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Effect of annealing temperature on structural properties of nanocrystalline $Tl_3(PW_{12}O_{40})$ thin films

S. R. Mane[1,]*, R. M. Mane[2], P. S. Patil[3] and P. N. Bhosale[2]

[1]*Department of Chemistry, Smt. K. R. P. Kanya Mahavidyalaya, Islampur 415 409, India*
[2]*Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur, India*
[3]*Thin Film Materials Laboratory, Department of Physics, Shivaji University Kolhapur, Kolhapur 416004, India*

[*]Corresponding author. E-mail: sambhaji_mane@rediffmail.com

ABSTRACT

Thallium (I) doped tungsten heteropolyoxometalate (HPOM) combinatorial thin films have been deposited on glass substrate using simple chemical bath deposition technique. The deposited films were annealed at 100 °C, 150 °C, 200 °C and 250°C. These annealed thin films were characterized by using SEM, EDAX, AFM, FT-IR, XRD and TGA-DTA techniques for their structural properties. SEM and EDAX results shows that, tungsten HPOM material is polycrystalline in nature and Tl (I) is intercalated in phosphotungustate anion. AFM studies on the films annealed at different temperatures reveal that the surface roughness increases with the increase in annealing temperature, suggesting an increase of crystallization with temperature. FT-IR study confirms the well formation of heteropolyoxometalate material under investigation. Various structural parameters such as lattice constants, crystallite size and grain size have been calculated and they are found temperature dependent. The lattice constant, crystallite size and grain size of tungsten HPOM material increases with increase in temperature. XRD pattern of annealed thin films shows better crystanality of tungsten HPOM material having simple cubic spinel structure. The TGA-DTA study revealed that, Tl_3 (PW_{12} O_{40}) material is thermally stable up to 265.12 °C. Copyright © 2013 VBRI press.

Keywords: Nanocrystalline; thin films; annealing; HPOM; tungsten*;* intercalation.

Sambhaji Mane is working as Associate Professor and Head in Chemistry at Smt. Kusumtai Rajarambapu Patil Kanya Mahavidyalaya, Islampur Maharashtra, India. He has published 13 research articles in international journals and 40 research articles in national and international conferences/symposia/workshops etc.

Popatrao Bhosale is working as Professor and Co - ordinator in Applied Chemistry, Shivaji University, Kolhapur, Maharashtra, India. He has published 20 research articles in international journals and 50 research articles in different national and international conferences/symposia/workshops etc.

Pramod Patil is working as Reader (Associate Professor), Department of Physics, Shivaji University, Kolhapur, Maharashtra, India since 1993. He has published 143 research articles in different international journals and 165 research articles in different national and international conferences/symposia/workshops etc.

Introduction

The heteropolyoxometalate (HPOM) materials of Vanadium, Molybdenum and Tungsten are an exciting class of materials whose properties are intermediate between atoms or molecules and bulk materials. They exhibit size dependent physical and chemical properties largely as a consequence of the confinement of their anionic nature and their unusual molecular structures [**1**]. Metal ion doped HPOM materials are technologically important due to its high electrical and thermal conductivities [**2**], redox ion exchange behaviors [**3-7**]. The applications of HPOM centre depend on their high charge and ionic weights. An enormous patent and journal literature is devoted to the applications of small number of heteropolyanions. The heteropolyanions of V, Mo, and W find applications in biochemical industrial catalysis, proton conductor [**8**], ion exchange materials, thin layer chromatography, materials for separation of amino acids [**9**]. Heteropolyoxometalates (HPOM), in addition to their considerable applications in catalysis and medicine, are attracting attention as compounds for advanced materials. The investigation on HPOM complexes with metal ions including Ln (III) ions has important significance due to their antiviral and anti-

HIV activity and potential applications in opto-electronic devices [**10**].

There is no single report available on thin films of thallium (I) doped tungsten heteropolyoxometalate prepared by using simple chemical bath deposition technique. So, in the present investigation, we are reporting preparation, characterization and effect of annealing temperature on structural properties of thallium (I) doped tungsten heteropolyoxometalate thin films.

