A new concept to prepare nanocomposite thin films is explored. Two chemical-based bottom-up steps are used to design functional films including (i) the block copolymer-assisted self-assembly of a porous matrix; and (ii) the impregnation of nanoparticles from a ferroic phase into the pores by supercritical CO$_2$ deposition. Porous nanopatterned BaTiO$_3$ thin films with ca. 17 nm thickness are prepared using a cost-effective sol–gel solution containing a block copolymer and evaporation-induced self-assembly methodology. Hexagonally arranged pores with a diameter of ca. 95 nm, running perpendicular to the substrate, are filled with Ni nanoparticles using the supercritical fluid deposition technique, obtained from the reduction of hydrated nickel nitrate in a supercritical CO$_2$–ethanol mixture at 250 °C. Small Ni nanoparticles of 21 ± 5 nm size are selectively deposited inside the pores of the porous matrix. Structural and magnetic properties prove the coexistence of both phases.

**Introduction**

Porous films may be seen as “bottom-up” platforms for nanotechnology.$^{1-3}$ Oxide-based porous films can find important applications in the microelectronics and photonics fields not only by nanofabricating functional ordered porous patterns with a lateral thickness below 100 nm,$^{4,5}$ but also by finding strategies to insert functional molecules or nanoparticles into the pores.$^1$

We have recently prepared and characterized the structure of nanoporous and nanopatterned thin films with PbTiO$_3$ composition using evaporation-induced self-assembly (EISA).$^6,7$ Over the last decade, EISA has been exploited for the preparation of mesoporous metal oxide thin films with periodicities in the sub-50 nm size range.$^2$ Besides the synthesis and structural characterization, we also demonstrated the positive effect of porosity on the local ferroelectric properties of PbTiO$_3$.$^6,7$ Well-ordered porous structures are excellent matrices to create multifunctional materials. We wish now to exploit the potential of these porous platforms, with vertically aligned pores perpendicular to the substrate, by depositing a magnetic material inside the pores of the ferroelectric patterned films. The vertical architectures of the composites should lead to enhanced properties compared to the layered structure as a consequence of the increase of the interfacial area between the two ferroic phases and of the reduced substrate clamping effect.$^8$

The deposition of the second magnetic phase within the small pores of a porous multimetallic oxide matrix is quite challenging because of the difficulties in filling the pores without covering the entire surface and achieving good interfaces between both crystallographic phases. In order to overcome these limitations, we proposed to use supercritical CO$_2$ as a solvent.

The use of supercritical fluids (SCFs) in Materials Science started in the beginning of the 90s as a means to produce nanomaterials.$^9-12$ Among all nanomaterials, the nanoparticles and nanostructured materials are the most explored areas.$^{10}$ The interest in using SCFs relies on their unique properties, high solvating power and excellent transport properties. Indeed, within the supercritical region, there is no phase boundary between the gas and liquid phases, meaning that there is a continuity in the physical properties of the fluid between the gas and liquid states.$^9$

The most frequently used supercritical fluid is carbon dioxide (CO$_2$). CO$_2$ is cheap, non-flammable, chemically inert, non-toxic and has a relatively low critical temperature and pressure ($T_c = 31 ^\circ$C, $P_c = 7.38$ MPa).$^{13}$ Supercritical CO$_2$ can dissolve a broad range of organometallic compounds.$^{14-16}$ Although pure CO$_2$ is not a good solvent for inorganic metal salts, hydrated metal nitrates and chlorides can be dissolved in
supercritical CO2 by adding a small amount of a polar solvent such as ethanol in CO2-ethanol solutions. These precursors are less toxic, cheaper and easier to handle than the nickel organometallic compounds.

Watkins et al. developed an SCF-based approach that consists of the deposition of metals and metal oxides by the chemical reaction of suitable precursors in an SCF within a high-pressure reactor. The reaction was generally initiated upon the addition of hydrogen (H2) or another reducing agent such as an alcohol. The Supercritical Fluid Depression (SCFD) technique was used previously to deposit Ni films onto planar and patterned silicon wafers using supercritical CO2 (scCO2) to achieve conformal films with high quality. The same approach was extended to deposit Ni nanoparticles into porous supports.

