

The structural and electrical properties of fluorine-doped tin dioxide ceramics Prepared by spark plasma sintering (SPS)

S. Malek^a, S. Baghshahi^{a,*}, R. Sarraf-Mamoory^b and Ali Nemati^c

^aDepartment of Materials Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

^bDepartment of Materials Engineering, Tarbiat Modares University, Tehran, Iran

^cDepartment of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

In this work, fluorine-doped tin dioxide ceramics were prepared by spark plasma sintering. In order to obtain a thin layer of fluorine-doped tin dioxide with high electrical conductivity and high optical transparency in the sputtering method, it is necessary to prepare a high density and high electrical conductivity target. To do so, tin dioxide powder and tin (II) fluoride powder were utilized to prepare the target. The concentration of fluorine was selected based on the mass ratio of tin (II) fluoride to tin dioxide and ranged between 0.04 and 0.24 (with 0.04 increments). After the powders were mixed, the target was made using spark plasma sintering. The best target had a mass ratio of tin (II) fluoride to tin dioxide of 0.16, with a relative density of 97% and an electrical resistance of $3 \times 10^{-4} \Omega \cdot \text{cm}$. This provided a suitable candidate for a target when using the sputtering method.

Key words: Fluorine-doped tin dioxide, Spark plasma sintering, Sputtering, Electrical resistance, Transparency.

Introduction

Fluorine-doped tin dioxide (FTO) and tin-doped indium dioxide (ITO) are two of the most widely used advanced engineering ceramics in the optic and electronic fields, as they possess desirable properties such as a high electrical conductivity coefficient [1]. Transparent conducting oxides have recently been used in solar cells. The thin films of transparent conducting materials, such as fluorine-doped tin dioxide, tin-doped indium oxide and antimony-doped tin dioxide are used in various fields, including solar cells, due to their combination of electrical, optical and chemical properties [1].

For years, tin-doped indium dioxide was extensively used as the transparent conducting film in dye-sensitized solar cells, but the high cost, along with the toxicity of indium and ITO's reduced electrical conductivity at high temperatures, were some of the problems that came with using it [2]. Therefore, less expensive and more efficient transparent conducting oxide films were required; FTO has recently been developed for use in solar cells and it has attracted the attention of a great many researchers and manufacturers. Cost-effectiveness (as there are no expensive elements in its composition), as well as high thermal and chemical stability, are some of the properties of

fluorine-doped tin oxide; it has also been reported to have more transparency for low-resistance plates in comparison with antimony [3].

The sputtering method is one of the most widely applied deposition methods in various industries, because it is capable of coating large surfaces relatively quickly and can compete with other methods [4]. Therefore, in order to achieve a thin homogenous layer with the proper characteristics using the sputtering coating method, a high density and conductivity target is needed [5]; this is also the objective of the current research paper.

There is a scarcity of research looking into FTO deposition on a solid target by means of the sputtering method, and the obtained films lack the optimum crystallinity. However, more optimally characterized films have been acquired over time by making changes to the solid target [6].

The densification of pure tin dioxide using conventional sintering is difficult for reasons such as the decomposition and evaporation of tin dioxide into SnO_2 (g) and $1/2\text{O}_2$ (g), which occurs during sintering [7]. The spark plasma sintering (SPS) method has reportedly been applied to achieve high-density SnO_2 -based ceramics [8, 9]. Some of the advantages of SPS over conventional sintering methods are the ability to use it for various materials, the production of high-density parts, the very short sintering time and the production of fine-grained ceramics, which can prevent the occurrence of deleterious intermediate phases and reduce SnO_2 evaporation [10, 11].

*Corresponding author:
Tel : +98-9122164225
Fax: +98-2833780073
E-mail: baghshahi@eng.ikiu.ac.ir

There are numerous mechanisms suggested for the SPS process, but the most common theory pertains to micro-spark plasma sintering. This is based on the foundation of an electrical load discharge and the instant production of plasma sparkles at a very high temperature within a fraction of second in a small local region between the powder particles [12, 13].

