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Effects of Powder Preparation and Sintering Procedure on Microstructure and Dielectric Properties of PLZT Ceramics

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Abstract: PLZT ceramics belong to one of the very important groups of functional materials that make a basis for the production of a large range of electronic devices. The microstructure and properties of ceramics depend on the powder preparation and thermal processing conditions. Various techniques have been used to obtain chemically homogeneous and fine starting powders. PLZT powders have been prepared by two different production routes: by a modified Pechini method, using a polymeric precursor method (PMM) and by a partial oxalate method. A two-step sintering process, including a hot pressing, was carried out at 1100 and 1200°C. Distinct phases obtained during the sintering process have been investigated by SEM and EDS techniques and dielectric properties such as permittivity and dielectric loss were measured in a frequency range from 1 to 20 kHz. A significant difference in microstructure and dielectric properties, depending on powder origin and sintering procedure, has been noticed.

Keywords: Sintering; Dielectric Materials; Microstructure.

Резюме: PLZT керамика принадлежит группе функциональных материалов, составляющих основу для получения широкой области электронных приборов. Структура и свойства керамики зависят от способа приготовления порошка и условий спекания. Для получения однородного и тонкого порошка используют различные методы. PLZT порошки получают методом Печины, т.е. методом полимерных исходных веществ и оксалатным методом. Двухступенчатый процесс спекания, включающий и горячее прессование, проведен при температурах 1100 и 1200°C. Структура и новополученные фазы исследованы методами СЭМ и ЭДС. Диэлектрическая проницаемость и диэлектрические потери измерены в диапазоне частот 1-20 кГц. Установлено, что микроструктура и диэлектрические свойства непосредственно зависят от способа приготовления порошка.

Ключевые слова: Спекание; диэлектрические материалы; микроструктура.

Садржај: PLZT керамика припада групи функционалних материјала који чине основу за добијање широког опсега електронских компонената. Структура и својства керамике зависе од начина припреме праха и услова синтеровања. За добијање хомогеног и финог

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праха користе се различите методе. PLZT прахови се могу добити Pechini методом, тј. методом полимерних прекурсора и оксалатном методом. Двостепени процес синтеровања, који укључује и топло пресовање, извршен је на температурама 1100 и 1200°C. SEM и EDS техником испитивана је микроструктура и новодобијене фазе. Диелектрична константа и тангенс угла губитака мерени су у фреквентном опсегу од 1-20 kHz. Микроструктура и диелектрична својства показују изразиту зависност од начина припреме праха.

Кључне речи: Синтеровање; диелектрични материјали; микроструктура.

1. Introduction

Increasing demands on high quality of PLZT ceramics, which are widely used due to their piezoelectric and electrooptic properties, have led to significant improvements in powder preparation and the subsequent sintering process. Hence the synthesis of high purity and ultrafine powder, with good chemical stability, is of primary importance for the production of specific design ceramics. PLZT ceramics, like other traditional ceramics, can be produced by a conventional sintering process, starting from oxides or carbonates, which are mechanically mixed, calcined, pressed and sintered at high temperature. When conventional sintering is used a high degree of agglomeration is observed which leads to a non-uniform microstructure of sintered ceramics. A new low-temperature powder preparation method, based on inorganic and/or organometallic precursors, has been developed in order to improve the chemical and optical stability of ceramics [1-4]. The procedure based on both mixed oxides and coprecipitation method is designed for PLZT ceramics, using liquid and oxide precursors. These wet-chemistry based routes, that include coprecipitation and sol-gel processes, are used for fabrication of ultrafine powders of PLZT ceramics. Well-known processes are the Pechini process and oxalate process [2, 4], which enable precise stoichiometry of materials.

The purpose of the present investigation is a comparative investigation of the microstructure and dielectric properties of PLZT ceramics obtained by two different methods of powder preparation. The powders prepared by a modified Pechini method and an oxalate method are sintered using conventional sintering and hot pressing.

