

Ferroelectric thin coatings *

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A review of the fabrication and characterization of thin ferroelectric films prepared by the sol-gel process since 1984 is presented. Single phase materials such as titanate, zirconate, niobate, tantalate and more complex relaxor ferroelectrics and mixed titanate and zirconate are reported and their properties are discussed in relation to electric and electro-optic applications.

1. Introduction

Non-linear dielectrics are an important class of materials which have large dielectric constants due to spontaneous alignment or polarization of electric dipoles. Among the 32 crystal point groups, 20 of them have one or more polar axes and can exhibit various polar effects such as piezoelectricity, pyroelectricity and ferroelectricity. Ten classes possess a unique polar axis and crystalline materials which cause them to present a spontaneous polarization within various temperature ranges. Since the permanent dipoles comprising their structure have temperature-dependent behavior, these materials are also called *pyroelectrics*.

The ferroelectric materials are a special category of pyroelectrics in which the spontaneous polarization can be reversed by the application of an electric field of magnitude less than the dielectric breakdown of the material. The actual

number of ferroelectrics is today in the thousands if we include the large number of ceramic solid-solution compositions.

Discovered by Valesek in 1920 in Rochelle salt, ferroelectricity underwent significant developments in the 1940s with the discovery of new materials such as single crystal and ceramic barium titanate [1]. In 1954, the ferroelectric lead zirconate titanate ceramic solid-solution compositions were developed [1] and a few years later complex compositions called relaxator or relaxor ferroelectric with high dielectric constant and broad peak in permittivity were found [2]. Ferroelectric materials have (a) high dielectric constant, (b) high piezoelectricity, (c) relatively low dielectric loss, (d) high electrical resistivity, (e) moisture insensitivity, (f) high electromechanical coupling, (g) fairly high pyroelectric coefficients and, in some cases, (h) good optical transparency and (i) high electro-optic coefficients which make them attractive for a variety of applications [3,4]. However the most outstanding feature of a ferroelectric ceramic is its hysteresis loop observed in a plot of polarization vs. electric field which describes the non-linear polarization switching [3]. The spontaneous alignment of electric dipoles occurring in these materials is often associated with a crystallographic phase change from a centrosymmetric non-polar lattice to a non-centro-

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symmetric polar lattice [3,4]. Barium titanate (BaTiO_3) is a typical example in which, in a ABO_3 perovskite-like structure, the Ti ions are surrounded by six oxygen ions in a TiO_6 octahedral configuration. At high temperature, the regular octahedron has a center of symmetry and the six Ti-O dipole moments cancel in antiparallel pairs. An off-center displacement of the Ti^{4+} against its negatively charged O^{2-} surroundings occurring at crystallographic phase changes results in a net permanent moment. These dipoles are ordered, giving a domain structure with a net spontaneous polarization within the domain [3,4].

The new relaxators have typical composition $\text{A}(\text{B}_1\text{B}_2)\text{O}_3$, where A may be Pb, B_1 may be Co, Sc, Fe, Mg, Cd, Zn and B_2 may be W, Ta, Nb. Therefore two or more species of ions occupy the same B site. The ferroelectric behavior is attributed to the disorder of ions occupying an octahedral position in the unit cell in a region of too small dimensions (~ 10 nm) to yield sharp phase transitions as seen in normal ferroelectrics [4]. As a result, the ferroelectric behavior is retained over a larger temperature range [4].

The ferroelectric properties of the ceramics are strongly affected by several effects such as grain size, aging and the presence of semiconducting species such as donor additives (usually compensated by A site vacancies), acceptor additives (compensated by oxygen vacancies) or isovalent additives [3,4].

The major compositional system used today by industry are centered around the PZT system and include PbZrO_3 - PbTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ + additives, $(\text{Pb,Sr})(\text{Zr,Ti})\text{O}_3$, $(\text{Pb,Ba})(\text{Zr,Ti})\text{O}_3$, $\text{Pb}(\text{Mg,Nb})\text{O}_3$ - PbZrO_3 , $\text{Pb}(\text{Co,Nb})\text{O}_3$ - PbZrO_3 - PbTiO_3 , PbTiO_3 + additive and $(\text{Pb,La})(\text{Zr,Ti})\text{O}_3$ [3].

