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Synthesis and Sintering of PLZT Powder Made by Freeze/Alcohol Drying or Gelation of Citrate Solutions

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Abstract

Citrate salts of PLZT 9/65/35 were prepared by drying (alcohol and/or freeze drying) and gelation of citrate solutions of PLZT. The decomposition of the citrate salts to form PLZT powder was studied by thermal analysis, X-ray diffraction, and scanning electron microscopy (SEM). It was found that the citrate salts of PLZT composition decompose in two separate stages; after decomposition, powder derived from alcohol dehydration, freeze drying and gelation have similar characteristics. Calcined powders in all cases consisted of 1 μm agglomerates with a surface area of approximately 11 m^2/g. Freeze drying and gelation are preferred over expensive alcohol dehydration. Dense pellets can be obtained from the citrate derived powder by a two stage pressureless sintering process.

1 Introduction

Lanthanum-doped lead zirconate titanate ceramics (PLZT), when fabricated as thin polished plates, have high optical transparency and exhibit excellent electro-optical characteristics.[1] As a result, many applications have been proposed in the field of electro-optics such as optical shutters, light modulators, memories and display devices.[2]

The production of high quality technical ceramics such as electro-optic PLZT components requires close control of powder characteristics such as purity, chemical homogeneity and particle-size distribution. By using chemical solution techniques for the preparation of multi-component powders, it is possible to produce fine, highly pure and homogeneous powders. The preparation of such PLZT powders via solution techniques has been demonstrated by several workers.[3–7] Another technique involves preparing multi-cation aqueous citrate solutions and co-precipitating PLZT citrate powder by alcohol dehydration of this solution.[8]

This method was first applied to the production of chemically homogeneous and fine $BaTiO_3$ powders[9] and later to the formation of PLZT and PZT powders.[8–10] In the alcohol dehydration process, droplets of a PLZT source solution are atomised into an alcohol bath to obtain PLZT citrate salt. The relative volumes of alcohol and source solution are critical; there must be at least 10 times greater volume of alcohol than solution to maintain the amount of water in the bath at a low level. The resulting powder can be filtered, and after drying, calcined to obtain PLZT.

Unfortunately, the alcohol dehydration technique is impractical because of the large volumes of expensive alcohol required which cannot be re-used without purification, and because of the susceptibility of the resulting salt to moisture absorption. Furthermore, the stoichiometry of the powder may be lost during co-precipitation. For instance, when co-precipitating titanium, 1% and 0.1% Ti remains in solution in ten-fold volumes of methyl and ethyl alcohol respectively.[9] This problem is prevented by using either freeze drying or gelation of the solution to yield the citrate salt.

The aim of the present study was to develop a technique which avoided the need for alcohol dehydration. PLZT citrate solutions were either (a) freeze dried, (b) alcohol dehydrated or (c) gelled. Freeze drying and alcohol dehydration yielded citrate powders while gelation led to a bulk citrate gel. All products were then calcined with the aim of forming PLZT powders.

The manufacture and decomposition of the citrate salts and the reaction mechanism to form PLZT powder is described. The properties and sinterability of powders obtained by freeze drying and gelation are compared to those of a powder made by alcohol dehydration.

2 Experimental Procedure

Lead oxide (PbO, >99·9%), lanthanum oxide (La_2O_3, >99·99%), zirconium oxychloride octahydrate ($ZrOCl_2 . 8H_2O$, >99%), titanium butoxide ($Ti[O(CH_2)_3CH_3]_4$, >99%) and citric acid (Analar grade) were used as starting materials. Citrate solutions of each of the cations La^{2+}, Pb^{2+}, Zr^{4+} and Ti^{4+} were prepared by mixing their respective oxides and hydroxides with a citric acid solution and using ammonia gas to regulate the pH so as to obtain a clear solution.[9] The individual citrate solutions were then combined to obtain source solutions of PLZT 9/65/35 with excess Pb^{2+} in order to provide 10 wt% excess PbO to the composition after calcination. The Cl^- anions arising from $ZrOCl_2 . 8H_2O$ used in the preparation of zirconium citrate solutions were removed by repeating the precipitation of ammonium zirconyl citrate in large volumes of ethyl alcohol; washing the precipitate; and re-dissolving in distilled water until there was no reaction with photographic paper. This chloride-free zirconium solution was then used to produce PLZT source solution. Removal of chlorides (Cl^-) from the solution is critical to obtaining single-phase product after calcination.[11,12]

By holding the temperature at 60°C for 16–20 h, PLZT solutions were gelled under magnetic stirring. The starting pH of the solutions was around 7. However, the pH gradually decreased below 6 due to ammonia loss at the gelation temperature, and a white precipitate formed in the solution at these low pH values. The precipitate was re-dissolved by adjusting the solution pH between 8 and 8·5 with ammonia solution. This process yielded translucent or transparent bulk citrate gel.