2. Experimental

Two kinds of ceramic samples were prepared according to formula $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$, where $x = 0.095$, $y = 0.65$ and $z = 0.35$, generally denoted as PLZT 9.5/65/35. The basic procedure for the powder preparation is a polymeric precursor method denoted the Pechini process starting from organometallic compounds. The first samples, denoted as PLZT (PMM), were obtained from powders prepared by the original pure Pechini method, and the second ones, denoted as PLZT (B), were prepared using a partial oxalate method starting from the Pechini process. In the first one, the organometallic complex is obtained starting from compounds as citrate solutions, i.e., such as La-, Ti-, Zr-citrates and from Pb-acetate, and after thermal treatment and calcination, the powder is milled and pressed into pellets. The precursor used to prepare PLZT powder by the partial oxalate method consisted of a Ti-Zr citrate solution and lead and lanthanum oxalate using the same procedure for preparation before thermal treatment as it was done for the pure Pechini process. After

thermal treatment in three steps and calcination the powder was also milled and pressed into pellets. The preparation procedure for both methods has been discussed previously in [5-6]. For comparison purposes PLZT samples doped with Nb and obtained by the Pechini method, were also investigated and are denoted as PLZT (Nb). One group of pellets was sintered at 1100 and 1200°C for 2 hours by a conventional sintering procedure (c.s.) and other group of pellets was hot pressed with a pressure of 40 MPa for the same time and temperatures. To minimize the loss of PbO during sintering, an oxygen gas atmosphere was used during sintering.

Microstructures of PLZT ceramics, obtained from different powders and sintering procedures were investigated by a scanning electron microscope, JSM 5300, JEOL, Japan, equipped with an EDS system (Energy Dispersive Spectroscopy). Densities were measured by the Archimedes method. Silver paste was applied on the samples for the measurements of dielectric properties. Permittivity and dielectric loss were measured using a HP 4276 LZC meter in the frequency range from 1 to 20 kHz at room temperature.

3. Results and Discussion

In this work PLZT ceramics were prepared according to the chemical formula $\text{Pb}_{0.905}\text{La}_{0.095}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.976}\text{O}_3$ with excess of 3.5 wt.% Pb. The role of excess PbO, which promotes liquid phase sintering, is very important in the initial and intermediate stage of sintering. As it has been reported [7-8] vaporization of PbO in the final stage of sintering is beneficial for the formation of lattice defects, which enhance the diffusion of atoms, thereby fully dense compacts may be obtained. Non-uniformity of the microstructure results partially from agglomeration of fine starting particles and partially from effective evaporation of PbO. It is also possible that due to evaporation of PbO and enhanced diffusion of ions, new phases rich in Pb and La are formed. The main characteristics for both methods are that completion of the phase formation finishes after calcination at 700°C, i.e., the powders exhibit only a pure PLZT phase. A significant difference in values of the specific surface area is noticed. They are higher in the powder obtained by the polymeric method. In all sintered samples a high degree of sintered density, up to 95 % of theoretical density, is achieved. The microstructures of as fired PLZT ceramics, obtained from powders prepared by the polymeric precursor method and sintered at 1100°C, are shown in Fig. 1.

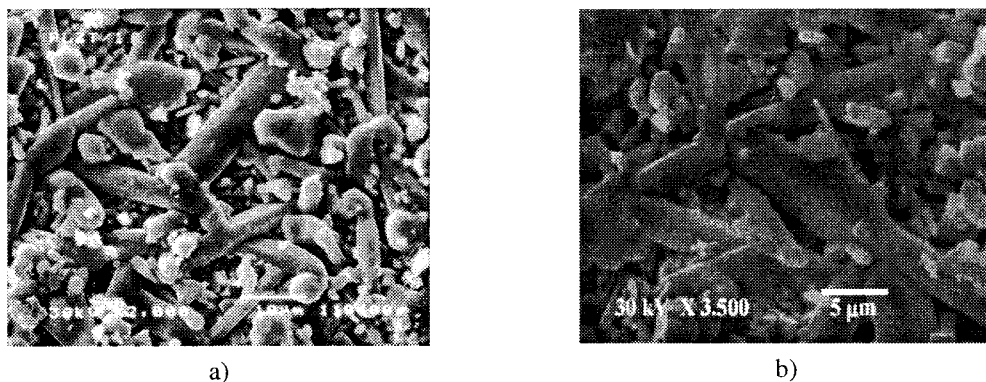


Fig. 1 SEM images of PLZT ceramics obtained by the Pechini method: a) hot pressed and b) conventional sintering.

