PRODUCTION AND PROPERTIES OF PLZT CERAMICS

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Introduction

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 [1]. The issue of homogeneity is particularly important for electronic ceramics, which generally consist of at least two metals [2]. The processing of electroceramics by means of chemical solutions has become increasingly important especially in the producing transparent PLZT ceramics of large size.

The purpose of the present study is: to work out 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 easy available and cheap.

At the first stage is obtained hydroxopolimer of TiO_2–ZrO_2–La_2O_3 by coprecipitation by 25% NH_4OH from mixed solution of corresponding metallic salts. At the second stage in the mixture of TiO_2–ZrO_2–La_2O_3 was introduced PbO.

Experimental

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 coordinate by hydroxo (OH^-) or aquo (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 : $[M\text{-}OH_2]^{z+}$ $[M\text{-}OH]^{(z-1)+} + H^+ \leftrightarrow [M{=}O]^{(z-2)+} + 2H^+$ [2,3].

To form a hydroxopolimer 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, pH about 9. From mixed solution of corresponding metallic salts $TiCl_4$, $ZrOCl_2$, $La(NO_3)_3$ by coprecipitation by 25% NH_4OH was obtained hydroxopolimer of TiO_2-ZrO_2-La_2O_3 as the curds-snow like deposit without any liquid phase. After calcination at 1000°C 4h was obtained white powder consisting of $TiO_2 \cdot ZrO_2 \cdot La_2O_3$ oxides. The reactions taking place in the process are as follows:

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

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

At the second stage in the white powder, consisting of mixed oxides of titanium, zirconium, lanthanum, was introduced PbO. The white powder of mixed Ti, Zr, La oxides was milled in $Pb(NO_3)_2$ solution of about 1.2 M concentrations for 10h in the ball mill. After milling suspension was coprecipitated by reagent consisted of 25% NH_4OH and 26% H_2O_2. Rapid reaction take place, Pb_3O_4 of brown color precipitated on the particles of mixed oxides powder. The obtained deposit after filtration by water pump was thermolysed at 600° 4h. PLZT amorphous nanopowder with perovskite structure was obtained. After the second calcination at 900° 1h a crystalline powder of PLZT was obtained. Reaction taking place in the second stage of process is as follows:

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

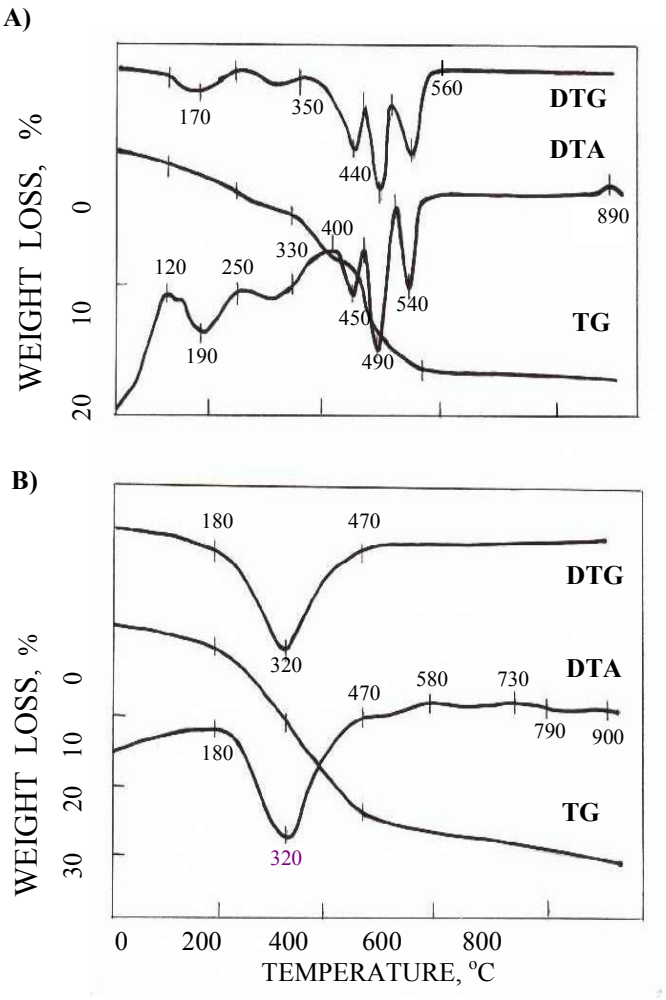


Fig.1. DTA curves:

A– synthesis of PLZT by peroxohydroxopolimer method;

B – formation process of LZT (first stage of peroxo-hydroxopolimer method).

