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Oriented nanocrystals in $SrLaMnTiO_6$ perovskite thin films grown by pulsed laser deposition

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ABSTRACT

We have fabricated $SrLaMnTiO_6$ thin films by PLD on different substrates ($SrTiO_3$, $LaAlO_3$ and Si). Their texture, width, homogeneity and morphology have been evaluated from XRD, SEM and complex impedance spectroscopy. The thickness ranged between 500 and 8800 nm depending on the synthesis conditions. The epitaxial growing could be interpreted in terms of two contributions of microstructural origin: a matrix part and some surface formations (hemi-spheres), with different texture and size distributions. The films were nanostructured and contained vertically aligned nanopores (VANPs) with a pore average size of 30–60 nm, which are very interesting for eventual SOFC anode applications. Magnetization results indicate an improved response respect to nano-sized powder samples.

1. Introduction

Polycrystalline ceramics have been widely recognized as important materials for both structural and electronic applications. Among them, rare-earth manganites have attracted considerable attention over the last decades in both, bulk and thin film form, due to attractive properties as CMR, MC effect, giant dielectric behaviour, multiferroic property, etc. It has been shown that different conditions of preparing materials of the nominally same composition, significantly affects the electronic behaviour. In this sense, the comparative study of samples synthesized and mechanized differently is of great interest in order to understand the intimate relationships between composition-structure and properties. On the other hand, for eventual applications in dielectric and/or magnetic devices, epitaxial or highly oriented thin films are often necessary. In this sense, development of comprehensive understanding on film growth of these types of materials will enable control over the crystal structure and permit them to be tailored for specific purposes [1,2].

Moreover, growth of a material as a thin film permits not only to fabricate complex ceramics on a scale and form compatible with electronic devices, but also provide a unique opportunity to create an internal crystallographic texture or epitaxial morphology [3] which could give rise to fascinating behaviour. Also the eventual preparation of artificial superstructures, e.g. CMR/Insulator/CMR, requires the previous fabrication of high quality thin films of the "active" material.

Among the processes for fabricating thin films, pulsed laser deposition (PLD) has emerged as a unique method to obtain epitaxial and nearly single crystal like thin films of multi-component oxides such as superconducting high Tc cuprates, ferroelectric, ferromagnetic, SOFC electrodes, dielectric oxides and their multilayers [4,5].

We have previously studied polycrystalline bulk samples of $SrLaMnTiO_6$ (SLMTO hereafter) synthesized from both the ceramic method and liquid-mix technique. It is an orthorhombic perovskite, S.G. *Pbnm*, which presents a long-ferromagnetic (FM) ordering, Fy mode, with Tc = 380 K, detected from both magnetization measurements and neutron diffraction data. Cations are randomly distributed in both A and B sublattice of the perovskite structure, i.e. it can be considered as a manganite with 50% of magnetic cations dilution in the octahedral sites. In this scenario, FM ordering has been interpreted in terms of fully polarized FM clusters embedded in a paramagnetic matrix, almost without any magnetic frustration. It is worth noting these especially interesting features in such a disordered system. Related to this fact, values of magnetoresistence up to 150% at 210 K have been measured, with a ΔH of 9 T [6,7].

The challenges encountered in fabricating thin ceramic films arise from the complexity of the materials in both composition and structure, especially when more than three cations must be incorporated within the structure, observing the stoichiometry maintenance. This paper reports on the fabrication of SLMTO thin films by PLD on different single-crystal substrates (Si, $LaAlO_3$ and $SrTiO_3$), and their characterization from XRD, scanning electron

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Table 1
Characteristics of the obtained SLMTO thin films.