Due to the submicron particle size and consequently high reactivity of the powder, a non-uniform microstructure was observed, for both sintering procedures (hot pressing and conventional sintering). It can be seen that the microstructure of PLZT (PMM) ceramics, especially on the edge of specimens, reveals three distinct phases: the first one, had randomly oriented elongated grains that have a high aspect ratio, the second one, had small columnar grains and the third phase mainly consisted of equiaxial grains. The microstructure indicated that starting sub-micron particle size powders, prepared by the Pechini process, caused exaggerated grain growth during sintering. After conventional sintering and/or hot pressing at 1200°C, the microstructure of the PLZT (PMM) material is almost uniform with an average grain size of 3-4 μm .

A quite outstanding microstructure was observed for PLZT (B) ceramics obtained by the oxalate method and hot pressing at 1200°C. In (Fig. 2a) a middle region in the sample is shown, where aggregates of very uniform cuboids crystals have developed. Development of these cuboid crystals could be noticed along borders of long grains, which are rich in the Pb phase. Needle shaped grains and pore rich polyhedral grains were also present. The microstructure of ceramic specimens, obtained by the oxalate method and conventional firing procedure, is uniform throughout the specimen and the size and shape of grains are almost identical (Fig. 2b). The average grain size is around 1-2 μm but no distinct grain boundaries can be observed. However, the presence of small pores, less than 1 μm , inside and between the grains is well illustrated.

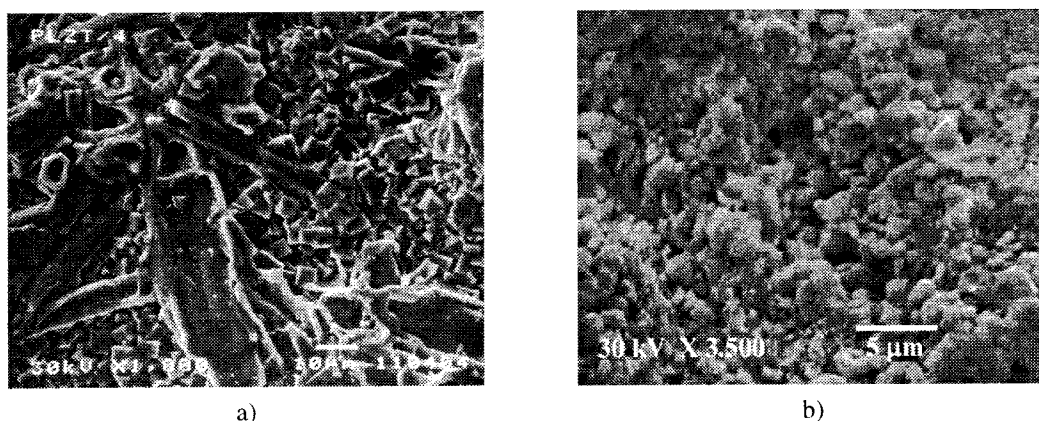


Fig. 2 SEM images of PLZT ceramics obtained by the oxalate method: a) hot pressed and b) conventional sintering.

Non-uniformity of microstructure, particularly on the edge of specimens, together with volatilization of PbO involves the formation of new phases. The composition of long, elongated grains in PLZT (PMM) and PLZT (B) samples is quite different. EDS spectrum for the PLZT (PMM) sample, obtained using a beam controller, shown in Fig. 3, showed that elongated grains, with a high aspect ratio, are rich in Pb and La phases. The Pb/Zr ratio in elongated grains is relatively higher compared to other regions in the sample (their EDS spectrum is given in Fig. 4). It is worth to say that, regarding the small concentration of La, which is less than 1 wt.%, La could not be detected by energy dispersive spectroscopy unless an inhomogeneous distribution and segregation of La are present. The corresponding EDS spectrum taken from the region with elongated grains in PLZT (B) ceramics (Fig. 5) clearly shows the presence of the newly formed phases rich in Pb and Zr with a trace of La.