Experimental

Preparation of solutions

Thin films of $Tl_3 (PW_{12} O_{40})$ were prepared by dissolving following AR grade chemicals in double distilled water.

a) 2% aqueous solution of Phosphotungustic acid $[H_3 (PW_{12} O_{40})]$.
b) 0.2%, aqueous solution of Thallous acetate (CH_3COO-Tl).
c) 0.2% aqueous solution of Polyacrylamide (PAM)

Fig. 1. Photograph of $Tl_3(PW_{12}O_{40})$ thin film.

Preparation of tungsten HPOM thin films

Thin films of $Tl_3 (PW_{12} O_{40})$ were prepared by using simple chemical bath deposition technique using following procedure. 90 cm^3 2 % aqueous solution of phosphotungustic acid was taken in 150 cm^3 capacity beaker having side arm and temperature of this solution was kept at 55 ^oC. The clean & dry glass substrates were fitted to bakelite substrate holder and dipped in the phosphotungustic acid solution. After five minutes 0.2% aqueous solution of thallous acetate was added drop wise through side arm in phosphotungustic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 1.5 h, there was white colored and uniform deposition of $Tl_3 (PW_{12} O_{40})$ on glass substrates (**Fig. 1**). As deposited thin films were dried at room temperature and dipped in 0.2% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. As deposited thin films after drying at room temperature were annealed at 100 ^oC, 150 ^oC, 200 ^oC and 250 ^oC temperatures and studied for their morphological and structural characterization using SEM, EDAX, AFM, FT-IR, XRD and TGA-DTA techniques. Thickness of the annealed films was measured by surface profiler and it was 371.80 nm.

The reactions involved during the growth of tungsten HPOM thin films are:

$$H_3 (PW_{12} O_{40}) \rightarrow (PW_{12}O_{40})^{3-} + 3H^+ \quad (1)$$

Phosphotungstic acid Phosphotungstate anion

$$3\ CH_3 – COO – Tl \rightarrow 3CH_3\text{- }COO^- + 3\ Tl^+ \quad (2)$$

Thallous Acetate Acetate ion

$$3\ CH_3\text{- }COO^- + 3H^+ \rightarrow 3CH_3\text{- }COOH \quad (3)$$

Acetate ion Acetic acid

$$H_3(PW_{12}O_{40})^{3-} + 3\ Tl^+$$

phosphotungstate anion Thallous ion

Ion by ion condensation ↓

$$Tl_3 (PW_{12} O_{40}) \quad (4)$$

Thallium (I) doped Tungsten HPOM.

The overall reaction is,

$$H_3 (PW_{12} O_{40}) + 3\ CH_3 – COO – Tl$$

$$p^H = 1.0 \downarrow \text{Temp.} = 55\ ^oC$$

$$Tl_3 (PW_{12} O_{40}) + 3CH_3\text{- }COOH \quad (5)$$

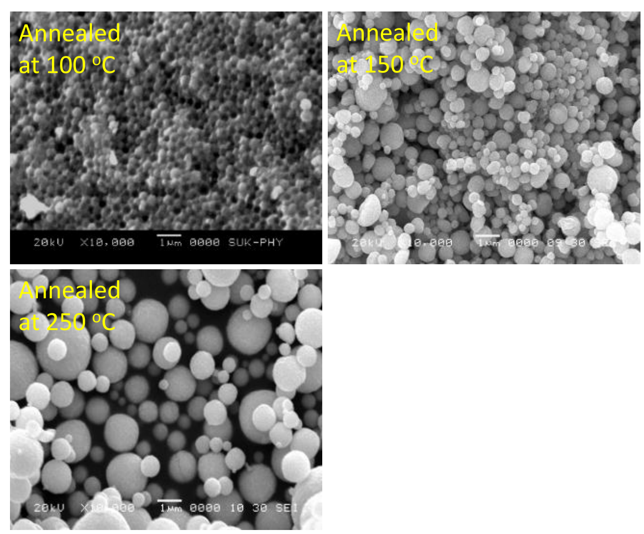


Fig. 2. Microphotographs of annealed $Tl_3(PW_{12}O_{40})$ thin films

Results and discussion

SEM results on external morphology

The microphotographs of annealed thin films are shown in **Fig. 2.** It indicates that $Tl_3(PW_{12}O_{40})$ material is polycrystalline in nature with uniform distribution of crystallites. It is found that, as the annealing temperature of the film increases crystallite size increases and we got spherical shaped crystals. The average crystallite size calculated by linear intercept technique was in the range 485.0 nm to 942.0 nm.

