Journal of Alloys and Compounds 509 (2011) 4127–4131

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effect of oxidant-to-fuel ratios on phase formation of PLZT powder; prepared by gel-combustion

Gurvinderjit Singh [a,*], V.S. Tiwari [a], Pragya Tiwari [b], A.K. Srivastava [b], P.K. Gupta [a]

[a] *Laser Materials Development and Devices Division, Raja Ramanna Centre for Advanced Technology, Indore-452 013, India*
[b] *Indus Synchrotrons Utlisation Division, Raja Ramanna Centre for Advanced Technology, Indore-452 013, India*

ARTICLE INFO

Article history:
Received 8 September 2010
Received in revised form
10 December 2010
Accepted 25 December 2010
Available online 31 December 2010

Keywords:
Oxide materials
Ferroelectrics
Chemical method
X-ray diffraction

ABSTRACT

Single phase, PLZT powder was synthesized using gel-combustion route. It has been observed that fuel-to-oxidant ratio affects the initial phase formation. Higher fuel content leads to direct formation of crystalline perovskite PLZT powder due to substantial rise in the temperature during the redox reaction. Perovskite PLZT phase formation takes place at 550 °C, without any intermediate phase formation, for stoichiometric fuel-to-oxidant ratio. The crystallite size was found to be independent of fuel-to-oxidant ratio when the ash is heated above 700 °C.

1. Introduction

Lanthanum modified lead zirconate titanate, $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})_{0.9775}O_3$ (PLZT) ceramic, has been known for its applications in electro-optical devices such as modulator, amplifier, and switches [1]. Conventionally, the PLZT powder is prepared at elevated temperature by solid-state reaction of constituent oxides. The reaction takes place at temperatures higher than 900 °C where substantial PbO loss is expected [2]. Moreover, multiple steps involved in this method, often leads to chemical and micro-structural inhomogeneities. These problems highly affect the reproducibility of the PLZT ceramics. Homogeneous and highly reactive, fine powder of PLZT can be obtained by solution chemistry routes like co-precipitation, sol–gel, and oxalate methods [3–7]. Many of these solution methods involve sophisticated techniques, expensive chemicals as well as complicated lengthy procedures. Among them the gel-combustion technique is facile, time saving and energy efficient for synthesis of ultra-fine powders. Usually the powder obtained from the gel-combustion has to be calcined for getting single phase PLZT powder. However, Roy et al. [8] have reported single step synthesis of PLZT powder using metal-PVA combustion. Gel-combustion involves an intimate blending of constituent ions and suitable fuel or complexing agent (citric acid, urea, glycine, etc.) in an aqueous media and an exothermic redox reaction between fuel and oxidizer (metal nitrates) [9]. The exothermic decomposition of fuel-oxidant precursors results in either the fine powder with required phase or semi-decomposed precursor with a considerable carbonaceous residue depending upon the nature of the fuel, pH of starting solution and oxidant-to-fuel ratio [8–13]. The powder characteristics are preliminary dependent on the flame temperature generated during the combustion which in turn is a function of nature of fuel and oxidant-to-fuel ratio. The effect of different fuels and fuel-to-oxidant ratio on crystallographic phases and powder characteristics was extensively investigated by Chavan and Tyagi [12] and Bedekar et al. [13] for many oxides. It was established that a careful control of fuel-to-oxidant ratio is necessary to get desired product. The optimal oxidant-to-fuel ratio depends upon the desired composition.

