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DAFTAR ISI HAL

LATTICE CONSTANTS ANALYSIS OF NIOBIUM AND GALLIUM DOPED LEAD ZIRCONIUM TITANATE CERAMIC BY VISUAL BASIC PROGRAM

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Abstract

Ceramic of $PbZr_xTi_{1-x}O_3$ (PZT), 1 % mass of niobium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PNZT) and 1 % mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT) were successfully deposited by solid solution method. The PZT, PNZT and PGZT ceramic were analyzed by x-ray diffraction (XRD). The XRD spectra was recorded on a Philips type PW 3701 diffractometer using CoK_α (λ_{co} = 1.7889 Å) radiation at 30 KV and 30 mA (900 watt). The spectra shows that PZT and PGZT ceramic are polycrystalline with tetragonal structure. The lattice constants analysis of the grown ceramics was analyzed by visual basic program. Using Cohen's and Cramer's algorithms in visual basic program, the lattice constants are a = b = 4.195 Å, and c = 4.306 Å; c a ratio = 1.026 for $PbZr_{0.525}Ti_{0.475}O_3$ ceramic; a = b = 4.187 Å, and c = 4.302 Å, c/a ratio = 1.027 for 1 % mass of niobium doped $PbZr_{0.525}Ti_{0.475}O_3$ ceramic; a = b = 4.185 Å, and c = 4.296 Å, c/a ratio = 1.027 for 1 % mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ ceramic, respectively. The reform value of the lattice constant of PNZT and PGZT ceramic is possibly associated with the anti site defects of Nb and Ga dopants.

Keywords : PZT, PNZT, PGZT, XRD, lattice constants, Cramer's method, Visual Basic Program.

1. Introduction

A pyroelectric infrared (IR) detector has advantages of wavelight independent sensitivity and can be operated at room temperature. It is also expected to provide various thermal observations for objects at near ambient temperature. Ceramic and thin film of $PbTiO_3$, $PbZr_xTi_{1-x}O_3$ have been used as pyroelectric IR detectors [1]. The merit of pyrosensor compared to other infrared sensor materials such as semiconductors as a wide range of response frequency; can be used at room temperature; shows quick

response in comparison with other temperature sensors and high quality materials for the pyrosensor is unnecessary [2].

$PbZr_xTi_{1-x}O_3$ ceramic can be grown by solid solution method [3 – 13]. The solid solution method is of particular interest because of its good control of stoichiometry, ease of fabrication and low temperature synthesis. It was reported that solid solution method derived is thermodynamically stable.

In this paper we report the fabrication of the $PbZr_{0.525}Ti_{0.475}O_3$ (PZT) ceramic, 1 % mass of niobium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PNZT) ceramic and 1 % mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT) ceramic by solid solution method. The PZT, PNZT and PGZT ceramics was examined by X-Ray diffraction. The lattice constant was analyzed by visual basic program, and the lattice constants obtained by using Cohen's and Cramer's algorithm are described.

2. Theory

The lattice constants analysis of the grown ceramics was analyzed by visual program using Cohen's and Cramer's algorithm. Cohen's method of determining lattice parameter is even more valuable when applied to tetragonal structure. The method provides a direct means of determining these parameters, although the equation are naturally more complex than those needed for cubic structure. Tetragonal phase takes on the relatively as Equation (1), (2), (3) : [14,15]

$$\lambda = 2d \sin\theta, \qquad (1)$$

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}, \qquad (2)$$

$$\begin{aligned} \sum \alpha \sin^2\theta &= C\sum\alpha^2 + B\sum\alpha\gamma + A\sum\alpha\delta, \\ \sum \gamma \sin^2\theta &= C\sum\alpha\gamma + B\sum\gamma^2 + A\sum\gamma\delta, \\ \sum \delta \sin^2\theta &= C\sum\alpha\delta + B\sum\gamma\delta + A\sum\delta^2. \end{aligned} \qquad (3)$$

where : d = interplanar spacing; a, c = the lattice constants; h, k, l = the planes indices; λ = wave length (λ_{Co} = 1.7889 Å); θ = the diffraction angle; $\alpha = h^2 + k^2$, $\gamma = l^2$; $\delta = 10 \sin^2 2\theta$; A, B, C = numerator, and D is a constant.

