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Influence of the Microwaves on the Sol-Gel Syntheses and on the Properties of the Resulting Oxide Nanostructures

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Abstract

Among the chemical methods in the liquid phase, the sol–gel technique is a versatile and efficient method for pure or doped metal oxide films or powders preparation, showing some advantages over other preparation techniques (high homogeneity, the possibility to introducing dopants in large amount, low processing temperature and control over the stoichiometry). Combining the sol–gel (SG) method with the effect of ultrasounds (US) or microwaves (MW) leads to improving the sol–gel procedure. The microwave-assisted sol–gel method is most frequently used for obtaining nanocrystalline, monodispersed oxide nanoparticles, or to transform amorphous gels into well-crystallized nanopowders. Less studied is the influence of the microwaves on the sol–gel reactions in solutions. The benefit of using microwave-assisted sol–gel preparation highly depends on the reagents used and on the composition of the studied systems. In the present chapter, results on the influence of the microwaves on the chemical reactions that take place during the sol–gel synthesis and on the properties of the resulted samples are discussed.

Keywords: sol–gel method, microwaves, reactions in solutions, oxide nanostructures, properties

1. Introduction

Although heavily exploited in recent decades, the domain of oxide nanostructures remains of interest to researchers throughout the world. This is because that the shapes and sizes of oxide nanomaterials greatly influence their properties, which is reflected in their use in the most diverse fields [1, 2]. Oxide nanostructures have applications in catalysis, energy storage, environmental decontamination, microelectronics, medical technology, ceramics, cosmetics, and so on [3–5].

Among the most studied branches of nanostructures are metal oxides, with representatives such as TiO_2 , ZnO , CuO , Fe_3O_4 , WO_3 , Cr_2O_3 , Co_3O_4 [6].

The structure, morphology, and properties of the oxide nanostructures depend significantly on the obtaining method. A large number of available synthesis methods underlies the continuous interest in obtaining oxide nanostructures that can be used successfully in specific areas [1, 7]. However, most of these methods are limited due to the use of toxic reagents, high processing temperatures, high vacuum, expensive equipment, or long reaction times [8, 9].

Although physical methods have the advantage of high reproducibility, chemical methods in the liquid phase are more often used to obtain oxide nanostructures due to their advantages, such as low production temperature, homogeneous mixing of precursors at the molecular scale, design and control of the physico-chemical properties of final products, depending on the precursors, and the experimental conditions used [10, 11].

Among the various chemical procedures, the sol-gel method gained increasing importance in the field of materials science because it is cheap, simple, allows the introduction of dopants in large quantities, ensures high purity, and homogeneity, allows control of size, shape, and size distribution of the obtained nanomaterials [12–14].

Lately, for the preparation of functional nanomaterials, more and more attention is being paid to the use of microwave as the energy source for carrying out a chemical reaction [1, 15]. The microwave (MW) assisted sol-gel method is reported to be a simple, cheap, faster, more energy-saving, and efficient process as compared to conventional heating methods [16–18]. The use of microwaves has received increased attention in the technological field because, among other things, it reduces the reaction time from days to minutes or hours, improves the properties of synthesized nanostructures, and allows obtaining oxide nanocrystalline films on various substrates [8, 19, 20].

The improved properties of the oxide nanostructures obtained by microwaves assisted sol-gel method could be correlated to the influence of the microwaves on the chemical reactions that take place during the sol-gel synthesis, leading to the formation of different molecular species. Results on the influence of the microwaves on the chemical reactions during the sol-gel synthesis will be discussed in the present chapter.

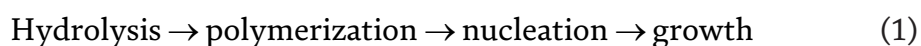
2. General consideration on the sol-gel chemistry

Among the chemical methods in the liquid phase, the sol-gel technique is a versatile and efficient method for pure or doped metal oxide films or powders, as well as for oxide compounds preparation [21–24].

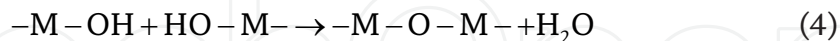
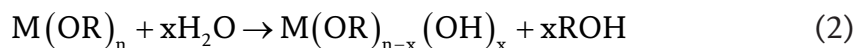
A comprehensive definition of sol-gel method assumes that the process represents the formation of an inorganic polymeric network by reactions in the solution at low temperatures. In the second step, by adequate thermal treatments, the conversion of the inorganic amorphous polymers takes place either into glasses or into crystalline materials [1, 22].

Based on the type of the precursors and the reaction medium used, two types of sol-gel processes were developed: on the bases of the alcoholic (organic) or aqueous medium.

According to Pierre [25] in both polymeric and aqueous sol-gel routes, the precursors undertake the succession of the following transformations in the presence of water:

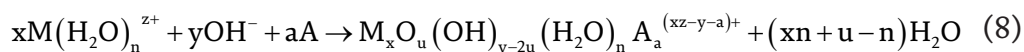
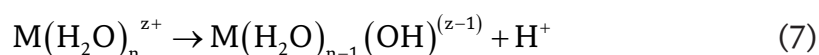
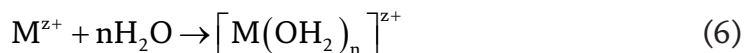


In the case of the **polymeric route**, using alkoxides (non-ionized precursors), the reactions that occur are the following:



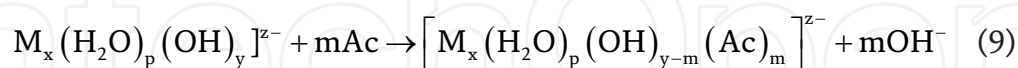
The **aqueous sol-gel route** has also two pathways: the colloidal route [26] and the aqueous route using different chelating agents [23, 26, 27].

In the case of the **aqueous route**, which starts from colloidal solutions in aqueous medium, the following reactions take place:



In the case of transition metals, it is more difficult to obtain gels, the metals having very high reactivity due to their higher electronegativity and their not satisfied coordination sphere.

To favor the gelling process, in case of the transition metals, chelating agents, as carboxylic acids or polyols, are used. A typical reaction is the following



It is important to underline that in all mentioned cases the reactions take place simultaneously, not consequently, and they are also reversible, fact that determines a complex composition of the sol-gel solutions.

Prior to gelation, the sol-gel solution can be used to obtain thin films by using simple techniques such as dip or spin coating [23, 28].

Besides the fact that it offers the possibility of obtaining both films and powders of metal oxides at nanometric dimensions, the sol-gel method has also some advantages over other preparation techniques. Such advantages are purity, homogeneity, the possibility to introducing dopants in large quantities, ease of manufacturing, low processing temperature, control over the stoichiometry, composition, viscosity [13, 27, 29] and, in the case of thin films, easy control of thickness, as well as the ability to cover large and different type of surfaces [30, 31].

