



---

---

## Stabilization Studies of Crystal Structure of Optimally Th-Doped Lead Zirconate Perovskite

**Khaled M. Elsabawy<sup>1,2,\*</sup>, Waheed F. El-Hawary<sup>2,3</sup>**

<sup>1</sup>Chemistry Department, Faculty of Science, Tanta University, 31725 - Tanta, Egypt

<sup>2</sup>Chemistry Department, Faculty of Science, Taif University, Taif City - 888, Alhawyah, Saudi Arabia

<sup>3</sup>Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

\*E-mail address: [khaledelsabawy@yahoo.com](mailto:khaledelsabawy@yahoo.com) , [ksabawy@hotmail.com](mailto:ksabawy@hotmail.com)

### ABSTRACT

The optimally thorium-doped  $\text{Pb}_{0.9}\text{Th}_{0.1}\text{ZrO}_3$  was selected for studying thorium doping effect on the structural parameters of lead zirconate crystal. The investigations were made on the low concentrations range of thorium doping  $0.0 \leq x \leq 0.25$  mole. The present investigations are concerned by confirming that thorium dopings play an important role as stabilizing agent inside internal structure of crystal lattice of  $\text{Pb}_{1-x}\text{Th}_x\text{ZrO}_3$  where  $x = 0.1$  mole. XRD-measurements indicated that Thorium dopant substitutes successfully on the A-sites of lead zirconate without damaging the main crystal structure at  $x = 0.1$  mole. Visualization and theoretical investigations were concerned by matching and comparison of bond distances, torsions on angles of investigated compound to clarify success of thorium doping on the perovskite structure.

**Keywords:** Crystal Structure; XRD; Visualization, Doping; Perovskite

### 1. INTRODUCTION

Complex lead-based perovskites with a chemical  $\text{PbB}'_1 = 2\text{B}''_1 = 2\text{O}_3$  formula have attracted considerable attention for many years because of their interesting physical properties

and wide industrial applications. Lead ytterbium niobate,  $\text{PbYb}_1 = 2\text{Nb}_1 = 2\text{O}_3$  (PYN), is a well known anti-ferroelectric with an ordered perovskite structure and its prototype crystal structure is space group  $\text{Fm}\bar{3}\text{m}$ . PYN is known to undergo 1<sup>st</sup>-order phase transition from the paraelectric to the antiferroelectric state at 302 °C [1,2].

Recently, Xu et al. reported that below the transition temperature, PYN has an ordered structure of orthorhombic symmetry with space group  $\text{Pbnm}$  and lattice parameters  $a_0 = 5.918$  Å,  $b_0 = 23.453$  Å and  $c_0 = 8.221$  Å [3,4]. For this compound, in addition to long range ordering of  $\text{Yb}^{3+}$  and  $\text{Nb}^{5+}$  ions in the B site, antiparallel displacements of  $\text{Pb}^{2+}$  ions in the prototype [110]p direction similar to PZ [5,6] are also confirmed from the superlattice reflections in the X-ray and electron diffraction patterns.

AFE materials have potential applications in micro-actuators, IR-detectors, digital memories, high energy storage capacitors and cooling devices [1-4]. Pure  $\text{PbZrO}_3$  (PZ) with a Curie point of 230 °C is the most stable AFE material at room temperature [5]. PZ-based materials in bulk and film forms are also the most extensively investigated AFE materials at present. There are a lot of reports on PZ-based AFE materials, such as:  $(\text{Pb},\text{La})\text{ZrO}_3$  (PLZ),  $(\text{Pb},\text{Ba})\text{ZrO}_3$  (PBZ),  $(\text{Pb},\text{Sr})\text{TiO}_3$  (PST),  $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr},\text{Ti},\text{Sn})\text{O}_3$  (PLZST) and  $(\text{Pb}_{0.99}\text{Nb}_{0.02})(\text{Zr},\text{Ti},\text{Sn})\text{O}_3$  (PNZST), and so on [6-14]. Most of the compounds with the general formula  $\text{ABO}_3$  have the perovskite structure [15] in which "A" may be a mono-, di-, or tri-valent cation and "B" may be a penta-, tetra-, or tri-valent cation [16]. Solid solutions of lead zirconate-titanate ( $\text{PbZrO}_3 - \text{PbTiO}_3$  system) attract the attention of researchers and developers in various fields of science and technology because of their potential applications in memories, microwave tunable capacitors, micro-electromechanical systems (MEMS), pyroelectric sensors and electro-optical switches [17-28].

Preparation of lead zirconate or (PZ) by conventional processes requires the use of high temperatures at which  $\text{PbO}$  volatility becomes significant. It is reported that the full development of pure  $\text{PbZrO}_3$  phase occurs after sintering at temperatures above 1200 °C for at least 2h in controlled  $\text{PbO}$  atmospheres [29-32]. PZ powders can also be prepared by wet-chemistry based process routes [29-38], which include chemical co-precipitation [33,34], micro-emulsion [35] and Sol-gel technique [36-38].

