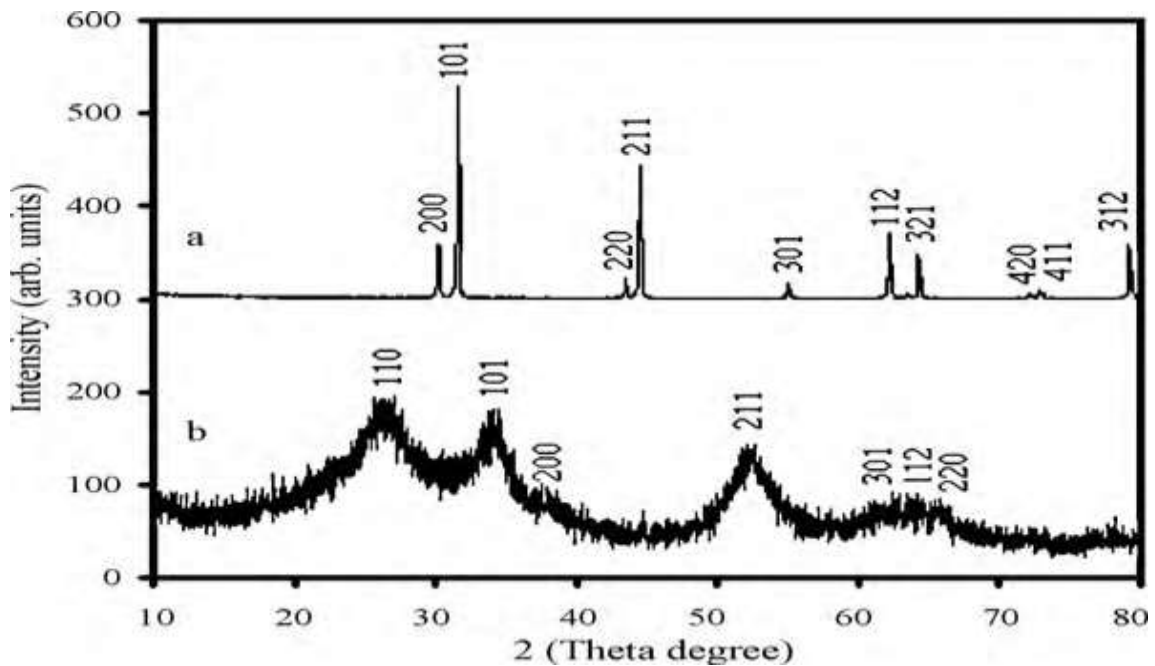


Figure 2: XRD spectra of (a) Tin target and (b) SnO<sub>2</sub> nanoparticles synthesized by laserablation in deionized water.

In order to conduct the absorbance, one of the cell filled with pure deionized water was kept as a reference and the other one was filled with deionized water solution containing SnO<sub>2</sub> nanoparticles. Figure (3) shows Uv-visible is spectrum of colloidal solution obtained by pulsed laser ablation of Sn in deionized water. SnO<sub>2</sub> exciton absorption peak located at 240nm is blue shifted relative to the bulk exciton absorption (532 nm). In the quantum confinement rang, the band gap of the particle increases resulting in the shift of absorption edge to lower wavelength, as the particle size decreases [13].