Alcohol dehydration was carried out by spraying source solution at a rate of 15 cm^3/min (compressed-air sprayer, Aldrich Z12, 630-6) into an ethanol (99%) bath which had a volume 20 times that of the solution to be sprayed in order to maintain the water content in the bath at a low level. The pH of the bath was adjusted between 4 and 4·5 with formic acid during co-precipitation. The white PLZT citrate precipitate was centrifuged from the bath, washed with ethanol and dried at 40°C for 18 h.

PLZT citrate powder was also produced by freeze drying. The source solution was frozen by spraying the solution into liquid nitrogen. Water was then removed from the solid particles of salt and ice sublimation in a freeze dryer (Edwards, Freeze Dryer Modulyo) at −50°C and 133 Pa for 48 h.

The powder surface area was determined by using a Micromeritics Gemini 2360 unit; morphology was examined by secondary electron imaging in a scanning electron microscope (SEM, Camscan series 2). Energy dispersive spectroscopy (EDS) was performed using a LINK AN 10000 system with a Be-window detector.

Decomposition of the citrate salt was studied by DTA and TG (Du Pont thermal analyst 2000, Stanton Redcroft TG-770) at a heating rate of 10°C/min in air. To identify the intermediate phases formed, powders were quenched after being held for 4·5 h at various temperatures in air (10°C/min heating rate), and were analysed by X-ray diffraction using Cu K_α radiation (Philips diffractometer equipped with 1710 diffractometer control unit operated at 40 kV and 30 mA). Due to the 4·5 h isothermal treatment, direct comparison between thermal analysis results and those of quenched samples is not possible.

The citrate gel was calcined by heating in air at 10°C/min to 300°C for 1 h. The resulting homogeneous black powder was ground and re-heated to 500°C at 10°C/min in nitrogen and held for another hour. The nitrogen atmosphere was then diluted by passing oxygen through the furnace, and the powder was further calcined for another 4 h.

Both alcohol- and freeze-dried powders were calcined by direct heating to the calcination temperature (500°C) without any intermediate steps (as was used when calcining the gel) and the atmosphere and thermal treatment times were the same.

The resulting powders were energy milled in 2-propanol with yttria-stabilized zirconia balls in polyethylene jars for an hour. Green pellets of 10 mm in diameter and 1 to 2 mm in thickness were then produced by uniaxial pressing at 130 MPa. A two stage sintering technique was used to densify the green pellets. In this technique the pellets were placed in an upside-down platinum crucible with a tight lid. A small amount of identical PLZT powder was used to prevent reaction between the pellets and the platinum crucible. The platinum crucible was flushed with oxygen and the samples were held at 1180°C for 1 h in an oxygen atmosphere. The samples were then transferred in a closed alumina crucible (the so-called double crucible technique, one inside the other) and re-sintered at 1125°C for 13 h in air. Heating and cooling rates were 400°C/h during sintering. This two-stage sintering technique is a modified form of the improved atmospheric sintering method reported by Snow.[13]

Grain size measurements were made using the linear intercept method[14] on samples thermally etched at 1050°C for 1 h in closed platinum crucibles. Optical transmission was determined by using a Perkin-Elmer 330 Spectrophotometer for wavelengths of 350 to 1050 nm on 0·2 mm thick samples polished to an optical finish with 0·25 μm diamond paste.