The solutions of the numerator A, B, and C from Equation (3) use Cramer's algorithm [16,17]. For the case of three equations with three unknowns numerator A, B, and C, Equation (3) become:

$$\left.\begin{aligned} a_1C + a_2B + a_3A &= a_4 \\ b_1C + b_2B + b_3A &= b_4 \\ c_1C + c_2B + c_3A &= c_4 \end{aligned}\right\}. \qquad (4)$$

where : $a_1 = \Sigma\alpha^2$; $a_2 = b_1 = \Sigma\alpha\gamma$; $a_3 = c_1 = \Sigma\alpha\delta$; $a_4 = \Sigma\alpha\sin^2\theta$; $b_2 = \Sigma\gamma^2$; $b_3 = c_2 = \Sigma\gamma\delta$; $b_4 = \Sigma\gamma\sin^2\theta$; $c_3 = \Sigma\delta^2$; $c_4 = \Sigma\delta\sin^2\theta$, can be reduced to the previous case by imbedding it in three dimensional space with a solution vector **x** (A, B, C) and row vectors **a** (a_1, a_2, a_3), **b** (b_1, b_2, b_3), **c** (c_1, c_2, c_3).

3. Experimental Procedure

Ceramic of $PbZr_xTi_{1-x}O_3$ (PZT), 1 % mass of niobium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PNZT 1%) and 1 % mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT 1%) were prepared by solid solution method. The PZT ceramic was prepared by mixing 2.65 grams lead titanate [$PbTiO_3$, 99 %], 3.35 grams lead zirconate [$PbZrO_3$, 99.7 %] and 20 ml aceton in a bowl for 1 hour, meanwhile, the PNZT 1% and PGZT 1% ceramics were made by

mixing a 2.65 grams lead titanate [$PbTiO_3$, 99 %], 3.35 grams lead zirconate [$PbZrO_3$, 99.7 %], 0.06 gram niobium oxide [Nb_2O_5, 99.9 %] and gallium oxide [Ga_2O_3, 99.9 %], respectively and 20 ml aceton in a bowl for 1 hour. The mixture was then pressed at 31.83 MPa for 5 minutes to form a pellet followed by a sintering at 850°C for 10 hours in a Furnace. The PZT, PNZT and PGZT ceramic were analyzed by x-ray diffraction (XRD). The XRD spectra was recorded on Philips type PW 3701 diffractometer using CoK_α (λ_{co} = 1.7889 Å) radiation at 30 kV and 30 mA (900 watt). The lattice constants analysis of the grown ceramics are analyzed by visual basic program using Cohen's and Cramer's algorithm. The flowchart of this experimental procedure is shown in Figure 1.

4. Results and discussion

A search in the ICDD-PDF database using the software available with the diffractometer was identified : PZT (PDF No° 33-0784) [18]. The peak positions of each phase were extracted by means of single-peak-profile-fittings. The remaining 12 intense peaks corresponding to the phase of interest, PZT, were readily indexed in a tetragonal cell. Table 1 contain the observed X-ray powder diffraction data for PZT, PNZT 1 % and PGZT 1%.

