Unveiling the efficiency of microwave-assisted hydrothermal treatment for the preparation of SrTiO₃ mesocrystals†

Luis F. da Silva, Ariadne C. Catto, Waldir Avansi Jr, Alexandre Mesquita, Lauro J. Q. Maia, Osmando F. Lopes, Máximo Siu Li, Mário L. Moreira, Elson Longo, Juan Andrés and Valmor R. Mastelaro

Material processing has become essential for the proper control, tuning and consequent application of the properties of micro/nanoparticles. In this case, we report herein the capability of the microwave-assisted hydrothermal (MAH) method to prepare the SrTiO₃ compound, as a case study of inorganic compounds. Analyses conducted by X-ray diffraction, X-ray photoelectron and X-ray absorption spectroscopies confirmed that the MAH route enables the formation of pristine SrTiO₃. The results indicated that the combination of thermal and non-thermal effects during the MAH treatment provides ideal conditions for an efficient and rapid synthesis of pristine SrTiO₃ mesocrystals. Scanning electron microscopy images revealed a cube-like morphology (of ca. 1 µm) formed via a self-assembly process, influenced by the MAH time. Additionally, photoluminescence measurements revealed a broad blue emission related to intrinsic defects, which decreased with the MAH synthesis time.

1. Introduction

The processing of ceramic materials with multifunctional properties has been attracting the attention of researchers, aiming to prepare micro/nanostructured inorganic semiconductors through the exploration of a variety of physical and chemical approaches. Despite their capability in obtaining such semiconductors, most of the approaches spend a large amount of energy and require long synthesis times. In this context, the microwave-assisted hydrothermal (MAH) route has been considered a clean, versatile, fast, and highly efficient method to obtain organic and inorganic compounds. Microwave energy has the potential to be ubiquitous and greatly contribute to the synthesis of materials in almost all areas of synthetic chemistry fields, considering that it requires short times and relatively low temperatures (usually <200 °C) in comparison with conventional heating methods. This route also contributes to suppressing side reactions, improving the degree of reproducibility.

In 1990, Komarneni and co-workers investigated the preparation of oxide materials via microwave-assisted treatment. They reported that this methodology improved the crystallization kinetics of various inorganic compounds. In the past few years, there has been increasing interest in improving the MAH route for the synthesis of micro/nanocrystals, since it provides not only a simple and fast way to obtain these materials, but also because its homogeneous heating minimizes thermal gradient effects with the formation of oriented structures with unique or enhanced properties.

De La Hoz and co-workers described that the importance of microwave irradiation during chemical synthesis could be related to thermal and non-thermal effects. According to the authors, the thermal effects are the solution superheating and the presence of hot-spots, while the non-thermal effects are the highly polarized electric field and those related to mobility and diffusion that increase the probabilities of effective contacts.
Motivated by such versatility and efficiency, the MAH method has been used to obtain different micro/nanocrystalline compounds.\textsuperscript{15,14,19,28–30} Strontium titanate (SrTiO\textsubscript{3}) has attracted attention because of its remarkable multifunctional properties.\textsuperscript{31–37} Moniruddin and co-workers demonstrated the potential of pristine SrTiO\textsubscript{3} nanoparticles as catalysts for the production of H\textsubscript{2} gas \textit{via} a water-splitting process.\textsuperscript{35} In the past decade, our research group studied the pristine and doped nanostructured SrTiO\textsubscript{3} applied as photocatalysts and a gas-sensing layer. To do so, different methodologies were used, such as electron beam vapor deposition, the polymeric precursor method, conventional hydrothermal routes and the MAH method.\textsuperscript{24,38–43} Regarding the MAH route, it was successfully used to prepare SrTiO\textsubscript{3} powders, allowing proper control over the crystal shape, photoluminescence properties and assembly process of the nanoparticles by an appropriate choice of titanium precursor as well as synthesis time.\textsuperscript{23,34,27,39}

In one of these previous studies, we demonstrated the relationship between structural properties and photocatalytic activity of SrTiO\textsubscript{3} obtained \textit{via} the MAH route, where we could observe a high disorder degree in the local structure around Ti atoms beyond the presence of some fivefold coordinated Ti atoms, leading to a photocatalytic improvement of the as-obtained samples of pristine SrTiO\textsubscript{3}.\textsuperscript{24} Following this line of research, the aim of this work is threefold: (i) to demonstrate the efficiency and potentiality of the MAH method in obtaining pristine SrTiO\textsubscript{3} crystals; (ii) to show the potential of this route for designing functional materials with superior properties and; (iii) to present and investigate the relationship between microwave-assisted hydrothermal treatment and photoluminescence properties. To achieve these purposes, different techniques such as X-ray diffraction (XRD), X-ray absorption near edge structure (XANES) spectroscopy, X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), photoluminescence (PL) spectroscopy, and field emission scanning electron microscopy (FE-SEM) were employed to characterize the obtained samples.

