Ferroelectric materials based on PZT ceramics

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1. INTRODUCTION

Ferroelectric materials offer a very wide range of useful properties for the electronic industry. First reports on ferroelectric ceramics date back to the 1920, and they followed the discovery of ferroelectricity phenomena in Seignette or Rochell Salt by Valasek [1]. These salts were observed to show the hysteresis of polarization and to undergo phase transitions from the polar to the non-polar phase. A huge leap in the research on ferroelectric materials came in the 1950, leading to the widespread use of barium titanate ($BaTiO_3$). Several years later, in the USA Smolenskii, Pepinsky and Mattias extended the list of ferroelectric crystals [2]. Since then, many other ferroelectric ceramics, including lead titanate ($PbTiO_3$), lead zirconate titanate ($Pb(Zr_yTi_{1-y})O_3$), lead lanthanum zirconate titanate ($(Pb_xLa_{1-x})(Zr_yTi_{1-y})O_3$) have been developed and utilized for a variety of applications.

Ferroelectric materials are an electrical analogy to ferromagnets, they can carry a permanent electric dipole moment. Ferroelectrics are non-polar above the Curie temperature (T_C) but are spontaneously polarized with a spontaneous lattice distortion below the Curie temperature. From this it follows that at a temperature $T > T_C$ the crystal does not exhibit ferroelectricity, while for $T < T_C$ it is ferroelectric [3]. On decreasing the temperature below the Curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. The spontaneous polarization is given by the value of the dipole moment per unit volume or by the value of the charge per unit area on the surface perpendicular to the axis of spontaneous polarization [4]. The axis of spontaneous polarization is usually along a given crystal axis. Only crystals with a unique polar axis (10 out of 21 non-centrosymmetric point groups - Fig. 1) show a spontaneous polarization vector P_S along this axis.

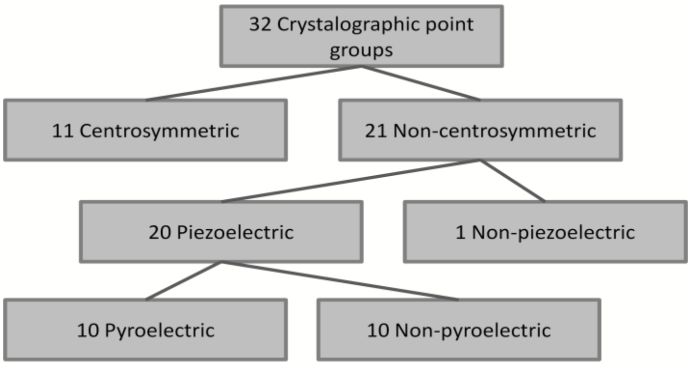

Fig. 1. Crystal symmetry

All ferroelectric materials are piezoelectric and pyroelectric (Fig. 2). However, not all pyro- or piezoelectrics are ferroelectric. Below the transition temperature ferroelectric and pyroelectric materials are polar and spontaneously polarize or possess an electric dipole moment. However, this polarity can be reoriented or reversed fully or in part through the application of an electric field.

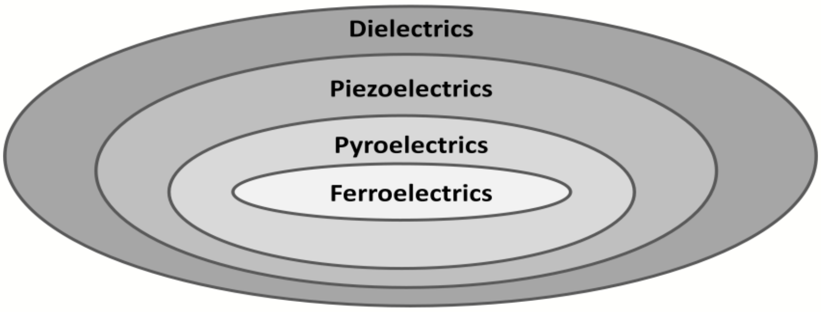

Fig. 2. Classification of ferroelectrics into the different classes of dielectric materials

2. FERROELECTRIC DOMAINS AND HYSTERESIS LOOP

Ferroelectric crystals possess regions with uniformly oriented spontaneous polarization called ferroelectric domains [5]. Within a domain, all the electric dipoles are aligned in the same direction (Fig. 3a). The region between two domains is called a domain wall. The ferroelectric domains are formed in order to minimize the electrostatic energy of the depolarizing fields and the elastic energy associated with the mechanical constraints, to which the ferroelectric material is subjected as it is cooled through the paraelectric-ferroelectric phase transition. These domains form in balance to the net polarization that would otherwise be present in a perfect crystal [6, 7].