Sample	t (h)	$d_{tg\text{-}subs}$ (cm)	Substrate	Thickness (nm)	Orientation
PD1	2	4.3	Si	750	Pollycrystal
PD2	1	4.3	Si	560	Partial [0 0 1]
PD3	2	4.3	LaAlO3	1150	Multiphasic
PD4	1	4.3	LaAlO3	730	Multiphasic
PD5	3	4.3	SrTiO3	4080	Partial [0 0 1]
PD6	3	3.3	SrTiO3	4800	Partial [1 1 1]
PD7	1	3.3	SrTiO3	2040	[0 0 1]+[1 1 1]
PD8	4	3.0	SrTiO3	5850	[0 0 1]+[1 1 1]
PD9	2+2	3.0	SrTiO3	8300	[0 0 1]

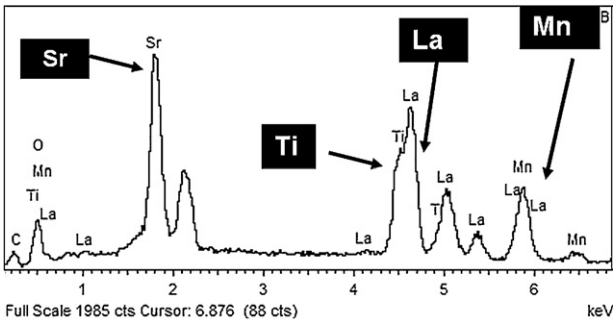

Fig. 1. EDS pattern for the PD8 thin film, i.e. SrLaMnTiO6 grown on $SrTiO_3$.

microscopy and complex impedance spectroscopy. The influence of the substrate in the epitaxiality and compositional and microstructural homogeneity are evaluated.

2. Experimental

Powders of SLMTO were prepared by the liquid-mix technique, with the experimental conditions detailed elsewhere [6]. Pressed pellets (size 13 mm diameter and 3 mm thickness) of these powders were prepared and sintered at 1373 K for 48 h. We will refer these samples as $SLMTO_{LM(I)}$. The thin films were deposited from these $SLMTO_{LM(I)}$ pellets on single crystals of Si, $LaAlO_3$ and $SrTiO_3$, in all cases with [1 0 0] direction. PLD technique (KrF excimer laser – 248 nm) was used to grow thin films. The target was placed in a rotating target holder in a vacuum chamber with a base pressure of 10^{-6} mbar. The substrates were mounted on a heater and in all cases we worked with fixed values of: Ar pressure = 0.3 mbar, T = 973 K, energy = 150 mJ, frequency = 15 Hz. These experimental conditions were selected after being previously optimized for similar compounds by us [5].

With comparative aim, nano-sized powders were prepared also by the liquid-mix technique but starting from organic precursors, Ti(IV) and Mn(III) acetylacethonates, and at lower temperatures (1073 K). Scanning images of these powder (referred as $SLMTO_{LM(II)}$) showed particle size of ca. 100 nm whereas for $SLMTO_{LM(I)}$ particles were sized of about 1 μm.

X-ray powder diffraction patterns were obtained at room temperature with a Siemens D-5000 diffractometer using Cu (Kα) radiation with λ = 1.5418 Å. Scanning electron microscopy (SEM) was performed using a JEOL JSM6335FEG, with resolution of 12 Å. Samples were prepared by covering with Au. In order to obtain surface and cross-section images, thin films were mechanically fractured using a diamond point. Semiquantitative chemical analyses were made from energy dispersive X-ray spectroscopy (EDS).

For a.c. electrical conductivity measurements, blocking electrodes were deposited on both sides of the thin films by platinum paint (previously dried at 1073 K) for measurements in the 300–773 K temperature range. The a.c. conductivity was obtained using a frequency analyzer (Solartron 1260) over a frequency range of 10^2–10^6 Hz.

3. Results and discussion

Nine different films have been prepared, named from PD1 to PD9, under the experimental conditions indicated in Table 1: time of deposition (t), target–substrate distance ($d_{tg\text{-}subs}$) and type of substrate.

EDS data showed a cationic ratio nominally equal to the expected one, within the experimental error, for films grown on Si and $SrTiO_3$. In contrast, for samples grown on $LaAlO_3$ (PD3 and PD4) a Ti-deficiency was detected, i.e. the XRD patterns showed characteristic reflections of different phases. Fig. 1 shows a representative EDS pattern for the stoichiometric films.