## 2. Experimental section

### 2.1. Synthesis and characterization of SrTiO\textsubscript{3}

To evaluate the effect of the MAH treatment on the preparation of the SrTiO\textsubscript{3} compound, two reaction mixtures were prepared, as reported in ref. 24. Strontium chloride (SrCl\textsubscript{2}·6H\textsubscript{2}O; 99.9\%) and titanium oxysulfate (TiO\textsubscript{2}SO\textsubscript{4}·xH\textsubscript{2}SO\textsubscript{4}·yH\textsubscript{2}O solution; 99.9\%) reagents purchased from Sigma-Aldrich Corporation were used. First, TiO\textsubscript{2}SO\textsubscript{4} and SrCl\textsubscript{2} (0.01 M, Sr:Ti = 1:1) were added to 50 mL of deionized water, followed by another 50 mL of 6 M KOH solution under constant stirring for 30 min. Afterwards, the reaction mixture was washed with deionized water and isopropyl alcohol, and then dried for 12 h at 80 °C. The obtained sample was labelled as SAM1.

#### 2.1.1. MAH synthesis vs. thermal annealing

In order to demonstrate the efficiency of the MAH synthesis compared to conventional thermal annealing, the sample SAM1 was weighted and then divided into three equal portions. Two portions were annealed in an electric oven under air atmosphere for 2 h, one at 300 °C, and the other at 750 °C, both at a heating rate of 10 °C min\textsuperscript{−1}. The last portion of the sample was maintained as-obtained, \textit{i.e.}, without any treatment.

#### 2.1.2. Longer MAH synthesis time

To study the influence of synthesis time, the precursor solution was heat-treated in the MAH system for 10 min (SAM2), 320 min (SAM3), and 640 min (SAM4). To this end, the reaction mixture was put into a 110 mL Teflon autoclave, which was in turn sealed and placed inside the custom-built microwave-assisted hydrothermal (MAH) system. The solution was then treated at 140 °C with a heating rate of 140 °C min\textsuperscript{−1} under an auto-generated pressure of 3 bar. At the end of the synthesis, the precipitated powder was washed and dried following the same procedure steps mentioned above.

### 2.2. Characterization techniques

The samples were characterized by X-ray diffraction (XRD) at 2θ = 20° to 60° with a step size of 0.02°, at a scanning speed of 2° min\textsuperscript{−1}, using CuK\textsubscript{α} radiation (Rigaku, RotaflexRU200B). The structure was refined using the Rietveld method and the General Structure Analysis System (GSAS) package with the EXPGUI graphical user interface. The average crystallite size was calculated from the full-width at half-maximum (FWHM) of the (110) XRD peak in the Scherrer equation.\textsuperscript{38} The FWHM value of the XRD peak due to instrumental broadening was considered using the Si sample as a reference. X-ray absorption near-edge structure (XANES) measurements were performed at the XAFS2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS). The Ti K-edge XANES spectra were collected in transmission mode at room temperature in the range of 4910 to 5200 eV with an energy step size of 0.3 eV around the edge, following the already reported experimental conditions.\textsuperscript{31,36,44} For the XANES analysis, the background was removed from all the spectra, which were then normalized by first extended X-ray absorption fine structure (EXAFS) oscillation using MAX software.\textsuperscript{45} X-ray photoelectron spectroscopy (XPS) analyses were performed on a ScientaOmicron (model ESCA+) spectrometer using monochromatic AlK\textsubscript{α} (hν = 1486.6 eV) radiation. The binding energies were corrected for charging effects by assigning a value of 284.8 eV to the adventitious C 1s line.

Morphological properties of the samples were characterized using a field emission scanning electron microscope (FE-SEM, Zeiss Supra35) operated at 5 kV in different magnifications. Room-temperature photoluminescence (PL) spectra were collected using a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier linked with a data acquisition system consisting of an SR-530 lock. All the samples were excited by 350 nm wavelength light from a krypton ion laser (Coherent Innova) and the nominal output power of the laser was kept at 200 mW.