In this paper, SnO_2 and SnF_2 powders were used to make the target. Then, SPS at a low temperature with a rapid sintering rate was used to obtain high-density FTO ceramics with high electrical conductivity.

Experimental Procedures

Tin dioxide (SnO_2), (supplied by Merck co.), and 99% pure tin (II) fluoride (SnF_2), (supplied by Acros Organics, Code No. 30850), were selected as the precursors for the preparation of the target required for the magnetron sputtering method.

To prepare the fluorine-doped tin dioxide powder, proper amounts of tin dioxide powder and tin (II) fluoride powder were mixed (Table 1). The fluorine concentration (the dopant) was selected based on the mass ratio of tin (II) fluoride to tin dioxide ranging between 0.04 and 0.24 (with a 0.04 increments). The target powders were blended with a planetary mill, rotating at a speed of 100 rpm, for two hours. Then, the target powder samples were calcined in a furnace at 400 °C for two hours. The specifications of the target powder samples, along with their code numbers are given in Table 1. In the coding, the number immediately following the letter "F" denotes the tin (II) fluoride to tin dioxide mass ratio.

The target powder samples were consolidated in a SPS system (SPS-20T-10) in the current investigation. The powders were poured into a graphite die with an inner diameter of 50 mm, after which the die was transferred into the SPS machine. The pulse pattern was kept constant and consisted of 12 pulses (with a pulse duration of 2 ms), followed by two periods of zero current. The axial pressure on the punches was 40 MPa during sintering; the whole pressure was exerted at the beginning from the heating step, before being unloaded during cooling. All of the samples were sintered at 950 °C at a heating rate of 20 °C per minute

Table 1. Target compositions by mass for the preparation of tin dioxide and fluorine doped tin dioxide thin films.

Powder target	Compound powder target mass (g)	
	Tin dioxide	Tin (II) fluoride
SnO_2	40	0
SnO_2 : F0.04	38.46	1.54
SnO_2 : F0.08	37	3
SnO_2 : F0.12	35.70	4.30
SnO_2 : F0.16	34.48	5.52
SnO_2 : F0.20	33.3	6.7
SnO_2 : F0.24	32.25	7.75

with a dwell time of up to six minutes in a vacuum (20 MPa), and they were allowed to slowly cool down at ambient temperature. To select the optimum temperature, the sintering was repeated under the above-cited conditions at both 850 °C and 1000 °C.

The density of the sintered FTO ceramics was measured according to the method proposed by Archimedes in water. Then, the relative density was computed based on the obtained density to theoretical density ratio. To determine the phase structures of the FTO powder and the sintered ceramics, X-ray diffraction (XRD, Scifert, model 3003PTS) was applied using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). The sample was scanned from 20 ° to 70 ° (2 θ) with a 0.02 step size.

The microstructures of the sintered FTO ceramics were observed using a field emission scanning electron microscope (FE-SEM, MIRA3TESCAN-XMU) and the grain size was estimated with Image J software.

To investigate and measure the electrical properties of the sintered FTO ceramics, including the electrical resistance, carrier concentration and hall mobility, the Hall Effect and the van der Pauw method were applied.

Results and Discussion

Phase composition of the FTO powder

Fig. 1 shows the XRD patterns of the FTO powder at different concentrations of fluorine dopant. The XRD results showed that the characteristic peaks of the cassiterite structure of SnO_2 crystals could be obtained by varying the tin (II) fluoride to tin dioxide mass ratio between the range of 0.04 and 0.24 (with 0.04 increments), without any significant structural changes. No obvious reflection peaks were detected as a result of impurities.

