

Contents lists available at ScienceDirect

Journal of Alloys and Compounds



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

Chemical synthesis, structural, thermo-physical and electrical property characterization of PLZT ceramics

A.R. James^{a,*}, Rajesh Kumar^b, PremKumar M.^a, K. Srinivas^c, V. Radha^d, M. Vithal^d, M. Vijayakumar^a

^a Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad 58, AP, India

^b Department of Nanotechnology, Anna University, Coimbatore, India

^c Advance Systems Laboratory, Kanchanbagh, Hyderabad 58, AP, India

^d Department of Chemistry, Osmania University, Hyderabad 7, India

ARTICLE INFO

Article history: Received 30 December 2009 Received in revised form 11 February 2010 Accepted 15 February 2010 Available online 23 February 2010

Keywords: Ferroelectrics Sol-gel synthesis X-ray diffraction Thermal analysis

ABSTRACT

The sol-gel process was employed to prepare (Pb_{1-x}La_x)(Zr_{1-y}Ti_y)O₃ (PLZT) ceramics with nominal composition (Pb_{0.92}La_{0.08})(Zr_{0.60}Ti_{0.40})O₃. X-ray diffraction results showed that the perovskite PLZT phase is formed at room temperature itself. The average size distribution of the particles was obtained by small angle X-ray scattering (SAXS). Nano-crystalline particles with a size of the order of ~30 nm were found. Morphological studies were carried out by SEM analyses to observe the grain structure. TG–DTA and DSC studies were used to analyze the thermal properties of the nano-powders, in order to understand the reaction kinetics in them. Poled bulk ceramic samples prepared from the sol-gel derived powders were subjected to electrical measurements, in order to determine the piezoelectric and electromechanical coupling coefficients.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In recent years the amount of research on the solution synthesis of ceramic materials has increased due to the potential advantages of better homogeneity, chemical purity and the wide variety of geometries that can be achieved – ranging from nanopowders to films, fibres or monoliths – which cannot be realized by solid-state processing [1]. The issue of homogeneity is particularly important for electronic ceramics, which generally contain at least two metal ions [2–4]. The processing of electroceramics by means of chemical solutions has become increasingly important especially in the production of transparent PLZT ceramics of large size (up to 100 mm diameter and more) [5]. Recent activities in ferroelectric materials, motivated by the latest advances in thin film growth processes, exploit several phenomena in ferroelectric materials including piezoelectricity, pyroelectricity, polarization switching and electro-optic activity [6,7]. In the perovskite oxide ferroelectric family, lead zirconium titanate (PZT) and lead lanthanum zirconium titanate (PLZT) are the well-known materials and are also the most important key materials used in the industry [7–10]. PZT doped with specific amount of La has been shown to be useful in many applications such as memories (DRAM and

E-mail address: james@dmrl.drdo.in (A.R. James).

FRAM), infrared detectors, electro-optic devices and surface acoustic wave devices and so forth. Modification of the PZT system by the addition of lanthanum sesquioxide has a marked beneficial effect on several of the basic properties of the material, such as increased squareness of the hysteresis loop, decreased coercive field, increased dielectric constant, maximum coupling coefficients, increased mechanical compliance, and enhanced optical transparency [11]. On account of the attractive properties of this material, in this paper, we report on the synthesis of PLZT ceramics via the sol–gel route on the nanometric scale and discuss the structure, thermo-physical and electrical properties of the same.

Another aspect of importance in this paper is that although, in general, irrespective of the synthesis methods, the morphology of nano-particles is mainly inferred from microscopy studies such as SEM/TEM, these techniques have certain limitations. One of the limitations of SEM/TEM is the small sampling volume. When used to analyze the size of a sample, in particular small particles, it is pragmatic to use another technique to corroborate the data obtained via microscopy. One such technique is the small angle X-ray scattering (SAXS) or dynamic light scattering. Scattering techniques sample a larger volume of the specimen and give information about the bulk properties of a sample. In the present study, SAXS technique has been applied to study the size, shape and distribution of particles from scattering data by means of the well-established 'indirect Fourier transformation'.

^{*} Corresponding author at: Defence Metallurgical Research Lab, D.R.D.O., Kanchanbagh, Hyderabad, AP 500058, India. Fax: +91 40 24340884.