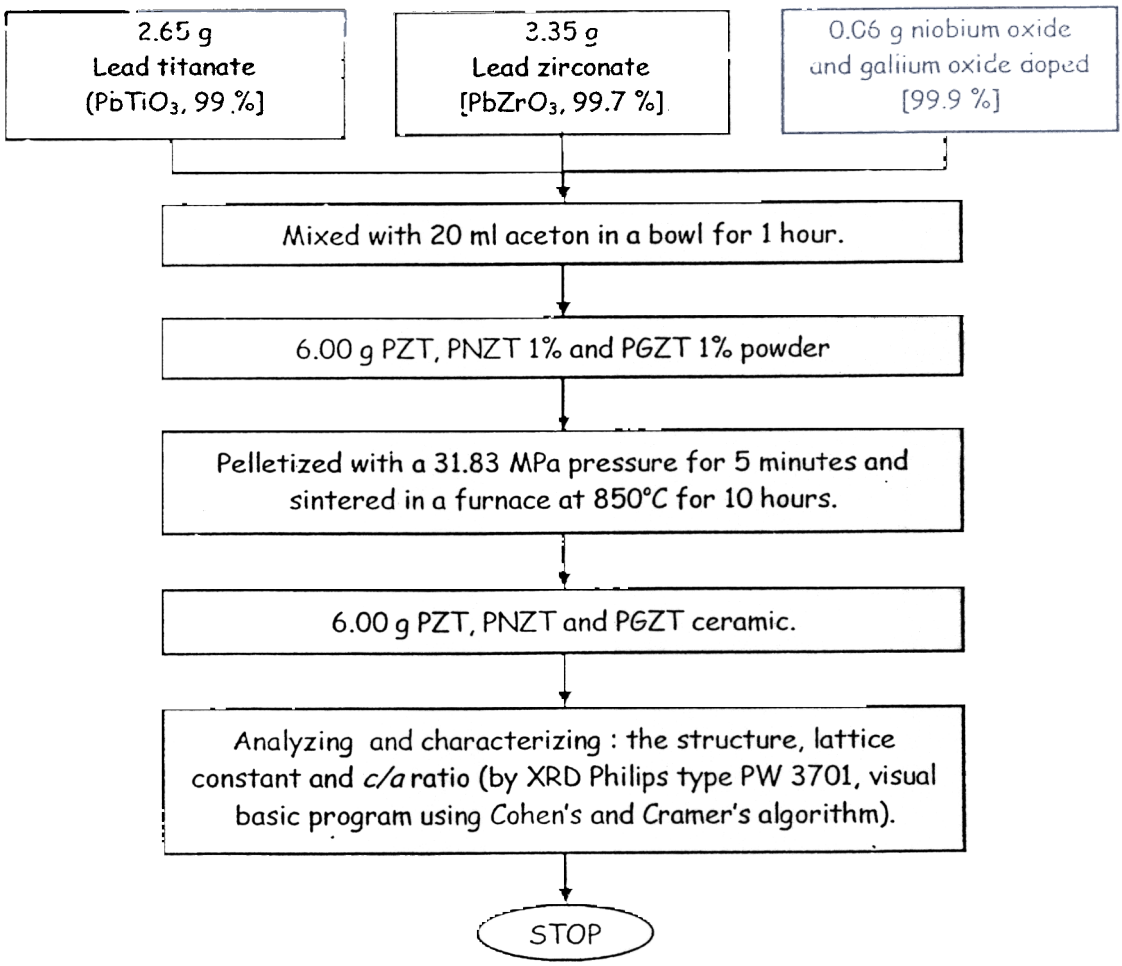

Figure Summary of sample fabrication and characterization.

Table 1. Observed X-ray powder diffraction data of PZT, PNZT 1% and PGZT 1%.

No	h k l	2θ (°)		
		PZT	PNZT (1%)	PGZT (1%)
1.	0 0 1	25.08	25.12	25.06
2.	1 0 0	26.02	26.00	26.06
3.	1 0 1	32.90	32.88	32.80
4.	1 1 0	36.38	36.36	36.30
5.	1 1 1	45.56	45.50	45.60
6.	0 0 2	50.64	50.54	50.64
7.	2 0 0	50.96	51.04	51.02
8.	1 0 2	58.20	58.28	58.28
9.	1 1 2	63.88	63.98	63.84
10.	2 1 1	64.98	65.06	64.94
11.	0 2 2	74.84	74.84	74.94
12.	2 2 0	76.76	76.86	76.82

Figure 2 shows XRD spectra of PZT, PNZT 1% and PGZT 1% ceramic tetragonal phase. The presence of intense diffraction peaks that correspond to (110) plane if compared with diffraction peaks from of (001), (100), (101), (111), (002), (200), (102), (112), (211), (022), and (220) planes implied that the PZT, PNZT and PGZT ceramic assessed a strong preferential orientation. Similar trends were observed in the XRD pattern of PZT, PNZT and PGZT deposited by solid solution method indicating preferential orientation [10,12,13].

