Nucl. Sci. and Tech., Vol.8, No. 3 (2018), pp. 14-19

Nuclear Science and Technology

Journal homepage: https://jnst.vn/index.php/nst

Hydrothermal synthesis and characteristics of lanthanum-doped $Pb(Zr_{0.65}Ti_{0.35})O_3$ ceramics

Nguyen Thanh Thuy, Nguyen Van Tung, Nguyen Trong Hung, Cao Duy Minh

Institute for Technology of Radioactive and Rare Elements, 48 – Lang Ha, Dong Da, Hanoi

Email: ntthuy.k51a@gmail.com

Abstract: Lanthanum-doped lead zirconate titanate (PLZT) powders were synthesized using the hydrothermal method. The influence of pH, reaction temperature and time, lanthanum concentration on the formation and characteristics of PLZT were investigated. Obtained powders were investigated using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) techniques and a dielectric analyzer. The results showed that $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})O_3$ with x= 0.0 – 0.1 were well formed under conditions: pH≥13, reaction time of 12hrs, reaction temperature of 180^{o}C. Dielectric constant of PLZT is higher than PZT. The grain size of the PLZT is found to be 1–3.5 µm.

Keywords: *PLZT, PZT, lanthanum, hydrothermal.*

I. INTRODUCTION

Lead, zirconium, titanium oxide - $PbZr_xTi_{1-x}O_3$ (PZT) is a solid solution of $PbTiO_3$ and $PbZrO_3$ [5,11]. In the perovskitec family, it is the well-known material and the most important materials in the industry. Depending on the purpose of use, PZT-based materials are doped by some elements such as rare earths, Mn, Fe, Cr, Sb, Zn… to enhance their properties [1,2]. PZT doped with specific amount of La has been shown to be useful in many applications such as memories (DRAM and FRAM), infrared detectors, electro-optic devices and surface acoustic wave devices and so forth [4]. Modification of the PZT system by the addition of lanthanum has a marked beneficial effect on several of the basic properties of the material such as decreased coercive field, increased dielectric constant, increased mechanical compliance, and enhanced optical transparency [7]. Therefore, the doped PZT-lanthanum is an attractive object for both basic and applied research.

The common methods used for the preparation of PZT and doped PZT powders are solid phase reaction, sol-gel, hydrothermal [4,8-12]. There are also methods such as co-precipitation, microwave [1,2,13]. Hydrothermal is one of the most popular methods to prepare PZT as well as other ceramic materials [4] because of its advantages such as simple operation, easy to implement, low reaction temperature (around 200^{o}C). It is also a superior method of low production cost due to energy and environmental considerations. Moreover, it is a simple method to prepare powders of single crystal with little post-treatments and good sinterability [9]. It is also a useful method for preparing nano-size ceramic materials.

In Vietnam, PZT doped rare earth elements were researched but a few results have been published [1-4]. Therefore, in this

https://doi.org/10.53747/jnst.v8i3.69
Received 12 December 2018, accepted 31 December 2018

study PZT doped lanthanum by hydrothermal method were investigated. The effect of the reactant preparation, pH, and temperature and time reaction on the PLZT forming was indicated. The effect of La doping on the dielectric and the crystallization of PLZT ceramics has been explored and reported in this research.

II. EXPERIMENTS

Each experiment was calculated to obtain 0.01 mol (about 3 g) PLZT as form $Pb_{1-x}La_x(Zr_{0,65}Ti_{0,35})O_3$ (x=0, 0.025, 0.05, 0.10 or lanthanum concentration in the function of Pb is 0, 2.5, 5.0, 10.0% mol respectively). High-purity chemicals of $ZrOCl_2.8H_2O$ (≥98%, German), $TiCl_3$ (15% in HCl media, German), $Pb(NO_3)_2$ (99%, China) La_2O_3 (99,99 – Vietnam), HNO_3 and KOH (PA, China) were used as starting materials. $La(NO_3)_3$ 0.1 M solution was obtained from La_2O_3 and HNO_3 5 M solution. Two routes to prepare the reactant mixtures before hydrothermal process in an autoclave were applied in this study.