^{0925-8388/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2010.02.132

2. Experimental details

Lead lanthanum zirconate titanate with nominal composition [(Pb_{0.92}La_{0.08}) $(Zr_{0.60}TiO_{0.40})O_3$ was prepared by the sol-gel method as described in the following lines. Stoichiometric amounts of nitrates of lead, lanthanum and zirconium i.e., [Pb(NO₃)₂], [La(NO₃)₃], [Zr(ONO₃)₂] of purity >99% were taken in aqueous solution and was designated as solution A. Stoichiometric amount of titanium dioxide [TiO₂] was dissolved in hydrofluoric acid (HF). Then ammonia solution was added drop wise to get a precipitate of titanium hydroxide. This precipitate was washed with double-distilled water to remove excess HF. The resultant precipitate was added to solution A. Then citric acid was added to this solution such that the mole ratio of citric acid: metal ion is 2:1. At this stage metal citrates were believed to be formed. The pH of the resultant metal citrate solution was adjusted to 6-7 by adding dilute ammonia solution drop wise. The solution was then slowly evaporated on a hot plate till a viscous liquid was obtained. At this stage ethylene glycol (gelating reagent) was added such that the molar ratio of citric acid to ethylene glycol was 1:1.2. This mixture was heated at 100 °C for 2-3 h with constant stirring. The temperature was increased to 160-180°C at the onset of solidification to obtain dry gel. The dried gel powders were subjected to X-ray diffraction studies using a Philips PW-3020 diffractometer to confirm phase formation. A scan rate of 2° min⁻¹ was used. The average size distribution of the particles can be obtained by using small angle X-ray scattering (SAXS) technique. This was done using a PW-3830 X-ray generator (Anton-Paar, Austria) operated at 40 kV and 50 mA with a Cu target. The scattering data collected were used to calculate the particle size, shape and distribution of the PLZT nano-particles. Initially the powders were dispersed in a solvent (toluene) and then this solution is subjected to ultrasonic vibration in order to separate the agglomeration of particles (since nano-particles are chemically highly reactive). Thereafter the powders were allowed to remain in suspension for about 24 h following which with the help of a syringe a part of the top of the solution was siphoned off and then injected into a quartz capillary tube for measurement. In addition, to estimate the particle size of the powders, the powders were examined via scanning electron microscopy.

Thermal analysis for the as-dried powders was carried out using a TG–DTA analyzer (TA Instruments, SDT 2960) in air between 30 and 1000 °C using a heating rate of $10 \circ$ C min⁻¹. In order to obtain further information about the reaction kinetics in the dried powders, differential scanning calorimetric (DSC) measurements of the as-dried powders were carried out using a DSC analyzer (TA Instruments, DS2920) between 30 and 600 °C with a heating rate of $10 \circ$ C min⁻¹ in air.

The sol-gel derived powders were stacked in crucible and calcined isothermally in air at 800 °C for 4 h and then cooled. The calcined powder was crushed and pressed into circular pellets of diameter 1 cm and thickness 1 mm using 2 mol% polyvinyl alcohol at a pressure of ~4 MPa using a hydraulic press. The pellets were sintered at 1200 °C for 4 h. During sintering, in order to prevent PbO loss, particularly at high temperatures, a small crucible containing PbZrO₃ with 10 wt% excess PbO was placed in a double crucible configuration. The entire assembly consisted of a doubly sealed alumina crucible with lids sealed with alumina powder as cement. All samples were coated with silver paste on the larger faces to make proper electrical contact. The sample geometries for measurement of the material properties were in conformity with the IEEE standards. Samples were electrically poled at a field of 15 kV cm⁻¹ for 15 min at 100 °C immersing the samples in a silicone oil (Dow Corning 704[®]) bath. Resonance data were acquired using an Agilent-E-4980 Precision LCR Meter, in the frequency range from 20 Hz to 2 MHz, on poled samples.

The elastic compliance s_{11}^E and coupling factor k_{31} can be expressed as follows:

$$\frac{1}{s_{11}^{E}} = 4\rho f_{\rm r}^2 l^2 \tag{1}$$

where f_r is the resonant frequency, l is the sample thickness and ρ is the density of the specimen (in meters). Similarly,

$$s_{11}^{D} = (1 - k_{21}^{2})s_{11}^{E}$$
⁽²⁾

$$k_{31}^2 = \frac{\psi}{1+\psi} \tag{3}$$

where

$$\psi = \frac{\pi}{2} \left[1 + \frac{f_a - f_r}{f_r} \right] \tan \left[\frac{\pi (f_a - f_r)}{2f_r} \right]$$
(4)

The frequency constant of the disks (radial mode disk) were also computed from resonance data using the relation:

$$N_{\rm t} = f_{\rm r} \times D \tag{5}$$

where *D* is the diameter of the disk. Piezoelectric constants are defined as partial derivatives evaluated at constant stress (*T*), constant field (*E*), constant displacement (*D*) and constant strain (*S*) and these boundary conditions can be thought as free, short circuit, open circuit and clamped response, respectively.

The dielectric polarization versus electric field measurements (P–E hysteresis loops) were conducted using a modified Sawyer–Tower circuit. P–E measurements were traced using a triangular waveform.



