Preparation and investigation of ferroelectric Pb(Zr\textsubscript{0.53}Ti\textsubscript{0.47})O\textsubscript{3} by modified Pechini method

Truong Van Chuong, Huynh Duy Nhan, Le Quang Tien Dung and Nguyen Duy Anh Tuan
Department of Physics, College of Science, Hue University, Vietnam
E-mail: truongvanchuong@yahoo.com

Abstract. This paper describes a new method, namely modified Pechini for one, for the preparation of nano-sized ferroelectric Pb(Zr\textsubscript{0.53}Ti\textsubscript{0.47})O\textsubscript{3} (PZT (53/47)) from low cost precursors. With this method, PZT (53/47) was prepared by microwave-assisted dissolving a pre-calcinated mixture of component oxides in dilute HNO\textsubscript{3} for a short time and precipitating in NH\textsubscript{4}OH solution (pH = 9-10). On the other hand, the ferroelectric thin films PZT (53/47) on Al substrates were also prepared. The films and the ceramic powders of PZT (53/47) were obtained with high quality in terms of structure and microstructure. The ferroelectric properties of thin films have also been investigated.

Keywords: Ferroelectric materials, PZT (53/47), microwave-assisted, Pechini method.

1. Introduction
The ferroelectric Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} (PZT), La-doped PZT (PLZT), and PbTiO\textsubscript{3} materials are attractive research subject not only in sense of basic research but also of applications such as in fabricating sensors and actuators. There are two common preparation methods for these compounds: a traditional solid state reaction and a sol-gel method. By using a solid state reaction, the title compounds are prepared from low cost starting materials but the prepared powders possess microscale average grain size. In contrast, the sol-gel method provides nanoscale average grain size but requires expensive precursors such as TiCl\textsubscript{4} or Ti(O(CH\textsubscript{2})\textsubscript{2}CH\textsubscript{3})\textsubscript{4} [1]. The advantages (nano-sized grains and low cost precursors) of these two method can be combined by applying the modified Pechini method [2]. With this method, from precursors (nitrate salts, ethylene glycol and citric acid), a fixed network enclosing the metal ions is formed and, as a result, the particles size is inhibited to grow. In addition, this method has the capability to prepare multicomponent compounds with high homogeneity.

For the preparation of ferroelectric PZT and PLZT materials by wet chemical route using TiO\textsubscript{2} as one of starting materials, the most difficult problem is the low solubility of TiO\textsubscript{2} in dilute HNO\textsubscript{3}. J. A. Eiras et al. proposed to make the PZT solutions from pre-calcinated PZT powders. However, due to the use of normal heating calcination methods it could not be dissolved totally PZT in dilute HNO\textsubscript{3} [3-5]. In this paper, we prepare and investigate the PZT (53/47) by dissolving calcined PZT (53/47) in dilute HNO\textsubscript{3} using microwave-assisted power. In addition, the Pechini method was also used to prepare the ferroelectric thin films.

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2. Experimental

2.1. Experimental setup

The microwave-assisted heating is a heat supplying technique by creating molecular oscillation at high speed. Its ability is to supply a homogeneous heat field similar to that of the hydrothermal process. This is a combination of normal calcination process and the heat due to rub of molecules. The heating process is performed immediate inside the sample. With microwave oven having the frequency of 2.45 GHz, the water molecules spin according to field and to be in contact with together 2.45 billion times per second, as a result, a very large and uniform heat field was created. The NE-5670 microwave oven was operated with the power of 500 W and the frequency of 2.45GHz. The low temperature microwave process device was described on figure 1.