The low surface tension, high diffusivity and low viscosities of CO2 solutions allow us to deposit or incorporate metallic nanoparticles into a wide variety of inorganic and organic substrates for microelectronic, optical and catalytic applications. Although the SCFD is a solution-based approach, the transport properties of SCFs, which are similar to those of a gas, afford the infiltration in the complex geometry and avoid the mass transfer limitations common to liquid phase reductions. The high solubility of the decomposition products in CO2 enhances the purity of the material deposited at low temperature by facilitating desorption of potential contaminants from its surface. Furthermore, the metal loading is easy to control by adjusting concentration, deposition time and pressure.

To the best of our knowledge, SCFD has never been used to prepare nanocomposite thin films. In this paper, the deposition of the nanopatterned BaTiO3 thin films using EISA onto planar silicon wafer, the deposition of Ni within the pores using SCFD, and the structural and physical characterization of the materials are described. We prove a new concept for the nanocomposite preparation using a full chemical scalable approach. This approach may be interesting for the design of multiferroic nanocomposite films, i.e. films exhibiting both magnetic spin and electric dipole ordering, in a vertical heterogeneous (1–3) arrangement as presented in Scheme 1. Multiferroics are very promising materials for modern electronics, especially high-density magnetic storage, sensors, and spintronics. Furthermore, single-phase multiferroics are scarce, and composite multiferroic thin films must be designed in a way which enhances cross-coupling properties that enable applications.

**Experimental**

**Nanopatterned thin film preparation**

Nanopatterned BaTiO3 thin films were prepared using an adapted sol–gel method and an evaporation-induced self-assembly methodology as described in ref. Poly(butadiene-(1,4 addition)-b-ethylene oxide) (PB51-b-PEO62), an amphiphilic block copolymer, with MW_{PB} = 51 000 g mol⁻¹ and MW_{PEO} = 62 000 g mol⁻¹, was used as a structure-directing agent. Three solutions were prepared. Solution A was prepared by the dissolution of barium hydroxide octahydrate (0.20 mmol, Merck, purity ≥ 98.0% w/w) in glacial acetic acid (8.93 mmol, Merck) at room temperature. Solution B was prepared by mixing 2,4-pentanediene (0.11 mmol, Fluka, purity 99.3% w/w) with titanium(iv) n-butoxide (0.20 mmol, Merck, 98.0% w/w) under stirring at room temperature. Afterwards, solutions B and C were added to solution A, forming the final solution. Nanopatterned BaTiO3 thin films were deposited by dip-coating onto planized silicon (Pt/TiO2/SiO2/Si) (Radiant Inc.) at 1.6 mm s⁻¹. All films were thermally treated in air at 350 °C for 5 min in order to complete the inorganic condensation (mesostructuration) of the matrix and to partially decompose the organic content. The films were also thermally treated at 600 and 700 °C for 2 min.

**Functionalization using scCO2**

Experiments were conducted in a ca. 100 mL stirred high-pressure reactor (Auto clave Eng. Inc.) in the batch mode. Several pieces of 1 cm × 1 cm of the nanopatterned BaTiO3 thin films were placed vertically inside the high-pressure reactor and in contact with the wall. The nickel(n) nitrate hexahydrate precursor (0.069 mmol, Sigma-Aldrich, 98.5% w/w) was previously dissolved in ethanol (68.50 mmol, Carlo ERBA) and placed in a vial allocated at the bottom of the reactor without coming into contact with the substrates.