The films were characterized from XRD data. A typical 2θ scan of polycrystalline SLMTO sample is shown in Fig. 2(a), with comparative aim. Partial "epitaxial" growth was obtained for most samples, being the preferred orientations the [1 0 0] and [1 1 1] directions of ideal cubic cell. As representative cases, XRD data for selected films, showing different preferred orientations, are shown in Fig. 2(b)–(e). It can be seen that these enhanced maxima coexist with all the perovskite reflections, i.e. a somewhat important random growth was obtained in all the cases. The most noticeable epitaxial distribution was found for the PD9 sample, see Fig. 2(f), in which the (1 0 0) reflections of the ideal cubic cell were observed to be the most intense ones. In this sense, $SrTiO_3$ seems to be the most appropriate substrate for obtaining epitaxial SLMTO films. In fact, this characteristic is rigorously only concerning the PD9 film, as the clear preferred orientation coincides with the substrate one. The compacity and thickness of the prepared thin films have been analysed by means of scanning microscopy. Figs. 3–5 show some representative images for PD6, PD7, PD8 and PD9. First, it was observed

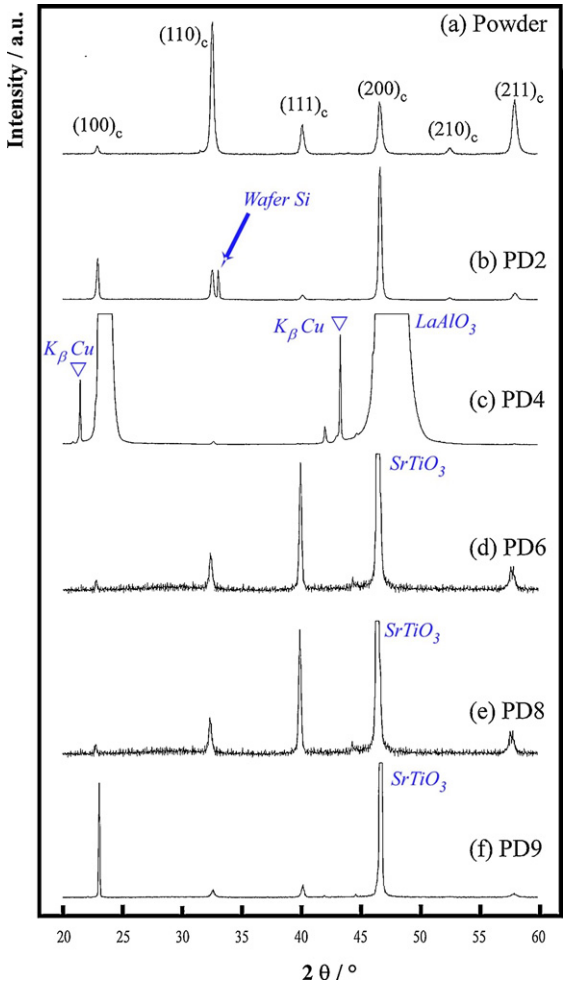

Fig. 2. XRD scans for $SrLaMnTiO_6$: (a) powder, (b) PD2, (c) PD4, (d) PD6, (e) PD8, and (f) PD9.

