Photochemical Solution Deposition of Lead-Based Ferroelectric Films: Avoiding the PbO-Excess Addition at Last

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The high activity (vapor pressure) of the PbO component has historically conditioned the research on lead-based ferro-piezoceramic compositions. Starting with bulk ceramics, the high annealing temperatures at which these materials are usually sintered (1250−1300 °C) lead to the irreversible volatilization of PbO from the system,[1] thus resulting in deviations from the nominal composition and detrimental densification and functionality of the ceramics. The addition of a certain excess of PbO to the material (5−15 mol %) was shown to compensate for the undesired lead loss during firing, and since then, manufacturing of lead-based ceramics has been inconceivable without this lead-excess addition. Furthermore, the low melting point of this compound (890 °C), as compared to the majority of refractory oxides, allows the formation of a PbO-rich liquid phase at elevated temperatures that enhances the mobility of the ions during the rearrangement of the solid network.[2] This produces high densification rates at the initial/intermediate stages of the process and promotes the formation of the final crystalline structure at lower sintering temperatures/times. Although much lower temperatures (600−700 °C) are employed in the thin-film technology, volatilization of PbO is also observed during the thermal processing of these materials. This can be explained mainly by two reasons. First, the particular thin-film conformation results in a high surface to volume ratio which can alter the physical conditions for the reactions (e.g., evaporation) occurring in the film. Thus, evaporation of lead oxide in films has been observed even at temperatures such low as 400 °C. Second, in the case of chemical solution deposition (CSD) methods, residual organic species remain in the gel film after solution deposition that must be pyrolyzed prior to the crystallization of the material at higher temperatures. The burning of these carbonaceous species requires oxygen consumption from the reaction atmosphere, and this could lead to low local values of oxygen partial pressure on the films.[3] Although the vapor pressure of the PbO component is still low at the usual processing temperatures of the films ($\sim 10^{-8}$ atm), elemental Pb can be easily volatilized at slighter reducing conditions ($\sim 10^{-6}$ atm).[4] Lead deficiency from the nominal composition of most perovskite films usually results in the appearance of secondary crystalline phases (e.g., fluorite, pyrochlore) whose nonferroelectric character leads to a deteriorated electrical response in the material.[5] When the lead loss is compensated by incorporating a PbO excess, then the volume of the perovskite phase present in the films is known to increase.[6] It is generally accepted that the PbO excess present in the amorphous film also leads to a decrease on the crystallization temperature of the ceramic material.[7] Some authors have pointed that the lead excess present in the films can act as a flux for crystal growth[8] or as a network modifier improving the mobility of the system,[9] thus enhancing crystallization kinetics. Anyway, additions of PbO excess to lead-based ferro-piezoelectric compositions (in both bulk ceramic and thin film conformations) remain representing the state-of-the-art in the preparation of these multifunctional materials. And one critical thought therefore flies over the heads of many researches today; the fabrication of full-crystalline lead-based ceramic films with optimum electrical properties seems to be unattainable without any PbO-excess addition.

Attending to the extensive literature, the former statement is almost true. To the best of the authors' knowledge, only one work reports on the preparation of homogeneous, single-phase perovskite films from stoichiometric solutions showing optimum ferroelectric properties. Two alternative firing strategies were then used by Lefevre et al.[10] to control the lead stoichiometry of sol−gel derived PZT films annealed at 650 °C. Both approaches are based on the replacement of the usual PbO-excess addition by increasing the PbO activity during firing. This was done either by using a PbO overcoat[4] on the surface of the films or by introducing PbO atmosphere powders[2b] in close proximity to the films. The resulting films showed phase-pure perovskite structures with dense and homogeneous microstructures and nearly ideal ferroelectric properties. One can think that if lead-based perovskite films were processed at lower annealing temperatures (<500 °C), volatilization of PbO from the system could be avoided. This is theoretically true, but then additional problems arise that make the task not really straightforward. Thus, the use of

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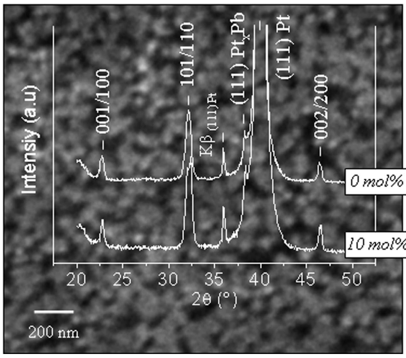

Figure 1. XRD pattern and SEM image of the PCT24 films with 0 mol % PbO excess prepared by PCSD at low temperature. Diffractogram corresponding to a counterpart film containing a 10 mol % PbO excess is also included.

