# APPENDIX

## Phases and structures of components in thesis

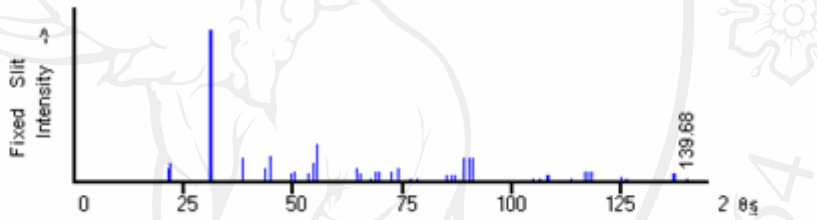
1. Lead zirconate titanate (PZT), tetragonal structure (JCPDS)

33-0784 Quality:
CAS Number:
Molecular Weight: 325.62
Volume[CD]: 67.54
Dx: 8.006 Dm:
Sys: Tetragonal

S.G.:
Cell Parameters:
a 4.036 b c 4.146
α β γ

SS/FOM: F30=15(0.060, 34)
I/Icor:
Rad: CuKa
Lambda: 1.5418
Filter: Ni
d-sp: diffractometer

Pb ( Zr0.52 Ti0.48 ) O3
Lead Zirconium Titanium Oxide
Ref: Kakegawa, K. et al., Solid State Commun., 24, 769 (1977)

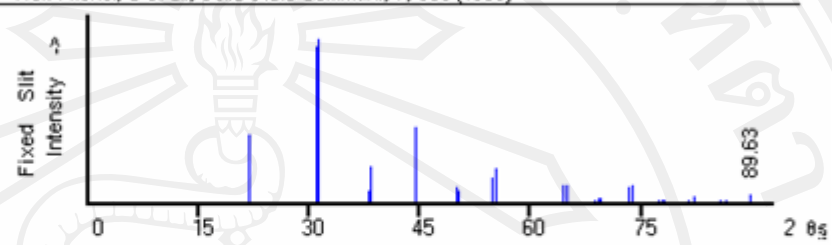



| 2θ | Int-f | h | k | l | 2θ | Int-f | h | k | l | 2θ | Int-f | h | k |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21.432 | 9 | 0 | 0 | 1 | 69.645 | 6 | 3 | 0 | 0 | 106.18 | 2 | 3 | 0 |
| 22.023 | 12 | 1 | 0 | 0 | 72.225 | 6 | 1 | 0 | 3 | 107.98 | 4 u | 4 | 1 |
| 30.942 | 100 u | 1 | 0 | 1 | 74.065 | 9 | 3 | 0 | 1 | 108.31 | u | 3 | 3 |
| 31.387 | u | 1 | 1 | 0 | 74.065 | 9 | 3 | 1 | 0 | 110.59 | 1 | 1 | 3 |
| 38.283 | 15 | 1 | 1 | 1 | 76.588 | 2 | 1 | 1 | 3 | 112.47 | <1 | 3 | 3 |
| 43.663 | 9 | 0 | 0 | 2 | 78.379 | 2 | 3 | 1 | 1 | 113.44 | 2 | 2 | 0 |
| 44.917 | 16 | 2 | 0 | 0 | 85.099 | 4 u | 2 | 0 | 3 | 116.41 | 6 u | 4 | 0 |
| 49.424 | 5 | 1 | 0 | 2 | 86.034 | u | 3 | 0 | 2 | 117.23 | u | 4 | 2 |
| 50.417 | 6 | 2 | 0 | 1 | 86.992 | u | 3 | 2 | 0 | 118.07 | u | 1 | 2 |
| 50.417 | 6 | 2 | 1 | 0 | 88.985 | 15 u | 1 | 2 | 3 | 121.16 | 1 u | 4 | 1 |
| 53.390 | 5 | | | | 90.023 | u | 3 | 1 | 2 | 121.86 | u | 4 | 2 |
| 54.734 | 12 | 1 | 1 | 2 | 91.089 | u | 3 | 2 | 1 | 124.79 | 3 | 2 | 3 |
| 55.524 | 24 | 2 | 1 | 1 | 96.092 | <1 | 0 | 0 | 4 | 126.13 | 2 | 3 | 3 |
| 64.434 | 9 | 0 | 2 | 2 | 99.627 | <1 | 4 | 0 | 0 | 133.60 | 1 | 2 | 2 |
| 65.398 | 5 | 2 | 2 | 0 | 100.31 | <1 | 1 | 0 | 4 | 136.84 | 5 u | 0 | 0 |
| 67.810 | 2 | 0 | 0 | 3 | 101.88 | <1 | 2 | 2 | 3 | 137.19 | u | 4 | 2 |
| 69.002 | 6 u | 2 | 1 | 2 | 102.99 | 1 | 3 | 2 | 2 | 139.68 | 2 | 3 | 0 |
| 69.645 | u | 2 | 2 | 1 | 104.60 | 2 | 1 | 1 | 4 | | | | |

