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SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE LEAD-ZIRCONIUM TITANATE BY TARTRATE PRECURSOR

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ABSTRACT

The present study aims at synthesis of lead - zirconium titanate (PZT) nanopowders via tartrate precursor methods. All the parameters affecting the synthesis conditions were studied and the optimum conditions were determined. The resultant powders were investigated by thermal analyzer (TG-DSC), X-ray diffraction analysis (XRD), Scanning electron microscope (SEM) and Energy Dispersive x-ray spectroscopy (EDX). The results showed that the perovskite phase was started to form at much lower annealing temperature ($> 490^{o}C$) and the powder consists mainly of $PbTiO_3$ and minor $PbZr_xTi_{1-x}O_3$, and small amounts of unreacted zirconium oxide and lead oxide. $PbTiO_3$ gradually decreased and $PbZr_xTi_{1-x}O_3$ gradually increased with the increase of annealing temperature up to $900^{o}C$ was $PbZr_xTi_{1-x}O_3$ the only detectable phase. Thermal analysis, XRD and EDX analysis indicated that perovskite phase was started to decompose at $> 950^{o}C$ due to the evaporation of lead.

KEYWORDS: Tartrate Precursor, Lead - Zirconium Titanate, PZT, Thermal Analysis, XRD, SEM, EDX

INTRODUCTION

Piezoelectric ceramic materials or what is called ferroelectric materials are materials that produce a voltage when stress is applied while a voltage across the sample will produce stress within the sample. Piezoelectric ceramics are important electronic materials that have a wide range of industrial and commercial applications. Piezoelectric materials are keys to many modern technologies. Computers use piezoelectric memories, security systems use pyroelectric sensors, cell phones used better dielectrics to improve antenna reception, optical communication components require electro-optic films and piezoelectric transducers are used for many purposes, ranging from microspeakers to medical ultrasound[1-3]. Among the piezoelectric materials, the perovskite group is the most important and thus the most widely studied because of their superior electrical properties[4-6]. Perovskite is usually expressed as ABO_3. Taking $PbTiO_3$ as an example [7,8], the structured consists of a corner-linked network of oxygen octahedra, creating an octahedral cage (B-site) and the interstices (A-sites). Ti^{4+} ions occupy the B-site while Pb^{2+} ions occupy the A-site.

Traditional materials design looks at measurable quantities, such as dielectric constant, or piezoelectric coefficient. Recently, however, the issue of environmental impact is becoming more important as a design parameter. This has spurred a search for alternative ferroelectrics to the many lead based system currently in use. The materials' performances are closely related to the ways they are processed. Synthesis method of ferroelectric powders has played a significant role in determining the microstructure, electrical and optical properties of ferroelectric ceramics [9–11]. Fully dense ferroelectric ceramics (>95% of theoretical density) are required by most applications, which are because of several reasons: Firstly, a full densification of ferroelectric ceramics ensures to achieve the maximized performance. For example, the dielectric constant of ferroelectric ceramics usually increases with increasing density. This is because the relative dielectric constant of pores/vacuums is unit. Secondly, the presence of pores is generally a cause of high loss tangent, since porosity could form provide conduction path for electricity and thus could be a main contribution to dielectric loss tangent,

as conduction loss. Moreover, electrical conduction caused by porosity is also responsible for degraded electrical breakdown strength. Optical properties of transparent ferroelectric ceramics are extremely sensitive to porosity. Pores reduced the transparency of ferroelectric ceramics by acting as scattering centers. Finally, mechanical strength, sometimes a critical requirement for some specific applications, such as piezoelectric transducers and actuators, is directly determined by the density of the materials used.

