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Microstructure-ferroelectric Properties Relationships in Sol–Gel Prepared Lanthanum Modified Lead Titanate Thin Films

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Abstract

Transmission electron microscopy is used to investigate the effect of the excess of PbO and the temperature of crystallization on the grain size of sol–gel lanthanum modified lead titanate thin films. Grain size is found to increase from ~100 nm to ~1 μm when the excess of PbO in the precursor solution is reduced from 20 to 10 mol%, but it is not significantly affected by raising the temperature from 650 to 700°C. Films ferroelectric characterization shows that the switchable polarization is higher in the films with a smaller grain size. This effect is explained by taking into account the presence of a tensile stress at the film–substrate interface, which clamps 90° domain walls. This stress is higher in coarse grained films, most of whose grains are in contact with the substrate, than in the fine grained films. Therefore, 90° domain wall movement is easier in fine grained films. © 1999 Elsevier Science Limited. All rights reserved

Keywords: (Pb,La)TiO_3, films, sol–gel processes, grain size, ferroelectric properties.

1 Introduction

Lanthanum modified lead titanate (PTL) ferroelectric thin films with low concentration of La have been studied[1–3] for their interest in infrared and electromechanical sensing, and actuating applications.

We have previously reported on the structural, microstructural and electrical properties of sol–gel prepared PTL films with a 8% of La on Si based substrates[4]. Single perovskite phase films were obtained when an excess of PbO was included in the precursor solution. These films present a random orientation and a significant porosity when a 10°C min^{-1} heating rate was used in the crystallization thermal treatment, and a mixed [001] [100] orientation and no porosity when a rate higher than 500°C min^{-1} (here referred to as rapid heating) was used. In this work, transmission electron microscopy (TEM) is used to study the films grain size, and how this parameter is affected by the preparation conditions. Ferroelectric data are also given, and the effect of a grain size of the order of the film thickness combined with the tensile stress at the film-substrate interface, on the reduction of the switchable polarization, is reported.

2 Experimental Methods

Films on Si based substrates were prepared[4] from precursor solutions with 10 and 20 mol% excess of PbO respect to the nominal composition, $Pb_{0.88}La_{0.08}TiO_3$. Amorphous films were crystallized with a 10°C min^{-1} rate and rapid heating. A temperature of crystallization of 650°C was used in the treatments with 10°C min^{-1}, and 650 and 700°C were tested with rapid heating.

Plan view specimens for TEM were prepared by a standard technique previously described,[5] and studied either in a JEOL JEM 2000 FX-II microscope working at 200 kV, or in a Philips CM30 one working at 300 kV. The dark field (DF) technique was used to estimate grain size. Images containing a number of grains that can be considered representative of the film microstructure, instead of just a few ones, are required. The DF images were formed with a portion of the rings of the selected area electron diffraction (SAED) patterns. An example of how the

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DF were obtained is shown in Fig. 1. In Fig. 1(a) and (b), a TEM image of a specimen and the corresponding SAED pattern are shown, respectively. The DF image of Fig. 1(c) is formed with the portion of the rings, which correspond to the (001)/(100), (110)/(101), (111) and (002)/(200) planes of the perovskite, contained in the circle in Fig. 1(b).

Electrical characterization was accomplished after 500 μm diameter Pt electrodes were deposited by sputtering on the films. The switchable polarization, P_{sw}, was evaluated by the measurement and integration of the switching current intensity. This magnitude is twice the remanent polarization from hysteresis loops, if saturation has been reached.

3 Results

3.1 Films treated with a 10°C min^{-1} rate

Traces of second phase has not been found neither by GIXRD nor by SAED in any of the films. In Fig. 2(a), a DF image of a film prepared from the solution with 10 mol% excess is shown. A grain size distribution from ~100 nm to ~1 μm is observed. In Fig. 2(b), a DF image of a film prepared from the solution with 20 mol% excess of PbO is shown. A grain size between ~60 and ~100 nm, much smaller than that of the film prepared from the solution with 10 mol% excess, is observed.