EDAX results on compositional analysis

In **Fig. 3.** typical EDAX spectrum of $Tl_3(PW_{12}O_{40})$ thin film annealed at 250 ^oC is shown which indicate that , Tl (I) is intercalated in Phosphotungustate anion[**11**]. The EDAX patterns show the presence of P, W, O and Tl in the films without any major impurity. Table 1 shows theoretical and practical atomic percentage of P, W, O and Tl. From **Table 1** it is found that theoretical and practical atomic percentages are in good agreement.

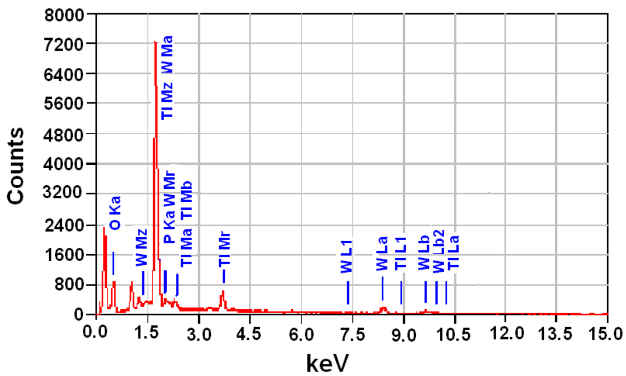
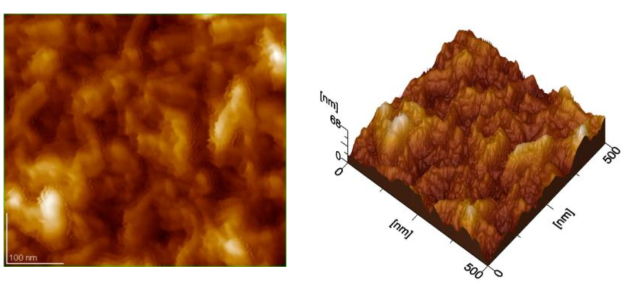


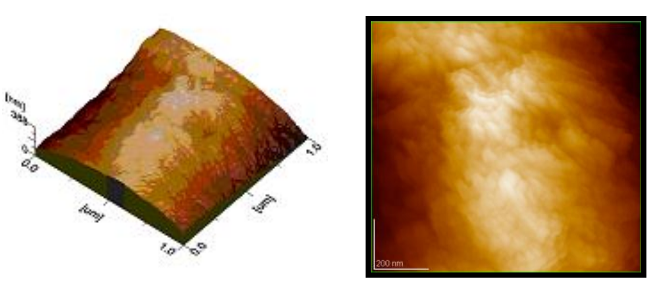
Fig. 3. Typical EDAX of $Tl_3(PW_{12}O_{40})$ thin film annealed at 250 ^oC.

Table 1. Compositional analysis of $Tl_3 (PW_{12} O_{40})$ by EDS.

Element	Theoretical Atomic %	Practical Atomic %
O	71.43	69.23
P	1.78	1.14
W	21.43	25.49
Tl	5.36	4.14



2D and 3D AFM images of $Tl_3 (PW_{12}O_{40})$ at 250 ^oC



3D and 2D AFM images of $Tl_3(PW_{12}O_{40})$ at 100 ^oC.

Fig. 4. AFM images for $Tl_3 (PW_{12}O_{40})$.

AFM study

The AFM images were recorded in order to study the effect of annealing temperature on surface morphologies of $Tl_3(PW_{12}O_{40})$ thin films deposited by optimizing various parameters. **Fig.4** shows 2D and 3D AFM images of $Tl_3(PW_{12}O_{40})$ thin films annealed at 100 ^oC and 250 ^oC . The AFM images are in well agreement with the SEM images recorded. All the results obtained from AFM data are consistent with SEM results. AFM studies on the films annealed at different temperatures reveals that the surface roughness increases with the increase in annealing temperature, suggesting an increase in crystallite size with temperature.