Densification and sintering behaviour of FTO ceramics

The SPS process used to consolidate the FTO powder was carried out at 950 °C for a holding period of six minutes in a vacuum, at a heating rate of 20 °C

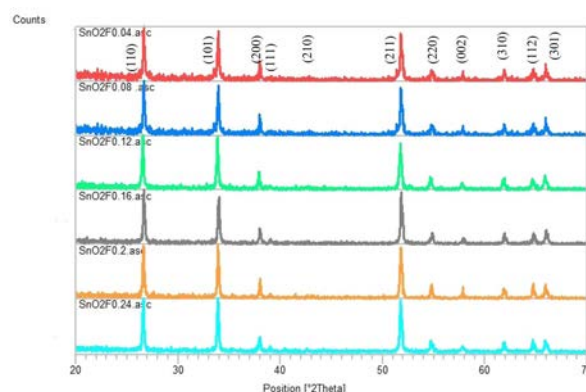


Fig. 1. XRD patterns for FTO powder with different F doping concentrations.

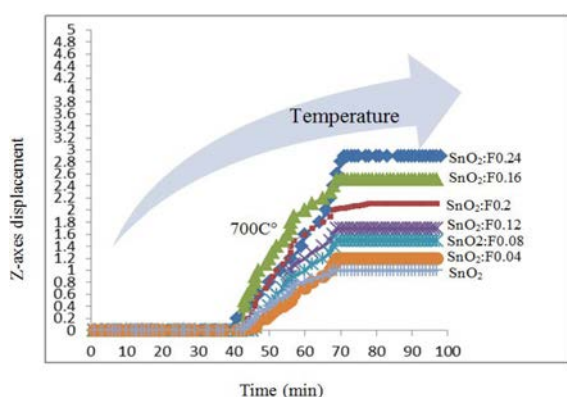


Fig. 2. Z-axis displacement curves of FTO powders curves as a function of the sintering time during the SPS (consolidated at 950 °C).

Table 2. Relative density of SPS as-sintered FTO ceramics.

Sample	Relative density (%)	
	850 °C	950 °C
SnO ₂	87.5	90
SnO ₂ : F0.04	89.2	91.5
SnO ₂ : F0.08	90.1	93.4
SnO ₂ : F0.12	91.3	95.6
SnO ₂ : F0.16	92.5	97
SnO ₂ : F0.20	91.7	96.4
SnO ₂ : F0.24	91	96

per minute. Fig. 2 illustrates the Z-axis displacement and displacement rate (dz/dt slope of curve) of FTO powders curves as a function of the sintering time during the SPS process when their sintering temperature is set at 950 °C. For FTO powders, the densification procedure starts at about 700 °C and the shrinkage stage begins slightly earlier and ends later as the fluorine concentration increases. This indicates the enhanced sintering potential of FTO powders especially for SnO₂ : F0.16 powder.

The results obtained for the relative density of the FTO ceramics at sintering temperatures of 950 °C and 850 °C are summarized in Table 2. It should be noted that the FTO powder was also consolidated at 1000 °C using the SPS method; however, the obtained FTO ceramics were brittle. The obtained FTO ceramics have low density at 850 °C. The FTO ceramics have a high density (91.5–97% d_{theor}) under the selected SPS conditions at 950 °C, while the density of pure SnO₂ ceramics is only 90%. The amount of fluorine dopant influences the density of the FTO ceramics. As the tin (II) fluoride to tin dioxide mass ratio increases within the range of 0.04 to 0.24 (with 0.04 increments), the density first increases before decreasing; the sample with a 0.16 weight ratio of tin (II) fluoride to tin dioxide had the highest relative density (97%) at 950 °C.

Phase composition and microstructure of FTO ceramics

Fig. 3 shows the XRD patterns of FTO ceramics

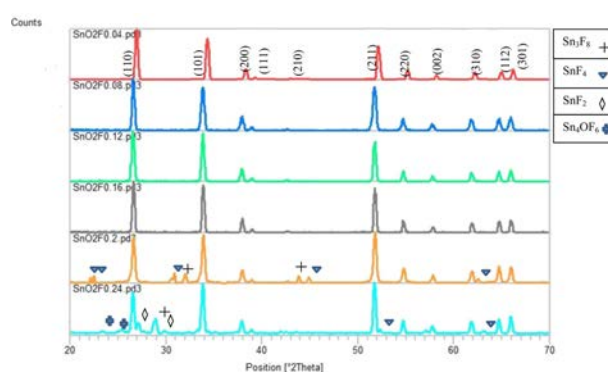


Fig. 3. XRD patterns for SPS as-sintered FTO ceramics.

