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TETRAGONAL TO CUBIC PHASE TRANSFORMATION IN TANTALUM OXIDE DOPED LEAD ZIRCONIUM TITANATE CERAMIC

Irzaman[1,*] and M. Barmawi[2]

[1]Laboratory of Material Physics, Department of Physics, FMIPA IPB,
Kampus IPB Darmaga Gedung Wing S Bogor, Indonesia – 16680
[2]Department of Physics, FMIPA ITB, Bandung Indonesia 40132
**Corresponding author e-mail: irzaman@yahoo.com, irzaman@dosen.fisika.net*

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ABSTRACT

Ceramic of tantalum oxide doped lead zirconium titanate $\lfloor (Pb_{1-y/2})(\mathrm{Zr}_x\mathrm{Ti}_{1-x-y}\mathrm{Ta}_y)\mathrm{O}_3 \rfloor$ (PTZT) ceramic were successfully deposited by solid solution method. The PTZT ceramic were analyzed by x-ray diffraction (XRD). The XRD spectra was recorded on a Philips type PW 3701 diffractometer using CuK_{α} (λ_{co} = 1.54056 Å) radiation at 30 KV and 30 mA (900 watt). The XRD spectra shows that for a tantalum oxide doped lead zirconium titanate $\lfloor (Pb_{1-y/2})(\mathrm{Zr}_x\mathrm{Ti}_{1-x-y}\mathrm{Ta}_y)\mathrm{O}_3 \rfloor$ ceramic with x = 0.525 and y = 0, 0.005, 0.01, and 0.015 has a tetragonal phase, and when x = 0.525 and y = 0.0108 it is in cubic phase. Increasing the tantalum oxide doping from 0 % to 1.5 % led to the decrease of c/a ratio The reform value of the lattice constant of PTZT ceramic is possibly associated with the anti site defects of Pb, Zr and Ta.

Keywords: *PTZT, dopant, ceramic, solid solution*

1. INTRODUCTION

A pyroelectric infrared (IR) detector has advantages of A pyroelectric ceramic and thin film film sensor is a thermal transducer based on the pyroelectric effect, i.e., as the sensor is exposed to infrared (IR) light, it absorbs radiation and its temperature rises from T °K to (T + ΔT) K, thus reducing the polarization, *P*, and enhancing the photo-current of the sensor[1)]. Therefore, the pyroelectric IR sensor has some advantages, compared to the photo-quantum-effect IR sensors fabricated with Si or GaAs materials that operate in very low temperatures unlike the pyroelectric IR sensor which can be operated even at room temperatures, has little wavelength dependence over a wide IR range, and a fast response[2)]. Among the pyroelectric materials, such as triglicine sulfate (TGS) and its isomers, lead zirconium titanate (PZT) possesses some excellent characteristics, i.e., large pyroelectric coefficient, small dielectric constant, and comparatively large pyroelectric figure of merit[2,3)].

Tantalum oxide doped lead zirconium titanate, $\lfloor (Pb_{1-y/2})(\mathrm{Zr}_x\mathrm{Ti}_{1-x-y}\mathrm{Ta}_y)\mathrm{O}_3 \rfloor$ has been of immense interest to those who use ferroelectric ceramic and thin films in pyroelectric sensor applications[3,4,5)]. The dielectric and pyroelectric properties of the materials can be tailored by varying the concentration of the dopant. Since the sensor performance significantly depends on these properties, the sensor performance can then be optimized.

In this paper we report on the fabrication of tantalum oxide doped lead zirconium titanate $\lfloor (Pb_{1-y/2})(\mathrm{Zr}_x\mathrm{Ti}_{1-x-y}\mathrm{Ta}_y)\mathrm{O}_3 \rfloor$ ceramic for x = 0.525 and y = 0, 0.005, 0.01, 0.0108, and 0.015. The crystalline structure related to the concentration of the dopant are described.

