

## **STUDY ON EFFECT OF ISOVALENT BARIUM IONS SUBSTITUTION ON STRUCTURAL FEATURES, FERROELECTRIC PROPERTIES AND BANDGAPS OF LEAD TITANATE**

Pwint Yi Thein<sup>1,\*</sup>, Lai Lai Khine<sup>2</sup>, Ye Myint Win<sup>3</sup>, Amy Than<sup>4</sup>,  
Mar Mar Myint<sup>1</sup> and Yin Yin Swe<sup>1</sup>

### **Abstract**

Isovalent Ba ions substituted lead titanate is studied by means of its structural features, ferroelectric properties and bandgaps. Analar grade PbO, TiO<sub>2</sub> and BaCO<sub>3</sub> are chosen and used as starting materials. Three starting materials are weighted and mixed by the stoichiometric composition: Pb<sub>(1-x)</sub>Ba<sub>(x)</sub>TiO<sub>3</sub>, where x = 0, 1 mol%, 2 mol%, 3 mol%, 4 mol% and 5 mol% respectively. The mixture powders are grinded by using agate mortar for each 5 hrs. Then, the mixture powders are conventionally sintered at 700°C for each 5 hrs. After first sintering process, the mixture powders are grinded again by using ball milling for each 5 hrs. Finally, the mixture powders are sintered at 700°C for each 5 hrs. X – rays diffraction technique is used to examine the phase formation and structural features of PbTiO<sub>3</sub>:Ba specimens. From the XRD studies, lattice constants, lattice distortion, unit cell volume, crystallite size and lattice micro strain are estimated. Ferroelectric properties of PbTiO<sub>3</sub>:Ba specimens are characterized by using Sawyer – Tower circuit. Spontaneous polarization, remanent polarization and coercive field of PbTiO<sub>3</sub>:Ba specimens are evaluated. Optical bandgaps of PbTiO<sub>3</sub>: Ba specimens are studied by using UV – Vis spectrophotometer. From the absorption spectra, bandgaps are calculated. XRD results indicates that, there are no significant change of tetragonal perovskite type PbTiO<sub>3</sub> structure after Ba substitution. A little changes of structural features are observed and it is due to appearance of micro strain and defects, dislocations and vacancies in host PbTiO<sub>3</sub> structure during the doping mechanism. Ferroelectric properties, such as spontaneous polarization, remanent polarization and coercive field slightly increase as additional Ba content increases, due to second- order hybridizations, caused by isovalent Ba ions in PbTiO<sub>3</sub> lattice. Optical bandgap of PbTiO<sub>3</sub> is enhanced when additional Ba content is raised. It is expected that, there are a quantum confinement effect in PT: Ba specimens.

**keywords:** PbTiO<sub>3</sub>, additional Ba content, structural features, ferroelectric properties, bandgap

### **Introduction**

Intensive research has been focused on ferroelectric materials in the last decade with particular emphasis on new processing and characterization techniques. Materials with perovskite - type crystalline structure are developed for their potential applications in the field of electronic, microelectronic and optoelectronic devices. In particular, the PbTiO<sub>3</sub> material has piezoelectric and ferroelectric properties at room temperature with bandgap of 3.4 eV in the tetragonal symmetry, special group P4mm and lattice parameters a = b = 3.904 Å and c = 4.152 Å [ Zelezly V. et al., 2016].

In the cubic symmetry, PbTiO<sub>3</sub> materials has spacial group Pm3m with lattice parameter a = 3.865 Å and bandgap is around 3.6 eV. PbTiO<sub>3</sub> has received special attention due to it's applications, such as pyroelectric infrared detectors, piezoelectric sensors, optical switches, DRAM and NVRAM devices. There is a tetragonal to cubic phase transition at ~ 490 °C in PbTiO<sub>3</sub>, which changes the piezoelectric and ferroelectric properties. Pure PbTiO<sub>3</sub> has large tetragonal

---

<sup>1</sup> Department of Physics, Nationalities Youth Resource Development Degree College, (Yangon), Myanmar.

<sup>2</sup> Department of Physics, University of Dagon, Myanmar.

<sup>3</sup> Department of Physics, Defence Services Academy, Pyin Oo Lwin, Myanmar.

<sup>4</sup> Department of Physics, University of Yangon, Myanmar.

\* - Corresponding author, Susan74june@gmail.com.

distortion at room temperature, approximately 1.064, which introduces a stress upon the cooling through the phase transition [Zelezly V. 2016; Moudavi S. J. and Pourhabib -Yekta A. 2011].