3 Results and Discussion

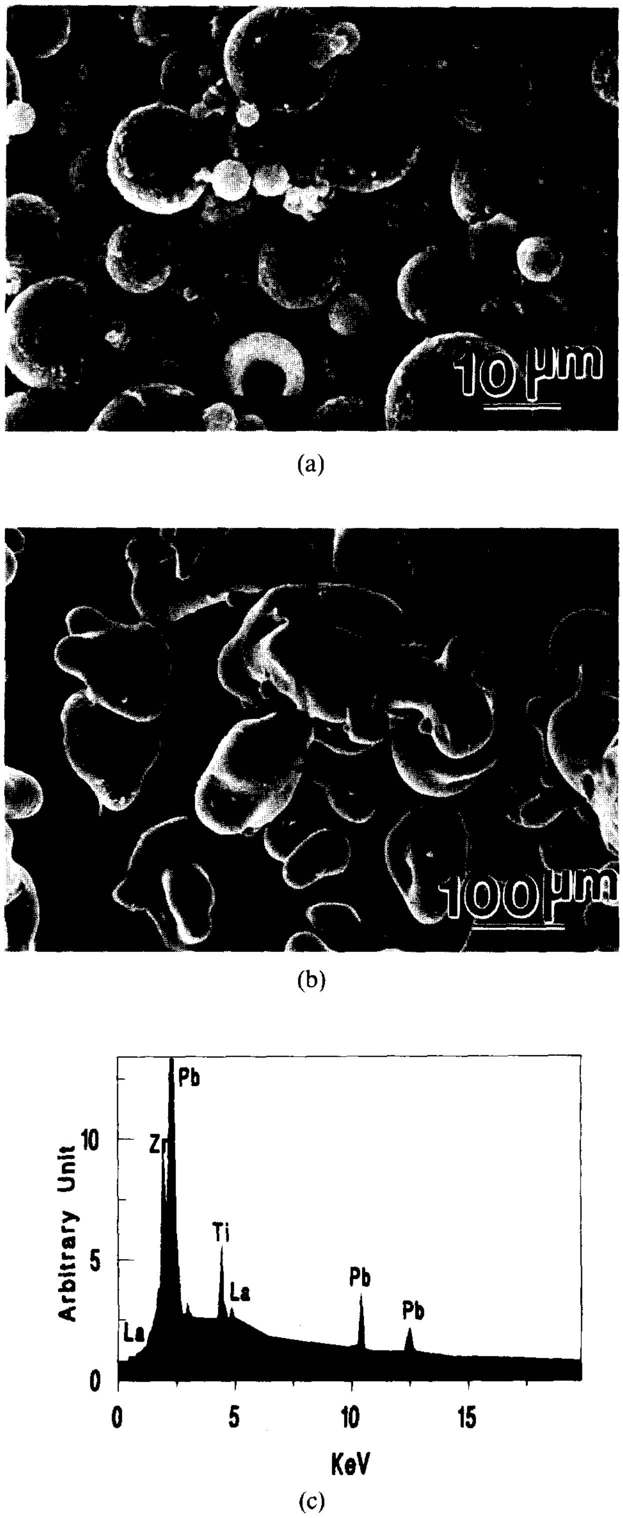
3.1 Processing and morphology of powders

3.1.1 Preparation of citrate solutions and gelation
The citrate route yielded a clear and colourless solution of each individual component of PLZT. No precipitation was observed when individual solutions were mixed together to obtain PLZT source solution of the desired composition. After gelation, the colour of the gel was cloudy white and all the solutions and gels were stable even after seven months storage in airtight plastic containers.

3.1.2 Alcohol- and freeze-dried powders
Both alcohol- and freeze-dried powders were white in colour and free flowing when fully dried. The alcohol-dried particles were spherical prior to calcination and 4–10 micron in size (Fig. 1(a)). While various particle shapes, such as globules and rods,[8,9] have been reported previously for alcohol-dried powders, spherical particles have not been obtained although this is simply achieved by control of the parameters when spraying the solution into the alcohol bath. TEM could not be used to resolve the fine structure of the powder due to rapid decomposition under the electron beam.

The freeze-dried powder consists of large 100-micron agglomerates which have the shape of deformed spheres (Fig. 1(b)). These agglomerates most likely formed due to partial melting upon freeze drying. This indicates that the freezing temperature of the solution (pH >7) is below −50°C at atmospheric pressure. The early stages of combination of the spherical particles to form agglomerates are indicated by the arrow (Fig. 1(b)).