The essential goal of present studies are studying the effect of low concentration thorium doping tetra-valent dopant ( $x = 0.1$  mole) on the A-site of perovskite on the stabilization of crystal structural of optimally Th-doped lead zirconate Tetragonal  $\leftrightarrow$  Orthorhombic Phase.

## **2. EXPERIMENTAL**

### **2. 1. Samples Preparation**

The optimally thorium-doped sample with general formula  $(\text{Pb}_{1-x}\text{Th}_x\text{ZrO}_3)$  where  $x = 0.1$  mole was synthesized by the conventional solid state method and sintering procedure using appropriate amounts of  $\text{PbCO}_3$ ,  $\text{Zr}(\text{CO}_3)_2$  and  $\text{ThO}_2$  each of purity >99%. The mixture were ground in an agate mortar for 1h. The finely ground powder were subject to firing at 800 °C for 20 hrs then reground and pressed into pellets under compressive strength 8 Ton/m<sup>2</sup> and the pellet dimensions were (thickness 0.2 cm & diameter 1.2 cm). Sintering were carried out at 850 °C for 48 hrs. Then the furnace is cooled slowly down to room temperature. 10%

more off-stoichiometric  $Pb_3O_4$  were used in order to compensate lead deficient due to its sublimation during sintering process.

### 2. 2. A. X-Ray diffraction (XRD):

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground powders of optimally thorium-doped sample with general formula  $(Pb_{1-x}Th_xZrO_3)$  where  $x = 0.1$  mole in the range ( $2\theta = 10-90^\circ$ ) using Cu-K $\alpha$  radiation source and a computerized [Steo-Germany] X-ray diffractometer with two theta scan technique. A visualized studies of crystal structure were made by using Diamond Molecular Structure version 3.2 package, Germany and Mercury 2.3-BUILD RC4-UK. A visualization study made is concerned by matching and comparison of experimental and theoretical data of atomic positions, bond distances, oxidation states and bond torsion on the crystal structure formed. Some of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting ICSD-Fiz-Karlsruhe-Germany.

## 3. RESULTS AND DISCUSSION

### 3. 1. Phase Identification

Fig. (1) displays the X-ray diffraction pattern of optimally Th-doped  $PbZrO_3$  ( $Pb_{1-x}Th_xZrO_3$ ) perovskite where  $x = 0.1$  mole. Analysis of the corresponding  $2\theta$  values and the inter-planar spacing  $d(\text{\AA})$  proved that, the compound mainly belongs to orthorhombic crystal structure  $a \neq b \neq c$  with *Cmmm* space group.

The unit cell dimensions were calculated using the parameters of the most intense X-ray reflection peaks and were found to be  $a = 11.8642 \text{ \AA}$ ,  $b = 12.09 \text{ \AA}$  and  $c = 8.6345 \text{ \AA}$  for the pure  $PbZrO_3$ . Even though PZ was first reported to be tetragonal [41] at room temperature, single-crystal studies revealed the structure to be orthorhombic [42]. The present XRD patterns of optimally thorium doped- PZ is in full agreement with results reported by Fang et al. [34] and Kong et al. [36].

It was observed that  $c$ -axis exhibits slight length compression by increasing Th-content as shown in Fig. (1a) due to ionic radius of Th-ion ( $Th^{4+} = 102 \text{ pm}$ ) which is smaller than that of Pb-ion such that,  $Pb^{2+} = 120 \text{ pm}$ .

Although most of the compounds with the general formula  $ABO_3$  have the perovskite structure as reported in [15] in which "A" may be a mono-, di-, or tri-valent cation and "B" may be a penta-,tetra-,or tri-valent cation [16]. In the present investigation tetravalent thorium succeeds within the investigated range to replace lead ( $Pb^{+m}$  where  $2 \leq m \leq 4$ ) in the main crystalline structure of perovskite without damaging the original orthorhombic perovskite crystal.

### 3. 2. Structure Visualization

To confirm the success of tetra-valent thorium to replace lead on the lattice structure of perovskite (A-site) a visualized crystal structure investigations were made depending upon single crystal data of lead zirconate supplied from ICSD-data bank Karlsruhe-Germany code number ICSD# 86443 [43] see Figs. 2a,b.

Fig. 2a shows 2D-framenet structure of orthorhombic perovskite structure displaying the different geometries of (Pb/Th) = A-sites and Zr = B-sites beside displaying the different orientation of polyhedron-zirconate inside unit cell of perovskite structure as clear in Fig. 2b.

Fig. 2c shows the indexed XRD-profile for pure lead zirconate with  $I_0$  index = {318} which lies at  $2\theta \sim 35.8$ . The most intense reflection peaks ( fingerprint ) of lead zirconate were represented by red circles as clear in Fig. 2c. It was noticeable that at two theta  $\sim 51.4$  there is doublet peak characteristics for lead zirconate perovskite structure indexed by {318}, the same doublet peak was observed also nearly in the same location in the visualized theoretical patterns constructed for thorium-doped zirconate as clear in Fig. 2d which confirm that thorium can substitute successfully on A-sites of perovskite structure without destroying the original orthorhombic phase.

