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PLZT—Synthesis, sintering and ceramics microstructure

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Abstract

Producing of PLZT powders by original two-stage co-precipitation method from mixed solution of inorganic salts $ZrOCl_2 \cdot 8H_2O$, $TiCl_4$, $La(NO_3)_3 \cdot 6H_2O$, $Pb(NO_3)_2$, was carried out. The sequence of phases formed during PLZT synthesis has been studied by X-ray and DTA analysis. Ceramic samples were prepared by two-stage hot-pressing technology. Dielectric, ferroelectric and optical properties have been measured. Ceramic microstructures were studied by SEM with energy dispersive analytical capability (EDX). The fine-grained microstructure was quite uniform with the average grain size of 5–7 μm, without internal or grain boundary porosity. The optical transmittance of ceramic plates (thickness of 0.3 mm) measured at wavelength of 630 nm reached 67–69%.

Keywords: Hot pressing; Powders-chemical preparation; Sintering; Electron microscopy; PLZT

1. Introduction

Traditionally, ferroelectric and electrooptical materials based on the system (Pb,La)(Zr,Ti)O_3 (PLZT) were amongst the first electroceramic materials that have been successfully densified to almost theoretical density.[1] By the application of hot pressing to powders prepared via the mixed oxide route, it is our experience that transparent ceramic of rather small size[2] (about 20 mm of diameter) could be obtained.

In recent years the amount of research into 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.[3] The issue of homogeneity is particularly important for electronic ceramics, which generally contain at least two metal ions.[4–6] The processing of electroceramics by means of chemical solutions has become increasingly important especially in the production of transparent PLZT ceramics of large size[2] (up to 100 mm diameter and more).

The purpose of the present study was as follows: (1) to develop an original two-stage coprecipitation method from mixed solutions of inorganic salts, as follows: $ZrOCl_2 \cdot 8H_20$, $TiCl_4$, $La(NO_3)_3 \cdot 6H_2O$, $Pb(NO_3)_2$, which are commercially available and cheap. At the first stage the hydroxypolymer of TiO_2–ZrO_2–La_2O_3 is obtained by coprecipitation with 25% NH_4OH from mixed solution of the corresponding metallic salts. At the second stage PbO was introduced into the mixture of TiO_2–ZrO_2–La_2O_3; (2) producing ceramic samples by hot-pressing technology, studying the microstructures of the ceramics, measuring the dielectric, ferroelectric and optical properties of the PLZT ceramic samples.

2. Experimental

Fig. 1 shows the flow chart for synthesis of PLZT powder by the peroxohydroxopolymer (PHP) method. The starting salts—$TiCl_4$, $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ were dissolved in water. Coprecipitation occurs when various cations in the solution precipitate simultaneously. Control of the solution conditions – concentration, temperature, pH, mixing – is essential in order to precipitate all the cations simultaneously and yield a perfectly mixed precursor. The metal ions are coordinated by hydroxy (OH^-) or aqua (H_2O) ligands, depending on the charge (z) of the metal cation and the pH of the solution. Cations with $z = 4$ form all types of complexes over the whole pH range: $[M-OH_2]^{z+}$ $[M-OH]^{(z-1)+} + H^+ \leftrightarrow [M=O]^{(z-2)+} + 2H^{+3,5}$. To form a