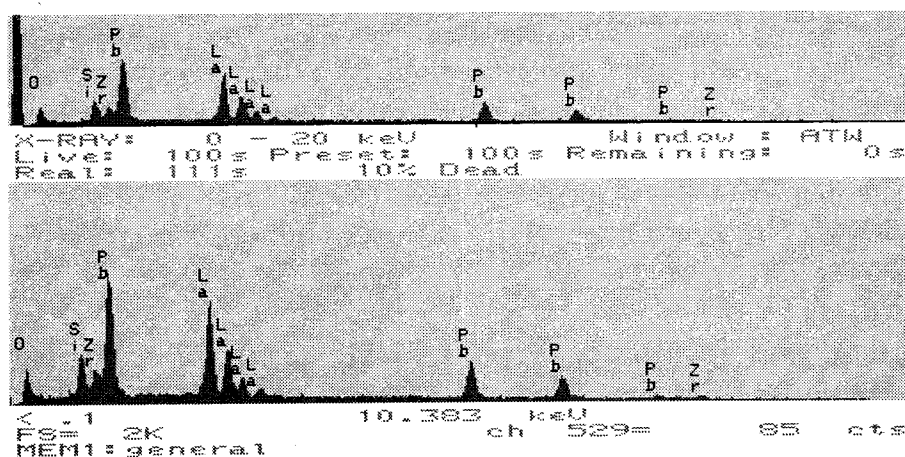


Fig. 3 EDS spectrum of elongated grains in PLZT (PMM) ceramics sintered at 1100°C for two hours.

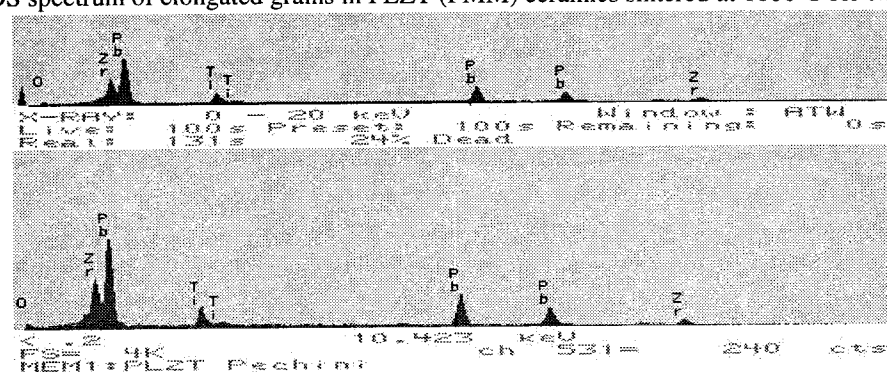


Fig. 4 EDS spectrum of small grains in PLZT (PMM) ceramics sintered at 1100°C for two hours.

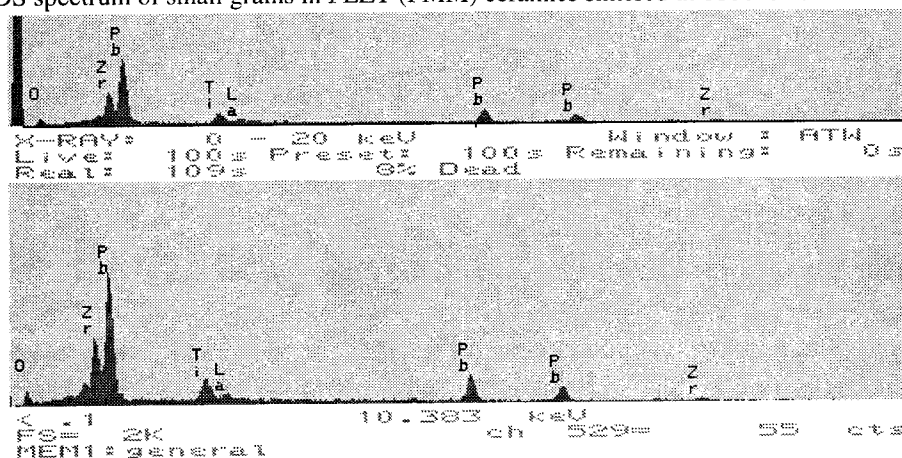


Fig. 5 EDS spectrum of elongated grains in PLZT (B) ceramics sintered at 1200°C for two hours.