Lately, ultrasonic [32, 33] or microwave irradiation [9, 17, 18, 34–36] in sol-gel oxide nanomaterials synthesis have become methods of interest because, in addition

to being cheap and environmentally friendly heating methods, offer the advantage of using shorter synthesis time, and allow the control of crystallinity, size and morphology of the resulted nanoparticles [9, 35].

3. Microwaves and their influence on the chemical reactions

Microwave radiation is a source of energy of great interest for chemical synthesis because, among other benefits, it has been observed that the use of microwaves improves the properties of obtained nanomaterials. The first reporting on the use of microwaves in a chemical synthesis dates back to 1986 [37]. Although initially microwaves have been applied in organic synthesis, lately their use has become quite widespread in obtaining inorganic products like metal oxides nanomaterials and metallic nanomaterials [38].

Microwaves are electromagnetic radiations located between infrared radiation and radio waves with frequencies between 300 MHz (100 cm) and 300 GHz (0.1 cm). For the nanomaterials synthesis in which aqueous solutions are used, 2.45 GHz frequency is commonly applied for microwave heating of the solutions, because water absorption is maximum at this value.

Subjected to a microwave field, the substances behave differently: absorb, transmit, reflect received radiation, or any combination of these three interactions. Polar substances absorb microwaves radiation, non-polar substances are transparent environments for this type of radiation, and electrical conductors reflect microwaves radiation. Therefore, microwave heating process is used for heating the materials which can absorb the microwave energy and convert it into heat especially by dipolar polarization or conduction mechanism [1, 39]. The interactions of polar molecules and ions with the electromagnetic field have already been described by many researchers. Shortly, the collisions resulting from the rotation of the dipoles during polarization and the load carriers during conduction give energy to the atoms and molecules from the solution in the form of heat [38, 39].

While conventional heating methods are slow enough and the heat transfer from the surface to the inner material or solution, producing non-homogeneous heating, microwave heating is done quickly because microwaves can penetrate the materials to a depth that depends on the dielectric properties of the material, heating them homogeneously [38]. Consequently, microwave heating can have certain benefits over conventional heating, like faster reaction, higher reproducibility, enhancement of product quality. It is instantaneous, with no heat dissipation effects, and advantageous for selective dielectric heating, as a result of the dielectric constant difference between the solvent and reactant [40].

In sol-gel synthesis, due to rapid and direct heating of the sample with microwave radiation, the instantaneous decomposition of the precursors and the obtaining of a supersaturated solution occur. In this way, the conditions for obtaining monodispersed nanoparticles (rapid and short nucleation in a supersaturated solution) can be obtained experimentally. At the same time, the *in-situ* approach of conversion of energy results in a minimized thermal gradient due to the fast heating rate consequently is providing perfect conditions for the uniform growth of nanocrystals [31, 41].

More, in the case of sol-gel synthesis using organic solvents, characterized by slow kinetics, microwave heating is an optimal method of increasing the rate of reaction [41].

From the research carried out so far, it has been observed that, by combining the sol-gel method with the microwave heating, the properties of the obtained oxide nanostructures are improved [9, 34].

Because the presence of MW, the interaction of the electromagnetic field with each molecule in the solution differs during the hydrolysis-condensation process, we can expect the formation of different molecular species as compared to the classical sol-gel synthesis.

4. Oxide nanostructures obtained by MW assisted sol-gel method

Up to now, there have been several reports regarding the synthesis of metal oxide nanomaterials by microwave-assisted sol-gel method. However, many of them have been performed using domestic microwave ovens, in which the reaction conditions cannot be accurately measured, making the experiments difficult to be reproduced.

According to the literature data, the MW irradiation in the sol-gel synthesis was used, most frequently, for precipitation of nanocrystalline metal oxides, for thermal treatment of amorphous oxide nanopowders as well as for drying and thermally treatment of the oxide films [36].

Less attention was given to study the reactions that take place in the sol-gel solutions during MW irradiation [42–45].

4.1 Pure and doped oxide nanostructures

A large number of oxides were prepared by sol-gel and microwave assisted sol-gel methods. Using MW irradiations of the solutions, preparation of several oxides were mentioned in the literature data, as MgO [46], RuO₂ [47], ZnO [16], ZrO₂ [48], WO₃ [49], SiO₂ [50], TiO₂ [35, 51]. The power of the used microwaves ranged from 140 W [51] to 850 W [47].

Among them, considerable interest is given to pure and doped TiO₂. The doping of TiO₂ was realized with a high number of elements, such as Cr [13], Ag [52], Au, Pt [14, 53], Sn-Cu-Ni [54], Fe, Pt, Pd [51] and V [55]. Doping TiO₂ with different elements the properties of the resulted nanostructures are improved, while using microwave assisted preparation, supplementary improvement was also observed.

Our studies regarding the influence of the microwaves on the reactions in the sol-gel solutions were published by Predoana et al. [42] in the case of TiO₂ and V-doped TiO₂ nanostructures.

The use of vanadium as a doping agent has a beneficial influence on the TiO₂ properties: it can reduce the band gap energy, enhance the absorption of visible light and increase the specific surface area of the powder. The mentioned properties are reflected mainly in its photocatalytic activity, previously presented by Huang et al. [55].

In our studies, the reagents used in the synthesis were titanium(IV) ethoxide Ti(OC₂H₅)₄ in the case of TiO₂, as well as, titanium(IV) ethoxide Ti(OC₂H₅)₄ and vanadylacetylacetonate VO(AcAc), for V-doped TiO₂. In both cases, ethanol C₂H₅OH as a solvent, 2,4 pentanedione (AcAc), as a chelating agent, and nitric acid HNO₃ as catalyst were used.

By the classical sol-gel method the reagents were mixed for 2 hours at room temperature. By the microwave-assisted sol-gel method, the same mixture was exposed for 5 min at 300 W and a frequency of 2.45 GHz.

The first important result of using the microwave-assisted sol-gel method is the significantly increasing of the stability of the prepared solutions against gelation, having a great advantage for multilayer film deposition. This effect was assigned to the formation of different molecular species.

The solutions were used for obtaining thin films and the resulted gels were investigated for their structural and morphological properties.

In our studies for **TiO₂ samples** synthesized by sol-gel and microwave-assisted sol-gel methods, the TG/DTG/DTA curves corresponding to the decomposition of the obtained gels are presented in **Figure 1**.

It could be noticed that the thermal decomposition of the gels is not essentially influenced by the method of preparation. Only a small increase of the thermal effect at 195° C is observed for the TiO₂ sample obtained by MW assisted sol-gel method. The fact could be explained by the positive influence of microwaves on the formation of the molecular species that decompose at the mentioned temperature.