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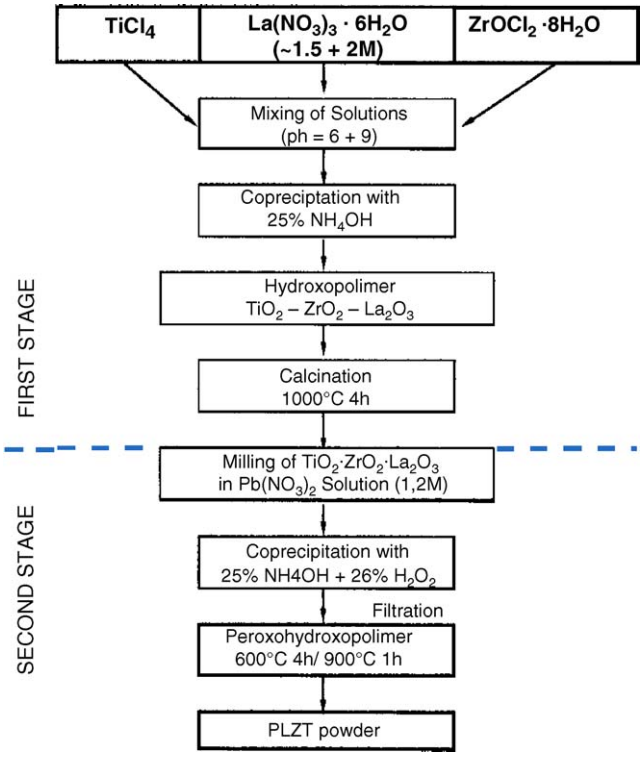

Fig. 1. Flow chart for synthesis PLZT powder by peroxyhydroxypolymer method.

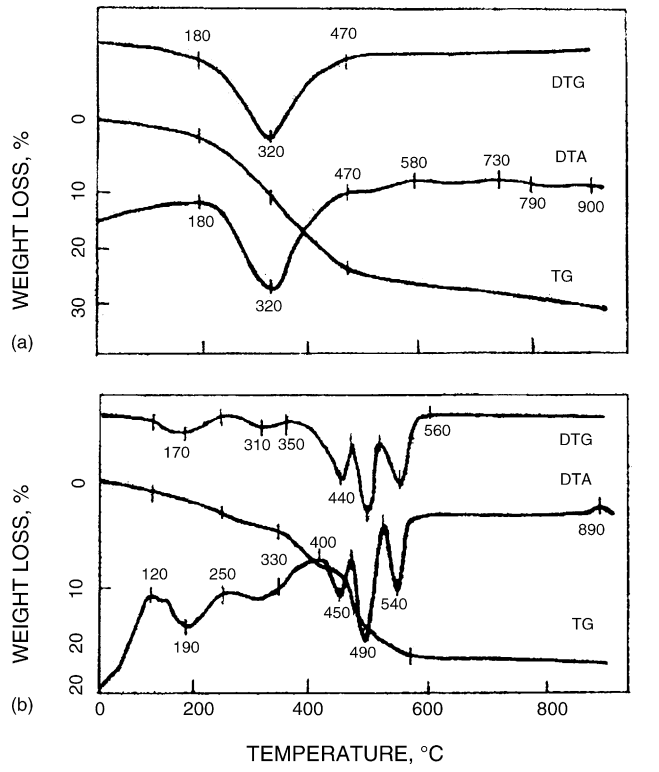

Fig. 2. DTA curves: (a) formation process of LZT (the first stage of peroxyhydroxypolymer method) and (b) synthesis of PLZT by peroxyhydroxypolymer method (the second stage).

hydroxypolymer the concentration of metallic cation had to be at least 1.5 g ion/l for titanium and zirconium and 2.4 g ion/l for lanthanum, with pH about 9. From a mixed solution of the corresponding metallic salts $TiCl_4$, $ZrOCl_2$, $La(NO_3)_3$ with 25% NH_4OH the hydroxopolymer of TiO_2–ZrO_2–La_2O_3 was obtained by coprecipitation as a curd-snow like deposit without any liquid phase. After calcination at 1000 °C for 4 h white powder consisting of $TiO_2{\cdot}ZrO_2{\cdot}La_2O_3$ oxides was obtained. The reactions taking place in the process are as follows:

$$TiCl_4 + ZrOCl_2 + La(NO_3)_3 + 9NH_4OH \rightarrow Ti(OH)_4 + ZrO(OH)_2 + La(OH)_3 + 6NH_4Cl + 3NH_4NO_3 \quad (1)$$

and

$$Ti(OH)_4 + ZrO(OH)_2 + 2La(OH)_3 \rightarrow TiO_2 + ZrO_2 + La_2O_3 + 6H_2O \quad (2)$$