The gel-combustion has been successfully used to synthesize PLZT nano-powders using citric acid as a fuel and metal nitrates as oxidant, for a fixed fuel-to-oxidant ratio, by Choy and Han [14]. They obtained perovskite phase PLZT at 550 °C without any intermediate pyrochlore phase formation. Another report by Cernea et al. [15] reveals that Nb doped PLZT by gel combustion method can lead to perovskite phase after annealing the powder at 600 °C. In this case powder transforms to the desired perovskite phase through an intermediate pyrochlore phase formation. However, none of these studies taken into consideration the effect of oxidant-to-fuel ratio on mechanism of phase formation. The aim of the present work is to study the effect of oxidant-to-fuel ratio on the phase formation sequence. We have used glycine as a fuel because it is known to act

---

* Corresponding author. Tel.: +91 0731 2488656; fax: +91 0731 2488650.
E-mail address: gjit@rrcat.gov.in (G. Singh).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.12.177

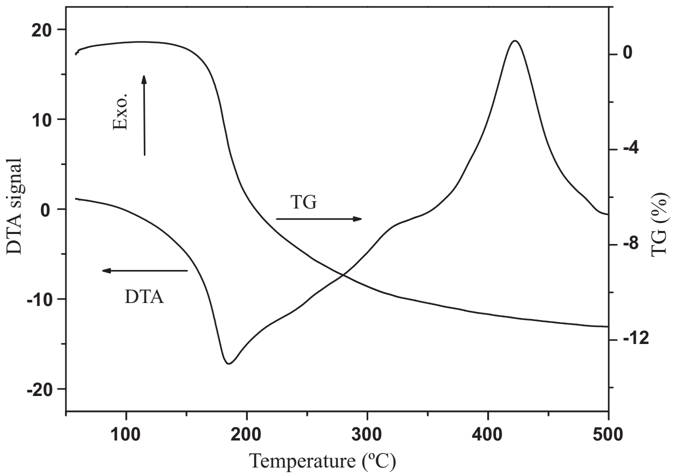

Fig. 1. DTA/TG of titanium hydroxide for estimation of Ti content.

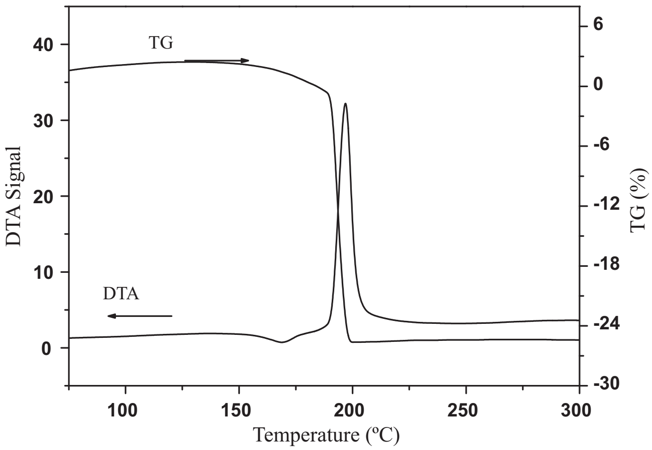

Fig. 3. DTA/TG of gel for stoichiometric nitrate-to-glycine ratio.

as a complexing agent for number of metal ions as it has a carboxylic acid group at one end and amino group at the other end [16]. Such zwiterionic character of a glycine molecule can effectively complex the metal ions of varying ionic size which helps to prevent them from selective precipitation and thus maintains the compositional homogeneity among the constituent. On the other hand, glycine also acts as a fuel in combustion reaction.

2. Experimental

High purity $TiO(NO_3)_2$, $ZrO(NO_3)_2$, $La(NO_3)_3{\cdot}6H_2O$, $Pb(NO_3)_2$, and glycine were used as starting materials. Oxy-nitrate of titanium and zirconium were prepared in two steps. First, hydroxides of titanium and zirconium were separately precipitated from diluted $TiCl_4$ and aqueous solution of $ZrOCl_2{\cdot}8H_2O$, respectively, using NH_4OH solution. The precipitates were thoroughly washed with DM water to remove the chloride ions. In the second step, the precipitates of titanium and zirconium hydroxides were dissolved in a minimum volume (~75 ml) of nitric acid. It has been observed that a pre-drying around 80 °C transform the zirconium hydroxides to hydrous zirconia ($ZrO_2{\cdot}nH_2O$) which was difficult to dissolve in nitric acid [17]. Therefore, a freshly prepared zirconium hydroxide was used to form its oxy-nitrate solution. Thermal gravimetric (Setaram, France) procedure was adopted to estimate the titanium dioxide (TiO_2) content in its hydroxide (Fig. 1). The decomposition of titanium hydroxide occurs between 150 and 350 °C and subsequent heating leads to exothermic peak near 400 °C due to the crystallization of titanium dioxide [18]. The content of TiO_2 estimated from the thermal gravimetric measurement was found to be 0.57 g of TiO_2 in 10 ml of $TiCl_4$ solution. The zirconium content was known from the molecular weight of $ZrOCl_2{\cdot}8H_2O$, therefore, gravimetric estimation was not required.