Generally, the densities of ferroelectric ceramics increase with increasing sintering temperature. However, too high temperature is not suitable for lead - containing ferroelectric materials, which is due the volatility characteristic of lead. High temperature also leads to abnormal grain growth (secondary grain growth). The presence of exaggeratedly grown grains is harmful to the performance for most ferroelectric ceramics. To effectively enhance the densification of ferroelectric ceramics at relatively low temperatures, various attempts have been made and have been widely reported in the literature. The main strategies that have been employed to reduce the sintering temperature of ferroelectric ceramics are the use of fine/ultrafine powders and the addition of sintering aids. Fine/ultrafine powders can be synthesized by various wet-chemical methods, as discussed later. Grain size is another important factor that determines the properties, such as dielectric constant, tetragonality (c/a ratio), phase transition temperature (TC), polarization, piezoelectric and pyroelectric coefficients, of ferroelectric ceramics [12- 14]. The variation in grain size with sintering temperature is similar to that of density, i.e. grain size increases with increasing sintering temperature. There is a critical grain size for most ferroelectric ceramics below which many properties, such as piezoelectric and pyroelectric, cannot be well developed. There is also a critical grain size beyond which most properties are saturated, i.e. the properties of ferroelectric materials do not always increase with grain size. Both critical sizes are depending on types of materials or compositions of given materials. In contrast to many other ferroelectrics, there is an anomalously high dielectric constant for ferroelectric ceramic materials of fine grains, which has not been fully understood till now [3,15].

It is well known that materials' performances are closely related to the ways they are processed. Synthesis method of ferroelectric powders has played a significant role in determining the microstructure, electrical and optical properties of ferroelectric ceramics. Ferroelectric powders were conventionally synthesized via a solid-state reaction process, using constituent oxides as the starting materials. Due to their relatively rough grains, these powders require relatively high sintering temperature to obtain ferroelectric ceramics with designed compositions and desired performances. This study focused on developing and understanding the synthesis behaviour of nanosized lead - zirconium titanate powders via organic carboxylic acid precursor methods.

The advantages of organic acid process are that the low cost starting materials, low synthesis temperature, fine microstructure, high performance, homogeneity, narrow particle size distribution and friendly environment procedure[16,17]. From our knowledge, no many data mentioned in literature about the synthesis of lead titanate nanopowders via organic acid precursors using titanium dioxide as a source of titanium. The process depend on the complexation of metallic salts with aqueous solution of organic acid, the formed complex solutions was evaporated at low temperature from 60 to $100^{o}C$ until viscous resin formed, the formed polymer resin was dried , then calcined at relatively low temperature from 600-$1100^{o}C$.

The present study aims at synthesis of lead - zirconium titanate ($PbZr_{0.6}Ti_{0.4}O_3$) nanopowders via organic acid precursor methods. Tartaric acid was used as source carboxylic acid. Thermal analysis of the un-annealed precursors was carried out. The effects of annealing temperature (600-$1100^{o}C$) on the phase formation and microstructure were investigated. The formed powders were characterized by X-ray diffraction analysis (XRD) and Scanning electron microscope (SEM).

EXPERIMENTAL WORK

The tartrate precursor method was applied for the preparation of Lead-Zirconium titanate ($PbZr_{0.6}Ti_{0.4}O_3$). The tartaric acid precursor technique involves the preparation of aqueous solution of the required cation, the chelation of cations in solution by addition of tartaric acid then, raising the temperature of the solution until formation the precursor. The precursor is calcined at low temperature compared by other methods to form the powders. The tartaric acid was not only used to form stable complexes with starting metallic ions but also it used as organic rich fuel. The process is very simple and available for most of piezoelectric materials. Pure chemical grade of Lead nitrate, Zirconium oxide, Titanium dioxide in the presence of stoichiometric amount of tartaric acid were used as starting materials. The mixtures of Pb-Zr-Ti solutions firstly prepared and then stirred for 15 minute on hot plate magnetic stirrer, followed with addition of an aqueous solution of tartaric acid to the mixtures with stirring. The solution was evaporated to $80^{\circ}C$ with constant stirring until dryness and then dried in a dryer at $100^{\circ}C$ overnight. The dried powders obtained as lead-zirconium titanate precursors. Thermal analysis of the un-annealed precursors was carried. The rate of heating was kept at $10^{\circ}C/min$ between room temperature and $1200^{\circ}C$. The measurements were carried out in a current of argon atmosphere.