For the electronic, microelectronic and optoelectronic applications, the properties of  $\text{PbTiO}_3$  based materials can be enhanced by substitutions of the alkali, rare - earth, and transition metals/materials in the perovskite type  $\text{PbTiO}_3$  based materials. At present, much attention has been paid to the lead based perovskite - type compounds and their solid solutions, due to a variety of physical properties and a wide range of industrial applications. Depending on the ionic/covalent radii and charge, ordering of cations may occur which gives rise to different structural and physical properties. Considerable amount of works has been carried out on A site, B site and A/B site in  $\text{ABO}_3$  - type  $\text{PbTiO}_3$  with different substituents. However, an annealing process is often accompanied by undesired secondary phases, such as substituent oxides. In the recent years, the substitutions of suitable ions either A, B and A/B site in the perovskite lattice has governed much attention [Scott J. F. 2008].

Among the suitable substituents, Ba ions are widely used to examine the structural, optical, magnetic, ferroelectric and piezoelectric properties of  $\text{PbTiO}_3$  [Zhen X. et al.,2012; Ponte F. M. 2016]. In this research work, Ba substituted  $\text{PbTiO}_3$  specimens are studied by means of its structural features, ferroelectric properties and optical bandgaps.

### Experimental Procedure

Additional Ba substituted  $\text{PbTiO}_3$  specimens are prepared by using conventional solid state sintering. Analar grade  $\text{PbO}$ ,  $\text{TiO}_2$  and  $\text{BaO}$  are used as starting materials. Three starting materials are weighted and mixed by the stoichiometric composition:  $\text{Pb}_{(1-x)}\text{Ba}_{(x)}\text{TiO}_3$ , where  $x = 0, 1 \text{ mol}\%, 2 \text{ mol}\%, 3 \text{ mol}\%, 4 \text{ mol}\%$  and  $5 \text{ mol}\%$  respectively. The mixture powders are grinded by agate mortar for each 5 hrs. After that, the mixture powders are conventionally sintered at  $700^\circ\text{C}$  for each 5 hrs. After first sintering, the mixture powders are grinded again by using ball - milling process for each 5 hrs. Then, the mixture powders are conventionally sintered again, for each 5 hrs. X - rays diffraction technique is used to determine the phase formation and structural features of the  $\text{PbTiO}_3$ : Ba specimens by means of Rigaku Multiflux with  $\text{Cu } k_\alpha$  monochromatic radiation ( $\lambda = 1.542 \text{ \AA}$ ).  $\text{PbTiO}_3$ : Ba specimens are scanned from  $2\Theta$  ( $\Theta = \text{Bragg's angle}$ ) in the range from  $10^\circ$  to  $70^\circ$  with a scanned speed of  $0.01^\circ/\text{sec}$ . Applied voltage and current of the Rigaku Multiflux are set to be 50 kV and 50 mA.

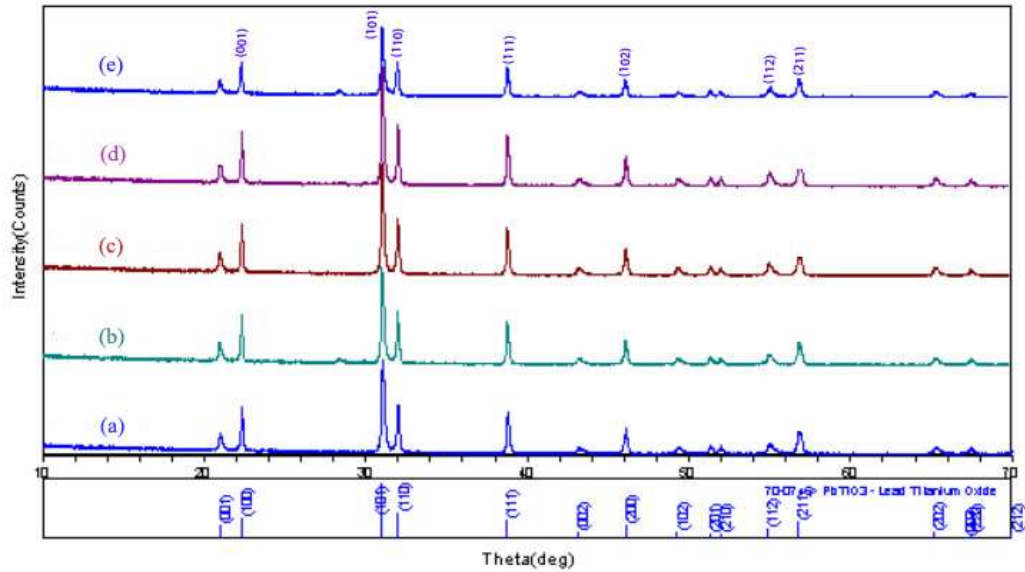
X - rays spectra are recorded at room temperature. From the x-rays spectra, lattice constants, lattice distortion, unit cell volume, crystallite size and lattice micro strain are estimated. Furthermore, effects of additional Ba substitution on lattice constants, lattice distortion and unit cell volume are studied.