Based on the TG/DTG/DTA results, the samples prepared by both methods were thermally treated at 450°C for 1 h. By X-ray diffraction of the samples thermally treated at this temperature only anatase phase was detected (according to

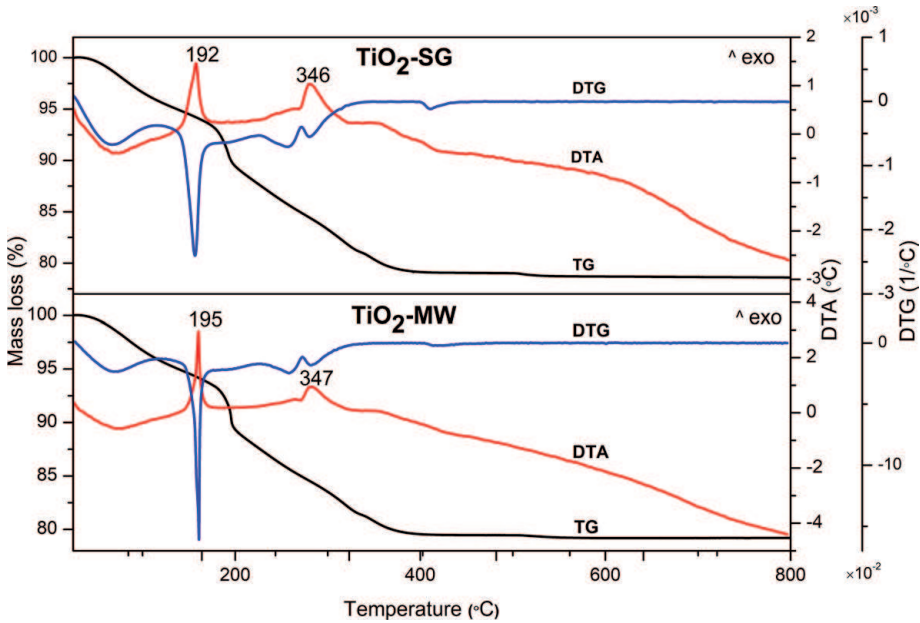


Figure 1. TG/DTG/DTA curves of the TiO₂ samples obtained by SG and MW methods [42] (Reproduced with the permission of Springer Nature).

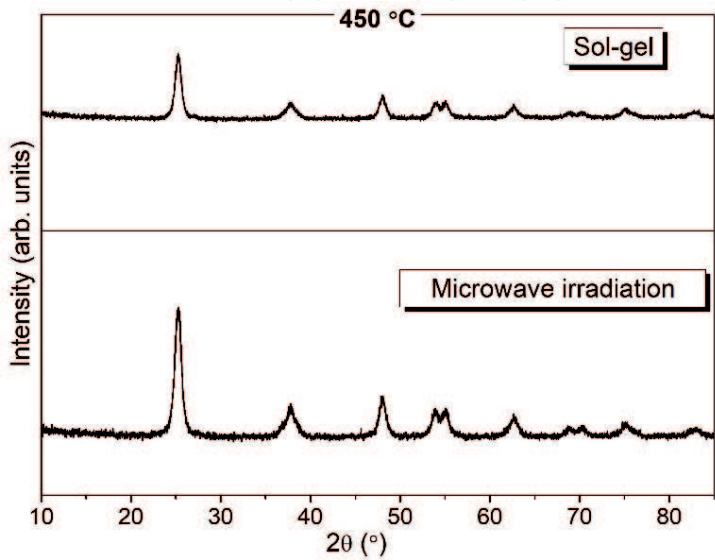


Figure 2. The XRD patterns of the TiO₂ samples obtained by SG and MW-assisted SG methods thermally treated at 450°C.

JCPDS card no. 21-1272), but a higher crystallinity is noticed in the case of sample obtained by MW-assisted procedure (**Figure 2**).

In the case of **the V-doped TiO₂** the TG/DTG/DTA measurements in the air are presented in **Figure 3** for the gel containing 2 mol% V. In this case, increased thermal stability and a more complex decomposition of the gels obtained by the microwave-assisted sol-gel method is observed.

Confirmations of the TG/DTG/DTA results on the gels with 2 mol% V were obtained by Differential Scanning Calorimetry (DSC). The obtained DSC curves are presented in **Figure 4**.

According to the DSC results, the thermal stability of the gel obtained from the solution prepared in the presence of microwaves, is significantly higher (with about 100°C), as compared with the gel with similar compositions, but obtained by the classical sol-gel method.

At the same time, the number and temperatures of the thermal effects are different in the two discussed cases underlying the different compositions of the gels obtained in the presence or the absence of the microwaves.

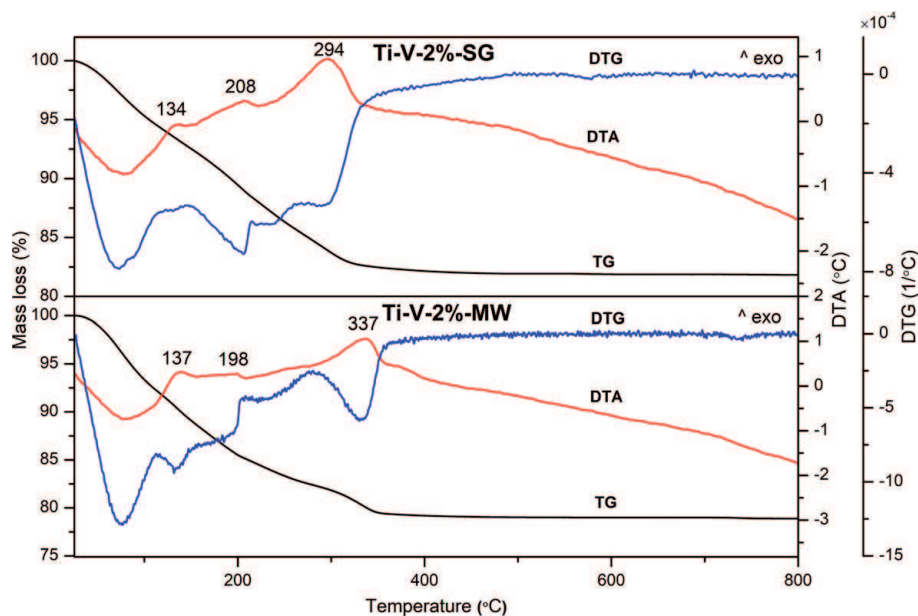


Figure 3. TGA/DTG/DTA curves of the V-doped TiO₂ samples obtained by SG and MW-assisted SG methods [42] (Reproduced with the permission of Springer Nature).

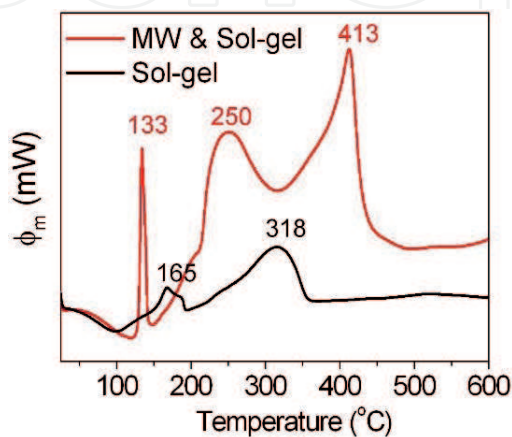


Figure 4. DCS curves of the V-doped TiO₂ obtained by SG and MW-assisted SG methods [43] (Reproduced with the permission from Springer Nature).