![Figure 1. The low temperature microwave-assisted processing system.](image)

2.2. Preparation sample

![Figure 2. The diagram prepared PZT (53/47) materials by modified with the Pechini method.](image)
The investigated sample under a general chemical formula of Pb(Zr_{0.53}Ti_{0.47})O_{3} (PZT (53/47) was obtained following the preparation procedure described in figure 2. The starting materials (PbO, ZrO_{2}, TiO_{2}), with an excess amount of 10 wt.% PbO in order to compensate the lost in weight during the firing, were used. The oxides were mixed and milled in 12 h and were then calcined in air at 850°C for 4 h. The calcined powder was given into a tank of dilute 10 wt.% HNO_{3} solution in a 250 ml glass jar, and was placed in the microwave oven and set at medium mode for 15 minutes. The PZT (53/47) material dissolved completely in dilute HNO_{3} solution, the obtained solution is transparent, forming the sol solution contained (Pb^{2+}, Zr^{4+}, Ti^{4+})(NO_{3})_{x}.

2.2.1. Preparation PZT (53/47) ceramic powders
The solution contained (Pb^{2+}, Zr^{4+}, Ti^{4+})(NO_{3})_{x} was cooled to room temperature and then under continuous agitation an aqueous NH_{4}OH solution was added, to promote the precipitation. The constituents were precipitated as Pb(OH)_{2}, TiO(OH)_{2} and ZrO(OH)_{2}. The precipitated slurry was obtained when the pH value of the solution was adjusted from 9 to 10.

2.2.2. Preparation PZT thin film
For preparation of the resin by the Pechini method, citric acid and ethylene glycol (citric acid/ethylene glycol = 45/55 in mol. %) were mixed with 100 ml from solution containing (Pb^{2+}, Zr^{4+}, Ti^{4+})(NO_{3})_{x}. The mixture was processed by microwave-assisted setting at medium mode for 2 minutes after that the solution compound is agitated for 12 h. A transparent resin of light yellow was obtained. Films of the resins PZT were deposited on hot substrates of Al at a speed of 0.5 mm/minute by dip coating method. The deposited films were previously heated on a hot plate before they were heat treated for crystallization.

3. Results and discussions

![Figure 3. DTA/TGA curves of the coprecipitated PZT powders.](image)

The endothermic peak on DTA curve (figure 3) at 368°C was related to the formation of the PZT and this formation ended up at 700°C. The PZT was formed without intermediate reactions and the mass lost of only 1.24 wt.% on TGA curve. This is affirmed by X-ray diffraction diagram (XRD) in figures 4 and 5. Figure 4a showed the XRD pattern of powders annealed at temperature of 600°C for 2 h. At this temperature the crystallization of PZT is not completely and pyrochlore phase is observed. The powders were crystallized completely at 700°C for 2 h and forming tetragonal phase at angles 44.5, 50, and 55° and rhombohedral at 21.7, 31.2, 38.2° (figure 4b).

Figure 5a shows the XRD pattern of a PZT film on Al substrates annealed at 550°C for 30 min. The tetragonal PZT phase is found with (100), (101), and (210) peaks at corresponding 2θ-angles of 21.9°, 31°, and 50.2°. Besides, the rhombohedral phase is also detected with peaks (101), (200) at 31°, 44.5°, respectively. However, the peak intensities are still low and the thin film may be only partially crystallized. The thin film annealed at 600°C for 30 min. (figure 5b) exhibits better crystallinity than film on figure 5a. The PZT film is completely crystallized with the coexistence of tetragonal and rhombohedral PZT phases.
Figure 4. X-ray diffraction diagram of PZT (53/47) ceramic powders prepared by modified Pechini method: (a) annealed at 600°C for 2 h and (b) annealed at 700°C for 2 h.

Figure 5. X-ray diffraction diagram of PZT (53/47) thin film on Al substrates prepared by modified Pechini method: (a) annealed at 550°C for 30 minutes and (b) annealed at 600°C for 30 minutes.

Figure 6. FESEM images of PZT (53/47) thin film on Al substrates prepared by modified Pechini method annealing at: (a) 600°C for 30 minutes, (b) 650°C for 30 minutes, (c) 700°C for 30 minutes.
Figures 6 a, b and c showed FESEM images of the PZT (53/47) thin films on Al substrates annealed at 600, 650, and 700°C for 30 minutes, respectively.