2. Ferroelectric thin films

Ferroelectric thin film synthesis is becoming an important field of activity. Despite the lack of commercial devices, the promise of economically important applications such as non-volatile, radiation hard ferroelectric random access memories, high K capacitors, actuators, SAW (surface

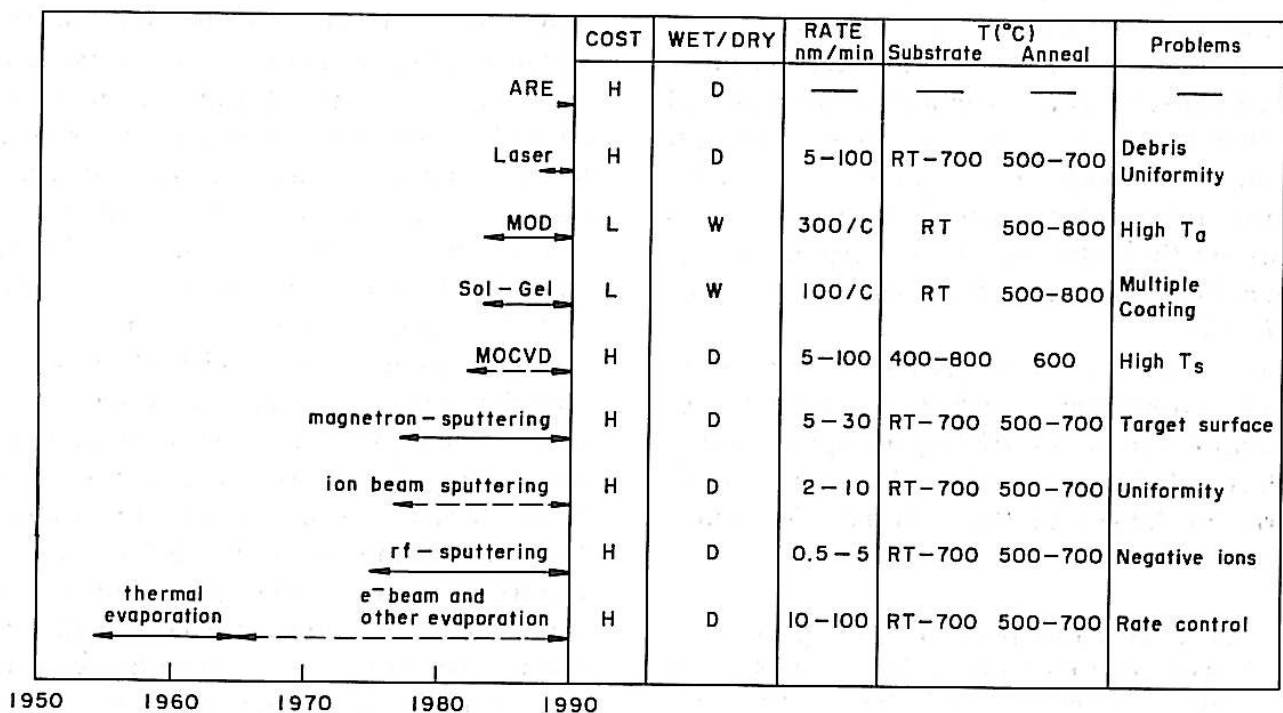


Fig. 1. History of the ferroelectric thin films and comparison of the most important features of techniques of preparation. MOCVD, MOD and ARE refer to metal organic chemical vapor deposition, metal organic decomposition and activated reactive evaporation, respectively. The solid lines indicate a more concerned activity (adapted from [13]).

acoustic waves) devices, acTFEL (thin film electroluminescent display), electro-optic devices, pyroelectric detectors, IR imagers, etc. [5–10] is without any doubt the important driving force. The availability of new synthesis techniques [13] such as sol–gel, laser deposition and metal organic chemical vapor deposition (MOCVD) is also stimulating new research and the knowledge obtained in the past years on the growth conditions suggest a promising future.