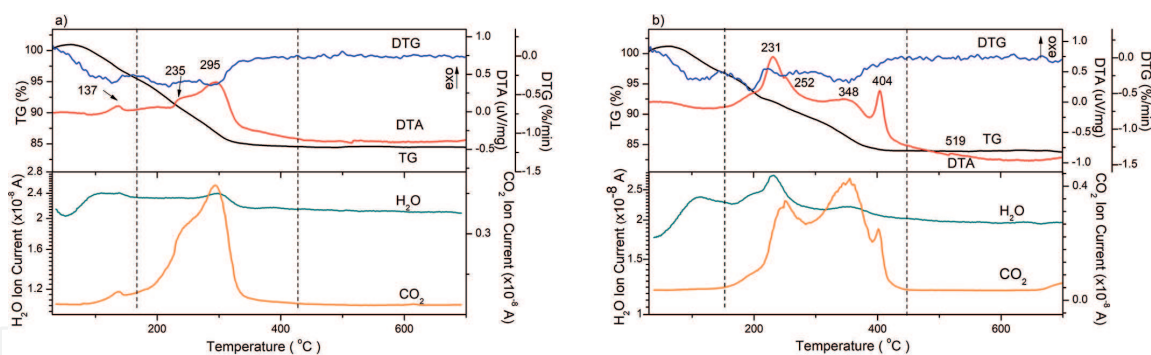


Figure 5. TG/DTG/DTA/EGA curves of V-doped TiO_2 obtained by (a) SG and (b) MW-assisted SG methods [42] (Reproduced with the permission of Springer Nature).

The TG/DTG/DTA/EGA measurements, presented in **Figure 5**, have confirmed, once more, the results discussed above, regarding the different thermal behavior of the gels obtained by the microwave-assisted sol-gel method.

In the case of the microwave-assisted sol-gel method the same gasses are evolved, namely H_2O and CO_2 , but a more complex thermal decomposition is observed, with different ratios among the two mentioned gases at the different temperatures. This result is assigned to the higher number of molecular species present in the gel, having different chemical composition and different thermal stability.

By X-ray diffraction of the V-doped TiO_2 with 2 mol% V samples thermally treated at 450°C (**Figure 6**) only anatase phase was detected (according to JCPDS card no. 21-1272). As in the case of un-doped TiO_2 , a higher crystallinity is noticed in the case of samples obtained by MW assisted procedure.

Before gelation, the solutions prepared in the presence and in the absence of MWs were used for thin film deposition by dip-coating on glass substrates [43].

In our studies for **the TiO_2 films** obtained by the sol-gel method, the SEM micrographs show surface cavities that were not observed in the case of microwave-assisted sol-gel films (**Figure 7a and c**).

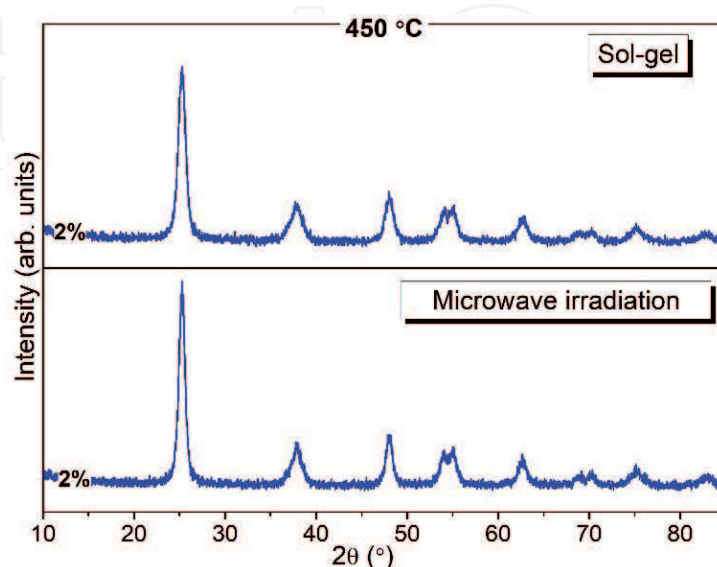


Figure 6. The XRD patterns of the V-doped TiO_2 samples obtained by SG and MW-assisted SG methods, thermally treated at 450°C .

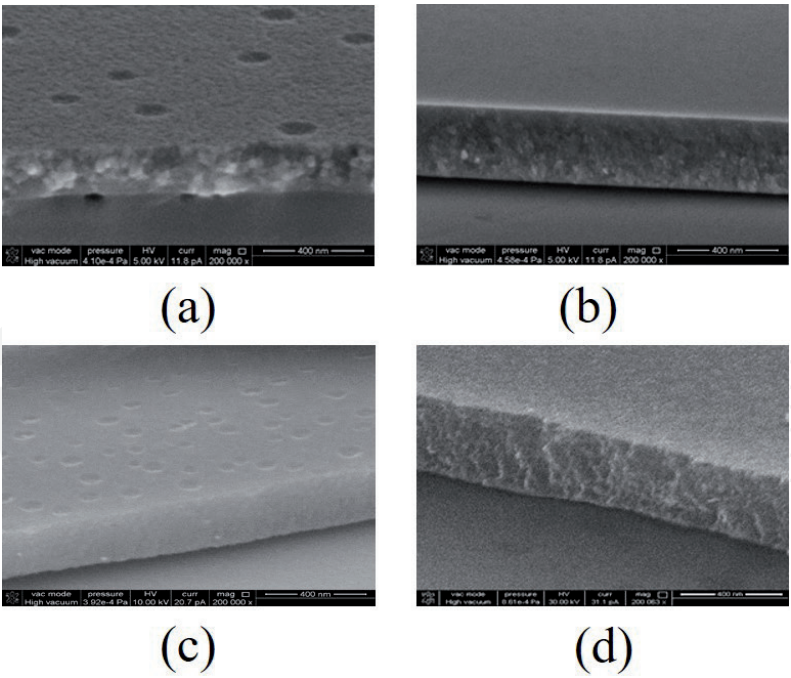


Figure 7.
SEM micrographs showing the film cross-section for samples (a) $(\text{TiO}_2)_{\text{SG}}$; (b) $(\text{TiO}_2)_{\text{MW}}$; (c) $(\text{V-dopedTiO}_2)_{\text{SG}}$; (d) $(\text{V-dopedTiO}_2)_{\text{MW}}$ [43].

The sol-gel TiO_2 based films present also a similar variation of the morphology according to the method of preparation. A more dense and homogeneous aspect is observed in the film obtained in the presence of microwaves (**Figure 7b and d**).