Both the freeze- and alcohol-dried powders have surface areas below 1 m^2/g as expected from the large particle size and smooth surfaces. Although particles are susceptible to electron beam damage, many EDS analyses obtained from individual particles indicate a homogeneous distribution of elements (Fig. 1(c)).



(a)

(b)

(c)

Fig. 1. Secondary electron imaging of (a) alcohol-dehydrated powder revealing its spherical morphology, (b) freeze-dried powder revealing some agglomeration and (c) EDS analysis taken from alcohol dehydrated spheres indicating a homogeneous distribution of the elements.

3.2 Decomposition of PLZT citrate salts

3.2.1 Thermal analysis
TG analysis (Fig. 2) indicates that PLZT citrate salts decompose in two separate stages. Previous work by Courty *et al.*[15] recognised the existence of two types of pyrolysis for the citrate–nitrate precursors. Type I was characterised by a con-

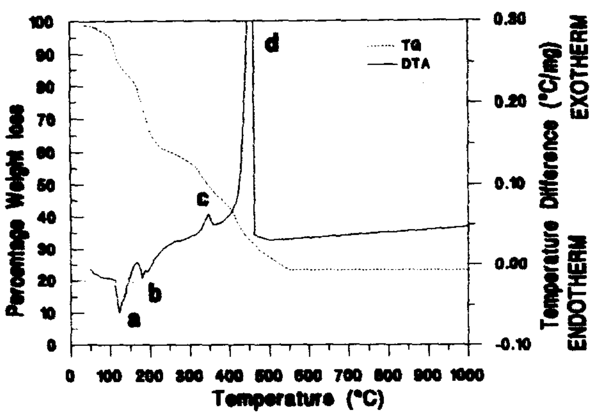


Fig. 2. DTA/TG of PLZT citrate gel. Similar curves result from alcohol-dehydrated and freeze-dried PLZT citrate salts.

tinuous and vigorous reaction which occurred with precursors containing metals with a strong catalytic activity in the oxidation process. Type I decomposition is characterised by a single-stage decomposition in TG. Type II is typified by two stages in which an intermediate decomposition step occurs as a result of the formation of a metastable semi-decomposed precursor which is thought to be a mixed citrate salt.

Citrate gel and alcohol/freeze-dried powders all showed very similar decomposition behaviour. TG and DTA (Fig. 2) indicate that the first stage of decomposition after the removal of water starts at around 120°C (endotherm a on Fig. 2), and continues until 180°C. This part of the decomposition was associated with a 20% weight loss. Samples quenched from 160°C indicated a yellow ochre intermediate phase which was amorphous (Fig. 3). Removal of ammonia and break up of some citrate chains is believed to occur at this stage.[16] The second stage of decomposition is indicated by an endothermic peak at 180°C (endotherm b on Fig. 2) and an associated loss of 25 wt% in a relatively small temperature range of 180°C to 225°C. Samples quenched from 200°C were dark brown to coffee coloured and still amorphous (Fig. 3). Most of the decomposition of the citrate chains occurs at this stage. From 225°C to 500°C, a gradual weight loss is detected due to the break up of any remaining citrate chains. Samples quenched from 300°C were black and still amorphous (Fig. 3) indicating almost complete break up of citrate chains and the presence of carbon as a decomposition product. DTA indicated an exothermic reaction at 340°C (exotherm c on Fig. 2) corresponding to the oxidation of Pb. The rate of weight loss increased after lead oxidation as indicated by TG (Fig. 2). This may imply that lead oxidation acts like a catalyst to ignite carbon oxidation. Exotherm d corresponds to vigorous oxidation of the remaining carbon. Samples quenched from 375, 505, 600, 700 and 800°C were yellow and crystalline (Fig. 3). This indicates that crystallisation of the powder is favoured by the heat produced by oxidation and occurred simultaneously. Although the onset temperature for this reaction was determined as 420°C by DTA, samples quenched from 375°C indicated that the reaction could start at lower temperatures if they were held isothermally for long times. No further DTA peaks were observed above 525°C and the weight remained constant from 530°C to 1000°C.