The comparison between theoretical pattern Fig. 2d and the experimental XRD-profile of thorium-doped lead zirconate Fig.1 ,2c one can concludes that there are moderate to strong fitting between the both profiles which confirm success of thorium doping within investigated range (0.05-0.25 mole) .

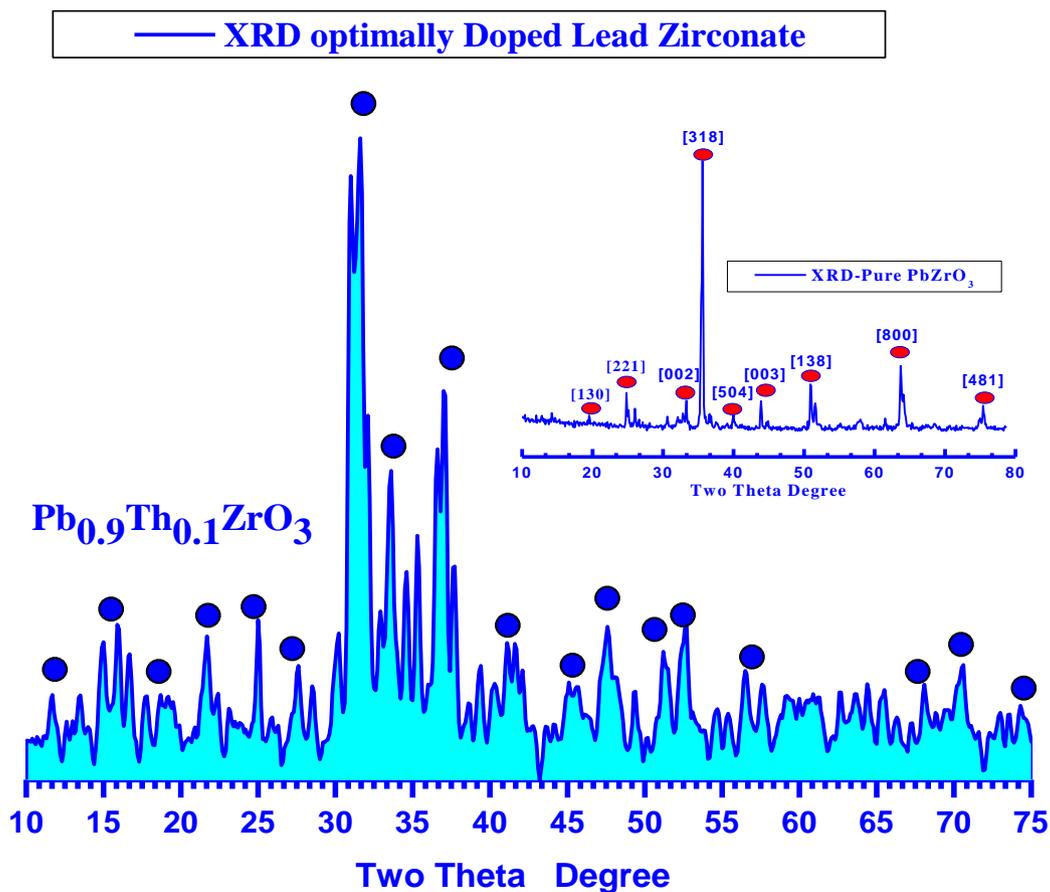


Fig. 1. RT- XRD patterns for optimally thorium-doped  $Pb_{0.9}Th_{0.1}ZrO_3$  .

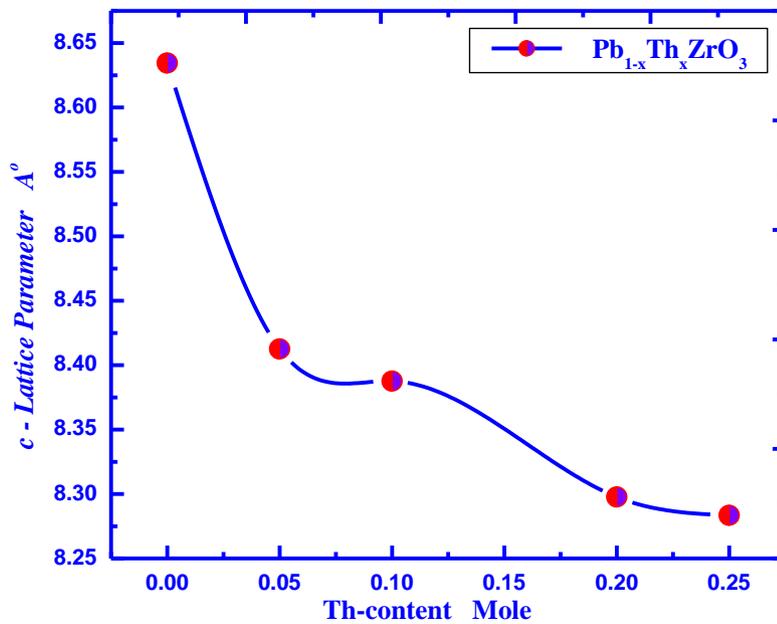


Fig. 1a. Variation of c-axis lattice parameter as function of thorium content.