Fig. 1. X-ray diffractogram of (a) dried gel powder and (b) sintered PLZT.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the sol-gel derived PLZT powders and Fig. 1(b) the sintered compact, indicating the formation of the PLZT in the single phase. It can be seen that Fig. 1(a) exhibits some peaks of crystalline PbO, in addition to the PLZT peaks. This indicates that some of the constituent oxides are still un-reacted. Besides the fact the sol-gel process resulted in a partial phase formation of PLZT (without any heat treatment). The strongest peak, at $2\theta \approx 29.17^{\circ}$, corresponds to the PbO (111) peak, which disappears after heat treatment. Fig. 1(b) is the diffraction pattern for the sintered PLZT pellet.

The results of the SAXS experiments are discussed in the ensuing paragraphs. The experimental scattering function I(q) was obtained for the samples are shown in Fig. 2(a). From the figure it is clear that samples are poly disperse in nature [12]. Fig. 2(b) shows the pair distances distribution functions as a function of r. It can be inferred from Fig. 2(b) that the PLZT (8/60/40) samples prepared via the sol–gel route have an average particle size of around 30 nm.

In the sol gel method, the particles obtained generally are spherical in shape whereas in other processes such as high energy ball milling, the shape of the particles deviates from sphericity, resulting in flaked or elliptically shaped particles. The particles seem to be free from agglomeration since only top solution was taken and injected into the quartz capillary tube. Whereas SAXS gives the average size of the particles, in SEM the estimation of particle size is rather localized to the region being seen under the microscope. Fig. 3(a) shows the SEM micrograph of the PLZT powders. Due to the very fine scale nature of the powders, agglomeration took place resulting in tightly packed agglomerates of size around 450 nm. The average particle size was found to be in good agreement with the SAXS result. The result of SEM and SAXS together confirm that the particles are nano-sized. The particles are spherically shaped as expected from the sol gel technique. Fig. 3(b) is the SEM micrograph of a fractured surface of sintered PLZT. The grain size of the PLZT ceramics was found to be $1-3 \mu m$. The ceramics show a well-sintered dense microstructure.

Fig. 4(a) shows the thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Curves for the sol–gel derived PLZT derived powders taken simultaneously in the temperature range of 30–1000 °C. The weight loss observed in TGA curves between 200 and 400 °C can be attributed to the removal of water and other volatiles. The TGA curve shows a sharp weight loss peak at 580 °C; this is due to the release of volatiles and onset of lead loss from the powders. The lead loss from the powders continued even beyond



Fig. 2. (a) Double logarithmic plot of the experimental scattering intensity, $\log I(q)$, versus the scattering vector $\log q$ for the PLZT as gel powdered sample. (b) Plot of the experimental pair distance distribution function, p(r), vs. size r for the as-dried gel PLZT sample.

this temperature up to 1000 °C. There is a significant weight loss from ~92% at 580 °C to ~7% at 1000 °C, whereas the weight loss due to removal of solvents and other volatiles in the temperature range of 200–580 °C is 4%. DSC data shown in Fig. 4(b) reconfirms the observations found in the DT–TGA analyses. The observed weight loss due to water and other volatiles from the sol–gel derived powders is observed from 300 to 400 °C. The area under the peak (endothermic peak at 350 °C) is attributed to the heat loss due to the vaporization of volatiles from the powder.

Resonance measurements were used to calculate several electromechanical parameters of the sol-gel derived PLZT ceramics. The resonant and anti-resonant frequencies were determined from the first minimum and maximum impedance peaks, respectively of the admittance vs. frequency scan and the graph is shown in Fig. 5. The figure shows the variation of the real part of admittance as a function of small signal voltage, with swept frequencies over a range from 100 to 300 kHz. These peaks were used to evaluate the values of various electromechanical and compliance coefficients for the sol-gel derived samples. The electromechanical coupling factor is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy, or conversely, converts mechanical energy into electrical energy. The planar coupling factor (k_p) was calculated and was found to be 0.35 (Fig. 5). A compilation of the other electromechanical and compliance coefficients is shown tabulated in Table 1.



(b)

Fig. 3. (a) SEM picture of dried gel powders. (b) SEM picture of fractured surface of



Fig. 4. (a) DTA/TG Curve for sol–gel derived powders. (b) DSC curve for the sol–gel derived powders.



Fig. 5. Admittance data plotted against the applied frequency, showing the resonance and anti-resonance peaks.

Table 1Electrical properties of PLZT-MCP samples.

Physical parameter	Value
Density (g/cm ³)	6.297
Kp	0.35
k ₃₁	0.20
$s_{33}^D (\times 10^{-12} \text{ m}^2/\text{N})$	7.52
$s_{11}^{\vec{E}}$ (×10 ⁻¹² m ² /N)	7.84
N _t (Hz m)	2250

The polarization versus electric field studies resulted in a relatively square shaped hysteresis loop with a Pr of ~17 $\mu C/cm^2$ and a coercive field of about 10 kV/cm Fig. 6. These values are comparable to ones reported by Kong et al. [13] on samples synthesized via the solid-state sintering route, but are significantly lower than those observed in samples synthesized via the high energy mechanochemical processing route by our group [14]. Application of higher electric fields was limited by the increased conductivity of the samples.