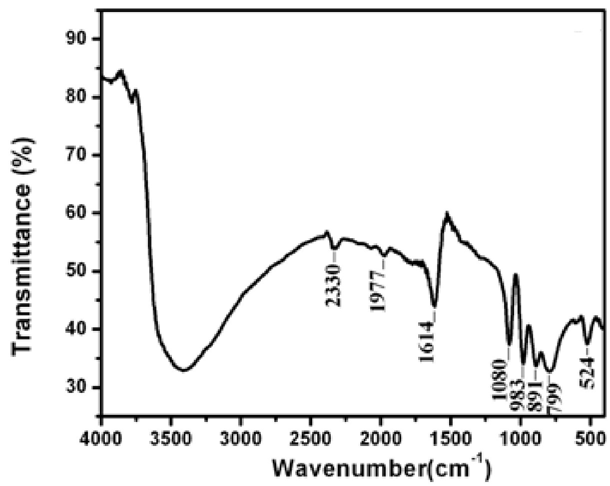


Fig. 5. FTIR Spectra of typical $Tl_3PW_{12}O_{40}$ sample.

FTIR Study

Fourier transform infrared (FTIR) spectra of typical $Tl_3(PW_{12}O_{40})$ sample was recorded from pressed KBr pellets using a Perkin-Elmer Spectrum-2000 FT-IR Spectrometer which is shown in **Fig. 5**. In our study, the IR spectrum of the present compound exhibits the characteristic frequencies of structure in the range 2330-524 cm^{-1}. After annealing the bands arising from the HPAs change obviously either in intensity, or in position. The frequency values (cm^{-1}) and assignment of FTIR bands observed for typical $Tl_3PW_{12}O_{40}$ sample is summarized in **Table 2**. The strong band at 3303 cm^{-1} was observed in IR spectra due to the water molecules involved in hydrogen bond interactions with HPA [**12-14**].

Table 2. Frequency values (cm^{-1}) and assignment of FTIR bands observed for $Tl_3PW_{12}O_{40}$.

Assignment	Frequency values (cm^{-1})
W-O-W ν_1	799
W-O-W ν_2	891
W=O	983
P-O	1080
H-O-H	3303

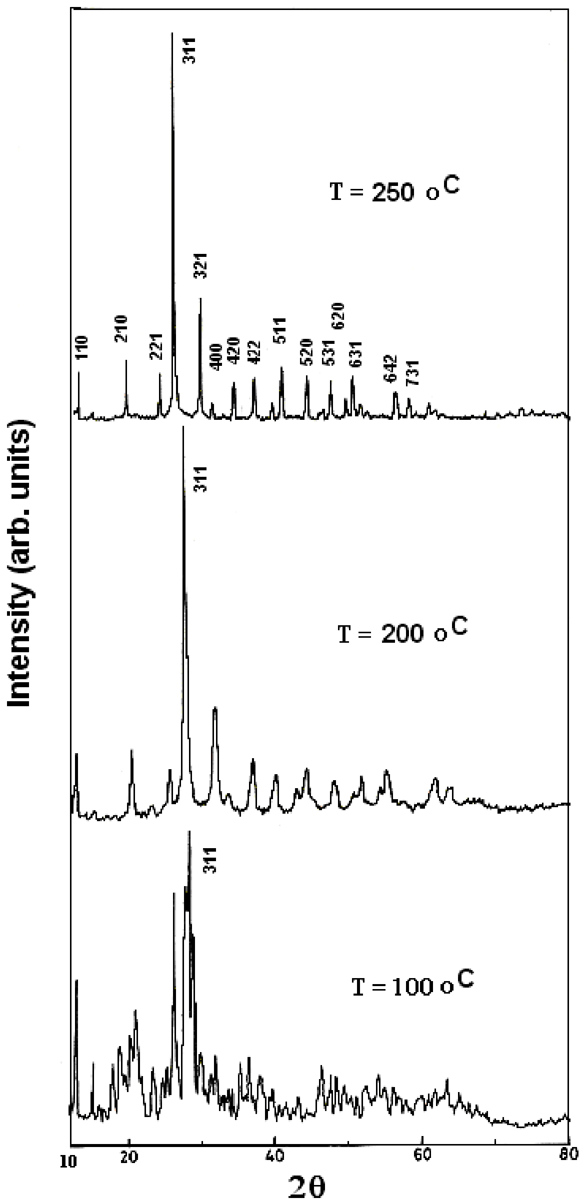


Fig. 6. X-ray diffractograms of $Tl_3(PW_{12}O_{40})$ samples annealed at 100 °C, 200 °C and 250 °C.