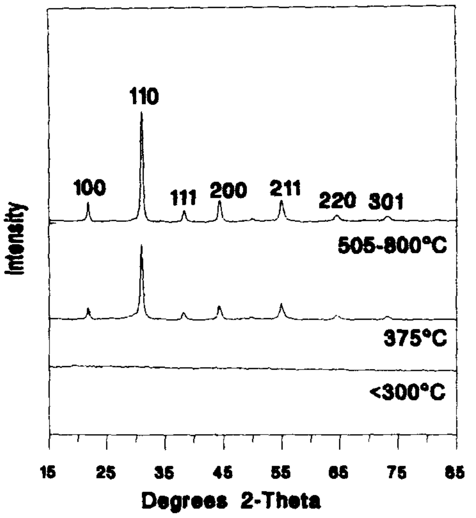
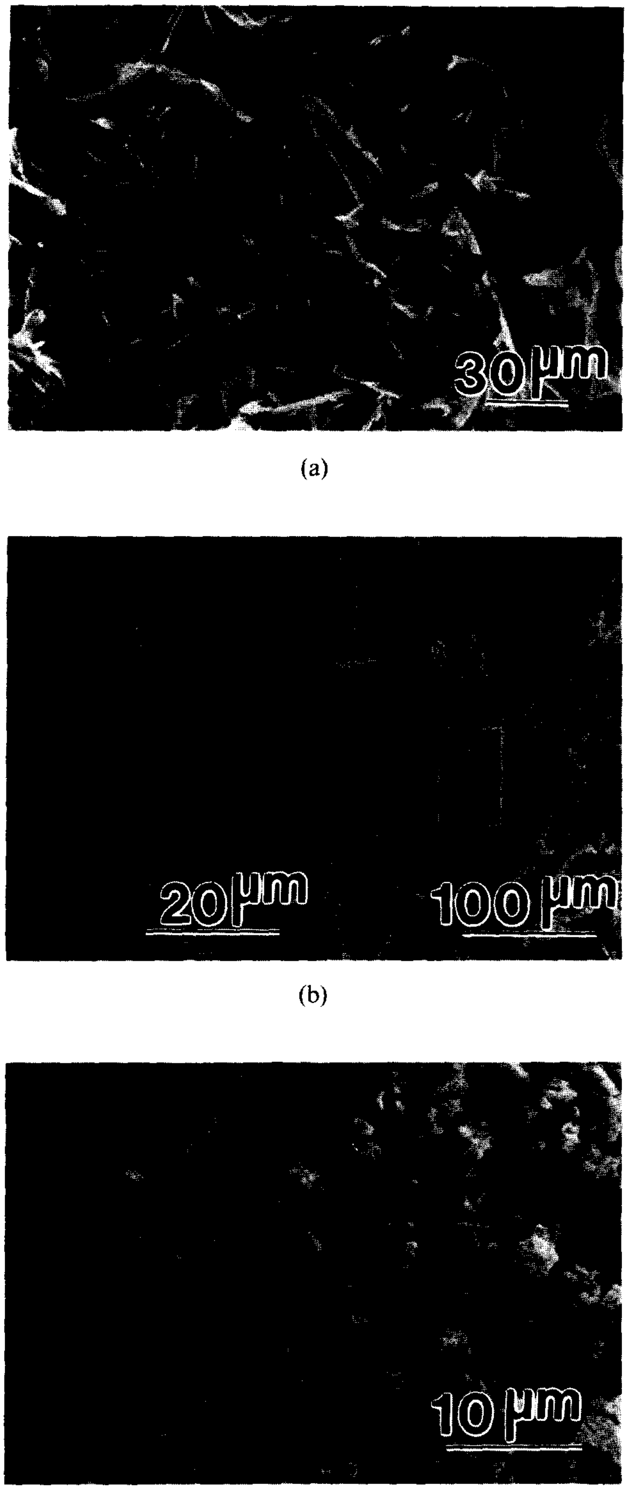


Fig. 3. X-Ray diffraction from citrate gel quenched from various temperatures after 4·5 h isothermal hold. No intermediate phases were observed during the crystallisation of PLZT.