Thickness values are around 200 nm both for TiO_2 and V-doped TiO_2 films, but slightly higher in the case of the films obtained from microwave-assisted sol-gel solutions.

The transmission spectra of obtained films are presented in **Figure 8** show optical transmittance values mainly over 80% in the visible range.

To explain the differences induced by the microwave-assisted sol-gel process on the properties of the resulted films, their influence on the starting solution, and the evolution of the sol-gel process, should be taken into consideration. Based on the results obtained up to now, it could be assumed that in the presence of microwaves, different and more stable molecular species are formed as compared to the classical sol-gel method and this a fact influences the properties of the resulted films.

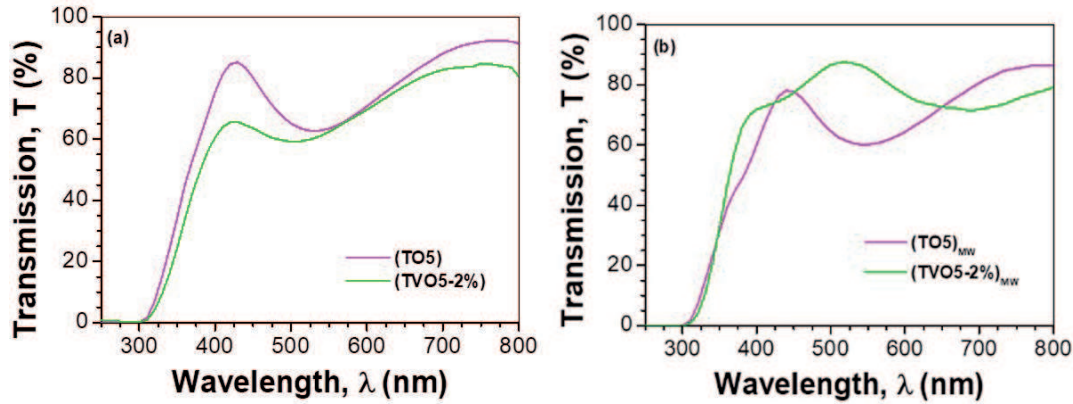


Figure 8.
Optical transmission of the TiO_2 and V-doped TiO_2 films obtained by (a) SG and (b) MW-assisted SG methods.

It was also observed that the effect of microwaves on the properties of the resulted materials is higher in the case of V-doped TiO_2 samples, fact that could be correlated to an enhancement of the reactions between Ti and V reagents during the sol-gel process in the presence of the microwaves.

As presented in the several references, **WO_3 based nanomaterials** are widely investigated in the field of electrochromic devices [56], gas sensing [57], and photocatalysis [58] in different morphologies and structures. Even though the sol-gel process has a long past and is an intensely researched method [59] the literature of sol-gel preparation of WO_3 using microwave-assistance is scarce. The following articles are all from the 2010s so further researches are to be expected.

Different nanostructures were prepared by microwave assisted sol-gel method with sodium tungstate as a precursor material by Kharade et al. [60–62]. The research group synthesizes various nanoparticles and nanofilms for electrochromic purposes. In 2012 WO_3 nanofilms were deposited on the FTO substrate, which was the first time used MW-assisted two-step process. In the first step, the preparation of the gel was conducted with microwave assistance, then in the second step, the deposition of the thin film occurred by a chemical growth set up. Scanning electron microscope (SEM) showed that the surface is coated with petal-like WO_3 nanodisks with dimensions of 450–600 nm length, 350–400 nm width, and 20–35 nm thickness. The X-ray diffraction (XRD) analysis (**Figure 9**) points out that WO_3 is in the hexagonal crystal form. Narrow and intense XRD peaks indicate that the material has good crystallinity and calculations determined that the crystal size is 71 nm, which is comparable to samples made by the regular sol-gel method [63]. X-ray photoelectron spectroscopy (XPS) revealed that the W:O ratio is non-stoichiometric(2.89). Electrochromic capabilities were determined with different electroanalytical methods [60]. Comparing this to a regular sol-gel method shows that the morphology of the surface, namely the platelet like nanodisks is nearly the same with a small difference in size (regular sol-gel platelets: 10–30 nm thick and few hundred nm lengths and width). However, to achieve the same crystallinity a 500°C annealing process is required for the regular sol-gel method, in contrast to the 150°C drying of the MW-assisted sol-gel method [64].

The same hexagonal WO_3 thin film was synthesized and its electrochromic properties were enhanced with different amounts of Ag nanoparticles [61]. The microwave-assisted sol-gel method was also used to produce WO_3/MoO_3 mixed

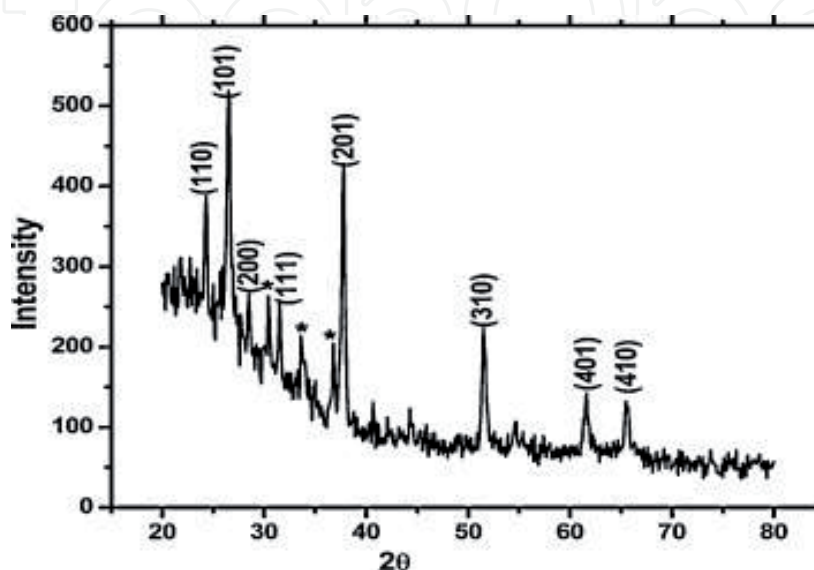


Figure 9.
X-ray diffractogram of the WO_3 thin film [60] (Copyright (2012), with permission from Elsevier).

oxide thin films. First, the WO_3 layer were produced with the two-step method explained earlier, then MoO_3 was deposited with vacuum evaporation [62].

Hilaire et al. [49] prepared WO_3 nanoparticles using a nonaqueous microwave-assisted sol-gel method for photoanodes. The synthesized nanoparticles were analyzed with FT-IR, which showed that no organic contaminant remained on the surface of the particles, but a weight indicates that there are a 4.4% water and organic residue after 800°C heating. XRD studies confirm the monoclinic crystal-line structure of the WO_3 nanoparticles.