2. MATERIALS AND METHODS

Small amount of dopants sometimes drastically change the lattice constants, dielectric, electromechanical, electrooptic properties and pyroelectric properties of ceramic and thin films. In this communication, the crystallographic deficiencies due to impurity doping in a $PbZr_xTi_{1-x}O_3$ perovskite crystal is considered. In the case of donor ions, Ta^{5+} in $PbZr_xTi_{1-x}O_3$, Pb deficiency[2)] is introduced as

$$\lfloor (Pb_{1-y/2})(\mathrm{Zr}_x\mathrm{Ti}_{1-x-y}\mathrm{Ta}_y)\mathrm{O}_3 \rfloor \qquad (1)$$

The exact relation between diffraction angle and the lattice constants depends on the crystal system involved. For cubic structure[6)] those relations are given by

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

and

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \qquad (3)$$

for tetragonal structure[6] those relations are given by

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}, \qquad (4)$$

and

$$\left.\begin{aligned} \sum \alpha \sin^2\theta &= C\sum \alpha^2 + B\sum \alpha\gamma + A\sum \alpha\delta, \\ \sum \gamma \sin^2\theta &= C\sum \alpha\gamma + B\sum \gamma^2 + A\sum \gamma\delta, \\ \sum \delta \sin^2\theta &= C\sum \alpha\delta + B\sum \gamma\delta + A\sum \delta^2, \end{aligned}\right\} \qquad (5)$$

where *d* is the interplanar spacing, *a* and *c* are the lattice constants, *h, k,* and *l* represents the plane indices. λ is the wavelength (Cu element = 1.54056 Å), θ is the diffraction angle, and $\alpha = h^2 + k^2$, $\gamma = l^2$, $\delta = 10 \sin^2 2\theta$, A = D/10, $\lambda^2/(4c^2)$, and $C = \lambda^2/(4a^2)$, while *A, B,* and *C* are the numerators. The solution for numerators *A, B,* and *C* are solved using Cramer's Method (CM)[7].

To make PZT ceramic, 5.3020 g of lead titanate [$PbTiO_3$, 99 %] and 6.6980 g of lead zirconate [$PbZrO_3$, 99.7 %] were initially mixed in a bowl for 6 hours, whereas 0.5 %, 1 %, 1.08 %, 1.5 % of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ (PTZT) ceramic were made by using a mixture of 5.3020 g lead titanate [$PbTiO_3$, 99 %] and 6.6980 g lead zirconate [$PbZrO_3$, 99.7 %] with 0.0600 g, 0.1200 g, 0.1296 g and 0.1800 g of tantalum oxide [Ta_2O_5, 99.9 %] respectively in a bowl for 6 hours. The mixture was then pressed at 31.43 MPa for 15 minutes to form a pellet followed by sintering at 850°C for 10 hours.

The structure of the grown films was analyzed by x-ray diffraction (XRD). The XRD spectra were recorded on a Diano type 2100E diffractometer using CuK_α radiation at 30 KV and 30 mA (900 watt).

3. RESULTS AND DISCUSSION

A search in the ICDD-PDF database using the software available with the diffractometer was identified : PZT (PDF No° 33-0784)[8]. The peak positions of each phase were extracted by means of single-peak-profile-fittings. The remaining 9 intense peaks corresponding to the phase of interest, PZT, were readily indexed in a tetragonal and cell. Figure 1 shows the XRD spectra 0 %, 0.5 %, 1 %, 1.08 % and 1.5 % of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ (PTZT) ceramic.

The presence of an intense diffraction peak corresponding to the (110) plane implied that the PZT and PTZT ceramic possessed a strong preferential orientation. Similar trends were also observed in PZT and PTZT ceramic fabricated by solid solution method[3].

The calculation of the lattice constant for 1 % tantalum oxide doped PZT [$Pb_{0.9950}(Zr_{0.525}Ti_{0.465}Ta_{0.010})O_3$] using CM as given in Eq. (2), (4), and (5) for numerators A, B, and C are

$$\left.\begin{aligned} 11.8478148 &= 320C + 7B + 335.6656A \\ 0.32640915 &= 7C + 2B + 10.6841A \\ 12.5447559 &= 335.6656C + 10.6841B + 361.3488A \end{aligned}\right\}. \qquad (6)$$