$\text{PbTiO}_3$ : Ba specimens are uniaxially pressed with 19.5 tons press into circular shape disc with 20 mm in diameter and 3.5 mm in thickness. Silver pastes are coated onto both surface of the specimens with the area of ( $7.06 \text{ mm}^2$ ). Sawyer - Tower circuit is used to characterized the ferroelectricity of  $\text{PbTiO}_3$ : Ba specimens. Thermal hysteresis loops were recorded on oscilloscope (Gwinstek, GDS -1152 A-U, 50 MHz). Applied voltage and frequency will set to 10Vpp and 10 kHz. Ferroelectric properties, such as spontaneous polarization, remanent polarization and coercive field of the  $\text{PbTiO}_3$ :Ba specimens are evaluated.

Optical bandgaps of the  $\text{PbTiO}_3$ : Ba specimens are determined by using UV - Vis spectrophotometer (UV 1800 Shimadzu) in the wavelength from 190 nm to 700 nm with 1.0 nm resolution and wavelength accuracy is  $\pm 0.01 \text{ nm}$ . UV 1800 consists of deuterium: tungsten halogen lamp source and attached with UV Probe. The optical bandgap measurement involves the excitation of electrons from valence band to conduction band using photons of selected frequency.

The process does not change the number of carriers involved and total numbers of carriers presented in the PbTiO<sub>3</sub>: Ba specimens remain the same. From the absorption spectra, optical bandgaps of PbTiO<sub>3</sub>: Ba specimens are studied.

### Results and Discussion



**Figure 1** XRD spectra of (a)PbTiO<sub>3</sub> : Ba (1 mol %)specimens (b)PbTiO<sub>3</sub>:Ba (2mol %) specimens (c)PbTiO<sub>3</sub> : Ba (3mol %) specimens (d)PbTiO<sub>3</sub>:Ba (4mol %) specimens and (e)PbTiO<sub>3</sub>:Ba (5mol %) specimens

X - diffraction spectra of PbTiO<sub>3</sub>: Ba specimens are shown in figure (1). Peak search algorithm, known as Jade software is used to identify the unknown peaks in this research work. Only diffraction peaks from polycrystalline, tetragonal, perovskite - type PbTiO<sub>3</sub> structure with reference (70 - 0746 > JCPDS file) are observed. In addition, (101) peak is the most intense peak, known as Bragg peak and a little shift of (101) peak position (2θ value) is obtained in all spectra. These results can be interpreted as additional Ba substituents are diluted into host PbTiO<sub>3</sub> structure. Furthermore, sharp diffraction peaks are found in all spectra. It is due to higher degree of crystallinity of PbTiO<sub>3</sub>: Ba specimens. From the x-rays spectra, lattice constants of the PbTiO<sub>3</sub>: Ba specimens are examined by using the equation (1):

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \tag{1}$$

Where, d = interplanar spacing

h, k, l = miller indices

a, c = lattice parameters

Interplanar spacing ‘d’ values from (110) and (101) planes are substituted in equation (1) and, lattice parameters ‘a’ and ‘c’ are estimated.

Unit cell volumes of PbTiO<sub>3</sub>: Ba specimens are estimated by using the equation (2):

$$\text{Unit cell volume} = a \times a \times c \tag{2}$$

Lattice constants, lattice distortion and unit cell volume of PbTiO<sub>3</sub>: Ba specimens are listed in table (1).

**Table 1** List of lattice constants, lattice distortion and unit cell volume of PbTiO<sub>3</sub>:Ba specimens.

Ba Content (%)	Lattice parameter “a (Å)”	Lattice parameter “c (Å)”	Lattice distortion	Cell Volume ( x 10 <sup>-30</sup> m <sup>3</sup> )
1	3.897	4.134	1.0608	62.792
2	3.899	4.131	1.0595	62.815
3	3.902	4.129	1.0582	62.859
4	3.905	4.126	1.0566	62.906
5	3.908	4.124	1.0553	62.971

Crystallite size and lattice micro strain of the PbTiO<sub>3</sub>:Ba specimens are investigated by using the Debye - Scherrer equations ( 3 ) and ( 4 ) :

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (3)$$

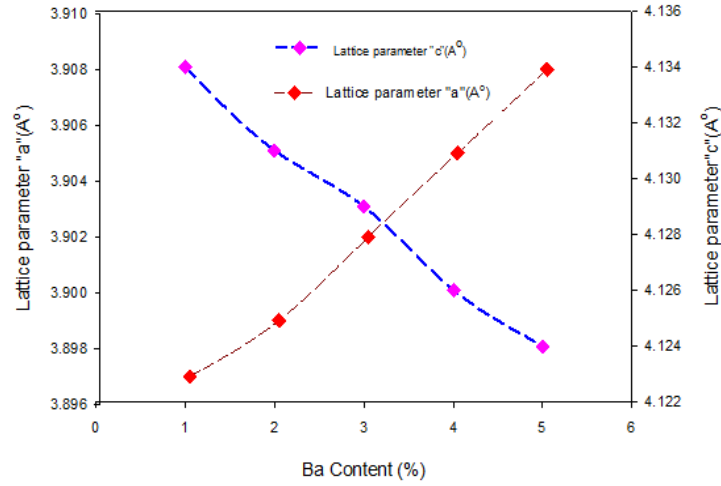
$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (4)$$

In this equation,  $\beta$  is full width at half of the most intense peak maximum (FWHM) and  $\lambda$  is the wavelength of the using X-ray and  $\theta$  is the peak position, is known as Bragg's angle.