Electron paramagnetic resonance (EPR) measurements of pristine SrTiO\textsubscript{3} samples were collected using a Bruker Elexys line model E-580 X-band spectrometer. The microwave frequency used was 9.5 GHz with a power of 8.025 mW. Measurements were taken at a temperature of 10 K with a magnetic field ranging from 500 to 4500 G.
3. Results and discussion

3.1. The efficiency of the MAH approach

XRD patterns of the samples SAM1 (before MAH treatment) and SAM2 (after MAH treatment) are shown in Fig. 1. The XRD pattern of SAM1 can be indexed to various crystalline phases identified as: SrTiO3 (JCPDS file 35-0734), SrSO4 (JCPDS file 05-0593), SrCl2·6H2O (JCPDS file 06-0073), SrCO3 (JCPDS file 05-0418) and K2Ti6O13 phase (JCPDS file 74-0275). In contrast, the XRD pattern of SAM2 reveals that when submitted to MAH treatment, it exhibits only reflections assigned to cubic perovskite SrTiO3 phase.14,46

Before MAH treatment, the reactants were mixed under alkaline conditions at room temperature to form the aforementioned crystalline phases, SrSO4 being the major phase found. This may be associated with the low solubility of SrSO4 under alkaline (Ksp = 3.8 × 10^-7) conditions.46 Nevertheless, when the reaction mixture undergoes MAH treatment, the pristine SrTiO3 phase can be obtained, as seen in Fig. 1. Some researchers described that the hydrothermal route, especially the microwave-assisted one, enhances the solubility and mobility of the ionic species as a result of water viscosity and polarization reductions related to the electric field component of the electromagnetic wave.14,46 Therefore, such a treatment is capable of solubilizing SrSO4, thus providing Sr(s) ions to react with Ti species, consequently forming pristine SrTiO3.

To confirm the efficiency of the MAH method to obtain the SrTiO3 pristine compound, the as-obtained sample SAM1 was annealed in an electric oven for 2 h at 300 °C, and 750 °C. The XRD patterns of the samples after thermal annealing are shown in Fig. 2. All the samples presented a mixture of crystalline phases. It is interesting to note that independent of the annealing temperature (in the range here investigated), the conventional heating was ineffective in providing the necessary conditions to obtain the pristine SrTiO3. Therefore, the presented results confirm the efficiency of the MAH method in synthesizing a pure SrTiO3 compound in a shorter time and at a lower temperature.

3.2. The influence of longer MAH synthesis time

To obtain further details on the processing of the SrTiO3 compound using the MAH method, we studied the influence of longer MAH synthesis time on the local structure around the Ti atoms, on the surface electronic structure, and on the PL emission of the compound. For this purpose, the reaction mixtures were treated in the MAH system at 140 °C for 10 min (SAM2), 320 min (SAM3) and 640 min (SAM4), where the synthesis parameters, such as pressure, heating rate and precursors and their concentrations, were kept constant. Fig. S1 and S2 (ESI†) shows the XRD patterns of samples SAM2, SAM3 and SAM4, all reflections being indexed to the cubic perovskite structure of the SrTiO3 phase (JCPDS file 35-0734) without any spurious phase.

The influence of MAH time on the crystallite size and the lattice parameter are presented in Table 1. A reduction of both structural parameters with MAH treatment time can be observed. The behavior can be attributed to the larger amount of energy provided during the MAH treatment, which corroborates to reduce the defects in the SrTiO3 network. Note that the literature reports an a0 value of approximately 3.905 Å.23,37

Fig. 3 shows the Ti K-edge XANES spectra of the samples SAM1, SAM2, SAM3 and SAM4 and the spectrum of the crystalline SrTiO3 (used as a reference compound) prepared via the polymeric precursor method, here designated as c-SrTiO3.38,42 The spectra revealed four pre-edge transitions, labeled as P1, P2, P3 and P4, as seen in the inset of Fig. 3. The physical origin of these electronic transitions is described elsewhere.24,36,42

First, it can be seen that the spectra of the samples synthesized via the MAH route (SAM2, SAM3 and SAM4) are quite similar to the c-SrTiO3 spectrum, which in turn is different from the SAM1 spectrum. Such results confirm that samples obtained

![Table 1](image)
via the MAH route have a structure similar to the c-SrTiO$_3$ reference at short-and medium-range order around Ti atoms.

Regarding the influence of MAH synthesis time, the analysis of the pre-edge region shows that the intensity of peak P2 is higher for samples obtained via the MAH method (SAM2, SAM3 and SAM4) than for c-SrTiO$_3$. Our research group has extensively investigated the local structure of ATiO$_3$ (A = Sr, Ba, Pb, or Ca) compounds using XAS spectroscopy. These investigations reveal that the intensity of the peak P2 is directly related to the local symmetry of Ti cations. Indeed, such an electronic transition is related to e$_g$ orbitals, linked to Ti-O bonding, being sensitive to symmetry variations in the Ti environment. Thus, the pre-edge region spectrum of c-SrTiO$_3$ (inset of Fig. 3) is typical of titanates, where it is possible to find Ti cations coordinated by six oxygen anions, i.e., formed by TiO$_6$ clusters. In contrast, it can be noticed that the peak P2 is more intense in SAM2, SAM3 and SAM4 than in c-SrTiO$_3$, suggesting the existence of a mixture of TiO$_5$/TiO$_6$ clusters in samples obtained via the MAH route, as illustrated in Fig. 3.

