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Hydrothermal Synthesis of $Pb_{1-1.5x}La_xZr_{0.5}Ti_{0.5}O_3$ (x = 0.01-0.06) Nanocrystallites

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Abstract: Nanocrystalline $Pb_{1-1.5x}La_xZr_{0.5}Ti_{0.5}O_3$ (x = 0.01-0.06, PLZT) powders with particle size from 30 to 150 nm were hydrothermally synthesized from the gels under mild conditions. The reaction conditions such as La content, reaction temperature and time were studied in detail and optimal conditions were established for synthesizing PLZT powders with different La contents. The effects of La content, alkali concentration, reaction temperature and time on the particle size were studied.

Keywords: Hydrothermal synthesis, PLZT powder, nanocrystallite.

Lanthanum doped lead zirconate titanate (PLZT) ceramics display excellent electrooptic and photostriction properties because of the existence of cavities in the perovskite structure[1-3]. The PLZT powders are conventionally prepared by solid state reaction[4-5], and the wet chemical methods such as sol-gel techniques are then introduced[6-7]. However, the homogeneity, morphology and size of the particles, which greatly affect the sinterability and the property of the resulting ceramics, are difficult to control due to the high temperature treatment during the preparation. Hydrothermal method, which was introduced to the synthesis of single and multi-component oxides in recent years, have attracted great interests for the advantages of minimum temperature required for crystallization and control the purity, morphology and size, phase composition of the resulting powders[8-9]. Many oxides have been successfully prepared by this method[10-12]. However, there was little information on the hydrothermal synthesis of PLZT powders except the hydrothermal preparation of niobium incorporated PLZT powder[13] and H. M. Cheng *et al.* studied the XRD patterns of hydrothermal PLZT powders[14] and revealed the formation of tetrahedral PLZT powder after treated at high temperature. In this work, phase-pure tetrahedral PLZT powder was hydrothermally prepared using xerogel as precursor with heat treatment.

$Ti(OC_4H_9)_4$, $Zr(OC_4H_9)_4$ and $Pb(OAc)_2$ which was obtained by recrystallization of $Pb(OAc)_2{\cdot}3H_2O$ from concentrated CH_3COOH were used as reactants. Firstly, the solution was prepared after the *n*-C_4H_9OH solution, in which the molar ratio of (Pb+La):Ti:Zr = 1.0:0.5:0.5 and the total metal ions concentration was 0.2 $mol{\cdot}L^{-1}$

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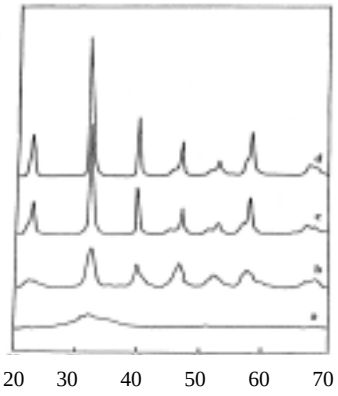
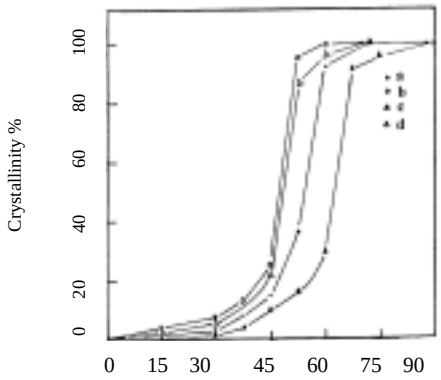
refluxed for 2 hours and cooled to room temperature, and then the mixture of *n*-butanol and water ($V_{n\text{-}C_4H_9OH}$ / V_{H_2O} = 8) was added under stirring until the molar ratio of H_2O to metal ions was up to 10. Then, the solution transformed to gel and the slight yellow xerogel powder was obtained after being dried under vacuum. The ground xerogel powder was added into NaOH solution (0.8-3.6 mol·L^{-1}) and treated at the designed temperature for a planned time in a stainless autoclave with teflon liner. After cooled to room temperature, the PLZT powder was obtained by filtration, washed with deionized water and dried at room temperature. The percent crystallinity was calculated according to the intensities of 110 reflections.

Figure 1 XRD patterns of PLZT (x = 0.02) powders obtained at different temperatures



100 (a), 120 (b), 140 (c) and 160°C (d)
Alkali concentration: 2.6 mol·L^{-1}
reaction time: 50 hours.