Phase composition and structure were determined using X-ray diffraction (XRD) analysis. The analyses were performed on a Brucker axis D8 diffractometer using Cu-K$_\alpha$ (λ =1.5406) radiation and secondary monochromator in the range 2θ from 10° to 70°. Identity of the phases present was determined by matching the experimental pattern with standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). The size and morphology of the synthesized particles were were directly imaged and determined using scanning electron microscopy (SEM). Qualitative analysis for the different elements in the $PbZr_{0.6}Ti_{0.4}O_3$ powders sample was used to clarify the distribution of each element in the perovskite powder by making maps for Pb, Zr, Ti and O while semiquantitatively analyzed for elemental composition (spot analysis) were conducted by Energy Dispersive x-ray spectroscopy (EDX)).

RESULTS AND DISCUSSIONS

Thermal decomposition studies of the precursors were analyzed using the DSC/TGA technique in air atmosphere at $10^{\circ}C/min$. Fig. 1 displays the DSC and TG curves of the tartrate precursor. The absorbed water can be removed by heating the tartrate precursor up to $150^{\circ}C$ which leads to a weight loss (wl) of ~3 wt% in TG curve. After dehydration of the tartrate precursor, the DSC/TG curve (Fig. 1) showed that the tartrate metal complex decomposition involves mainly two steps. The first exothermic peak (1) occured in the temperature range of $150–227^{\circ}C$ in the DSC curve along with an observed weight loss of ~ 40 wt% in TG curve, which is caused by the decomposition of the tartrate precursor into both metal oxide and gases (CO_2 and CO) through different steps. The 2nd and 3rd exothermic peaks (2&3) then occurs between 227 and $420^{\circ}C$, resulting in a further weight loss of~12 wt%, was most likely caused by the decomposition of carboxylates. Thereafter ($460^{\circ}C$), no further weight loss was evident in the TG curve, indicating the completion of the tartrate-chain decomposition process. However, the DSC curve showed a minor exothermic peak at temperatures of $490^{\circ}C$ (4). This peak was corresponding to the solid – solid interaction of PbO, ZrO_2 and TiO_2 to form a nanosized perovskite $PbZr_{0.6}Ti_{0.4}O_3$. In this case, nanosized $PbZr_{0.6}Ti_{0.4}O_3$ can be obtained at much lower temperature as compared to conventional ceramic method. The enlarge zone of this DSC curve showed that the exothermic peak started at $490^{\circ}C$ up to $950^{\circ}C$ may result from perovskite phase crystallization. The last endothermic peak started after $950^{\circ}C$ may be caused by the decomposition of the newly formed lead zirconium titanate oxide which will discuss latter in the XRD results of this work.

Powder XRD patterns of the annealed powders were given in Fig. 2. In general, the strongest reflections apparent in the majority of the XRD patterns indicated the formation of two lead zirconate titanate phases. These can be matched

with JCPDS file numbers 74-2495 and 89-1275 for the $PbTiO_3$ and $PbZr_{0.9}Ti_{0.1}O_3$, respectively. At annealing temperature 600^oC for 2h, the powder was consists mainly of perovskite $PbTiO_3$ and minor low intensity peaks of perovskite $PbZr_xTi_{1-x}O_3$, with two minor low intensity impurity peaks corresponding to zirconium oxide and lead oxide. A gradual disappearance of impurity peaks corresponding to zirconium oxide and lead oxide peaks with increase of calcinations temperature. Upon annealing at 800^oC, the phases of PbO and ZrO_2 had been found completely disappeared, and crystalline PZT of both perovskite phases ($PbTiO_3$ and $PbZr_{0.9}Ti_{0.1}O_3$) were the only detectable phases in the powder. Moreover, the XRD results clearly indicated a strong dependency of the amounts of the two majority perovskite phases ($PbTiO_3$ and $PbZr_{0.9}Ti_{0.1}O_3$) on calcinations temperature. The yield of the $PbTiO_3$ gradually decreased and the yield of the $PbZr_xTi_{1-x}O_3$ gradually increased with the increase of calcinations temperature up to 800^oC. At 900^oC, a perovskite $PbZr_xTi_{1-x}O_3$ was the only detectable phase. At 1000 & 1100^oC, a peak related to zirconium oxide was observed in the XRD patterns. As we observed from the thermal analysis (Fig. 1), perovskite phase was started to decompose at $> 950^oC$. The significant formation of the ZrO_2 peak by increasing the annealing temperature from 1000 to 1000^oC can be attributed to the partial dissolution in the lattice of perovskite phase yielding solid solution having the formula $Pb_yZr_{0.4}Ti_{0.4}O_3$ where y was a portion of $PbZr_{0.4}Ti_{0.4}O_3$ undergoing thermal decomposition to yielding its constituted oxides. The SEM micrograph of the produce perovskite phase produced at annealing temperature 600 (a & b) and 1100^oC (c & d), respectively were presented in Fig. 3. Different representative areas with different magnifications were taken to show the most important structures and phenomena.