Equation (1), (2), (3) using Cohen's algorithm in visual basic program for 1 % mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT 1%) ceramic produces numerator A, B, C as the following :

$$8.173389 = 136C + 36B + 223.771657A$$
$$4.843369 = 36C + 68B + 140.442026A$$
$$17.182691 = 223.771657C + 140.442026B + 487.642593A$$

When Equation (4) was carried out by using Cramer's algorithm in visual basic, we got the lattice constant of PGZT 1% ceramic as the following: $a = b = 4.185$ Å; $c = 4.296$ Å; c/a ratio = 1.027. The XRD spectra showed that the PZT, PNZT and PGZT ceramic were tetragonal structure. The calculated lattice constants and c/a ratio of PZT, PNZT and PGZT ceramic were given in Table 2. These values are in good agreement with those observed by other researchers [19,20]. The reform value of the lattice constant of PNZT and PGZT ceramic is possibly associated with the anti site defects of Nb and Ga dopants.

To understand this result, let us consider the crystallographic deficiencies due to impurity in a $PbZr_{0.525}Ti_{0.475}O_3$ (PZT) perovskite structure. The PZT perovskite structure can be simplified with general formula of ABO_3, where A is a monovalent or divalent metal (Pb^{2+}) and B is tetravalent or pentavelant (Ti^{4+} or Zr^{4+}), with the Pb atoms at the tetragonal corners, Ti or Zr atoms at the body centres, and the oxygen (O) atoms at the face centres. The reform value of the lattice constant of PNZT ceramic is due to the increasing dopant introduce Pb deficiencies in the $PbZr_{0.525}Ti_{0.475}O_3$ lattice as follow $Pb_{1-y/2}Zr_{0.525}Ti_{0.475-y}Nb_yO_3$. This donor doping causes the not easy reorientation of deficiency related dipoles. Whereas, the reform value of the lattice constant of PGZT ceramic is due to the increasing dopant introduce oxygen deficiencies in the $PbZr_{0.525}Ti_{0.475}O_3$

lattice as follow $PbZr_{0.525}Ti_{0.475-y}Ga_yO_{3-y/2}$. This acceptor doping causes the easy reorientation of deficiency related dipoles.

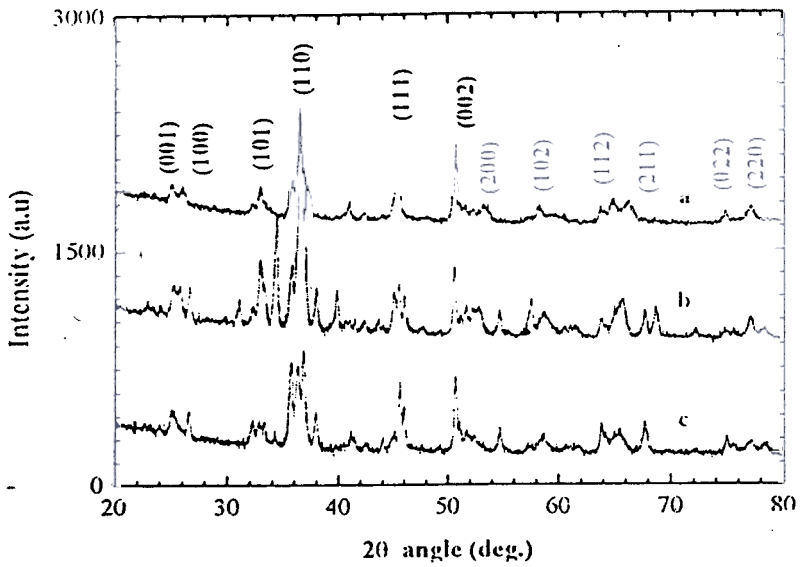

Figure 2. The XRD spectra of galiium oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ ceramic tetragonal phase.
(a) $PbZr_{0.525}Ti_{0.475}C_3$ (PZT) ceramic,
(b) 1% niobium oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ (PNZT) ceramic,
(c) 1% gallium oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT) ceramic.