Table 3. Lattice parameters for SPS as-sintered FTO ceramics.

Sample	Lattice parameters	
	a = b (Å)	c (Å)
SnO ₂	4.72	3.1750
SnO ₂ : F0.04	4.7402	3.1896
SnO ₂ : F0.08	4.7438	3.1923
SnO ₂ : F0.12	4.7451	3.1931
SnO ₂ : F0.16	4.7465	3.2078
SnO ₂ : F0.20	4.7482	3.2210
SnO ₂ : F0.24	4.7493	3.2530

doped with different concentrations of fluorine. As can be seen in Fig. 3, the SnO₂ phase is easily observable in the samples and the XRD patterns for samples SnO₂ : F0.04, SnO₂ : F0.08, SnO₂ : F0.12 and SnO₂ : F0.16 correspond to the JCPDS card No. 01-077-0450 cassiterite SnO₂. These XRD patterns for samples up to a weight ratio of tin fluoride to tin dioxide of 0.16 lend support to the idea that no extra phase has been created in the X-ray detection domain and that the low sintering temperature in the SPS method has prevented the formation of other harmful intermediary phases and decomposition of FTO system.

The results obtained for the lattice parameters of the FTO ceramics at a sintering temperature of 950 °C are summarized in Table 3. As can be seen, as The mass ratio of tin (II) fluoride to tin dioxide increases in the range of 0.04 to 0.24 (with 0.04 increments), it does not lead to an obvious change in the SnO₂ lattice parameters. This is because the radius of the fluorine ion (0.133 nm) is similar to the radius of the oxygen ion (0.140 nm), and the substitution of the fluorine ion by the oxygen ion does not lead to any considerable change in the lattice parameters, despite the fluorine ion being doped in tin dioxide. Therefore, the diffraction peaks of cassiterite SnO₂ do not appear to shift.

In the SnO₂ : F0.20 and SnO₂ : F0.24 samples in Fig. 3, the tin fluoride phase becomes detectable with the increase in dopant concentration corresponding to the JCPDS cards No. 01-075-2327 Sn₃F₈ phase, No. 01-085-2126 SnF₄ phase, No. 00-015-0744 SnF₂ phase