The first route is individual precipitation. As the first step, $Pb(NO_3)_2$ was dissolved into 25 ml de-ionized water and KOH 3 M was slowly added until the precipitation to obtain a precipitate of lead. $ZrOCl_2.8H_2O$ was dissolved in 25 ml de-ionized water in another beaker. $TiCl_3$ and $LaCl_3$ solutions were added into this beaker, with stirring (200 rpm), to get a mixture solution of Zr^{4+}, Ti^{3+} and La^{3+}. KOH 3 M was slowly added into this mixture solution to get a precipitate of zirconium, titanium and lanthanum. Then, two beakers were mixed with sintering (300 rpm). Finally, pH of the mixture was adjusted by using KOH 3 M.

The second route is co-precipitation. $ZrOCl_2.8H_2O$ and $Pb(NO_3)_2$ were dissolved separately in two beakers. $TiCl_3$ was added into the ZrO^{2+} solution and $LaCl_3$ was added into the Pb^{2+} solution. Then, the ZrO^{2+}/Ti^{3+} mixture was slowly poured with sintering (300 rpm) into the beaker which contains the Pb^{2+}/La^{3+} mixture. Finally, pH of the mixture was adjusted by using KOH 3 M.

Each reactant mixture was poured into an autoclave after 15 minutes stirring. The hydrothermal reaction was carried out at the temperature of 150 to 180°C in 12 to 48 hours. The obtained precipitate after hydrothermal process was filtered and washed with distilled water for several times to remove Cl^-, NO_3^- and K^+. The final products were obtained by drying the precipitate at 80°C in 24 hours.

Phase composition was analyzed by XRD (SIEMENS D5005). Morphology and particle size were analyzed by SEM (JEOL, JSM-IT100LV) and a size analyzer (PARTICA LA-950V2). For dielectric measurements, PLZT powders were pressed into discs (diameter ∼12 mm, ∼1 mm thick). Dielectric constant (ε) and dissipation factor (tanδ) were measured using an impedance analyzer (Autolab 30) in the frequency range 100Hz - 1 MHz at room temperature.

III. RESULTS AND DISCUSSION

A. Effect of the preparation of reactant mixtures on the PLZT forming

Because of variety of the starting chemicals, the mixing of starting material plays an important role in the formation and purity of final product. The presence of Cl^- (from $ZrOCl_2.8H_2O$ and $TiCl_3$) and Pb^{2+} (from $Pb(NO_3)_2$) lead to create $PbCl_2$ precipitate (reaction (1)) during mixing process. In this study, two routes to prepare the reactant mixtures (mentioned at paragraph II) were applied at pH of 13 and La of 10% mol (x=0.1). The hydrothermal process was occurred at 180°C for 48 hours.

XRD patterns in Fig.1 showed that $Pb_{0.9}La_{0.1}(Zr_{0,65}Ti_{0,35})O_3$ – PLZT crystal is formed in both precipitation routes. But pure PLZT crystal is formed only in case of co-precipitation. There are some impurities: ZrO_2, PbO exited in case of individual precipitation. In both cases the presence of $PbCl_2$ cannot be detected. This can be explained by reaction (2): $PbCl_2$ was converted to $Pb(OH)_2$ during pH adjustment by KOH solution. In fact, the solubility (K_{sb}) of $PbCl_2$ and $Pb(OH)_2$ are $1.7x10^{-4}$ and $1.42x10^{-20}$ respectively. Thus, the co-precipitation method is a better route to prepare pure PLZT powders.

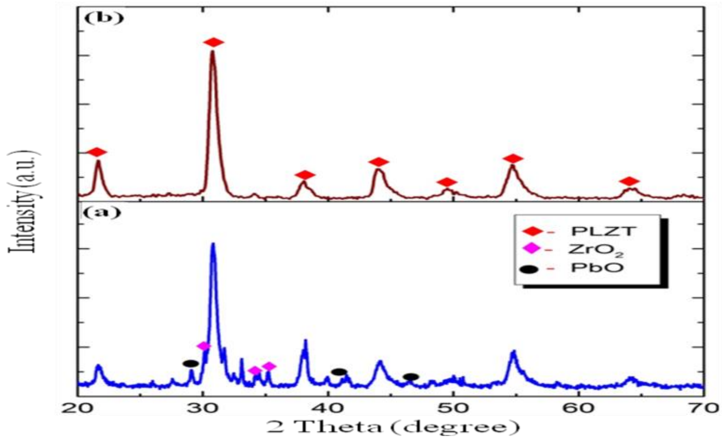

Fig.1. XRD patterns of materials obtained from individual precipitation (a) and co-precipitation (b).