It is important to note that although XRD results have confirmed a perfect long-range order for SrTiO$_3$ samples prepared via the MAH route, the XANES spectra indicate a local disorder structure in the environment around Ti cations, which is not affected by the synthesis time. The MAH system allows high reaction rates that favored here a fast crystallization of the SrTiO$_3$ phase. Despite exhibiting high order at long-range, this structure also presents a disorder in the local environment around Ti atoms.

The morphology of the as-obtained samples was studied via FE-SEM images. Fig. 4(a and b) show that SAM1 (without MAH treatment) consists of a non-homogeneous agglomeration of particles. These results are expected, since this sample contains different crystalline structures observed by XRD and XANES analyses. Fig. 4(c–f) reveal the formation of cube-like superstructures (or mesocrystals) as a consequence of the assembly of smaller cubes induced by MAH treatment. In this way, even with a longer MAH time, such as 320 min, the as-observed morphology remains similar. Nevertheless, for samples treated during 640 min (SAM4), the cubes became more homogeneous and well-defined exhibiting less assembled smaller cubes, as evidenced in Fig. 4(g and h).

It is known that the synthesis method plays an important role in order to obtain SrTiO$_3$ micro/nanostructures with different morphologies. Our research group reported that the mediation of this process occurs due to the presence of OH groups adsorbed on the nanocrystals, leading to the formation of a specific configuration in which such crystals organize themselves into desired patterns through an oriented attachment (OA) mechanism, which could produce a defective single crystal with a spherical or cubic shape. The presence of OH species on the sample surface was revealed by FTIR spectra, as displayed in Fig. S3 (ESI†).

Fig. 5(a) shows the XPS survey spectra of the representative samples SAM2 and SAM4 and the c-SrTiO$_3$ reference. The peaks in these spectra were indexed, revealing the presence of the elements Sr, Ti, O and C. Beyond the peaks previously observed in the SAM4 XPS spectrum, it is also possible to identify a small peak assigned to K, a remainder of the mineralizing source.

In the high-resolution Sr 3d XPS spectra shown in Fig. 5(b), it is possible to observe two strong peaks located at 132.6 eV and 134.3 eV, which correspond to Sr(n) species on the surface.
of the samples. The deconvolution of the Ti 2p XPS spectra, Fig. 5(c), reveals two main peaks at 458.3 and 464.0 eV attributed to Ti 2p 3/2 and Ti 2p 1/2 doublet core levels, whose binding energy values were assigned to Ti(IV) species in SrTiO3. The correspondent O 1s high-resolution spectra of SAM2 and SAM4 samples and that of the c-SrTiO3 reference compound were deconvoluted into three components, as illustrated in Fig. 5(d). The standard deviation value of the peak area was ca. ±1.5%. The spectra exhibited similar characteristics, with the peak at around 529 eV corresponding to the oxygen lattice at the SrTiO3 network. The second component located at approximately 531 eV was attributed to O2− and O0 ions in the oxygen-deficient regions caused by oxygen vacancies. Tan and co-workers investigated the surface properties of SrTiO3 nanocrystals applied as photocatalysts. The peak at around 532 eV was attributed to oxygen adsorbed to the sample surface. As seen in Fig. 5(d), the peak area attributed to oxygen vacancies is higher in the samples obtained via the MAH route when compared to the reference compound (c-SrTiO3), indicating the presence of a higher concentration of surface oxygen vacancies in these samples. Furthermore, it can be observed that the increase in the MAH time led to a decrease in this peak area, suggesting a reduction of the oxygen vacancies on the sample surface.

Fig. 6 shows the PL emission spectra of the samples SAM2, SAM3 and SAM4 and the c-SrTiO3 reference. All the spectra exhibit a broad-band emission centered at ca. 470 nm (2.64 eV). The broad blue emission band is typical of compounds exhibiting intermediate electronic levels within the band gap where the relaxation process occurs along several paths, either involving additional levels located at the top of the O 2p valence band and lower conduction band 3d orbitals of Ti23,31,38,62–65. Fig. 6 reveals a decrease in the PL intensity with MAH time, reaching a similar shape (intensity and profile) to the c-SrTiO3 spectrum. As suggested by XPS results related to O vacancies, this behavior confirms that longer MAH times favor a reduction in the concentration of intrinsic defects created during the rapid crystallization process of the SrTiO3 phase via the MAH method, which are probably oxygen vacancies. All these features show that the structural quality can be improved by increasing the reaction time, attaining the purpose of this work.