Crystallite size and lattice micro strain of PbTiO<sub>3</sub>: Ba specimens are listed in table (2).

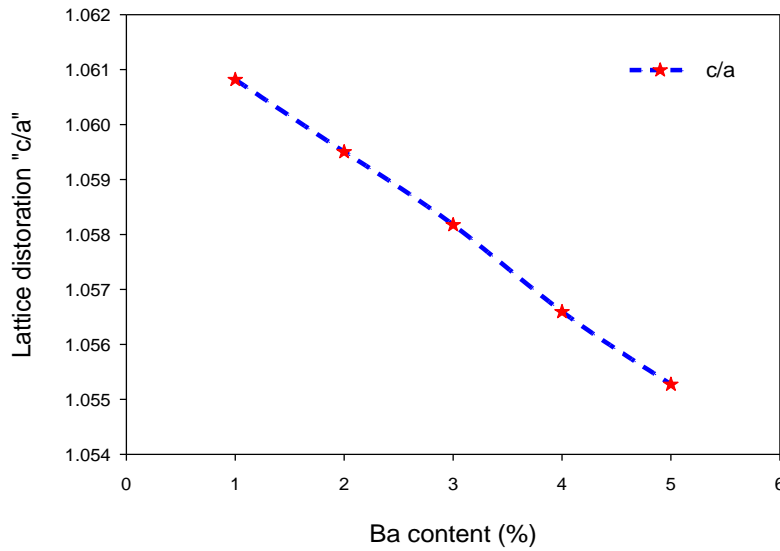
**Table 2** List of crystallite size and lattice micro strain of PbTiO<sub>3</sub>: Ba specimens.

Ba Content (%)	Crystallize size (nm)	Micro strain (x 10 <sup>-3</sup> )	FWHM of (101) plane (Rad) (x10 <sup>-3</sup> )
1	29.52	4.073	4.887
2	29.34	4.098	4.917
3	29.08	4.134	4.961
4	28.87	4.164	4.997
5	28.64	4.198	5.037



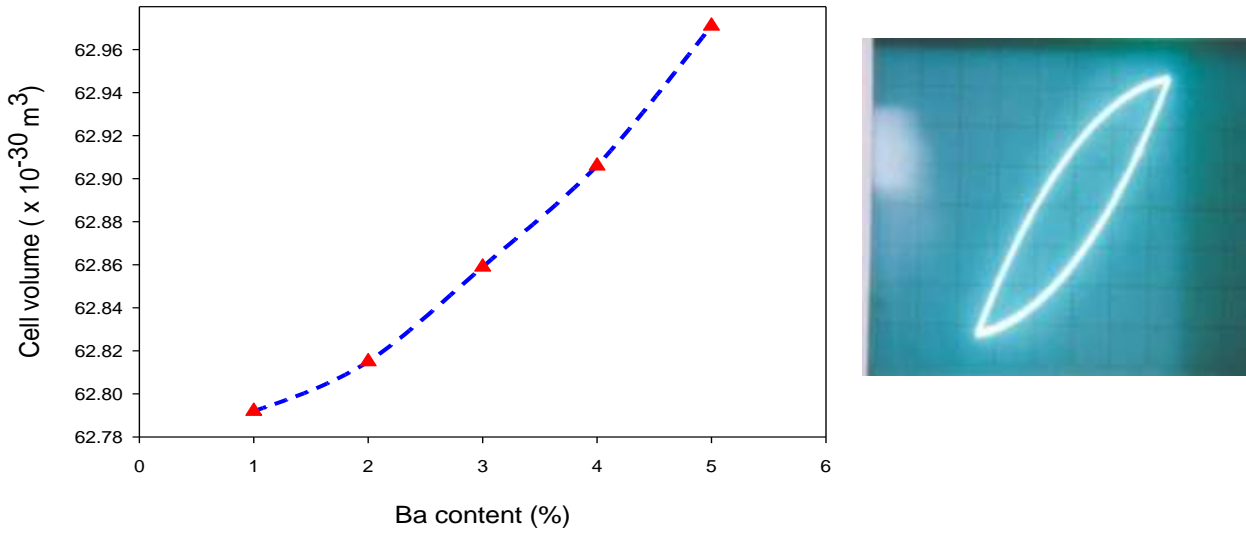
**Figure 2** Variation of additional Ba content with lattice constants of sPbTiO<sub>3</sub>:Ba specimens.

Figure (2) shows the variation of additional Ba content with lattice constants of PbTiO<sub>3</sub>:Ba specimens. It is obvious that, lattice constant "a" increases with increasing additional Ba content, on the other hand, lattice constant "c" decreases.