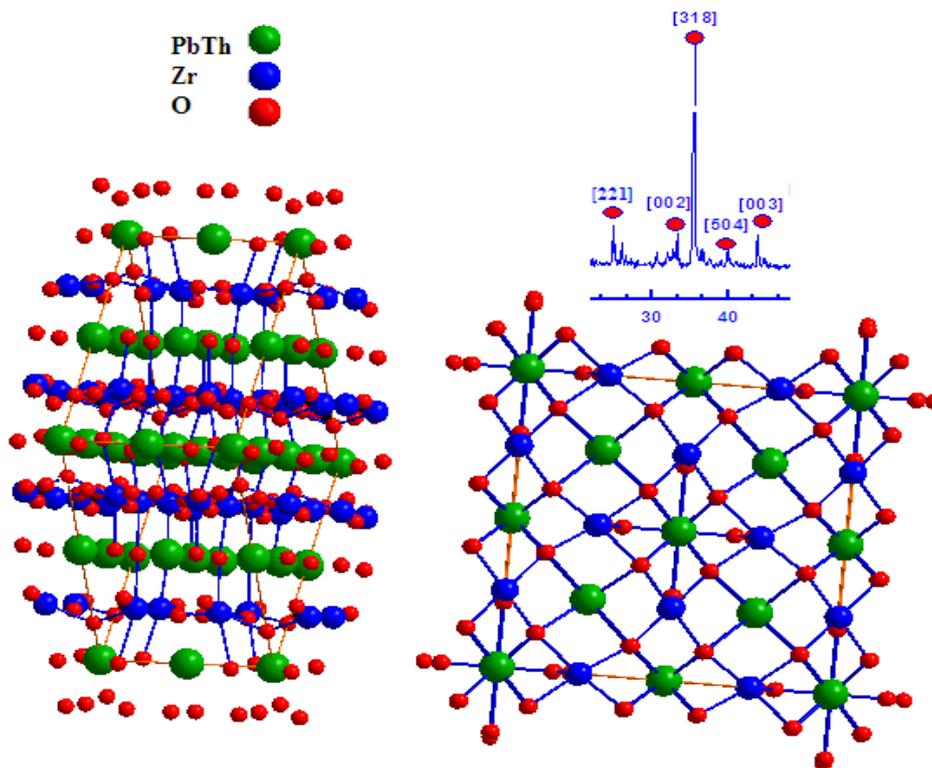


Fig. 2a. 2D-framenet and side view of thorium-doped lead zirconate perovskite unit cell.

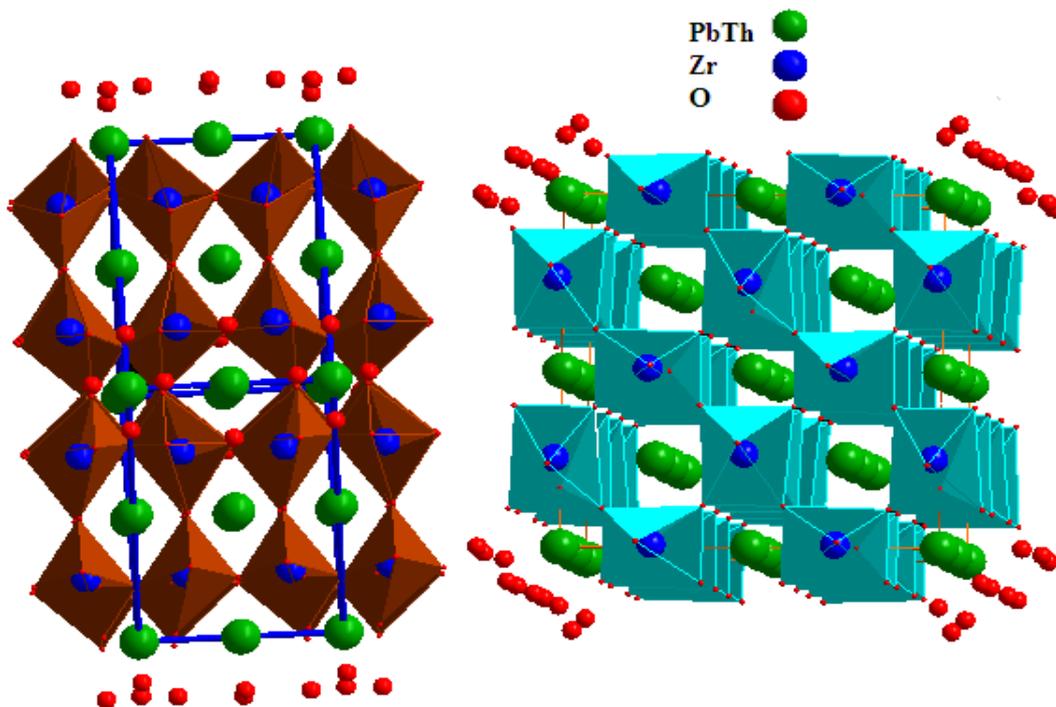


Fig. 2b. Unit cell of Th-doped zirconate displaying  $ZrO_6$ -polyhedral units.