The presence of oxygen vacancies, previously mentioned, was confirmed by using the electron paramagnetic resonance (EPR) technique. The EPR signal can be assigned to the paramagnetic oxygen vacancies, which allows the formation of intermediary energy levels in the SrTiO3 band gap, and consequently leads to broad PL emission presented in Fig. 6. Fig. 7 shows the electron paramagnetic resonance (EPR) spectra of samples SAM2, SAM3 and SAM4. The spectra present two EPR signals: the first one is located at ca. 3381.5 G, corresponding to the EPR g1 = 1.932 signal, while the second one is located at 3421.6 G, corresponding to the EPR g2 = 1.910 signal. Regarding their amplitudes, the EPR g1 signal presented values of approximately 0.1458, 0.2195 and 0.2435 for SAM2, SAM3, and SAM4, respectively. On the other hand, the EPR g2 signal values were of ca. 0.1870, 0.3057, and 0.1429 for SAM2, SAM3, and SAM4. Note that the behaviour of each center as a function of MAH time is quite different: intensity for g1 enhances with MAH time, and that of g2 exhibited a maximum for the
SAM3 sample. Based on these findings, it can be attributed that the competition of such centers (relative concentration) led to the reduction in PL emission intensity in the visible region (Fig. 6), and the maximum signal of $g_2$ can be assigned to the PL emission peak at ca. 440 nm for SAM3. In fact, the $g_2$ signal can be assigned to the peak at approximately 440 nm, and the $g_2$ to another one at approximately 510 nm. The sum of both emission bands shows a maximum around 470 nm for the SAM2 sample.

4. Conclusions

The main conclusions of the present work can be summarized as follows. (i) The results point out the capability of the MAH method in preparing pristine SrTiO$_3$ powders in a short time and at a relatively lower temperature. (ii) The combination of thermal and non-thermal effects present during MAH treatment provides ideal conditions for obtaining a pristine SrTiO$_3$ phase. (iii) The MAH method is not simply used to reduce the reaction time and temperature but also to suppress side reactions, improving the reproducibility. The results obtained by XRD, XANES and XPS techniques confirmed that this treatment is effective in eliminating spurious phases, unlike conventional annealing performed in an electric oven. (iv) FE-SEM images reveal that the crystal growth process along the MAH route occurs via an assembly process, forming crystalline SrTiO$_3$ powders with cube-like morphologies. XPS, EPR and PL results indicated that the increase in the treatment time contributes to a decrease in the defects found in the SrTiO$_3$ structure with concomitant enhancement of crystallization in the MAH route. (v) Finally, the present results go beyond the specific SrTiO$_3$ compound and can be extended to many ternary and more complex perovskite based oxides.

Author contributions

All authors have given the approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank Mr. Rorivaldo Camargo for operating the FE-SEM microscope and Prof. Otaciro R. Nascimento (IFSC/USP) for the EPR measurements. This research was partially performed at the Brazilian Laboratory of Synchrotron Radiation (LNLS; Project XAFS-20180311) and the Brazilian Nanotechnology National Laboratory (LNNano; Project XPS-22956), both in Campinas, SP, Brazil. The authors are also grateful for the financial support from the Brazilian research funding institutions CAPES (finance code 88887.197794/2018-00 and 001), CNPq (grant no. 442076/2014-2, 311463/2017-7 and 405140/2018-5), FAPEG and FAPESP (grant no. 2013/07296-2; 2017/12437-5). Prof. Juan Andrés acknowledges the financial support of the Universitat Jaume I (project UJI2016-25), the Generalitat Valenciana (project Prometeoi/2014/022, ACOMP/2014/270, and ACOMP/2015/1202), and the Ministerio de Economia y Competitividad, Spain, (Project CTQ2015-65207-P).