The interesting properties of ferroelectrics arise from the fact that it is possible to change the polarization and distortion through applied electric field or mechanical stress. The structure and the size of domains are dependent on the type and magnitude of distortion present in the perovskite crystal structure and other effects such as residual stress induced on cooling. The different states can coexist as domains in very intricate and characteristic domain patterns. These domains can be switched and therefore the domain patterns can be manipulated by application of the electric field and/or mechanical stress.

A very strong field could lead to the reversal of the polarization within a domain, known as domain switching [8]. The main difference between pyroelectric and ferroelectric materials is that the direction of the spontaneous polarization in ferroelectrics can be switched by an applied electric field. The polarization reversal can be observed by measuring the ferroelectric hysteresis as shown in Fig. 3b. As the electric field strength is increased, the domains start to align in the positive direction, giving rise to a rapid increase of the polarization (O-B).

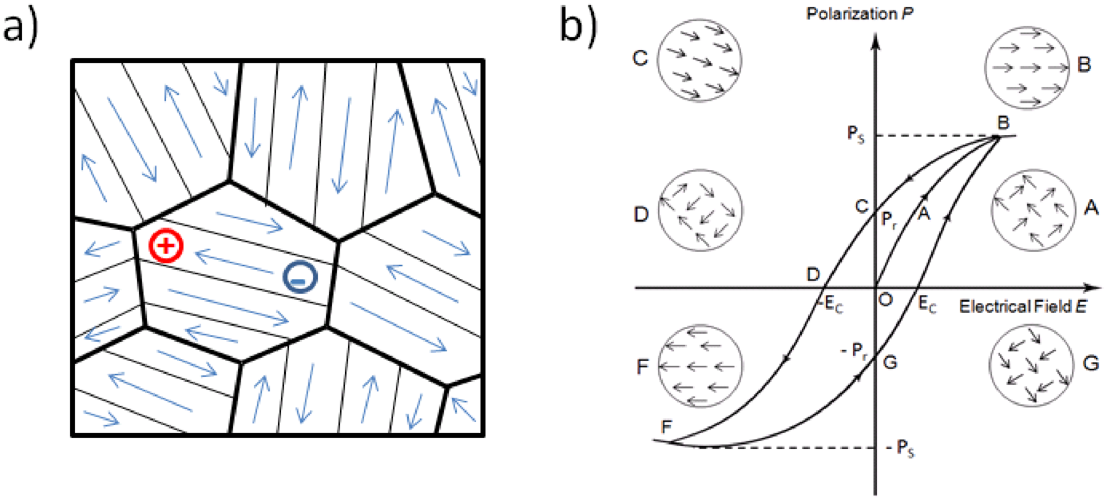

Fig. 3. (a) Orientation of polarization in ferroelectric domain; (b) Polarization vs. Electric Field (P-E) hysteresis loop for a typical ferroelectric crystal

3. PEROVSKITE STRUCTURE

The most interesting group of ferroelectric oxides is the perovskite oxides family. This group consists of numerous compounds with general composition of ABO_3, where A and B represent a different cation element or a mixture of two or more such elements. The physical properties of the entire family are extremely diverse: depending on the composition and cationic ordering, they can be metallic or dielectric and exhibit many different types of structural and ferroelectric order. The perovskite oxides that are ferroelectrics in bulk crystalline form are a subfamily within the entire group, other related compounds might have a tendency to a ferroelectric instability, which however may not be manifested in the bulk crystal due to the dominance of other, non-ferroelectric, competing types of order [9]. The ideal perovskite structure, which can be taken as the high-symmetry reference structure, features the structure of the high-temperature paraelectric phase for most ferroelectric perovskite oxides with a cubic lattice. As shown in Fig. 4, if the atom A is located at the corner of the cube, the B atom is at the center, than an oxygen atom is sited at the center of each face. Most perovskites are distorted and do not have the ideal cubic structure.