low temperatures is known to promote the formation of detrimental secondary phases in the films due to the *kinetically limited crystallization* concept.[9,11] In addition, low-temperature treatments of CSD derived layers usually lead to films in which an incipient ferroelectric phase is immersed into a matrix containing organic residuals still not decomposed. Both secondary nonferroelectric phases and the rest of the amorphous compounds strongly deteriorate the electrical response of the films. Such drawbacks were finally overcome by some authors of this work through the ultraviolet (UV) sol−gel photoannealing technique (photochemical solution deposition, PCSD).[12] Single-phase perovskite ($(Pb_{0.76}Ca_{0.24})TiO_3$ (PCT24) films with optimum ferro-, pyro-, and piezoelectric properties were then obtained at temperatures such low as 450 °C. Very recently (2008), we have additionally shown the feasability of this method to avoid the volatilization of hazardous lead from the ceramic composition of the films.[13] We must point out that the as-crystallized films used in that work contained a 10 mol % of PbO excess coming from the composition of the respective solution. Now, we report on the successful fabrication of PCT24 films derived from a *nominally stoichimetric* $(Pb_{0.76}Ca_{0.24})TiO_3$ solution (i.e., without using any PbO excess) by UV sol−gel photoannealing at 450 °C and with clear ferroelectric response. Details on the preparation of these films are given in the Supporting Information.

Figure 1shows the crystalline features of the PCT24 films here prepared by PCSD. Nanometric grains with an average size below 50 nm form the microstructure of these films. The presence of a single perovskite phase, with no appreciable amounts of secondary phases (fluorite, pyrochlore) or the rest of the amorphous compounds, can be inferred from the XRD pattern of the films. These results surmount the historical dependence on PbO-excess additions for enhancing the crystallization kinetics of lead-based ceramics, even more dramatic at low annealing temperatures. The processing of the gel film under high-intensity UV irradiation is the key point responsible for the prompt formation of the desired crystalline oxide phase at 450 °C without any PbO excess. Thus, (i) energetic photons coming from UV light produce the electronic excitation ($\pi \rightarrow \pi^*$) of the photosensible compounds present in the gel film, enhancing the decomposition of organic species in the material, and (ii) the UV-irradiation under O_2 atmosphere leads to the formation of ozone (O_3) and active oxygen (O^1D) species. Combustion of organic species is promoted by O_3 (ozonolysis), whereas O^1D can react with suboxides improving the stoichiometry and decreasing vacancies and defects in the film. (iii) Both electronic excitation and ozonolysis facilitate the rapid elimination of organic compounds from the film. As a result, the short-range diffusion of elements leading to the stabilization of metastable phases (fluorite, pyrochlore) in the film is overcome, and there is a high driving force to convert the amorphous film directly into the ferroelectric, perovskite crystalline structure at low temperatures.[11] Analogous to the PCSD films containing a 10 mol % excess of PbO (included in the XRD pattern of Figure 1), a diffraction peak at ~38.26° is detected which, in principle, can be ascribed to the (111) reflection of a Pt_xPb intermetallic phase (JCPDS-ICDD 6-574 file). The formation of this alloy is attributed to the reduction of Pb^{2+} to metallic Pb and subsequent reaction with the Pt bottom electrode. The low temperature used for the crystallization of the films would prevent the reoxidation of elemental lead and therefore, the Pt_xPb interlayer would remain in the heterostructure of the samples.[14]

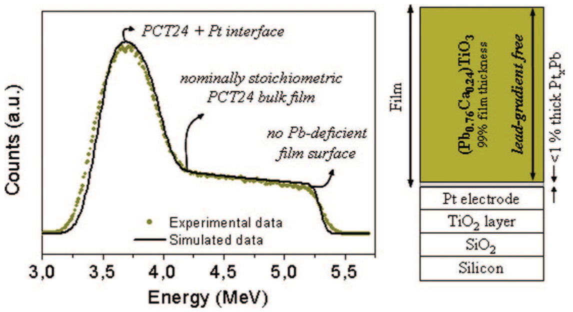

Figure 2. RBS spectra and respective heterostructure of the PCT24 films with 0 mol % PbO excess prepared by PCSD at low temperature.

The Rutherford backscattering spectra (RBS) obtained in the films of this work and their resulting heterostructure are depicted in Figure 2. An average elemental concentration of 0.76Pb + 0.24Ca + 1.00Ti + 3.00O is calculated from the simulation curve of the films. This concentration, within the experimental error, is equivalent to the nominal composition of the respective precursor solution, $(Pb_{0.76}Ca_{0.24})TiO_3$, denoting that evaporation of lead has not occurred in the films. These results demonstrate for the first time that phase-pure, crystalline, and stoichimetric films of lead-based multioxide compositions can be obtained without using any lead-excess source, neither in the solution nor in the engineering of the process (by using either film overcoats or atmosphere powders of PbO). As in the case of the PCSD films with a 10 mol % of PbO excess (see ref 13), a Pt_xPb interlayer between the film and the Pt electrode is required to fit both experimental and simulated curves. However, the thickness of this interface results in now less than the 1% of the total film thickness, in contrast to the 3% obtained in the films with lead excess.[13] This really low value leads us to believe that the formation of the Pt_xPb interlayer in the low-temperature processed films is practically suppressed when no PbO excesses are present in their microstructure during the fabrication process. The fact that the Pt_xPb intermetallic was clearly detected by XRD (Figure 1) despite its rather low concentration in the sample can be attributed to the high texture