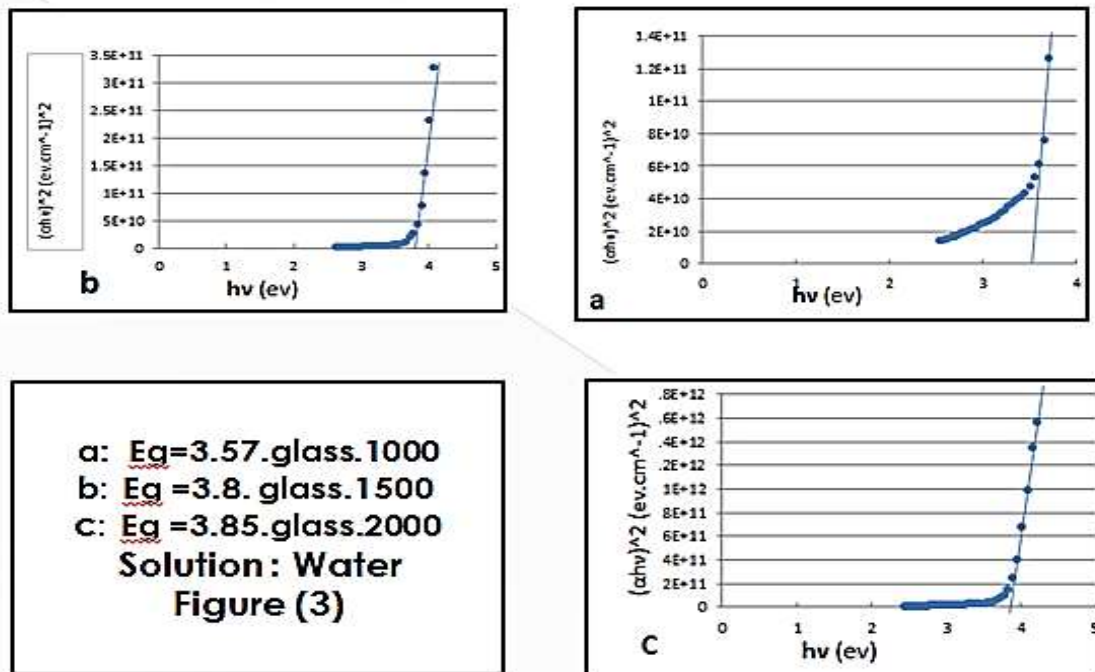


Figure 3: The  $(\alpha h\nu)^2$  Vs  $h\nu$  plots for SnO<sub>2</sub> NPs by PLA in liquid on glass substrate at (a) 1000 pulses, (b) 1500 pulses and (c) 2000 pulses with ( $\lambda= 532$  nm).

Figure (4) show the surface morphology of the colloidal suspension prepared by pulsed laser ablation in liquid on glass substrate, it's clearly obvious the plasma is intense enough to achieve its long life time and high temperature. in such a conditions, the space asymmetry of distributions is no longer predominant because the plume region is filled with a high density of species, Here the influence of aligned media will be much slighter, As a result the grain size increase and it shape close to a helical structure this result similar to other work[13, 14] the average grain size found to be about (218 nm) while the RMS value about ( 0.859 nm). AFM results show in the following figure (4).