The surface morphology of a PZT film deposited on Al substrates exhibits a dense microstructure. These films were prepared with 7 layers of coating and its average grain size of about 80 nm.

The EDS spectrum of PZT (53/47) powder annealed at 700°C for 2 h, showed the presence of all component chemical elements according to ratio of composition and no strange elements are detected (figure 7).

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| O K     | 21.38      | 69.83      |
| Ti K    | 6.58       | 7.18       |
| Zr L    | 15.02      | 8.60       |
| Pb M    | 57.03      | 14.38      |
| Totals  | 100.00     |            |

Figure 7. The EDS spectrum of PZT (53/47) powder prepared by modified Pechini method annealing 700°C for 2 h.

Figure 8 shows the hysteresis loops of the PZT (53/47) ceramics prepared from the coprecipitated powders and sintered at 950, 1000, 1050, and 1100°C for 3 h. The measured ferroelectric parameters of PZT powders are given in table 1. The results show that when the sintered temperature increased, the remanent polarization (P_r) also increased and the coercive field (E_c) decreased. The coercive field (E_c) decreased from 24 to 11 kV/cm and the remanent polarization (P_r) increased from 17 to 47 µC/cm².

| Sample      | The sintered temperatures and period | P_r (µC/cm²) | E_c (kV/cm) |
|-------------|-------------------------------------|--------------|-------------|
| M700-950    | 950°C – 3 h                         | 17           | 24          |
| M700-1000   | 1000°C – 3 h                        | 26           | 22          |
| M700-1050   | 1050°C – 3 h                        | 32           | 17          |
| M700-1100   | 1100°C – 3 h                        | 47           | 11          |

Figure 8. The ferroelectric hysteresis loops of ceramic samples.

Table 1. The ferroelectric parameters of ceramic samples prepared from the coprecipitated PZT powders.
Figure 9. Hysteresis loops of PZT films on Al substrates annealed at 500, 550, 600, 650°C for 30 minutes.

Table 2. The ferroelectric parameters of the PZT (53/47) thin films on Al substrates

| Thin films   | The annealed temperatures and period | $P_r$ ($\mu$C/cm$^2$) | $E_c$ (kV/cm) |
|--------------|-------------------------------------|------------------------|--------------|
| M500 – 30(Al)| 500°C – 30 minutes                   | 21                     | 50           |
| M550 – 30(Al)| 550°C – 30 minutes                   | 25                     | 47           |
| M600 – 30(Al)| 600°C – 30 minutes                   | 40                     | 25           |
| M650 – 30(Al)| 650°C – 30 minutes                   | 43                     | 23           |

From the table 2, one can see the remanent polarization ($P_r$) of the thin films on Al substrates is increased from 21 to 43 $\mu$C/cm$^2$ and the coercive field ($E_c$) decreased from 50 to 23 kV/cm. Generally, the PZT (53/47) thin films on Al substrates prepared by dip coating method exhibit good ferroelectric.

4. Conclusion

A new method, the modified Pechini method, was proposed and developed for preparation of ferroelectric ceramic powders and thin films. This method allows to make use of low cost precursors, like oxides or carbonates, and provides nano-sized prepared PZT powders or thin films. Another advantage of this method is the possibility of obtaining a source solution containing all constituents, with low crystallization temperature.

This method caused a full reaction of PZT (53/47) powders in diluted HNO$_3$, had no immediate reactions during the crystallization process from 367°C and completely crystallized to form the tetragonal and rhombohedral phases at 700°C. The prepared samples exhibit homogenous structure and microstructure and having the average particles size of about 80 nm for the ceramics as well as the thin films. These samples also show good ferroelectricity with the remanent polarization $P_r$ from 17 to 47 $\mu$C/cm$^2$ and the coercive field $E_c$ from 11 to 24 kV/cm for the ceramics, the remanent polarization $P_r$ from 21 to 43 $\mu$C/cm$^2$ and coercive field $E_c$ from 23 to 50 kV/cm for the films on Al substrates.

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