**Figure 3** Influence of additional Ba content on the lattice distortion (c/a) of PbTiO<sub>3</sub>:Ba specimens.

Figure (3) depicts the influence of additional Ba content on the lattice distortion (c/a) of PbTiO<sub>3</sub>:Ba specimens. It is studied that; lattice distortion is lowered when the additional Ba content is raised.

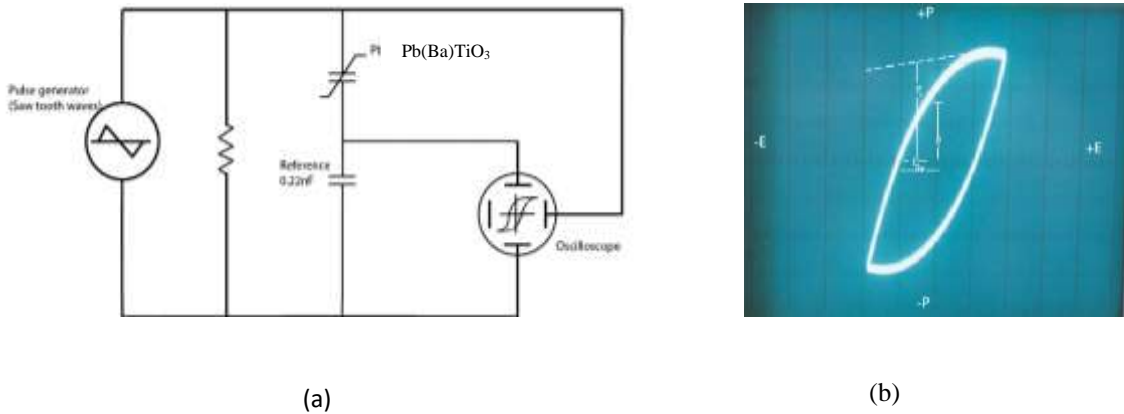


**Figure 4** Effect of additional Ba content on unit cell volume of PbTiO<sub>3</sub> : Ba specimens.

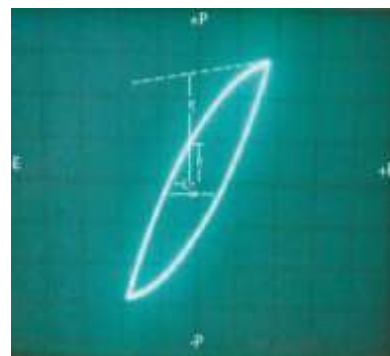
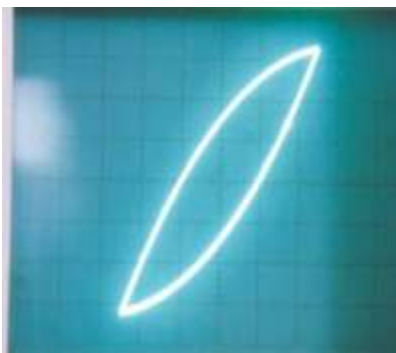
Figure (4) illustrates the effect of additional Ba content on unit cell volume of PbTiO<sub>3</sub>:Ba specimens. It is found that, unit cell volume slightly increases as additional Ba content increases.

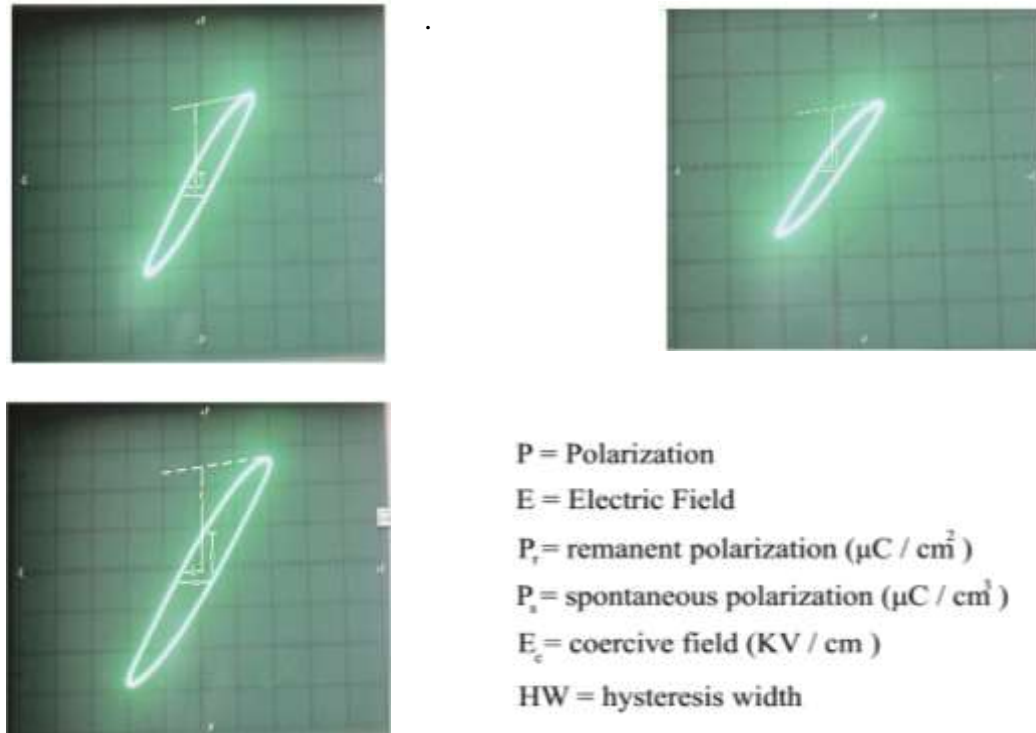
During the doping process, there are appearance of lattice micro strain, defects, dislocations and vacancies in host PbTiO<sub>3</sub> specimens. Consequently, variations of additional Ba content with structural features are observed.