Transmission electron microscopy (TEM) showed that the platelets like WO_3 nanoparticles size is 20–40 nm and thickness of 3 nm. Moreover, TEM measurements indicate that the WO_3 platelets face having the crystalline orientation of [0 0 2]. The WO_3 nanoparticles were used for the production of photoanodes, which was proven to be an efficient method for water splitting. The comparison of this result with another nonaqueous regular sol-gel method shows that the morphology of the particles differs, but this can be caused by the usage of a different solvent (dicarboxylic acid) and modifier (polyethylene glycol).

The regular method resulted in larger (58 nm) rod-like nanoparticles. The case of the WO_3 particle's crystallinity is similar to the thin layer's: without after annealing process, the MW assisted method provides better crystallinity [65].

It was also established [66] that microwave heating is more convenient than resistive heating to fabricate WO_3 nanoparticles with high specific surfaces and very small particle sizes also in the case of hydrothermal method of preparation. In our studies [67, 68] hexagonal structured WO_3 nanoparticles and wires were prepared using MW assisted hydrothermal process. SEM images are presented in the **Figure 10**.

The Au decorated h- WO_3 nanowires were prepared for photocatalysis. The pre-decorated WO_3 nanowires showed crystallinity and were composed of W and O only. The morphology also differs from nanodisks, the hydrothermally produced WO_3 took the form of nanorods with 10 μm length and 10 nm diameter.

Nevertheless, the Au decorated nanowires showed great photocatalytic activities. Nanowires and nanoparticles coated with TiO_2 using ALD were also

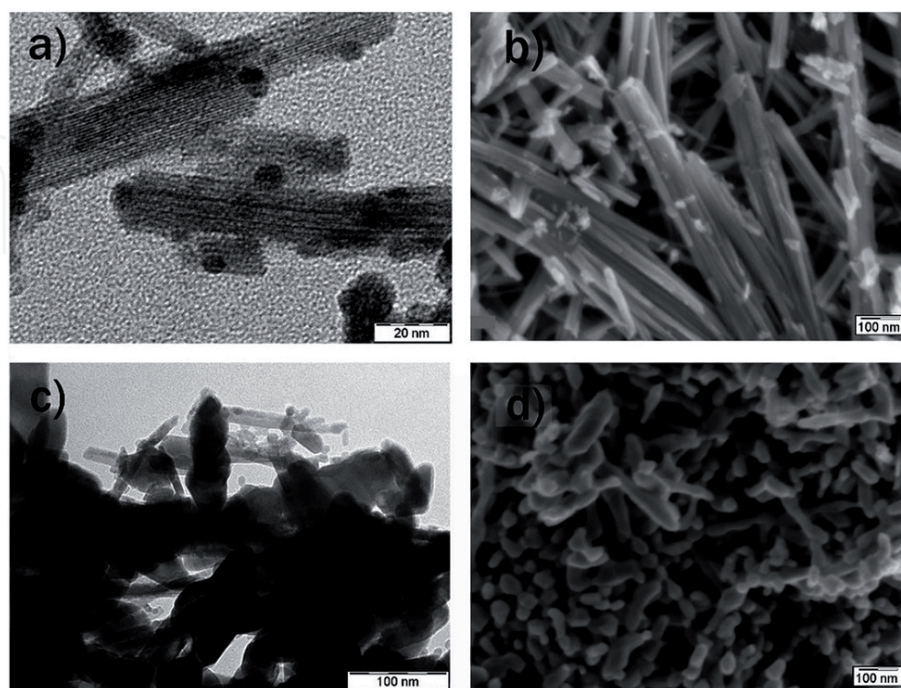


Figure 10.
SEM images of the (a, b) hexagonal WO_3 nanowire coated with TiO_2 and (c, d) monoclinic WO_3 nanoparticle coated with TiO_2 [67] (Reprinted with permission from [67] copyright from RSC Advances).

synthesized, but the characteristics of the non-coated samples were done. Hexagonal and monoclinic nanoparticles were prepared using controlled annealing of the samples.

Similarly, further annealing is needed to reach a comparable crystallinity, but for the monoclinic structure it's obligatory. The size of the crystals was 50–70 nm and 60–90 nm for hexagonal, and for the irregular shaped monoclinic WO_3 nanoparticles respectively. The hexagonal WO_3 nanowires were analogous to the earlier nanowire, several μm long and 5–10 nm diameter. The TiO_2 coated nanostructures proved to be efficient photocatalysts [67, 68].

4.2 Oxide compounds

Let us deal with the results regarding the synthesis by microwave-assisted sol-gel methods of the precursor powders for SrCu_2O_2 preparation.

The interest for the SrCu_2O_2 compound are connected to its possible applications as thermoelectric or full oxide electronic devices, solar cells, liquid-crystal displays, touchscreen, and so on [45].

Among the CuO -based p-type TCOs, Cu-Sr-O has received attention due to its wide direct band gap, and its potential use in transparent optoelectronic devices; such as light-emitting diodes, laser diodes, solar cells, display technology, and other technologies [69]. In most of the published reports, Cu based p-type TCO thin films are deposited by high vacuum processes which are costly. Some of the processes include pulsed laser deposition (PLD), reactive evaporation, magnetron sputtering, thermal co-evaporation and radio frequency [70–76]. To date, few studies have reported on the preparation of a Cu -based p-type TCO by a non-vacuum solution chemical route.

Roy et al. [77] used sol-gel and annealing methods to prepare Cu_2SrO_2 thin films. They used different oxygen pressure, annealing time, and temperature combinations to attempt to obtain phase pure Cu_2SrO_2 thin films. Copper (II) methoxide and triethanolamine were mixed in the ration 1:1. Pure Sr -metal was dissolved separately in distilled anhydrous isopropanol under argon. The Cu -solution was then mixed drop-wise into the Sr -solution while stirring. The mixture was stirred continuously for 2 hrs at room temperature. The sol was spin-coated on clean substrates with 3000 rpm for 30 s. The coated films were heated at 225°C for 2 min in the air for partial pyrolysis. This coating/heating cycle was repeated ten times to obtain films of the desired thickness of 500 nm. After deposition, the film was annealed further under controlled oxygen pressure. Different annealing procedures were used to avoid the presence of excess Cu_2O phase.

XRD analysis (**Figure 11b**) showed the films had a mixed-phase of excess Cu_2O and Cu_2SrO_2 after final reduced-oxygen pressure annealing. Films annealed at lower oxygen pressure (1.3×10^{-2} and 1.3×10^{-3} Pa) had similar phase composition and in all the three films Cu_2O formed as a secondary phase with Cu_2SrO_2 . For the film annealed at the highest oxygen pressure (1.3×10^{-1} Pa), CuSrO_2 was observed as the amount of Cu_2SrO_2 decreased and the intensity of the Cu_2O peaks did not change.

Both SEM and TEM images (**Figure 11a and c**) show that two phases are present. The light-gray particles (differing sizes) in the SEM and large particles in TEM images are the Cu_2SrO_2 phases. The dark gray phase in the SEM image is a mixture of small Cu_2SrO_2 and Cu_2O particles, as confirmed by the TEM images. The SEM and TEM images reveal that the Cu_2O and Cu_2SrO_2 phases are intermingled with each other.