B. Effect of pH on the PLZT forming

Because of very important role on the crystallization of PLZT, pH of reactant mixture before hydrothermal process was adjusted in range of 11 to 13. Each sample was treated at temperature of 1 80°C in 48 hours and lanthanum concentration of 10% mol.

It can be seen that Fig. 2 exhibits some peaks of ZrO_2, $PbZrO_3$ and $Pb_3(CO_3)_3(OH)_2$ in case of pH of 11 and 12. There are no peaks of PLZT at these conditions. It means that pH below 12 is not enough for the crystallization or forming of PLZT phase. Meanwhile, pure PLZT crystal is formed at pH of 13. Thus, pH≥13 is necessary to obtain pure PLZT powders.

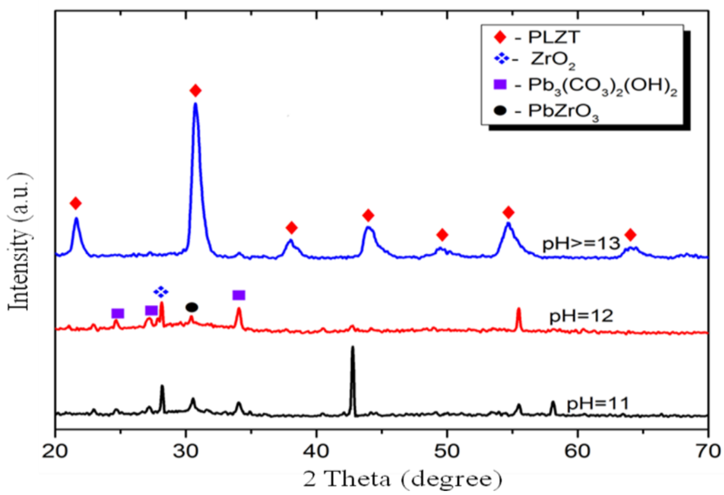

Fig. 2. XRD patterns of materials obtained at different pH.

The important role of the pH adjusting of reactant mixture before hydrothermal can be explained through the following reaction mechanism [4,9]:

$$Pb^{2+} + Cl^{-} = PbCl_2 \quad (1)$$

$$PbCl_2 + 2OH^{-} = Pb(OH)_2 + 2Cl^{-} \quad (2)$$

$$Pb^{2+} + 2KOH^{-} = Pb(OH)_2 + 2K^{+} \quad (3)$$

$$Ti^{3+} + 2OH^{-} + \tfrac{1}{2} O_2 + H_2O = Ti(OH)_4 \quad (4)$$

$$Zr^{4+} + 4OH^{-} = Zr(OH)_4 \quad (5)$$

$$La^{3+} + OH^{-} = La(OH)_3 \quad (6)$$

$$(1\text{-}x)Pb(OH)_2 + 0{,}35Ti(OH)_4 + 0{,}65Zr(OH)_4 + xLa(OH)_3 = Pb_{1-x}La_x(Zr_{0,65}Ti_{0,35})O_{3+x/2} + (3+x/2)H_2O \quad (7)$$

First is the forming of $Pb(OH)_2$, $Ti(OH)_4$, $ZrO(OH)_2$, $La(OH)_3$ (3)-(6). These reactions occurred during the pH adjustment process using KOH 3 M. Next, at the high pressure and temperature condition of reactor, $Pb(OH)_2$, $Ti(OH)_4$, $Zr(OH)_4$, $La(OH)_3$ participated in reaction and formed PZT material [7].