The required amount of $La(NO_3)_3{\cdot}6H_2O$, $Pb(NO_3)_2$ and NH_2CH_2COOH was dissolved in 100 ml of DM water and mixed with oxy-nitrate solutions of zirconium and titanium. The amount of each chemical was calculated for 5 g of PLZT(9/65/35) powder. The stoichiometric nitrate (oxidant)-to-glycine (fuel) ratio was calculated by balancing the oxidizing and reducing valances of glycine and metal nitrates [8]. The nitrate-to-glycine molar ratio for stoichiometric reaction was calculated to be 1:2.24 (i.e. 0.446). This implies that synthesis of one mole of PLZT powder requires 2.24 mol of glycine for stoichiometric redox reaction. Four different oxidant-to-fuel

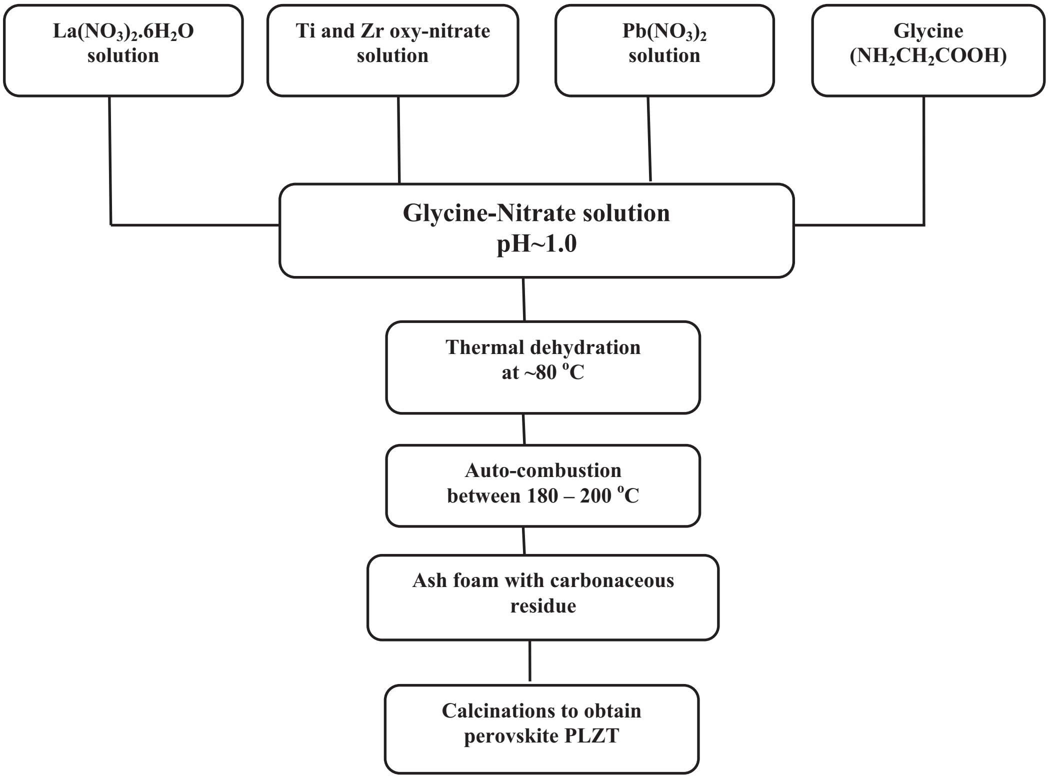

Fig. 2. Flow chart for synthesis of PLZT powder by gel-combustion method.