The reactor was then heated using a heating jacket connected to a PDI controller to 60 °C and then filled with CO2 (Air Liquide, purity > 99.99%) using a high-pressure syringe pump (Iscoc, Inc. Model 260D) thermostated at the same temperature up to 10.0 MPa. The temperature was measured using a K-type thermocouple. The pressure was measured using a pressure gauge. The mixture of the inorganic precursor with ethanol and scCO2 was kept under these conditions for 1 h. The percentage of ethanol in CO2 in the mixture was 9.5% mol. Then the reactor was heated at 250 °C for 2 h. The precursor dissolved in scCO2 impregnated the nanopatterned material and decomposed during heating. During these experiments, the pressure was kept below 30.0 MPa (which is the maximum pressure of the equipment) by venting a small amount of the CO2 solution from 100 °C. Then, the heater was turned off and the reactor was depressurized through a needle valve in 1 h. Ethanol acted as co-solvent favouring precursor dissolution and as a reducing agent at high temperature promoting the chemical reduction of the salt.

![Scheme 1](https://example.com/scheme1.png)  
**Scheme 1.** Representation of the potential multiferroic application of the developed nanocomposite thin films.
Characterization

The film microstructure was investigated by high-resolution SEM using a SU-70 Hitachi microscope. The average pore and nanoparticle sizes were determined using ImageJ software (version 1.45s). The values presented are average values taken from the measurement of at least fifty different particles. The Atomic Force Microscopy (AFM) and Magnetic Force Microscopy (MFM) measurements were obtained on a Nanoscope III, using Tap300 cantilevers with Al-coated tips (Budget Sensors, resonant frequency of 200–400 kHz, force constant of 20–75 N m⁻¹) and MESP cantilevers with CoCr-coated tips (Bruker, resonant frequency of 75–100 kHz, force constant of 2.8–5.0 N m⁻¹), respectively. The AFM images were collected in the contact mode. In the MFM measurements, the topography signals of the film surface were taken simultaneously with the deflection and phase signals and were collected in the non-contact mode. Since the results were obtained with the same type of cantilevers and under identical scanning and acquisition conditions, comparison between both films can be made. Magnetization measurements as a function of temperature and applied magnetic field were performed using a SQUID magnetometer (QD-MPMS). The thermal variation was measured at 200 Oe, increasing the temperature from 10 to 370 K after cooling the sample down to 10 K in zero applied field (zero field cooled – ZFC) or under the measurement field (field cooled – FC). Isothermal hysteresis loops were obtained at 35 K and 300 K for magnetic fields up to 5.5 T, which are parallel and perpendicular to the film surface. The diamagnetic components due to the substrate and to the porous BaTiO₃ film were subtracted from the measured magnetic moment.

Results and discussion

The pores of BaTiO₃ nanopatterned porous thin films were filled with Ni nanoparticles using the supercritical CO₂ deposition method according to schematic representation in Fig. 1d. Fig. 1 shows the top view SEM micrographs of nanopatterned BaTiO₃ thin films before (a–c) and after (e and f) functionalization with Ni and thermally treated at different temperatures. These micrographs are representative of the entire covered surfaces and exhibit the good quality of the hexagonal ordered porous structures. This pore order and periodicity result from the self-assembly of the micelles of the amphiphilic block copolymer, followed by the condensation of the inorganic species around the micelle arrays. Fig. 1a reveals an amorphous character of the structure after thermal treatment at 350 °C for 5 min. At this temperature, all pores are already open due to the complete decomposition of the block copolymer and to the very thin deposited layer of the nanopatterned BaTiO₃ films. During the thermal decomposition of the block copolymer, void motifs are thus created. The Pt grain structure of the Pt/TiO₂/SiO₂/Si substrate can already be observed, and this demonstrates that vertical pores are open. Upon thermal treatment at 600 °C, the well-ordered porous structure remained without the coalescence of the pores as seen in Fig. 1b. However, at 700 °C, some walls between the pores start to collapse and the coalescence of some pores takes place (Fig. 1c), despite the fact that, at this temperature, the well-ordered array is practically kept at a large scale. The XRD measurement (not shown) did not confirm the crystallinity of the BaTiO₃ film treated at 700 °C. Potential explanations for the absence of XRD signals may be: (i) the non-formation of the ferroelectric crystalline phase due to an inadequate inorganic/organic ratio or crystallization temperature; or (ii) the crystallites or the coherent volumes are too small to be detected using the XRD diffractometer. The preparation of crystalline BaTiO₃ thin films with a thickness below 2 nm using molecular beam epitaxy has been reported.