C. Effect of reaction time and temperature

Reaction time and temperature have an important role in hydrothermal process. Abothu [13] has successfully synthesized PZT under hydrothermal condition at 138°C in 2.5 hours with the presence of microwave in during hydrothermal process. In this study, the hydrothermal reaction was conducted at temperature of 150 and 180°C in 12 to 48 hours. La concentration was 10% mol and pH was 13.

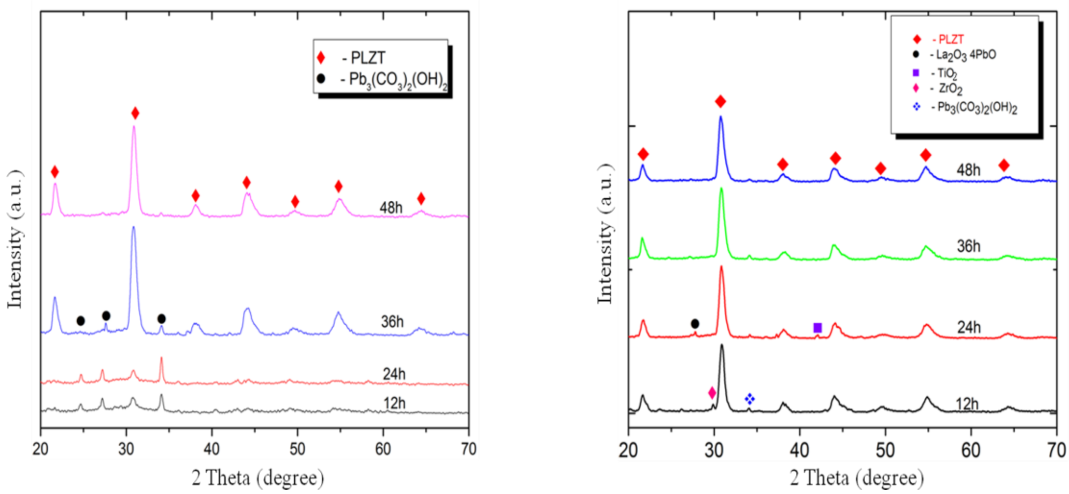

Fig. 3. XRD patterns of materials obtained at 150°C (left), 180°C (right).

Fig. 3 (left) shows that PLZT is formed at temperature 150°C in 36 hours, but it remained a small amount of ($Pb_3(CO_3)_3(OH)_2$). Pure phase of PLZT created in reaction time of 48 hours. During the reaction time of 12 to 24 hours, no peaks for PLZT are found. At this condition, only typical peaks for $Pb_3(CO_3)_3(OH)_2$ exist. At 180°C, the typical peaks of PLZT appeared in 12 hours (Fig. 3 (right)). However, the hydrothermal reaction is not completely, remaining some impurities with small content such as $Pb_3(CO_3)_2(OH)_2$, TiO_2, ZrO_2, $La_2O_3$4PbO. Pure phase of PLZT is formed when the reaction time is over 36 hours. Thus, the reaction temperature and time affect the formation as well as purity of PLZT crystal.

D. Effect of La concentration on dielectric constant and practice size

La concentration was adjusted from 0 to 10% mol to estimate the influence on characteristics of material. The hydrothermal process was conducted at 180°C in 48 hours.