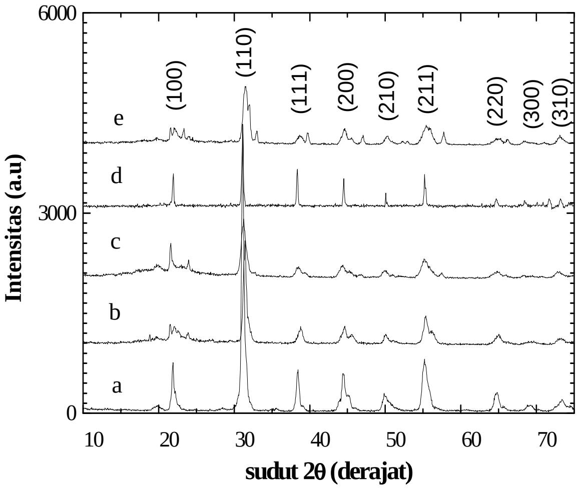

Figure 1. The XRD spectra of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ ceramic. (a) [$PbZr_{0.525}Ti_{0.475}O_3$] ceramic, (b) 0.5 % tantalum oxide doped [$Pb_{0.9975}(Zr_{0.525}Ti_{0.470}Ta_{0.005})O_3$] ceramic, (c) 1 % tantalum oxide doped [$Pb_{0.9950}(Zr_{0.525}Ti_{0.465}Ta_{0.010})O_3$] ceramic, and (d) 1.08 % tantalum oxide doped [$Pb_{0.9925}(Zr_{0.525}Ti_{0.460}Ta_{0.015})O_3$] ceramic. (e) 1.5 % tantalum oxide doped [$Pb_{0.9925}(Zr_{0.525}Ti_{0.460}Ta_{0.015})O_3$] ceramic

Table 1. The structure and the lattice constants of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ (PTZT) ceramic.

		PTZT				
		0 %	0.5 %	1 %	1.08 %	1.5 %
Lattice constant	a (Å)	4.094	4.122	4.075	4.068	4.248
	c (Å)	4.142	4.134	4.088		4.179
	c/a ratio	1.012	1.003	1.003	1.000	0.984
Structure		Tetra-gonal	Tetra-gonal	Tetra-gonal	cubic	pseudo tetra-gonal

The values produced by the CM for numerator C and B are 0.035726585 and 0.035501007, respectively. The lattice constant of $Pb_{0.9950}(Zr_{0.525}Ti_{0.465}Ta_{0.010})O_3$ ceramic is then $a = \lambda_{Cu}/(2\sqrt{C}) = 4.075$ Å; $c = \lambda_{Cu}/(2\sqrt{B}) = 4.088$ Å and *c/a* ratio = 1.003.

The XRD spectra (Figure 1) showed that PTZT ceramic were tetragonal and cubic in structure. The calculated lattice constants and *c/a* ratio are given in Table 1. Increasing tantalum oxide doped PZT from 0 % to 1.5 % led to the decrease of *c/a* ratio. This analysis is very important and appropriate for advanced research since it can yield compositions of tantalum oxide doped lead zirconium titanate for cubic phase (if *c/a* ratio is 1.00). Interpolating the tantalum oxide doped PZT from 1 % to 1.5 %, yielded the composition of tantalum oxide doped PZT for cubic phase at y = 1.08 %. Optimization of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ can result in tetragonal to cubic phase transformation ceramic. The calculation of lattice constants of PTZT (1.08 %) ceramic cubic phase (from XRD spectra is shown in Figure 1 (d)), using Equation (2), (3) and the lattice constants average calculated is $a = b = c = 4.068$ Å.

The smaller value of the c/a ratio for PTZT compared to those of PZT is possibly associated with the anti-site defects of Ta dopants. The reform value of the lattice constant of PTZT ceramic is possibly associated with the anti site defects of Pb, Zr and Ta.

4. CONCLUSIONS

X-ray diffraction was used to determine the orientation and crystalline structure of tantalum oxide doped lead zirconium titanate ceramic and thin film. Optimization of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ can result in tetragonal to cubic phase transformation ceramic. The 1.08 % of tantalum oxide doped $PbZr_{0.525}Ti_{0.475}O_3$ yielded cubic phase and exactly optimizing the concentration of the dopant can produce good crystalline ceramic.

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