Table 1
Effect of oxidant-to-fuel ratio in the formation of ash.

Oxidant:Fuel	Auto-ignition temperature (°C)	Colour of ash	Flame visibility	% Weight loss
1:2.24	188	Pale yellow	No flame	28
1:3.00	187	Dark brown	No flame	37
1:3.50	190	Black	Flame at centre	50
1: 4.00	188	Dark gray	Immense flame	63

ratios were used for the synthesis of PLZT powders are listed in Table 1. Different solutions for corresponding oxidant-to-fuel ratio were prepared and stirred for ~12 h in an oversize glass beaker for thorough mixing and then heated slowly on a hot-plate. These solutions resulted in highly viscous gel after thermal dehydration at 80 °C. In the next step the temperature of the hot-plate was raised to 200 °C where the gel swelled and self-ignited with the evolution of gaseous products. A smouldering like self-ignition occurs for oxidant-to-fuel ratios 1:2.24 (0.446) and 1:3.00 (0.333), while a visible flame appeared on the surface of gel for oxidant-to-fuel ratios 1:3.50 (0.286) and 1:4.00 (0.250). This process was carried out in a fume-hood with protective glass. The flow chart of the auto-combustion process is shown in Fig. 2. According to Chick et al. [16], for glycine–nitrate combustion, primarily N_2, CO_2, and H_2O are evolved as gaseous products. Taking this into consideration and using oxidizing and reducing valence of individual elements, the redox reaction during auto combustion for stoichiometric ratio can be expressed as follows:

$$0.91\mathrm{Pb(NO_3)_2} + 0.09\mathrm{La(NO_3)_2\ 6H_2O} + 0.975[0.65\mathrm{ZrO(NO_3)_2} + 0.35\mathrm{TiO(NO_3)_2}] + \frac{101}{45}\mathrm{NH_2CH_2COOH}$$

$$\downarrow$$

$$\mathrm{Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})_{0.975}O_3} + \frac{707}{225}\mathrm{N_2} + \frac{202}{45}\mathrm{CO_2} + \frac{1384}{225}\mathrm{H_2O}$$

The oxidant-to-fuel ratio for this reaction is 1:2.24. It has been observed that during auto-ignition process the large amount of gases evolve, as also shown in above equation. These gases dissipate the evolve heat and minimize the local sintering, making powder highly porous and frothy. A DTA/TG of the gel of stoichiometric ratio is shown in Fig. 3 for illustration. The auto-ignition remained for 5–10 s for all the oxidant-to-fuel ratios and resulted in voluminous powder called ash. The colour of ash changes from pale yellow to dark gray with increase in fuel content (Table 1). It has been observed that temperature of auto-ignition is independent of the oxidant-to-fuel ratio. However, the percentage weight loss during auto-ignition process increases with increase in the fuel content (Table 1). The ash produced with different oxidant-to-fuel ratios was annealed at different temperatures in air. The phase analysis was carried out using Rigaku's powder X-ray diffractometer. The crystallite size of the powder was calculated using Debye–Scherrer line profile analysis, and particle size of the same was determined using SEM (XL30CP, Philips) and TEM (CM200, Philips). The compositional investigations were carried out using energy dispersive X-ray (EDX) attachment on the SEM.