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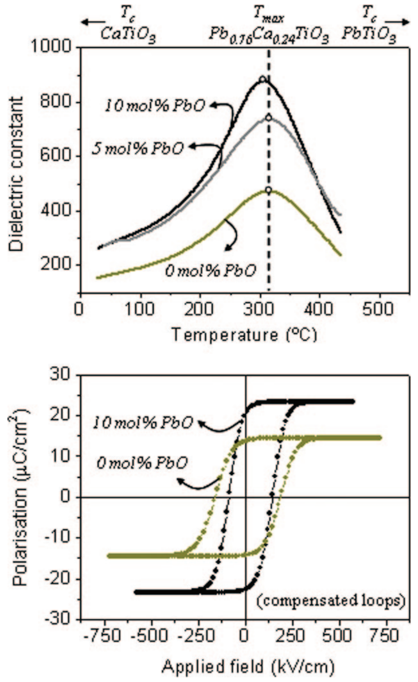

Figure 3. Electrical properties of the PCT24 films prepared by PCSD at low temperature and with different amounts of lead excess.

of this compound.[14] The decrease in the intensity of the (111)Pt_xPb peak in the films of this work with respect to the films with a lead excess supports that the formation of this alloy is significantly minimized in the former films. A homogeneous compositional profile is also deduced by RBS for the films (comprised of four layers) shown here, supporting the lack of compositional variations within the bulk material. A lead gradient with a concentration increasing from top to bottom was on the contrary found in the PCSD films containing a 10 mol % of PbO excess.[13] The tendency of lead to diffuse is in most cases responsible for the strong compositional gradients observed in lead-based ferroelectric films prepared by multilayered CSD methods. This produces variations on the physical properties of the material along the film thickness that can deteriorate the functionality of the device. Following the theory of diffusion of elements driven by chemical potential gradients, evaporation of lead at the surface (in films annealed at high temperatures) or formation of a Pt_xPb interlayer with the substrate (in films annealed at low temperatures) could be considered as the driving force for diffusion of this element within the film. Since neither lead volatilization nor practically formation of the Pt_xPb interlayer is here observed, a compositional lead gradient would be not expected in the films of this work, giving rise to the homogeneous compositional profile deduced by RBS.

Finally, the effect of the lead-excess content on the electrical properties of the PCSD films prepared at 450 °C can be evaluated from Figure 3. A clear ferro-paraelectric transition is observed for three films displaying different amounts of PbO excess in their composition. Note that the peak maxima of the curves corresponding to films containing 0 and 5 mol % of PbO excess are located at the same temperature, denoting that the remaining lead excess has not been incorporated into the $(Pb_{0.76}Ca_{0.24})TiO_3$ perovskite. Shifts in Curie point due to partial incorporations of PbO into perovskite lattices are a well-known fact reported for several lead-based ferroelectric ceramics. The slight shift observed in the transition temperature of the film containing a 10 mol % of PbO excess is more likely to be due to other considerations (e.g., mechanical stresses) rather than to deviations in the nominal composition of the film. The incorporation of PbO into the perovskite lattice of this film would displace its transition temperature toward higher temperatures (in the direction of that of pure $PbTiO_3$) and not to lower values as observed in the figure. Improved electrical properties are obtained in these films when a certain amount of lead excess is present within their microstructure. Some authors[7,15] have proposed that the remaining PbO excess can improve the interfaces of the films by avoiding the formation of low dielectric space charge layers and oxygen vacancies in the material.

On the other hand, the compositional gradient obtained in the PCSD films with PbO excess[13] could be related to the internal bias field inferred from the corresponding ferroelectric loop (see different E_c values with voltage sign). The presence of internal fields in the sample can lead to a faster imprint of the ferroelectric polarization. In spite of the drastic consequences associated with the use of low annealing temperatures and null amounts of lead excess, a remarkable ferroelectric response, with no internal bias fields, is obtained for the films of this work ($P_r = 14$ $\mu C/cm^2$, $E_c = 175$ kV/cm) which has not been reproducible before for any ferroelectric lead-based material processed under similar conditions. For example, an addition of 30 mol % of lead excess to the solution is observed to be necessary to crystallize PLZT films at temperatures near 500 °C.[7] Conversely, annealing temperatures of 650 °C together with certain strategic approaches (PbO atmosphere powders and PbO overcoats) is required to obtain single-phase ferroelectric PZT films from stoichiometric solutions with no lead excess.[10] The historical incompatibility between these two parameters (low processing temperatures and absence of PbO excess) has been finally overcome with the successful implementation of the UV sol−gel photoannealing technique.

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Supporting Information Available: Experimental details (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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