Figure 2 Crystallization curves of different PLZT powders at different temperatures



$Pb_{0.97}La_{0.02}Zr_{0.5}Ti_{0.5}O_3$ at 120 (a) and 140°C (b)
$Pb_{0.94}La_{0.04}Zr_{0.5}Ti_{0.5}O_3$ at 120 (c) and 140°C (d)

To study the effect of temperature on the crystallization of the PLZT powder, the reactions conducted at different temperatures while NaOH concentration, reaction time was 50 hours La content as held at 2.6 mol·L^{-1}, La/Pb = 2/97. **Figure 1** shows the XRD patterns of prepared powders. It can be seen that $Pb_{0.97}La_{0.02}Zr_{0.5}Ti_{0.5}O_3$ began to crystallize at 120°C, while 140°C was necessary to prepare phase-pure PLZT powder and the broaden of the XRD patterns was due to the small size of particle. Different from the report of Cheng *et al.*, tetrahedral PLZT powder could be hydrothermally obtained with heat-treatment at the temperature as low as 140°C. Furthermore, XRD patterns of the prepared powders with larger 2θ value comparing to the PZT powder show the decreasing of the cell parameters, which indicate La^{3+} incorporated into the PZT lattice replacement of Pb^{2+} [14]. In a word, raising temperature could accelerate the crystallization of PLZT particles. Further experiments were carried out to investigate the effect of La content. **Figure 2** shows the crystallization curve with different La content while other conditions were held constant. It indicates that increasing of La content did not favor the crystallization of the PLZT powder. With the increasing of La

content from 0.02 to 0.04, the time for prepare well-crystalline PLZT powder prolonged from 65 to 90 hours at 120°C.

Table 1 The optimal condition for synthesizing well-crystallized PLZT powders

x	0.01	0.02	0.04	0.06
Time at 120°C (h)	55	65	90	110
Time at 140°C (h)	40	55	65	80

NaOH concentration: 2.6 $mol \cdot L^{-1}$

Table 2 Particle size and BET surface area of PLZT ($Pb_{0.97}La_{0.02}Zr_{0.5}Ti_{0.5}O_3$) obtained at different conditions

Sample	Reaction conditions			Particulate properties	
	Temperature (°C)	time (h)	alkali concentration ($mol \cdot L^{-1}$)	Size* (nm)	Surface area ($m^2 \cdot g^{-1}$)
1	120	60	0.8	35±5	16.8
2	120	60	1.6	40±10	12.6
3	120	60	2.4	50±10	12.4
4	120	60	3.6	140±20	4.2
5	120	72	1.6	75±15	6.5
6	120	100	1.6	110±20	4.8
7	140	60	1.6	70±10	7.1
8	140	140	1.6	120±20	5.6
9	160	60	1.6	70±10	7.2

*Observed from TEM graphs

In summary, the optimal reaction conditions for synthesizing different La doped PLZT powders are listed in **Table 1**. Raising temperature favored the formation of PLZT, while the La content increasing did not. The radius of La^{3+} ion (0.117 nm)[15] is smaller than that of Pb^{2+} ion (0.133 nm)[16]. With the replacement of the Pb^{2+} ion by La^{3+} in the PLZT powder, the cavity formed and the lattice distortion took place. This distortion resulted a higher energy barrier to form PLZT crystallites and a critical condition was necessary for the formation of PLZT powder.

The particulate properties including particle morphology and size were investigated. TEM graphs indicated that the particles showed sphere-like morphology and **Table 2** lists the prepared $Pb_{0.97}La_{0.02}Zr_{0.5}Ti_{0.5}O_3$ particle size and BET surface area obtained at different reaction conditions. Most of the prepared particles were nanometer size. The particle size enlarged with the increasing of alkali concentration, reaction temperature and time. It usually includes two processes during the hydrothermal synthesis, which are nucleation and grain growth processes. If the reaction conditions favor the nucleation, small particles form and *vice versa*. It means that the increasing of alkali concentration and reaction temperature and time can accelerate the growth rate of the grain. A rapid grain growth relative to the nucleation resulted in the larger particles.

Chemical analysis by ICP technique indicated that the La, Pb, Zr, Ti contents of the

PLZT powders were in agreement with those in the gels within the measurement error.

In conclusion, phase-pure tetrahedral PLZT powders were hydrothermally prepared using $Ti(OC_4H_9)_4$, $Zr(OC_4H_9)_4$, $Pb(OAc)_2$ and $La(OC_2H_5)_3$ as starting materials. XRD patterns revealed La^{3+} replaced Pb^{2+} incorporated into the PZT lattice and. With the increasing of the La content the necessary reaction time prolonged, while increasing of alkali concentration and the temperature accelerated the crystallization of the PLZT.

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