2. Lead zirconate titanate (PZT), rhombohedral structure (JCPDS)

73-2022 Quality: C
CAS Number:
Molecular Weight: 328.22
Volume[CD]: 67.42
Dx: 8.085 Dm:
Sys: Rhombohedral
Lattice: Rhomb-centered
S.G.: R3m (160)
Cell Parameters:
a 4.070 b c
α 89.650 β γ
I/Icor: 9.39
Rad: CuKa1
Lambda: 1.54060
Filter:
d-sp: calculated
ICSD # : 024562

Pb Zr.58 Ti.42 O3
Lead Zirconium Titanium Oxide
Ref: Calculated from ICSD using POWD-12++, (1997)
Ref: Michel, C et al., Solid State Commun., 7, 865 (1969)

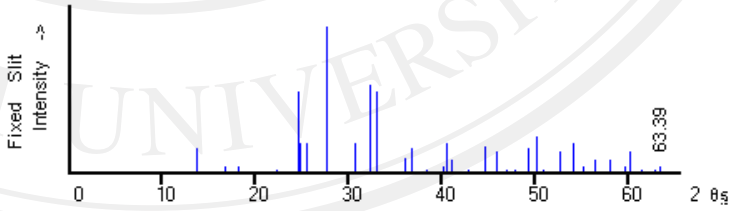



| 2θ | Int-f | h | k | l | 2θ | Int-f | h | k | l | 2θ | Int-f |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21.820 | 419 | 0 | 1 | 0 | 55.302 | 168 | $\bar{1}$ | 2 | 1 | 77.410 | 15 |
| 30.954 | 948 | $\bar{1}$ | 1 | 0 | 55.423 | 213 | $\bar{2}$ | 1 | 1 | 77.818 | 16 |
| 31.148 | 999 | $\bar{1}$ | 1 | 0 | 64.513 | 110 | $\bar{2}$ | 2 | 0 | 78.022 | 21 |
| 38.032 | 75 | $\bar{1}$ | 1 | 1 | 64.954 | 113 | $\bar{2}$ | 2 | 0 | 81.334 | 14 |
| 38.354 | 216 | $\bar{1}$ | 1 | 1 | 68.768 | 16 | $\bar{2}$ | 2 | 1 | 82.140 | 45 |
| 44.487 | 459 | 0 | 2 | 0 | 69.195 | 29 | $\bar{2}$ | $\bar{2}$ | 1 | 85.767 | 19 |
| 49.946 | 91 | $\bar{1}$ | 2 | 0 | 69.408 | 29 | $\bar{2}$ | 2 | 1 | 86.367 | 13 |
| 50.206 | 77 | $\bar{1}$ | 2 | 0 | 73.373 | 99 | $\bar{1}$ | 3 | 0 | 89.626 | 51 |
| 54.937 | 158 | 1 | 2 | 1 | 73.685 | 112 | $\bar{1}$ | 3 | 0 | | |

3. Lead tungsten oxide ($PbWO_4$), monoclinic structure (JCPDS)

16-0156 Quality: I
CAS Number:
Molecular Weight: 455.05
Volume[CD]: 355.01
Dx: 8.514 Dm: 8.465
Sys: Monoclinic
Lattice: Primitive
S.G.: P2$_1$/a (14)
Cell Parameters:
a 13.52 b 4.968 c 5.546
α β 107.7 γ
SS/FOM: F30=5(0.062, 94)
I/Icor:
Rad: CuKa
Lambda: 1.5418
Filter: Ni
d-sp:
Mineral Name:
Raspite