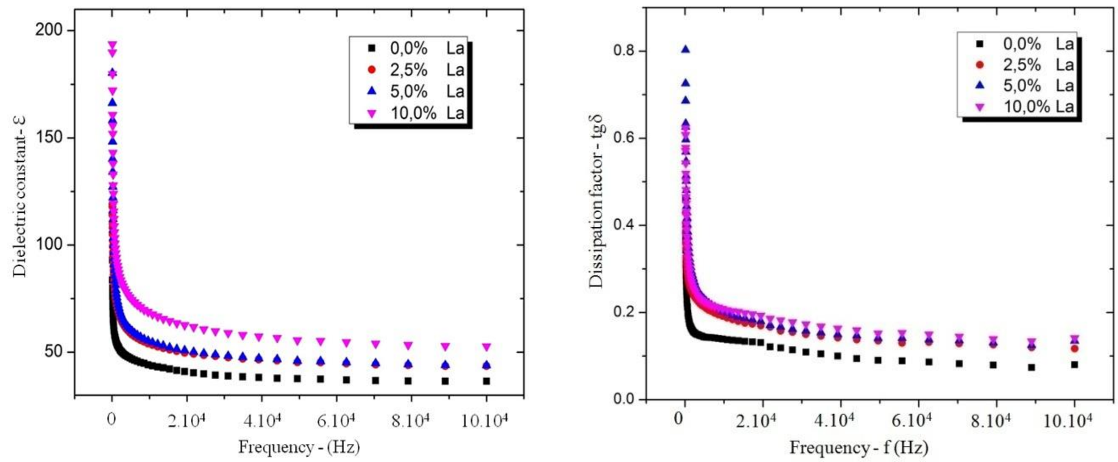

Fig.4. Dielectric constant (left) and dissipation factor (right) of PLZT in the presence of various concentrations of lanthanum.

Fig. 4 (left) shows that the dielectric constant and dissipation factor increase proportionally to lanthanum concentration. The dielectric constant PLZT at 100 Hz with La concentration of 0, 2.5, 5 and 10% mol are 93, 150, 180 and 193 respectively. Therefore, lanthanum improved significantly the dielectric constant of doped PZT in comparison to PZT. The increase of dielectric constant can be explained as a result of vacancies facilitating domain boundary motion, which in turn allows the relaxation of internal stresses and results in more efficient poling.

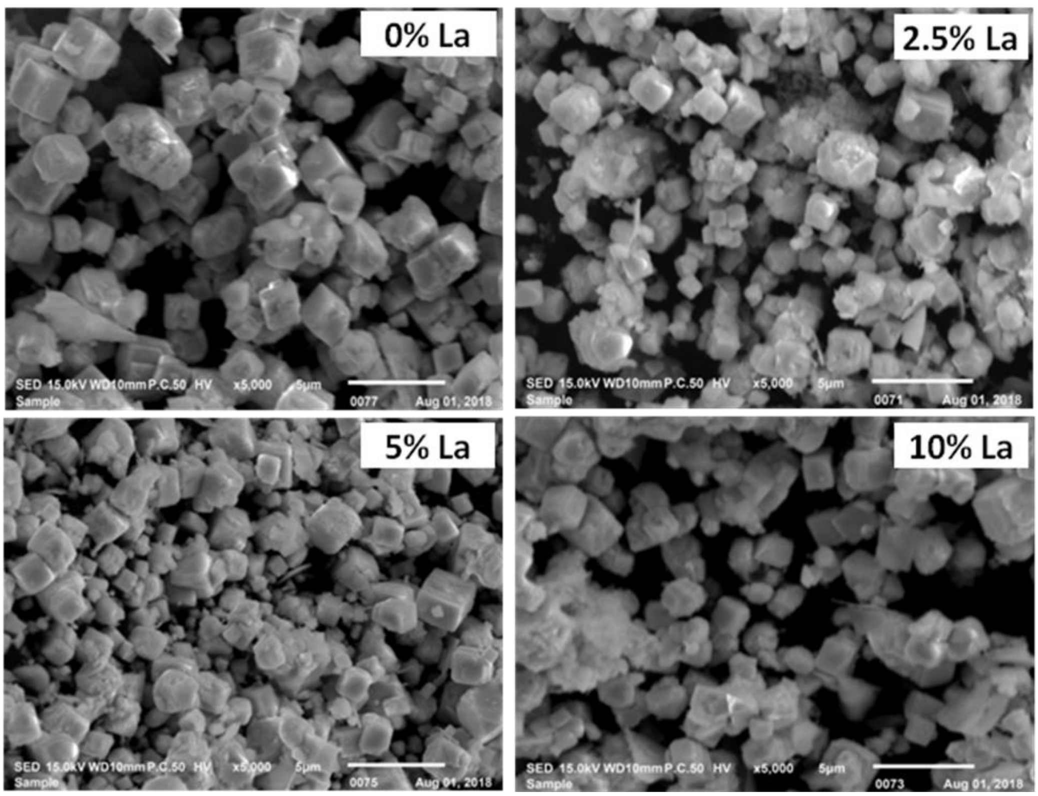

Fig. 5. SEM images of PLZT in the presence of various concentrations of lanthanum.