Table 2. The tetragonal structure and the lattice constants of PZT, 1% mass of niobium oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ (PNZT) ceramic and 1% mass of gallium oxide doped and $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT) ceramic by visual basic program.

		PZT	1% mass of niobium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PNZT 1%)	1% mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ (PGZT 1%)
Lattice constant	*a* (Å)	4.195	4.187	4.185
	c (Å)	4.306	4.302	4.296
	c/a ratio	1.026	1.027	1.027
Lattice Constants in literature [19]	*a* (Å)	4.036		
	c (Å)	4.146		
	c/a ratio	1.027		
Lattice constants in literature [20]	*a* (Å)	4.041		
	c (Å)	4.131		
	c/a ratio	1.022		

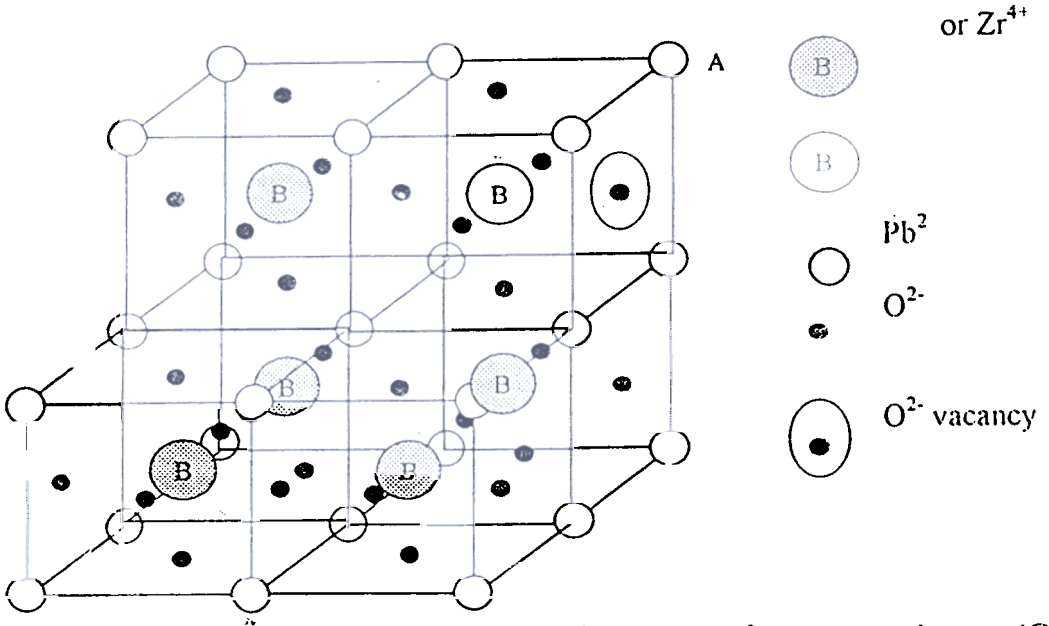

Figure. 3. Crystal deficiencies in PZT perovskite structure for acceptor dopants (Ga^{3}

These dipoles are generated by an Ga^{3+} ion (effectively negative charge) and an oxygen vacancy site (effectively positive charge) (Figure 3). Acceptor doping gallium-oxide more likely very effective for generating movable dipoles and domain pinning, since the oxygen ions are still movable even below the Curie temperature (e.g. at room temperature), because the oxygen and vacancy adjacent (only 2.8 Å) and hopping easily occurs [2].