Ferroelectricity of PT: Ba specimens is examined by using Sawyer - Tower circuit, as depicted in figure (5).



**Figure 5** (a) Sawyer - Tower circuit , and (b) estimation of P<sub>r</sub>, P<sub>s</sub>, and E<sub>c</sub>.





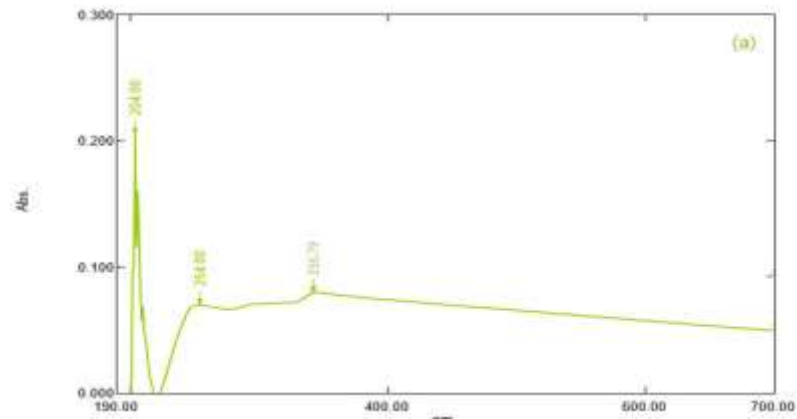
**Figure 6** Ferroelectric hysteresis loops of Ba modified PbTiO<sub>3</sub> structures of (a)PbTiO<sub>3</sub> : Ba (1 mol %)specimens (b)PbTiO<sub>3</sub>:Ba (2mol %) specimens (c)PbTiO<sub>3</sub> : Ba (3mol %) specimens (d)PbTiO<sub>3</sub>:Ba (4mol %) specimens and (e)PbTiO<sub>3</sub>:Ba (5mol %) specimens

According to first principle calculations on ferroelectric perovskite, hybridization between the electronic states of A or B ions and oxygen atom is essential for ferroelectricity. In addition, polarization in lead titanate arises from the distortion caused by 6s<sup>2</sup> lone pairs of Pb combined with the displacement of empty Jahn Teller (J T) Ti d<sup>6</sup> ions [Turik A. V. and Khasabov A. G. 2000] Situation, remanent, and coercivity are observed in all thermal hysteresis loops, as displayed in figure (6). Ferroelectric parameters, such spontaneous polarization, remanent polarization and coercive field are estimated and listed in table (3).

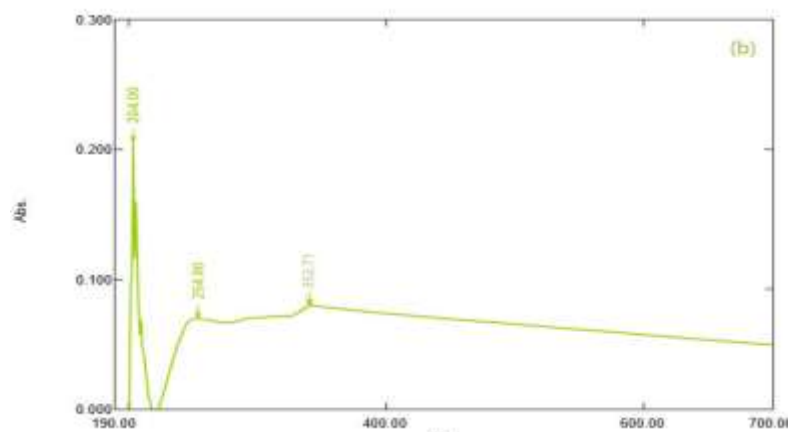
**Table 3** List of ferroelectric parameters of PbTiO<sub>3</sub>: Ba specimens.