In our case, the chemical-based preparation methodology and the low processing temperature would not only lead to a polycrystalline structure but also favor an incipient crystallization. Moreover, the combined effect of the thickness (~17 nm) with the porosity on the ferroelectric properties is unknown.

The analysis of the nanoscale ferroelectric properties was dismissed as a consequence of the lack of evidence of the crystalline structure. Despite the unclear crystallographic structure of the nanopatterned BaTiO₃ thin film thermally treated at 600 °C, the prepared nanopatterned thin films were used as matrices for studying the functionalization with Ni nanoparticles through the SCFD approach (Fig. 1d) to prepare a multifunctional material (Fig. 1e and f). Basically, the SCFD approach involved the dissolution of the Ni(NO₃)₂ salt in the CO₂–EtOH mixture and the exposure of the substrate to the solution. After incorporation of the precursor into the substrate surface, the metallic precursor was reduced to its metal form by heating at 250 °C. In this case, ethanol acted as both co-solvent and a reducing agent. Thus, from the SEM micrographs, Fig. 1e and f, no solvent residue or big nanoparticle clusters on the surface of the nanopatterned thin films were found. The presence of distinct nanoparticles only within the pores and more than one in the same pore can also be observed, suggesting that the particles’ coalescence was limited by the relatively low reduction temperature (Fig. 1e and f). The nanoparticles are only placed inside the pores as an effect of the grained structure of the exposed platinum substrate which may catalyze the reduction. Furthermore, Kondoh reported the selective deposition on metal surfaces. The author demonstrated that Ru films, deposited in scCO₂ fluid, grew only on conductive or metallized surfaces due to their ability to donate electrons, attracting the chemical species to adsorb. So, similarly Ni nanoparticles are deposited within the vertical pores of the BaTiO₃ film on the top of the platinum substrate, which attracts the nickel precursor and helps in its reduction.

The average pore diameter and nanoparticle sizes determined from SEM analysis are 95 ± 11 nm and 21 ± 5 nm, respectively. The nanoparticles seem to be very uniform as observed from Fig. 1e and f. The chemical composition of the nanoparticles was evaluated by EDX spectroscopy, confirming that nanoparticles are composed of Ni (Fig. 1g).

Fig. 2 shows the AFM measurements performed on the nanopatterned BaTiO₃ thin films thermally treated at 600 °C before (a) and after (b) functionalization with Ni. Similar to SEM micrographs, the images are representative of the entire covered surfaces and exhibit good quality arrays of hexagon-like ordered porous structures (Fig. 2a). Fig. 2b shows that more
than 70% of the pores of nanopatterned thin films are occupied by nanoparticles with ca. 21 nm diameter. Several nanoparticles have been deposited per pore, suggesting the selectivity of the deposition method. The pore size is in good agreement with that measured using the SEM micrographs. The wall thickness between the pores is 43 ± 10 nm showing the small importance of the wall area compared to the pore size (69 ± 2% porosity). As the AFM measurements were performed in the contact mode with high resolution tips at a tip height of 17 µm and a tip radius of <10 nm, the pore depth can be related to the film thickness. Thus, the thickness of the nanopatterned BaTiO₃ thin films is around 17 ± 2 nm. From the acquisition conditions and the relation between the pore depth and thickness, it is possible to observe that the pores reach down to the substrate and the pores are completely open and directed to the substrate as was observed in SEM micrographs. The RMS (root mean square) surface roughness for the nanopatterned thin films (Fig. 2a) is 5.1 nm. However, the AFM images for Ni functionalized nanopatterned BaTiO₃ thin films (Fig. 2b) present an RMS surface roughness of 3.0 nm. The decrease of the surface roughness proves that the pores are filled with nanoparticles, with a consequent flattening of the surface. As for crystalline BaTiO₃, the Ni
nanoparticles could not be identified by XRD. Again, due to the low film thickness, the Ni content may be below the resolution limit of the equipment.