At the second stage PbO was introduced into the white powder consisting of mixed oxides of titanium, zirconium, lanthanum. The white powder of mixed Ti, Zr, La oxides was milled in $Pb(NO_3)_2$ solution of approximately 1.2 M concentration for 10 h in a ball mill. After milling the suspension was coprecipitated by a reagent consisting of 25% NH_4OH and 26% H_2O_2. Rapid reaction takes place, and Pb_3O_4 (brown in colour) was precipitated on the particles of mixed oxide powder. The obtained deposit after filtration was heat treated at 600 °C for 4 h, yielding an amorphous PLZT nanopowder. After a second calcination treatment at 900 °C for 1 h a crystalline powder of PLZT was obtained. The main reaction taking place in the second stage of the process is:

$$3Pb(NO_3)_2 + 6NH_4OH + H_2O_2 \rightarrow Pb_3O_4 + 6NH_4NO_3 + 4H_2O \quad (3)$$

The sequence of phases formed during the synthesis of PLZT by the peroxyhydroxypolymer method was examined by DTA using a Hungarian "MOM" derivatograph. It was found that the reaction sequence for the synthesis of PLZT is complicated and multistage (Fig. 2). Fig. 2a shows the formation of LZT (the first stage of PLZT synthesis). The strong endothermal effects on the DTA curve in the temperature interval 180–470 °C are due to the decomposition of hydroxides, nitrates and chlorides, as suggested by the pronounced endothermal effect in the DTG curve with a minimum at 320 °C and corresponding mass loss (24.4%) on the TG curve. It shows that the most rapid reactions take place in this temperature interval. There is an accumulated weight loss of 31.9% in the process up to 1000 °C. The small exothermal effects on the DTA curve at 580, 730 and 900 °C appear to be due to crystallization processes (TiO_2, ZrO_2, La_2O_3).

In the second stage of the process there is evidence of five endothermal effects on the DTA curves with minima at 190, 330, 450, 490 and 540 °C, due to the decomposition of hydroxides, nitrates and chlorides (Fig. 2b). They are confirmed by relevant weight losses of 2.42, 1.21, 5.45, 4.09 and 4.09% (total 17.3%) on the TG curve. The decomposition process finished at 560 °C. The formation of PLZT solid solution takes place without any exothermal effect; a small unknown event was observed

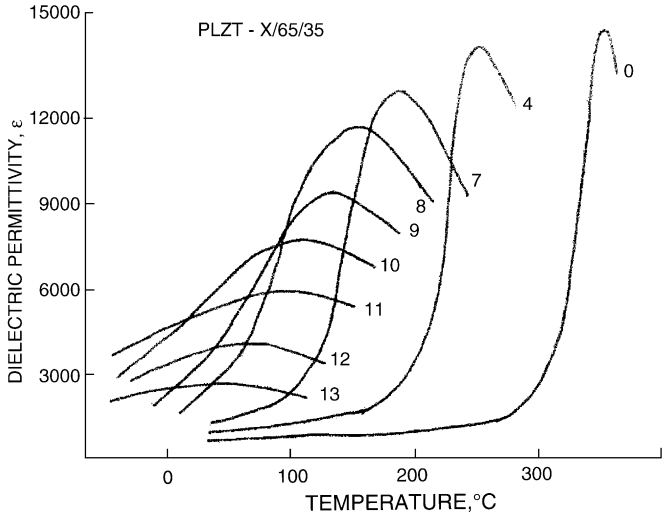

Fig. 3. Temperature dependence of dielectric permittivity $\varepsilon(T)$ for $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})O_3$ ceramics, measured at a frequency of 1 kHz. The numbers on the curves show the atomic percent of lanthanum.

at 890 °C. X-ray diffraction data show that PLZT formation takes place at 600–650 °C.

Transparent PLZT ceramics, of large size (up to 90 mm diameter), were produced by a two-stage hot-pressing sintering process, similar to that reported by Yoshikawa and Tsuzuki.[7] The first stage was performed at 1150–1180 °C for 1 h in vacuum with 20 MPa pressure. The second stage was performed at 1150–1200 °C for 1–40 h depending on size (15–90 mm diameter) at a pressure 20 MPa in air or in O_2 rich atmosphere.