5. Conclusions

We have investigated the dependence of gallium oxide doped lead zirconium titanate on lattice constants of PZT, PNZT and PGZT ceramic by using visual basic program in conjunction with Cohen's and Cramer's algorithm. The ceramic are polycrystalline in tetragonal structure with preferred orientation in (001), (100), (101), (110), (111), (002), (200), (102), (112), (211), (022), (220) crystal planes, and the crystalline quality of the grown ceramic significantly depends on the gallium oxide doped lead zirconium titanate. Using Cohen's and Cramer's algorithms in visual basic program, the lattice constants are $a = b = 4.195$ Å, and $c = 4.306$ Å; c/a ratio = 1.026 for $PbZr_{0.525}Ti_{0.475}O_3$ ceramic; $a = b = 4.187$ Å, and $c = 4.302$ Å, c/a ratio = 1.027 for 1 % mass of niobium doped $PbZr_{0.525}Ti_{0.475}O_3$ ceramic; $a = b = 4.185$ Å, and $c = 4.296$ Å, c/a ratio = 1.027 for 1 % mass of gallium doped $PbZr_{0.525}Ti_{0.475}O_3$ ceramic, respectively. The reform value of the lattice constant of PNZT and PGZT ceramic is possibly associated with the anti site defects of Nb and Ga dopants.

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References

T. Whitaker, "Focal Plane Arrays Fabricated from Compound Semiconductor Materials are at The Heart of Many Infrared Imaging Systems and Night Vision Cameras". *Compound Semiconductor*, 4 (4), 17 –23 (1998).

K. Uchino, "Ferroelectric Devices". *Marcel Dekker, Inc.* New York, 131 – 134 (2000).

N.J. Wu, Y.S. Chen, S. Dorderic, and A. Ignatiev, "Pyroelectric IR Sensor Based on Oxide Heterostructures on Si (100) and $LaAlO_3$ (100) Substrates". *Proceeding Third International Conference on Thin Film Physics and Applications*. SPIE Vol. 3175, 256 – 261 (1997).

4. K. Suu, "Preparation of (Pb,La)(Zr, Ti)O_3 Ferroelectric Films by RF Sputtering on Large Substrate. *Jpn. J. Appl. Phys.*, 35 (9B), 4967 – 4971 (1996).

Irzaman, A. Fuad, P. Arifin, M. Budiman dan M. Barmawi. "Analisis Strain Mikro dan Grain Size Bahan Pyroelektrik $PbTiO_3$". *Prosiding Simposium Fisika Nasional* XVIII, Serpong, 295 – 302 (2000).

6. N.A.K. Umiati, Irzaman, M. Budiman, dan M. Barmawi. "Efek Annealing pada Penumbuhan Film Tipis Ferroelektrik $PbZr_{0.625}Ti_{0.375}O_3$". *Jurnal Kontribusi Fisika Indonesia*. ITB Bandung, 12 (4), 94 – 98 (2001).

Irzaman, A. Fuad, P. Arifin, M. Budiman, M. Barmawi. "Pyroelectric Properties of Tantalum Oxide Doped Lead Zirconium Titanate (PTZT) Thin Films Grown by DC Unbalanced Magnetron Sputtering and Its Application for IR Sensor". *Prosiding Simposium Fisika Nasional*, Jurusan Fisika FMIPA ITS Surabaya, 2, 80 – 84 (2002).

8. Irzaman, Azizahwati, A. Fuad, P. Arifin, M. Budiman, M. Barmawi. "Surface Morphology of Lead Zirconium Titanate (PZT) Films". *Prosiding Pertemuan Ilmiah IPTEK Bahan 2002*, Pusapiptek Serpong, 205 – 209 (2002).

9. Irzaman, Y. Darvina, A. Fuad, H. Sutanto, P. Arifin, M. Budiman, M. Barmawi. "C-V Properties of Lead Zirconium Titanate ($PbZr_{0.525}Ti_{0.475}O_3$) Thin Films" *Prosiding Seminar Keramik Nasional*, Balai Besar Industri Keramik Bandung, Departemen Perindustrian dan Perdagangan, 1 – 9 (2002).

10. Y. Darvina, Irzaman, A. Fuad, H. Sutanto, P. Arifin, M. Budiman, M. Barmawi. "Crystalline Structure Analysis of Tantalum Oxide (Ta_2O_5) Doped Lead Zirconium Titanate ($PbZr_{0.525}Ti_{0.475}O_3$) Ceramic". *Prosiding Seminar Keramik Nasional*, Balai Besar Industri Keramik Bandung, Departemen Perindustrian dan Perdagangan, 17 – 25 (2002).