Pb W O4
Lead Tungsten Oxide
Ref: Sharp, University of California, Los Angeles, California, USA, Private Communication

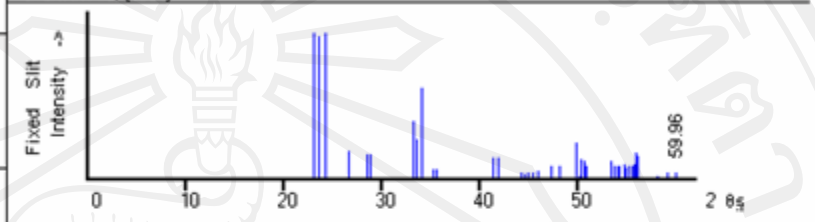



| 2θ | Int-f | h | k | l | 2θ | Int-f | h | k | l | 2θ | Int-f | h | k | l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13.772 | 16 | 2 | 0 | 0 | 32.438 | 60 | $\bar{2}$ | 0 | 2 | 44.637 | 18 | 2 | 1 | 2 |
| 16.823 | 4 | 0 | 0 | 1 | 33.117 | 55 | 4 | 1 | 0 | 46.049 | 14 | 6 | 1 | 0 |
| 18.216 | 4 | $\bar{2}$ | 0 | 1 | 36.160 | 10 | 0 | 2 | 0 | 47.111 | 2 | 5 | 1 | 1 |
| 22.229 | 2 | $\bar{2}$ | 1 | 0 | 36.773 | 16 | 4 | 0 | 1 | 47.955 | 2 | 3 | 2 | 1 |
| 24.598 | 55 | 0 | 1 | 1 | 38.436 | 2 | $\bar{5}$ | 1 | 1 | 49.310 | 16 | $\bar{2}$ | 0 | 3 |
| 24.779 | 20 | $\bar{2}$ | 0 | 1 | 40.167 | 4 | 0 | 2 | 1 | 50.357 | 25 | $\bar{5}$ | 2 | 1 |
| 25.612 | 20 | $\bar{2}$ | 1 | 1 | 40.581 | 20 | 2 | 0 | 2 | 50.929 | 2 | 4 | 0 | 2 |
| 27.668 | 100 | 4 | 0 | 0 | 41.142 | 8 | $\bar{1}$ | 1 | 2 | 52.727 | 14 | $\bar{4}$ | 2 | 2 |
| 30.724 | 20 | 2 | 1 | 1 | 42.902 | 2 | $\bar{3}$ | 2 | 1 | 54.140 | 20 | 8 | 0 | 1 |

4. Tungsten oxide ($WO_3$), monoclinic structure (JCPDS)

43-1035 Quality: C
CAS Number: 1314-35-8
Molecular Weight: 231.85
Volume[CD]: 422.88
Dx: 7.283 Dm:
Sys: Monoclinic
Lattice: Primitive
S.G.: P2$_1$/n (14)
Cell Parameters:
a 7.297 b 7.539 c 7.688
α β 90.91 γ
SS/FOM: F30=114(.0059, 45)
I/Icor: 5.04
Rad: CuKa1
Lambda: 1.54056
Filter:
d-sp: calculated

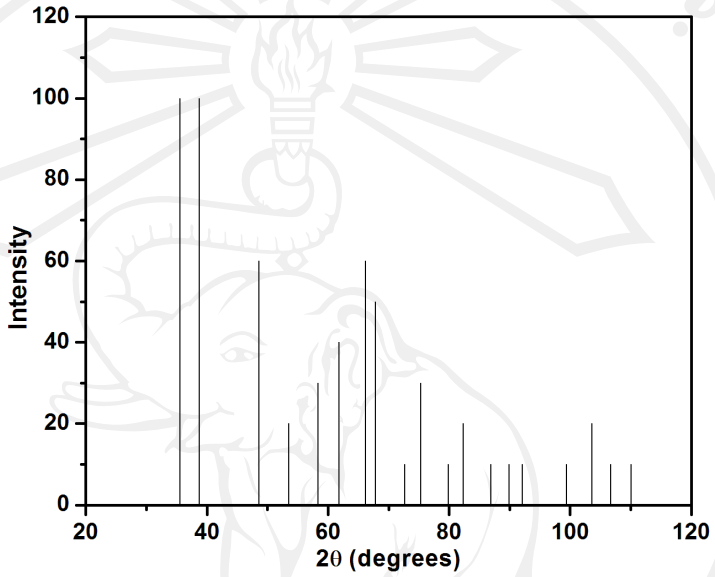
W O3
Tungsten Oxide
Ref: Grier, D., McCarthy, G., North Dakota State University, Fargo, North Dakota, USA, ICDD Grant-in-Aid, (1991)