In order to evaluate the magnetic behavior, the MFM measurements were performed in the Ni-functionalized nanopatterned BaTiO₃ thin films (Fig. 3). The topography and the phase are shown in Fig. 3a and b, respectively. The topography is very similar to the one obtained using SEM micrographs (Fig. 1) and AFM (Fig. 2), showing the well-ordered porous structure filled with Ni nanoparticles. However, no contrast coming from the magnetic nanoparticles can be observed in the phase image even at 5 nm from the surface (Fig. 3b), suggesting that the domains are oriented parallel to the surface and cannot be detected by our system that only operates out of plane.

Fig. 4 presents the magnetization measurements as a function of temperature and applied magnetic field. The diamagnetic components due to the substrate and to the BaTiO₃ film were subtracted. The data are normalized to the Ni volume, considering the mean values of film thickness (17 nm), film porosity (68%), pore diameter (95 nm) and the percentage of pores occupied by Ni nanoparticles (70%). Fig. 4a and b are consistent with a ferromagnetic behavior of Ni nanoparticles (Curie temperature above room temperature) with a wide size distribution. The maximum magnetization attained at 300 K (Fig. 4b) is 300 emu cm⁻³, and the coercive fields are around 150 Oe and 25 Oe at 35 K and 300 K, respectively. These values which are lower than the bulk values for Ni (~485 emu cm⁻³ and 100 Oe for saturation magnetization and coercive field, respectively, at 300 K) are attributed to the reduced size of the nanoparticles. Similar values have been reported for Ni nanoparticles. The field variation of the magnetization was also measured at 300 K with the magnetic field perpendicular to the film surface (Fig. 4c). In this case, in contrast to the parallel field configuration, a high susceptibility remains up to the highest
measured fields, indicating that there is a progressive alignment with the field of the Ni nanoparticles. This result is consistent with the fact that from MFM measurements the domains seem to be oriented parallel to the surface of the film, as an out-of-plane magnetic contribution was not detected within the pores.

Conclusions

Extremely well-patterned composite thin films were fabricated by an easy, chemical-based and scalable method, avoiding costly high-resolution lithography techniques and harmful etching processes. The composites are achieved in two steps: encompassing the design of a nanopatterned BaTiO₃ porous matrix, followed by the filling of the pores with nickel metal nanoparticles using the SCFD method. The nanopatterned thin films present a pore diameter size of ca. 95 nm and a thickness of ca. 17 nm. SEM, EDX and AFM proved the presence of nickel particles with ca. 21 nm size within the pores. Although through the MFM measurements it was impossible to confirm the magnetic behaviour due to the parallel orientation of the domains, SQUID measurements undoubtedly prove that a magnetic material was successfully deposited in the porous films of BaTiO₃.

The amount of the nanoparticles and their subsequent growth can be tuned by controlling the dissolution and reduction time, respectively. The chemical composition of the porous matrix and of the nanoparticles can be modified by the use of different inorganic precursors. This novel strategy of functionalization based on supercritical fluid deposition to create nanocomposite materials is very versatile and can open perspectives for the application of these materials as nanopatterned media (magnetic data storage devices) and multiferroic materials. A great leap forward in the multiferroic field is expected from alternative and cost-effective techniques, easy to be applied to extensive areas, in which the ferroelectric and the ferromagnetic components are arranged with long-range ordering and good control of the stoichiometric composition, phase distribution, interface and strain coupling between phases. Furthermore, nanocomposite thin films with small magnetic nanoparticles within the pores can also be used as a solution to avoid the magnetostatic interactions between neighboring magnetic domains in patterned magnetic media by the presence of the walls between the pores.

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References