In Fig. 3, the switchable polarization, P_{sw}, of a film prepared from the solution with a 10 mol%

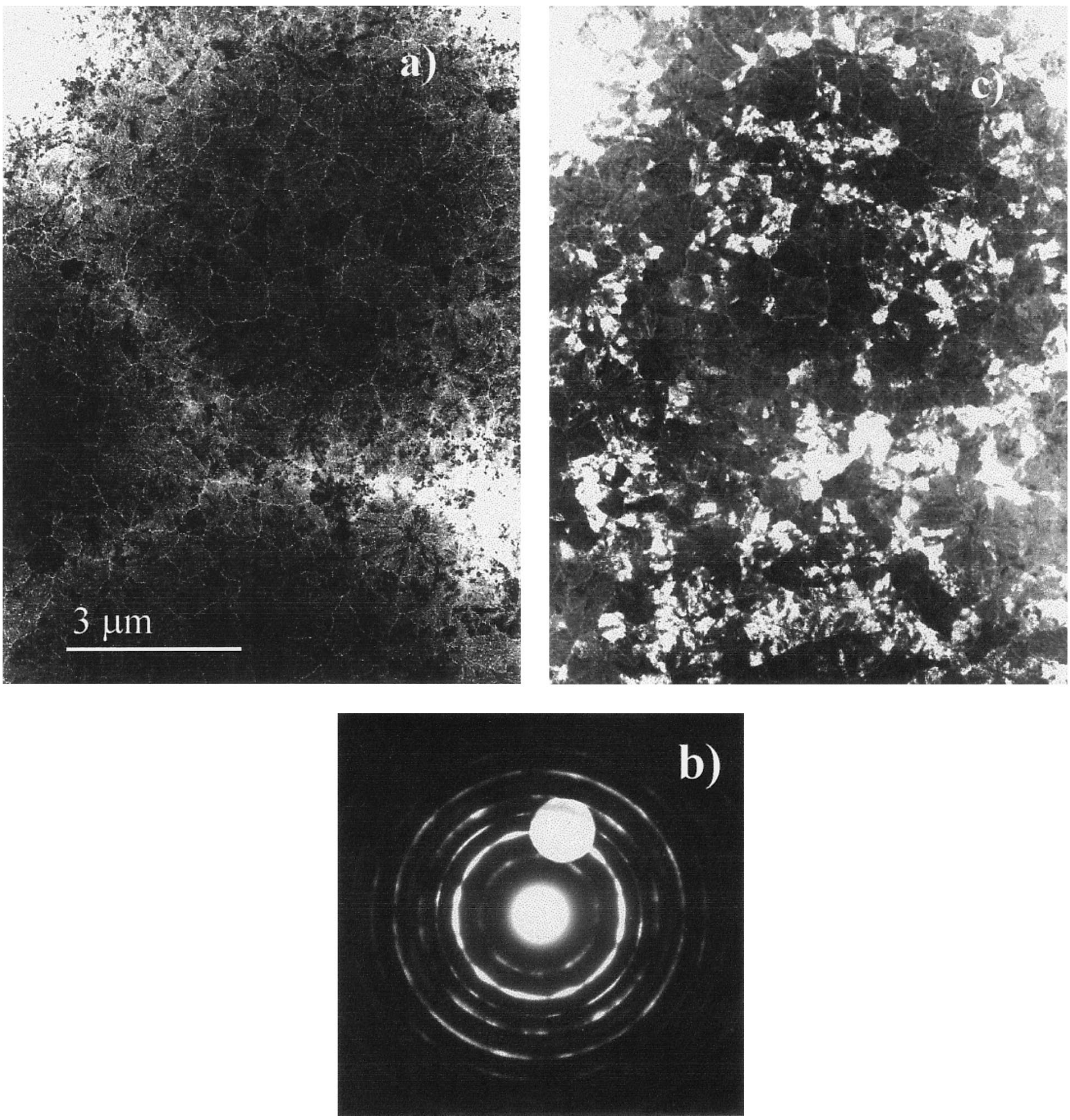

Fig. 1. (a) A TEM image of a PTL film, (b) corresponding SAED pattern, and (c) dark field image of the same area formed with the portion of the rings marked in (b).