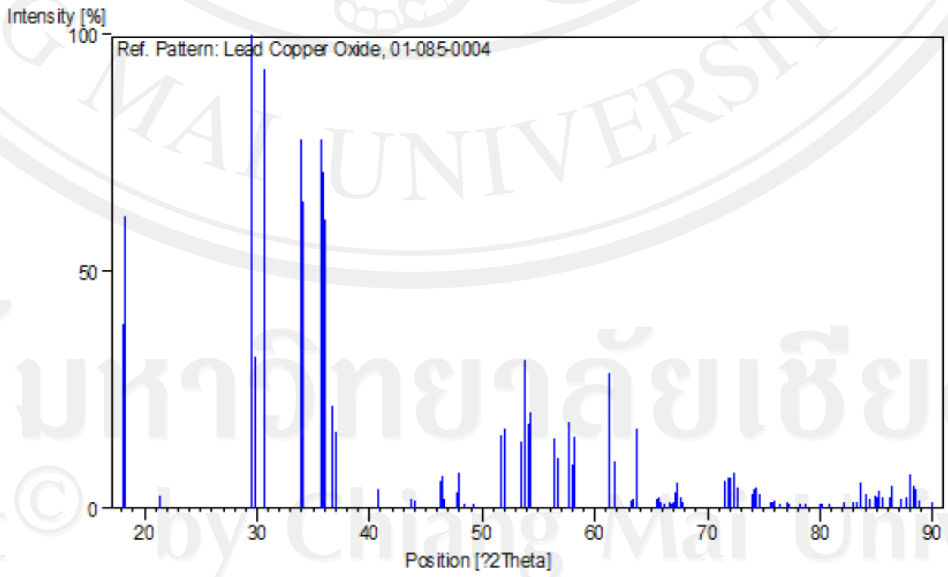

| 2θ | Int-f | h | k | l | 2θ | Int-f | h | k | l | 2θ | Int-f | h | k | l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16.896 | <1 | 1 | 1 | 0 | 37.344 | <1 | 1 | 0 | 3 | 48.867 | 1 | 0 | 1 | 4 |
| 20.595 | <1 | 1 | 1 | 1 | 38.627 | <1 | 3 | 0 | 1 | 49.413 | <1 | 2 | 2 | 3 |
| 23.119 | 100 | 0 | 0 | 2 | 38.887 | <1 | 3 | 1 | 0 | 49.771 | <1 | 0 | 4 | 1 |
| 23.586 | 97 | 0 | 2 | 0 | 38.887 | <1 | 1 | 1 | 3 | 49.814 | <1 | 2 | 3 | 2 |
| 24.380 | 99 | 2 | 0 | 0 | 38.992 | <1 | 3 | 0 | 1 | 49.948 | 24 | 1 | 4 | 0 |
| 26.002 | 1 | 0 | 1 | 2 | 39.276 | <1 | 1 | 1 | 3 | 49.948 | 24 | 4 | 0 | 0 |
| 26.314 | <1 | 0 | 2 | 1 | 39.727 | 1 | 1 | 3 | 1 | 50.216 | <1 | 2 | 3 | 2 |
| 26.595 | 19 | 1 | 2 | 0 | 40.490 | <1 | 3 | 1 | 1 | 50.240 | 2 | 3 | 2 | 2 |
| 28.615 | 16 | 1 | 1 | 2 | 40.854 | 1 | 3 | 1 | 1 | 50.341 | 13 | 1 | 1 | 4 |
| 28.937 | 17 | 1 | 1 | 2 | 41.443 | 14 | 2 | 2 | 2 | 50.742 | 12 | 1 | 1 | 4 |
| 29.140 | <1 | 1 | 2 | 1 | 41.906 | 14 | 2 | 2 | 2 | 50.839 | 9 | 3 | 2 | 2 |
| 33.266 | 39 | 0 | 2 | 2 | 42.632 | <1 | 0 | 2 | 3 | 51.373 | 1 | 1 | 4 | 1 |
| 33.575 | 27 | 2 | 0 | 2 | 42.972 | 1 | 0 | 3 | 2 | 51.473 | 1 | 1 | 4 | 1 |
| 34.155 | 62 | 2 | 0 | 2 | 44.277 | 4 | 3 | 2 | 0 | 52.331 | <1 | 1 | 3 | 3 |
| 34.155 | 62 | 2 | 2 | 0 | 44.669 | 3 | 1 | 2 | 3 | 52.767 | <1 | 4 | 1 | 1 |
| 35.393 | 6 | 1 | 2 | 2 | 44.669 | 3 | 1 | 3 | 2 | 53.153 | <1 | 4 | 1 | 1 |
| 35.670 | 6 | 1 | 2 | 2 | 44.926 | 4 | 1 | 3 | 2 | 53.485 | 12 | 0 | 2 | 4 |
| 35.670 | 6 | 2 | 1 | 2 | 45.396 | 4 | 3 | 1 | 2 | 53.485 | 12 | 2 | 0 | 4 |