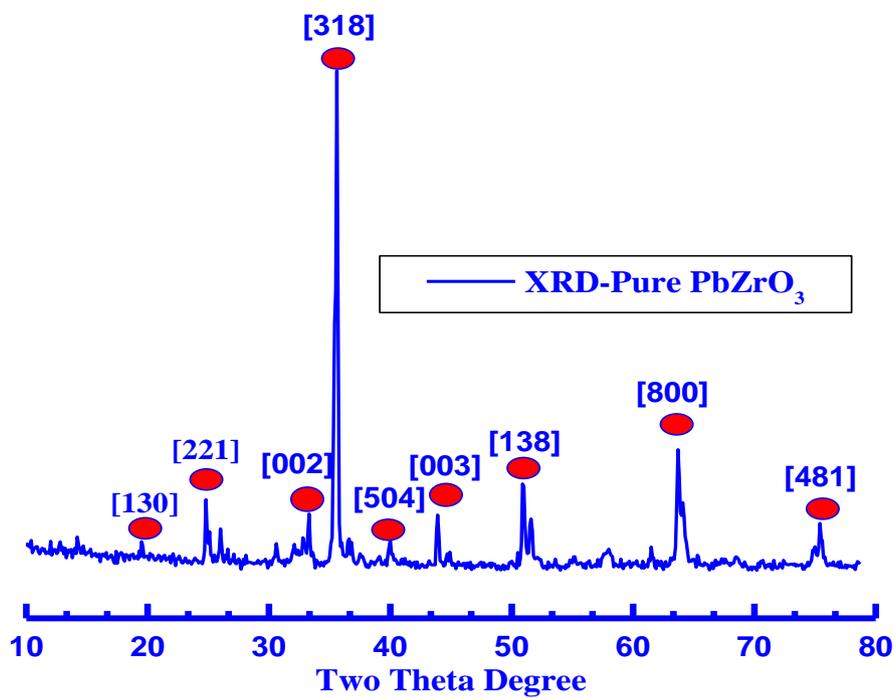
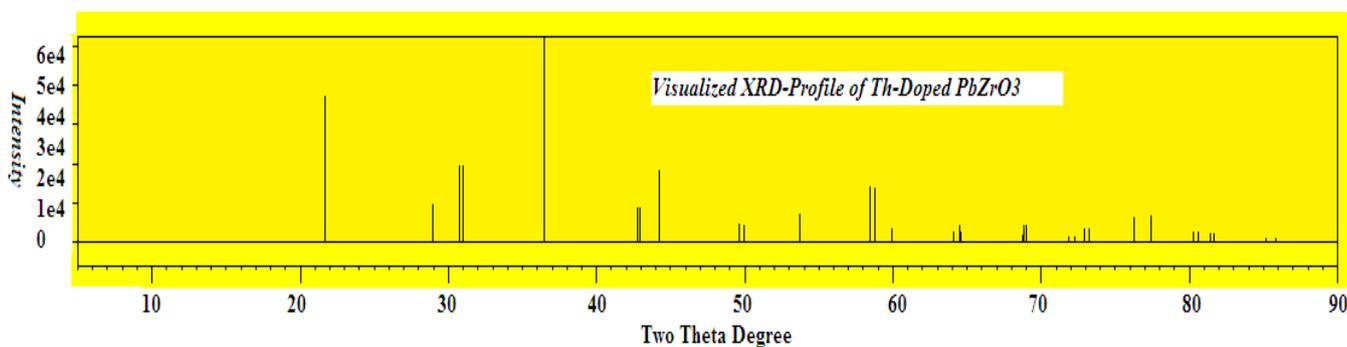


Fig. 2c. Indexed XRD-profile recorded for pure lead zirconate.



**Fig. 2d.** Visualized XRD-profile recorded for Th-doped lead zirconate.

Tables 1 & 2, show some selected bond distances and angles inside unit cell of Th-doped –perovskite zirconate. From Table 1 one can observe that there are five types of A-sites (Pb/Th) according to the data found with five different environment namely; Pb<sub>1</sub>/Th<sub>1</sub>, Pb<sub>2</sub>/Th<sub>2</sub>, Pb<sub>3</sub>/Th<sub>3</sub>, Pb<sub>4</sub>/Th<sub>4</sub> and Pb<sub>5</sub>/Th<sub>5</sub>, it was noticeable that the bond distances estimated for type one of A-sites (Pb<sub>1</sub>/Th<sub>1</sub>) were recorded and exhibited minimum bond distances with neighboring oxygen atoms as clear in Table 1 since b<sub>1</sub>/Th<sub>1</sub>-O<sub>1</sub> = 1.94 Å and Pb<sub>1</sub>/Th<sub>1</sub>-O<sub>5</sub> = 2.157 Å. While maximum bond distance were recorded for Pb<sub>5</sub>/Th<sub>5</sub>-O<sub>5</sub> which found to be equal 2.4836 Å.

These results are in full agreement with Fang et al. [34] who reported that the average bond distances recorded inside the crystal lattice of lead zirconate were found 2.47 Å for lead type 1 Pb<sub>1</sub>-O and 2.58 Å for lead type 2 Pb<sub>2</sub>-O respectively .