Notes and references

1. A. S. Bhatta, R. Guo and R. Roy, The perovskite structure - a review of its role in ceramic science and technology, Mater. Res. Innovations, 2000, 4, 3–26.
2. S. Komarneni, R. Roy and Q. H. Li, Microwave-hydrothermal synthesis of ceramic powders, Mater. Res. Bull., 1992, 27, 1393–1405.
3. H. Y. Hwang, Perovskites: Oxygen vacancies shine blue, Nat. Mater., 2005, 4, 803–804.
4. H.-J. Kim and J.-H. Lee, Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview, Sens. Actuators, B, 2014, 192, 607–627.
5. G. Zhang, G. Liu, L. Wang and J. T. S. Irvine, Inorganic perovskite photocatalysts for solar energy utilization, Chem. Soc. Rev., 2016, 45, 5951–5984.
6. L. F. da Silva, A. C. Catto, W. Avansi Jr., L. S. Cavalcante, V. R. Mastelaro, J. Andrés, K. Aguir and E. Longo, Acetone gas sensor based on α-Ag$_2$WO$_4$ nanorods obtained via a microwave-assisted hydrothermal route, J. Alloys Compd., 2016, 683, 186–190.
7. L. F. da Silva, A. C. Catto, W. Avansi Jr., L. S. Cavalcante, J. Andrés, K. Aguir, V. R. Mastelaro and E. Longo, A novel ozone gas sensor based on one-dimensional (1D) α-Ag$_2$WO$_4$ nanostructures, Nanoscale, 2014, 6, 4058–4062.
8. A. C. Catto, L. F. da Silva, M. I. B. Bernardi, S. Bernardini, K. Aguir, E. Longo and V. R. Mastelaro, Local Structure and Surface Properties of Co$_x$Zn$_{1-x}$O Thin Films for Ozone Gas Sensing, ACS Appl. Mater. Interfaces, 2016, 8, 26066–26072.
9. L. F. da Silva, W. Avansi Jr., A. C. Catto, J. E. S. Rodrigues, M. I. B. Bernardi and V. R. Mastelaro, The Role of Nb Addition in TiO$_2$ Nanoparticles: Phase Transition and Photocatalytic Properties, Phys. Status Solidi A, 2018, 125, 1800321.
10. D. Segal, Chemical synthesis of ceramic materials, 1997, vol. 7, pp. 1297–1305.
11. D. M. G. Leite, L. F. da Silva, A. L. J. Pereira and J. H. Dias da Silva, Nanocrystalline Ga$_1$-$\alpha$Mn$_x$N films grown by reactive sputtering, J. Cryst. Growth, 2006, 294, 309–314.
12. Y.-T. Tseng, J.-C. Lin, Y.-J. Ciou and Y.-R. Hwang, Fabrication of a Novel Microsensor Consisting of Electrodeposited ZnO Nanorod-Coated Crossed Cu Micropillars and the Effects of Nanorod Coating Morphology on the Gas Sensing, ACS Appl. Mater. Interfaces, 2014, 6, 11424–11438.
13. M. Baghbanzadeh, L. Carbone, P. D. Cozzoli and C. O. Kappe, Microwave-Assisted Synthesis of Colloidal Inorganic Nanocrystals, Angew. Chem., Int. Ed., 2011, 50, 11312–11359.
14. I. Bilecka and M. Niederberger, Microwave chemistry for inorganic nanomaterials synthesis, Nanoscale, 2010, 2, 1358–1374.
15. A. Goktaş, A. Tumbul and F. Aslan, Grain size-induced structural, magnetic and magnetoresistance properties of Nd$_{0.65}$Ca$_{0.33}$MnO$_3$ nanocrystalline thin films, *J. Sol-Gel Sci. Technol.*, 2016, **78**, 262–269.

16. Y.-H. Huang, Z.-G. Xu, C.-H. Yan, Z.-M. Wang, T. Zhu, C.-S. Liao, S. Gao and G.-X. Xu, Soft chemical synthesis and transport properties of La$_{0.8}$Sr$_{0.2}$MnO$_3$ granular perovskites, *Solid State Commun.*, 2000, **114**, 43–47.

17. A. Goktas, A. Tumbul and F. Aslan, A new approach to growth of chemically depositable different ZnS nanostructures, *J. Sol-Gel Sci. Technol.*, 2019, **90**, 487–497.

18. K. J. Rao, B. Vaidhyanathan and M. Ganguli, and P. a. Ramakrishnan, Synthesis of Inorganic Solids Using Microwaves, *Chem. Mater.*, 1999, **11**, 882–895.

19. A. de la Hoz, A. Diaze-Ortiz and A. Moreno, Microwaves in organic synthesis. Thermal and non-thermal microwave effects, *Chem. Soc. Rev.*, 2005, **34**, 164–178.

20. W. Shi, S. Song and H. Zhang, Hydrothermal synthetic strategies of inorganic semiconducting nanostructures, *Chem. Soc. Rev.*, 2013, **42**, 5714–5743.

21. Y.-J. Zhu and F. Chen, Microwave-Assisted Preparation of Inorganic Nanostructures in Liquid Phase, *Chem. Rev.*, 2014, **114**, 6462–6555.

22. A. L. J. Pereira, L. Gracia, A. Beltrán, P. N. Lisboa-Filho, J. H. D. da Silva and J. Andrés, Structural and Electronic Effects of Incorporating Mn in TiO$_2$ Films Grown by Sputtering: Anatase versus Rutile, *J. Phys. Chem. C.*, 2012, **116**, 8753–8762.