The first successful synthesis of micrometer thick film was realized by flash evaporation of BaTiO₃ in 1955 [11]. Since then, numerous materials and preparation techniques have been developed [3,4]. In 1970, the interest shifted toward PZT- and PLZT-type materials and most of the developments to date have been on these materials for applications in the field of electro-optic switches, silicon-base memory, piezoelectric, SAW devices and pyroelectric imagers [3]. The electrical properties of thin layers (such as P_r , E_c , K , etc.) are determined primarily by their composition, microstructure, thickness, substrate interaction, preferred orientation and presence of additional phase.

Film deposition techniques, which are numerous, influence the composition and the microstructure of the film. They can be divided into dry and wet processes. The dry processes include sputtering, evaporation and CVD and usually require hot substrates. They are relatively slow and expensive but allow greater ease of epitaxial film growth and are still widely used. The wet processes are metal organic deposition (MOD) and sol–gel and use unheated substrates or low temperature deposition. They are fast and inexpensive since they allow the preparation of 100–300 nm thick film per coating with good stoichiometry (fig. 1) [13].

Film thickness is a critical parameter since the dipole correlation length is usually of the order 10–50 nm along the polar axis and 1–2 nm along the non-polar direction [13]. Therefore, the alignment stability in thin coatings can be drastically affected.

Size effects were first studied for BaTiO₃ thin single crystals [12]. A decrease of the apparent dielectric constant was observed as the crystal

thickness decreases and higher fields were necessary to cause switching in thinner crystal. Such effects have been attributed to the presence of 0.1–1 μm thick surface layers having properties different from the bulk and showing either a space charge from ionic vacancies, exhaustion barriers, or interface charges preventing the surfaces from participating in polarization reversal. Substrate interaction such as metal electrode diffusion into the films may be dependent on the initial microstructure before annealing, and have important implications in wet processes since the layers are initially porous and amorphous [13]. These low permittivity interface layers which may vary with film material and substrate should be minimized. These phenomena are still an important topic of debate.

In this work, we review only the preparation of thin films < 10 μm thick by wet processes and their characterization. A review [13] discusses ferroelectric films produced by dry processes.

3. Solution-derived coatings

Solution deposition procedures are mainly sol–gel and MOD. The two methods are similar in that MOD involves the synthesis of solution containing high molecular weight precursors such as carboxylates which are deposited onto substrates for further heat treatment of densification and crystallization. However the solutions do not form complexes or networks.

The sol–gel method involves the preparation of a sol with polymerizable oligomers species which polymerize during spin- or dip-coating deposition. The formation of such networks can be very important for microstructure and crystalline phase development when the coatings are heat treated to obtain the crystalline ceramics. The sol–gel technique has been applied to the preparation of various types of ferroelectric thin films which include titanate and zirconate such as PbTiO₃, PbZrO₃, BaTiO₃, Pb(Zr,Ti)O₃ (PZT), PbLaZr titanate (PLZT), niobate such as LiNbO₃ [30–42], SrBa niobate (SBN), KNaSrBa niobate (KNSBN), PbBa niobate (PBN) and some ferroelectric relaxors such as PbMg niobate (PMN),

PbMgTi niobate (PMNT), PbFe niobate (PFN) and PbZrTi niobate (PZTN). Preparation methods and the main characteristics of the products are discussed below together with the literature references.

3.1. $PbTiO_3$ and $PbZrO_3$ [14–20]

Pure lead titanate and zirconate are not important technological materials; however they are the base constituents of important electrical and electro-optical ceramics such as PZT and PLZT and the preparation of $PbTiO_3$ and $PbZrO_3$ sols and thin films was an important step to obtain other materials. The precursor sol for $PbTiO_3$ film preparation was first developed by Budd et al. [14,15] by mixing a titanium methoxyethoxide precursor sol with a 2-methoxyethanol solution of dehydrated lead acetate and a solution of water-catalyst (acid or base)-methoxyethanol. An easier method based on the modification of titanium isopropoxide by acetylacetone to which lead acetate and acetic acid is added was later proposed [16]. Other preparation techniques have also been suggested [17,18]. The dielectric constant of the $PbTiO_3$ films was of the order of 23 and the refractive index was found to depend on thermal processing conditions. Amorphous layers with $n = 2.35$ have been prepared at 350°C and with crystallization at 450°C the index is 2.65 [19]. Planar optical waveguides 0.8 μm thick made with 10 $PbTiO_3$ layers deposited on SiO_2 substrates were reported [16]. Conventional heat treatment of $PbTiO_3$ deposited on GaAs wafer results in excessive diffusion of As into $PbTiO_3$ which degrades the electrical properties of the semiconductor and inhibits crystallization of the coating. Fast heating was found necessary to diminish the diffusion [20].