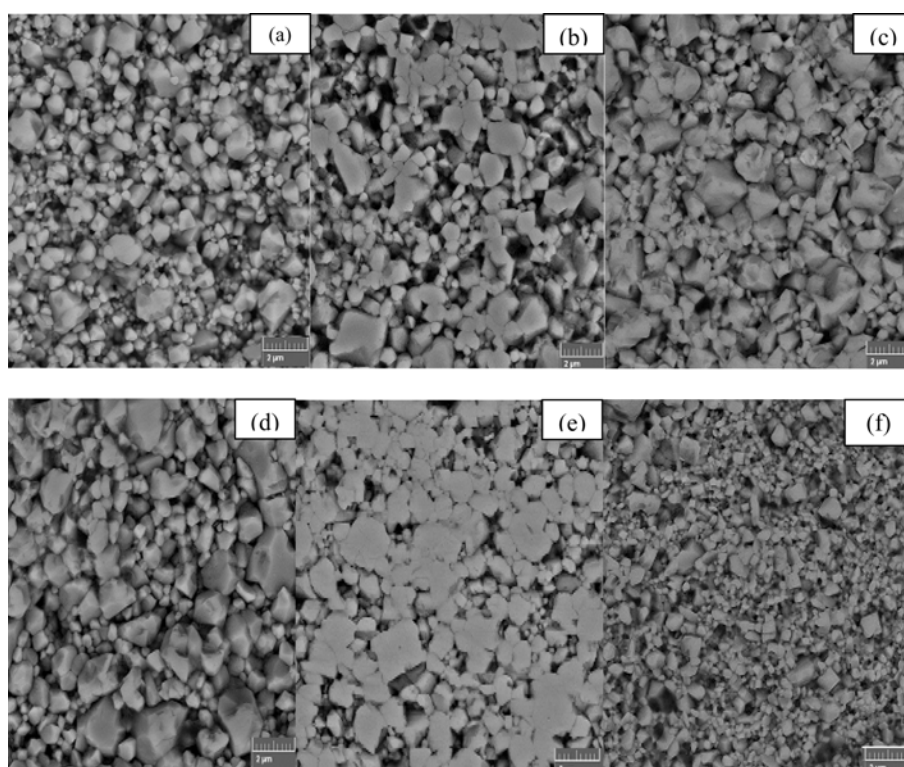


Fig. 4. FESEM photographs of the FTO ceramics sintered at 950 °C with different mass ratio of tin (II) fluoride to tin dioxide: (a) SnO_2 : F0.04, (b) SnO_2 : F0.08, (c) SnO_2 : F0.12, (d) SnO_2 : F0.16, (e) SnO_2 : F0.20, and (f) SnO_2 : F0.24.

and No. 01-082-2194 Sn_4OF_6 Phase.

The results of the FESEM photographs of the FTO ceramics sintered at 950°C are depicted in Fig. 4. The mean particle size of the FTO ceramics, obtained using Image J Software, are $0.80 \pm 0.5 \mu\text{m}$, $0.825 \pm 0.5 \mu\text{m}$, $0.922 \pm 0.5 \mu\text{m}$, $0.995 \pm 0.5 \mu\text{m}$, $0.910 \pm 0.5 \mu\text{m}$ and $0.62 \pm 0.5 \mu\text{m}$ for the FTO ceramics, SnO_2 : F0.04, SnO_2 : F0.08, SnO_2 : F0.12, SnO_2 : F0.16, SnO_2 : F0.20 and SnO_2 : F0.24 respectively. The grain growth in FTO ceramics is obvious and the results indicate that grain growth happens during the annealing and spark plasma sintering process.

The particle sizes of the FTO ceramics increased as the tin (II) fluoride to tin dioxide ratio increased to 0.16; after this, the particle sizes decreased due to the formation of tin fluoride phases. According to Table 2 and Fig. 4, the highest density (97%) was achieved for the sample with the code SnO_2 : F0.16.

From the perspective of spark plasma sintering, the transmittance of electrical current largely depends on the electrical conductivity of the compressed powder in the graphite die. With the insulating powder, the main current passes through the graphite die and a small fraction of the current passes through the particles. On the other hand, with conductive powders, the current is transmitted through the powder particles [14]. Tin dioxide is an n-type semi-conductor whose electrical conductivity increases with the addition of dopants [15, 16]. Thus, a large fraction of the main current passes through the compact FTO powder as compared

Table 4. Electrical conductivity properties for SPS as-sintered FTO ceramics.

Sample	Electrical resistance (ρ) (Ωcm)	Carrier concentration (n) (cm^{-3})	Hall mobility (μ) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
SnO_2	1.1	7.1×10^{17}	8.2
SnO_2 : F0.04	0.4	1.3×10^{18}	10.4
SnO_2 : F0.08	5×10^{-2}	8.3×10^{18}	14.6
SnO_2 : F0.12	9×10^{-3}	7.6×10^{19}	22.8
SnO_2 : F0.16	3×10^{-4}	4.5×10^{20}	40.5
SnO_2 : F0.20	3×10^{-3}	4.5×10^{20}	40.3
SnO_2 : F0.24	9×10^{-3}	4.4×10^{20}	40.2

to the compact tin dioxide powder. The electrical resistance of the tin dioxide and FTO ceramics are given in Table 4. Therefore, electrical discharge is a frequently observed phenomenon in the compact FTO powder in SPS, when compared to the compact tin dioxide powder.