The morphology and structure of perovskite was highly depends on the conditions under which they were formed. In all cases, homogeneous grains were observed in the specimens. Homogeneous small grains were observed in the sample fabricated at annealing temperature 600^oC (Fig. 3a-b) while relatively larger and homogeneous grains were observed at annealing temperature 1100^oC. Larger particles formed at higher synthesis temperature. Grain growth and opened pores were also observed (Fig. 3c). It seems that a number of grains are semi-fused into a larger grain, giving grains with a size of several microns. This grain growth can be attributed to the evaporation of lead and was enhanced as the annealing temperature was raised. It is known that the porosity of samples results from two sources, intra-granular pores and inter-granular pores (pores trapped within the grain). The inter-granular porosity mainly depends on the grain size. At higher annealing temperature, where the evaporation of lead is high and the grain growth rate is very high, pores may be left behind by rapidly moving grain boundaries, resulting in pores that are trapped inside grains (intra-granular pores) and intera-granular pores.

Qualitative analysis for the different elements in the $PbZr_{0.6}Ti_{0.4}O_3$ powders sample was used to clarify the distribution of each element in the perovskite powder by making maps for Pb, Zr, Ti and O as illustrated in Figs. 4-5. From these maps, it can be seen that the distribution of the four elements were almost the same indicating a good homogenous microstructure for the prepared $PbZr_{0.6}Ti_{0.4}O_3$ powders. $PbZr_{0.6}Ti_{0.4}O_3$ were semiquantitatively analyzed (spot analysis) by Energy Dispersive x-ray spectroscopy (EDX)) and their element compositions at annealing temperature 1000 and 1100^oC and were shown in Figs. 6. while the range of analysis of each element is given in Table 1. Four elements were detected. The Pb peak is related to PbO, the Zr peak is related to ZrO_2, and the Ti peak is related to TiO_2, while the oxygen peak is partially related to all these oxides.

Table 1 showed that the concentration of Pb at annealing temperature 1000^oC is higher than that at annealing temperature 1100^oC while the concentrations of Zr and Ti were increased with annealing temperature. This finding indicates that lead zirconium titanate undergoes thermal decomposition at higher annealing temperature and evaporation of lead was takes place.

CONCLUSIONS

Nanocrystalline powders of Lead zirconium titanate $PbZr_{0.6}Ti_{0.4}O_3$ perovskite were synthesized by tartrate precursor route. The effects of annealing temperature on the formation, and morphology were investigated. The results from thermal analysis, XRD, SEM and EDX studies are summarized as follows:

- The tartrate precursor of Pb-Zr-Tie mixture decomposed thermally in multistep weight loss up to about $460^{o}C$.

- perovskite $PbZr_{0.6}Ti_{0.4}O_3$ was started to form at much lower annealing temperature (~ $490^{o}C$)

- At annealing temperature $600^{o}C$, the powder consists mainly of $PbTiO_3$ and minor $PbZr_xTi_{1-x}O_3$, and small amounts of unreacted zirconium oxide and lead oxide.

- Perovskite phases ($PbTiO_3$ and $PbZr_{0.9}Ti_{0.1}O_3$) were the only detectable phases in the powder annealed at $\geq$ $800^{o}C$.

- $PbTiO_3$ gradually decreased and $PbZr_xTi_{1-x}O_3$ gradually increased with the increase of annealing temperature up to $900^{o}C$ was $PbZr_xTi_{1-x}O_3$ was the only detectable phase.