3. Results and discussion

3.1. Effect of oxidant-to-fuel ratio on the formation of perovskite PLZT powder

Fig. 4 represents the X-ray diffraction of ash obtained after auto-ignition for different oxidant-to-fuel ratios. The diffraction patterns for 1:2.24 and 1:3.00 ratios show the presence of crystalline lead nitrate and lead oxy-nitrate phases corresponding to the JCPDS card number 6-151 and 22-390, respectively. The traces of these un-decomposed nitrates are present because of very short time of auto-ignition (5–10 s). However, their content decreases with decrease in oxidant-to-fuel ratio and leading to the formation of lead oxide and the perovskite PLZT phase. Further decrease in oxidant-to-fuel ratio increases the content of PLZT phase in the ash. It can be inferred from Fig. 4 that the lead nitrate initially decomposes to lead oxide and then reacts with other constituents to form crystalline PLZT powder. It is known that the flame temperature during auto-ignition increases with increase in fuel content [8,9,19]. Therefore, the lead nitrate decomposes into PbO and forms PLZT at higher fuel content. An increase in the mass loss with fuel content (Table 1) also reflects the higher flame temperature and consequently higher gaseous evolution.

3.2. Evolution of perovskite PLZT powder by annealing the ash

To understand the mechanism of phase formation from ash to polycrystalline PLZT, we have carried out X-ray diffraction of ash annealed at various temperatures. Fig. 5 depicts the X-ray diffraction patterns at different temperatures for stoichiometric oxidant-to-fuel ratio. The formation of PLZT starts between 500 and 550 °C, without any intermediate pyrochlore phase formation. In addition to PLZT we observed the presence of crystalline PbO phase (Fig. 5). It is clear from Fig. 5 that content of PbO phase decreases gradually with increase in calcination temperature and it disappear for sample calcined above 550 °C. It implies that lead nitrate, present in the ash, initially converts to lead oxide and subsequently reacts with other constituents to form crystalline PLZT. Fig. 6 represents the DTA/TG of the ash for stoichiometric nitrate-to-glycine ratio. It shows that lead nitrate present in ash decomposes into lead oxide (PbO) between 300 and 450 °C (endothermic peak), with

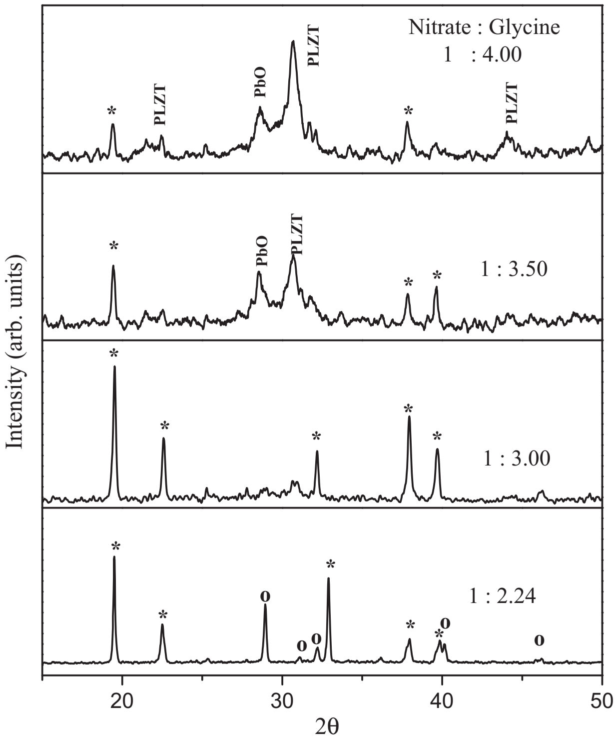

Fig. 4. Powder X-ray diffraction of as prepared ash for different oxidant-to-fuel ratios *$Pb(NO_3)_2$ JCPDS Card: 6-151; **o** – JCPDS Card: 22-390.