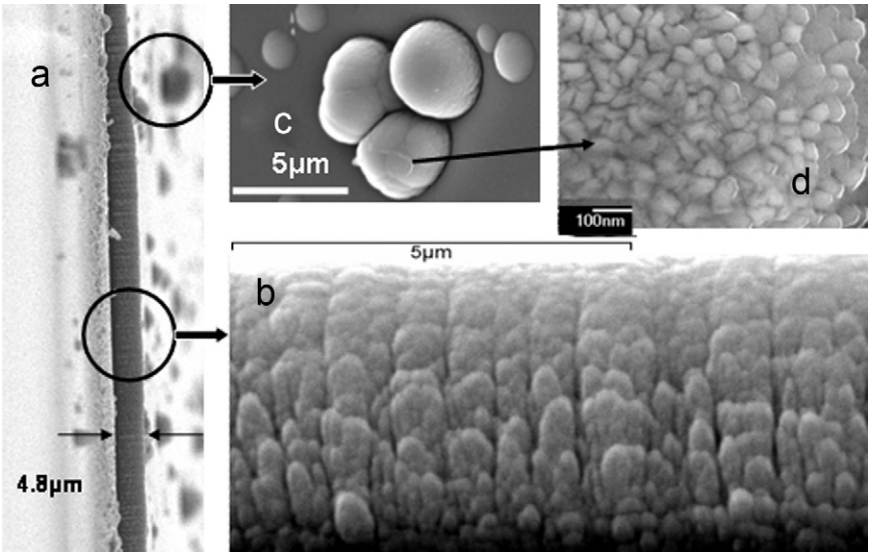

Fig. 3. SEM images for PD6.

that they were well grown over different substrate surfaces. From cross-section images a great homogeneity in the films was observed and thickness mean values were checked, and they are gathered in Table 1. For example, PD7 has ca. 2000 nm of mean thickness and PD8, 6000 nm; i.e. the thickness can be tuned by conveniently modifying the time of deposition. In this sense, $SrTiO_3$ seems to be the most appropriate substrate for obtaining epitaxial SLMTO films in a variable thickness range.

On the other hand, a detailed examination of the thin films structure revealed an interesting characteristic, especially appreciable in the cases presenting a somewhat important degree of "random" growth. As an example, a general overview of the PD6 film is given in Fig. 3(a). Its epitaxial growing (detected from XRD data) could be interpreted in terms of two contributions of microstructural origin, observed as a matrix part and some surface formations, differentiated with circles and zoomed in Fig. 3(b) and (c), respectively. While

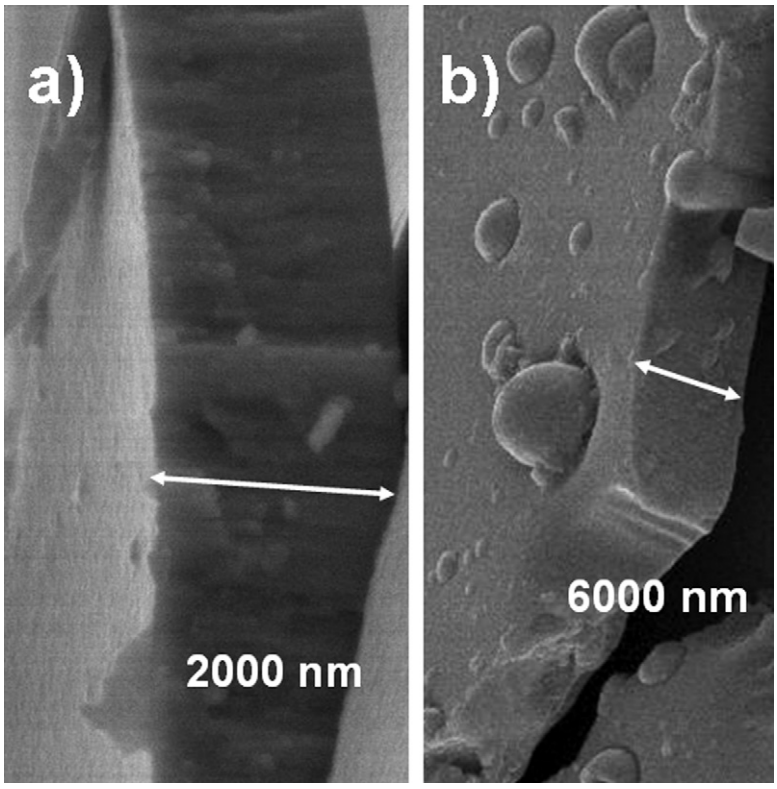

Fig. 4. SEM images for (a) PD7 and (b) PD8.

