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Mechanically activated PLZT ceramics: Structural and electrical properties

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ABSTRACT

Ultrafine powders of $(Pb_{0.92}La_{0.08})$ $(Zr_{0.60}Ti_{0.40})O_3$ (hereinafter designated as PLZT) have been synthesized from oxide powders using the high energy ball milling technique in air atmosphere. The powders milled in agate vials using Yttria stabilized Zirconia (YTZ) balls, were all about 20 nm in size. XRD revealed the formation of a significant amount of the perovskite PLZT phase at room temperature itself. The bulk ceramic samples were subjected to electrical poling, prior to performing resonance measurements on them, in order to determine the piezoelectric and electromechanical coupling coefficients. Poled samples exhibited large strains under the influence of applied electric fields, with limited hysteresis. The effect of powder refinement on the structural and electrical properties of PLZT ceramics are correlated in this paper.

1. Introduction

Among the various techniques for synthesis of nanocrystalline powders of complex oxides for use as advanced ceramics, the mechanochemical processing route has been found to be very effective and the simplicity that the process offers is an added advantage [1]. The reactivity of starting materials can be improved significantly by mechano-chemical processing and therefore the associated calcinations temperatures for the formation of the desired ceramic phases could be reduced very effectively. It has also been reported that the sintering temperatures of many systems were effectively lowered by 150–200 °C via this processing route without any deterioration of their properties [2–4].

Ferroelectric $Pb_{1-x}La_x$ $(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT) ceramics has attracted continuous attention in recent years due to its possible applications in memory elements [5]. The early measurements of the dielectric, pyroelectric, and electrooptic response in relaxor PLZT ceramics were followed by several more studies [6–9]. This paper reports the synthesis of nano-crystalline PLZT 8/60/40 using the high energy milling method and the structural and electronic properties of the same.

2. Experimental

Commercially available AR grade powders of Aldrich USA were used as starting materials in order to synthesize PLZT. PbO, La_2O_3, TiO_2 and ZrO_2 were used as starting oxides (all having purities > 99.9%). The raw materials were mixed with the appropriate amounts of $(Pb_{0.92}La_{0.08})(Zr_{0.60}Ti_{0.40})O_3$, and then milled with Yttria-stabilized Zirconia balls of 3 mm diameter (TOSOH, Japan) in an agate vial of 250 ml (usable) volume, using distilled water as milling medium. The milling lasted 5 h, with a pause for 1 min in every 5 min for cooling. The milled powders were dried at 500 °C for 2 h, to remove the water of adsorption. Powders were calcined at 800 °C for 4 h, in order to form the PLZT phase. The calcined powders were milled for a few minutes to crush any lumps that were formed during calcinations. These powders were cold isostatically compacted to a cylindrical rod at a pressure of 300 MPa and sintered at 1150 °C for 4 h. A small crucible containing $PbZrO_3$ with 10 wt.% excess PbO was placed in a double crucible, in order to prevent the PbO loss at high sintering temperature. The entire assembly consisted of a doubly sealed alumina crucible with lids sealed with alumina powder as cement. The phase formation of as-milled powders was determined by X-ray diffraction (XRD) studies, carried out on an X-ray diffractometer (Philips X'pert PW-3020) with step size of 0.02°. The average size distribution of the powders was analyzed by small angle X-ray scattering (SAXS) technique, using a PW-3830 X-ray generator (Anton-Paar, Austria) operated at 40 kV and 50 mA with a Cu target. The scattering data collected were used to calculate the particle size, shape and distribution of the PLZT nano-particles. A small quantity of the as milled powders was taken and dispersed in toluene and subjected to ultrasonic vibration to prevent agglomeration of these nano-particles (since nano-particles are chemically highly reactive). Thereafter the powders were allowed to remain in suspension for about 10–15 min following which, with the help of a syringe, a part of the top of the solution was

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siphoned off and then injected into a quartz capillary tube for measurement. In addition, to estimate the particle size of the powders, the powders were examined via scanning electron microscopy. Since the particle size was extremely fine and below the resolution of the SEM (LEO-440i), they were examined using a TEM to evaluate the particle sizes and they were found to be of the order of nanometers. The powder samples for TEM observation were prepared by dispersing in methanol and adding a few drops on carbon coated TEM grid. A FEI Tecnai 20G^2 TEM was used for observation of the powders. The density of the sintered ceramics was found using the Archimedes' method.

The sample geometries for measurement of the materials properties were in conformity with the IEEE standards [10]. All samples were polished and sputtered with gold on the larger faces for making proper electrical contact. Samples were electrically poled at a field of 40 kV cm^{-1} for 15 min at 100 °C immersing the samples in a silicone oil (DOW CORNING 704®) bath.

A Piezo-d meter of Sensor Technology Limited, Canada (SS01) was used to determine the piezoelectric charge coefficient on poled samples. A frequency of 190 Hz and force of 2 N was used during the measurement.