Looking at previously obtained results [5] some differences in grain size were observed. It is known that reproducibility of PLZT ceramics preparation by the conventional sintering procedure and hot pressing is a well-known problem. It is usually very difficult to maintain exactly the same experimental parameters during the whole procedure, especially starting from chemically prepared ceramic powders by the Pechini process. Besides, in the previous report opening of the microstructure was done by chemical and thermal etching and in the latter by chemical etching of PLZT ceramics.

A fairly uniform microstructure has been observed in Nb doped PLZT ceramics as illustrated in Fig. 6. The grain size ranged from 2-5 μm and nearly fully dense compacts of 97 % T.D. are obtained although some inner regions indicate the presence of intergranular

pores (Fig. 6b). The density of PLZT (Nb) was higher than for undoped PLZT ceramics. One of the reasons for higher density and small grain size microstructure is that sintering in doped PLZT proceeds at a temperature that is lower than the PbO volatilization temperature. The grain coarsening process at lower temperature is negligible and a uniform microstructure is obtained. The residual porosity is associated with small sized grains.

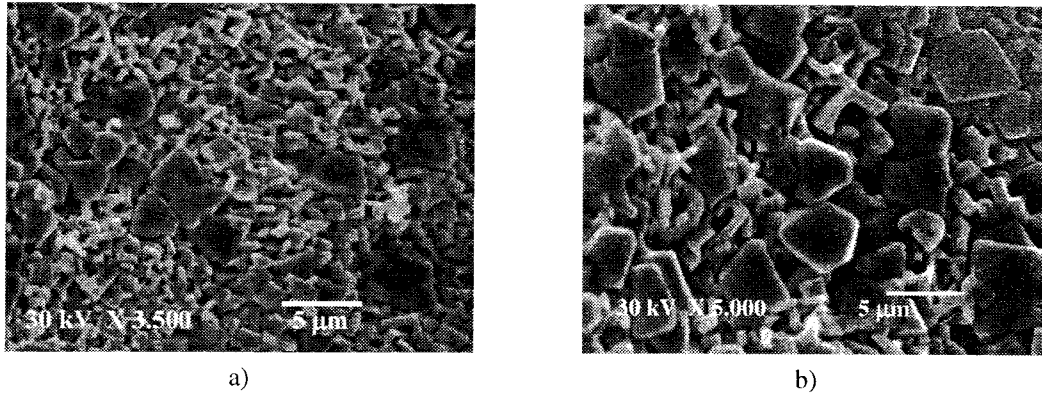


Fig. 6 SEM micrograph of Nb doped PLZT: a) outer and b) inner region.

The room temperature dielectric constant as a function of frequency for PLZT ceramics obtained from different powders is shown in Fig. 7. A common characteristic for all investigated samples is a slow monotonous decrease of the dielectric constant up to 5 kHz, thereafter the dielectric constant is almost constant.

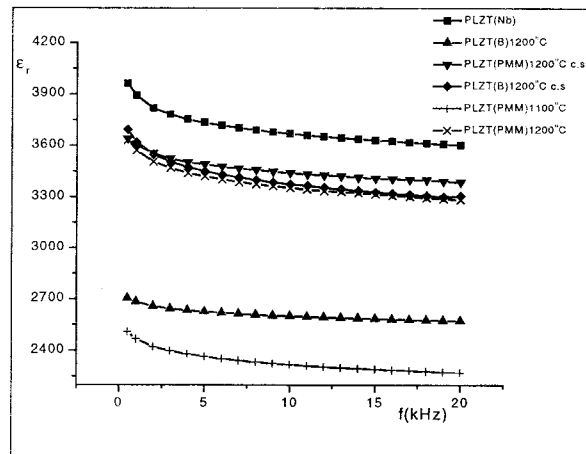


Fig. 7 Dielectric constant as a function of frequency.