23. M. L. Moreira, V. M. Longo, W. Avansi, M. M. Ferrer, J. Andrés, V. R. Mastelaro, J. A. Varela and É. Longo, Quantum Mechanics Insight into the Microwave Nucleation of SrTiO$_3$ Nanospheres, *J. Phys. Chem. C.*, 2012, **116**, 24792–24808.

24. L. F. da Silva, W. Avansi Jr, J. Andrés, C. Ribeiro, M. L. Moreira, E. Longo and V. R. Mastelaro, Long-range and short-range structures of cube-like shape SrTiO$_3$ powders: microwave-assisted hydrothermal synthesis and photocatalytic activity, *Phys. Chem. Chem. Phys.*, 2013, **15**, 12386–12393.

25. M. L. Moreira, G. P. Mambrini, D. P. Volanti, E. R. Leite, M. O. Orlandi, P. S. Pizani, V. R. Mastelaro, C. O. Paiva-Santos, E. Longo and J. A. Varela, Hydrothermal Microwave: A New Route to Obtain Photoluminescent Crystalline BaTiO$_3$ Nanoparticles, *Chem. Mater.*, 2008, **20**, 5381–5387.

26. J. Sun, W. Wang and Q. Yue, Review on Microwave-Matter Interaction Fundamentals and Efficient Microwave-Associated Heating Strategies, *Materials*, 2016, **9**, 231.

27. L. F. da Silva, W. Avansi Jr, M. L. Moreira, A. Mesquita, L. J. Q. Maia, J. Andrés, E. Longo and V. R. Mastelaro, Relationship between Crystal Shape, Photoluminescence, and Local Structure in SrTiO$_3$ Synthesized by Microwave-Assisted Hydrothermal Method, *J. Nanomater.*, 2012, **2012**, 890397.

28. I. Bilecka, L. Luo, I. Djerdi, M. D. Rossell, M. Jagodic, Z. Jaglicic, Y. Masubuchi, S. Kikkawa and M. Niederberger, Microwave-Assisted Nonaqueous Sol–Gel Chemistry for Highly Concentrated ZnO-Based Magnetic Semiconductor Nanocrystals, *J. Phys. Chem. C.*, 2011, **115**, 1484–1495.

29. G. A. Tompsett, W. C. Conner and K. S. Yngvesson, Microwave Synthesis of Nanoporous Materials, *ChemPhysChem*, 2006, **7**, 296–319.

30. M. Godinho, C. Ribeiro, E. Longo and E. R. Leite, Influence of Microwave Heating on the Growth of Gadolinium-Doped Cerium Oxide Nanorods, *Crysr. Growth Des.*, 2008, **8**, 384–386.

31. V. M. Longo, A. T. de Figueiredo, S. de Lazar, M. F. Gurgel, M. G. S. Costa, C. O. Paiva-Santos, J. A. Varela, E. Longo, V. R. Mastelaro, F. S. DE Vicente, A. C. Hernandez and R. W. A. Franco, Structural conditions that leads to photoluminescence emission in SrTiO$_3$: An experimental and theoretical approach, *J. Appl. Phys.*, 2008, **104**, 23515.

32. J. Li, S. Li, F. Liu, M. A. Alim and G. Chen, The origin of varistor property of SrTiO$_3$-based ceramics, *J. Mater. Sci.: Mater. Electron.*, 2003, **14**, 483–486.

33. O. K. Tan, W. Cao, Y. Hu and W. Zhu, Nano-structured oxide semiconductor materials for gas-sensing applications, *Ceram. Int.*, 2004, **30**, 1127–1133.

34. J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy and D. G. Schom, Room-temperature ferroelectricity in strained SrTiO$_3$, *Nature*, 2004, **430**, 758–761.

35. M. Moniruddin, K. Afroz, Y. Shabdian, B. Bizri and N. Nuraje, Hierarchically 3D assembled strontium titanate nanomaterials for water splitting application, *Appl. Surf. Sci.*, 2017, **419**, 886–892.

36. L. F. da Silva, O. F. Lopes, V. R. de Mendonça, K. T. G. Carvalho, E. Longo, C. Ribeiro and V. R. Mastelaro, An Understanding of the Photocatalytic Properties and Pollutant Degradation Mechanism of SrTiO$_3$ Nanoparticles, *Photochem. Photobiol.*, 2016, **92**, 371–378.

37. V. R. Calderone, A. Testino, M. T. Buscaglia, M. Bassoli, C. Bottino, M. Viviani, V. Buscaglia and P. Nanni, Size and Shape Control of SrTiO$_3$ Particles Grown by Epitaxial Self-Assembly, *Chem. Mater.*, 2006, **18**, 1627–1633.