Ginley et al. [78] used sol-gel and annealing to prepare pure phased Cu_2SrO_2 films. Stoichiometric amounts of aqueous solutions copper formate and strontium acetate were mixed in methanol and stirred. Triethanolamine was added, the

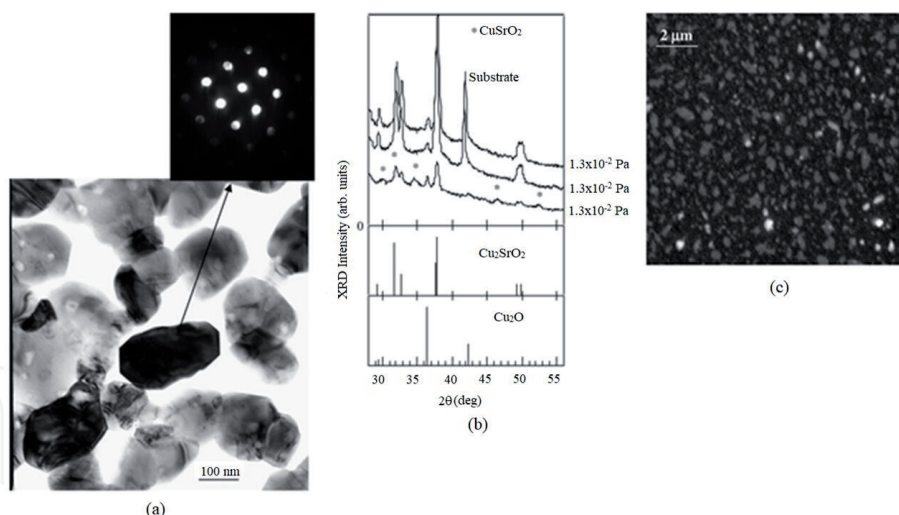


Figure 11.
 (a) TEM image, (b) XRD spectra (c) SEM image of the films after final annealing at 750°C under 1.3×10^{-2} Pa oxygen pressure [77] (Reproduced by the permission of Elsevier).

mixture stirred and evaporated at 80°C to form sol which was diluted by isopropyl alcohol and spin-coated on MgO (100) substrates for 20 s, at 3000 revs per min. The resulting films were annealed at 200°C temperature for 2 min and then pyrolyzed at 500°C for 2 min. The spin-coating and pyrolysis cycles were repeated 8–10 times. After the cycles, the films were first annealed at 750°C for 30 min in air and then at 775°C under 2.7×10^{-6} Torr oxygen. The films were characterized by XRD (Figure 12) and FTIR and showed to be phase pure.

Predoana et al., are the first to report the synthesis of Sr-Cu-O gels by microwave (MW) assisted sol-gel methods [45]. Pure strontium acetyl acetonate ($\text{Sr}(\text{C}_5\text{H}_7\text{O}_2)_2$) and copper (II) acetyl acetonate ($\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$) were used as precursors for strontium and copper, respectively. The 0.25 M aqueous solutions of $\text{Sr}(\text{C}_5\text{H}_7\text{O}_2)_2$ and $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ solution in absolute ethanol were mixed with triethanolamine, in the ratio 1:1. In the case of the sol-gel method, the starting solution was homogenized under vigorous stirring for 2 h at 80 C. For MW assisted sol-gel method, the same starting solution was homogenized by stirring and exposing to microwaves having power ~ 300 W and 2.45 GHz frequency for 5 minutes. The sol-gel and the microwave-assisted sol-gel prepared Sr-Cu-O were characterized by SEM, FTIR, XRD, and their thermal properties investigated by TG/DTA-MS in air, inert and reducing atmospheres.

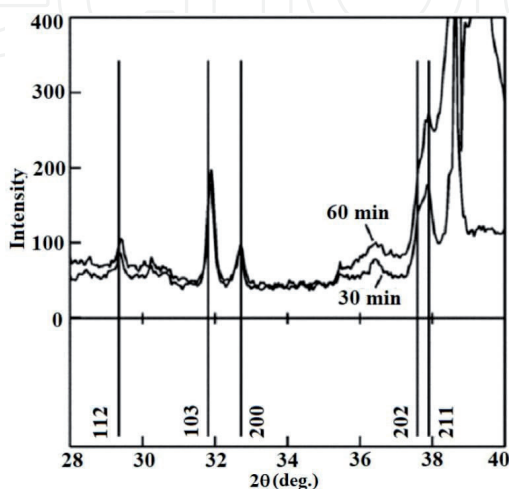


Figure 12.
 XRD patterns of Cu_2SrO_2 films as a function of processing time [78].