Crystallographic studies were made by X-ray diffraction analysis using a DRON-UM1 diffractometer with Co Kα radiation, and Feβ filter. Dielectric permittivity ε and $\tan\delta$ were measured using a HP4284 LCR instrument; the dielectric hysteresis loops were obtained by the Sawyer–Tower circuit in the quasi-static regime.

The optical transmittance of ceramic plates (thickness of 0.3 mm) measured at wavelength of $\lambda = 630$ nm reached 67–69%. It was found that the first stage of hot pressing improved the light transmittance of ceramic samples by 10–20%. An excess of PbO (1–3 wt%, depending on the size of the sample) was added to the powder mixture to compensate for loss of PbO during sintering. Any excess of PbO results in a liquid phase at the sintering temperature, just above 800 °C. A small amount of liquid phase has beneficial effect on the densification kinetics.[8,9]

Fig. 3 shows the temperature dependence of dielectric permittivity $\varepsilon(T)$ for PLZT-*X*/65/35 with $0 \le X \le 13.0$. The dielectric permittivity of PLZT decreases rapidly with increasing concentration of lanthanum. Simultaneously, the temperature of dielectric permittivity maximum T_m gradually decreases, almostly linearly. The dielectric permittivity curves show broad maxima near the phase transition, especially for compositions with $X > 7$.

Fig. 4 shows the dielectric permittivity as a function of temperature for PLZT-9.75/65/35, which evidences the strong dependence of the dielectric permittivity $\varepsilon(T)$ on frequency in the region of phase transition, characteristic to relaxor materials:

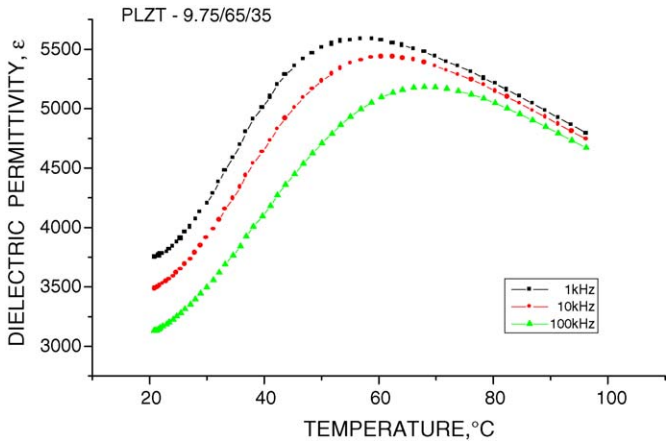

Fig. 4. Temperature dependence of dielectric permittivity $\varepsilon(T)$ of PLZT-9.75/65/65 ceramics, measured at different frequencies.

as the frequency increase, the value of ε_{max} decreases and T_{max} shifts to higher temperatures. In Fig. 5, it can be seen from the quasi-static loops of dielectric hysteresis of the PLZT-9.75/65/35 ceramics the value of full polarization reaches 10.0 μC/cm^2 at an applied field of 10 kV/cm.

The microstructure of PLZT ceramics was investigated by scanning electron microscope (SEM) with energy dispersive detector for X-rays (EDX) and microanalyser. Our studies concentrated on the effect of optimal processing conditions on the final microstructure. SEM images of PLZT with different content of lanthanum ($X = 13.0$, 9.75 and 8.5) are presented in Fig. 6. As a result of the combined thermal regimes, fine-grained material with an average grain size of 5–7 μm was obtained. Homogeneity varies slightly between the different compositions. However, the difference between the homogeneity and grain size of the different compositions is not significant enough to conclude there is any influence of composition. The fine-grained microstructure is quite uniform, with internal and grain-boundary porosity virtually nonexistent.