- Thermal analysis, XRD and EDX analysis indicated that perovskite phase was started to decompose at > $950^{o}C$ due to the evaporation of lead.

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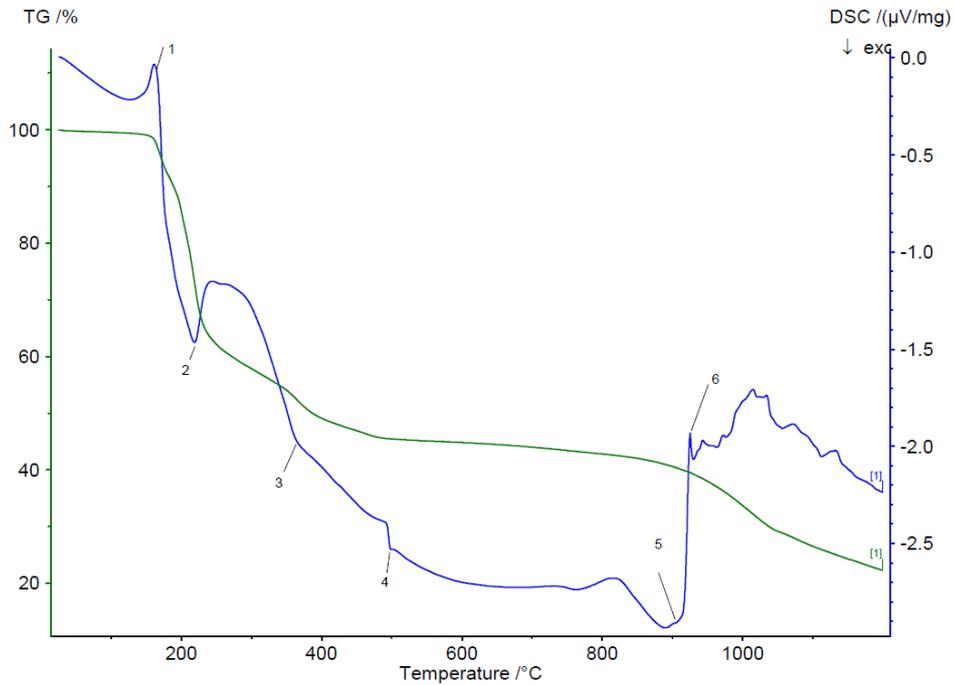
APPENDICES

Figure 1: Thermal Profiles (DSC-TG) of Mixture of Lead-Zirconium-Titanium Tartrate Precursors
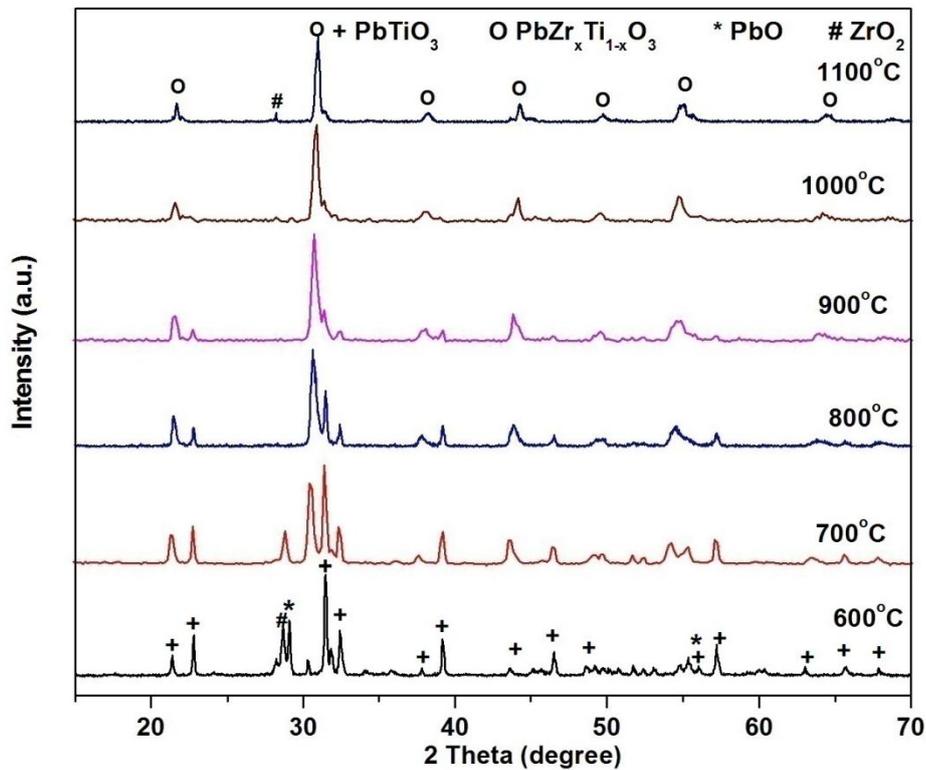