The analysis of bond distances and angles inside unit cell of Th-doped-lead zirconate indicated that there are two types of zirconium environment nominated as Zr<sub>1</sub> and Zr<sub>2</sub> as described in Table 2. This is beside six types of oxygen environment symbolized as O<sub>1</sub>, O<sub>2</sub>, O<sub>3</sub>, O<sub>4</sub>, O<sub>5</sub> and O<sub>6</sub> respectively .

It was noticeable that the bond distances between Zr-O recorded minimum for (Zr<sub>1</sub>-O<sub>3</sub> = 1.50 Å) and maximum one is for Zr<sub>1</sub>-O<sub>5</sub> with bond length = 2.22 Å while the other type was found to be 1.57 is for Zr<sub>2</sub>-O<sub>2</sub> and 2.029 for Zr<sub>2</sub>-O<sub>6</sub> respectively.

From Table 2 it was observed also that there are six types of oxygen symbolized as O<sub>1</sub>, O<sub>2</sub>, O<sub>3</sub>, O<sub>4</sub>, O<sub>5</sub> and O<sub>6</sub> are found inside lattice recorded bond distance values 1.83, 1.57, 1.5, 1.6, 2.007 and 2.029 Å for O<sub>1</sub>-Zr<sub>1</sub> , O<sub>2</sub>-Zr<sub>2</sub> , O<sub>3</sub>-Zr<sub>1</sub> , O<sub>4</sub>-Zr<sub>2</sub> , O<sub>5</sub>-Zr<sub>2</sub> and O<sub>6</sub>-Zr<sub>2</sub> Å respectively.

These results are compatible with average bond distances recorded for the two types of zirconium (Zr<sub>1</sub> and Zr<sub>2</sub> )-Oxygen inside crystal lattice reported in [34] for lead zirconate with small differences due to thorium doping effect. They [34] recorded the following bond distances for the two different types of zirconium Zr<sub>1</sub>-O<sub>2</sub> = 2.111 Å, Zr<sub>1</sub>-O<sub>1</sub> = 2.098 Å, Zr<sub>2</sub>-O<sub>3</sub> = 2.162 Å, Zr<sub>2</sub>-O<sub>4</sub> = 2.140 Å and Zr<sub>2</sub>-O<sub>5</sub> = 2.044 Å respectively .

The analysis of visualized structure concerning by XRD-pattern, bond distances, angles, torsion and lattice volume confirmed that stability of doped-lead zirconate lattice is relatively high specially there is no violation in most data recorded for thorium-doped- lead zirconate and consequently reflects success of thorium doping in the investigated range (x = 0.05-0.25 mole).

**Table 1.** Selected bond distances and angles inside crystal lattice of Th-doped-lead zirconate.

Atom <sub>1</sub>	Atom <sub>2</sub>	Sym. Oper.1	d <sub>1-2</sub>	Atom <sub>3</sub>	Sym. Opr.2	d <sub>1-3</sub>	Angle 213 <sup>^</sup>
Pb1 Th1	O1	-x, -y, z	1.9461	O1	x, y, z	1.9461	180.000
	O1	-x, -y, z	1.9461	O5	x, y, z	2.1570	124.046
	O5	x, y, z	2.1570	O5	x, -y, -z	2.1570	111.908
	O5	x, y, z	2.1570	O5	-x, y, -z	2.1570	97.369
Pb2 Th2	O6	0.5-x, 0.5-y, z	2.4102	O6	0.5+x, 0.5-y, -z	2.4102	118.991
	O6	0.5-x, 0.5-y, z	2.4102	O6	0.5-x, -0.5+y, -z	2.4102	115.995
	O6	0.5-x, 0.5-y, z	2.4102	O6	0.5-x, 0.5-y, -z	2.4102	85.581
	O6	0.5-x, 0.5-y, z	2.4102	O6	0.5+x, -0.5+y, -z	2.4102	180.000
Pb4 Th4	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5+x, -0.5+y, 1-z	2.2861	67.935
	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5+x, 0.5-y, 1-z	2.2861	101.369
	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5-x, 0.5-y, 1-z	2.2861	64.710
	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5-x, 0.5-y, z	2.2861	112.065
Pb5 Th5	O5	0.5-x, 0.5-y, z	2.4836	O5	0.5-x, 0.5-y, -z	2.4836	51.553
	O5	0.5-x, 0.5-y, z	2.4836	O5	x, y, -z	2.4836	180.000
	O5	0.5-x, 0.5-y, z	2.4836	O5	x, y, z	2.4836	128.447
	O5	x, y, -z	2.4836	O5	x, y, z	2.4836	51.553

**Table 2.** Selected bond distances and angles inside crystal lattice of Th-doped-lead zirconate.

Atom <sub>1</sub>	Atom <sub>2</sub>	Sym. Oper.1	d <sub>1-2</sub>	Atom <sub>3</sub>	Sym. Opr.2	d <sub>1-3</sub>	Angle 213 <sup>^</sup>
Zr1	O3	x, y, z	1.5066	O1	x, y, z	1.8329	140.289
	O1	x, y, z	1.8329	O5	x, y, z	2.2210	56.003
	O5	x, -y, z	2.2210	O5	x, y, z	2.2210	79.761
Zr2	O2	x, y, z	1.5781	O4	x, y, z	1.6000	153.370