Investigation of electrical properties

The results of the electrical conductivity properties of the sintered FTO ceramics at different fluorine dopant concentrations, including the electrical resistance (ρ), carrier concentration (n) and Hall mobility (μ), are presented in Table 4.

FTO is an n-type semiconductor. In fluorine-doped tin dioxide lattices, the F⁻ ion replaces the O²⁻ ion, thus acting as a donor and creating an electron. According to Table 4 and Fig. 5, the electrical resistivity first

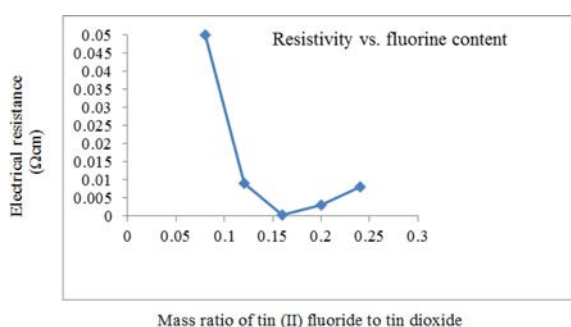


Fig. 5. The electrical resistivity of sintered FTO ceramics sintered at 950 °C with different mass ratio of tin (II) fluoride to tin dioxide in range of 0.08 to 0.24.

decreased as the tin fluoride to tin dioxide weight ratio increased to 0.16; however, the carrier concentration and Hall mobility increased and then electrical resistivity decreased. If a fluorine ion takes the place of the oxygen ion in the dioxide structure, this increases the electrical conductivity due to the creation of free electrons. The more fluorine ions that take the place of oxygen ions in the dioxide structure, the more free electrons will be produced and the more the electrical resistance decreases. Of course, if the dopants are increased based on Table 4, this gives an optimum limit.

Moreover, any increase further than 0.16 caused electrical resistivity to increase. If this value exceeded the optimum limit, the additional fluorine atoms that can no longer be dissolved in the tin dioxide structure by means of substitution cause the structure to become disordered and contributed to increase electrical resistivity. When fluorine took an interstitial position, it acted as an electron trap and reduced the carrier concentration [17]. Another outcome might be the formation of tin fluoride phases, and scattering beyond the boundaries that, in itself, causes an increase in electrical resistivity [18]. In current research, according to Fig. 3 and 4, increasing the mass ratio of tin (II) fluoride to tin dioxide to 0.2 and 0.24 leads to the formation of tin fluoride phases; therefore electrical resistivity increases.

The optimum limit of the tin fluoride to tin dioxide weight ratio was 0.16 in the current research paper and reached a minimum value of $3 \times 10^{-4} \Omega \cdot \text{cm}$ electrical resistivity. The low electrical resistivity of the sintered FTO ceramic with $\text{SnO}_2:\text{F}0.16$ code showed more current passed through the sample and more mass transport occurred due to SPS discharge in the void spaces [19]. This phenomenon described the high displacement rate for the $\text{SnO}_2:\text{F}0.16$ powder, shown in Fig. 2, which leads to the highest density of 97% for the sintered $\text{SnO}_2:\text{F}0.16$ ceramic.

Conclusions

Sintered fluorine-doped tin dioxide (FTO) ceramics

were prepared using the spark plasma sintering method at 950 °C, with a holding time of six minutes and a heating rate of 20 °C per minute. FTO ceramics with a 0.16 tin fluoride to tin dioxide mass ratio, with a high density (97% relative density) and high electrical conductivity $3 \times 10^{-4} \Omega \cdot \text{cm}$ was selected as target for use in magnetron sputtering.