Figure 2: XRD Patterns of $PbZr_{0.6}Ti_{0.4}O_3$ from lead-Zirconium-Titanium Tartrate Thermally Treated at Different Temperatures (600 -1100°C) for 2 h
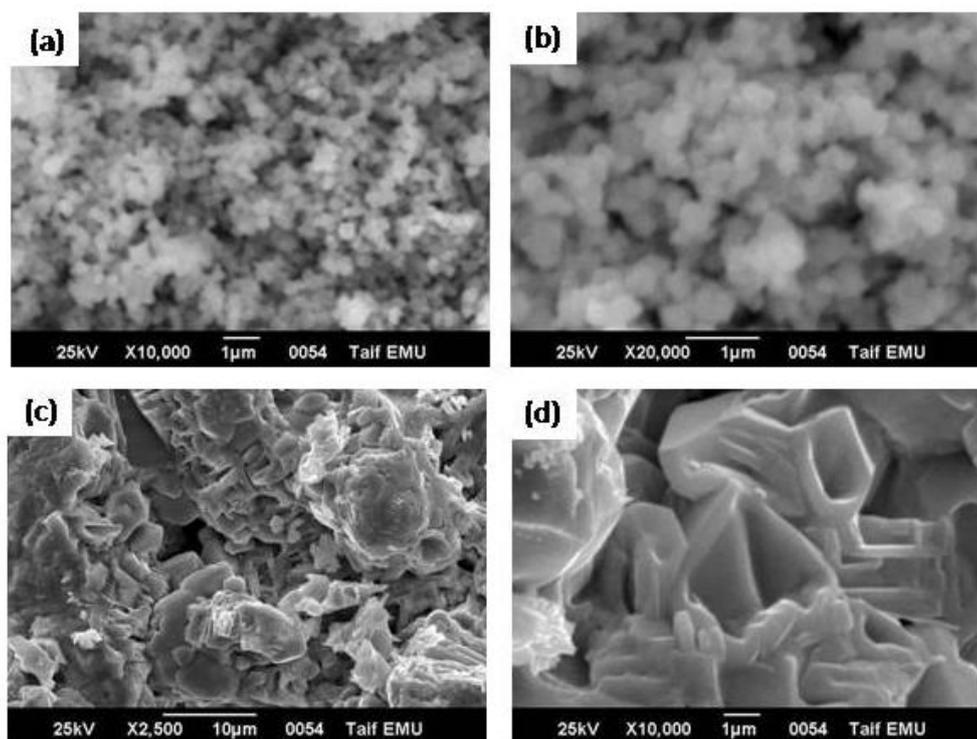