	<b>O4</b>	<b>x, y, z</b>	<b>1.6000</b>	<b>O5</b>	<b>-x, y, z</b>	<b>2.0079</b>	<b>94.843</b>
	<b>O5</b>	<b>-x, y, z</b>	<b>2.0079</b>	<b>O5</b>	<b>x, y, z</b>	<b>2.0079</b>	<b>73.944</b>
	<b>O6</b>	<b>-x, y, z</b>	<b>2.0294</b>	<b>O6</b>	<b>x, y, z</b>	<b>2.0294</b>	<b>78.010</b>
<b>O1</b>	<b>Zr1</b>	<b>x, y, z</b>	<b>1.8329</b>	<b>Zr1</b>	<b>x, -y, -z</b>	<b>1.8329</b>	<b>122.436</b>
	<b>O5</b>	<b>x, y, z</b>	<b>1.9338</b>	<b>O5</b>	<b>x, -y, -z</b>	<b>1.9338</b>	<b>135.099</b>
<b>O2</b>	<b>Zr2</b>	<b>-x, y, -z</b>	<b>1.5781</b>	<b>Zr2</b>	<b>x, y, z</b>	<b>1.5781</b>	<b>145.486</b>
	<b>O5</b>	<b>-x, y, -z</b>	<b>1.9460</b>	<b>O5</b>	<b>x, y, -z</b>	<b>1.9460</b>	<b>76.71</b>
<b>O3</b>	<b>Zr1</b>	<b>x, -y, 1-z</b>	<b>1.5066</b>	<b>Zr1</b>	<b>x, y, z</b>	<b>1.5066</b>	<b>158.142</b>
<b>O4</b>	<b>Zr2</b>	<b>-x, y, 1-z</b>	<b>1.6000</b>	<b>Zr2</b>	<b>x, y, z</b>	<b>1.6000</b>	<b>161.253</b>
<b>O5</b>	<b>O1</b>	<b>x, y, z</b>	<b>1.9338</b>	<b>O2</b>	<b>x, y, z</b>	<b>1.9460</b>	<b>109.573</b>
	<b>O2</b>	<b>x, y, z</b>	<b>1.9460</b>	<b>Pb1 Th1</b>	<b>x, y, z</b>	<b>2.1570</b>	<b>74.958</b>
	<b>Zr2</b>	<b>x, y, z</b>	<b>2.0079</b>	<b>Pb1 Th1</b>	<b>x, y, z</b>	<b>2.1570</b>	<b>106.153</b>
	<b>Pb1 Th 1</b>	<b>x, y, z</b>	<b>2.1570</b>	<b>O5</b>	<b>x, y, -z</b>	<b>2.1600</b>	<b>59.954</b>
	<b>Zr1</b>	<b>x, y, z</b>	<b>2.2210</b>	<b>O5</b>	<b>-x, y, z</b>	<b>2.4152</b>	<b>136.875</b>
<b>O6</b>	<b>Zr2</b>	<b>x, y, z</b>	<b>2.0294</b>	<b>Zr10.5</b>	<b>-x, 0.5-y, z</b>	<b>2.0946</b>	<b>164.190</b>
	<b>Zr1</b>	<b>0.5-x, 0.5-y, z</b>	<b>2.0946</b>	<b>Pb4 Th4</b>	<b>-0.5+x, 0.5+y, z</b>	<b>2.2861</b>	<b>98.639</b>
	<b>Pb4 Th 4</b>	<b>-0.5+x, 0.5+y,z</b>	<b>2.2861</b>	<b>Pb2 Th2</b>	<b>-0.5+x, 0.5+y, z</b>	<b>2.4102</b>	<b>82.106</b>
	<b>Pb2 Th 2</b>	<b>-0.5+x, 0.5+y,z</b>	<b>2.4102</b>	<b>O6</b>	<b>x, 1-y, z</b>	<b>2.4468</b>	<b>59.495</b>

#### 4. CONCLUSIONS

The conclusive remarks inside this article can be summarized in the following points;

- 1- Low concentrations range of thorium doping  $0.0 \leq x \leq 0.25$  mole are valid with high degree of success and stability.
- 2- The analysis of visualized structure concerning by XRD-pattern, bond distances, angles, torsion and lattice volume confirmed that stability of doped-lead zirconate lattice is relatively high specially there is no violation in most data recorded for thorium-doped- lead zirconate and consequently reflects success of thorium doping in the investigated range ( $x = 0.05-0.25$  mole).