A strain measurement system of Sensor Technology Limited, Canada-SS50 was used for measurement of the electric field induced strain. The SS50 strain measurement system uses a linear variable differential transformer (LVDT) to measure the absolute displacement over a 1.25 mm range. This is converted to strain in the system software by dividing by the appropriate sample thickness. The LVDT signal is sampled with 16-bit resolution. The system is used in conjunction with a high-voltage amplifier that has a peak voltage range of 4 kV. A uni-polar signal was used by applying half of a sinusoidal wave to the poled samples. The direction of application of electric field and the measurement direction (of displacement) were the same, hence a "33" type measurement was made, as per IEEE standards.

An Agilent E-4980 precision LCR meter was used to acquire resonance data in the frequency range from 100 kHz to 300 kHz on poled samples. The electromechanical coupling coefficient k_p can be expressed as follows:

$$k_p = \sqrt{\left[2.51\frac{f_a - f_r}{f_r} - \left(\frac{f_a - f_r}{f_a}\right)^2\right]} \quad (1)$$

where f_r is the resonance frequency and f_a is the anti-resonance frequency (Hz).

3. Results and discussion

High energy milling results in changes of free energy, leading to release of heat, constant formation of new surfaces, formation of different crystal lattice defects and initiation of solid-state chemical reaction. The accumulated deformation energy determines irreversible changes of crystal structure and consequently microstructure resulting in the change of their properties. The intrinsic advantage of this process is that the solid-state reaction is activated due to mechanical energy instead of the temperature. Fig. 1 shows the X-ray diffractogram of the as milled powders and sintered PLZT. It can be seen that the peaks of pervoskite PLZT are mostly present at the milled stage itself, i.e. without any heat treatment. The few extra peaks which do not belong to PLZT are of un-reacted PbO. The sintered PLZT XRD pattern shows completely crystallized perovskite phase formation. Since PLZT powders were subjected to high energy during the milling process, it is expected that the powders have a high degree of residual strain, and after sintering the strains got relieved resulting in a shift of the peaks. Further analyses would be required to get a better understanding of the same. A study of shrinkage as a function of sintering

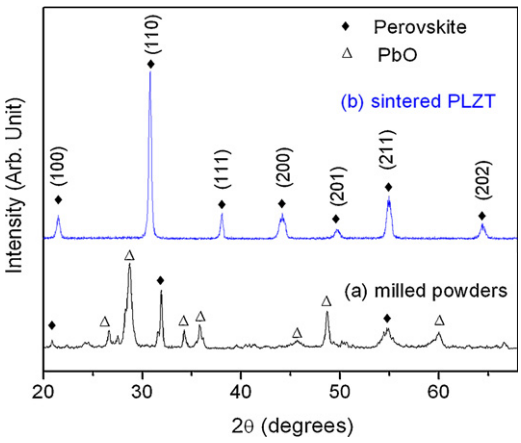

Fig. 1. X-ray diffractogram of (a) as milled powders and (b) sintered PLZT.

temperature and sintering time has been carried out and the sintering kinetics of PLZT ceramics have been studied and explained in detail in our previous work [12,14]. A study of density variation as a function of sintering temperature is yet to be done.

The results of the SAXS experiments are discussed in the ensuing paragraphs. Fig. 2(a) shows the pair distances distribution functions as a function of r. It can be inferred from Fig. 2(b) that the PLZT (8/60/40) samples prepared via the MCP route have an average particle size of around 19 nm, with the particle shapes deviating from sphericity.

In the sol gel method, the particles obtained are generally spherical in shape whereas in other processes such as high energy ball milling, the shape of the particles deviates from sphericity, resulting in flaked or elliptically shaped particles. The particles seem to be free from agglomeration since only top solution was taken and injected into the quartz capillary tube. Whereas SAXS gives the average size of the particles, in SEM the estimation of particle size is rather localized to the region being seen under the microscope.

It was shown that the chemical reactivity of starting materials could be improved significantly after mechanochemical activation and subsequently, the calcination temperature was reduced. Conventionally, PZT is calcined between 850 and 950 °C for 4–6 h, however, in this study, PZT was calcined at a temperature of 800 °C for 4 h. Besides, it was apparent that the mechanochemical treatment could enhance the reactivity of constituent oxides; however, the sintering process could not be avoided to develop the desired ceramics. The sintering temperature used in this work was 1200 °C, which is 50–100 °C less

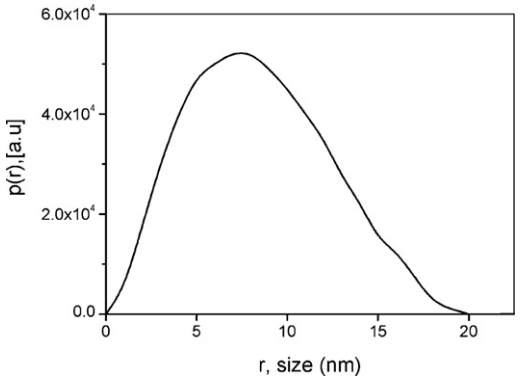

Fig. 2. Plot of the experimental pair distance distribution function, $p(r)$, vs. size r.