As can be seen in Fig. 7 the value of the dielectric constant is higher in samples obtained by the conventional sintering procedure (the samples are denoted as c.s.) compared to the hot pressed PLZT samples. The effect of sintering temperature on the dielectric constant in PLZT (PMM) ceramics is observed to be around 2500 at 1100°C and 3600 at 1200°C at 1 kHz, which can be correlated to the significant difference in their microstructures. For PLZT ceramics obtained by the oxalate method, no difference in the dielectric constant is found in regard to the sintering temperature. A fairly high dielectric constant of 4000 in Nb doped PLZT can be correlated to the small grain size and uniform microstructure in this material. A very coarse microstructure, observed in PLZT (PMM) and PLZT (B) contributes to the low dielectric permittivity in these samples. The difference in dielectric constants can be directly related to the variation in microstructure, size and composition of the grains.

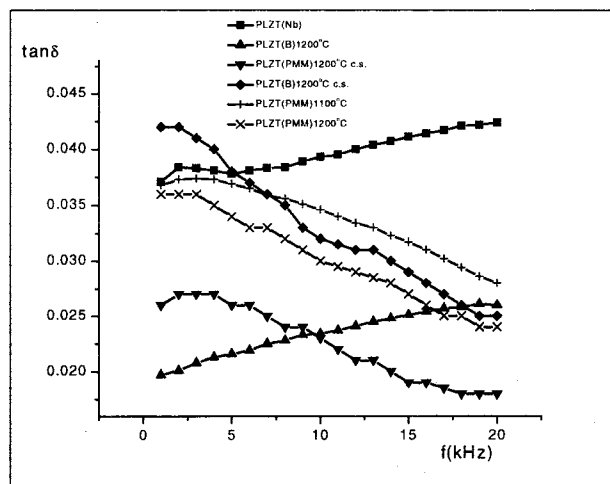


Fig. 8 Dielectric losses of PLZT ceramics as a function of frequency.

On the basis of dielectric loss measurements over a frequency range from 1 to 20 kHz presented in Fig. 8, it can be concluded that dielectric losses for all samples are very low, ranging from 0.020 to 0.042. The highest value of 0.042 at 1 kHz and a considerable change of $\tan \delta$ vs. frequency, from 0.042 to 0.025 at 20 kHz, are found in PLZT (B) samples obtained by conventional sintering. The unusual frequency dependence of $\tan \delta$, i.e., the increase of $\tan \delta$ with frequency is observed in hot pressed PLZT (B) and PLZT (Nb) samples. In contrast to the dielectric constant, that exhibits small changes within the frequency range and becomes constant at frequencies higher than 5 kHz, dielectric losses at room temperature mainly decrease with frequency. Regardless of the small differences in $\tan \delta$, the response of loss tangent to the compositional and microstructural uniformity was more sensitive and selective compared to the dielectric constant.

4. Conclusions

The effects of powder preparation and sintering procedure on the microstructural evolution of PLZT ceramics obtained by a modified Pechini method and partial oxalate process have been investigated. The microstructure of PLZT (PMM) samples sintered at 1100°C reveals the presence of three distinct regions in the samples in regard to the shape, size and composition of grains. Elongated grains with a high aspect ratio consist of Pb and La-rich phases and the Pb/Zr ratio is relatively higher compared to other regions in the sample. The corresponding EDS spectrum of elongated grains in PLZT ceramics, obtained by the oxalate process, reveals the presence of phases rich in Pb and Zr with a trace of La. The microstructure of PLZT (B) specimens using the conventional sintering procedure was uniform throughout the specimens and the size and shape of grains were almost identical. Room temperature dielectric constants of all investigated samples were in the range of 2500 to 4000, and were the highest in samples obtained by the conventional sintering procedure and in Nb-doped ceramics. The dielectric constant does not vary with frequencies above 5 kHz. In general, dielectric losses are very small and are in the range of 0.020 to 0.042 at 1 kHz. A frequency sensitivity of $\tan \delta$ was detected in all investigated samples. A slow increase of $\tan \delta$ vs. frequency was detected in hot pressed PLZT (Nb) and PLZT (B), compared to other samples that exhibit a decrease of $\tan \delta$ with frequency.

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