PLZT can be sintered to transparent/translucent ceramics that can be used as novel electro-optic materials and can be used for a variety of applications such as electro-optic switches. They were conventionally fabricated by either hot-pressing [11,15] or oxygen-atmosphere sintering via two-step or multiple-step pro-



Fig. 6. Ferroelectric polarization (*P*) vs. electric field (*E*) curve for the sol–gel derived PLZT ceramics.

cessing. Hot-pressing is very time consuming, with low through put, making the process very expensive. Furthermore, hot-pressing derived transparent PLZT ceramics have other unwanted properties, such as optical anisotropy caused by the residual strain and contamination coming from the hot-pressing die materials [11]. Alternatively, oxygen-atmosphere sintering is also widely used. Transparent PLZT ceramics derived from the solid-state reacted powders typically need a sintering temperature of 1250 °C and that too with a time duration of 60 h in flowing oxygen [8]. The high sintering temperature required by the solid-state reaction powders is due to the coarse PLZT powders. To reduce the sintering temperature, fine PLZT powders must be used [16]. Fine PLZT powders are usually synthesized via chemical methods or via the high energy milling process. Preparation of four-component PLZT via chemical process is still a challenge, while the high energy milling method has a problem with contamination. Nonetheless, in this study, we were successful in producing fine particle PLZT via a simple chemical processing route, with a possibility to scale up the same.

4. Conclusions

PLZT ceramics could be successfully prepared by the sol-gel processing route. The sol-gel process resulted in nano-sized powders with an average particle size of 30 nm. This was estimated by SAXS and SEM studies. SAXS measurements also revealed the sphericity of the particles synthesized by this process, unlike the flaky particles obtained by processes such as the high energy mechanical processing route. Thermal analysis studies in the form of TG-DTA and DSC studies were used to analyze the thermal properties of the nano-powders, in order to understand the reaction kinetics in them. The electrical property measurements were performed on poled bulk ceramic samples prepared from the sol-gel derived powders. The piezoelectric, electromechanical coupling coefficients and elastic compliance coefficients were determined from the resonance data. The process mentioned herein offers the promise to be scaled up although there is scope for improvement in the electrical property output.

Acknowledgements

This work was supported by Defense Research and Development Organization (DRDO), India. The authors thank ARCI for providing SEM images of some of the powder samples.

References

- D. Segal, Chemical Synthesis of Advanced Ceramic Materials, Cambridge University Press, Cambridge, 1989.
- [2] L.M. Brown, K.S. Mazdiyasni, J. Am. Ceram. Soc. 55 (1972) 541-544.
- [3] B. Malic, in: M. Kosec, D. Kuscer, B. Malic (Eds.), Conference Notes Book of Symposium Processing of Electroceramics, Jozef Stefan Institute, Ljubljana, 2003, pp. 41–52.
- [4] M. Yanovska, E. Turevska, N. Turova, M. Dambekalne, Bull. Acad. Sci. 23 (1987) 658-661.
- [5] A. Sternberg, The features of phase transitions and electrooptic properties of La-doped lead zirconate-titanate and lead scandate-niobate ferroelectric ceramics, Ph.D. Thesis, Institute of Physics, Latvian Academy of Sciences, 1978.
- [6] G.H. Haertling, Ferroelectrics 75 (1987) 25-55.
- [7] G.H. Haertling, J. Am. Ceram. Soc. 54 (1971) 1-11.
- [8] G.H. Haertling, C.E. Land, Ferroelectrics 3 (1972) 269-280.
- [9] X.H. Dai, Z. Xu, D. Viehland, Philos. Mag. B 70 (1994) 33-48.
- [10] C. Randall, D. Barber, R. Whatmore, P. Groves, Ferroelctrics 76 (1987) 311-318.
- [11] G.H. Haertling, J. Am. Ceram. Soc. 82 (1999) 797-818.
- [12] O. Glatter, J. Appl. Crystallogr. 10 (1977) 415-421.
- [13] L.B. Kong, J. Ma, R.F. Zhang, T.S. Zhang, J. Alloys Compd. 339 (2002) 167–174.
- [14] A.R. James, B.S.S. Chandra Rao, M. Pathak, S.V. Kamat, J. Subramanyam, Nanotechnology 19 (2008) 195201–195206.
- [15] M. Cerqueira, R.S. Nasar, E.R. Leite, E. Longo, J.A. Varela, Mater. Lett. 35 (1998) 166–171.
- [16] Y. Yoshikawa, K. Tsuzuki, J. Am. Ceram. Soc. 75 (1992) 2520-2528.