Ba Content (%)	Spontaneous polarization P <sub>s</sub> ( $\mu\text{C}\cdot\text{cm}^{-2}$ )	Remanent polarization P <sub>r</sub> ( $\mu\text{C}\cdot\text{cm}^{-2}$ )	Coercive field E <sub>c</sub> (kV cm <sup>-1</sup> )
1	11.4	2.4	3.6
2	11.6	2.6	3.9
3	11.9	2.8	4.1
4	12.2	3.1	4.3
5	12.6	3.4	4.6

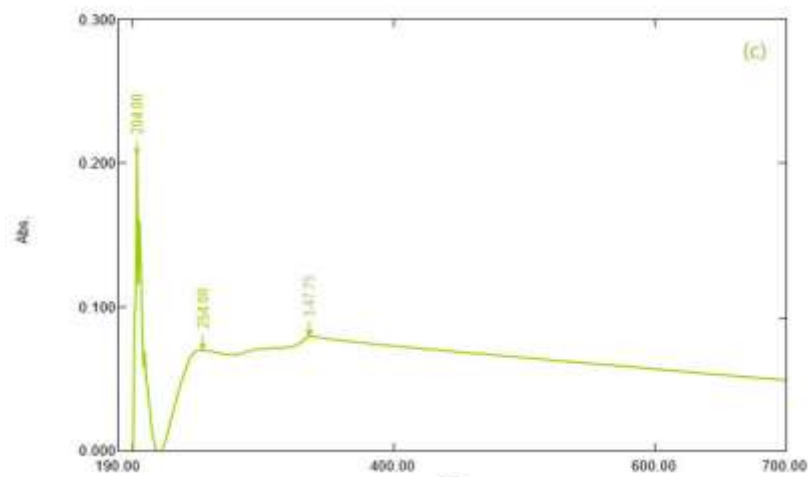
It is studied that, ferroelectric parameters are enhanced when additional Ba content is raised. It may be due to, second - order hybridizations between Ti - O and Pb (Ba) - O, lead to enhance the ferroelectricity in PbTiO<sub>3</sub>: Ba specimens.