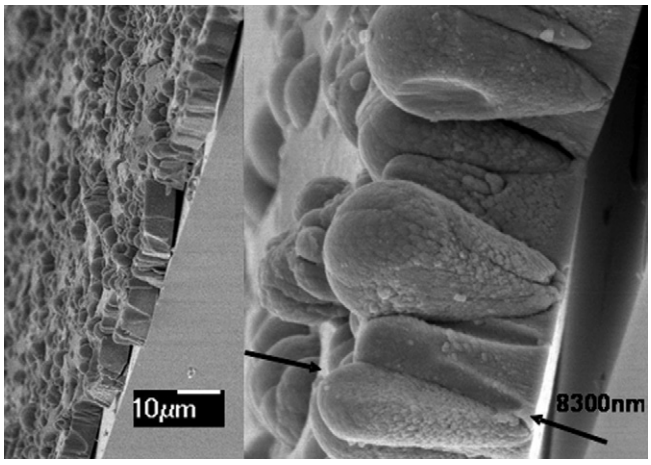

Fig. 5. SEM images of PD9.

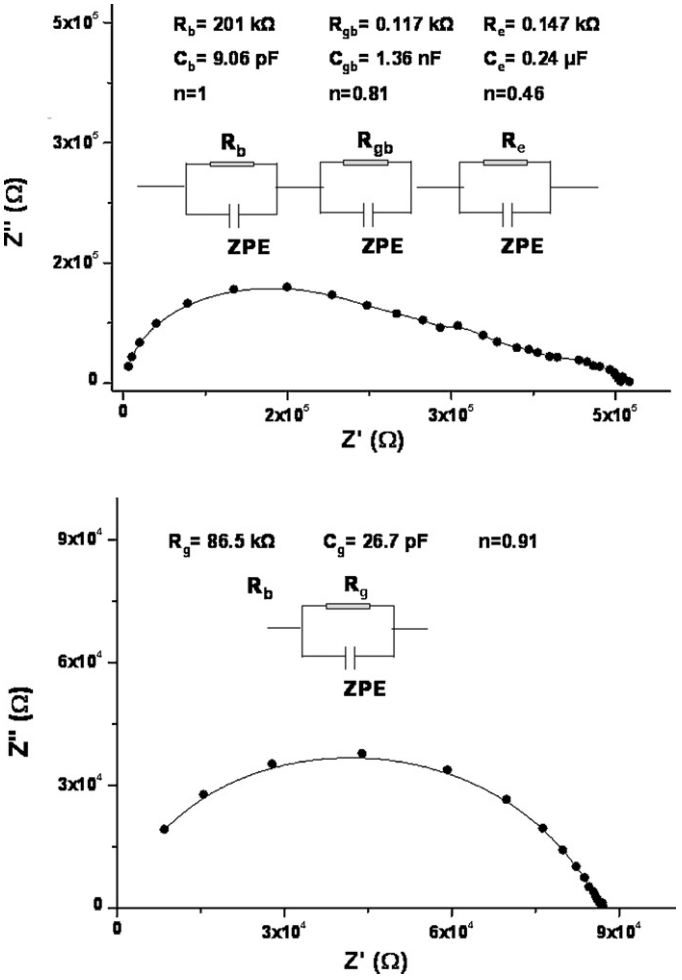

Fig. 6. Z''–Z' plots for PD8 at 800 K (a) before and (b) after annealing. Solid lines indicate the best fits obtained and the correspondent R, C and n values are gathered.

columnar-type packing of crystals is well observed in the matrix zone, Fig. 3(b), the compound grown in sphere-type morphology, as a consequence of the process known as splashing, Fig. 3(c), would be responsible on the random-part distribution of crystals. It is worth noting some interesting details in the microstructure of such spheres, as they present a marked texture exhibiting pyramidal grains in the surface with different size distributions, Fig. 3(d). As it can be observed, the films are nanostructured and contains the so called vertically aligned nanopores (VANPs) [8] with a pore average size of 30–60 nm. This relieves, very interesting for eventual anode applications, are observed in all films and they seem to be linked to the use of single crystals substrates [9,10]. Fig. 5 shows some representative SEM images for PD9, for which these sphere-type superficial formations are somewhat integrated in the thin film, presenting the same epitaxility in the whole sample. Having this in mind, splashing seems to be an important barrier for epitaxility in samples with lesser thickness and one-step grown. In this sense, the two steps treatment (2 h + 2 h) was revealed as convenient.