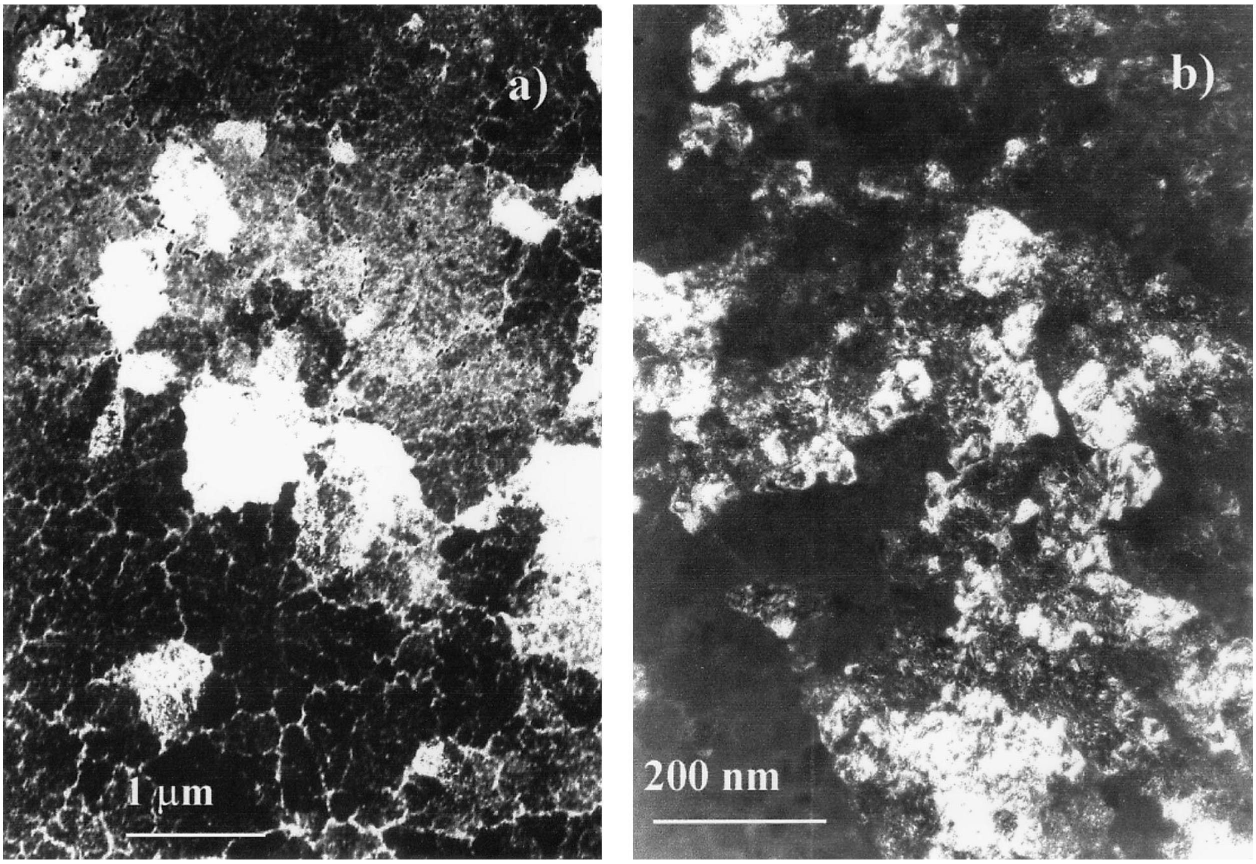

Fig. 2. DF images of PTL films prepared from the solution with (a) 10 mol% excess of PbO, and (b) 20 mol%, and crystallized at 650°C with 10°C min^{-1}.

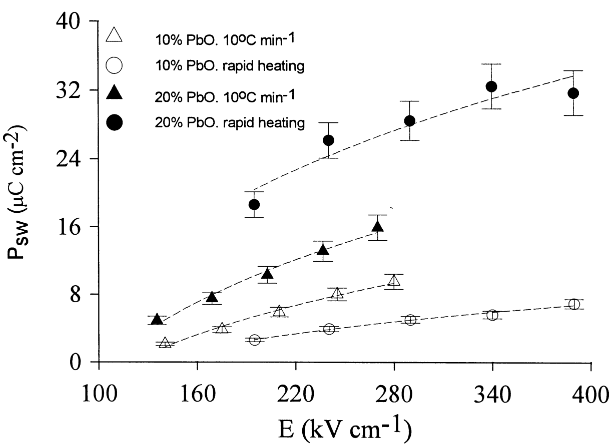

Fig. 3. Switchable polarization, P_{sw}, from the integration of the switching current intensity transients in PTL films.