3.2.2 X-Ray diffraction, surface area and SEM analysis

Many workers have investigated the reaction mechanism of formation of PZT solid solution from oxide precursor mixtures. Although these studies reached different conclusions, invariably intermediate phase(s), such as $PbTiO_3$,[17] $PbZrO_3$,[18] and a PbO solid solution[19] were observed prior to crystallisation of PZT. Figure 3 shows a series of XRD patterns obtained from citrate gel quenched from various temperatures after 4·5 h isothermal holds. XRD was not attempted for freeze/alcohol-dried powders since thermal analysis and calcination indicated that the crystallisation mechanism was identical to that of the gel. The powder remained amorphous up to 300°C and then apparently crystallised directly to single-phase PLZT by a vigorous oxidation/ decomposition reaction after 4·5 h at a temperature of 300–375°C. Brown & Mazdiyasni,[4] Duran & Moure,[20] Thomson[5] and Yoshikawa & Tsuzuki[21] reported 600°C, 550°C (16 h), 500°C (16 h), 450°C (14 h) respectively, as the minimum temperature (and time) required to obtain crystalline PLZT phases for their chemically prepared powders. In the present work, this minimum temperature was less than 375°C (4·5 h). No intermediate phases were observed and all the diffraction peak positions and intensities match



(a)

(b)

(c)

Fig. 4. SEM micrographs of citrate gel powder quenched from (a) 160, (b) 375 and (c) 500°C after 4·5 h at temperature indicating the powder morphology at various stages of decomposition.

with those reported for PLZT.[22] With increasing temperature, the peaks get sharper and stronger indicating an increase in crystallite size and amount.

The morphology of the citrate gel powder quenched from 160°C reveals large (30 μm) platy, angular particles with smooth surfaces (Fig. 4(a)). Their smooth appearance indicates that not much citrate decomposition has occurred at this temperature. After the strong oxidation of carbon at 375°C, the particles contain many micro-channels and pores presumably arising from decomposition of citrate chains (Fig. 4(b)). The large porous plates break up revealing many (1 μm) agglomerates after subsequent calcination at higher temperatures (Fig. 4(c)).

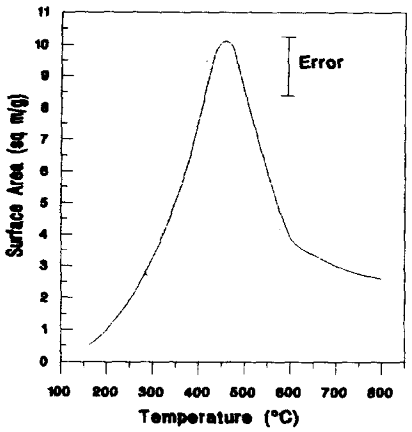


Fig. 5. Change in the surface area of powder with temperature during decomposition. Surface area was measured for powder quenched from various temperatures after 4·5 h isothermal hold of PLZT citrate gel.

Figure 5 shows the variation in the surface area of the calcined gel powder with temperature. Powder surface area increases sharply with increasing temperature up to around 500°C due to the decomposition of citrate salts to porous oxide powders and the fragmentation of the larger plate-like particles (Fig. 4(a)–(c)). A maximum surface area of 10·5 m^2/g was obtained at approximately 450–500°C. Powders calcined at higher temperatures showed decreased surface area due to particle coarsening. Therefore, the optimum calcination temperature was determined to be about 500°C for citrate salts of PLZT.

3.3 Calcination and densification of resulting powder

3.3.1 Calcination of citrate salts

Mulder[9] proposed that properly dried citrate powder does not melt during calcination and hence preserves its shape. However, the morphology of the alcohol and/or freeze-dried powders (Fig. 6), calcined at 500°C in nitrogen/oxygen diluted atmosphere indicates that the spherical shape was lost during calcination. Although the alcohol/freeze-dried powder appeared fully dried and free flowing (Fig. 1(a) and (b)), it was physically observed to melt at around 90°C. The shape of the calcined alcohol/freeze dried powders and their surface areas (11 m^2/g) were similar to those obtained from gel. It was thought that the melting of alcohol/freeze-dried powders might be prevented kinetically by rapid heating of the powder above the carbon combustion temperature. Consequently, some samples were heated to 700°C in