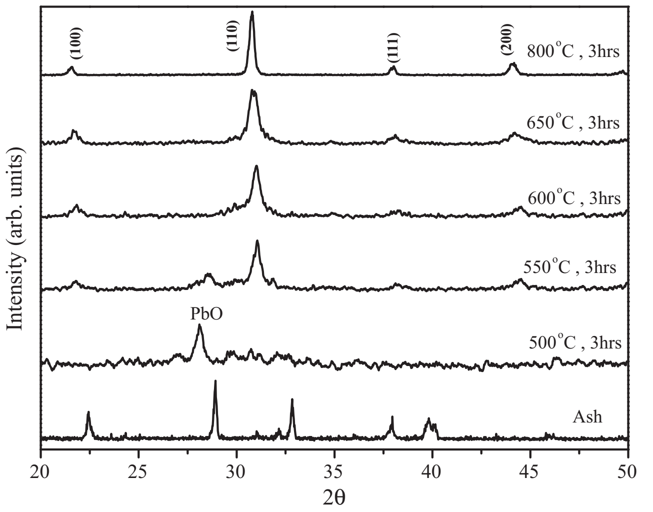

Fig. 5. Powder X-ray diffraction pattern of ash heated at different temperatures for stoichiometric oxidant-to-fuel ratio (1:2.24).

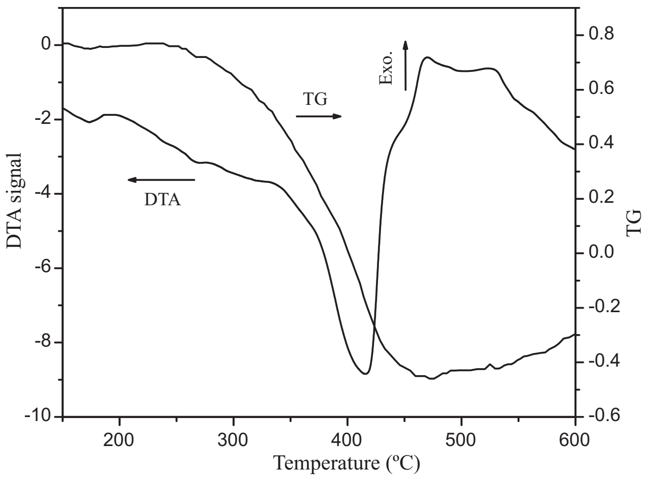

Fig. 6. DTA/TG of ash for stoichiometric nitrate-to-glycine ratio.

immediate crystallization around 470 °C (exothermic peak). The X-ray diffraction measurements, on ash annealed at different temperatures gives similar phase evolution behaviour as observed by increase in fuel content. The crystalline nature of PLZT increases with increasing temperature and is reflected in the width of the X-ray diffraction peaks. The powder annealed at 800 °C exhibit pseudo-cubic structure with lattice parameter 4.053(3)Å. Similar heat treatment was carried out on ash obtained from other fuel contents and it has been found that the transformation behaviour is similar for all fuel contents. More importantly, the ash for nitrate-to-glycine ratio 1:3.50 and 1:4.00, having sufficient amount of crystalline PLZT, shows insignificant change in the PLZT content up to 500 °C. Above 500 °C the transformation behaviour for both these fuel rich ashes is similar to that of 1:2.24 and 1:3.00 ratios. Though it is possible to form crystalline PLZT directly from self-ignition for higher fuel content, but further increase in PLZT concentration takes place by annealing the ash above 500 °C. This implies that the formation of crystalline PLZT is driven by the diffusion kinetics rather than fuel content. Higher fuel content may possibly increase the temperature of the reaction flame but the time may not be enough for the species to react and form crystalline PLZT powder.