Figure 3: Effect of Annealing Temperatures on the Microstructure of Synthesized PbZr$_{0.6}$Ti$_{0.4}$O$_3$ Powders Obtained from Tartrate Precursors Annealed for 2h. (a & b) 600 ^{o}C, (c & d) 1100°C
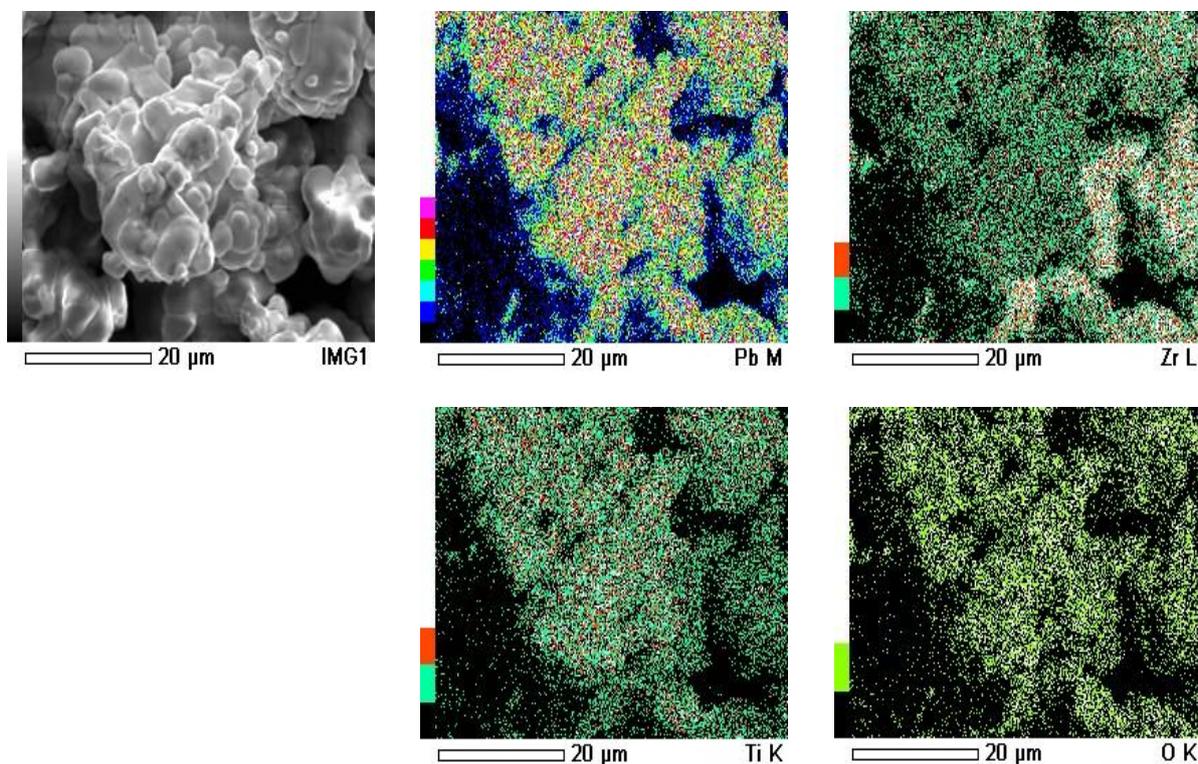