This fact was nicely corroborated by means of analysing complex impedance data. This technique permits to explore the homogeneity in the electronic response of the thin films. The obtained data showed that grain boundary melting for PD8 seems to require an annealing process of 723 K during 2 days, after fabrication. Before annealing, the impedance plots of PD8 revealed a response consisting in three interpenetrated semicircles. Fig. 6a shows, as an example, the Z''–Z' plot at 800 K before annealing. These three semicircles have been extensively related to bulk, grain boundaries and electrode in polycrystalline materials [8,11]. Effectively, they could be fitted to an equivalent circuit consisting in three RC parallel components, obtaining typical C values of 10^{-7}, 10^{-9} and 10^{-12} F for low, medium and high frequencies, respectively.

This behaviour is drastically changes once the annealing process has been completed. Fig. 6b shows the Nyquist plot obtained at 800K after annealing. As it can be observed, after the thermal treatment a single semicircle was obtained in the whole temperature range explored and activation energy values of ca. 0.30 eV could be calculated. Noticeably, the same typical semicircles were observed from room temperature up to 750 K for PD9, even with smaller values of electrical resistance, without requiring the annealing process. Nyquist plots for the raw PD9 film (without annealing) always consisted in one semicircle in the whole temperature range explored. Capacity values were coherent with bulk contribution. Fig. 7(a) shows these Z'' vs. Z' plots at intermediate temperatures ranging between 383 K and 443 K. The evolution of the real part of modulus with frequency is plotted in Fig. 7(b). Hence, the correspondent fits to a single RC element have been made, obtaining an activation energy of ca. 0.20 eV, clearly similar to that reported earlier for the bulk material (0.17 eV). Fig. 7(c) comparatively gathers the evolution of Z' and M'' with frequency for a selected temperature, showing that they both peak at the same frequency indicating a good homogeneity of the thin films.

Finally, preliminary magnetization measurements point to the stabilization of an enhanced magnetic response at low temperatures. Fig. 8 shows the variation of magnetization with temperature for selected films. The sharp increase in magnetization can be related to ferromagnetic interactions that are probably due to intergrain domains, as they seem to appear at both low temperatures and magnetic fields, coinciding with the intergrain contribution to magnetization. The importance of the grain boundaries role has been also pointed up in relation to the electronic behaviour of similar perovskite systems [12]. The inset of Fig. 8 includes the variation of magnetization with magnetic field for PD1 and PD9, compared to the obtained response for the polycrystalline $SLMTO_{LQ(I)}$ and $SLMTO_{LQ(II)}$ samples (microcrystals and nanocrystals, respectively) for comparison. It can be observed that the magnetic response for the nanosized material is improved when it is grown as a thin film. Some experiments are now in route in order to analyse this response.