3.2. $BaTiO_3$ [21–29]

This compound, widely used in the manufacture of capacitors and other compositions, such as BaTi_4O_9 , $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, presents interesting properties for microwave applications.

Most of the sol-gel processes have been developed to obtain powders and bulk ceramics [16].

Sols for thin film preparation have been prepared by mixing a solution of Ti isopropoxide diluted in isopropanol [21–23] or Ti-ethoxide [24,25] with an aqueous solution of Ba acetate. Acetic acid or acetylacetone was also added in order to avoid precipitation. Other preparations have been proposed [26]. The films deposited are amorphous to 450–500°C and have an electrical breakdown strength of the order of 9×10^6 V/cm which is larger than crystalline films ($\sim 10^5$ V/cm) [27]. Ferroelectric properties have been reported only after heat treatment at 800°C where a grain size of 0.1 μm can be obtained. The dielectric response is poor ($\epsilon \sim 50\text{--}90$, $\tan \delta = 2\text{--}3$) with a broad Curie point at 118°C [28,29].

Tuchiya et al. [26] obtained large dielectric constant ($\epsilon' \sim 1000$, $\tan \delta = 0.035$ at RT) for crack-free films deposited on Pt substrate and heat treated at 1000°C. The films have a typical P_s - E hysteresis with $P_s \approx 2.3 \mu\text{C m}^{-2}$, $P_r \sim 0.8 \mu\text{C m}^{-2}$ and a coercive field of 2.8 kV cm^{-1} .

3.3. $LiNbO_3$ [30–43]

Lithium niobate single crystal is a leading electro-optical material and is currently used for the realization of SAW devices, waveguides, modulators and switches [85]. However some of its outstanding properties such as the Curie point and the refractive indices are sensitive to fluctuations in stoichiometry. Single crystals are expensive and difficult to grow due to incongruent melting and the presence of Li-deficient solid solutions. Therefore the sol-gel process may be a good process to obtain suitable Li range contents at reduced temperatures for device optimization.

$LiNbO_3$ precursor sols have been prepared from ethanol- or methoxyethanol-based Li and Nb alkoxides solutions [30,31]. The films crystallized at a temperature as low as 400°C or less if an underlying fully crystallized film is first deposited or if the solution is deposited on single crystal of sapphire [32–34,36], $LiNbO_3$ [32], Al_2O_3 [34] and polycrystalline Pt [34,35]. Random orientation was obtained for deposition on Si(111) or Si(110) substrates due to the presence of an amorphous layer of native oxide. The heteroepitaxial growth with higher preferred orientation was found to be

promoted if small quantities of water were added for the alkoxide hydrolysis. Without water addition, crystalline material has been reported [36]. The grain size is typically in the range 0.1–0.5 μm depending on heating rate and composition [37].

Indices of refraction $n \sim 2.15$, are less than that of single crystal presumably due to residual porosity [31,38]. The dielectric constant is approximately 22 at audio frequencies with $\tan \delta = 0.005$ at 1 MHz [35]. The same techniques have also been applied to grow $\text{Li}(\text{Nb},\text{Ta})\text{O}_3$ [30,33,36,40–42] and $\text{Li}(\text{Nb},\text{Ti})\text{O}_3$ [34,43] with preferred orientation. Wave guide fabrication has been reported [42] but no data on attenuation were given. No report on electro-optic coefficients on these films are known.

For obtaining high quality epitaxial single crystal LiNbO_3 films for electro-optic applications, the non-sol-gel techniques are probably still better today [13]. The sol-gel method leads to large loss due to grain boundary scattering; however, it has potential for better reproducibility.