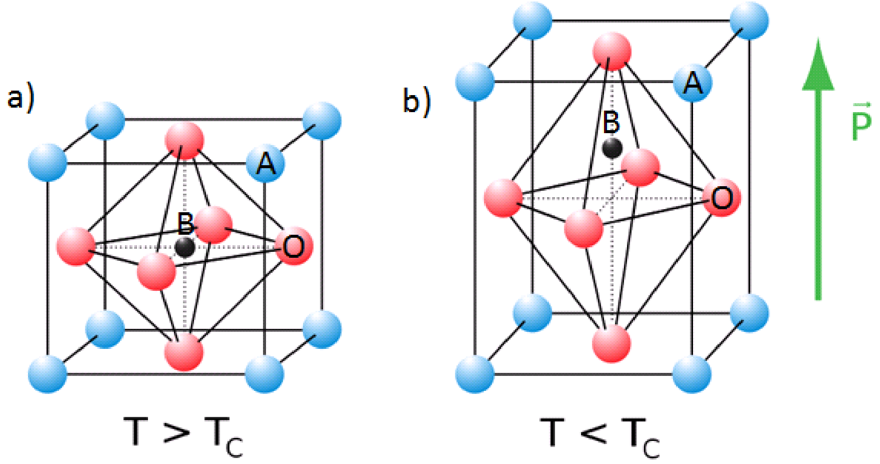

Fig. 4. Crystal structure of the ferroelectric materials: (a) high-temperature, paraelectric, cubic phase; (b) room-temperature, ferroelectric, tetragonal phases

4. PZT CERAMICS

Since their discovery, lead zirconate titanate solid solutions, $Pb(Zr_yTi_{1-y})O_3$ commonly labelled as PZT 100y/100(1-y), are widely recognized to represent a special group of perovskite-type $A(B'B'')O_3$ ferroelectric materials. PZT is an important material in the electronics industry. Its high dielectric constant and low dielectric loss factor over a wide range of temperature and frequency make it desirable as a dielectric material for the manufacture of capacitors, while its ferroelectric properties are exploited for applications such as piezoelectric transducers, sensors and actuators [10]. The aim of the present work is to study the electrical properties of PZT ceramics with particular composition given by the ratio Zr/Ti = 65/35. The materials were prepared by the standard mixed-oxide processing technique, starting from raw powders (TiO_2, ZrO_2 and PbO) of high purity grade (≥ 99.0% in every case). The mixed powders were calcined at 925°C for 3 h. Then, the so-prepared PZT powders were compacted into disk-shaped samples under a pressure of 200 MPa. Complete densification of PZT ceramics can be achieved by using various fabrication methods, such as hot pressing (*HP*) and pressureless sintering (*PS*) at temperatures of 1200°C and 1250°C, respectively.

Dielectric properties were measured on sintered pellets coated with high purity silver paste (to work as electrode) dried at 650°C for 1 h. Dielectric constant (ε) and dielectric loss ($tg\delta$) of the samples were obtained using a capacitance measuring as a function of temperature (from room temperature to 400°C) and frequency (from 100 to 10^6 Hz).

The microstructure of the sintered samples was examined using a scanning electron microscope QUANTA 3D FEG. The grain size was measured by using the line intercept method. The dielectric permittivity and dielectric loss of samples were measured by the Quadtech 1920 impedance meter.

The electric properties of ferroelectric ceramics depend on the microstructure and domain configuration. The microstructure of ceramics includes factors such as grain size or grain boundaries; density, porosity and homogeneity. Therefore, the microstructure studies of ferroelectric materials are very important. Main aim of this contribution is the measurement of the electrical properties of PZT ceramics as a function of the fabrication methods.

5. RESULTS AND DISCUSSION

Fig. 5 shows the scanning electron microscopy (SEM) images of the microstructure of PZT 65/35 ceramics. The samples were prepared by hot pressing method. It is seen from the Fig. 5 that they exhibit dense microstructure and the grains are distributed homogeneously. As shown in Fig. 5, the average grain size was calculated from the backscattered electron images. It increased from 3.7 µm to 9,3 µm for PZT $65/35_{HP}$ and PZT $65/35_{PS}$, respectively. The grain and in turn the domain size increased due to the sintering temperature increase up to 1250°C for the pressureless sintering process. For the PZT $65/35_{PS}$ the maximum grain size was about 15 µm.