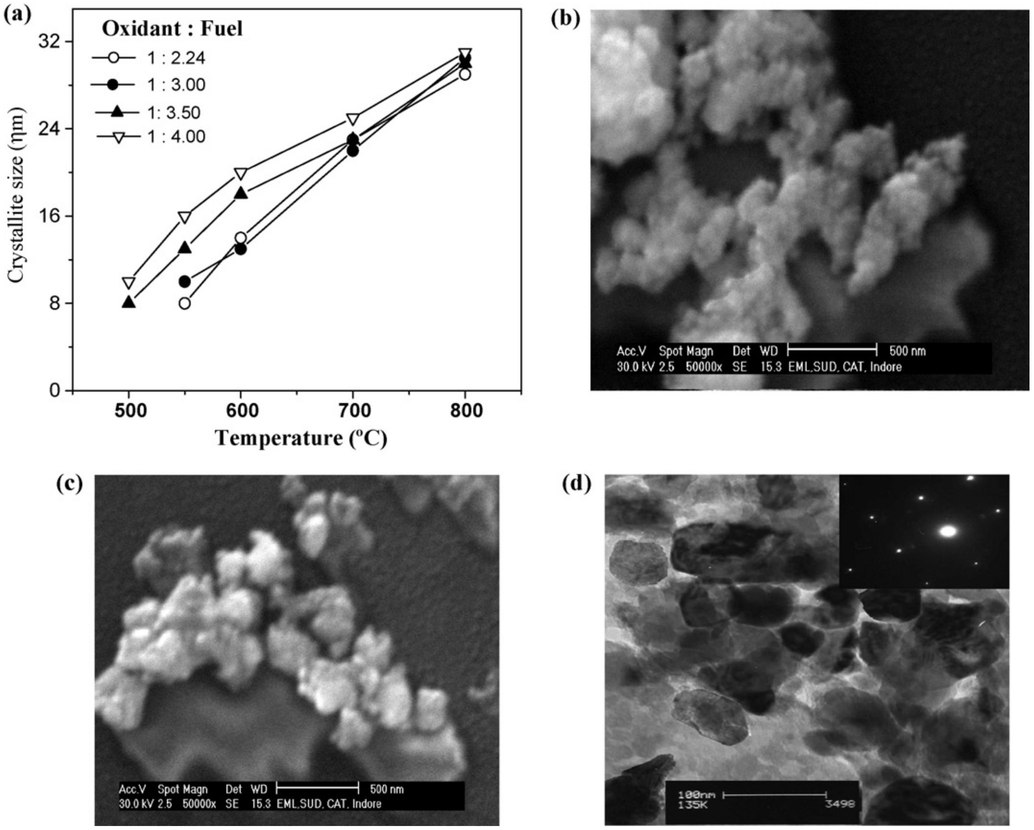

Fig. 7. (a) Temperature dependence of crystallite size for all fuel contents (b & c) SEM photographs of PLZT powder annealed at 800 °C for 1:2.24 and 1:4.00 oxidant-to-fuel ratio (d) TEM photographs of PLZT powder annealed at 800 °C for oxidant-to-fuel ratio 1:2.24.

3.3. Particle size analysis

Fig. 7a shows the temperature dependence of crystallite size of PLZT corresponding to different fuel contents. The crystallite size of the powder was determined by Scherrer broadening analysis of the X-ray diffraction profile. The half-width of Silicon powder was used as a standard to remove the instrument broadening. The crystallite size for all fuel contents increases with annealing temperature of the ash. The crystallite size for fuel ratio 1:3.50 and 1:4.00 is initially high due to the direct formation of crystalline PLZT during auto-ignition process. For fuel 1:2.24 and 1:3.00, no crystalline PLZT has been observed up to 500 °C, Although there is initial variation of crystallite size but for powders annealed at 800 °C the crystallite sizes are nearly the same and independent of fuel content. It is in the range 28–32 nm. These measurements imply that crystallite size of the PLZT powder is primarily dependent on the annealing temperature. With increase in fuel content the crystallite size increases while it become almost independent of oxidant-to-fuel ratio above 700 °C. The increase in the crystallite size conjectured due to high exothermicity for higher oxidant-to-fuel ratio. The high exothermicity increases the flame temperature during reaction causes grain growth in the particles.