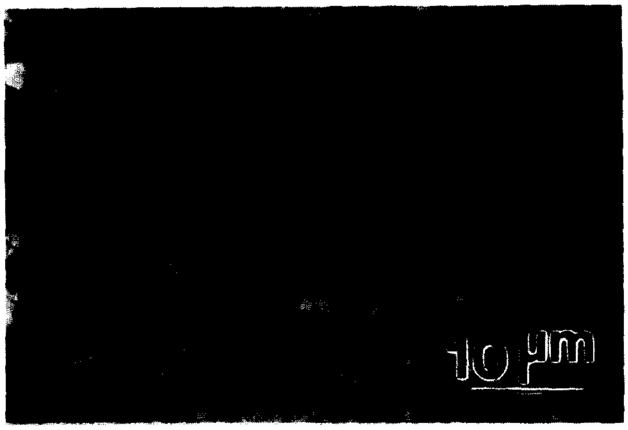


Fig. 6. SEM micrograph of calcined alcohol-dehydrated powder. A similar morphology was also observed for freeze dried powder.

less than 1 min and held for 15 min. However, the morphology of these rapidly decomposed powders was also not spherical.

3.3.2 Ceramic fabrication

After the first sintering stage, all samples were dull red, indicating the presence of excess PbO added to compensate PbO loss and to aid densification. There was no difference between the densification behaviour and final densities of the pellets prepared from alcohol/freeze dried or gel-derived powders. After the second sintering stage, pellets were pale yellow and their final densities were 97% of the theoretical density (which for this composition is 7·9 g/cm^3)[1].

Microstructures consisted of equiaxed grains (Fig. 7) with mean grain size 2·6 ± 0·2 micron. EDS analysis from various grains showed a homogeneous distribution of all elements in the microstructure. Figure 8 shows the variation of transmission percentage with wavelength. Pellets prepared from precipitated or gel-derived powders had similar microstructures and the transmission reached 62% in all cases. This transmission value compares reasonably with those reported for atmosphere sintered samples.[21]

Fig. 7. Scanning electron micrograph of thermally etched PLZT pellet made from gel-derived powder. The dense microstructure reveals equiaxed grains with mean grain size 2·6 micron. Similar densities and microstructure were observed in pellets made from powders prepared by alcohol or freeze drying.

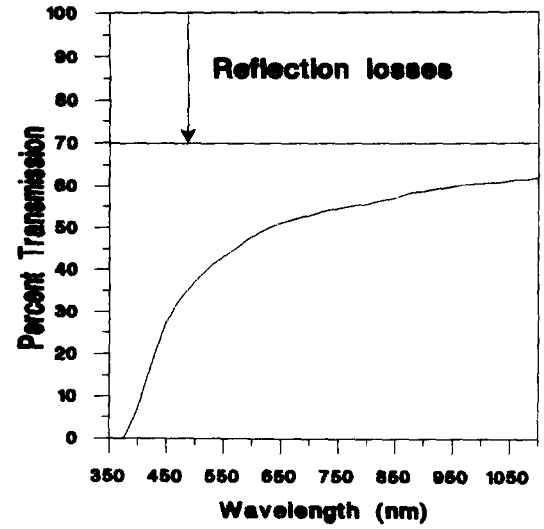


Fig. 8. Optical transmission of a 0·2 mm thick pellet. Maximum transmission was measured at 62%. This particular curve is from the gel-derived pellet with the microstructure given in Fig. 7.

4 Conclusions

(1) PLZT composition citrate salts manufactured by freeze/alcohol drying or gelation of citrate solutions decompose in a two-step process.
(2) Crystallisation of PLZT powder is catalysed by the heat evolved on oxidation of carbon present from citrate groups, occurring at temperatures below 375°C. This is a lower temperature than comparable methods have achieved. PLZT forms directly without any intermediate phase formations.
(3) The characteristics of the PLZT powders formed in each case (alcohol/freeze-dried or gelled) are similar. Alcohol dehydrated powder, however, is expensive to produce and stoichiometry may be lost. Consequently, powders derived from citrate gel or freeze drying are preferred.
(4) Dense and fine-grained ceramics can be made from the powders and lead to high homogeneity via a two-stage sintering process.