38. L. F. da Silva, L. J. Q. Maia, M. I. B. Bernardi, J. A. Andrés and V. R. Mastelaro, An improved method for preparation of SrTiO$_3$ nanoparticles, *Mater. Chem. Phys.*, 2011, **125**, 168–173.

39. L. F. da Silva, W. Avansi, M. L. Moreira, J. Andrés, E. Longo and V. R. Mastelaro, Novel Sr$_{1-x}$Fe$_x$O$_3$ nanocubes synthesized by microwave-assisted hydrothermal method, *CrystEngComm*, 2012, **14**, 4068–4073.

40. L. F. da Silva, M. I. B. Bernardi, L. J. Q. Maia, G. J. M. Frigo and V. R. Mastelaro, Synthesis and thermal decomposition of SrTi$_{1-x}$Fe$_x$O$_3$ (0.0 ≤ x ≤ 0.1) powders obtained by the polymeric precursor method, *J. Therm. Anal. Calorim.*, 2009, **97**, 173–177.

41. L. F. da Silva, V. R. Mastelaro, A. C. Catto, C. A. Escanhoela Jr., S. Bernardini, S. C. Zilii, E. Longo and K. Aguir, Ozone and nitrogen dioxide gas sensor based on a nanostructured Sr$_{0.65}$Fe$_{0.35}$O$_3$ thin film, *J. Alloys Compd.*, 2015, **638**, 374–379.

42. L. F. da Silva, J.-C. M’Peko, J. Andrés, A. Beltrán, L. Gracia, M. I. B. Bernardi, A. Mesquita, E. Antonelli, M. L. Moreira and V. R. Mastelaro, Insight into the Effects of Fe Addition...
A. Michalowicz, J. Moscovici, D. Muller-BouvetDiane and K. Provost, MAX: Multiplatform Applications for XAFS, J. Phys.: Conf. Ser., 2009, 190, 12034.

S. Aydogan, M. Erdemoğlu, A. Aras, G. Ucar and A. Özkan, Dissolution kinetics of celestite (SrSO₄) in HCl solution with BaCl₂, Hydrometallurgy, 2006, 84, 239–246.

A. C. Catto, L. F. da Silva, C. Ribeiro, S. Bernardini, K. Aguir, E. Longo and V. R. Mastelaro, An easy method of preparing ozone gas sensors based on ZnO nanorods, RSC Adv., 2015, 5, 19528–19533.

A. M. Ruiz, G. Dezanneau, J. Arbiol, A. Cornet and J. R. Morante, Insights into the Structural and Chemical Modifications of Nb Additive on TiO₂ Nanoparticles, Chem. Mater., 2004, 16, 862–871.

R. V. Vedrinskii, V. L. Kraizman, A. A. Novakovich, Ph. V. Demekhin and S. V. Urazhdin, Pre-edge fine structure of the 3d atom K x-ray absorption spectra and quantitative atomic structure determinations for ferroelectric perovskite structure crystals, J. Phys.: Condens. Matter, 1998, 10, 9561.

D. Barreca, D. Bekermann, E. Comini, A. Devi, R. A. Fischer, A. Gasparotto, C. Maccato, C. Sada, G. Sberveglieri and E. Tondello, Urchin-like ZnO nanorod arrays for gas sensing applications, CrystEngComm, 2010, 12, 3419–3421.

V. Krayzman, I. Levin, J. C. Woicik, D. Yoder and D. A. Fischer, Effects of local atomic order on the pre-edge structure in the Ti K X-ray absorption spectra of perovskite CaTi₁₋ₓZrₓO₃, Phys. Rev. B: Condens. Matter Mater. Phys., 2006, 74, 224104.

M. Ye, M. Wang, D. Zheng, N. Zhang, C. Lin and Z. Lin, Garden-like perovskite superstructures with enhanced photocatalytic activity, Nanoscale, 2014, 6, 3576–3584.

on the Local Structure and Electronic Properties of SrTiO₃, J. Phys. Chem. C, 2014, 118, 4930–4940.

M. Bender, E. Gagao, K. Natsakou, N. Katsaraki, V. Cimalla, G. Kiriakis, E. Fortunato, P. Nunes, A. Marques and R. Martins, Production and characterization of zinc oxide thin films for room temperature ozone sensing, Thin Solid Films, 2002, 418, 45–50.

M. L. Moreira, E. C. Paris, G. S. do Nascimento, V. M. Longo, J. R. Sambrano, V. R. Mastelaro, M. I. B. Bernardi, J. Andrés, J. A. Varela and E. Longo, Structural and optical properties of CaTiO₃ perovskite-based materials obtained by microwave-assisted hydrothermal synthesis: An experimental and theoretical insight, Acta Mater., 2009, 57, 5174–5185.