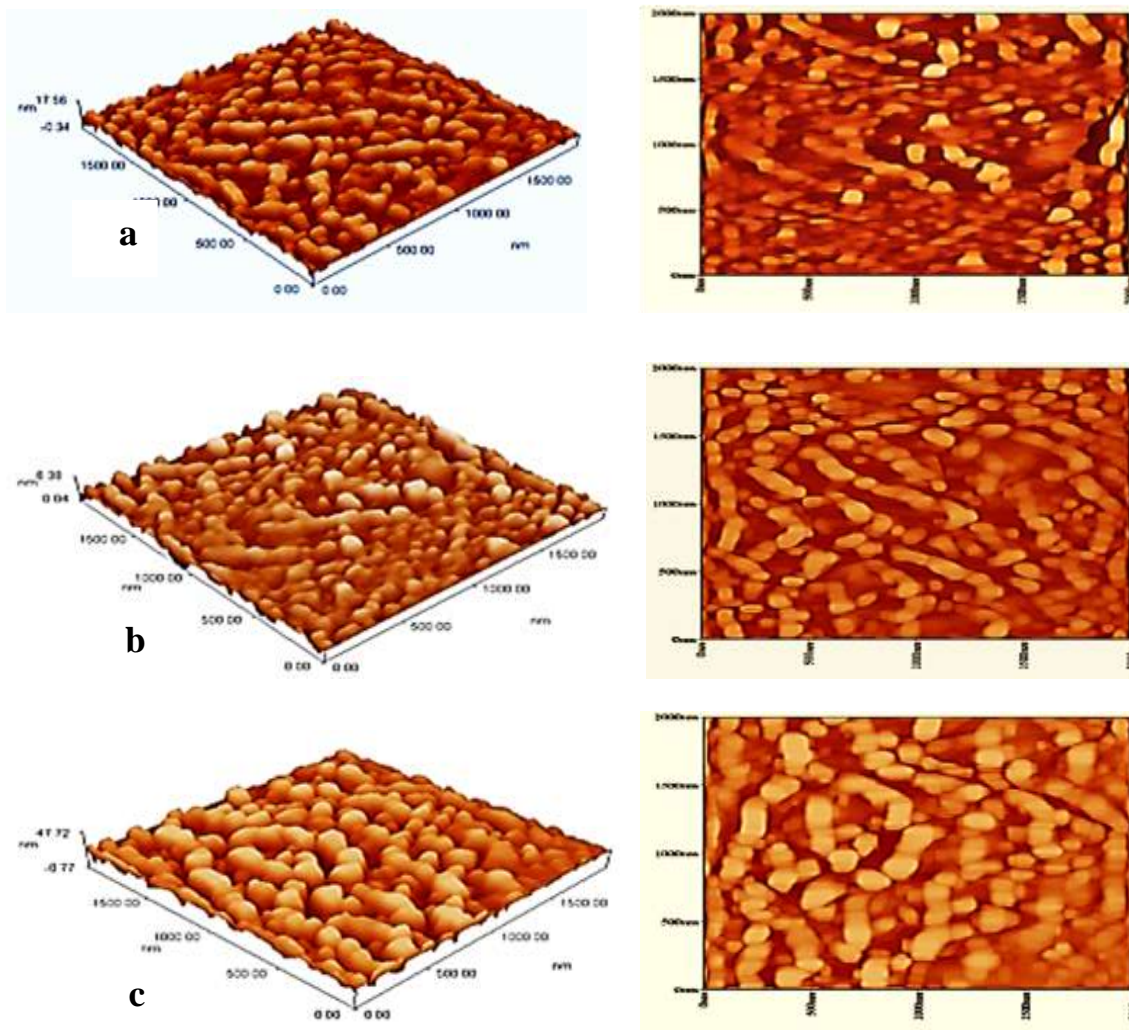


Figure 4: Typical 2D and 3D AFM images of SnO<sub>2</sub> NPs in DW, prepared by PLAL of (a) 1000 pulses, (b) 1500 pulses and (c) 2000 pulses.

Table 1: AFM images morphology experimental parameters of SnO<sub>2</sub>

Solvent	Pulse Laser	Avg. diameter (nm)	Ave. Roughness (nm)	RMS (nm)
DW	1000	77.54	0.715	0.859
	1500	94.53	1.89	2.19
	2000	97.91	5.48	6.51



Figure (5) shows the typical SEM morphology of fully dense cassiterite  $\text{SnO}_2$  samples as-prepared and calcined at  $300^\circ\text{C}$ . Previous studies on nanocrystalline  $\text{SnO}_2$  have shown that pure metastable tetragonal phase can be stabilized when the crystallite size is below a critical size primarily due to very low surface energy associated with it. When the crystallite size exceeds this size, the transformation of metastable phase to monoclinic one occurs due to a decrease in surface energy. The grain size obtained in the as-prepared  $\text{SnO}_2$  powder seems to be above the critical size needed to stabilize the metastable tetragonal phase. In the present study, monoclinic phase could not be stabilized probably due to high degree of agglomeration and annealing among nanocrystals, which can reduce the surface energy. In addition, high enthalpy generated due to the high amount of urea also facilitates agglomeration and annealing among nanocrystals that favors the tetragonal phase as observed by other researchers [15].

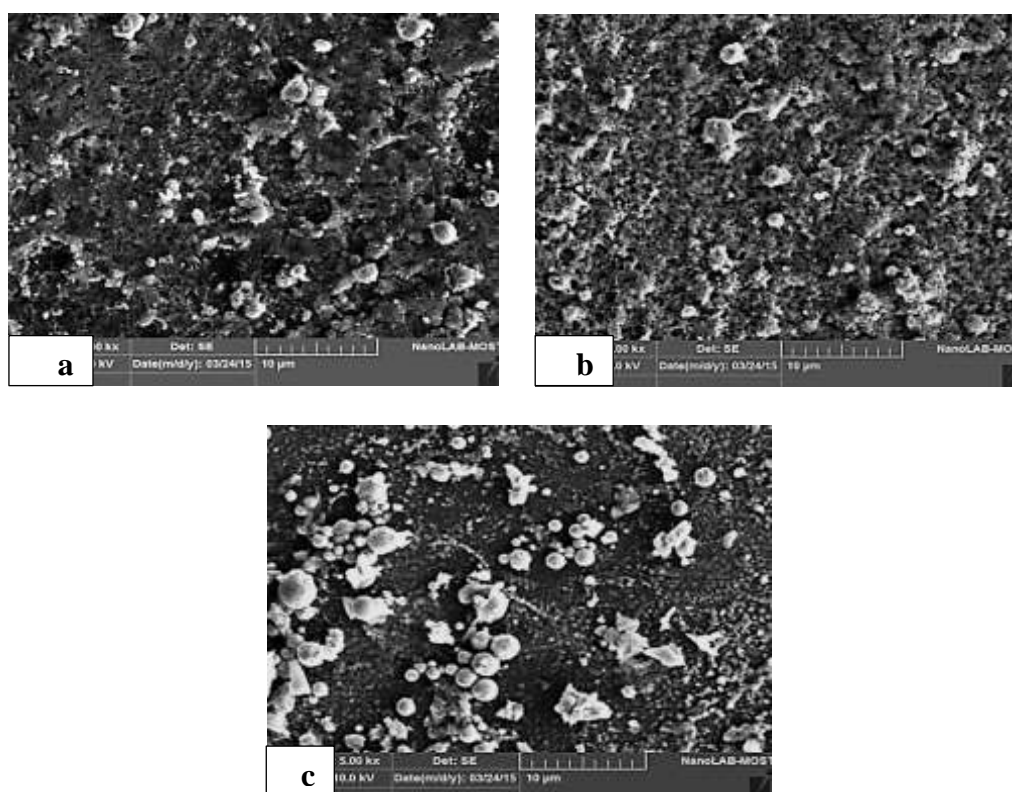


Figure 5: SEM image of  $\text{SnO}_2$  NPs in DW by PLAL of (a)=1000 Pulses, (b) =1500 Pulses, (c) =2000 Pulses at ( $\lambda= 532$  nm).