Fig. 7 (b & c) shows the SEM photographs of PLZT powder, annealed at 800 °C, for stoichiometric 1:2.24 and 1:4.00 nitrate-to-glycine contents. It has been observed that ultra-fine particles form agglomerates throughout the sample. The primary particles in clusters appear to have spherical shape and average size of 80 nm. The particle size calculated by X-ray line profile broadening is smaller than the observed by SEM. It is because the X-ray broadening reveals the size of the coherently scattering crystallites [20] rather than the particle size. The bigger size of the particle observed in SEM indicates that particles are having multiple coherently scattering crystallites. Transmission electron microscopy (TEM) of the powder for stoichiometric ratio is shown in Fig. 7d. The particle size distribution in the range of 30–100 nm was observed and the shape was not exactly spherical. The electron diffraction revealed a cubic structure as observed in X-ray diffraction.

4. Conclusion

Single phase, PLZT powder has been synthesized by gel combustion method. It is found that different oxidant-to-fuel ratios affect the initial phase formation. Perovskite phase formation in stoichiometric oxidant-to-fuel ratio (1:1.24) takes place after annealing the ash at 550 °C, without formation of any intermediate phase. However, for oxidant-to-fuel ratio 1:3.5 and 1:4.0 a direct perovskite phase formation occurs during the reaction process but the ash contains a mixture of crystalline PLZT along with other constituents. A complete conversion to crystalline PLZT phase occurs only after annealing the ash above 550 °C. The direct crystalline PLZT formation is related to the higher temperature generated during the reaction in fuel rich ratios. The crystallite size was found to increase with annealing temperature but it becomes independent of the oxidant-to-fuel ratio for sample annealed above 700 °C.

References

[1] G.H. Haertling, C.E. Land, J. Am. Ceram. Soc. 54 (1971) 1.
[2] C.G.F. Stenger, A.J. Burggraaf, J. Phys. Chem. Solids 41 (1980) 31.
[3] C.N.R. Rao, J.M. Honig, Preparation and Characterization of Materials, Academic Press, New York, 1981.
[4] K. Kitaoka, H. Kozuka, T. Yoko, J. Am. Ceram. Soc. 81 (1998) 1189.
[5] R.N. Das, A. Pathak, P. Pramanik, J. Am. Ceram. Soc. 81 (1998) 3357.
[6] W.D. Yang, Ceram. Int. 27 (2001) 373.
[7] H. Yamamura, M. Tanada, H. Haneda, S. Shirasaki, Y. Moriyoshi, Ceram. Int. 11 (1985) 23.
[8] S. Roy, S. Byaskh, M.L.N. Goswami, D. Jana, J. Subramanyam, Chem. Mater. 19 (2007) 2622.
[9] R.D. Purohit, S. Saha, A.K. Tyagi, J. Nucl. Mater. 288 (2001) 7.
[10] L.C. Pathak, T.B. Singh, S. Das, A.K. Verma, P. Ramachandrarao, Mater. Lett. 57 (2002) 380.
[11] R.D. Purohit, B.P. Sharma, K.T. Pillai, A.K. Tyagi, Mater. Res. Bull. 36 (2001) 2711.
[12] S.V. Chavan, A.K. Tyagi, J. Mater. Res. 19 (2004) 3181.
[13] V. Bedekar, S.V. Chavan, A.K. Tyagi, J. Mater. Res. 22 (2007) 587.
[14] J. Choy, Y. Han, Mater. Lett. 32 (1997) 209.
[15] M. Cernea, G. Montanari, C. Galassi, A.L. Costa, 17 (2006) 173.
[16] L.A. Chick, L.R. Pederson, G.D. Maupin, J.L. Bates, L.E. Thomas, G.J. Exarhos, Mater. Lett. 10 (1990) 6.
[17] G.K. Chuah, S. Jaenicke, Appl. Catal. A: Gen. 163 (1997) 261.
[18] B. Lee, S. Komarneni, Chemical Processing of Ceramics, 2nd edition, CRC Press, USA, 2005, pp. 147–149.
[19] S.R. Jain, K.C. Adiga, V.R. Pai Verneker, Combust. Flame. 40 (1981) 71.
[20] V.S. Tiwari, A.K. Singh, Dhananjai Pandey, Rev. Solid State Sci. 2 (1988) 173.