3.4. Other niobate films [38,44–46]

KNbO_3 , SrBa niobate (SBN), PbNa niobate (PBN) and KNaSrBa niobate (KNSBN) thin films have been prepared by Mackenzie and associates [38,44–46]. The solutions have been prepared by mixing metal alkoxides in appropriate conditions and the film have been processed by spin- or dip-coating technique on SiO_2 , n- or p-type Si and GaAs wafers. In the last two cases, a metal/ferroelectric film/semiconductor sandwich structure was formed. Preferentially oriented SBN film have been obtained by applying a dc electric field ($\sim 1 \text{ kV/mm}$) parallel to the surface of the film during heat treatment.

These films are not good insulators and all ferroelectric/silicon interfaces were found to possess I–V characteristics similar to a rectifying diode with p–n junction. This heterojunction effect is also responsible for photocurrent and photovoltaic effects observed with ITO/ferroelectric films/Si sandwiches. These effects can be utilized as detector or solar cell devices. Finally SBN thin films have been also used to record holographic grating by two-wave mixing. The Bragg diffraction

intensity measured at 632.8 nm was unusually large ($n \sim 1\%$) owing to the thickness of the film [46].

3.5. Relaxor ferroelectrics [47–53]

This class of ferroelectric materials has interesting structural and electrical properties. They are mainly observed in complex perovskites of the general formula $(A_1, A_2)(B_1, B_2)\text{O}_3$, where different cations can occupy the A and B sites, and where the relaxor behavior is associated with structures which have disorder in site occupation. Their preparation is relatively complex and the formation of a deleterious metastable pyrochlore phase ($A_3B_4O_{14}$) is difficult to avoid [53].

The MOD technique was tried but failed to prepare $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) thin layers. The first sol-gel PFN film was prepared on Si substrate by Quek and Yan [47]. A maximum dielectric constant of 81 (much lower than that of bulk material) was attributed by the authors to the presence of SiO_2 layers in series with the film. However their X-ray data show the presence of only the low dielectric constant pyrochlore phase. Okawada and co-workers [48,49] investigated the preparation of PMN and PFN from alkoxide precursors. The good perovskite phase was reported to form at $T > 600^\circ\text{C}$ and the phase development was found to depend on the heating rate and substrate type. The dielectric constant at 100 kHz measured for 0.5 μm thick PMN film was low ($\epsilon \approx 1800$) compared with bulk ceramic ($\epsilon \sim 16\,000$). More recently, PMN [50], $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$ (PMNT) [51–53] and $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$ (PZNT) [52,53] have been reported by Payne's group. The PMN synthesis involved preparation of a Pb precursor (Pb acetate) and a (Mg,Nb) double alkoxide (Mg powder and Nb ethoxide) sols, while lead zinc acetate methoxyethoxide was used for the PZN synthesis. Mixing of the two solutions gave a stable sol. PMNT and PZNT compositions were prepared by mixing PMN and PZN sols respectively and PT sols in adequate proportions.

Thin layers were deposited on Pt coated silicon substrates by spin-coating using a solution

containing the PMN sol, 2-methoxyethanol, water and NH_4OH [51–53]. Crack-free crystalline films with preferential orientation containing 99% of high perovskite phase have been obtained by fast firing at 800°C for 5 min. Small amount of pyrochlore phase has been observed. Fast-firing at lower temperature or at slower heating rates led to less perovskite content. The microstructure of the film was characterized by a bimodal grain size distribution ($0.5\text{--}1.0\ \mu\text{m}$ and $0.04\ \mu\text{m}$) [51–53]. The dielectric constant was of the order of 1000 to 1250 at room temperature, considerably less than bulk polycrystalline PMN ($\epsilon \sim 16000$). This low value was attributed to the presence of the residual pyrochlore phase as well as grain size, stress and interfacial effects. The dielectric constant was found to be dependent on the magnitude of the ac field applied, the effect of which was indicative of the presence of polar microregions, typical of relaxor ferroelectrics. Thin layer in the entire PMNT system have been prepared while the preparation of thin PZNT was limited to PT-rich composition [53]. High perovskite phase was again obtained for rapid heat treatment process. The highest dielectric constant was obtained for 90 PMNT ($\epsilon' = 2000$, $\tan \delta < 0.03$) and the layers exhibited polarization reversal [53]. The good properties exhibited by these coatings are promising for thin layer capacitors or memory applications.