#### **4. Conclusion**

Nanocrystalline SnO<sub>2</sub>, having normal molecule size of 3 nm was orchestrated in deionized water by PLAL method .

It was portrayed by X-ray diffraction, AFM, UV–visible, assimilation and photoluminescence. The XRD of the nanoparticles is ordered to rutile period of tin dioxide with no hint of an additional stag.



## **References**

- [1] S.B. Ogale, P.P. Patil, D.M. Phase, Y.V. Bhandarkar, S.K. Kulkarni, S.V. SmitaKulkarni, S.M. Ghaisas, Kanetkar, Synthesis of metastable phases via pulsed laser-induced reactive quenching at liquid–solid interfaces, *Phys. Rev. B* 36 (1987).
- [2] G.W. Yang, Laser ablation in liquids: applications in the synthesis of nanocrystals, *Prog. Mater. Sci.* 52 (2007) 648–698.
- [3] A. Diéguez, A. Romano-Rodríguez, J.R. Morante, U. Weimar, M. Schweizer-Berberich, W. Gopel, Morphological analysis of nanocrystalline SnO<sub>2</sub> for gas sensor applications, *Sens. Actuators B: Chem.* 31 (1996) 1–8.
- [4] N. Kudo, Y. Shimazaki, H. Ohkita, M. Ohoka, S. Ito, Organic–inorganic hybrid solar cells based on conducting polymer and SnO<sub>2</sub> nanoparticles chemically modified with a fullerene derivative, *Solar Energy Mater. Solar Cells* 91 (2007) 1243–1247.
- [5] C. Choudhury, H.K. Sehgal, Chemical vapour deposited SnO<sub>2</sub>:Sb heat mirror coatings for cylindrical solar collectors, *Energy Convers. Manage.* 29 (1989) 265–272.
- [6] M. Ruske, G. Brauer, J. Pistner, U. Pfafin, J. Szczyrbowski, Properties of SnO<sub>2</sub> film prepared by DC and MF reactive sputtering, *Thin Solid Films* 351 (1999) 146–150.
- [7] Y. Ning, W. Jianhua, G. Yuzhong, Z. Xiaolong, SnO<sub>2</sub> nanofibers prepared by sol–gel template method, *Rare Met. Mater. Eng.* 37 (2008) 694–696.
- [8] J. Ahmed, S. Vaidya, T. Ahmad, P.S. Devi, D. Das, A.K. Ganguli, Tin dioxide nanoparticles: reverse micellar synthesis and gas sensing properties, *Mater. Res. Bull.* 43 (2008) 264–271.
- [9] S.H. Luo, Q. Wan, W.L. Liu, M. Zhang, Z.T. Song, C.L. Lin, Paul K. Chu, Photoluminescence properties of SnO<sub>2</sub> nanowhiskers grown by thermal evaporation, *Prog. Solid State Chem.* 33 (2005) 287–292.
- [10] J. Pal, P. Chauhan, Structural and optical characterization of tin dioxide nanoparticles prepared by a surfactant mediated method, *Mater. Charact.* 60 (2009) 1512–1516.

- [11] C. Liang, Y. Shimizu, T. Sasaki, N. Koshizaki, Synthesis of ultrafine SnO<sub>2</sub>-xnanocrystals by pulsed laser-induced reactive quenching in liquid medium, *J. Phys. Chem. B* 107 (35) (2003) 9220–9225.
- [12] M.A. Gondal, Q.A. Drmosh, Z.H. Yamani, M. Rashid, Synthesis of nanostructured ZnO and ZnO<sub>2</sub> by laser ablation process using third harmonic of Nd:YAG laser, *Int. J. Nanoparticles* 2 (2009) 142–146.
- [13] T.W. Kim, D.U. Lee, D.C. Choo, J.H. Kim, H.J. Kim, J.H. Jeong, M. Jung, J.H. Bahang, H.L. Park, Y.S. Yoon, J.Y. Kim, *J. Phys. Chem. Solids* 63 (2002) 881.
- [14] David R. Lide, ed., *CRC Hand book of Chemistry and Physics*, CRC Press, Boca Raton, FL, 2005.
- [15] M. Kojima, F. Takahashi, K. Kinoshita, T. Nishibe, Ichidate, *Thin Solid Films* 392 (2001) 349.