**Figure 7 (a)** UV-Vis absorption spectrum of PbTiO<sub>3</sub>:Ba ( 1 mol %) specimens

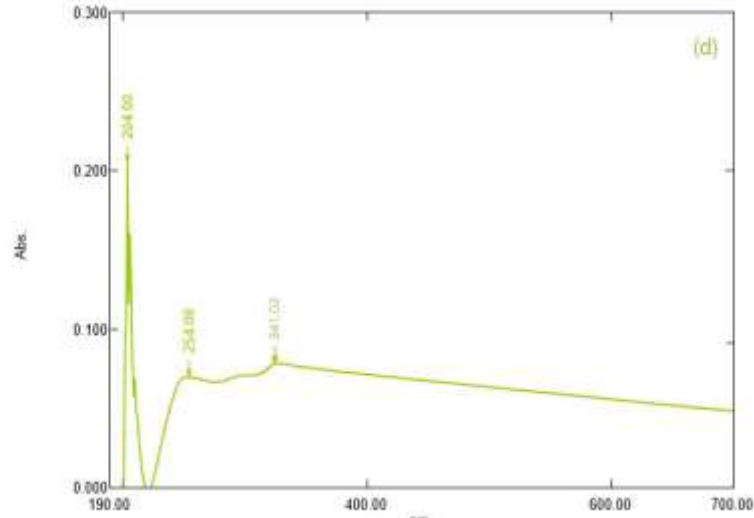


**Figure 7 (b)** UV-Vis absorption spectrum of PbTiO<sub>3</sub>:Ba ( 2 mol %) specimens

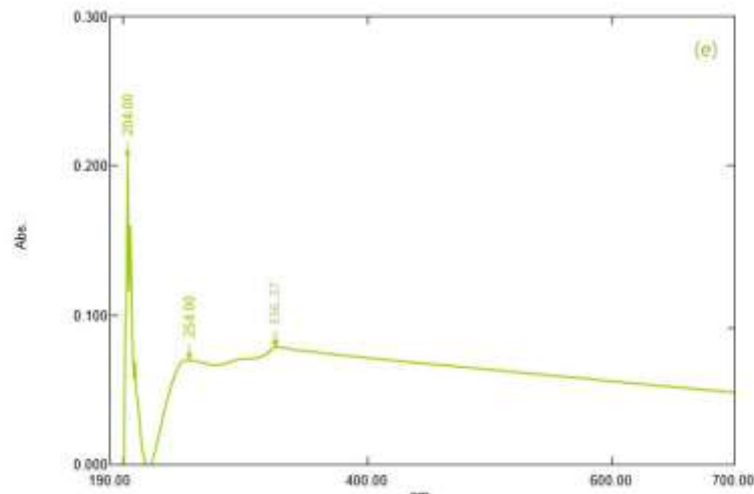


**Figure 7 (c)** UV-Vis absorption spectrum of PbTiO<sub>3</sub>:Ba ( 3 mol %) specimens.





**Figure 7 (d)** UV-Vis absorption spectrum of PbTiO<sub>3</sub>:Ba ( 4 mol %) specimens.



**Figure 7 (e)** UV-Vis absorption spectrum of PbTiO<sub>3</sub>:Ba (5 mol %) specimens.

Figure (7) shows the optical absorption spectra of PbTiO<sub>3</sub>: Ba specimens. It is obvious that absorbance increases with increasing additional Ba content. Optical bandgap is the exciton energy which determine the onset of vertical inter band transition. An exciton is a bound state of an electron and hole which are held together by electrostatic Coulomb force. An exciton forms when a photon is absorbed by a semiconductor (PbTiO<sub>3</sub>: Ba), so optical bandgap is threshold for photons to be absorbed. From the optical absorption spectra, bandgap is estimated by using the following equation (5):

$$E_c = \frac{hc}{\lambda} \tag{5}$$

Where, h = Planck ' s constant,

c = speed of light and

λ = wavelength in nm, which is the absorption edge value from the spectra.

Optical bandgaps of PbTiO<sub>3</sub> : Ba specimens are listed in table ( 4).

**Table 4 List of optical bandgaps of PbTiO<sub>3</sub>: Ba specimens.**

Ba Content (%)	Edge value from absorption spectrum (nm)	Optical bandgap (eV)
1	356.79	3.46
2	352.71	3.50
3	347.75	3.55
4	341.02	3.62
5	336.37	3.67

It is studied that, optical bandgap increases as additional Ba content increases in PbTiO<sub>3</sub> specimens. It is expected that, there are quantum confinement effect in PbTiO<sub>3</sub>: Ba specimens. The quantum confinement is observed when the particle size (in nano scale) decreases in confining dimension makes the discrete energy level and ultimately bandgap energy also increases. It is also believed that, the conduction band is dominated by Ti<sup>4+</sup> cations, the valence band is mainly by oxygen anions.

### Conclusion

Additional Ba substituted PbTiO<sub>3</sub> specimens are studied by means of its structural features, ferroelectric behavior and optical bandgaps. Structural features of PbTiO<sub>3</sub>:Ba specimens are examined by using x - rays diffraction technique. XRD results indicate that, there are no considerable change of tetragonal, perovskite - type PbTiO<sub>3</sub> structure after Ba substitutions. A little change of structural features is observed and it is due to appearance of lattice micro strains, defects, dislocations and vacancies in host PbTiO<sub>3</sub> structure during the doping process. Ferroelectricity of PbTiO<sub>3</sub>:Ba specimens is investigated by using Sawyer - Tower circuit. Ferroelectric parameters are enhanced when the additional Ba substitution is raised in PbTiO<sub>3</sub> specimens. It is possibly due to second - order hybridizations between Ti - O and Pb (Ba) - O are responsible for the enhancement of ferroelectric parameters in PbTiO<sub>3</sub>: Ba specimens. Optical bandgaps of PbTiO<sub>3</sub>:Ba specimens are studied by using UV - Vis spectrophotometer. Optical bandgap increases as additional Ba content increases in PbTiO<sub>3</sub> specimens. It is expected that, there are quantum confinement effects in PbTiO<sub>3</sub>:Ba specimens. PbTiO<sub>3</sub> : Ba specimens are potential candidate for dynamic random access memory ( DRAM ) and non-volatile random access memory ( NVRAM ) devices.

### Acknowledgement

The authors would like to thank the Universities ' Research Center (U R C, University of Yangon for XRD investigations and AMTT Co.Ltd. for UV - Vis spectrophotometer examination

## References

- Moudai S. J. and Pourhabib - Yekta A. (2011); " A First Principle Calculation of the Structural and Optical Properties of PbTiO<sub>3</sub> in Paraelectric Phase ", Chinese Journal of Physics, vol 50 (4), pp 628 - 637.
- Ponte F. M. et al., (2016); "Structural, Optical and Piezoelectric Properties of (Pb,Ba)(Ti,Fe)O<sub>3</sub> Perovskite: A Macroscopic and Nanoscale Properties Approach ", Journal of Materials Chemistry, vol 4, pp 9331 - 9342.
- Scott J. F. (2008); " Ferroelectrics Go Banana ", Journal of Physics Condensed Matter, vol 20, 021001.
- Turik A. V. and Khasabov A. G. (2000); " Origin of Ferroelectricity in PbTiO<sub>3</sub> " Ferroelectrics, vol 237 (1), pp 64 - 71.
- Zelezly V. et al., (2016); " The Variation of PbTiO<sub>3</sub> Bandgap at Ferroelectric Phase Transition ", Journal of Physics Condensed Matter, vol 28, 025501.
- Zhen X. et al., (2012);" Doping and Phase Transformation of Single Crystal Pure Perovskite PbTiO<sub>3</sub> Fibers with TiO<sub>6</sub> Edge Shared Octahedra ", Crystal Engineering Communication, vol 14, pp 4520 - 4524.