excess of PbO is shown at increasing electrical fields. P_{sw} increases with field, from 2 to 9.5 μC cm^{-2} for fields from ~135 to ~275 kV cm^{-1}. In the same figure, P_{sw} of a film with a 20 mol% excess is also shown. The trend is the same, but the figures are always higher than in the former case. P_{sw} increases from 5 μC cm^{-2} at 135 kV cm^{-1} to 16 μC cm^{-2} at 275 kV cm^{-1}.

3.2 Films treated with rapid heating

In Fig. 4(a) a DF image of a film prepared from the solution with 10 mol% excess is shown. A grain size distribution from ~100 nm to ~1 μm, similar to that of films prepared from the same solution but treated with 10°C min^{-1}, is observed. In Fig. 4(b) a DF image of a film prepared from the solution with 20 mol% excess of PbO, and crystallized at 650°C, is shown. A grain size between 50 and 150 nm, much smaller than that of the film with 10 mol% excess, is observed. Finally, in Fig. 4(c) is shown the DF image of a film prepared from the latter solution but crystallized at 700°C. There are no differences in grain size with respect to the one crystallized at 650°C.

In Fig. 5, a TEM image of the film with the higher grain size, i.e. the one prepared from the solution with 10 mol% excess of PbO, is shown. In the image, a 90° domain structure is observed within the grains. This structure is specially clear in this type of films.

*P*sw of the films prepared from the solutions with 10 and 20 mol% excess and crystallized at 650°C with rapid heating is also shown in Fig. 3 at increasing fields. The maximum field attained is higher in these films because they are thinner (410 nm) than the ones treated with 10°C min^{-1} (580 nm). Trends are the same observed in the latter ones; P_{sw} increases with field in the whole range, and it is always higher in those prepared from the solution with 20 mol% excess.

4 Discussion

Results show that the grain size is higher in the films prepared from the solution with a 10 mol% excess of PbO, in which many of the grains are larger, up to 1 μm, than the film thickness (500 nm); than in films prepared from the solution with 20 mol% excess of PbO, in which grain sizes between 50 and 150 nm exist, well below the film thickness. These trends are not affected neither by the crystallization heating rate