Irzaman, H. Darmasetiawan, M. Hikam, and M. Barmawi. "Micro Strain and Particle Size Analysis of PZT Ceramic and Thin Films". Prosiding Seminar Nasional Hamburan Neutron dan Sinar-X, P3IB Batan, Puspiptek Serpong, (2003).

12. Irzaman, Y. Darvina, A. Fuad, P. Arifin, M. Budiman, and M. Barmawi. "Physical and

Pyroelectric Properties of Tantalum Oxide Doped Lead Zirconium Titanate $[Pb_{0.9950}(Zr_{0.525}Ti_{0.465}Ta_{0.010})O_3]$ Thin Films and Its Application for IR Sensor". Phys. Stat. Sol.(a), **199** (3), 416 -424 (2003).

13. Irzaman, Y. Darvina, P. Arifin, M. Budiman, and M. Barmawi. "Micro Strain and Particle Size Analysis of Tantalum Oxide Doped Lead Zirconium Titanate (PTZT) Ceramic". Prosiding *Prosiding Seminar Keramik Nasional II*, Balai Besar Industri Keramik Bandung, Departemen Perindustrian dan Perdagangan, 132 – 140 (2003).
14. B.D. Cullity, Elements of X-ray Diffraction, Second Edition, *Addison Wesley Publishing Company Inc.*, London, 26(1978).
15. C. Suryanarayana and M.G. Norton, X-ray Diffraction : A Practical Approach, *Plenum Press, London,* 46 (1998).
16. M.R. Spiegel. Advanced Mathematics for Engineers and Scientific, *McGraw-Hill International Book Company*, New York, (1983).
17. G.B. Arfken and H.J. Weber. Mathematical Methods for Physicists, Fourth Edition, *Academic Press, Inc*, San Diego, 156 – 158 (1995).
18 JCPDS, Powder Diffraction File (Set 1 – 5), International Centre For Diffraction Data. CD- Room, (1997).
19. Kakegawa, JCPDS-International Center for Diffraction Data (JCPDS-ICDD), (1995).
20. F.J. Jona and G. Shirane, Ferroelectric Crystal, *Dover Publications, Inc.*, New York, 242 (1993).

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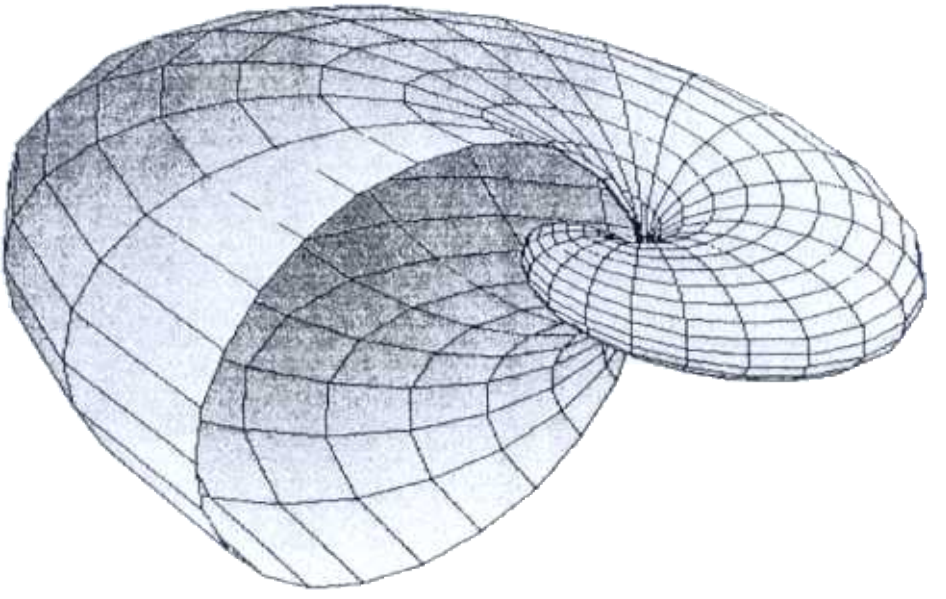

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