Figure 4: Microstructure Maps for Constituent Elements in of Synthesized PbZr$_{0.6}$Ti$_{0.4}$O$_3$ Powders Obtained from Tartrate Precursors Annealed at 1000°C for 2h
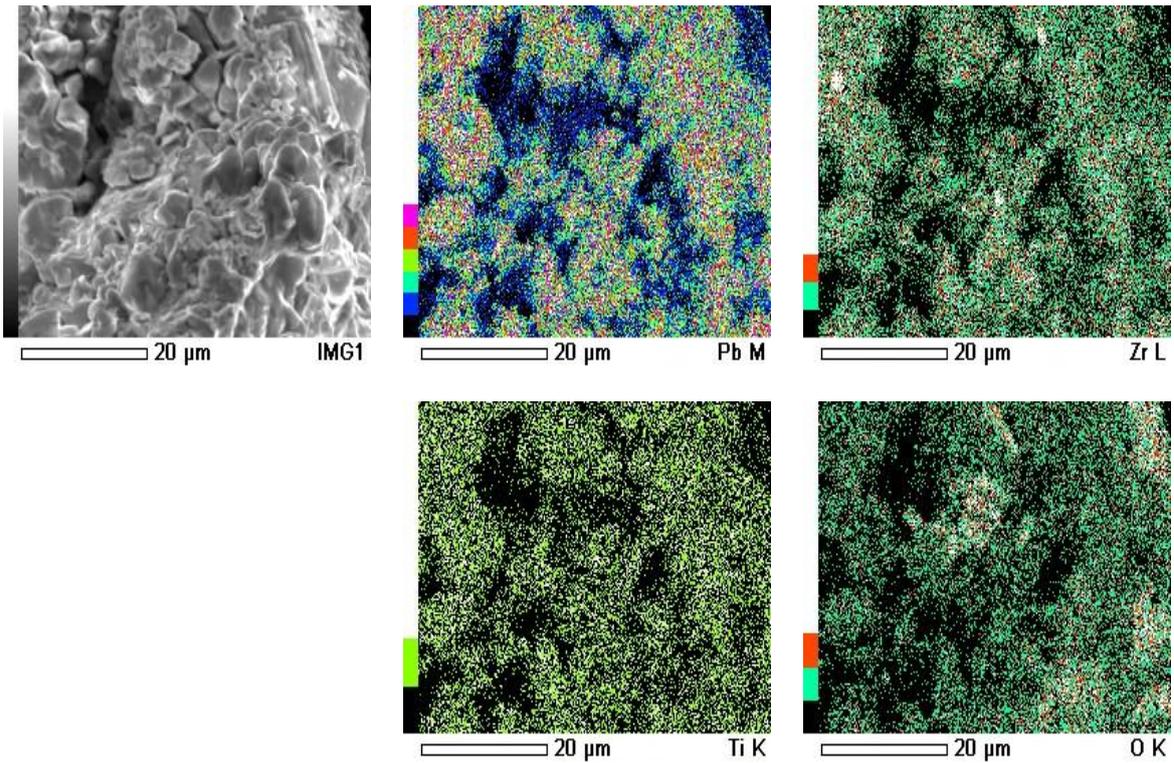
Figure 5: Microstructure Maps for Constituent Elements in of Synthesized PbZr$_{0.6}$Ti$_{0.4}$O$_3$ Powders Obtained from Tartrate Precursors Annealed at 1100°C for 2h
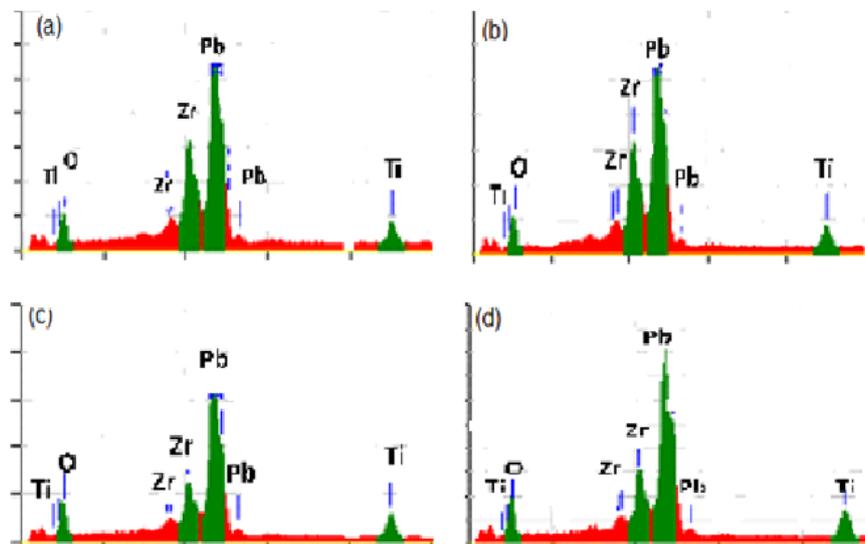

Figure 6: EDX Spectra of Synthesized PbZr$_{0.6}$Ti$_{0.4}$O$_3$ Powders Obtained from Tartrate Precursors Annealed for 2h (a & b) 1000 ^{o}C, (c & d) 1100°C

Table1: Spot Analysis Range of Constituent Elements in the PbZr$_{0.6}$Ti$_{0.4}$O$_3$ Phase, wt-%

Annealing Temperature(^{o}C)	Mass%		
	Pb	Zr	Ti
1000	65.26 – 66.44	15.81 - 15.94	6.61 - 6.94
1100	62.78 - 65.61	17.84 - 20.26	7.10 – 7.15