3.6. PZT and PLZT

One of the ferroelectric materials currently under investigation for use as non-volatile computer memory is lead zirconate titanate (PZT) which is a solid solution of composition of PbZrO_3 and PbTiO_3 . The first sol–gel PZT of composition $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ was prepared by Fukushima et al. in 1984 [54] using sol of Pb 2-ethylhexonate, Zr acetylacetonate and Ti tetrabutoxide in a butanol solution.

Later Payne's group [55,60] described a process using Pb acetate and Zr and Ti alkoxide dissolved in basic methoxyethanol. They obtained crystalline PZT after annealing at temperatures greater than 500°C [55]. A coercive field of $4 \times 10^6\ \text{V/m}$ and remanent polarization of $0.36\ \text{C/m}^2$

has been reported for PZT [47,53]. Similar results are reported by Chen et al. [56], Lipeles et al. [57], Yi et al. [58] and others [59–62], using the same process. Due to the excellent results reported, many other groups have entered the field and published numerous reports during the past two years [38,44,46,63–80].

Active works are now underway to develop sol–gel PZT thin film capacitors for integration with GaAs junction field effect transistor (JFET) circuits to yield non-volatile programmable random access memories [63,75] and ULSI DRAM (dynamic random access memories) cell [72,74]. Film processing was found to be very important. Excess Pb (up to 5 mol%) and fast heating rates ($> 50^\circ\text{C}/\text{min}$) increase the perovskite content and improve the ferroelectric properties of the film fired at 600°C . Slower heating rate ($\leq 15^\circ\text{C}/\text{min}$) results in an extensive formation of the undesired pyrochlore phase $\text{A}_2\text{B}_2\text{O}_7$.

However, several important questions require further studies. In these lead-based ceramics thin films, non-stoichiometric surface regions to a depth of $\sim 150\ \text{\AA}$ were detected with high Pb concentration and deficiency of O, Zr, Ti [76]. Oxygen diffusion may have some effects on the endurance and retention properties of the capacitors which typically show 30% reduction in spontaneous polarization after 10^9 cycles. However, PZT films prepared by sputtering or sol–gel process show similar frequency dependence in ϵ' and ac conductivity. Similar results had been observed in sol–gel PbO-TiO_2 , $\text{Bi}_2\text{O}_3\text{-TiO}_2$ thin layers [77]. Although low sintering temperatures are used (typically $650^\circ\text{C}/15\ \text{min}$), metal electrode diffusion has also been observed.

PLZTs are lanthanum-modified lead zirconate–titanates of composition ABO_3 , where Pb or La occupy the A sites at the cubic (pseudo-cubic) unit cell corners, the Zr or Ti occupies the B sites at or near the cell center and O is located on the cell faces [4]. Depending on the composition and temperature, the crystal structure of PLZT is either rhombohedral or tetragonal and the unit cells are reversible dipoles. This latter feature is the important attribute for making non-volatile IC memories. A field applied across the film can pole the otherwise randomly ori-

ented domains in one of two possible directions which will correspond to the binary 0 or 1 of a digital memory [85].

Few papers exist on preparation of PLZT thin films by wet chemistry. Recent works reported using either the MOD technique [81,82] or the sol-gel process [83,84]. In this last case, the sol preparation was the technique employed by Budd et al. [14] with some modifications. The films have been deposited on various substrates and their IR spectra and electrical characteristics were measured.

PZT and PLZT are also important materials for electro-optic applications. In thin film form, they are promising materials for surface optical wave devices because of their high electro-optic coefficients compared with those of LiNbO_3 [85]. To our knowledge no work has been reported with sol-gel films.

4. Conclusion

Ferroelectric thin films are important materials for various electronic and electro-optic applications but today commercial products are absent. Their preparation by wet processes (MOD or sol-gel) started in 1984 and works have been reported for single phase titanates (PbTiO_3 , BaTiO_3), zirconate (PbZrO_3), niobates (LiNbO_3 , NbO_3), tantalate (LiTaO_3) and more complex perovskite system such as PMN, PMNT, PZN, PZNT and others such as SBN, PBN, KNSBN, PZT and PLZT. An almost exhaustive review of the literature on sol-gel preparation and characterization and properties is reported. The future looks promising but the ideal compositions and film microstructure remain open questions, particularly for Pb-based materials. These crucial problems are common to all deposition processes.

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