References

1. E. Fortunato, D. Ginley, H. Hosono, and D.C. Paine, "Transparent Conducting Oxides for Photovoltaics", *MRS Bull.*, 32 (2007) 242-247.
2. T. Ogi, "Characterization of dip-coated ITO films derived from nanoparticles synthesized by low-pressure spray pyrolysis", *J. Nanopart. Res.*, (2006) 8: 343.
3. B. Lia, L. Huang, B. Ming Zhou, N. Fei Ren, and D. Bowub, "Surface Morphology and Photoelectric Properties of Fluorine-Doped Tin Oxide Thin Films Irradiated with 532 Nano second Laser", *Ceram. Int.*, 40 (2014) 1627-1633.
4. M. Girtan, A. Bouteville, and G.G. Rusu, "Preparation and properties of $\text{SnO}_2:\text{F}$ thin films", *J. Optoelect. Adv. Mat.*, 8 (2006) 27-30.
5. M. Seo, Y. Akutsu, and H. Kagemoto, "Preparation and properties of Sb-doped SnO_2 /metal substrates by sol-gel and dip coating", *Ceram. Int.*, 33 (2007) 625-629.
6. H. Cachet, "Films and powders of fluorine-doped tin dioxide", *Fluorinated Materials for Energy Conversion*, Chapter 22, 513-534
7. E. R. Leite, J. A. Cerri, E. Longo, J. A. Varela and C. A. Paskocima, "Sintering of Ultrafine Undoped SnO_2 Powder", *J. Eur. Ceram. Soc.*, 21 (2001) 669-675.
8. O. Scarlat, S. Mihailescu, G. Aldica, M. Zaharescu, and J. R. Groza, "Enhanced Properties of Tin (IV) Oxide Based Materials by Field Activated Sintering", *J. Am. Ceram. Soc.*, 86 (2003) 893-897.
9. J. R. Zhang, X. J. Xu, X. H. Li, L. Gao, and J. Sun, "Fabrication of antimony doped tin oxide ceramics by spark plasma sintering technique", *Chin. J. Inorg. Chem.*, 26 (2010) 1100-1104.
10. Z. A. Munir and D. V. Quach, "Electric current activation of sintering: a review of the pulsed electric current sintering process", *J. Am. Ceram. Soc.*, 94 (2011) 1-19.
11. M. Omori, "Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS)", *Mat. Sci. Eng. A*, 287(2000)183-188.
12. F. Chen, Sh. Yang, J. Wu, Jorge A. G. Perez, Q. Shen, J. M. Schoenung, E. J. Lavertnia, and L. Zhang, "Spark plasma sintering and densification mechanisms of conductive ceramics under coupled thermal/electric fields", *J. Am. Ceram. Soc.*, 98(2015) 732-740.
13. Y. J. Wu, J. Li, X. M. Chen, and K. Kakegawa, "Densification and microstructures of PbTiO_3 ceramics prepared by spark plasma sintering", *Materials Science and Engineering A*, 527 (2010) 5157-5160.
14. L. E. Smart and E. A. Moore, *Solid State Chemistry: An Introduction*, CRC Press, 2005.
15. J. Robertson and B. Falabretti, "Electronic structure of transparent conducting oxides", in *Handbook of Transparent Conductors*, D. S. Ginley, Ed., p. 27, Springer Science, Business Media, Limited liability company, 2010.
16. U. Anselmi-Tamburini, S. Gennari, J. E. Garay, and Z. A. Munir, "Fundamental investigations on the spark

- plasma sintering/synthesis process: II. Modeling of current and temperature distributions”, *Mat. Sci. Eng. A*, 394(2005)139-148.
17. B. Zhang, Y. Tian, J. X. Zhang, and W. Cai, “The role of oxygen vacancy in fluorine-doped SnO₂ films”, *Physica B*, 406 (2011) 19: 791-796.
 18. S. J. Ikhmayies and R. N. Ahmad-Bitar, “Using HF rather than NH₄F as doping source for spray-deposited SnO₂ thin films”, *J. Cent. South Univ.* 19 (2012) 791-796.
 19. J. Wu, F. Chen, Q. Shen, J. M. Schoenung, and Li. Zhang, “Spark plasma sintering and densification mechanisms of antimony-doped tin oxide nanoceramics”, *J. Nano Mat.*, 2013 (2013) 1-8.