| 36.040 | 1 | 2 | 2 | 1 | 45.749 | 1 | 3 | 2 | 1 | 53.722 | 8 | 3 | 1 | 3 |
| 36.206 | 1 | 2 | 1 | 2 | 46.042 | 5 | 3 | 1 | 2 | 54.155 | 9 | 0 | 4 | 2 |
| 36.296 | 1 | 2 | 2 | 1 | 47.258 | 9 | 0 | 0 | 4 | 54.259 | 8 | 2 | 0 | 4 |
| 36.962 | <1 | 1 | 0 | 3 | 48.247 | 9 | 0 | 4 | 0 | 54.775 | 10 | 2 | 4 | 0 |

5. Copper oxide (CuO), monoclinic structure (JCPDS)

   File no. 02-1040




6. Lead copper oxide ($Pb(Cu_2O_2)$), monoclinic structure (ICSD)



**Thermal expansion**

| Materials | Thermal expansion ($\times 10^{-6}$ $K^{-1}$) | Ref |
|---|---|---|
| **PZT** | $\alpha$ll = -4 to -6 (parallel to polarization )<br>$\alpha\perp$ = 4 to 8 (perpendicular to polarization ) | **1A** |
| **$WO_3$** | $\alpha_a$ = 23.3<br>$\alpha_c$ = 7.1 | **2A** |
| **CuO** | $\alpha$ = 4.3 | **3A** |

**References**


[1A] CTS Electronic components

[2A] W.L. Kehl, R.G. Hay and D. Wahl, The structure of tetragonal tungsten trioxide, *J. Appl. Phys*., **23** (1952) 212-215.

[3A] T.D. Dzhafarov, M. Altunbas and O. Gorur, The high-temperature thermal expansion of BiPbSrCaCuO superconductor and the oxide components ($Bi_2O_3$, PbO, CaO, CuO), *J. Mater. Sci*., **31**[8] (1996) 2207-2212.

**Sol-gel chemistry**

The sol-gel reaction consists of hydrolysis and condensation reactions.

**Hydrolysis:**

$$M(OR)_x + H_2O \rightarrow HO - M(OR)_{x-1} + ROH \quad \textbf{(1)}$$

$$M(OR)_x + xH_2O \rightarrow M(OH)_x + xROH \quad \textbf{(2)}$$

**Condensation (alcohol elimination):**

$$(RO)_{x-1}M - OH + RO - M(OR)_{x-1} \rightarrow (RO)_{x-1}M - O - M(OR)_{x-1} + ROH \quad \textbf{(3)}$$