The influence of the thermal treatment conditions is very important in the formation of high-quality PLZT ceramics.[8,9] An excess lead significantly increased density and transparency

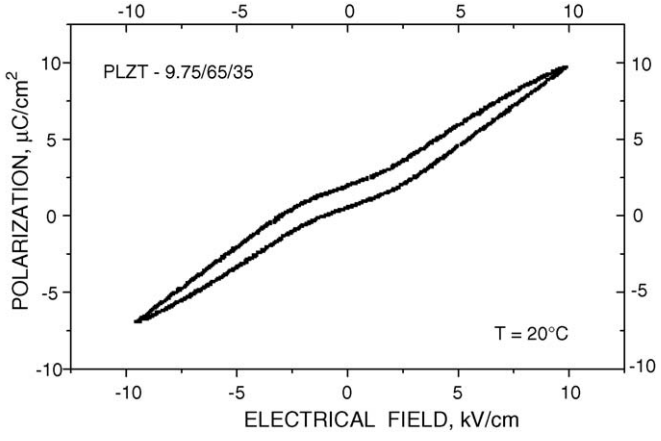

Fig. 5. Polarization hysteresis in PLZT-9.75/65/65 ceramics as function of applied field at 20 °C.

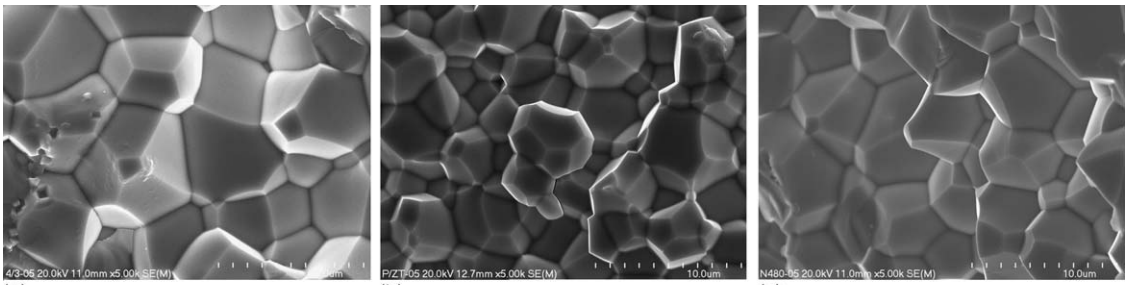

Fig. 6. SEM micrographs of PLZT ceramics prepared with different amounts of lanthanum: (a) La = 13; (b) La = 9.75 and (c) La = 8.

of ceramics. The most important effect on the size and homogeneity of grains is the sintering time. Long sintering times promote mass transport and a considerable increase in the grain size. EDX analysis of individual grains in different compositions indicated a homogeneous distribution of all the basic elements in the ceramics. Chemical analysis of PLZT ceramics by emission microanalyzer for Pb, Zr, Ti and La agreed well with the nominal composition of PLZT, except PbO. The maximum deficiency of PbO from stoichiometry is 2–3 wt%.

3. Conclusions

A new method – peroxyhydroxypolymer – was developed and applied for the preparation of PLZT powders by two-stage coprecipitation. The principle advantage of this method is the possibility of using less expensive materials—inorganic salts $TiCl_4$, $ZrOCl_2{\cdot}8H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Pb(NO_3)_2$, making the preparation cost lower than those for sol–gel and other methods. Additional advantages of this method are that a two-stage synthesis as PbO was introduced in the mixing of oxides (zirconium, titanium and lanthanum) at low temperature. From the synthesis procedure at 600 °C 4 h a fine-grained precipitated almost amorphous powder was obtained, which could easily be milled in a mortar, resulting in a homogeneous powder after calcination. As a result, high density and transparent ceramics were obtained. An excess lead oxide (about 3%) significantly increased density and transparency of ceramics. The first stage of hot-pressing (in vacuum) improves the light transmittance of ceramic samples by 10–20%. A fine-grained ceramic with the average grain size of 5–7 μm was obtained. The ceramic microstructure is quite uniform, with internal and grain-boundary porosity virtually nonexistent. The optical transmittance of hot-pressed plates (thickness of 0.3 mm) measured at wavelength of $\lambda = 630$ nm was 67–69%.

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