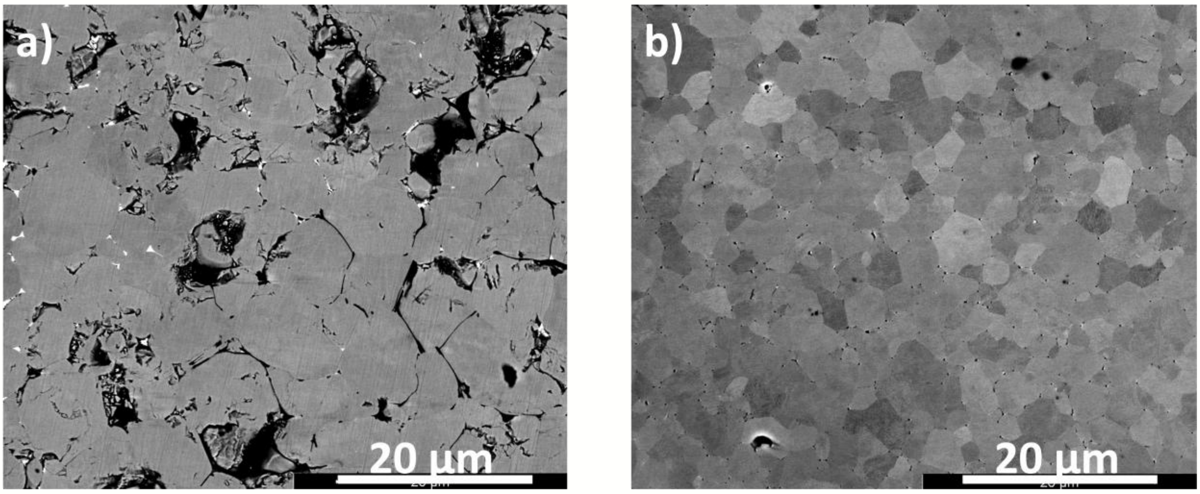

Fig. 5. Scanning electron micrographs (fractured surfaces) of PZT 65/35:
(a) pressureless sintering; (b) hot pressure

Fig. 6a illustrates the temperature dependences of the dielectric permittivity (ε) for the PZT samples at 1 kHz frequency. These samples show dielectric peaks characterizing the ferro- to paraelectric phase transition at T_C. It can be seen that the permittivity of PZT $65/35_{HP}$ is higher than that of PZT $65/35_{PS}$ and T_C decreases from 372°C to 356°C. The value of loss tangent decreases from 0.013 to 0.012 for $Pb(Zr_{0.65}Ti_{0.35})O_3$ HP. In general, all samples exhibit a good thermal stability of the dielectric properties with the loss tangent smaller than 0.06 at 1 kHz.

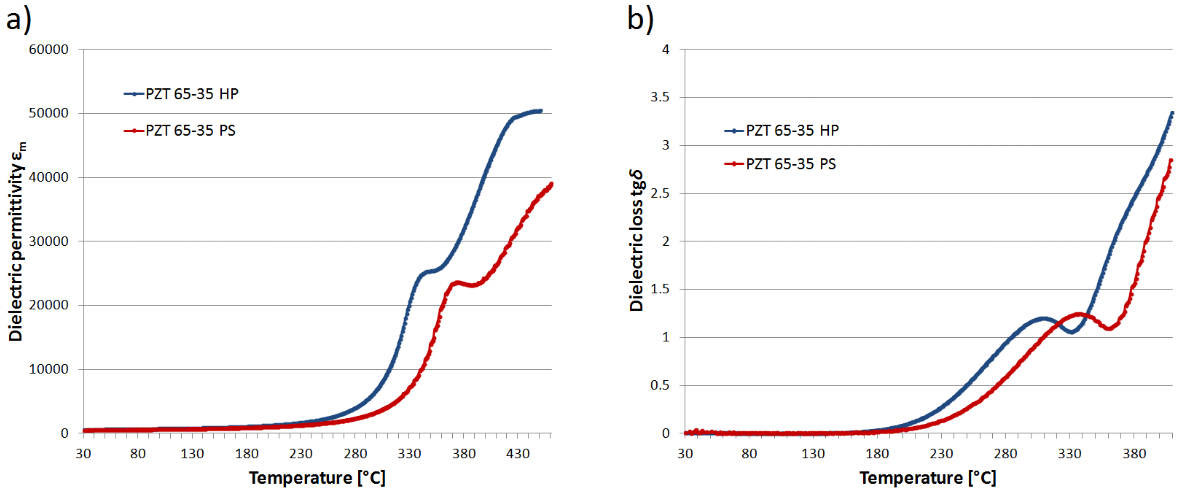

Fig. 6. (a) Dielectric permittivity; (b) dielectric loss as a function of temperature measured during heating for PZT ceramics

6. CONCLUSIONS

The grain size, domain structure and electrical properties are greatly affected by sintering temperature under conventional furnace annealing. Compared with conventional pressureless sintering the samples prepared by hot pressing method exhibit higher permittivity and lower dielectric loss, which makes them suitable for applications involving high frequency output. The ferroelectric Curie temperature was found to decrease with the decrease of the sintering temperature. Consequently, the effect of the grain size on the electric properties is found to strongly depend on the compositions and sintering conditions.

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