The sequence of phases formed at synthesis of PLZT by peroxohydroxo-polimer method was examined by DTA. Investigation was made by a Hungarian "MOM" derivatograph. It was found that the process of synthesis is very complicated and multistage. Evident 5 endothermal effects on the DTA curves with minimumes at 190°C, 330°C, 450°C, 490°C, 540°C are due to the process of decomposition of hydroxides, nitrates and chlorides. They are confirmed by relevant weight loss of 2.42%, 1.21%, 5.45%, 4.09%, and 4.09% (summary 17.3%) of mass on the TG curve. The decomposition process finished at 560°C. The formation of PLZT solid solution take place without any exothermal effect, a small unknown one was observed at 890°C. X-ray diffraction data show that PLZT formation take place at 600° - 650°C. At Fig.B was studied formation process of LZT (the first stage of PLZT synthesis). The strong endothermal effect on DTA curve tested in the temperature interval from 180° – 470°C are due to the process of decomposition of hydroxides, nitrates and chlorides as suggested by the pronounced endothermal effect at DTG with minimum at 320°C and corresponding loss of mass (24.4%) on the TG curve. It shows that the most rapid reaction take place in this interval of temperature. The summary weight loss of mass was 31.9%, process take place till 1000°C. The little exothermal effects on the DTA curve at 580°C, 730°C and 900°C evidently is due to crystallization process of oxides (TiO_2, ZrO_2, La_2O_3).

Transparent PLZT ceramics of large size (up to 90 mm of diameter) were produced by two-stage hot-pressing sintering. The first stage was performed at 1150°C – 1180°C about 1h at forvacuum by 20 MPa pressure. The second stage was performed at 1150°C- 1200°C for 1 – 40h depending on size (15 – 90 mm diameter) at pressure 20MPa in air or rich in O_2 atmosphere.

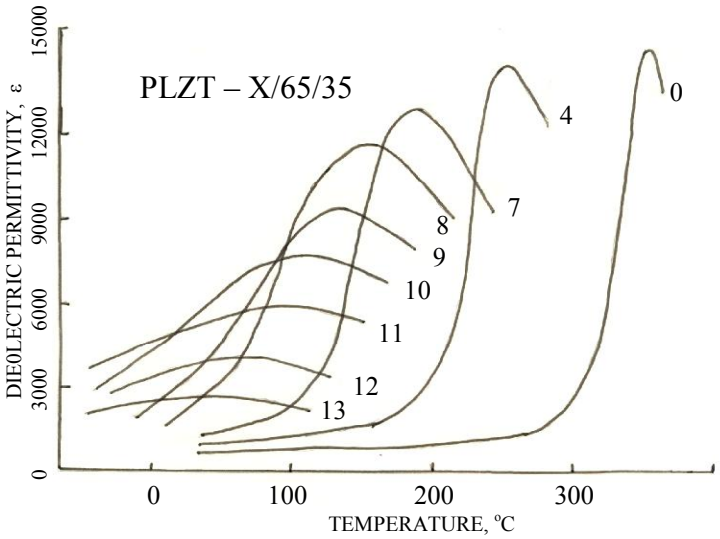


Fig.2. Temperature dependence of dielectric permittivity ε(T) for $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})O_3$ ceramics, measured at frequency 1kHz. The numbers at curves show at.% of lanthanum.

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 tanδ were measured using a HP4284 LCR instrument, the dielectric hysteresis loops were obtained by the Sawyer – Tower circuit in quasistatic regime.

The optical transmittance of ceramic plates (thickness of 0.3 mm) measured at wavelength of λ=630 nm reached 67-69%. It is found the first stage of hot-pressing improve the light transmittance of ceramic samples for 10 – 20%. An excess amount of PbO (1 – 3 wt%) was added to the powder to compensate loss of PbO during sintering

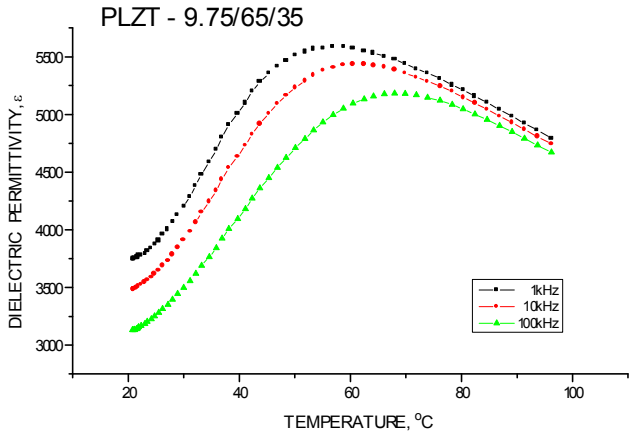


Fig 3. Temperature dependence of dielectric permittivity ε(T) in PLZT–9.75/65/65 ceramics, measured at different frequency.