**Condensation (water elimination):**

$$(RO)_{x-1}M - OH + HO - M(OR)_{x-1} \rightarrow (RO)_{x-1}M - O - M(OR)_{x-1} + H_2O \quad \textbf{(4)}$$

*Note: R is an alkyl group ($-C_nH_{2n+1}$)

Thus, the sol-gel reaction for **$Ti(OCH(CH_3)_2)_4$** could be

$$Ti(OCH(CH_3)_2)_4 + H_2O \rightarrow HO - Ti(OCH(CH_3)_2)_3 + OCH(CH_3)_2OH \quad \textbf{(Hydrolysis)}$$

$(OCH(CH_3)_2)_3Ti - OH + HO - Ti(OCH(CH_3)_2)_3 \rightarrow (OCH(CH_3)_2)_3Ti - O Ti(OCH(CH_3)_2)_3 + H_2O$ **(Condensation)**

The sol-gel reaction for **$Zr(OCH_2CH_2CH_3)_4$** could be

$Zr(OCH_2CH_2CH_3)_4 + H_2O \rightarrow HO - Zr(OCH_2CH_2CH_3)_3 + OCH_2CH_2CH_3OH$ **(Hydrolysis)**

$(OCH_2CH_2CH_3)_3Zr - OH + HO - Zr(OCH_2CH_2CH_3)_3 \rightarrow (OCH_2CH_2CH_3)_3Zr - O Zr(OCH_2CH_2CH_3)_3 + H_2O$ **(Condensation)**

However, the characterization of the sol structure by NMR spectroscopy by Nimit Sriprang and his colleagues suggested that the gels consisted of the metal ions and bonded THOME, acetylacetonate and acetate residues with several possible complex M – O – M bridges as shown below.