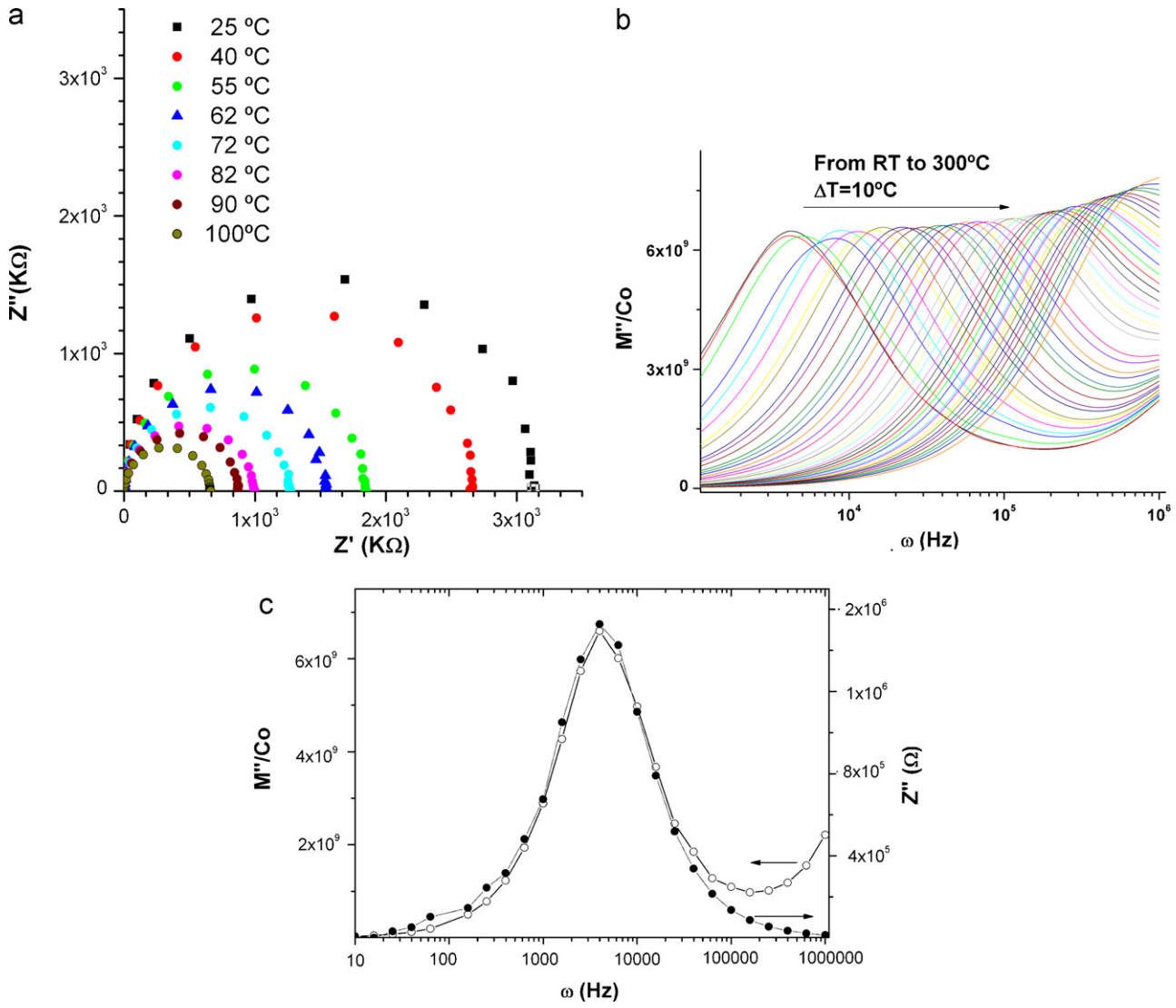

Fig. 7. (a) Nyquist plots for PD9 at selected temperatures, (b) evolution of modulus with frequency, (c) comparison of the variation of M'' and Z'' with frequency at 500 K.

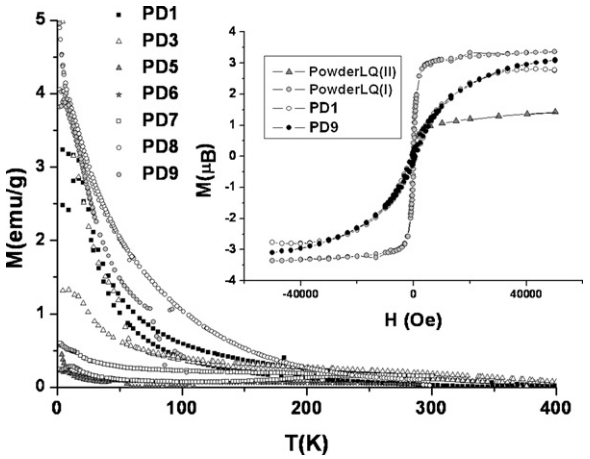

Fig. 8. M vs. T for selected films, under 500 Oe. Inset: M vs. H for PD1 and PD9 thin films, and for powder pellets $SLMTO_{LQ(I)}$ and $SLMTO_{LQ(II)}$.

4. Conclusions

STO substrate is revealed as the most adequate one in order to grow homogeneous and epitaxial SLMTO films. Thickness can be tuned by modifying the time of deposition. Other parameters as distance target-substrate seem not to be relevant at this respect. The two-step treatment (PD9) permits both to avoid the surface splashing effects related to random growth, and to obtain conductive films without requiring an annealing treatment.

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