## References

- [1] S.E. Park, K. Markowski, S. Yoshikawa and L.E. Cross, *J. Am. Ceram. Soc.* 80 (1997), 407.
- [2] J. Parui and S.B. Krupanidhi, *J. Appl. Phys.* 100 (2006), pp. 044102.
- [3] Z.K. Xu, J.W. Zhai and W.H. Chan, *Appl. Phys. Lett.* 88 (2006) 132908.
- [4] G.R. Love, *J. Am. Ceram. Soc.* 73 (1990) 323.
- [5] S. Chattopadhyay, P. Ayyub, V.R. Palkar, M.S. Multani, S.P. Pai, S.C. Purandare and R. Pinto, *J. Appl. Phys.* 83 (1998) 7808.
- [6] S.S.N. Bharahwaja and S.B. Krupanidhi, *Thin Solid Films* 423 (2003) 88.
- [7] B.M. Xu, Y.H. Ye and L.E. Cross, *J. Appl. Phys.* 87 (2000) 2507.
- [8] J.W. Zhai, M.H. Cheung, Z.K. Xu and X. Li, *Appl. Phys. Lett.* 81 (2002) 3621.
- [9] H.W. Chen, C.R. Yang, J.H. Zhang, Y.F. Pei and Z. Zhao, *J. Alloys Compd.* 486 (2009) 615.
- [10] X.H. Hao and J.W. Zhai, *J. Cryst. Growth* 310 (2008) 1137.
- [11] X.H. Hao, J.W. Zhai and X. Yao, *J. Cryst. Growth* 311 (2008) 90.
- [12] L.B. Kong, J. Ma, W. Zhu and O.K. Tan, *J. Alloys Compd.* 322 (2001) 290-297.
- [13] P. Charoonsuk, S. Wirunchit, R. Muanghlua, S. Niemcharoen, B. Boonchom and N. Vittayakorn, *J. Alloys Compd.* 3 (2010) 23-28.
- [14] X.H. Hao, Z.Q. Zhang, J. Zhou, S.L. An and J.W. Zhai, *J. Alloys Compd.* 501 (2010) 358-361.
- [15] R. Smoluchowski and N. Kurti "Solid State Physics-vol.5: Structure, Properties, &Preparation of Perovskite-Type Compounds", Pergamon Press Inc., (1969) 3-11.
- [16] A. Wold and K. Dwig "Solid State Chemistry" Chapman and Hall Inc., (1993) 127, 136, 137.
- [17] J.F. Scott, C.A. Araujo, *Science* 246 (1989) 1400.
- [18] Y.H. Xu, *Ferroelectric Materials and Their Applications*, North-Holland, Amsterdam, (1991) 206.
- [19] R. Watton, P. Manning, *Proc. SPIE* 3436, (1998) 541.
- [20] V.E. Wood, J.R. Bush, S.D. Ramamurthi, S.L. Swartz, *J. Appl. Phys.* 71 (1992) 4557.
- [21] K.D. Preston, G.H. Haertling, *Appl. Phys. Lett.* 60 (1992) 2831.
- [22] W.G. Liu, J.S. Ko, W.G. Zhu, *Infrared Phys. Technol.* 41 (2000) 169.
- [23] D. Dimos, C.H. Muller, *Annu. Rev. Mater. Sci.*, 28 (1998) 397.
- [24] D.L. Polla, *Microelectron. Eng.*, 29 (1995) 51.

- [25] Y. Nemirovsky, A. Nemirovsky, P. Mural, N. Setter, *Sensors Actuators A* 56, (1996) 239.
- [26] G. Heartling, *J. Am. Ceram. Soc.*, 82 (1999) 797.
- [27] K. Singh, *Ferroelectrics*, 94 (1989) 433.
- [28] M.T. Lanagan, J.H. Kim, S. Jang, and R.E. Newnham, *J. Am. Ceram. Soc.* 71 (1988) 111.
- [29] K. Wakino, M. Murata, and H. Tamura, *J. Am. Ceram. Soc.*, 69 (1986) 34-37.
- [30] W.N. Lawless, *Phys. Rev. B*, 30 (1984) 6555-6559.
- [31] D.M. Ibrahim and H.W. Henniek, *Trans. J. Br. Ceram. Soc.*, 80 (1981) 18-22.
- [32] Y.S. Rao, C.S. Sunandana, *J. Mater. Sci. Lett.*, 11 (1992) 595-597.
- [33] E.E. Oren, E. Taspinar and A.C. Tas, *J. Am. Ceram. Soc.*, 80(10) (1997) 2714-2716.
- [34] J. Fang, J. Wang, S. Ng, L. M. Gan, C. Quek and C.H. Chew, *Mater. Lett.*, 36 (1998) 179-185.
- [35] B. Matthes, G. Tomandl and G. Werner, *J. Eu. Ceram. Soc.*, 19,6-7, (1999)pp.1387-1389.
- [36] L.B. Kong, J. Ma, W. Zhu and O.K. Tan, *Materials Letters*, 49(2) (2001) 96-101.
- [37] S.S.N. Bharadwaja, S.B. Krupanidhi, *Thin Solid Films* 423 (2003) 88-96.
- [38] Z.G. Hu, F.W. Shi, T. Lin, Z.M. Huang, G.S. Wang, Y.N. Wu, J.H. Chu, *Physics Letters A*, 230 (2004) 478-486.

( Received 24 November 2015; accepted 12 December 2015 )