Fig. 5 shows that all samples have a clear grain boundary grains. The grain size of the PLZT is found to be 1–3.5 µm. The results from size analyzer show the decrease of medium grain size with the increase in La concentration in the sample (3.5 µm with 0% to 2.9 µm with 10% mol La). Due to the decrease in grain size, the fraction of dipoles at its interface also increases. The increase in number of dipoles and the lattice strain result in increase in the ferroelectric and piezoelectric properties or dielectric constant [5].

IV. CONCLUSIONS

PZT doped La with $Pb_{1-x}La_x(Zr_{0,65}Ti_{0,35})O_3$ formula was successful prepared by hydrothermal method. The effect of precipitation method, pH, lanthanum concentration, temperature and time were also investigated. Pure PLZT phase was formed when pH ≥ 13; the reaction time was higher than 36 hours at 180°C or higher than 48 hours at 150°C. The grain size was smaller than 3.5 µm, the dielectric constant increased proportional to the La concentration. The dielectric constant of PLZT was 193 at 1 kHz in case of La 10% mol in comparison to 93 of PZT.

REFERENCES

[1]. Phan Dinh Gio, "*Study on the physical characteristics of two and three components ferroelectric ceramics based on PZT doped by La, Mn, Fe*". Doctoral thesis, 2007.

[2]. Than Trong Huy, "*Study on the fabrication and characteristics of piezoelectric ceramics* $[(1-x)Pb(Zr,Ti)O_3 + xPb(Mn_{1/3}Nb_{2/3})O_3]$ *x = 0 ÷ 12%mol (PZT-PMnN) doped by La*". Doctoral thesis, 2014.

[3]. Thanh Thuy Nguyen et al., "*Elaboration and dielectric property of modified PZT/epoxynanocomposites*". Polymer Composites 37, 455-461, 2016.

[4]. Nguyen Xuan Hoan et al., "*Study on synthesis of the lead zirconate titanate powder by the hydrothermal method*". Vietnam Journal of Science and Technology 48 (2A), 414-418, 2010.

[5]. P. Kour et al., "*Enhanced ferroelectric and piezoelectric properties in La-modified PZT*". Ceramics Applied Physics A, 122:591, 2016.

[6]. H.D.Sharma et al., "*Effect of rare earth ions on the structural parameters of modified PLZT ceramics (5/65/35)*". Journal of Materials Science Letters 15, 1424-1426, 1996.

[7]. A. R. James et al., "*Chemical synthesis, structural, thermo-physical and electrical property characterization of PLZT ceramics*". Journal of Alloys and Compounds 496, 624–627, 2010.

[8]. Irinela et al., "*Ferroelectric ceramics by sol-gel methods and applications: a reviews*". J. Sol-gel Science 64, 571-611, 2012.

[9]. Yao-Jung Lee et al, "*Phase-formation mechanism for hydrothermally synthesizing lanthanum-modified lead zirconate titanate powders*". Journal of Crystal Growth 178, 335-344, 1997.

[10]. D. Lui, H. Zhang, W. Cai, X. Wu, L. Zhao, "*Synthesis of PZT nanocrystalline powder by a modified sol-gel process using zirconium oxynitrate as zirconium source*". Materials Chemistry and Physics 51, 186-189, 1997.

[11]. T. Lamcharfi et al., "*Dielectric and relaxation studies in hydrothermal processed PLZT ceramics*". M. J. Condensed Matter 6, No.1, 2005.

[12]. S. N. Shannigrahi et al., "*Structural, electrical and piezoelectric properties of rare-earths doped PZT ceramics*". Indian Journal of Pure & Applied Physics 37, 359-362, 1999.

[13]. Isaac Robin Abothu et al., "*Processing of* $Pb(Zr_{0.52}Ti_{0.48})O_3$ *(PZT) ceramics from microwave and conventional hydrothermal powders*". Materials Research Bulletin 34 No.9, 1411–1419, 1999.