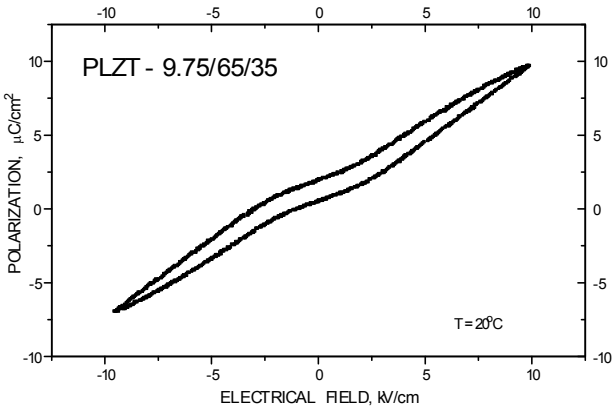


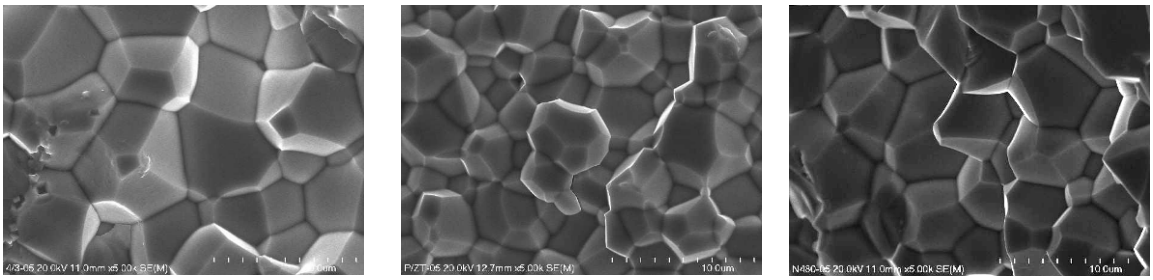
Fig.4. Polarization hysteresis in PLZT–9.75/65/65 ceramics as function of applied field at 20°C.

In Fig.2 is performed temperature dependence of dielectric permittivity ε(T) for PLZT - X/65/35 with $0 \geq X \leq 13.0$. The value of dielectric permittivity of PLZT decreases rapidly with increasing the concentration of lanthanum. Simultaneously the temperature of dielectric permittivity maximum Tm gradually decreases, almostly linearly (≈ 24.5 grad./at.%). The dielectric permittivity curves show broad maximum near phase transition, especially for compositions with X > 7.

Fig.3 shows the dielectric permittivity vs. temperature curves for PLZT - 9.75/65/35, which evidence the strong dependence of the dielectric permittivity ε(T) on frequency in the region of phase transition, characteristic to relaxor materials: as the frequency grows, the value of ε_{max} decreases and T_{max} shifts to higher temperatures.

As seen from the quasi-static loops of dielectric hysteresis of the PLZT - 9.75/65/35 ceramics (Fig.4). SEM images of PLZT with different content of lanthanum (X = 13.0, 9.75 and 8.5) were presented in Figure 1a, b and c. As a result of following thermal regimes the fine-grained material with the average grain size of 5 - 7 μm was obtained. Homogeneity varies slightly among the different compositions, slightly more - uniform grain size. However, the difference between the homogeneity and grain size of the different compositions is not significant enough to conclude any influence of composition. The fine-grained microstructure is quite uniform, with internal and grain-boundary porosity virtually nonexistent.

The influence of the thermal conditions is very important in the formation of high-quality PLZT ceramics. An excess lead significantly increased density and transparency of ceramics. The most important effect on the size and homogeneity of grains has sintering time. Long sintering times promote mass transport and considerable increases in the grain size..The example of EDS analysis, obtained for one of the grains for different compositions indicated a homogeneous distribution of all the basis elements of the ceramics within the grains. Chemical analysis of PLZT ceramics by emission microanalyzer for Pb, Zr, Ti and La agreed well with the nominal composition of PLZT.



a) b) c)

Figure 1. SEM micrographs of the PLZT ceramics with different content of lanthanum:
a) La = 13, b) La = 9.75, c) La = 8.5.

Conclusion

A new method – peroxohydroxopolimer – 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 $TiCl_4$, $Pb(NO_3)_2$, $ZrOCl_2 \cdot 8H_2O$, $La(NO_3)_3 \cdot 6H_2O$, making the preparation cost lower than those for sol-gel and other methods. Additional advantages of this method are two-stage synthesis as PbO was introduced in mixing of oxides (zirconium, titanium and lanthanum) at low temperature. From the synthesis procedure at 600^oC 4h a fine-grained precipitated almost amorphous powder was obtained, which could be easily milled in a mortar, resulting in a homogeneous powder after calcination. The optical transmittance of hot-pressed plates (thickness of 0.3 mm) measured at wavelength of λ =630nm reached almost theoretical, 67 –69%.

References

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