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References

1. Heartling, G. H. & Land, C. E., Hot-pressed (Pb, La) (Zr, Ti) O_3 ferroelectric ceramics for electro-optic applications. *J. Amer. Ceram. Soc.*, **54**(1) (1971) 1.
2. Heartling, G. H., Electro-optic ceramic and devices. In *Electronic ceramic, properties devices and applications*, ed. L. M. Levinson. Marcel Dekker, Inc., New York, 1988, pp. 454–81.
3. Heartling, G. H. & Land, C. E., Recent improvements in the optical and electro-optic properties of PLZT ceramics. *Ferroelectrics*, **3** (1972) 269.
4. Brown, L. M. & Mazdiyasni, K. S., Cold pressing and low temperature sintering of alkoxy-derived PLZT. *J. Amer. Ceram. Soc.*, **55** (1972) 541.
5. Thomson, J. R., Chemical preparation of PLZT powders from aqueous nitrate solutions. *Bull. Amer. Ceram. Soc.*, **53** (1974) 421.
6. Yamamura, H., Tanada, M., Haneda, H., Shiraska, S. & Mariyashi, Y., Preparation of PLZT by oxalate method in ethanol solution. *Ceramic Int.*, **11** (1985) 23.
7. Lin, W. K., Jo, M. S. & Chang, Y. H., Chemical preparation of PLZT powders by the carbonate method. *Ceramic Int.*, **14** (1988) 223.
8. Li, C. E., Ni, H. Y. & Yin, Z. W., Preparation of active powder for electronic ceramics by alcohol dehydration of citrate solutions. In *Ceramic Powders*, ed. P. Vincenzini. Elsevier Scientific Publishing Company, Amsterdam, 1983, pp. 593.
9. Mulder, B. J., Preparation of $BaTiO_3$ and other ceramic powders by co-precipitation of citrates in alcohol. *Amer. Ceram. Soc. Bull.*, **49**(11) (1970) 990.
10. Bastos, C. M. R., Jafelicci, JR. M., Varela, J. R. & Zaghette, M. A., Preparation of PZT powder from citrates. In *Ceramics Today—Tomorrow's Ceramics*, ed. P. Vincenzini. Elsevier Science Publisher B. V., 1991, pp. 1983–90.
11. Akbas, M. A. & Lee, W. E., Preparation of PLZT powder by a citrate gel technique. *Brit. Ceram. Proc.*, **52** (1994) 139.
12. Wang, H., Hall, D. A. & Sale, F. R., Phase homogeneity and segregation in PZT powders prepared by thermal decomposition of metal—EDTA complexes derived from nitrate and chloride solutions. *J. Amer. Ceram. Soc.*, **75**(1) (1992) 124.
13. Snow, G. S., Improvements in atmosphere sintering of transparent PLZT ceramics. *J. Amer. Ceram. Soc.*, **50**(9) (1973) 25.
14. Mendelson, M. I., Average grain size in polycrystalline ceramics. *J. Amer. Ceram. Soc.*, **52**(8) (1969) 443.
15. Courty, P. H., Ajot, H., Marcilly, C. & Delmon, B., Oxydes mixtes ou en solution solide sous forme tres divisee obtenus par decomposition thermique de precurseurs amorphes. *Powder Technol.*, **7** (1973) 21.
16. Anderton, D. J. & Sale, F. R., Production of conducting oxide powders by amorphous citrate process. *Pow. Metall.*, **1** (1979) 14.
17. Chandratreya, S. S., Fulrath, R. M., & Pask, J. A., Reaction mechanisms in the formation of PZT solid solutions. *J. Amer. Ceram. Soc.*, **64**(7) (1981) 422.
18. Yamaguchi, T., Cho, S. H., Hakomori, M. & Kuno, H., Effect of raw materials and mixing methods on the solid state reactions involved in fabrication of electronic ceramics. *Ceramurgia Int.*, **2**(2) (1976) 76.
19. Hiremath, B. V., Kingon, A. I. & Biggers, J. V., Reaction sequence in the formation of lead zirconate–lead titanate solid solutions: Role of raw materials. *J. Amer Ceram. Soc.*, **66** (1983) 790.
20. Duran, P. & Moure, C., High density PLZT ceramics prepared chemically from different raw materials. *Am. Ceram. Soc Bull.*, **64**(4) (1985) 575.
21. Yoshikawa, Y. & Tsuzuki, K., Fabrication of transparent lead lanthanum zirconate titanate ceramics from fine powders by two-stage sintering. *J. Amer. Ceram. Soc.*, **75**(9) (1992) 2520.
22. Keve, E. T. & Bye, K. L., Phase identification and domain structure in PLZT ceramics. *J. Appl. Phys.*, **46**(2) (1975) 810.