XRD measurements

X-ray diffractograms of Tl_3 $(PW_{12}O_{40})$ samples annealed at 100 °C, 200 °C and 250 °C are presented in **Fig. 6**. Increase in temperature shows better crystanality of tungsten HPOM material. The presence of planes (110), (210),(221), (311), (321), (400), (420), (422), (511) (520), (531) (620), (631), (642), (731) in the XRD pattern of $Tl_3(PW_{12}O_{40})$ sample annealed at 250 °C shows that the material is polycrystalline in nature with simple cubic spinel structure. The crystallite size of $Tl_3(PW_{12}O_{40})$ material was determined by considering most intense peak (311) using Debye-Scherer formula [**15-19**] which lies in the range 15.80 to 20.14 nm. The calculated and observed values of interplaner distances are in good agreement [**8**]. The values of lattice constant (a) vary from 11.17 to 11.29 A^0. From X-ray diffractograms and **Table 3** it is clear that, the lattice constant, crystallite size of tungsten HPOM material increases with increase in temperature.

Table 3. Effect of annealing temperature on crystallite size, lattice constant and average crystallite size of $Tl_3(PW_{12}O_{40})$ material.

Temp. (°C)	Crystallite size 'D' from XRD (nm)	Lattice constant 'a' (A0)	Average crystallite size from SEM (nm)
100	15.80	11.17	485
150	15.92	11.20	687
200	19.13	11.24	856
250	20.14	11.29	942

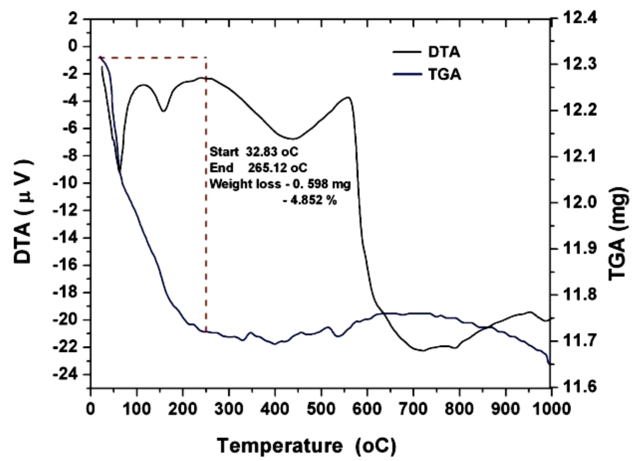


Fig. 7. TGA-DTA curves for as deposited $Tl_3(PW_{12}O_{40})$ thin films.

TGA-DTA measurements

Thermal stability of the film was determined by TGA-DTA measurements. TGA- DTA measurements were carried out in nitrogen atmosphere on TG-DTA-DSC-SDT- 2960 TA. Inc.-USA makes thermogravimetric analyzer with heating rate of 10 °C / min.

Fig. 7 shows the TGA and DTA curves for as deposited $Tl_3(PW_{12}O_{40})$ thin films. The endothermic peaks were observed at 62.12, 157.87, 433.64, 713.45 °C and exothermic peaks were observed at 110.86, 240.12, 556.10, 952.45 °C on the DTA curve, only one weight loss region could be observed at 265.12 °C for $Tl_3(PW_{12}O_{40})$ material. The acid forms of HPAs are usually obtained with large amounts of water of crystallization, and most of these water molecules are released below 100 °C. Decomposition, which takes place at 350-600 °C is believed to occur according to

$$H_3PW_{12}O_{40} \rightarrow (1/2)\ P_2O_5 + 12WO_3 + (3/2)\ H_2O \qquad (6)$$

Hodnett and Moffat assumed that this decomposition proceeded via $PW_{12}O_{38}$ in the case of $H_3PW_{12}O_{40}$. The thermal stability also depends on the environment. In a reducing atmosphere heteropolycompounds decompose more rapidly. The coexistence of oxygen and water vapor enhances the stability at high temperatures and sometimes causes the reformation of the heteropolystructure from a decomposed mixture. TGA-DTA curves show that, $Tl_3PW_{12}O_{40}$ material is thermally stable up to temperature 265.12 ^oC [**17-20**].