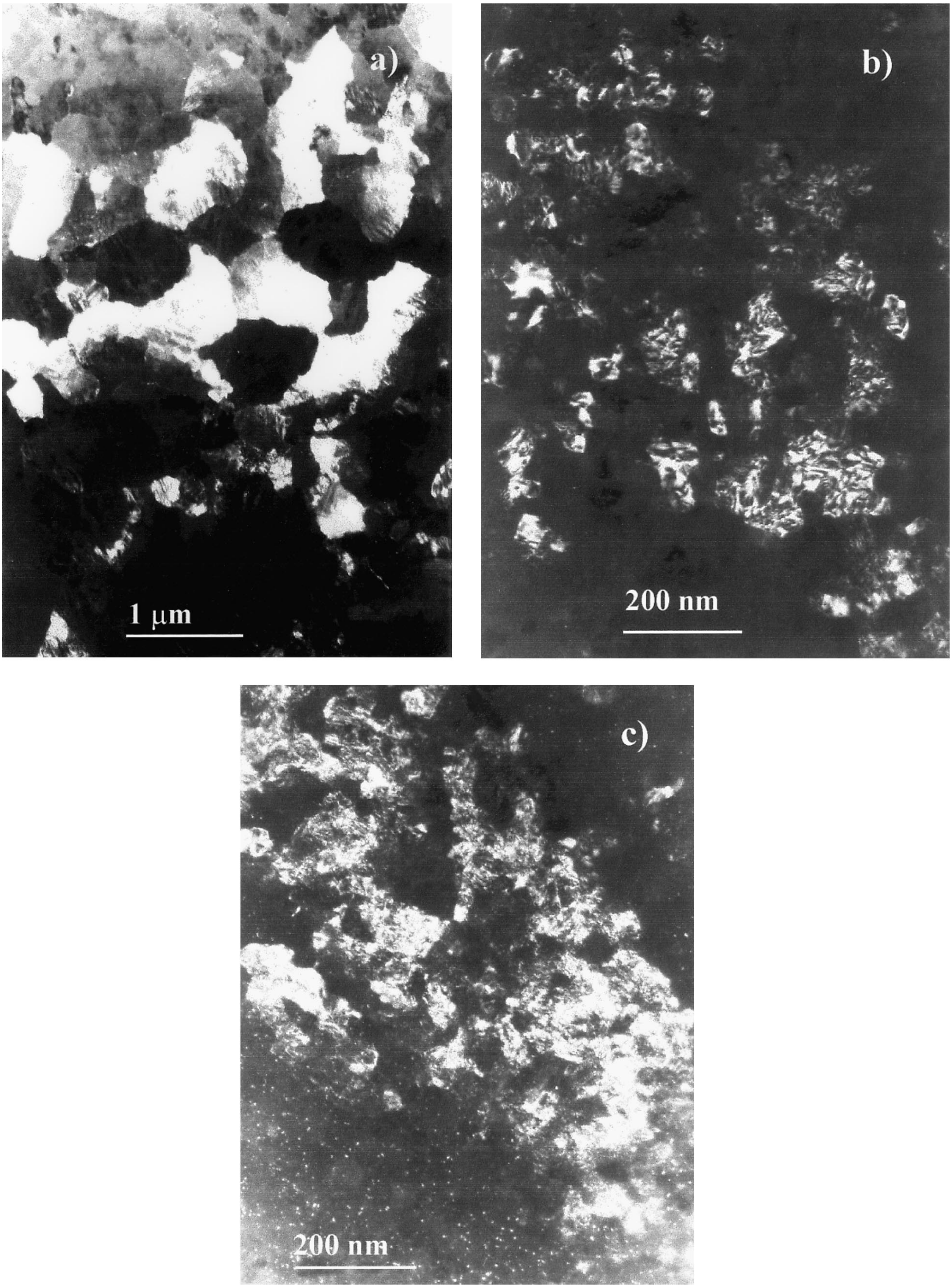

Fig. 4. DF images of PTL films prepared from the solution with (a) 10 mol% excess of PbO, and (b) 20 mol%, and crystallized at 650°C with rapid heating. (c) as (b), but crystallized at 700°C.

Fig. 5. TEM micrograph of the film prepared from the solution with 10 mol% excess of PbO, and crystallized at 650°C with rapid heating, showing the presence of domain twinning.

nor by the temperature of crystallization. Therefore, we have obtained two types of single perovskite phase films with very different grain size: One of them is formed by non-textured films with a significant porosity, and the other is formed by non-porous films with a mixed [001] [100] orientation.

In these films, it has been observed that the switchable polarization increases when the grain size decreases.

We propose the following explanation in order to understand the differences in switchable polarization between the films with different grain size. This explanation considers the presence of a tensile stress at the film substrate interface, as reported before for sol–gel derived lead-based perovskite thin films on silicon substrates.[6,7] 90° domain walls are clamped by this tensile stress. This effect is more significant when the grains are attached to the substrate, and therefore, in films with a grain size close to the film thickness, than in fine grained films. Tuttle *et al.*[8] have also shown that 90° domain switching was negligible in columnar lead zirconate titanate (PZT) films, which will be the extreme situation.

The presence of 90° domains in the PTL is a necessary condition for this explanation. TEM has provided clear evidence of their presence in coarse grained films (see the typical herringbone pattern shown in Fig. 5), although they cannot be observed so easily in fine grained films.

5 Conclusions

Single perovskite phase, lanthanum modified lead titanate thin films (PTL) with grain sizes between 100 nm and 1 μm, can be prepared by a diol-based sol–gel technique on Si based substrates by varying the excess of PbO included in the precursor solution. The tensile stress developed during films preparation causes the partial clamping of the 90° domain walls, the effect more significant in coarse grained films than in fine grained ones. Because of this, fine grained films have higher values of the switchable polarization than coarse grained films, and are preferred for applications requiring a high electrical polarization, as those are based on the pyro and piezoelectric properties of the films.

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