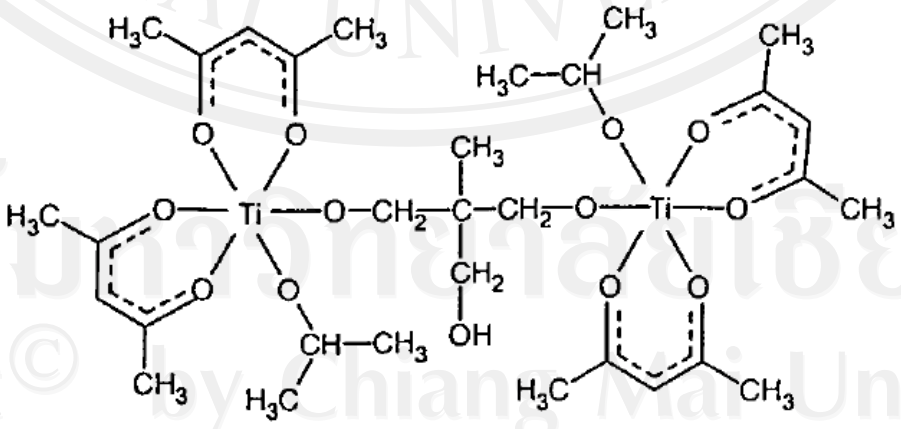



**Figure 1A** Dimer structure illustrates basic structural principles of titanium sol-gel [4A].

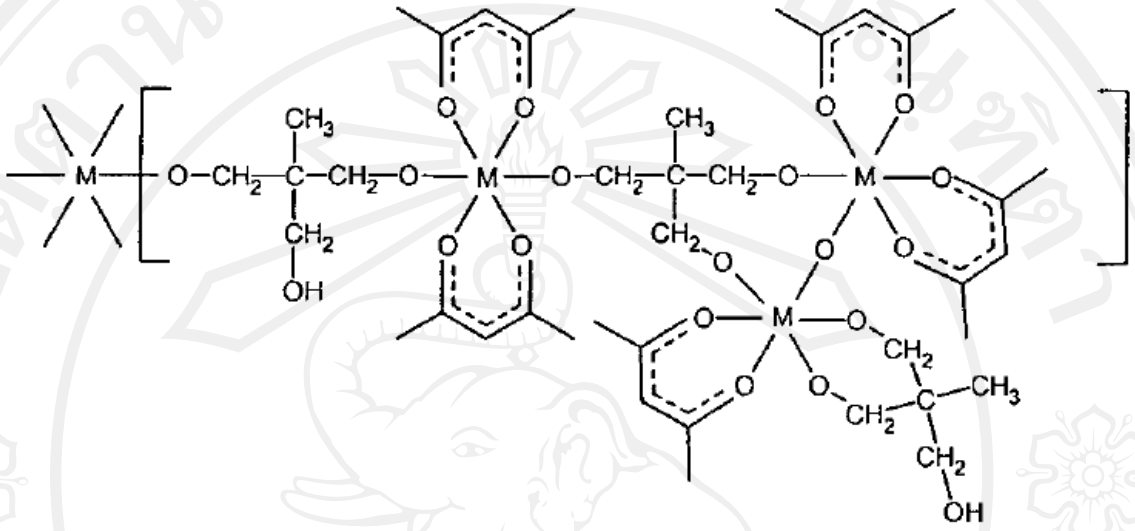


**Figure 2A** Dimer structure illustrates the basic structural principles of zirconium sol-gel [4A].

**References**

[4A] N. Sriprang, D. Kaewchinda, J.D. Kennedy and S.J. Mine, Processing and sol chemistry of a triol-based sol-gel route for preparing lead zirconate titanate thin films, *J. Am. Ceram. Soc*., **83**[8] (2000) 1914-1920.

# VITA

| | |
|---|---|
| **Name** | Miss Tharathip Sreesattabud |
| **Date of Birth** | 25 February, 1984 |
| **Education** | B.Sc. (Materials Science), Chiang Mai University, Chiang Mai (2002 - 2005)<br>M.Sc. (Materials Science), Chiang Mai University, Chiang Mai (2006 - 2007)<br>Ph.D. (Materials Science), Chiang Mai University, Chiang Mai (2008 - 2013) |
| **Scholarship** | Sandwich Program (CHE-PhD-SW), Ph.D. Scholarship from the Office of the Higher Education Commission, Thailand (2008-2011) |

**International Publications:**

**(1)** **T. Sreesattabud**, B.J. Gibbons, A. Watcharapasorn and S. Jiansirisoomboon, Synthesis and characterization of PZT thin films embedded with $WO_3$ nanoparticles by a hybrid chemical solution route, *Integrated Ferroelectric*, **139** (2012) 40-47.

**(2)** **T. Sreesattabud**, B.J. Gibbons, A. Watcharapasorn and S. Jiansirisoomboon, Effect of donor and acceptor dopants on fatigue properties in PZT thin films, *Ceramics International*, **39** (2013) 521-524.

**(3)** **T. Sreesattabud**, B.J. Gibbons, A. Watcharapasorn and S. Jiansirisoomboon, Phase and electrical properties of PZT thin films embedded with CuO nano-particles by a hybrid sol-gel route, *Electronic Materials Letters*, **9** (2013) 409-412.

**International Conferences and Meetings:**

**(1)** **T. Sreesattabud**, A. Watcharapasorn, M. Naksata and S. Jiansirisoomboon, Preparation 0-3 composite structure of PZT/$WO_3$ system, 1st Chiang Mai - Kyoto Symposium on Materials Science and Technology (CK1), 2-4 December 2010, Chiang Mai, Thailand.

**(2)** **T. Sreesattabud**, A. Watcharapasorn, M. Naksata and S. Jiansirisoomboon, Effect of annealing temperature and lead content on crystallization and dielectric property of triol sol-gel derived PZT thin films, Nano Thailand 2010, 18-20 November 2010, Pathumthani, Thailand.

**(3)** **T. Sreesattabud**, A. Watcharapasorn, and S. Jiansirisoomboon, Effect of lead content on crystallization and electrical properties of triol sol-gel derived PZT thin films, The 6$^{th}$ Pure and Applied Chemistry International Conference 2012 (PACCON 2012), 11-14 January 2012, Chiang Mai, Thailand.

**(4)** **T. Sreesattabud**, B.J. Gibbons, A. Watcharapasorn, M. Naksata and S. Jiansirisoomboon, Fabrication and Characterization of PZT/CuO Thin Film, Special International Workshop and Symposium on Emerging Frontiers in Multiferroics and Electronic Metamaterials (INAMM), 9-10 December 2012, Pattaya, Thailand.