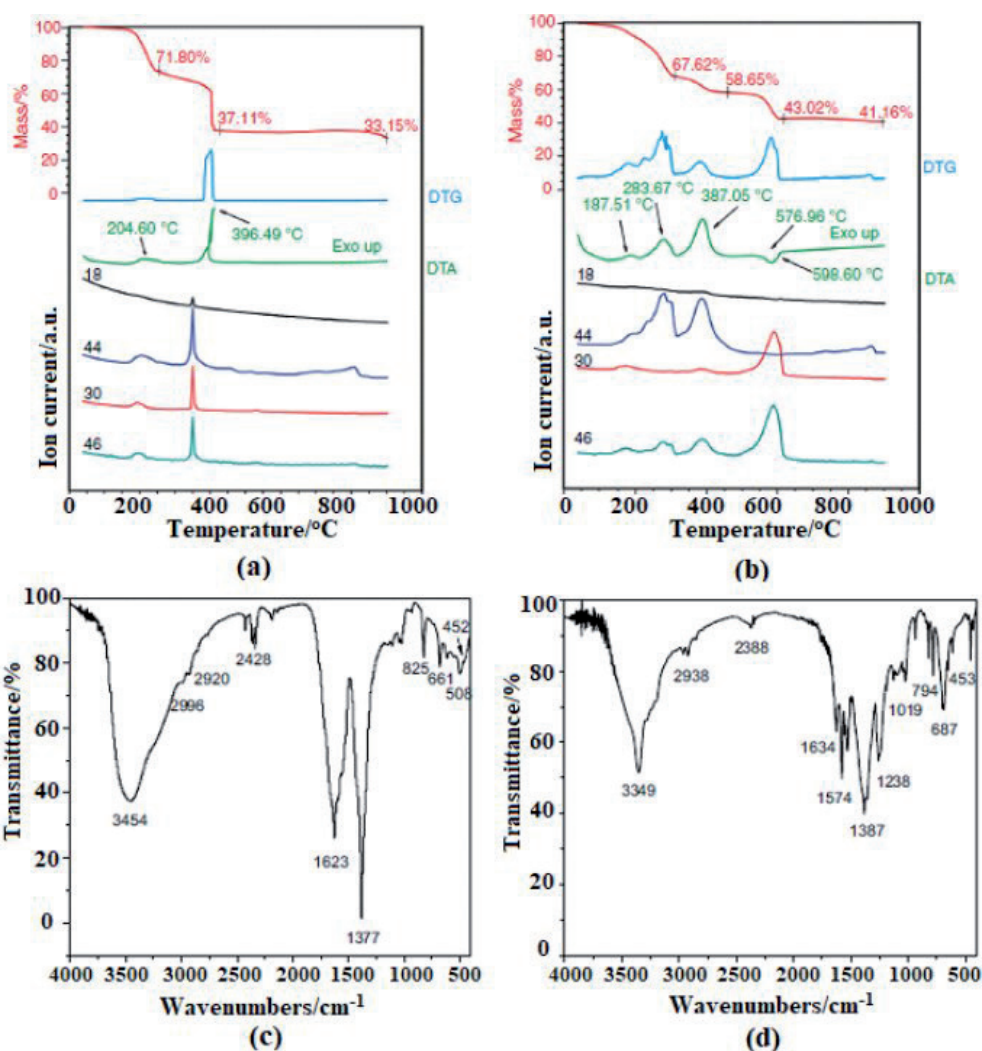


Figure 13.

Thermal decomposition in air (a) sol-gel synthesized sample, (b) MW assisted sol-gel synthesized sample, (c) FTIR spectra of sol-gel synthesized sample, (d) FTIR spectra of MW assisted sol-gel synthesized sample [45] (Reproduced by the permission of Elsevier).

In the experimental conditions presented above pieces of gels of different size, and blueish-green color were obtained for both preparation methods. The results obtained by TG/DTA-MS analysis (**Figure 13a** and **b**) of the obtained gels demonstrated the influence of MW on the sol-gel synthesis. MW treated samples had one more mass loss step when heated in air attributed to complex compositions of the resulted gels that contain a higher number of molecular species with higher thermal stability. The results were confirmed with the FTIR spectra (**Figure 13c** and **d**) showing more vibration bands for the samples prepared by the MW sol-gel method, assigned according to [79–81].

Based on the XRD patterns of the residues (**Figure 14**), the final product is composed of a mixture of phases that depend on the synthesis route and the annealing conditions.

For samples annealed in air, Sr–Cu–O phase was also present for the sol-gel synthesized sample, while the MW sample had CuO as the main component. In different atmosphere (N₂ and H₂/Ar) several compounds (Sr₂CuO₃, SrO and CuO) are present in varying amounts. Only traces of SrCO₃ can be detected. In all annealing atmospheres, in the case of the samples synthesized by MW-assisted sol-gel method, powders with a lower degree of crystallization is formed. This result could be attributed to the formation of a higher number of molecular species with higher thermal stability.

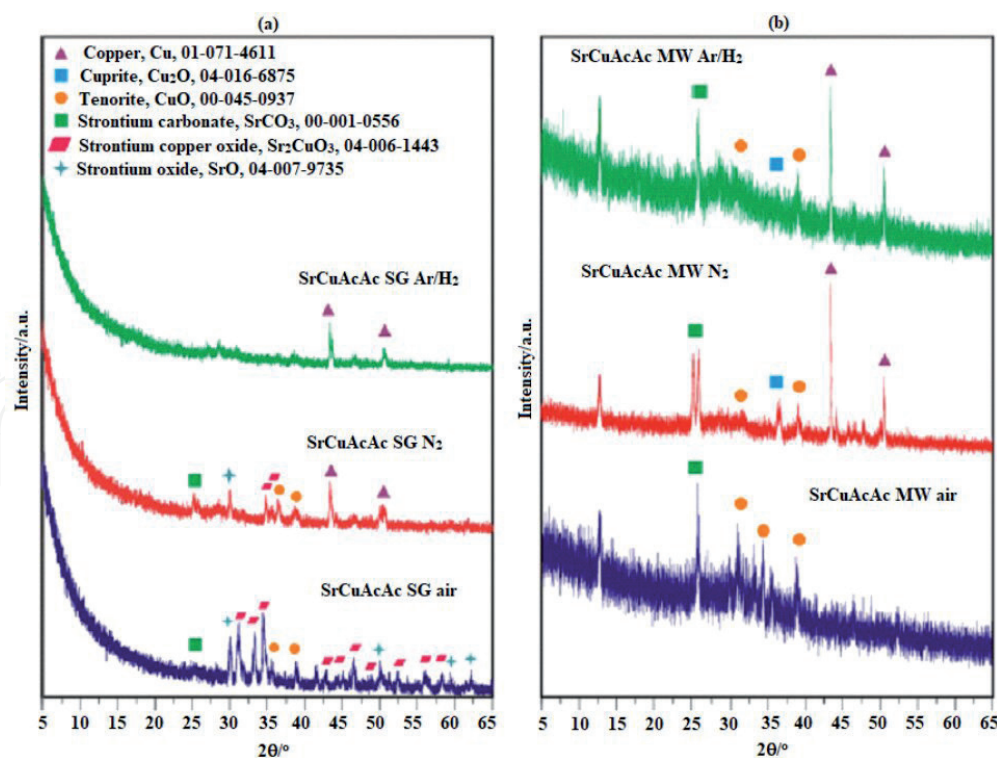


Figure 14.
 (a) XRD patterns of sol-gel synthesized samples (b) MW-assisted sol-gel samples annealed at 900°C in air, N₂ and 5% H₂/95% Ar [45].

The powders prepared in the mentioned conditions are intended to be investigated as precursors for SrCu₂O₂ compound preparation.

The presented results are important revealing the effect of MW on the reactions that take place during the sol-gel synthesis but should be considered preliminary. Direct methods of the solutions investigations, as High-Pressure Liquid Chromatography (HPLC), are underway in order to bring more information on the sol-gel chemistry in the presence and the absence of microwaves.

5. Conclusions

The interest of using microwaves in obtaining oxide nanostructures by reactions in solutions is rather high, leading to obtaining powders or films with enhanced properties.

According to the literature data, the MW irradiation in the sol-gel synthesis was used, most frequently, for precipitation of nanocrystalline metal oxides, for thermal treatment to crystallize the amorphous oxide nanopowders as well as for drying and thermally treatment of the oxide films.

However, the influence of the microwaves on the chemical reactions that take place during the sol-gel synthesis is less investigated.

Results regarding the formation of pure or doped nanostructures, as well as oxide compound, by sol-gel method in the presence or absence of microwave are presented.

The main results of the studies have shown that in all cases in the presence of microwave formation different molecular species is observed with a positive influence on the properties of the resulted nanostructure.

The advantage of using the MW-assisted sol-gel method is a more shorter time of synthesis and obtaining nanostructures with improved properties.

The obtained results are of interest, but could be considered preliminary and systematic studies on the chemical processes induced by the microwaves should be continued.

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