Conclusion

Thin films of $Tl_3PW_{12}O_{40}$ were prepared by using simple chemical bath deposition technique. X-ray diffraction study confirms well formation of HPOM material with simple cubic spinal structure and nanocrystalline nature. Increase in temperature shows better crystanality of tungsten HPOM material. Average crystallite size by SEM, crystallite size and lattice constant of the material increases with increase in temperature. It is found that these structural parameters are found to be temperature dependent. Hence after annealing $Tl_3PW_{12}O_{40}$ material we get good stoichiometric and pure tungsten heteropolyoxometalate material which can be used for device applications.

Reference

1. Sun, Y.H.; Xu, J.Q. ; Ling, Y.; Cui, X.B. ; Yong, L. *J. Mol. Str*. **2005**, 740, 193-201
   DOI: 10.1016/j.molstruc.2005.01.028
2. Lisnard, L. ; Dolbecq, A.; Mialane, P. ; Marrot, J.; and Secheresse F. *Inorganica Chimica Acta* **2004,** 357, 845-852.
   DOI: 10.1016/j.ica.2003.09.007
3. Marosi, L.; Cifre, J. ; and Otero, C. *J. Powder Diffraction* **2003,** 18, 236.
   DOI: 10.1154/1.1575762
4. Yamse. T. *Chem. Rev*. **1998** 98 307.
5. Feng,W. ; Zhang, T. ; Liu,Y.; Lu, R. ; Guan, C. ; Zhao, Y. and Yao J. *Mater. Chem. Phy*. **2003 ,**77, 294-298.
   DOI: 10.1016/S0254-0584(01)00604-6
6. Keita, B.; Nadjo, L. *J. Mat. Chem. Phy*. **1989,** 22, 77.
   DOI: 10.1016/0013-4686(94)00294-B
7. Feng, W.; Zang,T. ; Liu,Y. ; Lu, R. ; Zhao, Y. ; Li, T. and Yao, J. *J. Solid State Chem.* **2002,** 169,1.
   DOI: 10.1016/S0022-4596(02)00009-9
8. Mioc, U.; Todorovic, M.; Davidovic, M.; Colomban, P. and Holclajtner, I. *J. Solid State Ionics* **2005,** 176, 3005.
   DOI: 10.1016/j.ssi.2005.09.056
9. Fujibayashi, S.; Nakayama, K. ; Hamamoto, M. ; Sakaguchi,S. ; Nishiyama, Y. and Ishii, Y.*J. Mol.Cat.- A: - Chemical* **1996,** 110,105.
   DOI: 10.1016/1381-1169(96)00060-X
10. M. Pope, A. Muller *(Eds.) Polyoxometalates: - Kluwer Academic, Dordrecht.* **1994**.
11. M. Pope, *Heteropoly and Isopolyoxometalates, Springer, Berlin* **1983**
12. Thanganathan, U. and Nogami, M. *J. Chem. Mater*. **2007,**19,3604.
    DOI: 10.1021/cm070567f
13. Ranga, R. G. and Rajkumar, T. *Catal. Lett*. **2008,** 120, 261.
    DOI: 10.1007/s10562-007-9279-2
14. Ranga, R. G. and Rajkumar, T. *J. Colloid Interface Sci*. **2008,** 324,134.
    DOI: 10.1016/j.molcata.2008.08.008
15. Klug, H.; Alexander, L. ; *X-ray diffraction procedure For Polycrystalline and Amorphous Materials, 2nd Edition. Wiley-Interscience, New York*, **1974,** 656.
16. Cullity, B. D. *Ele. of X-ray Diff., Addison-Wesley Publishing Company*, **1956,** 471.
17. Hayashi, H. and Moffat. J. *Catl*. **1982,** 77, 473.
    DOI: 10.1016/0021-9517(83)90146-X
18. Hayashi, H. and Moffat, J. *J Catl*. **1983,** 83,192.
    DOI: 10.1006/jcat.1998.2389
19. Hodnett, B.K. and Moffat, J.B. *J Catl*. **1984,** 88, 253.
    DOI: 10.1016/0021-9517(84)90001-0
20. Uda, T.; Haile, S.M. *Electrochem. Solid State Lett*., **2005** 8A 245.
    DOI: 10.1134/S1023193511050090